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Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident

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The Fukushima Daiichi nuclear power plant (DNPP) accident caused massive releases of radioactivity into the environment. The released highly volatile fission products, such as ^{129m}Te, ^{131}I, ^{134}Cs, ^{136}Cs and ^{137}Cs were found to be widely distributed in Fukushima and its adjacent prefectures in eastern Japan. However, the release of non-volatile actinides, in particular, Pu isotopes remains uncertain almost one year after the accident. Here we report the isotopic evidence for the release of Pu into the atmosphere and deposition on the ground in northwest and south of the Fukushima DNPP in the 20–30 km zones. The high activity ratio of ^{241}Pu/$^{239+240}$Pu (> 100) from the Fukushima DNPP accident highlights the need for long-term ^{241}Pu dose assessment, and the ingrowth of ^{241}Am. The results are important for the estimation of reactor damage and have significant implication in the strategy of decontamination.

On March 11, 2011, a catastrophic earthquake (M 9.0) occurred in the northwest Pacific about 130 km off northeastern Japan, followed by a gigantic tsunami, which caused serious damage of the electric system of the Fukushima Daiichi nuclear power plants (DNPP). As a consequence, the cooling systems of nuclear reactors failed, resulting in hydrogen explosions on March 12 and 14 in the Unit 1 and 3 reactors, respectively. On March 15, other explosions happened in the Unit 4 reactor building and the Unit 2 reactor. These explosions of the Fukushima DNPP caused serious releases of radionuclides into the atmosphere[1–3]. The released high volatility fission products including ^{129m}Te, ^{131}I, ^{134}Cs, ^{136}Cs and ^{137}Cs were carried together with the air parcel, and subsequent wet and dry depositions, caused accumulation of them on the ground[4,5]. Consequently, their released amounts and distributions on the ground, as well as the impact on the environment have been studied to provide scientific basis for radiation dose estimation and prediction of their behavior and fate in the environment. For the non-volatile radionuclides, Pu isotopes attracted great public attention in the Fukushima DNPP accident because Pu isotopes present a large risk for internal radiation exposure via ingestions of contaminated agricultural crops, in particular for ^{241}Pu (a beta-emitter, $T_{1/2} = 14.4$ years), with its decay, the ingrowth of ^{241}Am (alpha and gamma-emitter, $T_{1/2} = 432.7$ years) will present a new radiation risk. In addition, the accurate determination of Pu isotopic composition may provide important information for the estimation of reactor damage, considering the fact that high radiation levels make it impossible to directly measure damage to the melted reactor cores[6]. As discussed by Powers et al.[7] after the Chernobyl accident, isotope compositions and activity ratios of different radionuclides could be useful to obtain information on the situation of the nuclear fuel, such as the fuel burn-up and the inventory of radionuclides in the reactor, and thus on the accident mechanisms. For the Fukushima DNPP accident, a preliminary investigation found no significant increase of activities of $^{239+240}$Pu in the soil samples, and ^{241}Pu, the principle isotope contributing to the dose due to external exposure from radioactivity deposition after the accident, was not considered, although the ^{238}Pu/$^{239+240}$Pu activity ratio suggested possible Pu contamination in the northwest of the Fukushima DNPP[8]. Therefore, the release of Pu isotopes into the environment from the Fukushima DNPP accident needs to be clarified.

According to the air dose monitoring data from the MEXT (Ministry of Education, Culture, Sports, Science and Technology) and the atmospheric dispersion simulation by SPEEDI (System for Prediction of Environmental Emergency Dose Information), a high concentration plume of released radionuclides moved to the northwest from the power plant during the daytime on March 15, 2011, and a large amount of radionuclides were deposited on the ground by precipitation[5]. In addition, on March 21, 2011, high deposition rates were observed in the Kanto

Plain, i.e., Ibaraki, Tochigi, Saitama, and Chiba Prefectures and Tokyo[9]. To understand any deposition of Pu isotopes on the ground and to elucidate its isotopic composition, we collected surface soil samples for the determination of activities of ^{137}Cs and Pu, and Pu atom ratios (^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu) in: Chiba, Kamagaya, and Mito Cities in the Kanto Plain; the Evacuation-Prepared Area (J-Village, 20 km south of Fukushima DNPP); and the Deliberate Evacuation Area (S1, in Katsurao Village, 25 km WNW of Fukushima DNPP; S2, in Namie Town, 26 km NW of Fukushima DNPP; and S3, in Iitate Village, 32 km NW of Fukushima DNPP) (Fig. 1). The determination of Pu isotopes was done using a sector-field ICP-MS[10]. Details of the separation and purification of Pu are described elsewhere (see Methods Section).

