

# Temporal Variations of Global Fallout-Derived Plutonium and $^{137}\text{Cs}$ in River Water in Japan

Katsumi Hirose<sup>1\*</sup> and Michio Aoyama<sup>2</sup>

<sup>1</sup>Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan

<sup>2</sup>Institute of Environmental Radioactivity, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan

## Abstract

Temporal variations of global fallout-derived plutonium and  $^{137}\text{Cs}$  concentrations in river water in Japan were examined using a composite dataset for 1966–1987 (1966–1987 for  $^{239,240}\text{Pu}$ , 1978–1987 for  $^{137}\text{Cs}$ ). Plutonium and  $^{137}\text{Cs}$  concentrations in Japanese river water exhibited exponential decreases during the sampling periods, with the exception of  $^{137}\text{Cs}$  concentrations immediately after the Chernobyl nuclear reactor accident in 1986. The apparent half-decrease time of dissolved  $^{137}\text{Cs}$  ( $1.9 \pm 0.3$  years), which means a time that radionuclide concentrations in river water decrease to a half, was similar to that for dissolved  $^{239,240}\text{Pu}$  for the same period, whereas the apparent half-decrease time of particulate  $^{239,240}\text{Pu}$  ( $4.5 \pm 2.2$  years) was longer. Temporal changes in dissolved  $^{239,240}\text{Pu}$  and  $^{137}\text{Cs}$  in river water can be explained by direct contribution of radionuclides from rainwater and leaching of radionuclides from surface-layer soil particles on land.

## Introduction

Plutonium and  $^{137}\text{Cs}$  released into the atmosphere by atmospheric testing of nuclear weapons and nuclear disasters involving nuclear reactor accidents such as the Chernobyl nuclear reactor accident and Fukushima Daiichi Nuclear Power Plant (FDNPP) accident have been deposited on land surfaces by both wet and dry deposition [1,2]. As a result of radioactive fallout from atmospheric nuclear tests, about 11  $\text{kBq m}^{-2}$  and 44  $\text{Bq m}^{-2}$  of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  have been deposited on land surfaces in Japan during 1945–1985 [3,4]. Most anthropogenic radionuclides deposited on land surfaces were initially adsorbed onto surface soil particles, although adsorption reactions between soil particles and radionuclides differ between radionuclides; typically plutonium reacts with biogenic organic matter including microorganisms [5–7], whereas radiocesium adsorbs onto clay minerals [8–11]. Subsequently, the anthropogenic radionuclides gradually migrated within terrestrial environments. A portion of radionuclides in terrestrial environments was transported into the ocean via river runoff and aeolian processes involving radionuclide-bearing dust particles [12]. After the 1986 Chernobyl and 2011 FDNPP accidents, migration of anthropogenic radionuclides in the terrestrial environment has been major concern to assess radiological effects, in which river runoff of the anthropogenic radionuclides are one of the most important processes [6,11,13,14].

In order to have better understanding of the long-term river runoff processes of anthropogenic radionuclides, it is necessary to have long-term monitoring results of concentrations of anthropogenic radionuclides in river water. Monitoring results for anthropogenic radionuclides derived from atmospheric nuclear explosions would provide a good opportunity to study the long-term riverine processes. Except the large-scale nuclear reactor accidents, most of the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in river water originated from global fallout, although anthropogenic radionuclides have been discharged into several rivers from nuclear facilities, including nuclear reactors and nuclear fuel reprocessing plants. In this connection, concentrations of anthropogenic radionuclides in river water have been determined so that the effects of radioactive discharge from nuclear facilities can be assessed [15–18]. In Japan, most nuclear facilities are located in coastal areas. Therefore, until the 2011 FDNPP accident, there is no obvious

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source of contamination of  $^{137}\text{Cs}$  and plutonium in major Japanese rivers except as a result of radioactive fallout originating from atmospheric nuclear tests. The source of anthropogenic radionuclides in Japanese river water until 2011 is primarily global fallout from atmospheric nuclear testing. Miyake and Tsubota [19] and Miyake et al. [20] reported concentrations of  $^{137}\text{Cs}$  and plutonium in major Japanese rivers and suggested that only a small portion of  $^{137}\text{Cs}$  and plutonium that was deposited on land surfaces is leached by river water because  $^{137}\text{Cs}$  and plutonium is tightly adsorbed on soil particles, as shown by large partition coefficients for plutonium between soil particles and the aqueous phase [21].

The dynamics of chemical constituents, including radionuclides, trace metals, and nutrients, are often complex in river systems [22]. River water comes from three sources: overland flow, groundwater, and subsurface stormflow. Precipitation plays an especially important role in overland flow. Chemical and biological interactions that control element concentrations vary among rivers, as does the source of river water. Although complex chemical processes occur in rivers, a major process in river systems is the leaching of elements from the land surface [22–24]. Precipitation is another important factor because it is a direct source of anthropogenic radionuclides, as shown by the increase in  $^{137}\text{Cs}$  concentrations in river water immediately after the Chernobyl accident [21]. However, factors controlling anthropogenic radionuclides in rivers remain poorly understood. Before these factors can be examined, however, temporal variations of the global fallout-derived  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in major Japanese rivers must be analyzed. However, little information is available on long-term variations of the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in river water because of a lack of long-term monitoring of anthropogenic radionuclides in rivers.

