

# Plutonium isotopes derived from Nagasaki atomic bomb in the sediment of Nishiyama reservoir at Nagasaki, Japan

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## Abstract

The source of plutonium in sediments deposited at Nishiyama reservoir at Nagasaki was characterized by their  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio. The average ratio was approximately 0.03, except in two layers. The main source of the plutonium was the Nagasaki atomic bomb. The plutonium continues to flow into the reservoir even now. The  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in two layers were higher than the average, which showed that plutonium in these layers were made of those of nuclear tests added to those of the atomic bomb.

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## 1. Introduction

Plutonium isotopes and  $^{137}\text{Cs}$  are artificial nuclides and have long half-lives ( $^{239}\text{Pu}$ :  $2.411 \times 10^4$  yr,  $^{240}\text{Pu}$ :  $6.564 \times 10^3$  yr,  $^{137}\text{Cs}$ : 30.07 yr). When these nuclides are released, these are kept in the environment. Their environmental behavior is, therefore, of interest from the viewpoint of radioecology. Nagasaki city is one of the oldest areas where plutonium isotopes and  $^{137}\text{Cs}$  were released when the plutonium atomic bomb was exploded on August 9, 1945.

Sakanoue (1987) and Mahara et al. (1988) found high levels of  $^{239+240}\text{Pu}$  in sediments of Nishiyama reservoir at Nagasaki (Fig. 1(a)), about 3 km east of the hypocenter, which experienced the ‘black rain’ formed from the detonation of Nagasaki atomic bomb. They reported that the plutonium isotopes were derived from the atomic bomb. However nuclear tests conducted after the detona-

tion of the atomic bomb scattered plutonium isotopes and fission products in the world. The nuclides fell in the reservoir and were added into the sediment. Thus, the concentrations in the sediments cannot identify whether the origin of the nuclides is the atomic bomb or nuclear tests.

As the isotopic composition of plutonium depends on its origin, isotopic ratios, especially  $^{240}\text{Pu}/^{239}\text{Pu}$ , are used to understand the origin of plutonium. The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in source materials of nuclear weapons are different according to the date when the weapons were made. The ratio in the fallout depends on the design of the weapons and the scale of explosion; the ratios during the nuclear tests ranged from 0.09–0.34 (Koide et al., 1985). At present, the integrated ratio in the fallout is 0.176 (Krey et al., 1976). The determination of the ratio would be a powerful tool for understanding sources of plutonium in the sediments.

This paper is intended to report sources of plutonium isotopes in the sediment of the Nishiyama reservoir. We determined  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio in core sediments and also measured concentrations of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$ . These

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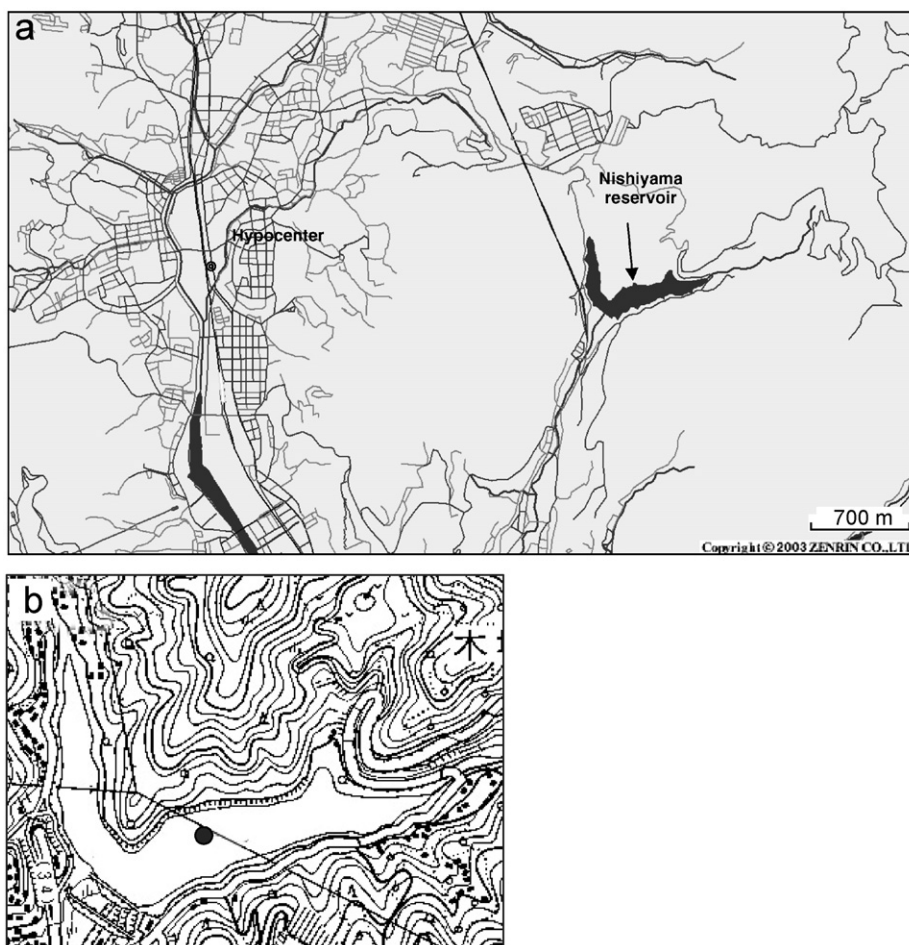


