



Characterization of Pu concentration and its isotopic composition in a reference fallout material

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ABSTRACT

Because there is no reference material for fallout plutonium isotope monitoring, preparation of such a material is necessary for quality control of fallout radionuclides analysis for atmospheric environmental studies. In this work, we report the characterization of Pu activity and its isotopic composition in a reference fallout material prepared by the Meteorological Research Institute (MRI), Japan. This material was prepared from samples collected at 14 stations throughout Japan in 1963–1979, with reference values of ^{137}Cs , ^{90}Sr and $^{239+240}\text{Pu}$ activities. We analyzed the activities of $^{239+240}\text{Pu}$ and ^{241}Pu , and the atom ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ using an isotope dilution sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS). The $^{239+240}\text{Pu}$ activities in this fallout material using acid leaching and total digestion were 6.56 ± 0.20 mBq/g and 6.79 ± 0.16 mBq/g, respectively. Atom ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ were 0.1915 ± 0.0030 and 0.1922 ± 0.0044 , respectively. Both $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios were slightly higher than those of global fallout, which could be attributed to the deposition of fallout radionuclides resulting from the Chinese nuclear weapons tests conducted in the 1970s. The dominant host phases of $^{239+240}\text{Pu}$ were found to be organic matter-sulfides (70%) with a relative high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio, and Fe–Mn oxides (19%) using a sequential extraction method.

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1. Introduction

Plutonium in the environment mainly originates from atmospheric nuclear weapons tests, accidental releases (for example, the Chernobyl nuclear accident in 1986), and nuclear fuel reprocessing. In particular, the global cumulation of $^{239+240}\text{Pu}$ released from atmospheric nuclear explosions is estimated to be 15 PBq since the 1960s (Hirose et al., 2004). After the cessation of atmospheric nuclear weapons tests, $^{239+240}\text{Pu}$ in atmospheric deposition decreased according to stratospheric residence time of radioactive debris. However, a long-term monitoring record of atmospheric deposition of Pu concentration and isotopes in Japan has shown that the decline in the deposition has almost ceased since 1988 (Hirose et al., 2008). Hence, it is obvious that the plutonium is supplied from reservoirs other than the stratosphere. A resuspension process, in which radioactive materials deposited on the ground are suspended

again in the air along with soil particles by storm activity, is suggested as the major one controlling the deposition of Pu as well as other anthropogenic radionuclides (Rosner and Winkler, 2001; Hirose et al., 2003; Igarashi et al., 2003, 2009; Akita et al., 2008; Fujiwara et al., 2007; Fukuyama and Fujiwara, 2008).

As a useful geochemical tracer, Pu isotope ratios have been used in various environmental studies, such as tracing the sources of radioactive contamination (Mitchell et al., 1997; Muramatsu et al., 2001; Ketterer et al., 2004; Yamamoto et al., 2004; Hamilton et al., 2008), revealing the transport process of aerosols in the atmosphere, and studying ongoing environmental changes, for instance, erosion and desertification (Hirose et al., 2003; Choi et al., 2006). Since the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio is characteristic for various Pu sources, information on the activity of Pu as well as the isotopic composition are very important for better understanding resuspension and long-range transport of radioactive materials in the environment. Large-scale aeolian dust events such as *Kosa* which carry many suspended soil particles originating from the Asian desert and arid region has been linked to the deposition of Pu in Japan and Korea since the early 1990s (Hirose et al., 2003). The concentration of Pu in fallout samples collected in both countries showed the maximum value in the spring.

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Since the present environmental radioactivity level is becoming extremely low, quality control in determining the Pu isotopes in fallout samples is increasingly important. So far, there has been no reference material available for fallout Pu isotope ratio analysis. In this work we report the characterization of $^{239+240}\text{Pu}$ activity and its isotope composition ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios) in a reference fallout material prepared by the Meteorological Research Institute (MRI), Japan with reference value of ^{137}Cs , ^{90}Sr and $^{239+240}\text{Pu}$ activities (Otsuji-Hatori et al., 1996). This reference fallout material was obtained from samples which were collected in 1963–1979. Plutonium isotopes were analyzed using isotope dilution SF-ICP-MS combined with a high-efficiency sample introduction system (APEX-Q). For the separation and purification of Pu isotopes, we employed a two-stage anion-exchange chromatography. We used the acid leaching and total digestion methods to compare whether there was any difference in Pu activity and its isotope composition between the two methods. Plutonium in the fallout samples may exist in different oxidation states, which could result in their complexation by a variety of different chemical species, thus affecting their partitioning behavior (Fuger, 1992). In order to identify the solid phase reservoirs of Pu isotopes in the fallout samples for a better understanding of the partitioning behavior of Pu in the environment, the sequential extraction technique described by Tessier et al. (1979) was adopted to determine the major host phases of Pu isotopes in the reference fallout material.