**\*Corresponding Author:** Prof. Katsumi Hirose, Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan; E-mail: [hirose45037@mail2.acccsnet.ne.jp](mailto:hirose45037@mail2.acccsnet.ne.jp)

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In this paper, we report data obtained in Environmental Radiation Survey (ERS) project, Japan and examine the temporal variation in previously reported <sup>137</sup>Cs and <sup>239,240</sup>Pu concentrations in major Japanese rivers [20,25] in order to elucidate behaviors of global fallout-derived radionuclides in the terrestrial environment.

### Background

Meteorological Research Institute (MRI) have conducted the ERS project since 1957 to monitor the environmental effects of anthropogenic radionuclides derived from atmospheric nuclear testing. This project revealed temporal changes of deposition fluxes of anthropogenic radionuclides due to global fallout; the maximum deposition fluxes of <sup>137</sup>Cs and <sup>239,240</sup>Pu occurred in 1963 after the large-scale US and former USSR atmospheric nuclear tests in 1961-62, and although since Nuclear Test-Ban Treaty in 1963 these deposition fluxes decreased exponentially according to the stratospheric residence time of radioactive aerosols, the radioactive deposition fluxes varied due to Chinese atmospheric nuclear tests conducted until 1980 [2,3]. Terrestrial environment was contaminated by deposition of the anthropogenic radionuclides from global fallout [26]. It is important to assess the effects of the anthropogenic radionuclides in the terrestrial environment. MRI had conducted the research project entitled Behavior of Transuranic Elements in the Environment during the period of 1978 - 1988, in which <sup>137</sup>Cs and <sup>239,240</sup>Pu concentrations in major rivers in Japan were measured. Figure 1 shows the temporal variations of annual deposition fluxes of <sup>137</sup>Cs and <sup>239,240</sup>Pu observed at Tsukuba, Japan during the period of 1978 - 1988, in which the annual <sup>137</sup>Cs and <sup>239,240</sup>Pu deposition fluxes, ranged from 0.067 (in 1985) to 135 Bq m<sup>-2</sup>y<sup>-1</sup> (in 1986) and from 0.026 (in 1985) to 0.27 Bq m<sup>-2</sup>y<sup>-1</sup> (in 1977), respectively varied more than one order of magnitude.

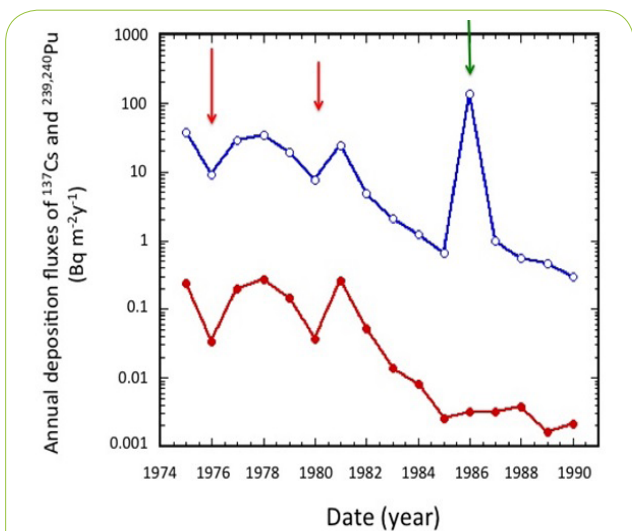


Figure 1: Temporal variations of annual deposition fluxes of <sup>137</sup>Cs and <sup>239,240</sup>Pu observed at Tokyo (1986 - 1980) and Tsukuba (1980 - ). Red arrows show Chinese thermonuclear tests (21<sup>st</sup>: 4 Mt, Nov. 1976; 26th : 0.6 Mt, Oct. 1980). Green arrow shows the Chernobyl accident.

### Sampling

Sampling of water was carried out in 24 rivers in Japan during the period of 1978 - 1988: Ishikari and Teshio (Hokkaido Island); Omono, Kitakami, Mogami, Shinano, Tone, Fuji, Tenryu, Kiso, Kuzuryu, Yura, Yodo, Asahi, Gou, Hii, and Ohta (Honshu Island); Yoshino (Shikoku Island); and Chikugo, Ohono, Sendai, Kuma, Ohyodo, and Gokase

(Kyushu Island) rivers. Locations and sampling sites are shown in Figure 2. Sampling period of each river is shown in Table 1. The sampling site on each river was selected to avoid industrial and urban pollution as well as inflowing seawater. A water sample of 1000 L was collected from each river. The water was filtered through a fine membrane filter (Millipore HA, pore size of 0.45 μm and diameter of 293 mm) immediately after collection.

