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Behavior of Plutonium and Americium in Soils

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The depth profiles and the particle size dependencies of the distributions of ^{239,240}Pu and ^{241}Am in soil have been studied in comparison with those of ^{137}Cs to obtain information on clarifying their behaviors and fates under the natural conditions. It was found that the concentrations of ^{239,240}Pu and ^{137}Cs in soil decrease exponentially with increasing the depth, and over 80% of these fall-out radionuclides is accumulated in the upper 10 cm of the soils. The concentration of ^{241}Am was measured by non-destructive γ-spectrometry using Ge-LEPS up to the depth of 6.5cm for two soil cores. The activity ratios of ^{241}Am/^{239,240}Pu were found to be in the range from 0.25 to 0.30 for one core sample, while rather high values, *i.e.*, 0.63-0.75, were obtained for another one. The particle size discrimination of surface soil showed that the concentrations of ^{239,240}Pu and ^{137}Cs increase steadily with the particle size from coarse sand to clay fraction, while that of ^{241}Am doesn't show such a tendency. These facts suggest that the behavior of ^{241}Am in soil may be different from that of ^{239,240}Pu and ^{137}Cs.

INTRODUCTION

The soil, closely associated with the ecosystem of terrestrial environs, accumulates the artificial radionuclides originating from the nuclear weapons and the nuclear facilities. Among these radionuclides, plutonium is recognized as a very radiotoxic substance[1]. Behavior of plutonium in soil is a matter of concern from the view point of environmental radioactivity since the production of this element is now increasing rapidly due to the atomic power generation. Environmental plutonium is serious in two exposure pathways, that is, the resuspension subjected to inhalation and the uptake by plants subjected to injestion. The environmental ^{241}Am, the amount of which is increasing steadily with times by *in-situ* build-up from short-lived parent ^{241}Pu, will play an

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important role in near future. Although basic studies on the behavior of plutonium in soil have been investigated by many authors[2] and a number of monitoring data are now available, only a few studies have been made for ^{241}Am in soil[3-5].

The purpose of this study is to clarify the behavior and the distribution patterns of fall-out ^{239,240}Pu and ^{241}Am in soil under the natural conditions in comparison with ^{137}Cs in the coastal areas of Japan Sea where it snows heavily during the winter season. For this purpose, the soil samples accumulating rather high levels of fall-out radionuclides were subjected to investigate the depth profiles and the particle size dependencies of fall-out radionuclides. The amount of the total organic carbon was also measured to examine the characteristics of the soil.

MATERIALS AND METHODS

Samples: The measurements of environmental radioactivities have been made extensively by *In-Situ* γ-spectrometry using a portable Ge(Li) detector in many locations to evaluate the exposure rates along with the contents of natural and artificial radionuclides[6,7]. The results from *In-Situ* γ-spectrometry showed that the accumulation of fall-out radionuclides was rather high in the natural forests or the points nearby the eaves where snow and rain water might potentially be collected from large area by the roof. In order to investigate the depth profiles of fall-out radionuclides, soil samples up to a depth of 20–30 cm were collected from three locations, Oguroi and Kohno (southern part of Fukui Pref.), and Tatsunokuchi adjacent to Low Level Radioactivity Laboratory (LLRL) (Ishikawa Pref.). The soil samples from Kohno were collected from the area nearby the eaves of a temple, and those from Oguroi and LLRL were collected from relatively flat area in the forest. The soil sample to investigate the particle size dependencies of the distributions of fall-out radionuclides was collected from Kohno up to a depth of 5 cm in the area of 50×50 cm. Besides these samples, sea sample collected from the sea floor in Nyu Bay (Fukui Pref.) and the surface soil collected from the moderately flat ridge of Mt. Kanmuri about 1100 m above sea level (Fukui Pref.) were also analysed. All samples obtained were air-dried. After pebbles and fragments of the plants were removed, the soil samples were pluverized to be sifted out through the standard sieves of 2 mm in diameter and then stored in plastic bottles.