2. Experimental

2.1. Sampling and preparation of the reference material

The reference fallout material was prepared by the Meteorological Research Institute (MRI), Japan to ensure their monitoring quality for the radioactive fallout. Details on the preparation were described previously (Otsuji-Hatori et al., 1996). In brief, monthly atmospheric depositions (total deposition = wet + dry) were collected at 14 sites of the Japan Meteorological Agency (JMA) monitoring network during the period of 1963–1979, using a plastic open surface collector with surface area of 0.5 m². After evaporating to dryness, each sample was subjected to γ -ray measurement, and then about one-third of each sample was used to prepare the reference material. Each sample was combined and dried at 110 °C to remove moisture, then the sample was pulverized in a porcelain rolling pot mill at 2500 rph for about 6 h. After passing through a 150 mesh sieve, the sample was divided into 16 portions (hereafter called splits), and each split was subdivided into about 60 portions (hereafter called numbers). Each number was bottled in a 50 ml vial. In total, about 1000 bottles of reference material, each of which contains 4 g of the sample, were obtained. Numbers 6–30, 12–63, 16–9, 14–8 and 14–59 were used in this study. The contents of stable elements in this reference fallout material were originally measured by ICP-AES or ICP-MS (Otsuji-Hatori et al., 1996). As the data were obtained by the analysis of the sample in a single bottle, the data in Table 1 just give the information on the concentration levels of these elements.

2.2. Determination of Pu isotopes

2.2.1. Instrumentation

To determine Pu isotopes in the reference fallout sample, we used the SF-ICP-MS (Finnigan Element 2, Bremen, Germany) in a low resolution (LR) mode in order to utilize the maximal instrument sensitivity. We used an APEX-Q high-efficiency sample introduction system (Elemental Scientific Inc, Omaha, NE, USA) with membrane desolvation unit (ACM) and a conical concentric nebulizer. Additionally, the normal skimmer cone was replaced by a high-efficiency cone (X-cone, Thermo Finnigan), further increasing the sensitivity of SF-ICP-MS. The details on the optimization of APEX-Q-ICP-SF-MS for determination of Pu isotopes have been described previously (Zheng

Table 1

Concentrations of stable elements in the 'Reference Fallout Material'^a.

Element	Concentration	
	ICP-AES (mg/g)	ICP-MS ($\mu\text{g/g}$)
Be		0.53 ± 0.03
Na	41.45 ± 0.51	
Mg	11.60 ± 0.09	
Al	26.03 ± 0.05	
K	7.58 ± 1.43	
Ca	63.00 ± 0.51	
Ti	11.38 ± 0.07	
Mn	0.80 ± 0.02	
Fe	31.24 ± 0.40	
Cu	8.69 ± 0.03	
Zn	4.51 ± 0.02	
Sr	0.26 ± 0.00	264 ± 2
Cs		5.62 ± 0.05
Ba	0.37 ± 0.00	

^a Data cited from Otsuji-Hatori et al., 1996. Errors are SD of triplicated measurements.

and Yamada, 2006). The activity of $^{239+240}\text{Pu}$ was calculated from the mass concentration obtained by the isotope dilution SF-ICP-MS using the specific activity of each isotope.

2.2.2. Sample preparation for Pu determination

Reference materials, Radionuclides in Pacific Ocean Sediment IAEA-368 (obtained from International Atomic Energy Agency) and Ocean Sediment Radionuclide Standard NIST-4357 (obtained from the National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) were used to validate the analytical method. We employed both acid leaching and total digestion to release Pu isotopes from the reference fallout sample.

