4.31 Isotope ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ in soil samples from different areas

Yasuyuki Muramatsu$^1$, Satoshi Yoshida$^1$ and Shinnosuke Yamazaki$^2$

$^1$National Institute of Radiological Sciences: Anagawa 4-9-1, Inage, Chiba, 263-8555 Japan
$^2$Tokyo Nuclear Service Inc.: Ueno 7-6-5, Taito-ku, Tokyo, 110-0005 Japan

ABSTRACT

Plutonium concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in soil samples from Japan and other areas in the world (including IAEA standard reference materials) were determined by ICP-MS. The range of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios observed in 21 Japanese soil samples was 0.155 - 0.194 and the average was 0.180 ± 0.011, which is comparable to the global fallout value. A low ratio of about 0.05, which is derived from Pu-bomb, was found in samples from Nishiyama (Nagasaki) and Mururoa Atoll (IAEA-368), while a high ratio of about 0.31 was found in a sample from Bikini Atoll (Marshall Islands). The ratio for Irish Sea sediment (IAEA-135) was 0.21, which was higher than the global fallout value, suggesting the influence by the contamination from the Sellafield facility. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in soils from the Chernobyl area were determined, and the ratio was found to be very high (about 0.4), indicating the high burn-up grade of the reactor fuel. These results show that the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio can be used as a finger print to identify the source of the contamination.

Keywords
Plutonium, ICP-MS analysis, isotope ratio, soil, different areas

1. INTRODUCTION

Plutonium is one of the most important radionuclides in the field of radioecology. There are different anthropogenic sources of Pu in the environment [1]. Atomic weapons testing introduced the major deposited fraction of Pu to the global environment. High Pu levels are known for the nuclear weapons testing sites such as in the Marshall Islands, Mururoa Atoll, Nevada and Semipalatinsk. In the Nishiyama area (Nagasaki/Japan) elevated Pu concentrations were observed [2]. Plutonium has also been released into the environment through operation or accidents at nuclear facilities such as Sellafield/UK, Kyshtym/Russia, Chernobyl/Ukraine, etc. The deep-sea disposal of packaged waste around the Farallon Islands (California/USA) and in the North Atlantic would be potential contamination sources in the marine environment. Accidental burn-up of the SNAP9A satellite in 1964 also released Pu, which was used for the battery, into the atmosphere.

However, there is only a limited volume of quality data available on the isotope compositions of Pu (specifically, $^{240}\text{Pu}/^{239}\text{Pu}$ ratio). This is mainly due to the fact that $^{239}\text{Pu}$ and $^{240}\text{Pu}$ have similar alpha energies and cannot be easily resolved by alpha spectrometry. We have developed a reliable method...
for the determination of $^{239}$Pu and $^{240}$Pu by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) [3].

In this paper, we report the analytical methods for Pu by ICP-MS, $^{240}$Pu/$^{239}$Pu ratio in soil (or sediments) samples from different areas (e.g. Japan, Chernobyl, the Marshall Islands) and the differences in the $^{240}$Pu/$^{239}$Pu ratios according to the soil profile.

2. MATERIALS AND METHOD

Analytical procedures used were based on the method reported previously [3, 4]. Only a brief description is given here. Samples (1-10 g, depending on the concentration level) were mixed with a known amount of $^{242}$Pu tracer (CRM 130, New Brunswick Laboratory) in a Pyrex beaker and treated with 8 M HNO$_3$ (more than 8 times the sample weight). Special attention should be paid to the high production of CO$_2$ bubbles during the acid dissolution step to avoid loss of sample. The beaker was covered with a watchglass and boiled on a hot plate (180-200°C) for about 5 hours. The warm supernatant (leachate) was then filtered through a glass fiber filter. The residue in the beaker was treated again with 8 M HNO$_3$ for about 30 minutes, then filtered. This leaching procedure was usually repeated at least twice. The filtrates were collected in a beaker, and heated on a hot plate until a thick wet paste was obtained. The paste was then dissolved in HNO$_3$, and diluted with deionized water to adjust the solution to 8 M HNO$_3$. Chemical form of plutonium was converted to tetravalent Pu (IV), which is the only retainable form in the chromatography column, with NaNO$_2$. Sample solution was loaded onto the column containing 2 mL of Dowex 1X8 at a speed < 2 mL min$^{-1}$. The resin was washed with 40 mL of 8 M HNO$_3$, then with 40 mL of 10 M HCl. Finally, plutonium was eluted from the column using 40 mL of NH$_4$Cl (5%)-10 M HCl solution which reducing Pu (IV) to Pu (III). In order to remove iodine, the eluant was treated with 4 mL of HNO$_3$ and 1 mL of H$_2$O$_2$, and the solution heated to dryness. The residue was then dissolved in 4% HNO$_3$ and plutonium isotopes measured by ICP-MS using a quadrupole-type mass spectrometer (Q-ICP-MS; Yokogawa PMS-2000) and also high resolution-type (HR-ICP-MS; Finnigan Element).