Fig. 1. Sampling point in Nishiyama reservoir at Nagasaki, Japan: (a) hypocenter of the Nagasaki atomic bomb and Nishiyama reservoir, (b) sampling point of core in Nishiyama reservoir.

results make it possible to determine the depth profile of these nuclides released from the atomic bomb.

## 2. Experiment

### 2.1. Samples

Sediment core was collected with a Mackereth-type core sampler at Nishiyama reservoir as shown in Fig. 1(b) in December 1999. After observation of the horizon in the core, the core was cut into slices 2 cm each in thickness. The sediment was dried and homogenized.

### 2.2. Determination of $^{137}\text{Cs}$ by $\gamma$ -spectrometry

The sediment samples (20 g) were analyzed for their  $^{137}\text{Cs}$  content by using HP-Ge detector (LOAX60450/30P, Ortec, USA), the counting efficiency of which were calibrated by measuring two standard reference materials (NIST SRM4350B: River sediment, SRM 4354: Fresh-water lake sediment). The measured activity of  $^{137}\text{Cs}$  in the sediments samples was decay corrected to the sampling date (December 20, 1999).

### 2.3. Chemical separation of Pu

Before ICP-MS measurements, plutonium was chemically isolated from soil matrix. The chemical separation and the measurement by ICP-MS were operated in the clean rooms (ISO class 5 and 6, respectively) of the CLEAR in JAEA. This facility has the ability to measure the isotopic ratio of trace amounts of uranium and plutonium in environmental samples (Magara et al., 2000). The procedure used for Pu leaching was based on the method reported by Muramatsu et al. (1999). The supernatants resulting from four steps of leaching with 8 M  $\text{HNO}_3$  were dried to salt and then the salt was dissolved in 3 ml of 8 M  $\text{HNO}_3$ , which was followed by filtration through a Teflon membrane filter (pore size: 0.45  $\mu\text{m}$ , DISMIC, Advantec, Japan) to remove any residue. The beaker was rinsed twice with 1 ml of 8 M  $\text{HNO}_3$ . All the three filtrates were mixed and sodium nitrite (200 mg) was added. The solution was left overnight to adjust Pu to the tetravalent state.

Plutonium purification was carried out with anion-exchange resin (75–150  $\mu\text{m}$ , MCI GEL CA08P, Mitsubishi Chemical, Japan) in a 1 ml column. After resin was pre-treated with

8 M HNO<sub>3</sub> to be NO<sub>3</sub><sup>-</sup> form, plutonium in the solution was loaded onto the resin. The resin was rinsed sequentially with 8 M HNO<sub>3</sub> (2 ml), 9 M HCl–0.1 M HNO<sub>3</sub> (7 ml) and then 9 M HCl (5 ml). Plutonium was stripped from the resin as Pu(III) with 3 ml of 9 M HCl–0.1 M NH<sub>4</sub>I. To complete the reduction to Pu(III), another 4 ml of the elutant was loaded into the column, and the column was plugged to prevent from spilling the solution and was left for 3 h. Then the remaining elutant was passed and collected.