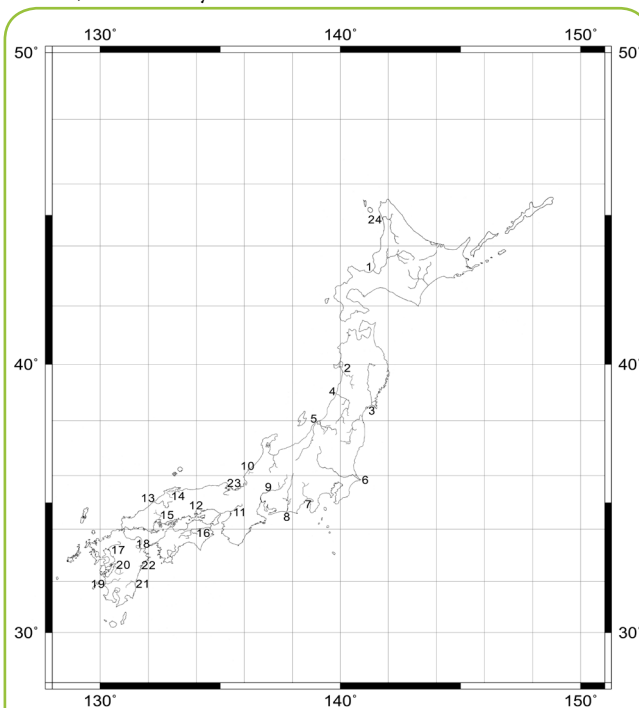


Figure 2: Locations and sampling sites for 24 rivers in Japan. 1., Ishikari; 2., Omono; 3., Kitakami; 4., Mogami; 5., Shinano; 6., Tone; 7., Fuji; 8., Tenryu; 9., Kiso; 10., Kuzuryu; 11., Yodo; 12., Asahi; 13., Gou; 14., Hii; 15., Ohta; 16., Yoshino; 17., Chikugo; 18., Ohono; 19., Sendai; 20., Kuma; 21., Ohyodo; 22., Gokase; 23., Yura; and 24., Teshio.

Name of river	Sampling time	<sup>239,240</sup> Pu (mBq m <sup>-3</sup> )		Dissolved <sup>137</sup> Cs (Bq m <sup>-3</sup> )
		Dissolved	Particulate	
Kitakami	Aug. 1966	25±3 <sup>a</sup>	21±2 <sup>a</sup>	
Mogami	Aug. 1966	67±4 <sup>a</sup>	21±2 <sup>a</sup>	
Shinano	Oct. 1966	8.5±0.7 <sup>a</sup>	14±1 <sup>a</sup>	
Kiso	Oct. 1966	19±2 <sup>a</sup>	11±1 <sup>a</sup>	
Tone	Nov. 1966	154±7 <sup>a</sup>	7.8±0.7 <sup>a</sup>	
Yodo	Aug. 1967	2.6±0.4 <sup>a</sup>	4.8±0.4 <sup>a</sup>	
Asahi	Aug. 1967	9.6±0.7 <sup>a</sup>	8.5±0.7 <sup>a</sup>	
Yoshino	Aug. 1967	19±2 <sup>a</sup>	12±1 <sup>a</sup>	
Ishikari	Oct. 1978	10±1 <sup>b</sup>	5.2±0.4 <sup>b</sup>	0.65±0.10 <sup>c</sup>
Kitakami	Oct. 1978	3.3±0.4 <sup>b</sup>	5.6±0.4 <sup>b</sup>	1.27±0.18 <sup>c</sup>
Mogami	Oct. 1978	11±1 <sup>b</sup>	1.5±0.2 <sup>b</sup>	2.15±0.30 <sup>c</sup>
Shinano	Oct. 1978	1.9±0.4 <sup>b</sup>	1.1±0.1 <sup>b</sup>	1.56±0.10 <sup>c</sup>
Kiso	Oct. 1978	10±1 <sup>b</sup>	5.9±0.4 <sup>b</sup>	0.58±0.09 <sup>c</sup>
Yodo	Oct. 1979	0.7±0.4 <sup>b</sup>	3.0±0.4 <sup>b</sup>	1.37±0.20 <sup>c</sup>
Yoshino	Oct. 1979	1.1±0.4 <sup>b</sup>	4.8±0.4 <sup>b</sup>	0.28±0.06 <sup>c</sup>
Asahi	Oct. 1979	0.4±0.2 <sup>b</sup>	0.37±0.04 <sup>b</sup>	0.99±0.15 <sup>c</sup>

Continued....