Results

The results of activities of ^{137}Cs, $^{239+240}$Pu, and ^{241}Pu, the atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu, and the activity ratio of ^{137}Cs/$^{239+240}$Pu in the soil and litter samples were summarized in Table 1. Data of ^{137}Cs activity for the J-Village samples were cited from Tagami et al.[11], and data for global fallout and soil in Tokyo and Sapporo were cited from Kelley et al.[12]. Pu isotopic composition data for atmospheric fallout in Japan were cited from Zhang et al.[13], and for the Chernobyl accident from Muramatsu et al.[14] and Ketterer et al.[15], respectively. For the samples collected in Fukushima Prefecture, activities of $^{239+240}$Pu ranged from 0.019 to 1.400 mBq/g, within the typical global fallout $^{239+240}$Pu activity range of 0.15 to 4.31 mBq/g observed in Japanese soils before the Fukushima DNPP accident[16]. However, high activities of ^{241}Pu ranging from 4.52 to 34.8 mBq/g were detected in samples of the J-Village surface soil (0–2 cm) and of litter at sites S2 and S3 (Table 1). ^{241}Pu was released into the environment through atmospheric nuclear weapons tests in the last century. Due to its short half-life of 14.4 years, the activity of ^{241}Pu in Japanese soils is quite low (ca. 1.2 for ^{241}Pu/$^{239+240}$Pu activity ratio, ^{241}Pu decay corrected to March 15, 2011). Therefore, the finding of high ^{241}Pu activities in these samples suggested an additional Pu input. The ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios found in these samples ranged from 0.303 to 0.330 and from 0.103 to 0.135, respectively. They were significantly higher than those of global fallout (0.180±0.007, 1σfor ^{240}Pu/^{239}Pu atom ratio, and 0.00194±0.00014, 1σ for ^{241}Pu/^{239}Pu atom ratio)[12] and the atmospheric fallout deposition in

