Characteristics of Fall-out Plutonium in Soil

M. YAMAMOTO, T. TANII and M. SAKANOUE*

School of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa 920-11, Japan
*Low Level Radioactivity Laboratory, Kanazawa University
Tatsunokuchi-machi, Nomi-gun, Ishikawa Pref. 923-12, Japan
(Received September 2, 1980)

Plutonium in Soil/Soil Organic Materials/Leaching of Plutonium

Two kinds of samples have been tested to investigate the adsorption of plutonium in soil under natural conditions. In a soil sample containing only about 5% of organic materials, no significant leaching of plutonium was observed with three kinds of extractants, namely, 1N-ammonium acetate, 5%-EDTA and 0.1N-sodium citrate, while some plutonium was leached with 0.1N-citric acid. The results of solubility tests made with natural soil organic acids, namely, humic and fulvic acids, showed that solubilization of plutonium by these acids is unlikely to occur in this soil sample. On the other hand, in another soil sample rich in organic materials (about 50%), significant leaching of plutonium was observed with all the extractants tested. The leaching of plutonium was especially very high with 0.1N-sodium citrate (about 60%); sodium citrate showing an initial pH of 8.4 probably solubilized some of organic materials present. Experiments made on extraction of organic materials with alkali solution also suggested that as much as 60-70% of plutonium in this soil sample was associated with some organic acids, whose carbon content was assumed to be 30-40% of the total organic carbon in the soil sample. This finding is very important from a view point of the uptake of plutonium by plant because plutonium associated with such organic acids is presumed to exist abundantly in cultivated soils which are quite rich in organic materials.

INTRODUCTION

Among various long-lived alpha emitters present in the environment, plutonium isotopes are especially important because they are very radiotoxic. Although extensive studies have been made on the distribution and the depth profiles of plutonium in soils, there have been only a few reports which studied the fractionation of adsorbed plutonium into various soil constituents.

It is well known that humic acids present in soil or water enhance the solubilities of both metal ions and hydrous oxide, and that chelate organic materials play an important role in the uptake of trace metals by plant. Trace characterization study to elucidate mainly the chemical state of trace element in a sample has been emphasized for the environmental contamination with heavy metallic elements. Such a trace
characterization study over soil plutonium is now intensively desired to predict its distribution and biological availability.

This paper describes the characteristics of fall-out plutonium in soil under natural conditions. Soil samples accumulating rather high levels of fall-out radionuclides were collected in the coastal area of Japan Sea where much snow-fall occurs in winter season, and solubilities of plutonium in these samples with natural organic acids, mineral acids and chelate agents were examined. Furthermore, the fraction of plutonium associated with organic materials in soil samples was estimated.

SAMPLES AND EXPERIMENTAL METHODS

Sample

Surface soil samples were collected at two places where relatively high levels of fall-out radionuclides were accumulated. One sample was collected from the ground surface under the eaves of temple at Kohno (35°30'N, 135°29'E) in southern part of Fukui Pref. Snow and rain water from the large roof must pass over the ground surface. Another sample was collected from a moderately flat ridge about 1100 m above sea level at Mt. Kanmuri (35°46'N, 136°25'E) in Fukui Pref. The soil from Kohno contains only about 5% organic materials, and against this, the soil from Mt. Kanmuri has an exceptionally high concentration of organic materials, reaching about 50%. Besides these soil samples, a sea sediment sample was collected from the sea floor of Nyu Bay (35°42'N, 135°58'E) in Fukui Pref. All of these samples are the same as those described in previous report, in which are shown the depth profiles and the particle size dependences of several fall-out radionuclides, such as $^{239,240}$Pu, $^{241}$Am and $^{137}$Cs. After large rocks and plant fragments were removed, the soil samples were air-dried and then were sieved through a 500-μm screen. Kohno sample was furthermore sieved through a 250-μm screen to remove finer pebbles. As for sea sediment, the fraction below 37 μm was used for study because previous work had shown that plutonium was concentrated in the smaller size fractions. Each specimen was blended for 24 hr by a ball-mill, and the following contents of plutonium ($^{239,240}$Pu) were found respectively for each sample, that is, 0.108 pCi/g. dry for Kohno sample, 0.495 pCi/g. dry for Mt. Kanmuri sample and 0.188 pCi/g. dry for Nyu Bay sample.

