

## Strong association of fallout plutonium with humic and fulvic acid as compared to uranium and $^{137}\text{Cs}$ in Nishiyama soils from Nagasaki, Japan

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To investigate the formation of mobile organic plutonium, we analyzed the plutonium contents of the fulvic (FA) and humic (HA) acids from the soil samples obtained at Nishiyama, Nagasaki, Japan. The percentages of the plutonium bound strongly to HA and to FA vs. the total plutonium in the soil were 5–10% and 1%, respectively, at the depth of 0–0.1 m, much higher values than those of  $^{137}\text{Cs}$  and uranium. After being weathered for 51 years under a temperate climate, the initial high-fired oxides of fallout plutonium have become as chemically reactive plutonium from nuclear fuel reprocessing plants.

### Introduction

Fifty-two years have passed since a plutonium bomb (Pu-bomb) was dropped on the rich temperate ecosystem of Nagasaki, Japan in 1945. After its detonation, radioactive fallout consisting of unexpended plutonium and fission products was deposited by “black rain”, the highest fallout deposition rate being in the Nishiyama area. As a consequence, 98 % of the  $^{239+240}\text{Pu}$  and 50% of the  $^{137}\text{Cs}$  in Nishiyama soil samples examined in 1990 originated in the Pu-bomb.<sup>20</sup>

We have investigated the migration of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  released from the Nagasaki Pu-bomb in the geosphere,<sup>28</sup> hydrosphere,<sup>27</sup> and regional<sup>18,19</sup> and global<sup>20,22</sup> levels. The distributions of the radionuclides emitted from this bomb to the environment have been well clarified by these investigations. Unresolved problems concerning the mechanisms which govern the migration and speciation of the fallout radionuclides in the environment, however, remain.

Previous measurements showed that a small portion of the  $^{239+240}\text{Pu}$  underwent very low sorption by the Nishiyama soil;<sup>28</sup> 3% of the  $^{239+240}\text{Pu}$  moved downward a maximum of 4 m in the soil profile. In contrast, the downward movement of  $^{137}\text{Cs}$  in the same soil profile was less than 0.4 m.

Several mechanisms cause fast migration of Pu in the environment. Species of Pu that have high mobility in an oxic environment are organic complexes of tetravalent Pu (Pu(IV)) or pentavalent Pu (Pu(V)) under the absence of strong complex ligands.<sup>5</sup> LESSIVAGE,<sup>6</sup> the mechanical wash of small mineral particles down the soil profile, also may contribute to the movement of Pu in soils. Translocation of Pu with suspended particles was important in semi-arid, alkaline soils from the Rocky Mountains (USA) in which 90% of Pu in the soil solution was associated with suspended particles

(>0.45  $\mu\text{m}$  diameter). The migration of Pu with suspended particles, however, does not adequately explain the highly mobile Pu fraction in Nishiyama because fallout radionuclide Cs, which is often associated with soil particle fractions with small diameter,<sup>17</sup> did not move with Pu.

The effect of organic ligands and living organisms are probably important in the Nishiyama soil which contains organic matter (organic carbon content 10–15% at 0–4 cm depth) and various microbes.<sup>16</sup> Some bacteria and fungi produced metabolites which formed Pu complexes with increased mobility in soil columns.<sup>40</sup> Low molecular aliphatic acid (e.g., oxalic acid and formic acid)<sup>14</sup> and yellow organic acid<sup>12</sup> with high mobility are found from forest soils. Complex of metal with these organic compounds are important in metal transport within the aquatic environment.<sup>4</sup> The swiftly moving Nishiyama Pu fraction probably is a Pu-organic complex which formed in topsoil rich in organic matter and therefore has little interaction with the soil strata.

