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A study of characteristics of cumulative deposition of fallout Pu in environmental samples

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Abstract : This paper describes the cumulative deposition of fallout Pu in soil and lichen at the present time and give the characteristics of fallout Pu deposits in the soil. In the soil of the forest, the accumulated depositions of ^{239,240}Pu were estimated to be in the range of 34.0 to 101.2 Bq m^{-2} with an average value of 65.3 ± 21.6 Bq m^{-2}. The average inventory of ^{239,240}Pu in the forest was calculated to be two times higher than that in the hill. Also, the deposited activities of ^{239,240}Pu in cultivated soil were significantly lower than those in the hill or forest. However, the cumulative depositions of fallout Pu in the volcanic ash soil on Cheju Island were much higher than those in the forest and hill soils. The measured activity concentrations of Pu isotopes in lichens and mosses showed large variations, due to characteristics of species and life span of lichen and moss colonies. From depth profiles, it was found that most of the fallout Pu has been accumulated in upper 10 cm layer of soil. Except for a few cases, the concentrations of ^{239,240}Pu in soil tended to decrease exponentially with increasing soil depth. Among parameters affecting the cumulative deposition of fallout Pu, organic substances and rainfall play an important role in the retention and relative mobility of fallout Pu in the soil. However, pH showed a weak correlation with the deposition of fallout Pu in the soil. From sequential leaching experiments, Pu was found to be associated predominantly with the “organic” and “oxy-hydroxy” fractions. Both the activity ratios of ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu in soils, lichens and mosses and the atomic ratios of ^{240}Pu/^{239}Pu in soils are close to those observed in the cumulative deposit global fallout from nuclear weapon testings. The results obtained from this research make it possible to interpret and predict the behavior of fallout Pu under natural conditions.

Keywords : cumulative deposition, fallout plutonium, activity ratio, soil, moss

1. Introduction

As a consequence of nuclear weapon tests in the atmosphere in the past, many nuclides were released into the environment. Most of the radioactive elements produced by atmospheric nuclear tests decay so rapidly that only a few elements with long half-lives may remain in the soil at the present time. Plutonium has been produced in greater quantity than any other transuranic element such as neptunium, americium and curium in the environment.

The contamination level of fallout Pu in the

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environment due to atmospheric fallout is highly variable with time and geographic location. The behavior of Pu is very complicated, and is largely dependent on the physicochemical properties of the soil, the chemical forms of the nuclides themselves, and the biological and physico-chemical processes in a given environment. In the terrestrial environment, the soil is a principal reservoir of the artificial radionuclides and acts as a medium for migration processes. This is because the soil accumulates the artificial radionuclides originating from nuclear weapons and nuclear facilities. When plutonium isotopes deposited by fallout come in contact with the soil, most of them bind so strongly to soil particles that become nearly immobile. Plutonium isotopes are caught not only by adsorption on reactive sites on clay minerals soil particles, ion exchange and precipitation as hydroxide or sulfide, but also by a complex formation with organic compounds. Also, lichens and mosses have been reported to be good biological indicators of fallout nuclides from nuclear accidents and from nuclear weapon tests, owing to their relatively high accumulation capacity for radionuclides.[1-6]

Fallout Pu belongs to a group of man-made radionuclides that attract the attention of radioecologist because of their high radiotoxicity, long half-lives, high chemical reactivities and long residence in biological systems. ^{239,240}Pu and ^{238}Pu are long lived α-emitting radionuclides, whereas the relatively short-lived β-emitting ^{241}Pu ($t_{1/2}$=14.35 y) decays into the long lived α-emitting ^{241}Am ($t_{1/2}$=482 y). Though the radiotoxicity of ^{241}Pu itself is much lower than that of the alpha emitting plutonium isotopes, ^{241}Pu decays to ^{241}Am which is a highly radiotoxic alpha-emitting nuclide and has a long residence time in animals and man. The radioactivity ratio of ^{241}Am to ^{239,240}Pu in the environment will increase in the long run due to the decay of ^{241}Pu. Therefore, information on the cumulative distribution of plutonium isotopes in the environment is essential for dose assessments.

Owing to their long half-lives (^{239}Pu : 24,131 y, ^{240}Pu : 6,569 y, ^{238}Pu : 87.8 y) and the abundant fallout deposited especially in the northern hemisphere, fallout Pu is detectable in environmental samples for many years. This paper describes the cumulative deposition of fallout Pu in the soil and lichen at the present time and the characteristics of fallout Pu deposits in the soil. The results from this study can be used as reference data in case of an accident in nuclear facilities as well as to elucidate the behavior of fallout Pu in the environment.

2. Materials and Methods

2.1. Soil sampling and preparation

The sampling area is very important to the determination of fallout Pu contamination levels in the terrestrial environment. In this field study, soil samples were collected from 17 sites in South Korea. All the sampling sites were selected on flat areas, if possible, in order to minimize the possibility of precipitation run-off. Soil sampling was carried out from 1998 to 2001. At each site, 2 to 8 soil samples were taken with a core sampler (4.5 cm in diameter) with an area of about 50 m × 50 m to the depth of about 20 cm or 30 cm. It is enough to estimate the cumulative depositions of fallout Pu to a depth of 20 cm. However, sampling depth in the volcanic soil of Cheju island were taken to a depth of 30 cm. Several preliminary experiments on volcanic soils showed that a sampling depth of 20 cm is insufficient to determine the inventory of fallout Pu due to the characteristics of the volcanic ash soil. For investigating the depth profile of fallout Pu in soils, with a shovel soil column which have an area of about 30 cm × 30 cm and the depth of about 20 cm was made and sliced into section 2 or 5 cm thick from top layer until 20 cm. Soil samples were dried at 110°C for 48 h after removing pebbles and fragments of plant root from the samples, and then sieved through a 1.0 mm screen. Lichens from rocks, mosses from stones and soils were collected at 9 sites within a 5 km radius of the sampling site in the autumn of 1995. Each sample was composed of 5-10 subsamples collected within an area of 50 m × 50 m. After extraneous plant materials such as tree bark and other foreign matters were removed, the collected samples were air-dried at 35°C and were used for analysis. The organic matter content was determined using the loss-on-ignition method with an ashing temperature of 550°C for 24 h. The pH was measured with a glass electrode in a 1 : 5 suspension of soil and water.