2.2.2.1. Acid leaching. Ocean sediment CRM IAEA-368 (ca. 0.1 g), SRM NIST-4357 (ca. 0.7 g) and the reference fallout sample (ca. 0.6 g) were weighed out and spiked with yield tracer ^{242}Pu (1 μg). The dried sample mixed with 50 ml 8 M HNO_3 was heated in a Pyrex beaker on a hotplate (180–200 °C) for at least 4 h. The warm supernatant was filtered through a glass-fiber filter, and the filtrate was heated on a hotplate until a thick, wet paste was obtained. The wet paste was dissolved by concentrated HNO_3 (13.2 M), and then the acidity was adjusted to ca. 8 M HNO_3 by adding de-ionized water. After that 0.2 M NaNO_2 was added, the samples were heated in a water bath at 40 °C for 30 min, the sample was then ready to run onto the first anion-exchange column.

2.2.2.2. Total digestion. Ocean sediment CRM IAEA-368 (ca. 0.1 g), SRM NIST-4357 (ca. 0.3 g) and the reference fallout sample (ca. 0.3 g) were weighed out in 100 ml Teflon beaker and spiked with yield tracer ^{242}Pu (1 μg). A mixture of concentrated HNO_3 (40 ml) and HF (10 ml) was added to each sample, followed by digestion on a hotplate at 180 °C–200 °C. After digestion, the sample was evaporated to dryness, and then to remove any HF, it was heated after adding of 3 ml HClO_4 until the HClO_4 fumed. Next, 3 ml of concentrated HNO_3 were added, and the solution was evaporated to dryness, this step was repeated two times. The dried sample residue was dissolved in 50 ml 1 M HNO_3 , and 4 mg Fe^{2+} (0.2 ml of 20 mg Fe/ml in 1 M HNO_3) were added as carrier. In order to adjust the oxidation of Pu to Pu(III), 2.5 ml of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (80 g/l) were added to the solution. The sample solution was heated on a hotplate at 90 °C for 2 h, and cooled to room temperature. After co-precipitating Pu with $\text{Fe}(\text{OH})_3$, the precipitate was magnetically stirred for 2 h, and then allowed to settle overnight. The supernatant was siphoned from the precipitate and then centrifuged at 3000 rpm for 1 h. The precipitate was dissolved with 1.5 ml concentrated HNO_3 , the solution was added with 50 ml 8 M HNO_3 and 0.4 g NaNO_2 . After heating in a water bath at 40 °C for

15 min, the sample was then ready to run on the first pre-conditioned anion-exchange column.

2.2.2.3. Chromatographic separation and purification of Pu. We employed the same chromatographic separation and purification procedure for the sample solutions obtained from the leaching and total digestion methods. Sample solution was loaded onto the column (AG 1×8 anion-exchange column, 2.5 ml), which was pre-conditioned with 10 ml of 8 M HNO₃–0.2 M NaNO₂. After a sequential washing step with 60 ml 8 M HNO₃ and 50 ml 10 M HCl, Pu was eluted with 50 ml NH₄I (0.1 M)–HCl (8.5 M) and collected in a 100 ml Teflon beaker. The solution was evaporated to dryness, then repeatedly treated with aqua regia (2×1 ml) and concentrated HCl (2×1 ml), respectively. After dissolving in 3 ml HCl–H₂O₂ (100 ml concentrated HCl with the addition of 0.1 ml 30% H₂O₂), the solution was heated in a water bath at 40 °C for 1 h. Then the sample solution was loaded onto the second column (AG-MP-1 M anion-exchange column, 2.5 ml) which was pre-conditioned with 7.5 ml HCl–H₂O₂ solution. After washing with 20 ml 8 M HNO₃, Pu was eluted by 10 ml concentrated HBr. The purified Pu sample solution was heated on a hotplate until a few drops of HBr solution remained, 1 ml of concentrated HNO₃ was added to destroy any HBr, the solution was evaporated to dryness, and then dissolved in 4% HNO₃ (0.75 ml) for SF-ICP-MS analysis. The chemical yield for total Pu obtained by this method was 70 ± 8%.

2.2.3. Sequential extraction

About 1 g reference fallout samples were used to identify the host phases of ²³⁹⁺²⁴⁰Pu. The sequential extraction was carried out according to the method described by Tessier et al (1979). As summarized in Table 2, Pu isotopes were extracted into five fractions: (F1) exchangeable; (F2) bound to carbonate; (F3) bound to Fe–Mn oxides; (F4) bound to organic matter-sulfides; and (F5) residual. After sequential extractions were completed, ²⁴²Pu (1 pg) tracer was added to the obtained fractions. They were evaporated to dryness, and 50 ml 1 M HNO₃ were added. Then, following the Fe(OH)₃ co-precipitation and ion-exchange chromatography chemical procedure described above, the sample was prepared in 4% HNO₃ for Pu isotope analysis using SF-ICP-MS.