The migration of Pu in Nishiyama soil is governed by dynamically varying, complex conditions. Bacterial populations, which decompose soil organic matter to various organic ligands that bind with Pu, are abundant in this soil (more than 100 strains),<sup>16</sup> and may have contributed to the remobilization of Pu. Conversely, the bacterial populations themselves sorb Pu, thereby reducing its movement in the environment.<sup>21</sup>

Actinide elements (Pu, uranium and others) form a complex with the organic matter in natural environments.<sup>3,2,10,26,25,29,32</sup> In contrast,  $^{137}\text{Cs}$  shows little interaction with soil organic materials.<sup>31</sup> High concentrations of  $^{239+240}\text{Pu}$  from atmospheric fallout were found in the humic acid (HA) and fulvic acid (FA) extracted from lake sediments;<sup>3,2</sup> whereas, 3% of the fallout Pu remained in water columns.<sup>39</sup> A high concentration of  $^{239+240}\text{Pu}$ , discharged from the

Sellafield nuclear fuel reprocessing plant, Cumbria, UK, was present in the HA and FA of Cumbrian soil samples.<sup>26</sup> Uranyl ions ( $\text{UO}_2^+$ ) have high ability to form a complex with humic substances in groundwater.<sup>15</sup> Despite all these findings, it is not clear whether such organic actinide complexes remain stable over a period of years in temperate climate ecosystems in which dynamically varying environmental conditions are present.

Identification of the chemical speciation of organic Pu in groundwater is often difficult because of the scarcity of methods to separate such Pu compounds from the environmental samples without changing their original chemical forms. As the mass concentration of Pu is low (e.g.,  $1 \cdot 10^{-9} \text{ kg/m}^3$  of  $^{239+240}\text{Pu}$ ) even in considerably polluted soil solutions,<sup>24</sup> the chemical form of organic Pu in environmental matrices must be investigated by procedures such as molecular size fractionation and association with resins which are not specific to a certain chemical form. For example, a compound which might be a Pu-organic complex was found in the large molecular weight fraction separated from polluted groundwater by ultrafiltration.<sup>5</sup> Radionuclide fractions (e.g.,  $^{60}\text{Co}$ ) separated from groundwater by anion exchange resin are considered to be organic metal complexes with high mobility.<sup>11</sup> Separation techniques such as ultrafiltration and anion-exchange that have been used to separate organic metal compounds are not, however, always specific for organic compounds and may recover inorganic compounds such as clay minerals or iron hydroxide particles which carry Pu and an anionic complex of Pu from groundwater.

Our objective was to evaluate the organically bound  $^{239+240}\text{Pu}$  fraction in Nishiyama soil from Nagasaki, Japan, more than 50 years after the deposition of nuclides. The Nishiyama area has been exploited and is inhabited, and only a small area (a few  $\text{km}^2$ ) remains undisturbed since World War II, but a mobile Pu fraction had been reported there,<sup>28</sup> and artificial Pu that was discharged for first time to a human environment has been preserved. Although the speciation of the Pu in groundwater is of interest as to the mobility of Pu compounds, the Pu concentration in groundwater from Nishiyama was low ( $1 \cdot 10^{-20} \text{ kg/m}^3$  or  $2.4 \cdot 10^{-8} \text{ Bq/m}^3$ ),<sup>28</sup> and direct observation of Pu speciation in the groundwater was difficult due to the restricted obtainable sample size and the detection limit of the alpha-spectrometry analysis. It was more practical to measure the speciation of Pu in the topsoil where the mobile Pu probably was generated than to investigate speciation of Pu in the groundwater. We, therefore, measured  $^{239+240}\text{Pu}$ ,  $^{137}\text{Cs}$  and natural uranium in the HA and FA of soil samples taken from 0–10 cm depth. The association of organic matter with Pu was compared to that for the fallout  $^{137}\text{Cs}$  and natural uranium in the soil. Our findings provide information on variation in the chemical species of Pu with time, and should help to clarify the

mechanisms of mobile Pu formation in natural environments.

## Experimental

### Soil samples

Soils were sampled in October 1996 at Nishiyama, Nagasaki where "black rain" containing high concentrations of fission products and unexpended Pu ( $37.5 \text{ g}$ )<sup>20</sup> had fallen after the 1945 Pu-bomb explosion. The area was destroyed by fire after the detonation of the bomb but its ecosystem recovered relatively quickly, and the sampling area is now covered by an oak forest.

The sampling point is on a moderate slope near the peak of a hill. Soil was collected at two points (stations A and B), from depths of 0 to 0.04 and 0.04 to 0.1 m, after removal of a layer of undecomposed litter. The soil color was dark brown, and the pH was 4.9 to 5.1. Organic carbon in the samples was 10–15% at the 0–0.04 m depth, and 5% at the 0.04–0.1 m depth. Its value was obtained by dry combusting an oven-dried soil sample at  $375 \text{ }^\circ\text{C}$  for 16 hours. The percentage of organic carbon in the soil then was calculated using the empirical equation for Japanese soil:<sup>13</sup>

$$y = 0.458x - 0.4 \quad (1)$$

where  $y$  is the amount of organic carbon in the soil, and  $x$  the decrease in the soil mass after combustion.