2.2. Extraction procedures

The chemical characterization of plutonium in soil was studied using the sequential extraction techniques.[7,8] Air-dried 50 g soil samples were shaken for 24 h with an appropriate amount of extractant, as presented in *Table* 1, and the mixture was centrifuged at 4,000 rpm for 60 min. The supernatant was filtered and any residue on the filter paper returned to the sample using the next extractant as a wash solution. A suitable aliquot of the leachate was transferred to a beaker and evaporated to dryness. After adding ^{242}Pu as a yield tracer into the sample, the samples wet-ashed with nitric acid until organic-free. The dried residue was dissolved in 8 M HNO_3, then subjected to a radiochemical analysis for ^{239,240}Pu.

2.3. Determination of plutonium isotopes

An aliquot of 100 g soil and 20 g moss were calcined at 550°C for 24 h to eliminate organic matter. After adding ^{242}Pu as a yield tracer (Isotopes Products Laboratories, USA), a leaching procedure using 8 M HNO_3/0.9 M HF and 5 M HNO_3/1 M $Al(NO_3)_3$ solution was performed. Pu fraction was separated from most matrix components by extraction with 0.2 M TOPO (trioctyl phosphineoxide) in cyclohexane. After backextraction of the Pu fraction with ascorbic acid/hydrochloric acid, trace elements and disturbing alpha-emitting radionuclides of natural or man-made origin were separated radiochemically by coprecipitation of the Pu with lanthanium fluoride and an anion-exchange step.[9] The purified plutonium isotopes were electrodeposited from the electroplating solution[10] on a polished stainless steel disc and measured by α-ray spectrometry. After α-spectrometric measurement Pu isotopes electrodeposited on the stainless steel planchet were dissolved in 60 ml 8 M HNO_3. For removing Fe and Ni dissolved from the stainless steel, the acid solution was loaded on an anion exchange column. The plutonium was eluted with 10 ml of 0.36 M HCl/0.01 M HF. The purified Pu isotopes was subjected to ^{241}Pu measurement[11] by a low background liquid scintillation counter (Quantulus 1220). Also, for determining the atomic ratios of ^{240}Pu/^{239}Pu, the stainless steel planchet electroplated Pu isotopes was dissolved in 8 M HNO_3. Using an anion exchange column, Pu fraction was purified from Fe and Ni dissolved from the stainless steel. The atomic ratios of ^{240}Pu/^{239}Pu were measured by a high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Micromass, Manchester, UK). The separation scheme is presented in *Fig.* 1. The detection limit was 0.0063 Bq/kg-dry for soil and 0.031 Bq/kg-dry for moss in 86000 seconds of counting time in the alpha spectrometry.

3. Results and Discussion

3.1. Inventory of fallout Pu in soil

In *Table* 2, the cumulative deposition of fallout Pu in the soil samples are summarized in terms of

Table 1. Extractant volume per gram of sample used in sequential extraction

Fraction	Reagents	pH	Volume (ml g^{-1})
Exchangeable and water soluble	0.05 M $CaCl_2$	6.0	20
Specifically adsorbed	0.5 M CH_3CO_2H	2.8	20
Organically bound	0.1 M $Na_4P_2O_7$	9.7	100
Oxide/hydroxide bound	0.175 M $(CO_2\ NH_4)_2$/0.1 M (CO_2H_2)	3.1	75
Residual	HF/HNO_3	1.4	70