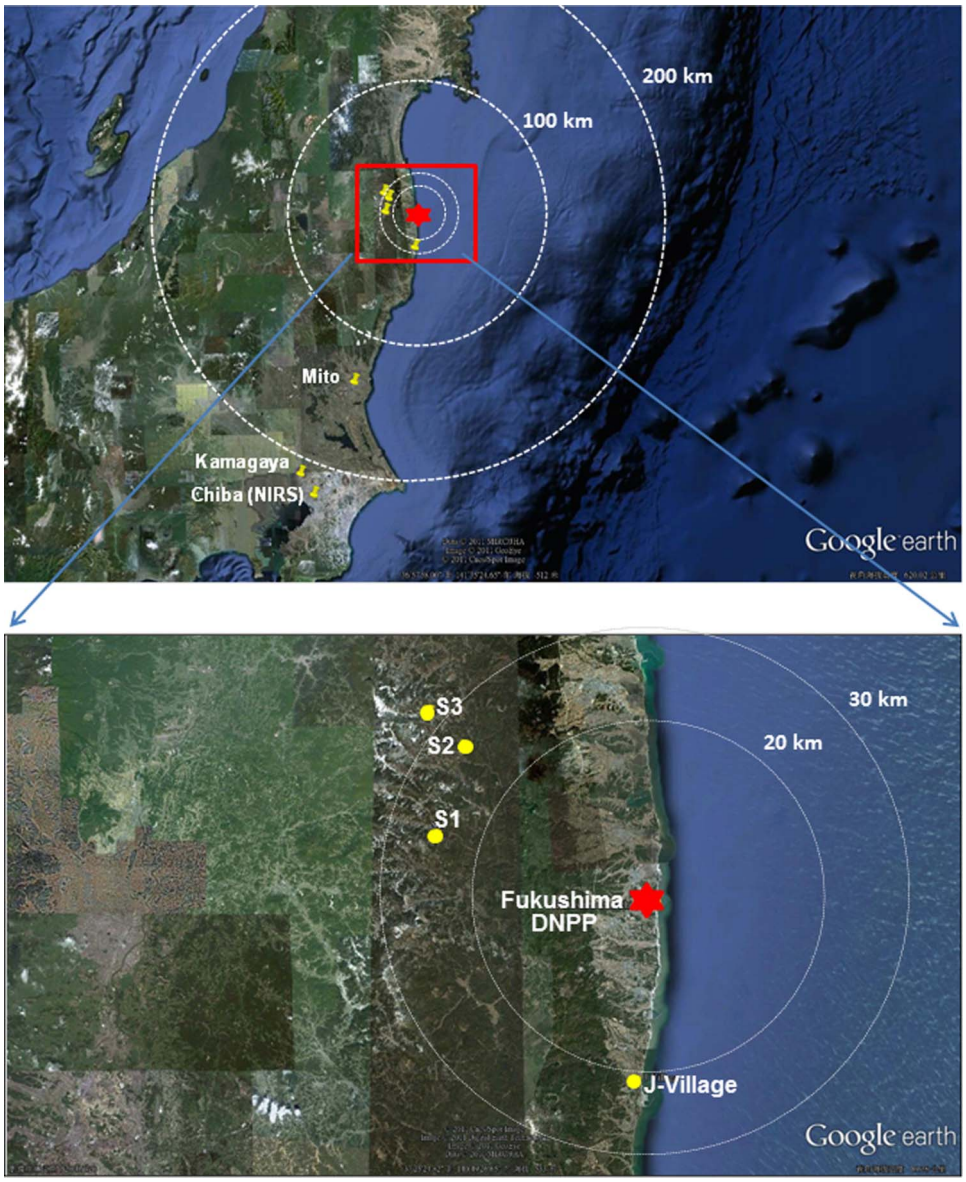

Figure 1 | **Map showing the locations of soil sampling sites.**

Table 1 | Activities of $^{239+240}$Pu, ^{241}Pu and ^{137}Cs, and atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu in soil and litter samples

Sample	Sampling date	Location	$^{239+240}$Pu activity (mBq/g)	^{241}Pu activity (mBq/g)[a]	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	^{137}Cs activity (mBq/g)	^{137}Cs/$^{239+240}$Pu ratio
S1-Litter	2011/5/20	WNW 25 km	0.019±0.003	ND	ND	ND	148000±1350	7.79×10^{6}
S1-Soil (0–1 cm)	2011/5/20	WNW 25 km	0.215±0.006	ND	0.171±0.013	ND	1693±48	7.87×10^{3}
S2-Litter	2011/5/20	NW 26 km	0.329±0.011	34.8±2.7	**0.323±0.017**	**0.135±0.012**	1416000±4230	4.30×10^{6}
S2-Soil (0–1 cm)	2011/5/20	NW 26 km	1.163±0.033	ND	0.177±0.013	ND	21410±360	1.84×10^{4}
S3-Litter	2011/5/20	NW 32 km	0.184±0.011	20.2±4.2	**0.330±0.032**	**0.128±0.034**	4649000±9070	2.53×10^{7}
S3-Soil (0–1 cm)	2011/5/20	NW 32 km	1.400±0.023	ND	0.144±0.006	ND	17060±250	1.22×10^{4}
J-Village surface soil (0–2 cm)	2011/4/20	S 20 km	0.059±0.004	4.52±0.56	**0.303±0.030**	**0.103±0.013**	11480±540[b]	1.95×10^{5}
J-Village surface soil (5–7 cm)			0.024±0.004	ND	ND	ND	630±30[b]	2.63×10^{3}
J-Village surface soil (10–12 cm)			0.026±0.003	ND	ND	ND	140±10[b]	5.38×10^{3}
Mito surface soil (0–1 cm)	2011/8/9	SW 130 km	0.020±0.004	ND	ND	ND	1443±22	7.22×10^{4}
NIRS soil 1 (0–1.5 cm)	2011/4/14	SW 220 km	0.070±0.006	ND	0.209±0.031	ND	898±15	1.28×10^{4}
NIRS soil 2 (0–0.5 cm)	2011/4/22		0.042±0.004	ND	0.173±0.031	ND	2887±30	6.87×10^{4}
NIRS soil 3 (0–1 cm)	2011/4/14		0.100±0.006	ND	0.198±0.017	ND	694±14	6.94×10^{3}
NIRS soil 3 (1–3 cm)			0.117±0.008	ND	0.200±0.029	ND	50±6	4.27×10^{2}
NIRS soil 3 (3–5 cm)			0.133±0.011	ND	0.199±0.035	ND	ND	ND
NIRS soil 3 (5–13 cm)			0.097±0.006	ND	0.186±0.028	ND	ND	ND
Kamagaya soil 1 (0–2 cm)	2011/8/7	SW 230 km	0.081±0.008	ND	0.195±0.036	ND	1311±20	1.62×10^{4}
Kamagaya soil 2 (0–2 cm)	2011/8/7		0.235±0.012	ND	0.171±0.019	ND	11429±88	4.86×10^{4}
Kamagaya soil 2 (2–5 cm)			0.223±0.059	ND	0.172±0.034	ND	1045±87	4.67×10^{3}
Global fallout		(30–71°N)			0.180±0.007	0.00194±0.00014[c]		
		(0–30°N)			0.178±0.010	0.00188±0.00039[c]		
Atmospheric fallout in Japan	1963–1979				0.1922±0.0044	0.00287±0.00056[c]		
Soil in Tokyo, Japan	1970/1971				0.1755±0.0012	0.00171±0.00010[c]		
Soil in Sapporo, Japan	1970/1971				0.1765±0.0011	0.00183±0.00011[c]		
Chernobyl accident					0.408±0.003	0.123±0.007[d]		

[a] ^{241}Pu decay corrected to 15 March 2011.
[b]Data cited from Tagami *et al.*[11].
[c] ^{241}Pu decay corrected to 1 January 2000.
[d] ^{241}Pu decay corrected to 1 May 1986.
Data for global fallout and soils in Tokyo and Sapporo are cited from Kelley *et al.*[12]. Data for atmospheric fallout in Japan are cited from Zhang *et al.*[13].
Data for the Chernobyl accident are cited from Muramatsu *et al.*[14] and Ketterer *et al.*[15].