### Reagents

The nitric and hydrochloric acids used were of commercial AA-100 grade (prepared for class 100 environments by Tama Chemical Co., Tokyo, Japan), or were purified by sub-boiling in a class 100 environment at the laboratory of the National Research Council, Ottawa, Canada. Hydrofluoric and perchloric acids of AA-100 grade were obtained from Tama Chemical Co. The NaOH used to extract HA was microselect grade (Fluka, Buchs, Switzerland).

### Sample preparation and analysis

The alkaline reagent used to extract the soil organic matter also extracts iron hydroxides and clay minerals which probably contain Pu and other heavy metals owing to their high surface reactivity.<sup>35</sup> Purification of HA and FA to eliminate such iron hydroxide and clay mineral impurities and the preservation of the organically bound Pu fraction were our prime concerns. We, therefore, used repeated centrifugation, filtration, dialysis and acid washes with  $0.1 \text{ M HCl} + 0.3 \text{ M HF}$ . Purification using resins (XAD resins, Roam and Harth Co.) which have an affinity for organic materials was not done in order to avoid the possibility of eliminating the organically bound Pu fraction.

HA was extracted by adding 0.5% NaOH to the soil sample then heating it at 85 °C for 30 minutes under an N<sub>2</sub> atmosphere. To maximize the extraction of organic matter, the NaOH-to-soil ratio was optimized; i.e., 30 ml of 0.5% NaOH was added to a soil sample containing 100 mg organic carbon. The sample size was reduced to 7.5 g if the amount that contained 100 mg of organic carbon exceeded 7.5 g. The total amount of soil subjected to extraction was 80 to 250 g depending on the sampling point and depth (Table 1). The extract was centrifuged twice at 10,000 rpm and 4 °C for 30 minutes. The supernatant was filtered through a 0.45 µm-pore Teflon membrane filter to remove large soil particles, and the filtrate acidified to pH 1 with HCl. The supernatant was condensed in a vacuum then dialyzed until no chloride ion was detected on titration with Ag(NO)<sub>3</sub>, after which it was freeze-dried giving FA as a powder. The precipitate was further purified by again dissolving it in NaOH then re-precipitating it twice with HCl. The final precipitate was shaken with 0.1M HCl + 0.3M HF for a few days to remove any precipitated or loosely bound metals on the HA fraction. Lastly, it was rinsed with double-distilled water, dialyzed until no chloride ion was detected on titration with Ag(NO)<sub>3</sub>, then freeze-dried at 30 °C giving HA as a powder.

The radioactive <sup>137</sup>Cs in the HA, FA and soil samples was analyzed in two parallel high purity germanium semi conductor detectors with anti-coincident background reduction (Canberra-Packard, Ottawa, Canada). <sup>239+240</sup>Pu was analyzed by alpha-particle spectrometry after ashing of the sample at 600 °C, acid leaching, concentration, purification and electroplating on a polished stainless steel disc. The

respective detection limits for <sup>137</sup>Cs and <sup>239+240</sup>Pu in the samples were better than 50 and 0.02 Bq/kg, with a counting error of ±10%.

After decomposition of the soil samples with hydrofluoric, perchloric and nitric acids (HA and FA with nitric acid) in sealed Teflon vessels under microwave irradiation, the natural uranium in the soil samples, HA and FA were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with an HP-4500 machine manufactured by Yokogawa Analytical Systems, Tokyo, Japan. The analytical error was less than 2% for uranium in the standard sediment sample, SRM4354, purchased from the National Institute of Standards and Technology, Gaithersburg, USA. The detection limit for uranium in the ICP-MS measurement was better than 0.4 ppb for HA and FA, and better than 0.04 ppb for the soil.

## Results and discussion

Table 2 shows the concentrations of <sup>239+240</sup>Pu, natural uranium and <sup>137</sup>Cs in the soil, HA and FA samples for depths of 0–0.04 and 0.04–0.1 m at stations A and B in Nishiyama, Nagasaki.