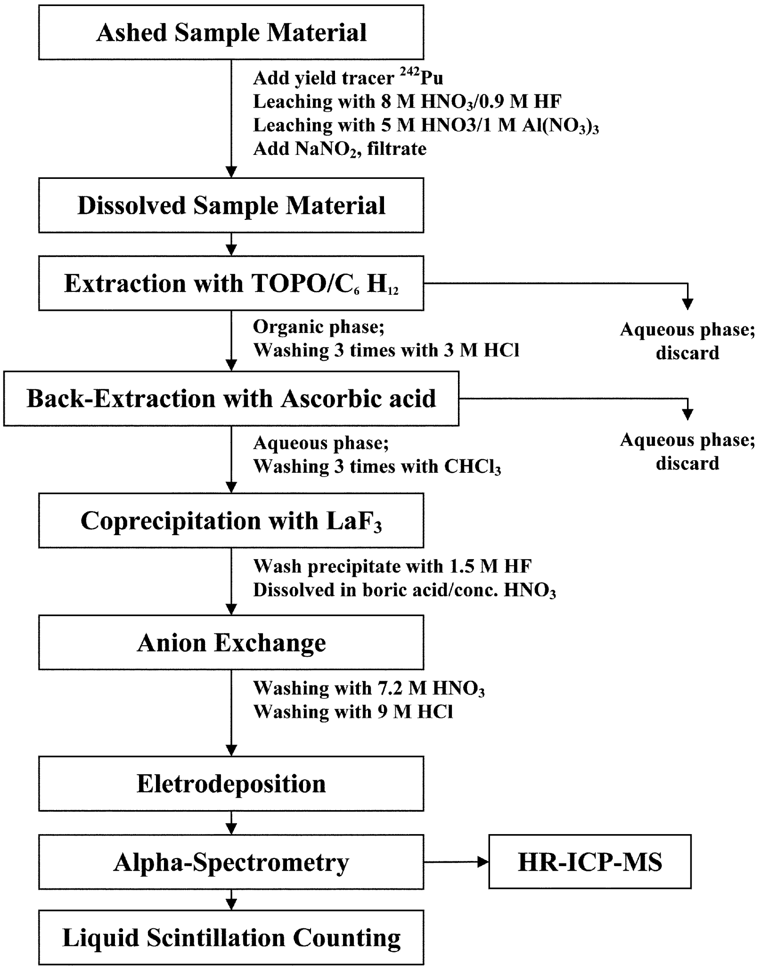

Fig. 1. Analytical procedure for separation of fallout Pu in the environmental sample.

activities per unit area (Bq m^{-2}). The inventory represented as Bq m^{-2} is much more meaningful than the observed activity concentrations (Bq kg^{-1}), because the observed activity varies with parameters such as soil type, topography, water content, mineralogy and rate of soil erosion. The typical spectra of Pu in the forest soil are shown in *Fig.* 2. In *Fig.* 2-a, the alpha peaks of ^{242}Pu, ^{239,240}Pu and ^{238}Pu are well resolved and the spectrum is free from contributions due to various thorium and uranium isotopes. Also, typical liquid scintillation spectra of Pu are shown in *Fig.* 2-b, in which beta spectrum of ^{241}Pu is clearly separated from α spectrum of ^{239,240}Pu and ^{238}Pu. However, the alpha peaks of ^{242}Pu, ^{239,240}Pu and ^{238}Pu can not be separated in liquid scintillation counting, because the energy resolution is rather poor for α-particles in liquid scintillation counting.

There seems to exist considerable difference in the cumulative deposition of fallout Pu in the soil as presented in *Table* 2. The Pu contamination level in the terrestrial environment varies with geographic location, as shown in *Fig.* 3. Therefore, a sampling area is very important to cumulative deposition of fallout Pu. The deposition of fallout Pu on the soil depends on rainfall and removal processes such as wind erosion, resuspension, runoff and uptake in vegetation. The lowest values were found for the

Table 2. Inventory of fallout Pu in soils

Sampling Type	Location		LOI[a] (%)	Rainfall (mmy^{-1})	pH	Inventory of fallout Pu (Bq m^{-2} ± 1σ)[b]			Activity ratio	
	^{0}N	^{0}E				^{239,240}Pu	^{238}Pu	^{241}Pu	^{238}Pu/^{239,240}Pu	^{241}Pu/^{239,240}Pu
Arable 1	36.4	127.5	4.2	1360	3.5	21.2 ± 2.9	3.1 ± 0.12	<87	0.146	-
Arable 2	36.2	128.1	4.9	1170	4.2	10.9 ± 1.2	<0.4	<65	-	-
Arable 3	35.3	129.1	4.5	1271	4.7	13.0 ± 1.1	<0.5	<66	-	-
Arable 4	34.7	127.4	3.9	1341	3.8	12.3 ± 1.9	0.3 ± 0.07	<55	0.024	-
Mean value						14.4 ± 4.0	1.7 ± 1.9	-	0.118	-
Hill 1	38.1	128.0	6.0	1266	6.2	27.7 ± 3.0	0.9 ± 0.12	124 ± 14	0.032	4.48
Hill 2	37.3	127.6	5.7	1304	4.7	30.1 ± 2.3	1.2 ± 0.10	126 ± 10	0.040	4.19
Hill 3	36.7	126.4	4.8	1216	4.4	18.3 ± 2.0	<0.8	<78	-	-
Hill 4	36.4	128.7	7.5	1274	5.0	20.8 ± 1.8	<0.5	<64	-	-
Hill 5	35.8	129.2	12.4	1272	4.7	22.9 ± 1.9	<1.0	<91	-	-
Hill 6	35.7	128.2	8.0	1011	4.5	28.5 ± 3.2	2.1 ± 0.15	100 ± 11	0.074	3.51
Hill 7	35.1	127.81	9.6	1257	5.9	27.0 ± 2.1	0.7 ± 0.11	92 ± 10	0.026	3.41
Hill 8	34.5	126.6	4.5	1360	5.1	11.1 ± 1.2	<0.6	<70	-	-
Mean value						23.3 ± 6.0	1.2 ± 0.60	111 ± 15	0.052	4.76
Forest 1	37.8	128.8	10.8	1580	5.0	50.5 ± 3.9	1.8 ± 0.16	157 ± 12	0.036	3.11
Forest 2	37.4	128.8	11.0	1357	4.8	84.1 ± 6.51	1.9 ± 0.231	244 ± 19	0.023	2.90
Forest 3	37.4	126.9	11.5	1307	4.3	101.2 ± 10.9	7.1 ± 0.55	192 ± 21	0.070	1.90
Forest 4	37.1	128.9	12.2	1190	4.9	64.4 ± 8.1	1.6 ± 0.33	245 ± 31	0.025	3.80
Forest 5	36.5	127.2	13.7	1311	4.7	87.9 ± 6.9	1.4 ± 0.28	448 ± 35	0.016	5.10
Forest 6	36.5	127.7	6.8	1250	5.5	71.1 ± 6.1	4.1 ± 0.26	299 ± 26	0.058	4.21
Forest 7	36.0	126.8	10.7	1311	4.9	55.2 ± 4.2	1.9 ± 0.36	259 ± 18	0.034	3.63
Forest 8	35.7	126.5	10.6	1280	4.3	34.0 ± 4.2	1.1 ± 0.16	122 ± 15	0.032	3.59
Forest 9	35.4	126.7	9.4	1249	5.1	39.0 ± 4.1	1.2 ± 0.15	164 ± 17	0.031	4.21
Mean value						65.3 ± 21.6	2.5 ± 1.95	237 ± 92	0.038	3.63
Volcanic ash 1	33.8	126.4	44.3	1998	6.9	420.1 ± 18.1	22.4 ± 0.80	1150 ± 54	0.053	2.74
Volcanic ash 2	33.8	126.5	39.1	1799	5.9	228.9 ± 10.4	4.20 ± 0.53	1232 ± 43	0.018	5.38
Volcanic ash 3	33.7	126.4	40.7	1804	6.4	258.3 ± 12.9	5.91 ± 0.50	1093 ± 50	0.023	4.23
Mean value						302.4 ± 84.1	10.8 ± 10.0	1158 ± 70	0.036	3.83