Name of river	Sampling time	<sup>239,240</sup> Pu (mBq m <sup>-3</sup> )		Dissolved <sup>137</sup> Cs (Bq m <sup>-3</sup> )
		Dissolved	Particulate	
Chikugo	Oct. 1979	31±2 <sup>b</sup>	1.9±0.1 <sup>b</sup>	0.94±0.14 <sup>c</sup>
Tone	Feb. 1980	58±4 <sup>b</sup>	1.9±0.1 <sup>b</sup>	0.59±0.10 <sup>c</sup>
Ohono	Oct. 1980	0.6±0.1 <sup>c</sup>	0.7±0.07 <sup>c</sup>	0.30±0.06 <sup>c</sup>
Hii	Sep. 1981	ND	4.8±0.4 <sup>c</sup>	0.31±0.06 <sup>c</sup>
Gou	Sep. 1981	0.7±0.1 <sup>c</sup>	0.85±0.07 <sup>c</sup>	0.21±0.05 <sup>c</sup>
Ohota	Sep. 1981	0.4±0.1 <sup>c</sup>	1.0±0.1 <sup>c</sup>	0.33±0.06 <sup>c</sup>
Shinano	Oct. 1982	0.4±0.1 <sup>c</sup>	3.0±0.4 <sup>c</sup>	0.14±0.04 <sup>c</sup>
Omono	Oct. 1982	0.9±0.1 <sup>c</sup>	2.7±0.3 <sup>c</sup>	0.23±0.05 <sup>c</sup>
Mogami	Oct. 1982	2.8±0.3 <sup>c</sup>	2.4±0.2 <sup>c</sup>	0.27±0.06 <sup>c</sup>
Kiso	Oct. 1983	11±1 <sup>c</sup>	1.1±0.1 <sup>c</sup>	0.11±0.03 <sup>c</sup>
Fuji	Oct. 1983	1.1±0.1 <sup>c</sup>	0.3±0.04 <sup>c</sup>	0.03±0.02 <sup>c</sup>
Tenryu	Oct. 1983	1.1±0.1 <sup>c</sup>	0.52±0.07 <sup>c</sup>	0.18±0.04 <sup>c</sup>
Fuji	Oct. 1984	0.21±0.05 <sup>c</sup>	0.48±0.07 <sup>c</sup>	0.06±0.02 <sup>c</sup>
Tenryu	Oct. 1984	0.4±0.04 <sup>c</sup>	0.7±0.1 <sup>c</sup>	0.07±0.03 <sup>c</sup>
Yura	Oct. 1984	0.5±0.07 <sup>c</sup>	0.9±0.1 <sup>c</sup>	0.01±0.02 <sup>c</sup>
Kiso	Oct. 1984	0.37±0.04 <sup>c</sup>	1.0±0.1 <sup>c</sup>	0.14±0.04 <sup>c</sup>
Tone	June 1985	2.2±0.3 <sup>d</sup>	0.67±0.13 <sup>d</sup>	0.69±0.10 <sup>d</sup>
Ishikari	Oct. 1985	0.33±0.07 <sup>d</sup>	1.6±0.3 <sup>d</sup>	0.033±0.018 <sup>d</sup>
Kitakami	Oct. 1985	–	0.63±0.14 <sup>d</sup>	0.085±0.03 <sup>d</sup>
Tone	Nov. 1985	0.08±0.03 <sup>d</sup>	0.56±0.10 <sup>d</sup>	0.126±0.038 <sup>d</sup>
Tone	Feb. 1986	1.51±0.26 <sup>d</sup>	0.52±0.10 <sup>d</sup>	0.39±0.08 <sup>d</sup>
Tone	June 1986	0.3±0.07 <sup>d</sup>	1.63±0.22 <sup>d</sup>	1.39±0.10 <sup>d</sup>
Ishikari	Aug. 1986	–	0.52±0.10 <sup>d</sup>	0.57±0.10 <sup>d</sup>
Kuzuryu	Oct. 1986	–	0.67±0.12 <sup>d</sup>	1.04±0.10 <sup>d</sup>
Kiso	Nov. 1986	0.11±0.03 <sup>d</sup>	0.52±0.10 <sup>d</sup>	0.49±0.09 <sup>d</sup>
Tenryu	Nov. 1986	–	0.37±0.07 <sup>d</sup>	0.14±0.05 <sup>d</sup>
Fuji	Nov. 1986	0.59±0.1 <sup>d</sup>	0.22±0.06 <sup>d</sup>	0.063±0.029 <sup>d</sup>
Tone	Oct. 1986	0.04±0.01 <sup>d</sup>	0.52±0.09 <sup>d</sup>	0.46±0.06 <sup>d</sup>
Tone	Feb. 1987	0.06±0.02 <sup>d</sup>	1.30±0.21 <sup>d</sup>	0.52±0.10 <sup>d</sup>
Kiso	Oct. 1987	–	–	0.25±0.05 <sup>c</sup>
Tenryu	Oct. 1987	–	–	0.05±0.03 <sup>c</sup>
Fuji	Oct. 1987	–	–	0.05±0.03 <sup>c</sup>
Ishikari	Oct. 1987	–	–	0.11±0.04 <sup>c</sup>
Teshio	Oct. 1987	–	–	0.19±0.04 <sup>c</sup>
Kitakami	Oct. 1987	–	–	0.29±0.06 <sup>c</sup>
Tone	Oct. 1987	–	–	0.27±0.06 <sup>c</sup>

Table 1: Concentrations of <sup>137</sup>Cs and dissolved and particulate <sup>239,240</sup>Pu in Japanese river water.

Uncertainty is one sigma of counting error.

a: from Miyake et al., 1973; b: from Hirose and Sugimura, 1981; c: unpublished data; d: from Hirose et al., 1990.

## Methods

Analytical procedures to determine concentrations of <sup>137</sup>Cs and <sup>239,240</sup>Pu in river water have been described in detail elsewhere [21]. In our work, we analyzed <sup>137</sup>Cs and <sup>239,240</sup>Pu concentrations in 500-L samples of filtered river water. <sup>137</sup>Cs was concentrated by adsorption onto ammonium molybdophosphate (AMP) under acidic conditions (pH = 2). The AMP precipitate was separated from water by decantation and filtration. After being dried at 110°C, precipitate was packed in a 50-ml plastic container. <sup>137</sup>Cs counting was carried out by gamma spectrometry, comprising a Ge semiconductor detector and a 4096 ch pulse-height analyzer. The energy dependent efficiency of the Ge detector was determined with a <sup>152</sup>Eu standard source or a mixed

standard source of <sup>60</sup>Co, <sup>133</sup>Ba and <sup>137</sup>Cs. The <sup>137</sup>Cs activity was measured at 661 keV. The geometric parameters were determined by using a laboratory standard AMP precipitate with known <sup>137</sup>Cs content. Chemical yield of <sup>137</sup>Cs dissolved in river water was measured from weight recovery of the AMP precipitate. Uncertainty accompanied with analytical procedure was less than 5 %.