| Element   | Mt. Kanmuri | Kohno |
|-----------|-------------|-------|
|           | H. A        | F. A  | H. A |
| Carbon    | 51.20       | 42.45 | 47.69 |
| Hydrogen  | 4.54        | 3.33  | 4.22 |
| Oxygen    | 40.12       | 47.64 | 43.53 |
| Nitrogen  | 3.77        | 2.28  | 3.83 |
| Ash       | 0.37        | 4.30  | 0.73 |
The humic and fulvic acids used for the leaching tests of plutonium in soil sample were extracted from the two kinds of soils. The method of extraction and purification was reported in detail elsewhere. Elementary compositions of humic and fulvic acids and their ash contents are shown in Table 1. Infrared spectra of these organic acids were measured. They were similar to those reported by Kumada and Aizawa.

General Experimental Method

1) Solubility of soil plutonium: Solubility of soil plutonium with several selected reagents were tested in the following way. Each soil or sediment sample of 10 g was suspended in the reagent solution of 100 and/or 300 ml in a polyethylene bottle. The bottle was sealed, and then was continuously shaken for 20 hr (72 and 300 hr partly) being kept at 27±1°C by a thermostat. After this procedure, the suspended soil was separated by centrifugation at 36,000 rpm for 60 min. This ultra-centrifugation makes even colloidal clay particle precipitate. Since the plutonium content in the leachate was expected to be extremely low, the sedimentary residue obtained was subjected to a radiochemical analysis for $^{239, 240}$Pu.

In the leaching experiments with soil organic acids, each 10 g of the Khono sample was suspended in the organic acids solution of 100 ml or 150 ml in the polyethylene bottle. The bottle was sealed, and then was continuously shaken for 20 to 330 hr being kept at 27±1°C by a thermostat. The sedimentary residue obtained by centrifugation was subjected to a radiochemical analysis for $^{239, 240}$Pu. The content of organic acid in the leachate was determined spectrophotometrically, and pH determination was also made.

2) Plutonium associated with soil organic acid: To ascertain the presence of plutonium in organic fraction, soil samples were treated with alkali to extract organic acids. Both 0.1 N-sodium hydroxide solution and mixed solution of 0.1 N-sodium hydroxide and 0.1 N-sodium pyrophosphate (expressed as mixed solution hereinafter) were used as reference extractant for organic acids. The flow scheme of this experiment is shown in Fig. 1. The resultant three fractions, namely, the sedimentary residue, humic and fulvic acid fractions, were subjected to a radiochemical analysis for $^{239, 240}$Pu and the determination of the amount of total organic carbon as follows.

3) Analyses of $^{239, 240}$Pu and total organic carbon in each fraction: The following procedure of the radiochemical analysis of plutonium is almost the same as that described in a previous report. Plutonium in the sedimentary residue was leached out by hot concentrated nitric acid after adding the known amount of $^{236}$Pu as a yield tracer, and then isolated from chemical elements other than plutonium by means of an anion exchange resin in the nitrate form. The plutonium are electroplated onto a stainless steel disc cathode. As for the solutions of humic and fulvic acid fractions, these solutions were heated almost to dryness, and then decomposed by nitric acid and hydrogen peroxide. The resultant residue was treated with the same manner as the sedimentary residue. The amount of $^{239, 240}$Pu on the electroplated disc was measured by alpha spectrometry using a surface barrier type of Si(Au) detector. The chemical yield of
$^{239,240}$Pu was determined from the recovery of $^{239}$Pu.

The amount of total organic carbon in sedimentary residue, and both humic and fulvic acid fractions were determined by Tyulin's method\textsuperscript{19}.

