

Organic Association of the Fallout radionuclides in the Soil

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ABSTRACT

In order to investigate organic association of fallout cesium, strontium and plutonium in the soil, soil samples influenced by fallout from nuclear weapon testings were treated with alkali (0.1 M-sodium hydroxide solution) to extract organic acids. After extraction, the resultant three fractions (*sedimentary residue*, humic and fulvic acid fractions) were subjected to the γ -ray spectrometric analysis for ^{137}Cs , and radiochemical analysis for ^{90}Sr and $^{239,240}\text{Pu}$. Alkali extraction experiments showed that a lot of $^{239,240}\text{Pu}$ was extracted to organic acids from the soil samples, whereas most of ^{137}Cs and ^{90}Sr remained in residual fraction. Less than 10% of the total ^{137}Cs and ^{90}Sr was found in the organic fraction. The concentrations of ^{137}Cs and ^{90}Sr associated with humic fractions were higher than those with the corresponding fulvic fractions. It was found that more than 40% of the total $^{239,240}\text{Pu}$ was associated with the organic fraction of soils. In contrast with ^{137}Cs and ^{90}Sr , $^{239,240}\text{Pu}$ associated with fulvic fractions was much higher than in humic fractions.

1. INTRODUCTION

Most of the fallout nuclides was relatively strong associated with silicate

materials. Though the fallout radionuclides associated organic substances were small, organic substances is very important in understanding the behavior and characteristics of fallout Pu in soil under natural condition, because it affected the retention and migration of fallout Pu under actual environment.

There are a variety of organic compound in soil. The majority of organic compounds found in soils are humic substances, which are formed through an ill-defined process that depends on several parameters like climate, parent materials, vegetation, microbial flora.[1]

Humic substances are complex mixtures of high molecular weight organic species of unknown structure. They are further classified into three fractions according to their solubilities in aqueous solutions of different acidities. Fulvic acid are soluble at all pH's; humic acids are soluble at high pH but insoluble at low pH. Humic acid and fulvic acid are similar structurally, differing mainly by virtue of the higher molecular weight (humic acid) and greater number of functional groups like carboxyls (fulvic acid).

Of importance in the migration of radionuclides in geological media is the strong complexing and redox interaction of humic materials to metal ions. However, the quantitative investigations of complexes between the humic and fulvic acid and the fallout radionuclides are very difficult because the humic and fulvic acid is a heterogeneous polyelectrolytic materials, and characteristics of humic and fulvic acid are dependent on its original source and the methods of isolation and purification. Also, it is very difficult to predict the behavior and characteristics of fallout Pu, unlike most fission products, in soil on the basis of their known chemical properties, because they have no stable counterparts, and can exist simultaneously in several valences.

In this study, organic association of the fallout radionuclides under nature condition is investigated. These results could elucidate the migration of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$ in soils under natural condition.

2. EXPERIMENTAL SECTION

2.1 Extraction of humic and fulvic fraction from the soil

To ascertain the presence of fallout radionuclides in soil organic fraction, soil samples were treated with alkali to extract organic acids. 40 g of soil was mixed with 400 ml of 0.1 M-sodium hydroxide solution in a polyethylene bottle. The resultant three fractions, namely, the sedimentary residue, humic and fulvic acid fractions, were subjected to a radiochemical analysis for ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$.

2.2 Determination of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$

^{137}Cs was analyzed by γ -ray spectrometric analysis. A HPGe detector with counting efficiency of 25 %, FWHM of 1.7 KeV was used. The counting efficiency was calibrated by using the mixed sources (Amersham, UK) in suitable substrates and geometries. The corresponding γ -ray spectra were analyzed using the Omnigam Software.

After the γ -ray spectrometry, the resultant three fractions for $^{239,240}\text{Pu}$ and ^{90}Sr analysis were calcined at 550°C for 24 h to eliminate organic matter. $^{239,240}\text{Pu}$ in the calcined samples was dissolved in nitric acid and purified by TOPO extraction and anion exchange[2]. Finally, $^{239,240}\text{Pu}$ was electrodeposited from HCl/oxalate solution on a polished stainless steel disc and measured by α -ray spectrometry.

Also ^{90}Sr in the calcined samples was extracted using Crown Ether/Chloroform[3]. The β -activity measured in a continuous flow gas proportional counter calibrated with a ^{90}Sr and ^{90}Y standard.