[a] Loss of ignition

[b] n = 4

cultivated soil, while the highest values were obtained for the volcanic ash soil. The deposited ^{239,240}Pu in the cultivated soil were significantly lower than those in the hill or forest. This means that agricultural practices such as the irrigation, the plowing and chemical products (fertilizers, pesticides, etc) may have reduced plutonium concentrations. The cumulative deposition of ^{239,240}Pu in the soil of the hill was estimated in the range of 11.1 to 30.1 Bq m^{-2} with an average value of 23.3 ± 6.0. In the forest soil, the accumulated depositions of ^{239,240}Pu were estimated in the range of 34.0 to 101.2 Bq m^{-2} with an average value of 65.3 ± 21.6. The average inventory of ^{239,240}Pu in the forest is two times higher than that in the hill. This means that the fallen leaves in the deep forest accumulate fallout radionuclides in the nearby soil. The deciduous leaves of a tall tree on the ground increase not only the effective surface area for deposition of fallout but also the amount of humic substances which may easily associate with the fallout radionuclides. Also, the mean value of cumulative deposition of ^{239,240}Pu in the hill and

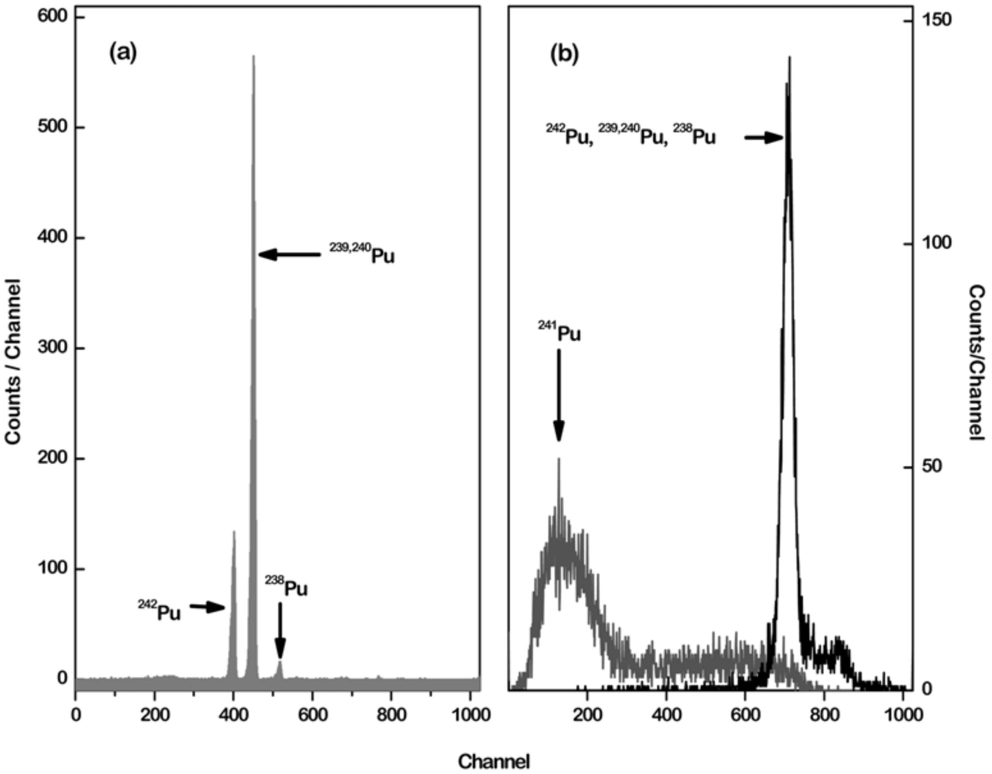

Fig. 2. Typical alpha spectra (a) and liquid scintillation spectra (b) in the soil.

forest soil, 45.5 Bq m^{-2}, is close to fallout values reported by UNSCEAR[12] for the north temperate zone (30-50 N°). However, the cumulative depositions of fallout Pu in the volcanic ash soil on Cheju Island were much higher than those in forest and hill soils. This difference may suggest that the deposition rate can be influenced by meteorological condition and topographical features of the earth's surface, such as soil type, organic substances or clay content.[13] The annual precipitation on Cheju Island is more than 1800 mm, about 1.5 times higher than that on the Korea peninsular, and is one of the reasons why the accumulation of fallout radionuclides is much higher than in other sites of Korea. When rain falls on volcanic ash soil, which has the high porosity and permeability of lavas, it percolates easily through the volcanic soil. The loss of nuclides by rainwater rolling off on the volcanic soil is smaller than for other soil types. Also, due to the high CEC (cation exchange capacity) and organic matter content of volcanic soil, the fallout radionuclides in volcanic soil are somewhat tightly associated with soil particles and organic matter.