Measurement: Samples of 30–50 g were compressed to make a disc shape counting source by a 10 ton test press and subjected to γ-spectrometry by a Ge(Li) detector with energy resolution of 1.8 keV FWHM and efficiency of 16% relative to 7.6 cm×7.6 cm NaI(Tl) at 1.33 keV. The minimum detectable concentration of ^{137}Cs is 0.01 pCi/g for a 50 g soil sample by 10^3 minutes of counting. After the Ge(Li) measurements, some of the soil sample were further analysed for ^{241}Am by a planar type Ge-LEPS (Low Energy Photon Spectrometer) of 32 mmϕ×10 mm thick with energy resolution of 450 eV at 59 keV. This detector is very effective for the measurements of low energy γ-rays[8]. Appropriate corrections due to the self-adsorption were made for the attenuation of

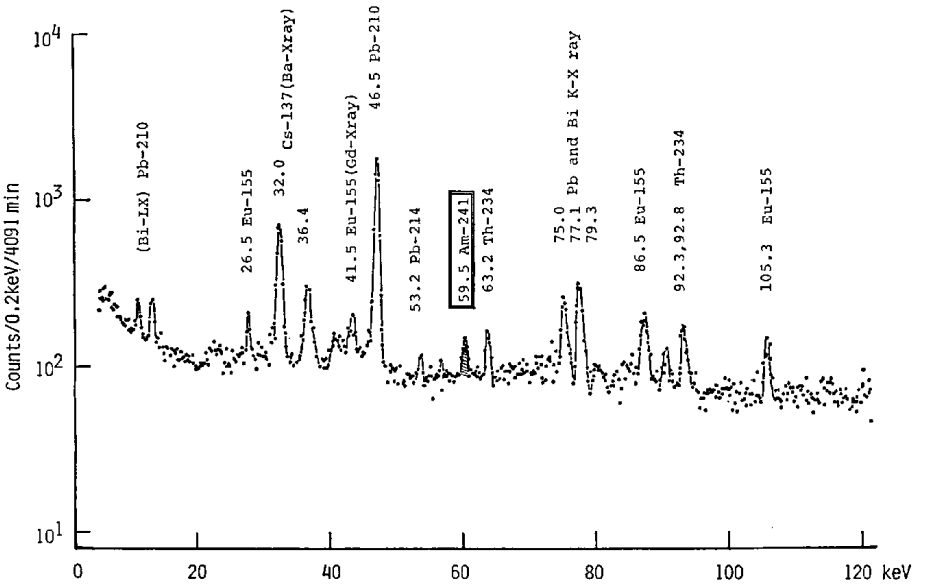

Fig. 1. Photon spectrum of non-destructive LEPS measurements of soil.
Detector: Intrinsic Germanium ($32\,mm^{\phi} \times 10\,mm^{t}$).
Sample: 53.1 g (Surface soil collected from Kohno).

this low energy gamma ray by the soil mass. A typical example of this LEPS spectrum is shown in Fig. 1, from which it is seen that ^{241}Am is clearly detected by the LEPS measurement together with other fall-out radionuclides, such as ^{137}Cs, ^{155}Eu and ^{210}Pb*. The minimum detectable ^{241}Am concentration is 0.01-0.005 pCi/g for a 50 g sample by 4×10^3 minutes counting.

Afterward, the soil sample of 20-40 g was subjected to the radiochemical analysis for $^{239,240}Pu$. The procedures of radiochemical separation of plutonium are described in detail in eleswhere[9]. The amount of $^{239,240}Pu$ was measured by an α-spectrometry using surface barrier type Si(Au) detector. The chemical yield of plutonium was determined by using ^{236}Pu as a yield tracer and was usually ranging from 60 to 80%. The minimum detectable concentration by 10^3 minutes of counting is 0.02 pCi/sample by considering the variation in counts due to ^{236}Pu tracer and background.

The total amount of organic carbon was determined by means of Tyulin's method[10]. The approximate amount of the total organic matter can be calculated by multiplying the total organic carbon by the carbon factor of 1.7[10].