RESULTS AND DISCUSSION

1) Solubility of plutonium in soil and sediment

For the purpose of clarifying the nature of plutonium adsorbed in soil or sediment matrices, a series of extraction experiments were carried out using several leaching reagents. The leaching experiments with 1N-ammonium acetate would provide information about plutonium taking an exchangeable form. On the other hand, since organic reagents such as EDTA (Ethylenediaminetetraacetic acid) and citric acid make a organic complex with plutonium strongly, the leaching experiments with these reagents would provide information about whether the solubilization of plutonium is caused or not by similar complexing materials present in soil or sediment. As sodium citrate solution at...
pH of 8.4 suppresses the decomposition of carbonate\(^{14}\), comparison of the result of extraction experiment obtained using sodium citrate with that obtained using citric acid would provide information about whether plutonium carbonate exists or not. The results of the extraction experiments are given in Table 2 in terms of the plutonium activity ratio of the sedimentary residue obtained after extraction to the original sample.

**Table 2.**

Activity Ratio of Plutonium of the Sedimentary Residue obtained after Extraction to the Original Soil or Sediment

| Location | Extractant Volume (ml) | Activity Ratio of the unextractable Plutonium |
|----------|------------------------|-----------------------------------------------|
|          |                        | Ammonium Acetate | EDTA | Citric Acid | Sodium Citrate |
| Pu-239,240 |                        | IN: pH=7.0 | 5%: pH=7.0 | 0.1N: pH=2.4 | 0.1N: pH=8.4 |
| Kohno    | 100                    | 1.01/7 (6.7) | 0.94/7 (6.8) | 0.85/8 (3.0) | 0.99/8 (7.6) |
| Sep. 1978| 300                    | 1.01/8 (6.9) | 0.94/8 (7.0) | 0.84/8 (2.8) | 0.97/8 (7.4) |
| Surface Soil 0.108/4 pCi/g (<250 μm) | 100 | 0.62/6 (2.6)* |     |     |     |
|          | 100                    | 0.62/7 (2.5)** |     |     |     |
| Mt. Kanmuri | 100                | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |
| May 1978 | 100                    | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |
| Surface Soil 0.046/25 pCi/g (<500 μm) | 100 | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |
| Nyo Bay | 100                    | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |
| Dec. 1975 | 100                | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |
| Sediment 0.188/9 pCi/g (<37 μm) | 100 | 0.86/8 (6.1) | 0.71/8 (6.4) | 0.72/8 (2.5) | 0.33/9 (5.6) |

The number behind slant denotes the statistical error originating from counting: 1.01/7 = 1.01 ± 0.07. The value of pH after leaching is given in the parenthesis. *: 72 hr, **: 300 hr.

For Kohno sample, no significant leaching of plutonium was found in the extractions with ammonium acetate, EDTA and sodium citrate. The results obtained with 100 ml extractant were quite similar to those obtained with 300 ml extractant. The extraction with citric acid showed that about 30% of plutonium was leached by 72 hr extraction, and no increase was observed in further 300 hr extraction. These results suggest that plutonium in Kohno sample doesn't take exchangeable form but is likely to be in carbonate matrices. The slight solubility of plutonium with citric acid may suggest the presence of plutonium in the form solubilized with such a similar complexing materials present in soil.

On the other hand, in the case of Mt. Kanmuri sample rich in organic materials, leaching of plutonium was higher for all the reagents tested, especially much higher for sodium citrate, than in the case of Kohno sample. In the case of the extraction with sodium citrate, pH values in the suspended solutions from Kohno sample (pH: 7.6) and Mt. Kanmuri sample (pH: 5.6) were different. The supernatant solutions obtained
with ammonium acetate, EDTA and citric acid were colored light brown, while that with sodium citrate was colored dark brown. The prominently low pH value may be due to the fact that sodium citrate in an initial pH of 8.4 solubilizes some of the organic materials. From the observation that as much as 60% of plutonium was leached with sodium citrate by shaking for a short time (20 hr), it is considered that a part of plutonium present in this sample was associated with organic materials. This problem is discussed further in the following section.