The supernatant from the <sup>137</sup>Cs analysis was used for the plutonium analysis. After the addition of MgCl<sub>2</sub> and CaCO<sub>3</sub>, plutonium was concentrated as a coprecipitate of (Mg, Ca)(OH)<sub>2</sub> by adding a NaOH solution. The precipitate was then dissolved with concentrated HCl. The plutonium was separated and purified using an anion exchange resin. The concentration of particulate <sup>239,240</sup>Pu concentration in river water was determined by analyzing the residue collected on the membrane filter during filtration of the sample. The residue was digested and dissolved with concentrated HNO<sub>3</sub> and HCl as it was heated on a hot plate. Particulate <sup>239,240</sup>Pu was separated and purified using an anion exchange resin.

Each plutonium fraction was dissolved in 1 ml of a 2 M HCl solution and transferred into an electroplating cell by using 20 ml of ethanol. Plutonium was electrodeposited onto a stainless steel disc. <sup>239,240</sup>Pu counting (alpha energy: 5.157 MeV (<sup>239</sup>Pu), 5.168 MeV (<sup>240</sup>Pu)) was done by alpha spectrometry, comprising silicon solid-state detectors and a multichannel pulse-height analyzer. Energy calibration and detector efficiency were carried out with a laboratory standard uranium disc (alpha energy: 4.202 MeV (<sup>238</sup>U), 4.775 MeV (<sup>234</sup>U)) and a <sup>241</sup>Am standard disc (alpha energy: 5.486 MeV). The chemical yield was determined by adding a known amount of <sup>236</sup>Pu.

## Results and Discussion

The concentrations of <sup>137</sup>Cs and <sup>239,240</sup>Pu in major Japanese rivers during 1966–1987 are shown in Table 1. The <sup>137</sup>Cs and <sup>239,240</sup>Pu concentrations in river water show large spatial variability, as summarized in Table 2. The results suggest that complex processes, such as spatial variability of time-dependent atmospheric deposition fluxes of anthropogenic radionuclides, water–land surface interactions, and chemical conditions of river water, control the radionuclide concentrations in the rivers.

Year	<sup>239,240</sup> Pu range	Calc.	<sup>137</sup> Cs range	Calc.
	mBq m <sup>-3</sup>		Bq m <sup>-3</sup>	
1966	8.5–154	30		
1967	2.6–19	13		
1978	1.9–11	5.4	0.6–2.2	0.78
1979	0.4–30	2.2	0.3–1.4	0.36
1980	0.8–58	0.8	0.07–0.59	0.22
1981	0.04–1.3	4.9	0.11–0.33	0.51
1982	0.4–2.8	1.0	0.14–0.27	0.18
1983	1.1–11	0.54	0.03–0.18	0.15
1984	0.06–0.48	0.52	0.015–0.21	0.14
1985	0.33–0.67	0.34	0.03–0.69	0.12
1986	0.04–1.5	0.35	0.06–1.4	0.10*
1987			0.05–0.52	0.12

Table 2: Concentration ranges and calculated values of <sup>239,240</sup>Pu and <sup>137</sup>Cs dissolved in Japanese river water.

\* The effect of the Chernobyl fallout was removed from this calculation.

The data used in this work are scattered temporally and spatially. It is difficult to extract detailed behaviors of anthropogenic radionuclides in individual rivers because of limited data. Therefore, we used a composite dataset to analyze temporal variations of anthropogenic radionuclides in Japanese rivers.

#### Temporal variations in concentrations of $^{137}\text{Cs}$ and $^{239,240}\text{Pu}$ in rivers

Temporal variations in concentrations of dissolved  $^{137}\text{Cs}$  in major Japanese rivers during 1978–1987 are shown in Figure 3. Dissolved water decreased exponentially from 1978 to 1985, although rather large spatial variations occurred. Assuming that the dissolved  $^{137}\text{Cs}$  concentrations in the rivers decrease as an exponential function according to first-order kinetics, we have a best fit curve of an equation ( $C_{R, \text{river}} = A \exp(-\lambda t)$ ;  $C_{R, \text{river}}$ : the concentration of radionuclide in river water,  $t$ : time,  $A$  and  $\lambda$ : constants). We calculated an apparent half-decrease time (HDT:  $T_{1/2} = 0.693/\lambda$ ) of the dissolved  $^{137}\text{Cs}$  in Japanese river water from the  $\lambda$  value. The apparent HDT of river  $^{137}\text{Cs}$  was  $1.9 \pm 0.3$  years during 1978–1985.

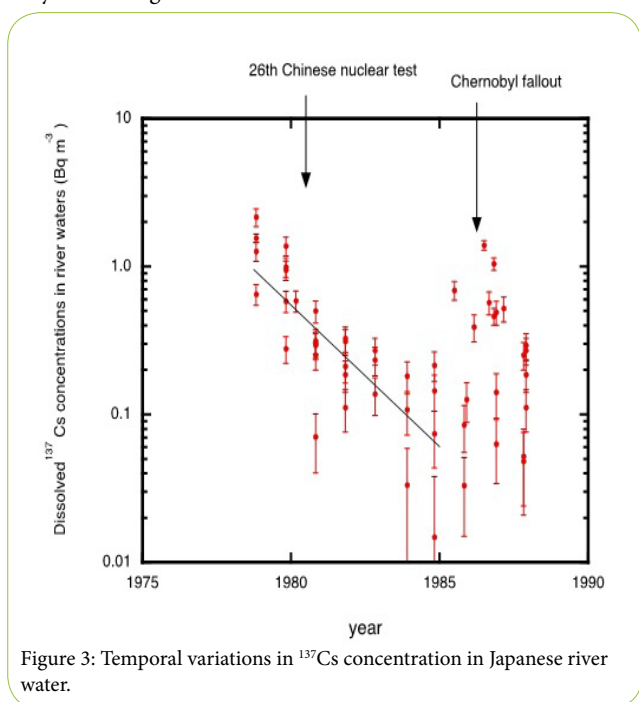


Figure 3: Temporal variations in  $^{137}\text{Cs}$  concentration in Japanese river water.