3.2. Concentrations of fallout Pu in lichens and mosses

Lichens and mosses are known to strongly accumulate a great variety of radionuclides from atmospheric contamination due to their complex surface, slow growth rate and slow metabolic activity. As presented in *Table* 3, the ^{239,240}Pu concentrations observed here ranged from 2.23 to 4.70 (average 3.85) Bq/kg-dry in lichens and from 0.20 to 2.25 (average 0.65) Bq/kg-dry in mosses. The measured activity concentrations of Pu isotopes in lichens and mosses showed large variations. It may come from deposition influenced by meteorological conditions and characteristics of lichens and mosses such as species and life span of lichens and mosses colonies. Also, mosses or lichens growth is

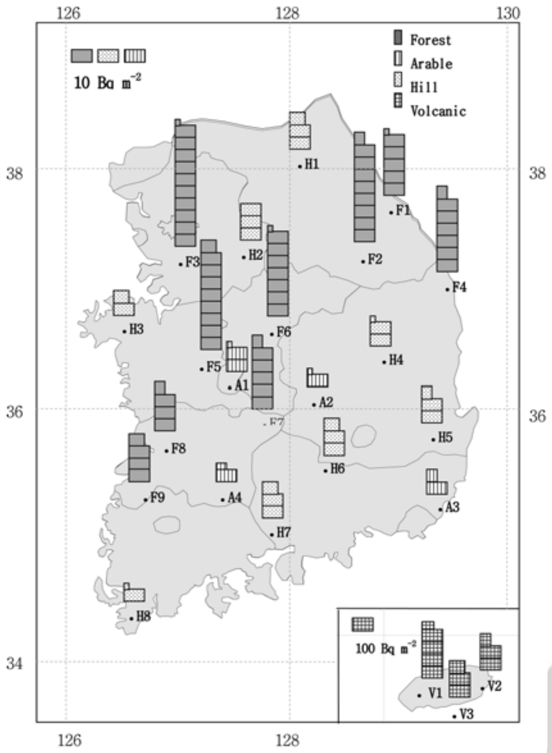

Fig. 3. Cumulative depositions of ^{239,240}Pu in terrestrial soils.

indicated to cause enhanced ‘dilution’ of the radionuclide concentration.[14,15] The concentrations of fallout Pu in mosses on the soil were found to be lower than those on the stone, due to the relatively active growth rate of mosses in the soil. Also, the concentrations of fallout Pu in lichens were higher than those in mosses. Mihok *et al.,* showed that the effective half-life of ^{137}Cs was 10 y in lichens and 4 y in mosses.[16] This result can be used to elucidate behavior of fallout Pu in mosses and lichens. That is, lichens are more effective than mosses as an accumulator of the airborne Pu pollution, because of longer effective half-life. Therefore, it seems that lichens are a more efficient bioindicator of radionuclides than mosses. However, for clearly elucidating behavior of fallout Pu in the lichens and mosses, the effect of resuspension should be considered.

3.3. Factors affecting cumulative deposition of fallout Pu

The large number of factors such as organic substances, rainfall, and pH affects fallout Pu in the soil. The contents of organic matter, rainfall and pH in the soil samples are shown in *Table* 2. Regression analysis was used to investigate a possible correlation between the concentration of the radionuclides and the content of organic matter in the soil.

As shown in *Fig.* 4, the correlation between the organic matter content and the concentration of fallout Pu is highly significant, and its correlation coefficients was 0.95. This means that organic substances in the soil reduce the efficiency of removal processes. Due to its large cation exchange capacity, the organic matter content is a characteristic factor that has a significant influence on the dynamics of fallout-originated radionuclides in the soil.[17-21] Therefore, it must be certain that fallout Pu

Table 3. Concentration of fallout Pu in lichens and mosses

Sample Type	Location		Concentration (Bq kg dry^{-1} ±1σ)[a]		
	^{0}N	^{0}E	^{239,240}Pu	^{238}Pu	^{241}Pu
Lichens growing on rock (ULJIN)	37.1	128.9	4.70 ± 0.71	0.20 ± 0.030	8.5 ± 1.9
Mosses growing on soil (KONGJU)	36.5	127.2	0.39 ± 0.04	0.01 ± 0.001	1.8 ± 0.35
Mosses growing on stone (KIMJE)	35.7	126.5	2.25 ± 0.12	0.12 ± 0.009	7.3 ± 1.2
Lichens growing on stone (MUJU)	36.0	126.8	2.23 ± 0.10	0.10 ± 0.006	9.5 ± 1.0
Mosses growing on soil (HADONG)	35.2	127.8	0.32 ± 0.03	<0.004	1.3 ± 0.20
Lichens growing on rock (SENGSAN)	33.8	126.5	4.61 ± 0.65	0.19 ± 0.027	15.5 ± 1.5
Mosses growing on soil (YEIJU)	37.3	127.6	0.20 ± 0.03	<0.004	1.8 ± 0.35
Mosses growing on soil (TAEJON)	36.4	127.5	0.24 ± 0.05	<0.004	1.8 ± 0.35
Mosses growing on stone (YANGGU)	38.1	128.0	0.49 ± 0.07	0.02 ± 0.005	<0.44