The analytical sensitivities of the alpha-spectrometry measurement of <sup>239+240</sup>Pu and of the ICP-MS measurement of natural uranium were sufficient for the analysis of the samples. <sup>137</sup>Cs was well detected in the soil, but not in the HA and FA samples, in spite of the highly sensitive gamma-spectrometry system with anti-coincident background reduction and the long counting time (2.5–7·10<sup>5</sup> s) used.

Table 1. Amount of soil subjected to extraction, HA and FA obtained, and their ash contents (in %)

Sampling location	Soil subjected to extraction, g	HA obtained, g	Ash content of HA, %	FA obtained, g	Ash content of FA, %
Station A 0–4 cm	84.8	2.39	0.4	0.57	1.2
Station A 4–10 cm	246.4	1.718	1	1.51	12
Station B 0–4 cm	126.4	2.34	0.6	1.22	0.4
Station B 4–10 cm	190.8	1.77	0.6	2.34	8.5

Table 2. Radioactivities (in Bq/kg) of <sup>239+240</sup>Pu, natural uranium and <sup>137</sup>Cs in the soil, humic and fulvic acid samples from Nishiyama, Nagasaki, Japan

Sampling location	<sup>239+240</sup> Pu, Bq/kg			Natural uranium, Bq/kg			<sup>137</sup> Cs, Bq/kg		
	Soil	HA	FA	Soil	HA	FA	Soil	HA	FA
Station A 0–4 cm	9.2	31.0	5.5	34.9	14.8	2.7	103	<9	<47
Station A 4–10 cm	14.9	73.8	16.8	39.2	48.8	63.4	121	<11	<17
Station B 0–4 cm	20.0	96.0	35.1	36.8	20.7	0.7	148	<12	<20
Station B 4–10 cm	21.5	102.8	21.4	39.2	20.1	50.6	108	<18	<8

The  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  concentrations in the Nishiyama soils agreed with previous measurements.<sup>20,28</sup> As shown in Table 2, the respective radioactivity levels of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  were 9–22 and 100–150 Bq/kg in the soil. Background radionuclide concentrations, measured 100 km east of the hypocenter of the Nagasaki Pu-bomb,<sup>20</sup> are 0.04 to 1.02 (average 0.15) Bq/kg for  $^{239+240}\text{Pu}$ , and 20–40 Bq/kg for  $^{137}\text{Cs}$ . The concentrations of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  in the Nishiyama soil, therefore, are 60–150 and 2.5–7.5 times higher than their respective background values. Evidently, radioactive remains of the Pu-bomb have been preserved in the surface soil for more than 50 years.

The de-ashing of HA was successful as the ash content obtained study was 0.4–1% (Table 1). The de-ashing of FA also was successful (ash content 0.4–1%) for the extract from soil sampled at 0–0.04 m depth, but it was not very successful (ash content 9–11%) for the extract from samples at 0.04–0.1 m depth (Table 1) because of the higher mineral content of the soil at that depth.

In spite of the acid wash and other purification procedures used, a high concentration of Pu was retained in HA (31–102 Bq/kg-organic, 3–5 times higher than that in the soil) as compared with uranium (15–55 Bq/kg-organic, about equal to the concentration in the soil) and  $^{137}\text{Cs}$  (not detected, less than 2–9 Bq/kg-organic). The acid wash process with 0.1M HCl + 0.3M HF was expected to remove virtually all the Pu and uranium loosely associated with the organic matter, owing to the exchange with hydronium ions, the dissolution of impurities precipitated on the surface of HA, and the formation of a Pu and uranium fluoride complex. The results indicate that the Pu retained after purification is strongly associated with HA. Part of the Pu detected in the HA probably was incorporated into the organic structure during the formation of HA from litter, therefore it was not readily dissociated in the acid solution.

The soil organic matter with which a considerable amount of  $^{239+240}\text{Pu}$  is associated has been formed by rich litterfalls from the oak forest that covers the sampling sites. Alteration of the landscape, such as destruction of the forest and subsequent depletion of litterfalls would lead to a decrease in soil organic matter and might drastically change the chemical speciation of Pu in the soil.