It is likely that temporal changes in the  $^{137}\text{Cs}$  concentrations in river water respond to changes in atmospheric deposition fluxes. When we compared the apparent HDT of the river  $^{137}\text{Cs}$  with that of the atmospheric deposition flux (Figure 1), we found that the apparent HDT of the river  $^{137}\text{Cs}$  is slightly longer than that of the corresponding atmospheric deposition flux by  $1.2 \pm 0.3$  years for the same period. After the Chernobyl accident in April 1986, the  $^{137}\text{Cs}$  concentrations in river water increased by an order magnitude compared to the concentrations in previous years. The increase in the  $^{137}\text{Cs}$  concentrations in river water in 1986 resulted from the Chernobyl fallout, as indicated by the detection of  $^{134}\text{Cs}$  [21]. On the other hand, there was no effect on the  $^{137}\text{Cs}$  concentrations in river water in 1981 following the 26th Chinese atmospheric nuclear test, which was conducted in October 1980.

Temporal variations in dissolved  $^{239,240}\text{Pu}$  concentrations in major Japanese rivers from 1978 through 1987 are shown in Figure 4.

Dissolved  $^{239,240}\text{Pu}$  concentrations in river water exponentially decreased from 1966 to 1987, although large spatial variations occurred. We calculated an apparent HDT of dissolved  $^{239,240}\text{Pu}$  in Japanese river water, assuming that the dissolved  $^{239,240}\text{Pu}$  concentrations decrease as an exponential function, of  $3.4 \pm 0.6$  years during 1966–1986. After the Chernobyl accident in April 1986, the  $^{239,240}\text{Pu}$  concentrations in river water showed no increase, which is likely because there was only small contribution on deposition of Chernobyl-derived plutonium in Japan in contrast to  $^{137}\text{Cs}$  [27].

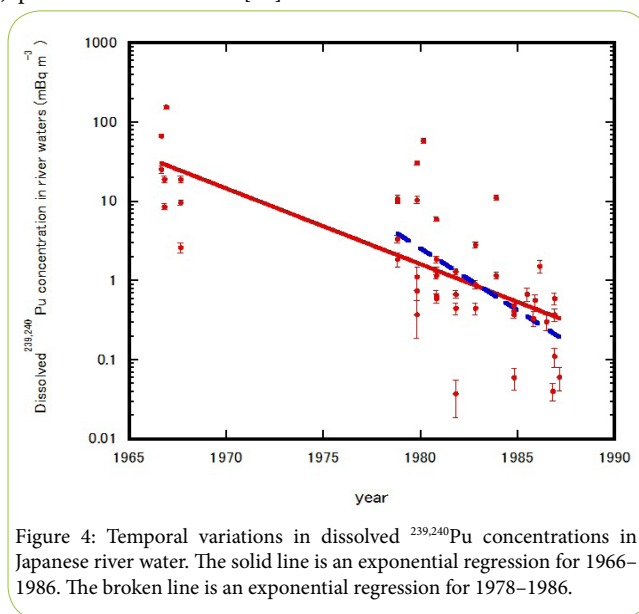


Figure 4: Temporal variations in dissolved  $^{239,240}\text{Pu}$  concentrations in Japanese river water. The solid line is an exponential regression for 1966–1986. The broken line is an exponential regression for 1978–1986.

The temporal variation of the particulate  $^{239,240}\text{Pu}$  concentrations in major Japanese rivers during 1978–1987 is shown in Figure 5. Both dissolved and particulate  $^{239,240}\text{Pu}$  concentrations in river water exponentially decreased from 1966 to 1986. We calculated an apparent HDT of particulate  $^{239,240}\text{Pu}$  in Japanese river water, assuming that the particulate  $^{239,240}\text{Pu}$  concentrations decrease as an exponential function, of  $4.5 \pm 0.7$  years during 1966–1986. The apparent HDTs of dissolved and particulate river  $^{239,240}\text{Pu}$  were thus longer than that of the atmospheric deposition rate (2.7 years) for the same period.

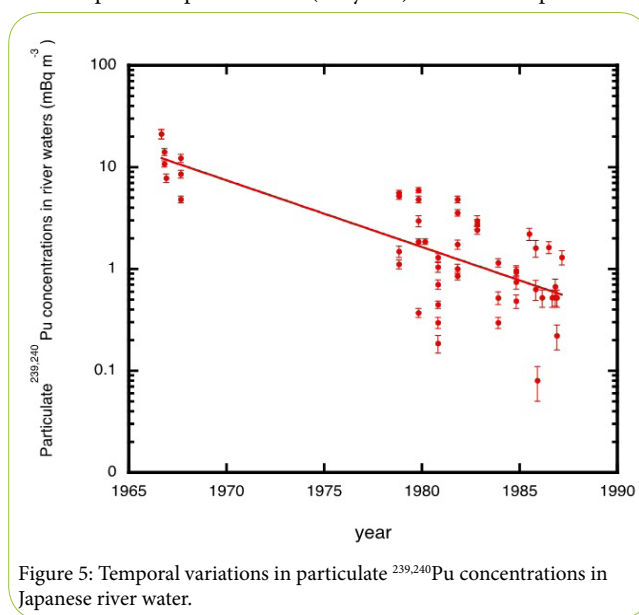


Figure 5: Temporal variations in particulate  $^{239,240}\text{Pu}$  concentrations in Japanese river water.