In order to decompose any organic material and expel iodine completely from the collected fraction, the solution was heated at 200 °C on a hot-plate, and then the solution to which 15 M HNO<sub>3</sub> was added was heated again until the residue became colorless. The residue was dissolved in 3 ml of 9 M HCl–0.1 M HNO<sub>3</sub> and 200 mg of sodium nitrite was added to it. The solution was left overnight for plutonium valence adjustment, and then second purification was carried out in the same manner mentioned above, except the rinsing step; 9 M HCl–0.1 M HNO<sub>3</sub> (4 ml) and 9 M HCl (3–5 ml). Finally, the residue was dissolved in 3 ml of 0.32 M HNO<sub>3</sub>, a solution suitable for ICP-MS measurement.

#### 2.4. Determination of <sup>239+240</sup>Pu and <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio by ICP-MS

The instrument used was high-resolution ICP-MS (ELEMENT1, ThermoElectron, Germany) with Guard Electrode, operated in electrostatic scanning mode (E-scan) with a resolution ( $M/\Delta M$ ) of 300. A PFA micro-flow nebulizer was used as a sample introduction system. The plutonium isotopic standard (NIST SRM 947) was used to

correct the mass bias of the instrument. Concentrations of <sup>239</sup>Pu and <sup>240</sup>Pu were calculated by isotopic dilution method using a <sup>242</sup>Pu spike. Details of the operation conditions and the method of mass bias correction were reported by Magara et al. (2002).

### 3. Results and discussion

The depth profiles of the <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio and the concentrations of <sup>239+240</sup>Pu and <sup>137</sup>Cs in the core are shown in Fig. 2(a) and (b) respectively. Sediments at the depth of 150–200 cm have considerably low <sup>239+240</sup>Pu concentrations, which induce large uncertainties of the ratios. Considering <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios in sediments located the upper and lower side of 150–200 cm, we could not conclude that the ratios in the sediments at the depth of 150–200 cm have significant difference from the other ratios in sediments located the upper and lower side. Thus, the ratios in the core are almost constant within the error of 2σ, except peak (1) and peak (2). The average of the ratios is approximately 0.03, which is considerably lower than the global fallout value of 0.176 reported by Krey et al. (1976). It was reported by Rokop et al. (1996) that the ratio of the source material of atomic bombs before 1960 was less than 0.01. The plutonium used for the Nagasaki atomic bomb had a ratio of the same level and neutron capture reactions at the explosion increased the ratio. In the case of nuclear tests which had occurred after the detonation of the Nagasaki atomic bomb and which are the main origin of global fallout, the ratio of the source material is higher (about 0.06) (Rokop et al., 1996) and the scale of explosion is bigger resulting in the sufficiently