[a] n = 3

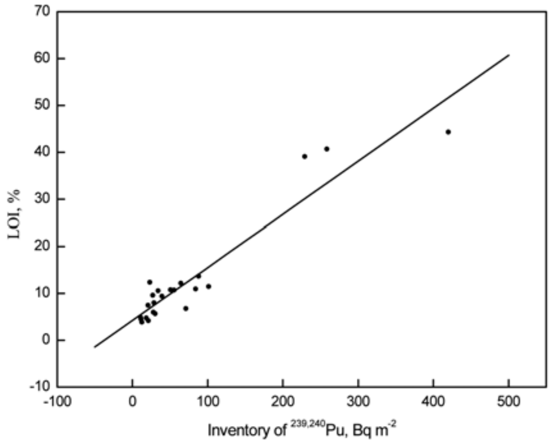

Fig. 4. The correlation between cumulative depositions of ^{239,240}Pu and organic substances in soils. Regression equation: Y = 0.11 X + 4.24; r = 0.95.

easily associates with the organic substances as forms of surfaces coatings and complexing. High concentration of fallout Pu found in the soil with high organic content must be attributed to these phenomena.

Rainfall is known to influence deposition of fallout Pu by worldwide fallout, and could be used as an indicator of the distribution of these nuclides in soil.[22] Precipitation scavenging is an important mechanism which brings the debris of nuclear explosions in the atmosphere to the earth's surface. The correlation between rainfall and deposition of fallout Pu in the forest and volcanic soil was found to be highly significant (r = 0.90). In the deep forest, removal processes of fallout Pu, such as wind erosion, resuspension and runoff are less efficient than those in the hill, because of geographic location. Also, the loss of nuclides by rainwater rolling off on the volcanic soil is smaller than for other soil types due to characteristics of volcanic ash soil. However, the correlation of rainfall with the cumulative deposition of fallout Pu in the soil of hill was found to be weak (r= -0.44). The weak correlation indicates that removal process, such as the outflowing loss of

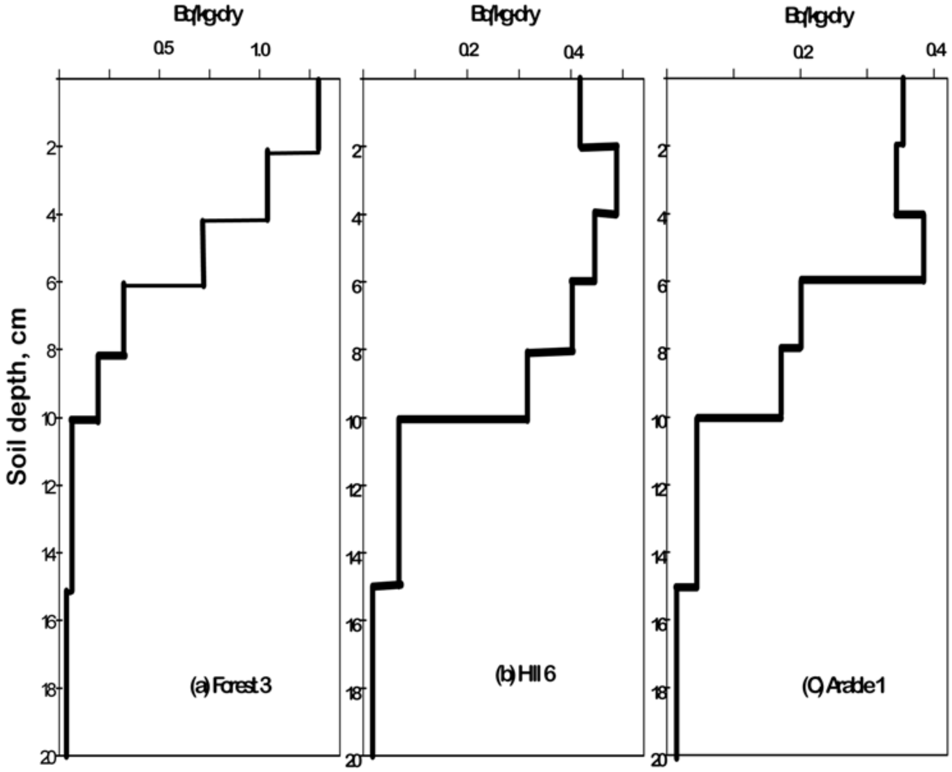

Fig. 5. Depth profiles of ^{239,240}Pu in soils.

the fine particle fraction adsorbing the radionuclides by heavy rain, partial soil erosion and wind erosion, have affected desorption of fallout Pu in hill soil.

The pH value affects adsorption and solubilization processes of radionuclides in soil. The influence of the pH on the fallout Pu concentration in soil was studied by means of a linear correlation analysis. The correlation between fallout Pu and pH was not significant (r = 0.15). The weak effect of pH on the distribution of radionuclides has been reported in the previous literature.[21,23] The weak correlation may imply that pH has no influence on the retention of fallout Pu in the soil in the given range of pH, or the pH effect is masked by the action of the other parameters affecting fallout Pu mobility in the soil.[24]

3.4. Depth profiles of ^{239,240}Pu

Fallout radionuclides move downward in soil column after the deposition on the soil surface. The depth profile of the fallout radionuclides can give information on the retention and migration of the radionuclides.