The particle size discrimination of surface soil was performed simply by dispersing the soil sample in distilled water and passing the suspension through a set of standard sieves down to 53 μm in diameter. The finer fraction below 53 μm down to less than 2 μm was separated by applying Stoke's law of particle settling by assuming the density

* Most of ^{210}Pb detectable in surface soil is originated from the decay of airborne ^{222}Rn.

of the soil to be 2.65 g/cm^3. Each fraction thus separated was air-dried at about 105°C for 24 hours in a drying oven, then, pluverized and stored in plastic bottles till being subjected to further series of experiments. The contribution of the particle size in each fraction to the total soil was measured by using an apparatus of the particle size analyser (Shibata : Model-SA-2).

RESULTS AND DISCUSSION

In the previous work[11], accumulation levels of world wide fall-out ^{239,240}Pu and ^{137}Cs in Wakasa district (southern part of Fukui Pref.) were measured to be ranging from 1.8 to 3.7 mCi/km^2 and 134-307 mCi/km^2 respectively in the surface soils up to a depth of 20 cm. As the extension of this work, the depth profiles of these radionuclides and the particle size dependencies of their distributions in soils have been studied in the present paper. The depth profiles of ^{239,240}Pu and ^{137}Cs in the three core samples measured are shown in Fig. 2, together with those of ^{241}Am, natural radionuclides of ^{40}K, ^{238}U and ^{232}Th, and total organic carbon. Here, radioactive equilibrium is assumed for ^{238}U and ^{232}Th decay chain series. As seen in Fig. 2, the concentrations of ^{239,240}Pu and ^{137}Cs decrease smoothly with increasing of the depth, and their distribution patterns can

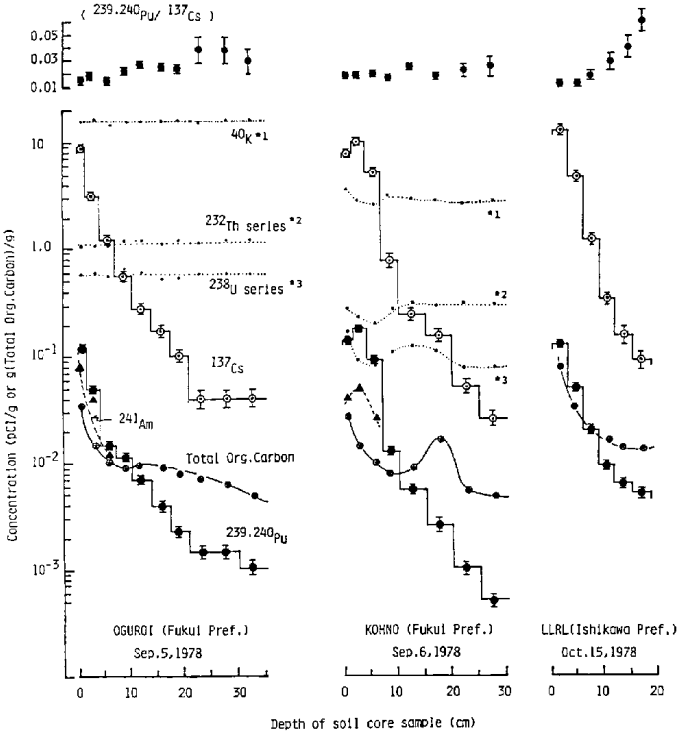

Fig. 2. Depth profiles of radionuclides and total org. carbon in soils and activity ratio of ^{239,240}Pu/^{137}Cs.