3. Results and discussion

The reference fallout material prepared by the MRI consists of fallout material collected in 1963–1979 at 14 sites covering a wide area of Japan. Because the covered area is sufficiently wide, the material represents a fairly average composition of fallout material in Japan (Otsuji-Hatori et al., 1996). The highest yearly global fallout deposition was observed in 1963 due to a series of large-scale atmospheric nuclear tests conducted by the former Soviet Union in

1961–1962. During the period from 1964 to 1980, 22 atmospheric nuclear weapons tests were conducted by China at Lop Nor, and from 1966 to 1974, 41 atmospheric nuclear weapons tests were conducted by France at Mururoa and Fangataufa Atolls in the South Pacific Ocean (UNSCEAR, 2000). About 40% of the samples making up the reference fallout material were collected during 1963–1970. Therefore, this reference fallout material contains an important part of the global fallout originating from the former Soviet Union nuclear detonations, the Chinese atmospheric nuclear weapons tests and the French atmospheric nuclear weapons tests in the South Pacific Ocean, and can be regarded as one representative for fallout radioactivity in Japan since 1963. Precise determination of Pu isotopes in this material could strengthen the quality control for atmospheric radioactivity monitoring and be of benefit to understanding the fallout Pu isotopic signature after 1963, which could provide an important baseline crucial to the assessment of possible future additional non-fallout input Pu into the environment.

In order to obtain precise and accurate Pu activity and its isotope composition in the reference fallout material, the employed analytical methods were validated by the analysis of IAEA-368 and NIST-4357. As summarized in Table 3 (the data are presented with an expanded uncertainty using a coverage factor of 2), for both the HNO₃ extraction and HNO₃–HF–HClO₄ digestion methods, the experimentally established values of ²³⁹⁺²⁴⁰Pu activities (31.8–32.1 mBq/g for IAEA-368, *n* = 3; 9.20–9.44 mBq/g for NIST-4357, *n* = 3) are in good agreement with the certified values (31.0 mBq/g, 95% confidence interval of 29.0–34.0 mBq/g for IAEA-368; 10.4 ± 0.2 mBq/g, 95% confidence interval of 9.2–13.3 mBq/g for NIST-4357). Also, the atom ratios of ²⁴⁰Pu/²³⁹Pu obtained in our study (0.0320 ± 0.0012–0.0320 ± 0.0016 for IAEA-368; 0.2329 ± 0.0130–0.2363 ± 0.0098 for NIST-4357) are in good agreement with the values reported (0.030–0.043 for IAEA-368; 0.233–0.244 for NIST-4357) (Zheng et al., 2004; Kim et al., 2004; Yoshida et al., 2007; Hrnccek et al., 2008). We used quite a small sample size, 0.7 g for acid leaching and 0.3 g for total digestion, the ²³⁹⁺²⁴⁰Pu activities we obtained (9.20–9.44 mBq/g) are still within the 95% confidence interval of 9.2–13.3 mBq/g for NIST-4357, suggesting that due to the good homogeneity of this reference material, small sample size can be used for analysis although it is recommended in the NIST-4357 certificate that a sample size of 10 g be used for comparison with the certified massic activity and uncertainty.

3.1. Pu activity and atom ratio in the reference fallout material

To characterize the Pu isotope composition in the reference fallout material, both acid leaching and HNO₃–HClO₄–HF digestion were conducted for samples from different splits: No. 6–30, No. 12–63, No. 16–9, No. 14–8, and No. 14–59. The results of Pu activities of ²³⁹⁺²⁴⁰Pu and ²⁴¹Pu, and atom ratios of ²⁴⁰Pu/²³⁹Pu and ²⁴¹Pu/²³⁹Pu in the reference fallout material are presented in Table 4. The data are presented with an expanded uncertainty, which includes the uncertainties of sample weight, the amount of ²⁴²Pu tracer and the ICP-MS measurement for Pu isotopes, using a coverage factor of 2. The activities of ²³⁹⁺²⁴⁰Pu in the 5 measured samples range from 6.40 to 6.64 mBq/g, with an average of 6.56 ± 0.20 mBq/g, for the acid leaching method. For the total digestion method, ²³⁹⁺²⁴⁰Pu activities range from 6.66 to 6.85 mBq/g, with an average of 6.79 ± 0.16 mBq/g. The deviations of the data set for acid leaching and total digestion methods are rather small (less than 2%), which indicates good homogeneity of the reference fallout material. For ²⁴¹Pu activities, they range from 12.2 to 13.8 mBq/g, with an average of 12.7 ± 1.4 mBq/g for acid leaching method, and from 10.8 to 13.0 mBq/g, with an average of 12.1 ± 2.2 mBq/g for the total digestion method. Due to the short half-life of ²⁴¹Pu (14.3 y), its determination by ICP-MS has been a great challenge. The counts for ²⁴¹Pu determination are much lower than those of ²³⁹Pu and ²⁴⁰Pu isotopes, which results in