The depth distributions of ^{239,240}Pu in the top 20 cm soil layer for three typical sites are shown in *Fig.* 5. As shown in *Fig.* 5-a, the concentration of ^{239,240}Pu in the forest soil decreases nearly exponentially as the depth of soil increases. Most of ^{239,240}Pu is accumulated in top 10 cm layer of soil. The contribution of the upper layer to total inventory of ^{239,240}Pu were more than 90%. When the fallout Pu deposited by fallout comes in contact with soil, most of them are bound so tightly to soil particles that they are nearly immobile. Many fallout Pu are caught not only by adsorption on reactive sites on clay minerals soil particles. Also, fallout Pu is so easily associated with the organic or inorganic substances in the form of surface coatings and complexing that its downward migration is limited. Lee and Lee reported that for the forest soil, about 30% of the total plutonium was found in the organic (humic and fulvic) fraction. For the volcanic soil, about 45% of the total plutonium was found in the organic fraction.[25] Also, Lee and Lee supposed that a lot of insoluble ^{239,240}Pu associated with high molecular weights of humic acids seems to restrict its mobility,[25] though a small position of soluble ^{239,240}Pu complexed with fulvic acids seems to enhance its mobility.

However, as a result of the physicochemical reactions such as the solubility of plutonium compounds in water surrounding the soil particles under conditions of moderate rainfall, a small portion of fallout Pu moves slowly into the deeper soil. The downward movement of the fallout radionuclides deposited on soil surfaces depends on many parameters such as chemical forms of the radionuclides, physicochemical properties of the soil, the rainfall, and the biological and physicochemical processes in the natural environment. In the soil environment, complex formations occur by the interaction of fallout Pu with surfaces, surface coatings, colloidal materials and complexing ligands. When Pu (IV) is stabilized by naturally occurring ligands such as humic and fulvic acid, Pu can remain in the soluble state.[26] The complexation may influence the mobility of the fallout radionuclides. Hence, investigating the association of the fallout radionuclides with organic acids, it may be possible to interpret the mobile tendency of fallout radionuclides in the soil. Also, the physical transport of very small soil particles associated with the fallout radionuclides and bioturbation by the earthworm into deeper soil layers may affect migration of the fallout radionuclides. However, it seems that pH has little influence on the retention and migration of fallout Pu in the soil, as described above.

A somewhat different pattern in the depth profile was observed in the hill soil as shown in *Fig.* 5-b. The maximum concentration of ^{239,240}Pu was found not in the top layer but in the second layer of 2-4 cm depth. This may be explained by the downward percolation through the soil due to the rainwater. Also, removal processes have influence on the depth profile in the soil. Resuspension, runoff, soil erosion and wind erosion in the surface layer of hill sometimes reduce the concentration of ^{239,240}Pu in the top layer. In *Fig.* 5-c, ^{239,240}Pu concentrations in the cultivated soil were significantly lower than those found in the forest soils studied presently and were rather constant up to the depth of 8-10 cm below. This may be due to the effect of tillage carried out in these plots.[27] This tillage, mixing the soil, must have disturbed the distribution of ^{239,240}Pu in the whole profile.

3.5. Chemical characterization of fallout Pu in the soil

The results of the sequential extraction of plutonium from each surface soil are presented in *Table* 4. The sequential leaching scheme used here differentiates between the labile “exchangeable” and “adsorbed” fraction and the much more inert “organic”, “oxide” and “residual” phases. However, redistribution and incomplete extraction of fallout Pu may occur as a result of the chemical treatments used, such that absolute concentration within each fraction may not be reliable.[28] Also, sodium pyrophosphate is used as a organic extractant as well as a dispersant for clays, and its use sometimes may consequently result in an overestimate of the organically bound fraction.[18] Nevertheless, this procedure used to determine the dominant chemical characterization, if the results are cautiously interpreted, could elucidate the behavior of fallout Pu in the soil.

^{239,240}Pu was associated predominantly with the “organic” and “oxy-hydroxy” fractions. Despite major difference in soil type, plutonium behaviour is similar in the soil samples. The observed order of association is:

Organic > Oxide > Residual > Exchangeable >Adsorbed

This trend is very similar to that reported by Livens and Baxter for Cumbrian soils.[18] The dominant association in each fraction was with organic materials. More than 50% of total ^{239,240}Pu activity was associated with organic substances. Murdock *et al.* found that more than 90% of ^{239,240}Pu to total ^{239,240}Pu was associated with the organic and oxy-hydroxy fraction in the marine sediment, less than 5% of ^{239,240}Pu associated with its residual fraction.[28] This means that ^{239,240}Pu in the terrestrial soil such as Korean and Cumbrian soils is much more inert to leaching agents than the marine sediment. Also, a small amount of ^{239,240}Pu was found in the exchangeable fraction. This implies that Pu oxide/hydroxide species adsorb strongly to soil surfaces and not easily replaced by competing cations or other positively charged species. Hence, in the short term, the mobility of fallout Pu into the soil may be due to physical redistribution processes rather than geochemical processes. But it is suggested that, after a long time have passed, redissolution of plutonium-binding phases by waterlogging, microbial transformation of organic substances and other processes may influence the mobility of fallout Pu in the soil.

3.6. Activity ratios of fallout Pu

The activity ratios of ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu may vary over a wide range depending on the source of the release and therefore this ratio may be utilized to identify the different sources of release. As shown in *Table* 2, the mean activity ratio of ^{238}Pu/^{239,240}Pu in soils except for cultivated soil was calculated to be 0.042. This value is very close to

Table 4. Percentage activity of ^{239,240}Pu associated with different geochemical species in different sampling type.