Table 1
Depth Distribution of Fall-out Plutonium and Cesium in Soils (% of Total)

OGUROI			KOHNO			LLRL		
Depth (cm)	^{239}Pu	^{137}Cs	Depth (cm)	^{239}Pu	^{137}Cs	Depth (cm)	^{239}Pu	^{137}Cs
0-1.5	24.2	28.7	0-1.5	19.3	19.7	0-3	53.2	59.4
1.5-4.0	34.3	35.6	1.5-4.0	46.4	46.8	3-6	25.1	28.7
4.0-6.5	10.4	14.3	4.0-6.5	24.7	24.3	6-9	11.0	8.1
6.5-10	12.0	9.4	6.5-10	4.8	5.2	9-12	4.7	2.2
10-13.5	7.0	4.5	10-15	2.8	2.1	12-15	3.3	1.0
13.5-17	4.0	2.8	15-20	1.2	1.3	15-18	2.7	0.6
17-20.5	2.4	1.8	20-25	0.5	0.4			
20.5-25	2.1	1.0	25-30	0.3	0.2			
25-30	2.1	1.0						
30-35	1.5	0.9						
Accumulation (mCi/km^2)	3.2	195		9.0	505		5.1	404

generally be approximated by exponentially decreasing functions. Table 1 gives the percentage contributions of each depth fraction and the total accumulations of ^{239,240}Pu and ^{137}Cs per unit area. The contributions of top 10 cm of surface soil for ^{239,240}Pu and ^{137}Cs are as high as 81% and 88% for Oguroi, 95% and 96% for Kohno and 91% and 97% for LLRL, respectively. Hardy and Krey[12] have reported that 95% of fall-out plutonium are concentrated in upper 15 cm of the soil collected from the temperate zone of United States. On the contrary, the concentrations of natural radionuclides are nearly constant showing the uniformity of the soil, though small dips and humps of the depth profiles are observed in the shallow layer of Kohno sample. The amount of total organic carbon is very high in the top layer and decreases gradually with increasing of the depth except for Kohno sample, which shows a characteristic peaking at 15-20 cm layer.

Most of ^{239,240}Pu and ^{137}Cs in the soil are derived from the large scale nuclear testing carried out in the periods of 1956-1958 and 1961-1963. The concentrations of ^{239,240}Pu and ^{137}Cs in the top layer of 0-1.5 cm or 0-3 cm are ranging from 0.11 to 0.17 pCi/g and 7.7 to 11.5 pCi/g, respectively. And, total accumulation calculated from the depth profiles are 3.2-9.0 mCi/km^2 for ^{239,240}Pu and 195-505 mCi/km^2 for ^{137}Cs. The annual rainfall in Fukui and Ishikawa Prefs. is as high as 2500 mm which is about 1.7 times higher than that in Tokyo (the coastal area of Pacific Ocean), and this is one of the reason that the accumulation of fall-out radionuclides is much higher in the coastal area of Japan Sea. Among three core samples, the Kohno sample contains rather high amount of ^{239,240}Pu and ^{137}Cs. This should be due to the fact that the Kohno sample was collected from the point just near the eaves of a temple, therefore, fairly large amount of fall-out radionuclides might be supplied by the snow and the rain precipitated on the

roof. Furthermore, the depth profiles of fall-out radionuclides for Kohno samples show a little different pattern that the maximum concentration is found not at the top layer but at the second layer of 1.5-3.0 cm in depth. This may be explained either by the outflowing loss of the fine particle fraction absorbing higher amount of radionuclides, or by the downward percolation through the soil due to the rainwater and melted snow. The similar depth profiles have also been observed by the recent studies on the peat core samples collected from the boggy field of Oze in Gunma Pref.[13]

The activity ratios for $^{239,240}Pu/^{137}Cs$ shown in the upper part of Fig. 2 have rather constant values of 0.018 ± 0.004 up to the depth of 20 cm for Oguroi and Kohno samples, but the soil samples below 20 cm show slightly increasing tendency, though the statistical errors of counting is rather high (30-50%). The increasing tendency of this ratio with increasing of a depth is apparently observed for the soil from LLRL. These increasing tendencies can be explained by the differences of mobilities and half-lives of plutonium isotopes ^{239}Pu, ^{240}Pu and ^{137}Cs. It is well-known that the ^{137}Cs once adsorbed on the soil particles is very hard to remove from the soil even by using aqua regia, whereas, fall-out plutonium can easily be extracted from the soil by using nitric acid (8-10 M) reflecting the different chemical states of plutonium and ^{137}Cs on the surface of the soil. The higher ratio of $^{239,240}Pu/^{137}Cs$ in the deeper soil layer can also be caused by the decay of ^{137}Cs, if the downward percolation of these fall-out nuclides through deeper layer occurs in a period of time scale comparable to the half-life of ^{137}Cs.