It is of interest to know whether a difference of riverine behaviors between anthropogenic radionuclides exists. The apparent HDTs of dissolved and particulate river  $^{239,240}\text{Pu}$  were calculated for the same sampling period as for  $^{137}\text{Cs}$  because comparison of apparent HDTs between the different sampling periods is misleading. The calculated apparent HDTs of the dissolved and particulate river  $^{239,240}\text{Pu}$  were  $1.9 \pm 0.5$  and  $4.5 \pm 2.2$  years, respectively. There was no significant difference in the apparent HDTs of the dissolved river  $^{239,240}\text{Pu}$  and  $^{137}\text{Cs}$ , whereas the apparent HDT of the particulate river  $^{239,240}\text{Pu}$  was slightly longer than that of the dissolved  $^{239,240}\text{Pu}$ . These findings suggest that the trends in the concentrations of anthropogenic radionuclides dissolved in Japanese rivers during 1966–1987 primarily reflect their atmospheric deposition fluxes, although they might be mitigated by land surface–water interactions. In fact, marked high  $^{137}\text{Cs}$  concentrations in river waters occurred in high deposition flux area after the Fukushima Daiichi Nuclear Power Plant accident [28].

#### Factors controlling dissolved $^{137}\text{Cs}$ and $^{239,240}\text{Pu}$ concentrations in river water

To have better understanding of factors controlling  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations dissolved in river water is important because dissolved form of radionuclides is directly related to biological uptake and chemical reactions occurring in river water. It is likely that chemical processes such as adsorption and desorption controls dissolved  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in river water. In addition to the chemical processes, another process is direct input of water-soluble  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in river water due to atmospheric deposition [21]. To examine factors controlling concentrations of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  dissolved in river water, we plotted the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in river water against the corresponding annual mean concentrations in rainwater. The annual mean radionuclide concentrations in rainwater were calculated from corresponding annual deposition fluxes and annual precipitation amounts [3]. The results are shown in Figure 6.

The concentrations of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  dissolved in river water increased with those in rainwater. We propose a simple two-compartment model to explain the relationship between  $^{137}\text{Cs}$  and

$^{239,240}\text{Pu}$  concentrations in rainwater and river water. Two pathways may control the concentrations of radionuclides in river water; as a pathway, anthropogenic radionuclides may be directly contributed into river from rainfall, and as another pathway, they may be leached into river from the soil by rainwater. We assumed that the total volume of river flow per year is approximately equal to the annual amount of precipitation falling on a river drainage basin. The annual total amount of dissolved radionuclides flowing out by river,  $F_{R,R}$ , is given by the following equation:

$$F_{R,R} = C_{R,river} S_d P = S_d f D_R + S_d P C_{R,L} \quad (1)$$

where  $C_{R,river}$ ,  $S_d$ , and  $P$  represent the concentration of radionuclides dissolved in river water, surface area of watershed, and annual precipitation amount, respectively.  $D_R$ ,  $f$ , and  $C_{R,L}$  represent the annual deposition of radionuclides in the drainage basin, direct contribution of rain water to river water, and the radionuclide concentration leached by rainwater from soil, respectively. The radionuclide concentration leached by rainwater is determined from the partition constant and the radionuclide concentration in soil, assuming that partition equilibrium is established between water and soil phases, according to the following equation:

$$C_{R,L} = K_{R,d}^{-1} C_{R,s} \quad (2)$$

where  $K_{R,d}$  represents the radionuclide partition coefficient between soil and water phases in ml/g, and  $C_{R,s}$  represents the radionuclide concentration in soil. Taking into account that most of the radionuclides deposited on the land surface are tightly adsorbed onto soil particles, the radionuclide concentration in soil is given as  $C_{R,s} = D_T d^{-1} \rho^{-1}$ , where  $D_T$  is the cumulative amount of radioactive deposition,  $d$  is the vertical migration depth of radionuclides in the soil layer, and  $\rho$  is the density of surface soil. Finally, the radionuclide concentration in river water can be represented by the following equation:

$$C_{R,river} = f D_R P^{-1} + K_{R,d}^{-1} D_T d^{-1} \rho^{-1} \quad (3)$$

where  $D_R P^{-1}$  represents the radionuclide concentration in rainwater. The second term in equation (3) is approximately constant because most of the anthropogenic radionuclide deposition occurred in the early 1960s. The partition coefficients of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  have been determined for river suspended matter [11,21,24] and soil [8,29]. According to previous results [8,21,24,29],  $K_{R,d}$  values (unit:  $\text{ml g}^{-1}$ ) of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  between water and soil phases are on the orders of  $10_4$  and  $10_5$ , respectively; the  $K_{R,d}$  value of  $^{239,240}\text{Pu}$  is greater than that of  $^{137}\text{Cs}$ . Large variability occurs in the  $K_{R,d}$  values because they depend on chemical and mineralogical compositions and particle size of soil (or sediment) [11,24] and chemical properties of dissolved matter in water.