Fraction	Percentage activity of ^{239,240}Pu in fraction		
	Hill 5[a]	Forest 3[a]	Volcanic ash 1[a]
Exchangeable and water soluble	2.1 ± 0.8[b]	3.9 ± 1.1	3.0 ± 0.7
Specifically adsorbed	2.2 ± 0.9	2.7 ± 0.1	1.2 ± 0.6
Organically bound	51.1 ± 2.1	60.4 ± 3.4	69.2 ± 3.3
Oxide/hydroxide bound	31.4 ± 1.0	20.7 ± 1.6	18.4 ± 1.1
Residual	13.2 ± 0.8	12.3 ± 1.0	8.2 ± 0.7

[a] n = 4
[b] Error is 1σ

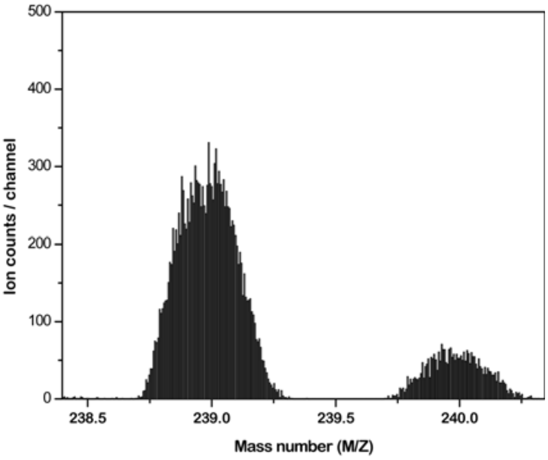

Fig. 6. Typical HR-ICP-MS spectra of ^{239}Pu and ^{240}Pu in the forest soil.

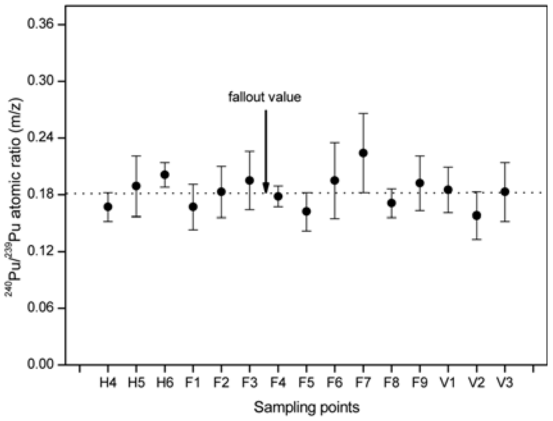

Fig. 7. Atomic ratios of ^{240}Pu/^{239}Pu measured by HR-ICP-MS in soil.

0.04, the typical value of world-wide fallout in the environment after the SNAP-9A satellite accident in 1964.[29] Also, the mean activity ratio of ^{241}Pu/^{239,240}Pu was found to be 4.1. This value is in good agreement with the recently reported activity ratio of ^{241}Pu/^{239,240}Pu influenced by the fallout from nuclear weapon testings.[30] Also, the activity ratios of ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu in lichens and mosses were found to be similar to those in soils. Therefore, the contribution of Chernobyl-derived plutonium in Korea was negligible relative to the cumulative depositions derived from weapon testings, considering that the reported value of ^{238}Pu/^{239,240}Pu was 0.42 in the Chernobyl fallout over Germany[31] and that of ^{241}Pu/^{239,240}Pu was 95 in the Chernobyl fallout over Finland.[32]

A typical spectrum obtained by HR-ICP-MS for ^{239}Pu and ^{240}Pu in the forest soil (F3) is shown in *Fig.* 6. The peak of ^{239}Pu was clearly separated from that of ^{240}Pu, although the difference of mass number is only 1. Also, the atomic ratios of ^{240}Pu/^{239}Pu measured by HR-ICP-MS in soils are shown in *Fig.* 7. The atomic ratios of ^{240}Pu/^{239}Pu in the soil were found to be in the narrow range of 0.158-0.224 with a mean value of 0.183. The mean atomic ratio of ^{240}Pu/^{239}Pu in the soil is very close to the value of 0.18 commonly accepted for global fallout from the atmospheric nuclear weapon tests.[33,34] These atomic ratios of ^{240}Pu/^{239}Pu were remarkably lower than those influenced by the Chernobyl accident.[35] However, the atomic ratios of ^{240}Pu/^{239}Pu in the soil were significantly higher than those contaminated by weapon-grade plutonium.[36] Therefore, the atomic ratios of ^{240}Pu/^{239}Pu is useful as an “indicator” to discriminate the origin of Pu from different sources.

4. Conclusions

In this work the cumulative depositions of fallout Pu were measured in the soil and lichen at present time and investigated characteristics of fallout Pu deposits in the soil. From this present investigation, the following conclusions are drawn.

The average ^{239,240}Pu deposition of in the forest was two times higher than that in the hill. The ^{239,240}Pu deposition in the cultivated soil were significantly lower than those in the hill or forest. The cumulative depositions of fallout Pu in the volcanic ash soil were much higher than those in forest and hill soils. The measured concentrations of Pu isotopes in lichens and mosses showed large variations. The concentrations of fallout Pu in lichens were higher than those in mosses.

From depth profiles, it was found that most of the fallout Pu has been accumulated in the layer of top 10 cm layer of soil. The concentrations of ^{239,240}Pu in soils showed the tendency of decreasing exponentially with increasing soil depth. Among parameters affecting the cumulative deposition of fallout Pu, organic substances and rainfall play an important role in the retention and relative mobility of fallout Pu in the soil.

From the sequential leaching experiments, ^{239,240}Pu was associated predominantly with the "organic" and "oxy-hydroxy" fractions. This result may be elucidated the migration of fallout Pu in the soil.

The activity ratios of ^{238}Pu/^{239,240}Pu and ^{241}Pu/^{239,240}Pu in soils, lichens and mosses and the atomic ratios of ^{240}Pu/^{239}Pu in soils are close to those observed in the global fallout of nuclear weapons testing.

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