The amount of Pu in the FA from the 0–0.04 m depth (5.5–35 Bq/kg-organic, about twice the concentration in the soil) was less than in HA, but still considerable, as compared with the amounts of uranium (0.7–2.7 Bq/kg-organic, 20–50 times lower than in the soil) and  $^{137}\text{Cs}$  (not detected, less than 8–50 Bq/kg-organic).

The ratio of the  $^{239+240}\text{Pu}$  concentration in the soil to that in HA, as well as the ratio of the soil to FA is similar to the reported values,<sup>3,26</sup> despite the marked differences in the organic carbon contents of the soils, the initial chemical forms of Pu, the different HA and FA purification procedures (which probably led to the different ash contents of the samples) in those reports. For example, ALBERTS et al.<sup>3</sup> reported that the concentrations of fallout  $^{239+240}\text{Pu}$  in HA (13–15 Bq/kg) extracted from sediments of Lake Michigan were approximately 2–3 times those in the whole sediments, even though the organic carbon content of the sediment was less than 0.5%. The concentrations of  $^{239+240}\text{Pu}$  from the Sellafield nuclear fuel-reprocessing plant found in the HA (31000 Bq/kg) and FA (7700 Bq/kg) extracted from gley soil (organic carbon content 3.0%), respectively, were 5 times and almost the same as that in the soil.<sup>26</sup>

Our comparison shows that the  $^{239+240}\text{Pu}$  in the Nishiyama soil, the initial form of which was probably high-fired oxides<sup>8</sup> formed at several thousand degrees Centigrade in the fireball of the Pu-bomb, has been weathered for more than 50 years under a temperate climate and has become as chemically labile as the Pu discharged from a nuclear fuel reprocessing plant.<sup>3</sup>

Figures 1 and 2, respectively, show (in %) the  $^{239+240}\text{Pu}$ ,  $^{137}\text{Cs}$  and natural uranium fractions in soil bound to HA and to FA. These fractions are averages of calculations made from the following equation at stations A and B in Nishiyama:

$$X = c_{org} / (m/m_{SOM}) / c \quad (2)$$

where  $c_{org}$  is the concentration of the element contained in a unit mass of HA or FA (unit/kg-SOM),  $m_{SOM}$  is the amount of HA (kg) extracted from  $m$  (kg) of a soil sample (Table 1), and  $c$  is the concentration of the element in a unit mass of the soil sample (unit/kg). Data in Figs 1 and 2 are expected to give a low bound value for organically bound fractions because 100% recovery of HA or FA from a soil sample, i.e., obtaining a minimum  $m/m_{SOM}$ , would be difficult, even though our extraction method has been optimized to obtain maximum recovery (see Experimental).

The percent of elements bound to HA or FA is in the descending order of Pu > U >  $^{137}\text{Cs}$  (Figs 1 and 2). Ten percent of the  $^{239+240}\text{Pu}$ , 1% of the uranium and less than 1% of the  $^{137}\text{Cs}$  in the Nishiyama soil were associated with HA; whereas 1% of the  $^{239+240}\text{Pu}$ , 0.05–1% of the uranium and less than 0.2% of the  $^{137}\text{Cs}$  were associated with FA in the same samples.

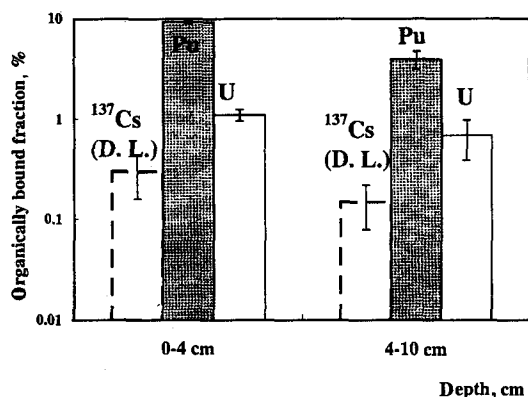


Fig. 1. Fractions (%) of elements bound to humic acid. The percent of <sup>137</sup>Cs shown was estimated from the detection limit of the gamma-ray measurement because no <sup>137</sup>Cs was detected in the humic acid samples during the 3–8 days of counting. D. L.: detection limit