The concentrations of ^{241}Am measured with a LEPS are given in Table 2. Most of the environmental ^{241}Am is produced by *in-situ* build-up by the decay of short-lived ^{241}Pu and its concentration is steadily increasing with time, though a small fraction of ^{241}Am is originally included as a fall-out component. The activity ratio of $^{241}Am/^{239,240}Pu$ gives us information about the relative mobility of these nuclides in soil. The ratios in

Table 2
Depth profiles of ^{239}Pu, ^{241}Am and ^{137}Cs in soils and sediment*

Location	Depth (cm)	Concentration (pCi/g)			Am-241 / Pu-239	Pu-239 / Cs-137
		Pu-239	Am-241	Cs-137		
KOHNO (Sep.6, 1978)	0-1.5	0.135/9	0.041/5	7.72/27	0.30	0.017
	1.5-4.0	0.173/8	0.044/4	9.82/14	0.25	0.018
	4.0-6.5	0.091/5	0.027/4	5.03/6	0.30	0.018
OGUROI (Sep.5, 1978)	0-1.5	0.115/9	0.073/4	8.25/9	0.63	0.014
	1.5-4.0	0.047/6	0.031/3	2.96/6	0.66	0.016
	4.0-6.5	0.014/1	0.011/3	1.17/3	0.75	0.012
Mt, KANMURI (May 8, 1978)	0-5	0.495/30	0.108/16	11.5/2	0.22	0.043
NYU BAY (<37 μm)* (Aug. 2, 1975)	0≃10	0.188/11	0.060/23	0.79/3	0.32	0.24

The number behind slant denotes the statistical error of counting: $0.135/9=0.135\pm0.009$.

Kohno samples are ranging from 0.25 to 0.30 and nearly the same values of 0.22 and 0.32 are obtained for the soil sample rich in organic matter collected from Mt. Kanmuri and the sea sediment of less than 37 μm fraction collected from Nyu Bay, respectively. These values agree well with those obtained by Krey *et al.*[4] for fall-out sample. Though the activity ratios of $^{239,240}Pu/^{137}Cs$ for Oguroi samples are almost the same as those of Kohno samples, the ratios of $^{241}Am/^{239,240}Pu$ are ranging from 0.63-0.75, which are about 2-3 times higher than those for other ones. It seems rather difficult to find a reasonable explanation for this anomalously high $^{241}Am/^{239,240}Pu$ ratios for Oguroi samples. Fowler and Essigton[14] have shown the relative higher mobility of ^{241}Am than that of plutonium isotopes based on the variation of $^{241}Am/^{239,240}Pu$ ratios with the depth in the soil. If we apply the higher mobility of ^{241}Am to the Oguroi case, it seems reasonable to consider that the excess ^{241}Am is supplied from the sloping surface just nearby the sampling point of Oguroi samples. In order to elucidate this problem, further investigations must be performed for the deeper layer of Oguroi soil and for the soil from sloping surface adjacent to the sampling point.

The particle size discrimination was made for the surface soil collected from Kohno. The particle size dependencies of the distributions of $^{239,240}Pu$ and ^{241}Am is very interesting in view of the adsorption and the resuspension processes of fall-out radionuclides. The measured concentrations of $^{239,240}Pu$, ^{241}Am and ^{137}Cs and their activity ratios in each size fraction are given in Table 3. And in Table 4, the percentage distributions of particle size, organic carbon, fall-out and natural radionuclides are summarized. As seen from Table 3, the concentrations of $^{239,240}Pu$ and ^{137}Cs increase apparently with decreasing of the size of soil particles, and for the clay fraction less than 2 μm these values are as high as 0.485 pCi/g and 9.87 pCi/g, respectively. On the other hand, rather scattered values ranging from 0.019 to 0.032 pCi/g are obtained for ^{241}Am concentrations. The correlation between ^{241}Am concentration and the particle size is not

Table 3

The concentration of ^{239}Pu, ^{241}Am and ^{137}Cs among each size fraction in surface soil (0-5 cm depth) collected from KOHNO, Fukui, Pref., in Dec. 4, 1978.