We calculated the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations dissolved in the Japanese river water from the corresponding annual mean concentrations in rainwater, using  $K_{R,d} = 8 \times 10^4$ ,  $D_T = 5000 \text{ Bq m}^{-2}$  (radioactive decay is corrected at 1980),  $d = 0.2 \text{ m}$ , and  $\rho = \text{cm}^{-3}$  for  $^{137}\text{Cs}$ ; and  $K_{R,d} = 3 \times 10_5$ ,  $D_T = 44 \text{ Bq m}^{-2}$ ,  $d = 0.2 \text{ m}$ , and  $\rho = 1.5 \text{ g cm}^{-3}$  for  $^{239,240}\text{Pu}$ . The cumulative amounts of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  were observed values in Meteorological Research Institute [3]. Both of the vertical migration depths of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in soil layers were determined to be about 0.1 m in non-cultivated areas [30]. In this calculation, we assumed that the vertical migration depth for  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  is about 0.2 m, which is a typical cultivated depth in paddy fields, because drainage areas in Japan include cultivated areas

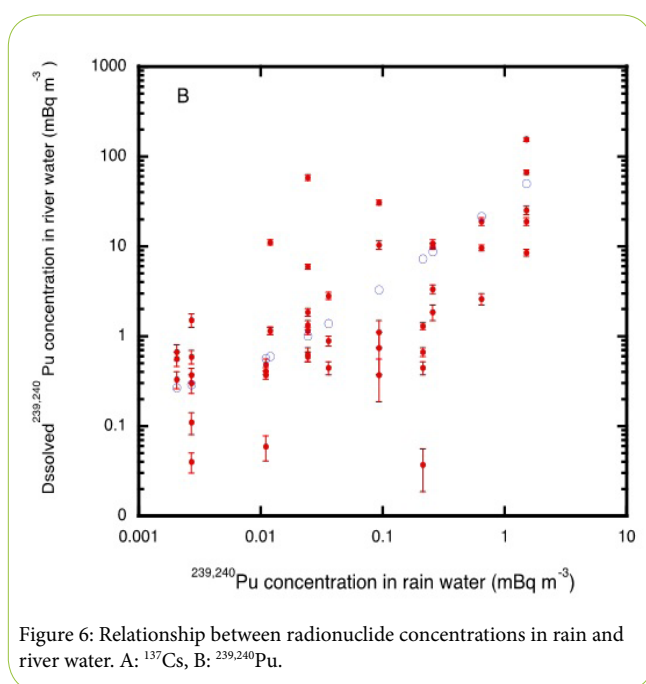
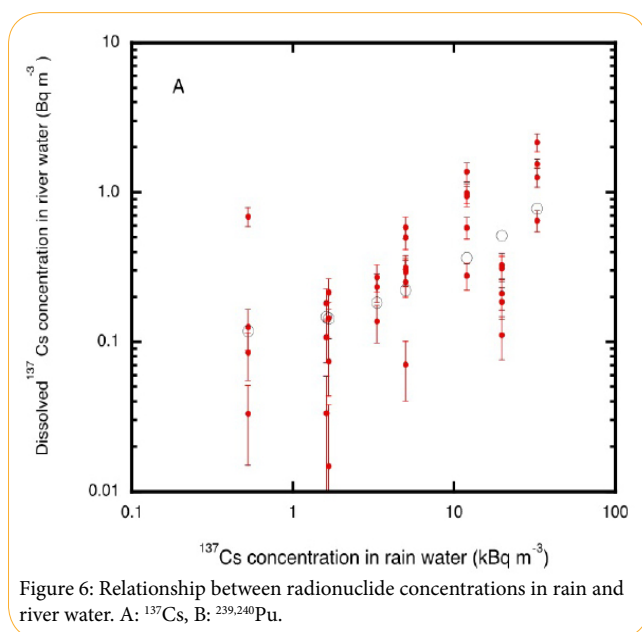


Figure 6: Relationship between radionuclide concentrations in rain and river water. A:  $^{137}\text{Cs}$ , B:  $^{239,240}\text{Pu}$ .



as well as non-cultivated areas. When the direct contribution from rainwater in rivers is about 2% [19,20], the calculated  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in the Japanese river water have the values shown in Table 2 and as open circles in Figure 6. As a first approximation, the calculated results based on the two-compartment model can explain the temporal trend of the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations dissolved in Japanese river water.

## Conclusions

Concentrations of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in major Japanese rivers during 1966–1987 are summarized in this paper. The concentrations exhibited rather large spatial variability, as shown in Table 2. Therefore, we examined temporal variations using a composite dataset. Both  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in Japanese river water exponentially decreased during 1966–1987, with the exception of the  $^{137}\text{Cs}$  concentrations after the Chernobyl accident. We calculated the apparent half-decrease times of river  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  from their temporal changes. The apparent half-decrease time of dissolved  $^{137}\text{Cs}$  ( $1.9 \pm 0.3$  years) was similar to that of dissolved  $^{239,240}\text{Pu}$  ( $1.9 \pm 0.5$  years) in the same period. The apparent half-decrease time of particulate  $^{239,240}\text{Pu}$  was longer ( $4.5 \pm 2.2$  years). Temporal changes in dissolved plutonium and  $^{137}\text{Cs}$  in major Japanese rivers can be explained by the direct effect of atmospheric deposition fluxes and leaching processes from land surfaces when the partition coefficients of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  are known. These findings suggest that, because atmospheric deposition fluxes of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  are low, the  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  concentrations in Japanese river water might be primarily governed by leaching of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  from surface soils of drainage basins during the period of the 1990s and 2000s.

## Competing Interests

The authors declare that they have no competing interests.

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