Concentrations of $^{239}$Pu and $^{240}$Pu were calculated from the results using isotope dilution methods. Three separate measurements of each solution digest were performed—normally the internal precision of these measurements was around ± 5%. A plutonium isotopic standard (NIST-947) with a known $^{240}$Pu/$^{239}$Pu ratio was also used to check the accuracy of the isotopic ratio measurements, and to correct for any mass bias.

3. RESULTS AND DISCUSSIONS

3.1 $^{240}$Pu/$^{239}$Pu ratios in Japanese soil samples

Analytical results for 21 Japanese soil samples collected from different places showed that the concentrations of Pu ($^{239+240}$Pu) ranged from 0.15 – 4.3 Bq/kg (dry weight basis). The concentrations in surface soils collected from forests were higher than those from agricultural fields. The range of $^{240}$Pu/$^{239}$Pu atom ratios observed in the Japanese soil samples was 0.155 – 0.194 (excluding
Nishiyama/Nagasaki sample) and the average was 0.180 ± 0.011. These values were comparable to the global fallout value of 0.176 ± 0.014 reported by Krey [5], which was based on the mass-spectrometric measurements of various soils (about 60) collected world-wide. Variation between the lowest to highest ratio might be due to the influence of different fallout events, since a variety of nuclear weapons has been tested world-wide. Differentiation of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio might also occur during the migration of Pu in the environment (e.g. in soil), because chemical species of Pu would depend on individual fallout.

In order to know the vertical distribution of Pu in soil, samples were collected at 4 different depths (0-2cm, 2-5cm, 10-20cm and 20-30cm) at the same point in a pine forest in Aomori Prefecture. It was observed that Pu concentration was markedly higher in the surface soil layer (specifically in the 0-5 cm depth) than in deeper layers (see Table 1). This suggested that the migration of Pu into lower soil layers was very slow and most of Pu is still retained in the surface soil for more than 30 years after the fallout peak (around 1963). A tendency was observed for the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio to increase with depth, although the differences were not so large. If these differences had been statistically significant, there could be a possibility that species having a higher $^{240}\text{Pu}/^{239}\text{Pu}$ ratio migrated in the soil faster than those having a lower ratio. However, it is necessary to analyze more samples from different areas, before we can confirm this hypothesis. There was also a possibility that the difference of the isotope ratios and the Pu chemical forms were related to the different origin of the fallout, which were influenced by the type and scale of the explosion.

Table 1 Concentrations of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ and their atom ratios in soils from a forest in Aomori Prefecture (on a dry weight basis).

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>$^{239}\text{Pu}$ (Bq/kg)</th>
<th>SD</th>
<th>$^{240}\text{Pu}$ (Bq/kg)</th>
<th>SD</th>
<th>$^{239+240}\text{Pu}$ (Bq/kg)</th>
<th>SD</th>
<th>$^{240}\text{Pu}/^{239}\text{Pu}$ (atom ratio)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-2</td>
<td>1.88 ± 0.020</td>
<td></td>
<td>1.14 ± 0.012</td>
<td></td>
<td>3.02 ± 0.023</td>
<td></td>
<td>0.166 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>2-5</td>
<td>1.62 ± 0.015</td>
<td></td>
<td>1.01 ± 0.019</td>
<td></td>
<td>2.62 ± 0.024</td>
<td></td>
<td>0.170 ± 0.004</td>
<td></td>
</tr>
<tr>
<td>10-20</td>
<td>0.45 ± 0.008</td>
<td></td>
<td>0.29 ± 0.003</td>
<td></td>
<td>0.74 ± 0.008</td>
<td></td>
<td>0.174 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>20-30</td>
<td>0.09 ± 0.001</td>
<td></td>
<td>0.06 ± 0.002</td>
<td></td>
<td>0.15 ± 0.002</td>
<td></td>
<td>0.194 ± 0.005</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Comparison of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios from different areas

The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios analyzed by us for samples originating from several different areas (including IAEA standard reference materials) are summarized in Figure 1. Details on the samples from the Chernobyl area and from the Marshall Islands were published elsewhere [6, 7].