Table 2
Fractions and reagents used for sequential extraction.

Fractions	Extraction reagent	Temperature (°C)	Time (h)
F1 exchangeable	1 M MgCl ₂ , pH 7	Room	1
F2 carbonate	1 M CH ₃ COONa (CH ₃ COOH) ^a	Room	5
F3 Fe–Mn oxides	0.04 M NH ₂ OH·HCl in 25% (V/V) CH ₃ COOH, pH 2 (NaOH) ^a	96	6
F4 organic-sulfides	30% H ₂ O ₂ in 0.02 M HNO ₃ pH 2 (HNO ₃) ^a	85	2
	30% H ₂ O ₂ , pH 2 (HNO ₃) ^a	85	2
	3.2 M CH ₃ COONH ₄ in 20% (V/V) HNO ₃	Room	0.5
F5 residual	HNO ₃ /HF/HClO ₄	200	

^a Reagent used to adjust pH.

Table 3
Analytical results of $^{239+240}\text{Pu}$ and ^{241}Pu activity, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio in ocean sediment reference materials, IAEA-368 and NIST 4357 (The data are presented with an expanded uncertainty using a coverage factor of 2).^a

HNO ₃ extraction				
Sample	$^{239+240}\text{Pu}$ (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	^{241}Pu (mBq/g)	$^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio
IAEA-368	32.1 ± 0.8	0.0320 ± 0.0012	6.75 ± 2.52	0.00019 ± 0.00004
NIST-4357	9.44 ± 0.19	0.2363 ± 0.0098	70.9 ± 5.9	0.01324 ± 0.00070
HNO ₃ + HF + HClO ₄ digestion				
Sample	$^{239+240}\text{Pu}$ (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	^{241}Pu (mBq/g)	$^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio
IAEA-368	31.8 ± 0.6	0.0320 ± 0.0016	7.71 ± 5.31	0.00026 ± 0.00010
NIST-4357	9.20 ± 0.25	0.2329 ± 0.0130	69.0 ± 14.5	0.01314 ± 0.00172
Certified and/or information values (data in parentheses indicate 95% confidence interval)				
Sample	$^{239+240}\text{Pu}$ (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ [#] atom ratio	^{241}Pu (mBq/g)	$^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio
IAEA-368	31.0 (29.0–34.0)	0.030–0.043	–	–
NIST-4357	10.4 ± 0.2 (9.2–13.3)	0.233–0.244	–	–

^a ^{241}Pu decay corrected to 1st. January 2000. [#] $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios from Zheng et al., 2004; Kim et al., 2004; Yoshida et al., 2007; Hrnccek et al., 2008.

the relatively high uncertainty for ^{241}Pu data (5.5 % and 9.1 % for acid leaching and total digestion methods, respectively).

Fig. 1 compares the activity of $^{239+240}\text{Pu}$ of the reference material obtained using acid leaching and total digestion methods with the reference value. The activity of $^{239+240}\text{Pu}$ of the reference fallout material samples for the leaching method was 6.56 ± 0.20 mBq/g, which accounts for 96.6% of the $^{239+240}\text{Pu}$ activity in the total digestion method (6.79 ± 0.16 mBq/g). Lee et al. (2004) reported similar results for sediment samples. Although a *t*-test revealed that the two methods are non-equivalent to each other, the difference of the obtained $^{239+240}\text{Pu}$ activities between these two methods is less than 3.5%, suggesting that the acid leaching method is generally acceptable to analyze the radionuclides in fallout samples. The activities of $^{239+240}\text{Pu}$ obtained by acid leaching and total digestion methods are similar to the reference value (6.52 ± 0.42 mBq/g) given by the MRI (Otsuji-Hatori et al., 1996), demonstrating the accuracy of our methods for the quantitative determination of Pu isotopes in fallout at ultra-trace levels.