For the sea sediment from Nyu Bay, ammonium acetate didn't leach any plutonium. This fact suggests that plutonium in the sediment doesn't take exchangeable form. The complexing with EDTA or citric acid leaches about 40-50 of plutonium from the sediment, but sodium citrate doesn't leach plutonium. Significantly different results were obtained for the extractions with citric acid and with sodium citrate. This suggests that some plutonium is in carbonate matrices. The results obtained by complexing reagents suggest that the solubilization of plutonium adsorbed on sediment may occur with similar complexing materials present in the marine environment.

In all cases, plutonium in soil and sediment is unlikely to be present in the simple exchangeable form. The nature of fall-out plutonium adsorbed on soil surface is influenced largely by the physico-chemical properties of soil, and, furthermore, chemical and biochemical changes taking place in the environment. On the basis of the data from two kinds of soils, one might conclude that amount of organic materials in soil have an important influence on the nature of plutonium in soil under natural conditions.

2) Leaching of plutonium with natural organic acids

In contrast with the data as mentioned above, the data on the leaching experiments made with natural soil organic acids seems to be very interesting to study the migration of plutonium in soil. For this experiments, Kohno sample containing only a little organic materials was used, because plutonium originally bound to the organic materials might be leached if the experiments is made with Mt. Kamnuri sample rich in organic materials. The results of a series of leaching experiments with 100 ppm fulvic acid are summarized in Fig. 2 along with those with 1000 ppm humic and fulvic acids.

As seen in Fig. 2, the fulvic acid doesn't leach the plutonium in soil under the condition studied. The value of pH in suspension didn't change so much because of the buffering action of soil. As shown in the lower part of this Fig., the fulvic acid content in supernatant solution obtained by ultra-centrifugation decreased to 30% of the added fulvic acid after 20 hr. And then the content decreased slightly and reached about 10% of the original value after 330 hr. The similar decreases were also observed by the leaching experiments with 1000 ppm humic and fulvic acids for 160 hr period. Since humic and fulvic acids are adsorbed scarcely on polyethylene bottle, these decreases of organic acids are mainly due to the coagulation and the sorption on the soil. Therefore, even if plutonium in soil should form soluble complex with organic acids and may be dissolved into the solution, such complex seems to be removed soon from the solution by coagulation and sorption on soil. These results are consistent with
those obtained by the leaching test of plutonium and americium in Rocky Flats soil sample with fulvic acid reported previously by Cleveland and Rees15'. However, it may not be ruled out the possibility of solubilization of plutonium for longer period of contact.

3) Plutonium associated with natural organic acids

From the above mentioned point of view, it is important to ascertain whether plutonium exists in organic form or not under natural conditions. The two kinds of soil samples were treated with both 0.1N-sodium hydroxide solution and the mixed solution to extract organic acids. As seen in Fig. 3, showing the percentages of plutonium and total organic carbon in each fraction, plutonium was detected in both humic and fulvic fractions of two kinds of soil samples. For Kohno sample by leaching with sodium hydroxide or the mixed solution, 4.3% or 6.8% of the total plutonium was found respectively for the organic fractions, which corresponded to 35% or 39% of the total organic carbon in original soil. On the other hand, for Mt. Kanmuri sample by leaching with sodium hydroxide or the mixed solution, as much as 72% or 61% of the total plutonium was found respectively for the organic fractions, which corresponded to 33% or 41% of the total organic carbon in original soil. Though the large difference isn't clearly observed in leaching of plutonium and organic acids between with sodium hydroxide and with the mixed solution, the leaching with the mixed solution tends to increase the plutonium amount in fulvic fraction, and against this, to decrease the plutonium amount in humic fraction. This may be explained by the fact that plutonium is liable to form complexes with phosphate ions in the mixed solution. Taking into account the results of these leaching experiments, it may be concluded that these experiments show the
presence of plutonium bound to organic acids in soil, especially in Mt. Kanmuri sample.

For the sediment from Nyu Bay, 6.5% of plutonium was found in the leaching fraction with 0.5%-sodium hydroxide solution, although the leaching of plutonium wasn't observed with 30%-hydrogen peroxide.