The value for surface soil collected from Austria (IAEA-SOIL-6) was 0.191 ± 0.005, which was somewhat larger than the Japanese soil, but within the range of the global fallout value of 0.176 ± 0.014 reported by Krey [5].

Ocean sediment from Mururoa Atoll (IAEA-368) had a value of 0.04 ± 0.008. This suggested that Pu was derived from the testing of a Pu-bomb in which $^{239}\text{Pu}$ was enriched. However, the $^{240}\text{Pu}/^{239}\text{Pu}$
atom ratio for samples from the Marshall Islands (IAEA-367) showed a high value of about 0.30, although the concentration of $^{239+240}$Pu in these two marine sediments was similar. The high $^{240}$Pu/$^{239}$Pu atom ratio for samples found for the Marshall Islands sample was similar to the ratio reported by Komura et al. [8] measured in two samples of Hemp-palm leaves (0.338±0.051 and 0.318±0.033) used in the Japanese fishing boat, No. 5 Fukuryu-Maru (Lucky Dragon), which was directly contaminated in a thermonuclear bomb test at Bikini Atoll. The difference of the atom ratio observed in Mururoa Atoll and the Marshall Islands may be due to the type of the weapons tested. Since several different tests were probably carried out in both islands, we could not conclude that the values mentioned here were representative for these areas; they are just for examples based on our analytical results in standard reference materials.

The ratio obtained for the Irish Sea sediment sample (IAEA-135) of 0.211 was higher than the global fallout value. The higher value would be influenced by the contamination from the Sellafield facility. Our value was comparable to the ratio (0.20) reported by Yamamoto et al. [9] in a sediment sample originating from the Sellafield area. Fish flesh from the Irish Sea (IAEA-134) showed a similar value of 0.200 to the Irish Sea sediment sample, suggesting that the origin of the contamination seemed to be the same.

The very low value of the $^{240}$Pu/$^{239}$Pu atom ratio (0.04) observed in the sample collected from Nishiyama/Nagasaki indicated the influence of Pu from the bomb dropped in August 1945. The low ratio observed in a sample from Kyshtym of about 0.07 indicated the Pu was related to the contamination due to the release of nuclear materials from the nearby military facility.
Analytical results for surface soil samples collected from the 30 Km zone of the Chernobyl reactor showed very high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of about 0.41 [6]. There were almost no differences in the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios between the samples analyzed in our study, although the $^{239+240}\text{Pu}$ levels varied very widely, i.e. 6.3 - 1430 Bq kg$^{-1}$, depending on the distances from the reactor and also on the soil layers. The ratio observed in the Chernobyl area was much higher than that attributed to weapons fallout. This high ratio should be related to the high burn-up grade of the reactor fuel. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratio observed might be used in identifying the distribution of the Chernobyl-derived Pu in the environment.

As already mentioned that the average $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in global fallout was around 0.18; it is interesting to consider which significant sources (nuclear weapons types, etc.) contributed to this ratio. In our previous study [7] on Pu analysis in soil samples from the Marshall Islands, we saw there was a large variation of $^{240}\text{Pu}/^{239}\text{Pu}$ ratios, depending on the type of devices having tested. For example, samples from Bikini Island (Bikini Atoll) had a high $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.302-0.306. This Island received direct contamination from the fallout originating from the Castle-BRAVO thermonuclear test (15 Mt) at Namu Island (Bikini Atoll) in March 1954. On the other hand, the very low $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.065 with a high Pu concentration (1420 Bq kg$^{-1}$) was observed in a sample from Runit Island (Enewetak Atoll), in which Pu bombs were tested. As mentioned above, one $^{240}\text{Pu}/^{239}\text{Pu}$ ratio found in Nishiyama/Nagasaki was also very low, 0.037, due to the influence of Pu bomb fallout. If we consider the mixture of Pu isotopes from the above-mentioned two major sources, Pu bombs and thermonuclear bombs, the mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio might be similar to the average ratio found in global fallout. However, data are still lacking on source specific $^{240}\text{Pu}/^{239}\text{Pu}$ ratios from different nuclear weapons tests, including thermonuclear tests other than the BRAVO bomb.

The determination of the Pu isotope ratio is important in understanding the source of the nuclide and the ratio can be used as a finger print in the environmental monitoring of Pu.

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