Table 4

Analytical results of $^{239+240}\text{Pu}$ and ^{241}Pu activity, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio in the reference fallout material (the data are presented with an expanded uncertainty using a coverage factor of 2).^a

Sample	$^{239+240}\text{Pu}$ (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	^{241}Pu ^a (mBq/g)	$^{241}\text{Pu}/^{239}\text{Pu}$ atom ratio
HNO ₃ extraction				
No. 6–30	6.40 ± 0.15	0.1896 ± 0.0082	12.3 ± 5.5	0.00259 ± 0.00064
No. 12–63	6.59 ± 0.15	0.1906 ± 0.0068	12.2 ± 6.0	0.00250 ± 0.00078
No. 16–9	6.53 ± 0.17	0.1929 ± 0.0078	12.8 ± 6.6	0.00265 ± 0.00088
No. 14–8	6.63 ± 0.17	0.1913 ± 0.0078	13.8 ± 5.8	0.00282 ± 0.00078
No. 14–59	6.64 ± 0.19	0.1931 ± 0.0076	12.2 ± 4.8	0.00249 ± 0.00064
Average ^b	6.56 ± 0.20	0.1915 ± 0.0030	12.7 ± 1.4	0.00261 ± 0.00026
HNO ₃ + HF + HClO ₄ digestion				
No. 6–30	6.82 ± 0.23	0.1927 ± 0.0008	13.0 ± 5.6	0.00308 ± 0.00086
No. 12–63	6.66 ± 0.23	0.1916 ± 0.0112	13.0 ± 7.9	0.00314 ± 0.00116
No. 16–9	6.82 ± 0.19	0.1951 ± 0.0104	10.8 ± 5.5	0.00258 ± 0.00084
No. 14–8	6.78 ± 0.23	0.1924 ± 0.0140	12.7 ± 6.8	0.00301 ± 0.00104
No. 14–59	6.85 ± 0.25	0.1890 ± 0.0156	10.9 ± 9.0	0.00255 ± 0.00136
Average ^b	6.79 ± 0.16	0.1922 ± 0.0044	12.1 ± 2.2	0.00287 ± 0.00056
Global fallout (Kelley et al., 1999)				
30–71°N		0.180 ± 0.007		0.00194 ± 0.00014
0–30°N		0.178 ± 0.010		0.00188 ± 0.00039

^a ^{241}Pu decay corrected to 1st January 2000.

^b The average data are presented with unbiased 2 SD for the data set.

For the $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios in the reference fallout material, as summarized in Table 4, there is no significant difference for the two methods we employed. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios for the acid leaching and total digestion methods ranged from 0.1896 to 0.1931, with a mean of 0.1915 ± 0.0030 ($n=5$) and 0.1890–0.1951, with a mean of 0.1922 ± 0.0044 ($n=5$), respectively. The $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios ranged from 0.00249 to 0.00282, with a mean of 0.00261 ± 0.00026 ($n=5$) and $0.00255\text{--}0.00314$, with mean of 0.00287 ± 0.00056 ($n=5$), respectively. The $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios observed in this study are slightly higher than the global fallout values of 0.180 ± 0.007 and 0.00194 ± 0.00014 in the northern hemisphere (30–71 °N) (Kelley et al., 1999). As mentioned above, the reference fallout sample is composed of the fallout material collected at 14 sites covering a wide area of Japan during the period of 1963–1979. Therefore, the reference fallout material can be regarded as one representative for global fallout plutonium in these years. The Chinese above-ground level nuclear tests started from 1964, and ended in 1980, which overlapped with the sample collection period. Although from 1966 to 1974, 41 atmospheric nuclear weapons tests were conducted by France, the influence of these tests on the atmospheric deposition of radionuclides in the northern hemisphere could be limited as these tests were conducted at Mururoa and Fangataufa Atolls in the southern hemisphere. Thus, the reference fallout material to some extent reflected the atmospheric deposition of radionuclides resulting from the Chinese nuclear tests. Similarly,