Size Range (μm)	Concentration (pCi/g)			$\frac{\text{Am-241}}{\text{Pu-239}}$	$\frac{\text{Pu-239}}{\text{Cs-137}}$
	Pu-239	Am-241	Cs-137		
2000-710	0.0725/44	0.022/4	3.69/7	0.31	0.020
710-250	0.0816/45	0.024/3	4.49/13	0.29	0.018
250-125	0.0999/55	0.019/2	5.35/7	0.19	0.019
125- 53	0.0956/65	0.032/3	5.00/8	0.35	0.018
53- 20	0.1209/89	0.023/3	5.35/8	0.20	0.023
20- 5	0.1735/134	0.029/4	6.22/8	0.17	0.028
5- 2	0.1666/115	0.032/5	8.34/11	0.19	0.020
<2	0.4851/188	0.031/5	9.87/10	0.07	0.048

The number behind slant denotes the statistical error of counting: $0.0725/44 = 0.0725 \pm 0.0044$.

Table 4
Contributions (%) of Radionuclides, Org. Carbon and Weight by Particle Size in Surface Soil (0-5 cm depth) collected from KOHNO, Fukui Pref., in Dec. 4, 1978.

Size Range (μm)	Weight	Org. Carbon	^{239}Pu	^{241}Am	^{137}Cs	^{210}Pb	^{226}Ra	^{208}Tl	^{40}K
2000-710	7.2	6.2	3.7	6.0	4.6	6.2	7.4	6.3	6.0
710-250	9.4	7.5	5.5	8.6	7.3	8.1	8.9	7.7	6.5
250-125	12.5	11.9	8.9	9.0	11.6	12.4	11.4	10.8	11.7
125- 53	17.5	16.6	12.0	21.2	15.2	16.5	20.5	15.0	15.1
53- 20	22.0	21.4	19.0	19.2	20.5	20.0	23.2	19.7	21.2
20- 5	16.7	18.1	20.7	18.4	18.0	21.7	14.3	21.5	20.1
5- 2	9.1	11.8	10.8	11.0	13.2	10.5	8.7	12.2	12.4
<2	5.6	6.5	19.4	6.6	9.6	4.6	5.6	6.8	7.0

clearly observed, though slightly increasing tendency may be seen.

As for the percentage contribution of each fraction given in Table 4, all radionuclides except ^{239,240}Pu show relatively similar contributions to weight percentage, to which the contribution of the total organic carbon was also similar. The percentage contribution of ^{239,240}Pu in the clay fraction is 19.4% of the total, which is higher than other radionuclides. For ^{239,240}Pu, the percentage contributions by the particle size in various soil samples and sea sediments have been reported[9,15]. As for the sea sediment, the highest contributor is generally fine particles such as clay, but those for soil samples differ mainly due to the differences of soil properties and the source of the plutonium with which soil has been contaminated. In our experiments, since the particle size discrimination of the soil sample was made only by dispersing the soil particles using the distilled water, the complete dispersion might not be attained. In this case, the real fine particles such as clay and silt might remain apparently as coarser particles. To examine this effect, 10 g of soil sample was dispersed by using sodium hexametaphosphoric acid as a dispersing agent. And it is found that the percentage contribution of clay fraction increased by about 2.5 times. Considering this effect and the results shown in Tables 3 and 4, it is concluded that the highest contributor of fall-out plutonium is the clay fraction with large surface area per unit weight. Because the concentration of ^{239,240}Pu in the fine silt and clay fractions is relatively high, the contribution of the fine particles blown up from the soil surface must be considered to estimate the internal exposure due to inhalation.

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