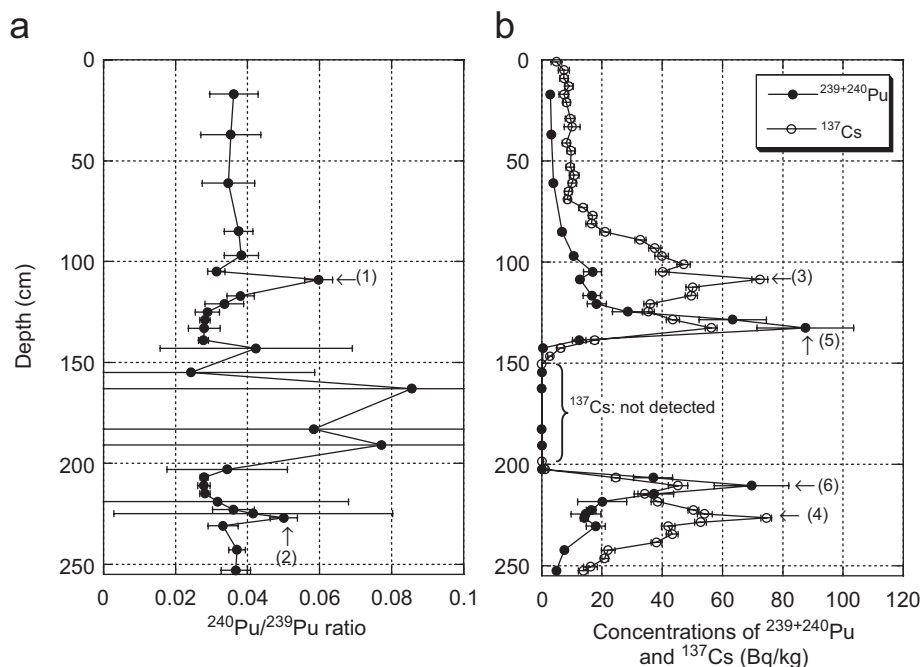


Fig. 2. Depth profiles of the <sup>240</sup>Pu/<sup>239</sup>Pu ratio, <sup>239+240</sup>Pu and <sup>137</sup>Cs in the sediments; (a) <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio, (b) concentrations of <sup>239+240</sup>Pu and <sup>137</sup>Cs. (1) Error: 2σ, (2) (1)–(6): peak of <sup>240</sup>Pu/<sup>239</sup>Pu ratio or each elemental concentration.

higher ratios of nuclear tests fallout (0.09–0.34) (Koide et al., 1985). Therefore, the obtained lower ratios in the core indicate that the main source of plutonium isotopes was not the nuclear tests fallout but the atomic bomb dropped at Nagasaki. Notice that sediments at the depth of 0–100 cm have  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios which is comparable to the values (0.020–0.042) in surface soils collected at the basin of the reservoir, see Komura et al. (1984), Yamamoto et al. (1985) and Muramatsu et al. (2003). This means that the soils flow into the reservoir and continue to supply the plutonium isotopes of the atomic bomb even now. However concentrations of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  have decreased, which shows amounts of inflow of the plutonium isotopes and  $^{137}\text{Cs}$  have reduced.

The ratios found in the peak (1) and peak (2) are  $0.060 \pm 0.004$  and  $0.050 \pm 0.004$  respectively, which were significantly higher than the average ratio in the other samples. It must be noted that these ratios were lower than those of global fallout. It is likely at these peaks that the plutonium released from the nuclear tests was significantly mixed with the atomic bomb plutonium. The contribution of the atomic bomb plutonium for these layers was estimated to be 79% at the peak (1) and 86% at the peak (2) respectively under the assumption that the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of the atomic bomb was 0.03 and that of the fallout was 0.176. The layers where peaks of the ratio were found have peaks of concentrations of  $^{137}\text{Cs}$ ; (3) and (4), whereas concentrations of  $^{239+240}\text{Pu}$  are low (Fig. 2(b)). It was reported that the activity of  $^{137}\text{Cs}$  released from the nuclear tests was two orders higher than that of  $^{239+240}\text{Pu}$  (UNSCEAR, 2000). Therefore, it shows that  $^{137}\text{Cs}$  of the nuclear tests fallout was added into each layer as with plutonium isotopes and made the peaks.

The depth profile of  $^{239+240}\text{Pu}$  had two big peaks at positions (5) and (6) (Fig. 2(b)). If data of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the sediments were unavailable, one might regard the upper peaks (5) and the deeper peaks (6) as the trace of nuclear tests and the atomic bomb, respectively. However the results of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios at these peaks revealed that the plutonium isotopes in the each sediment were dominated primarily by contributions from the atomic bomb. This indicated that the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio is useful as an indicator to identify the origin of plutonium.

In addition, the  $^{239+240}\text{Pu}$  peak (6) is positioned up the ratio peak (2) and the  $^{137}\text{Cs}$  peak (4) composed of nuclides released from the nuclear tests. This means that the plutonium isotopes released the atomic bomb in the  $^{239+240}\text{Pu}$  peak (6) was deposited after the nuclear tests. It is appropriate that plutonium isotopes reached the reservoir at the time of the detonation is deposited in sediments below this core analyzed.

#### 4. Conclusion

In the present work, the source of plutonium isotopes in sediments collected in the Nishiyama reservoir has been

determined by means of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio. The main source is the Nagasaki atomic bomb. The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the sediments are comparable to those in soils around the reservoir. The soils have been a source of the plutonium isotopes supply for the sediments a long period of time. Two layers in sediments have not only plutonium isotopes and  $^{137}\text{Cs}$  of the atomic bomb but also those of nuclear tests. Sediment deposited soon after the detonation of the atomic bomb might lie under the sediment in this study. This warrants future work of the measurement of the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio in deeper layer of the sediments. Nonetheless, determination of the source of plutonium isotopes in the sediment of the Nishiyama reservoir will allow us to understand behavior of the plutonium isotopes released from the Nagasaki atomic bomb.

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