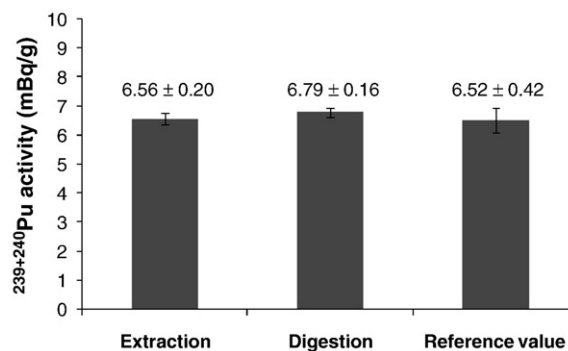


Fig. 1. Comparison of $^{239+240}\text{Pu}$ activities obtained by using HNO₃ extraction and HNO₃-HF-HClO₄ digestion with the reference value for the reference fallout material. The error bar shown in the figure is the unbiased 2 SD.

relatively high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios were observed in Lake Chenghai sediment core samples in the layer corresponding to the period of 1968–1981, and Zheng et al. (2008) suggested that the sediment in this layer to some extent reflected the deposition of radionuclides resulting from the Chinese tests. Although the atom ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in fallout may vary, depending upon the specific weapon design and the test yield, the Chinese atmospheric nuclear tests may have enhanced the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio compared with the global fallout value of 0.18. This speculation is supported by the fact that for the 21st nuclear explosions test which was the largest yield Chinese thermonuclear test (4 Mt) conducted on 17 November, 1976, the atom ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ was 0.224 ± 0.002 in the debris (Leifer and Toonkel, 1981). In addition, Warneke et al. (2002) observed a small increase in the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio during the late 1970s in Rothamsted grass, and they attributed this increase to the Chinese nuclear tests.

Plutonium deposition in Japan has stayed at a fairly constant level since 1985, and showed a typical seasonal variation with high levels in spring. This phenomenon was attributed to the resuspension of soil particles originated from the East Asian desert and arid areas (Igarashi et al., 2003; Lee et al., 2006). During the period of June 2001 to April 2002 in Korea, the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio for five Yellow Sand samples had a mean value of 0.191 ± 0.014 , which is similar to what we observed in the reference fallout material, and indicates that the atmospheric resuspension of soil particles plays an important role in the behavior of Pu in the environment (Choi et al., 2006). The atom ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in the reference fallout material samples may be regarded as an average value corresponding to the Chinese nuclear tests, and Pu isotopic composition can be used as an important geochemical proxy to understand the variation of radionuclides deposition in Korea and Japan since the late 1980s, and support the hypothesis that resuspension is the major process controlling the deposition of Pu as well as other anthropogenic radionuclides (Rosner and Winkler, 2001; Hirose et al., 2003; Igarashi et al., 2003, 2009).

3.2. Distribution of $^{239+240}\text{Pu}$ activity and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio among different host phases

The distribution percentages of $^{239+240}\text{Pu}$ activity in reference fallout sample, No. 12-63, treated with sequential extraction among the host phases are shown in Fig. 2. The dominant host phases of $^{239+240}\text{Pu}$ are found to be organic matter-sulfides (70%) and Fe–Mn oxides (19%). Our results suggest that the organic matter-sulfides fraction and redox sensitive elements (Fe/Mn) play important roles in the partitioning of Pu. Small amounts of $^{239+240}\text{Pu}$ are found in the carbonate (6%) and

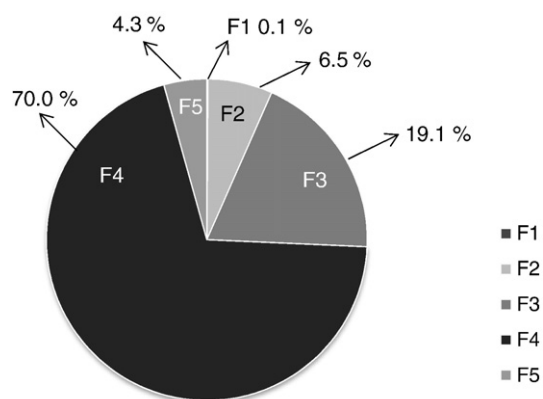


Fig. 2. Distribution of $^{239+240}\text{Pu}$ among extraction fractions for the reference fallout sample No.12-63. F1, exchangeable; F2, bound to carbonate; F3, bound to Fe–Mn oxides; F4, bound to organic matter-sulfides; and F5, residual. Only one sequential extraction experiment was done to obtain these results.