As for the presence of plutonium-organic complex in soil, there are some reports by using solid chelating resin (Chelex 100) and DTPA (Diethyleneetriaminepentaacetic acid). Such studies have also shown the evidence that a part of plutonium present in soil was in organic form. However, it has not yet been clarified how much fraction of plutonium is associated with the organic materials. Therefore, studies on this point must be made furthermore. In this aspect, it is particularly interesting that as much as 60-70% of plutonium in Mt. Kanmuri sample is associated with organic acids. Studies for cultivated soils rich in organic materials seem to be necessary to understand how much organic form of plutonium become available to plant with time.

**Fig. 3.** Distributions (%) of plutonium and total organic carbon in each fraction, that is, sedimentary residue (S.R), humic acid (H.A) and fulvic acid (F.A) fractions.
ACKNOWLEDGEMENT

The authors wish to thank Mr. T. Kitagawa, Mr. S. Igarashi and Mr. H. Takayama. Division of Radioactivity, Fukui Prefectural Institute of Public Health, for supplying the soil sample of Mt. Kanmuri and for measuring a part of plutonium. This work was supported by a Grant in Aid for Scientific Research, Ministry of Education, Science and Culture (1979).

REFERENCES

1. J. C. Nenot and J. W. Stather (1979) The toxicity of plutonium, americium and curium. Pergamon Press.
2. J. H. Harley (1979) Plutonium in the environment—A Review. J. Radiat. Res., 21: 83-104.
3. E. A. Bondietti, S. A. Reynolds and M. H. Shanks (1976) Interaction of plutonium with complexing substances in soils and natural waters. In: Transuranium Nuclides in the Environment (IAEA-SM-199) : 273-287.
4. M. Schnitzer and S. M. Khan (1972) Humic substances in the environment. Marcel Dekker, New York, N.Y.
5. H. L. Ong and R. E. Bisoue (1968) Coagulation of humic colloids by metal ions. Soil Sci., 106: 220-224.
6. G. L. Picard and G. T. Felbeck, Jb (1976) The complexation of iron by marine humic acid. Geochim. Cosmochim. Acta, 40: 1347-1350.
7. Trace Analysis—A New Design of Submicro Analysis (1978) A special issue of KAGAKU, 78/November, Kagaku-Dōzin (in Japanese).
8. M. Yamamoto, S. Yamamori, K. Komura and M. Skanoue (1980) Behavior of plutonium and americium in soil. J. Radiat. Res., 21: 204-212.
9. M. Yamamoto, M. Matsui, S. Igarasi, M. Yoshioka, H. Hayakawa and T. Kitagawa (1979) Distribution and behavior of \(^{239}\text{Pu}\), \(^{137}\text{Cs}\) and \(^{60}\text{Co}\) in the sediment at Urazoko Bay. J. Radiat. Res., 20: 264-275.
10. E. L. Bertha and G. R. Choppin (1977) Interaction of humic acids with Eu (III) and Am (III). J. Inorg. Nucl. Chem., 40: 655-658.
11. K. Kumada and K. Aizawa (1958) The infra-red spectra of humic acids. Soil Plant Food, 3: 152-159.
12. K. Kumada and K. Aizawa (1959) The infra-red spectra of soil components. Soil Plant Food, 4: 181-188.
13. Methods of soil analysis. Part 2: Chemical and microbiological property. (1965) American Society of Agronomy, Inc., Madison, Wisconsin.
14. T. Tamura (1976) Physical and chemical characteristics of plutonium in existing contaminated soils and sediments. In: Transuranium Nuclides in the Environment (IAEA-SM-199) : 213-219.
15. J. M. Cleveland and T. F. Rees (1976) Investigation of solubilization of plutonium and americium in soil by natural humic compounds. Environ. Sci. Tech., 10: 802-806.
16. M. Yamamoto and T. Kitagawa (1978) The concentrations of \(^{239,240}\text{Pu}\) and \(^{134}\text{Cs}\) in sediments. Report of Fukui Prefectural Institute of Public Health, 14: 30-46 (in Japanese)