3. RESULTS AND DISCUSSIONS

The results of the concentration of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$ in the Volcanic and Shale soil, and leaching experiments using 0.1 M-sodium hydroxide are summarized

in Table 1. In case of the volcanic soil 1 and 2 in Cheju island, the concentration of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$ are 2 or 3 times higher than that in other forest site. This result is explained by geological and geographical location of sampling. Cheju island has more precipitation than any other area. When rain falls on the volcanic soil which has the porosity and permeability of the lavas, it easily percolate on the volcanic soil. The loss of nuclides by rainwater rolling off on the volcanic soil is smaller than that on other soil. Also the organic matter (more than 40 %) forms complexes with fallout radionuclides such as plutonium compound and fix fallout radionuclides in the soil[4].

As a result of leaching experiments using 0.1 M-sodium hydroxide, the observed order of percentage activity in the Residue fraction is:

$$^{137}\text{Cs} > ^{90}\text{Sr} > ^{239,240}\text{Pu}$$

The above results show that some inorganic components of soil, particularly clay minerals such as mica and kaolin, have a large capacity of adsorbing and fixing Cs in the soil and thereby ^{137}Cs once adsorbed on the soil particle is very hard to be removed from the soil by using the leaching reagent.

It is interesting to compare the concentrations of ^{137}Cs , ^{90}Sr and $^{239,240}\text{Pu}$ for the Humic and Fulvic fraction, since the concentration of the fallout radionuclide in each fraction could deduce the relative binding site between humic and fulvic acid and the fallout radionuclide. As shown in Table 1, the concentrations of ^{137}Cs and ^{90}Sr in the Humic fraction are higher than that in the Fulvic fraction, though the concentrations of ^{137}Cs and ^{90}Sr in the Humic and Fulvic fraction are low. But the concentrations of $^{239,240}\text{Pu}$ in the Fulvic fraction is about two times higher than those in the Humic fraction. The above result is explained by ionic size of Cs^+ , Sr^{2+} and Pu^{4+} and physico-chemical characteristics of humic and fulvic acid. Generally, the hydration energy of Pu^{4+} (ionic radius : 0.90 Å) is higher than that of Cs^+ (ionic

radius : 1.84 Å) and Sr²⁺ (ionic radius : 1.27 Å), since the hydration energy is inversely proportional to the radius. The hydrated Pu compound (Pu(H₂O)₆⁴⁺) is so large in size that it is relatively adsorbed on the fulvic acid, because the humic acid is more bulky than the fulvic acid that steric effect keep from binding with bulky hydrated Pu compound. Also the PEC (proton exchange capacity) in the fulvic acid is about two times higher than that in the humic acid[5]. This means that the concentration of acidic functional groups of fulvic acid like carboxyls is much higher than those of the corresponding humic acid. Therefore, fallout Pu associated in fulvic acid is much higher than that in humic acid, as fulvic acid have more binding site like carboxyls than humic acid. However, though the percentage activity is very low, Cs⁺ ion is more adsorbed on the humic fraction than the fulvic fraction, because the higher molecular weights of the humic acid than that of the fulvic acid tend to trap small Cs⁺ ion like weak electrostatic force in humic acid structure.

4. REFERENCES

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Table 1. Concentration of ^{137}Cs , $^{239,240}\text{Pu}$ and ^{90}Sr in humic fraction, fulvic fraction and residue.

Soil Type	Fraction	Concentration (Bq kg ⁻¹)					
		^{137}Cs	^{90}Sr	$^{239,240}\text{Pu}$	^{137}Cs	^{90}Sr	$^{239,240}\text{Pu}$
Volcanic 1 (0~5 cm)	Total	211.5	33.8	6.19	6.26	0.029	0.183
	Humic	7.90 (3.7) ^a	7.57 (22) ^a	0.96 (16) ^a	1.04	0.122	0.127
	Fulvic	2.73 (1.3)	4.33 (13)	1.60 (26)	0.51	0.586	0.370
	Residue	188.2 (89)	24.6 (73)	3.45 (56)	7.65	0.018	0.140
Volcanic 2 (0~5 cm)	Total	154.4	36.8	4.13	4.19	0.027	0.112
	Humic	5.54 (3.6) ^a	- _b	0.41 (10) ^a	- _b	0.074	- _b
	Fulvic	1.84 (1.2)	-	0.63 (15)	-	0.342	-
	Residue	149.5 (97)	-	2.99 (72)	-	0.020	-
Shale (0~4 cm)	Total	78.9	34.4	1.82	2.29	0.023	0.053
	Humic	4.51 (5.7) ^a	3.65 (11) ^a	0.22 (12) ^a	0.81	0.049	0.060
	Fulvic	1.28 (1.6)	2.24 (7)	0.31 (17)	0.57	0.242	0.138
	Residue	71.5 (91)	25.7 (75)	1.19 (65)	3.29	0.017	0.055

a : Percentage activity of each fraction to total activity

b: Analyzing