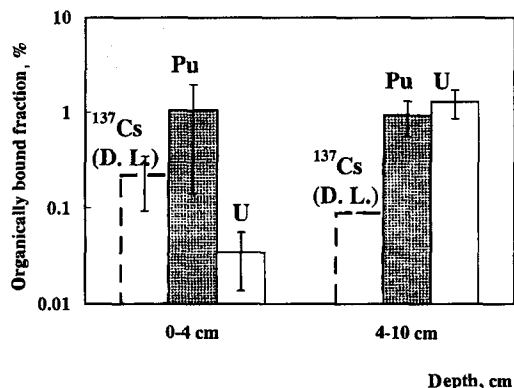


Fig. 2. Fractions (%) of elements bound to fulvic acid. The percent of <sup>137</sup>Cs shown was estimated from the detection limit of the gamma-ray measurement because no <sup>137</sup>Cs was detected in the fulvic acid samples during the 4–8 days of counting. D. L.: detection limit

In FA the association of Pu with impurities was small because the higher ash content of the FA at 0.04–0.1 m depth (9–11%) than at 0–0.04 m depth (0.4–1%) did not affect the percent of the associated Pu (Fig. 2). In contrast, the ratio of the association of uranium with FA was much higher at the 0.04–0.1 m than the 0–0.04 m depth (Fig. 2). These findings show that the association of Pu with impurities (probably iron hydroxides and clay minerals in the soil) in the FA from the 0.04–0.1 m depth, is low compared to that of uranium. A similar conclusion has been reported in Reference 23.

The association of a soil element with soil organic matter probably is governed by a two-step process: (1) dissolution or desorption of the element from a solid to an aqueous phase; and (2) formation of a complex between the element in the aqueous phase and the soil organic matter. If the percentage of an element

associated with the soil organic matter (e.g., Figs 1 and 2) is low, the reason may be that the concentration of the element in the aqueous phase is low or that in that phase the element reacts very little with the soil organic matter.

In our study, Pu and uranium, actinide elements known to have a high affinity for organic matter, had considerably different affinities for soil organic matter. This may be because of the higher affinity of Pu for the HA and FA from Nishiyama, because the Pu from the bomb, probably PuO<sub>2</sub>, was more soluble than uranium which is an impurity in silicate minerals,<sup>30</sup> or because the uranium concentration in the aqueous phase was low due to the higher solid to liquid distribution coefficient of uranium than Pu (although this is contrary to reported results).<sup>36</sup> The mechanisms for these affinities will be clarified in future investigations.

Remobilization of Pu with the downward migration of FA, which contains at least 1% of the Pu in the soil (see Fig. 2), is possible. FA with its low molecular weight is considered more mobile than HA, because, on the basis of Traube's rule, "The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series".<sup>1</sup> Moreover, the sorption of humic substances to lab-synthesized iron minerals is reported to be less significant for smaller-weight molecules.<sup>37,38</sup> The origin of the mobile Pu in the soil, 3% of the total <sup>239+240</sup>Pu deposited in the Nishiyama soil,<sup>28</sup> can be explained by this mechanism. The remobilizations of uranium and <sup>137</sup>Cs with FA would be less significant, because the associations of these elements with FA are lower than the association of Pu.

## Conclusions

The association of <sup>239+240</sup>Pu with HA and FA in the Nishiyama soil of Nagasaki, Japan is marked as compared with the associations of uranium and cesium in samples from the 0–0.1 m depth. At least 5–10% and 1% of the <sup>239+240</sup>Pu and 1% and 0.05–1% of the natural uranium in the soil were strongly associated with HA and FA, respectively, whereas, the <sup>137</sup>Cs bound to HA and FA was negligible.

As we de-ashed the HA by repeated centrifugation, filtration, acid-washes with 0.1M HCl + 0.3M HF and dialysis prior to the radioactivity analysis, the Pu retained in our HA fraction is very strongly associated with the organic ligands in this humic acid.

A comparison of our findings with those of previous reports shows that the Pu in the Nishiyama soil, (the initial form of which probably is a refractory mineral formed at several thousand degrees centigrade in the fireball of the Pu-bomb), has been weathered for more than 50 years under a temperate climate and now is as chemically labile as the Pu discharged from a nuclear-fuel reprocessing plant.<sup>3</sup>

The remobilization of Pu as an FA–Pu complex is possible because the FA from Nishiyama soil contains at least 1% of the Pu in that soil. This can explain the presence of the mobile fraction of Pu previously found in the Nishiyama soil.<sup>28</sup>

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