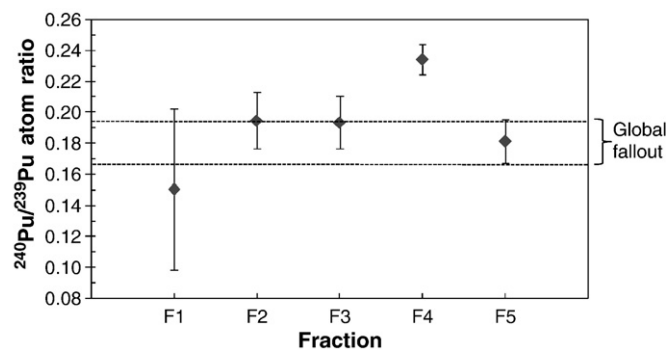


Fig. 3. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio distribution among extraction fractions of the reference fallout sample No. 12-63. F1, exchangeable; F2, bound to carbonate; F3, bound to Fe–Mn oxides; F4, bound to organic matter-sulfides; and F5, residual. The data are presented with an expanded uncertainty using a coverage factor of 2. Only one sequential extraction experiment was done to obtain these results.

residual phases (4%), respectively. Only 0.1% Pu is found in the exchangeable fraction, showing that Pu bound to the exchangeable phase is negligible in the reference fallout material. Plutonium in the residual phase, formed by the fusion of weapon components and soil silicates during the surface tests can only be released by total digestion using the mixture of $\text{HNO}_3\text{--HClO}_4\text{--HF}$. About 4% Pu is found in the residual phase, which is consistent with the result that the activity of $^{239+240}\text{Pu}$ for the leaching method accounts for 96.6% of $^{239+240}\text{Pu}$ activity in the total digestion method, indicating that the acid leaching technique can release Pu bound to all the host phases, except that in the residual phase. It should be noted that the apparent partitioning of Pu into the various extraction phases may also result from slow dissolution kinetics of Pu compounds together with the difference of relative solubilities in each of the solvents, therefore, Pu may be not actually associated with different phases in the reference fallout sample.

A comparison of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios among the five fractions of reference fallout sample No. 12-63 and the global fallout is shown in Fig. 3. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio ranges from 0.151 to 0.234. A noteworthy feature is that the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in most fractions (F2, F3 and F5) falls within the range of global fallout, while a low $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.151 and a high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.234 are found in F1 and F4 fractions, respectively. For F4, the strong extraction reagents of H_2O_2 and HNO_3 are used to release Pu bound to the target phase of oxidizable, organic matter-sulfides (Kenna 2009). Whether Pu isotope fractionation occurs during this sequential extraction process or this oxidizable, organic matter-sulfides phase specifically adsorbs Pu with higher $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio, at present, it is not clear to us. Further studies are needed to address these questions.

4. Conclusions

Using the sensitive isotope dilution SF-ICP-MS technique, we made accurate and precise determination of Pu activity and its atom ratios to characterize the Pu isotope composition in the reference fallout material prepared by MRI based on the fallout samples collected throughout Japan during the period from 1963 to 1979. The main conclusions can be summarized as follows:

- Although a *t*-test revealed that the acid leaching and the total digestion methods were non-equivalent to each other, the difference of the obtained $^{239+240}\text{Pu}$ activities between these two methods was less than 3.5%, suggesting that the acid leaching method is generally acceptable to analyze the radionuclides in fallout samples. The $^{239+240}\text{Pu}$ activities for acid leaching and total digestion methods were 6.56 ± 0.20 mBq/g and 6.79 ± 0.16 mBq/g, respectively, showing good agreement with the reference value of 6.52 ± 0.42 mBq/g.

- ii) The $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios found in the reference fallout material were slightly higher than those of global fallout values, indicating the influence of Chinese nuclear tests in the 1970s in the fallout samples. These results support the hypothesis that the fallout deposition of Pu in Japan and Korea since the late 1980s was mainly controlled by resuspension of soil particles.
- iii) One sequential extraction experiment was conducted for Pu in the reference fallout sample. The preliminary results suggested that the dominant host phases of $^{239+240}\text{Pu}$ were organic matter-sulfides (70%) and Fe–Mn oxides (19%). Further study is needed to verify this observation.

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