Japan from 1963 to1979 (0.1922±0.0044, 1σ for $^{240}Pu/^{239}Pu$ atom ratio, and 0.00287±0.00056, 1σ for $^{241}Pu/^{239}Pu$ atom ratio)[13], indicating new Pu input from the Fukushima DNPP accident. We noted that in the surface soil (0–1 cm) under the litter layer at sites S3 and S2, no ^{241}Pu was determined and $^{240}Pu/^{239}Pu$ atom ratios were 0.144 and 0.177, respectively, close to the global fallout value of 0.180. This phenomenon indicated that the released Pu deposited in the litter layer, had not reached the underlying surface soil by May 2011 when the samples were collected. We considered that the atom ratios of $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ found in the litter layer reflected the isotopic composition of the released Pu from the Fukushima DNPP accident.

Discussion

Compared to the Pu isotopic composition seen after the Chernobyl accident[14,15], the Fukushima accident Pu had a slightly higher $^{241}Pu/^{239}Pu$ atom ratio, but lower ratio of $^{240}Pu/^{239}Pu$ (Fig. 2). However, due to the large amount of $^{239+240}Pu$ (about 8.7×10^{13} Bq) released from the Chernobyl accident[17], the activity ratio of $^{241}Pu/^{239+240}Pu$ of the Chernobyl accident (83±5)[15,18] is much lower than that of the Fukushima DNPP accident (107.8, average of S2 and S3 litter, ^{241}Pu decay corrected to March 15, 2011). The Pu atom ratios increase with the increase of the fuel burn-up time in the reactor. The relatively higher $^{241}Pu/^{239+240}Pu$ activity ratio of the Fukushima DNPP accident might be because of the damage to the Unit 3 reactor, which had a mixed core, containing both uranium fuel and mixed uranium and plutonium oxide (MOX) fuel; the latter was about 6% of the core fuel. The additional production of ^{241}Pu from the ^{239}Pu fuel may have enhanced the $^{241}Pu/^{239+240}Pu$ activity ratio and $^{241}Pu/^{239}Pu$ atom ratio inside the reactor during normal operation before the accident.

The atom ratios of $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ found in the surface soil of J-Village were slightly lower than those in litter samples in Namie Town (S2) and Iitate Village (S3) in the NW direction of the Fukushima DNPP. The plot of $^{241}Pu/^{239}Pu$ vs. $^{240}Pu/^{239}Pu$ for the data of Table 1 for the global fallout, the soil in J-Village and the litter at sites S2 and S3 could be described by a linear function ($r^2=0.9901$): $^{241}Pu/^{239}Pu = 0.9024\times(^{240}Pu/^{239}Pu)-0.1656$ (Fig. 2). It indicated that the Pu in J-Village surface soil (0–2 cm) contained a small proportion of global fallout Pu.

Using a two end-member mixing model (see Methods Section) based upon the work of Krey[19], we found the percentage of Fukushima-derived $^{239+240}Pu$ in the J-Village soil was 87 %; and the other 13 % $^{239+240}Pu$ was of global fallout origin. We noted that Pu activities in the J-Village surface soil were ca. one order of magnitude lower than those in northwest of Fukushima DNPP.

In the samples that showed Pu contamination from the Fukushima accident, we detected extremely high ^{137}Cs activities. They ranged from 1.15×10^4 to 4.65×10^6 mBq/g (Table 1). The activity ratios of $^{137}Cs/^{239+240}Pu$ for these samples ranged from 1.95×10^5 to 2.53×10^7, and they were 1–3 orders of magnitude higher than that of the Chernobyl accident (770, ^{137}Cs corrected for decay to June, 1997)[14], indicating that the release of $^{239+240}Pu$ from the Fukushima DNPP accident was very small. This was supported by the $^{239+240}Pu$ activity data in Table 1; even in the samples with high ^{137}Cs contamination, the detected $^{239+240}Pu$ activities were still in the typical activity range of the global fallout. To understand the differences of Pu emissions between the Fukushima DNPP accident and the Chernobyl accident, we made a rough estimation on the amount of atmospheric release of Pu and the percentage of core inventory released. The estimation was made based on the average of $^{137}Cs/^{239+240}Pu$ activity ratios (1.48×10^7) observed in litter samples

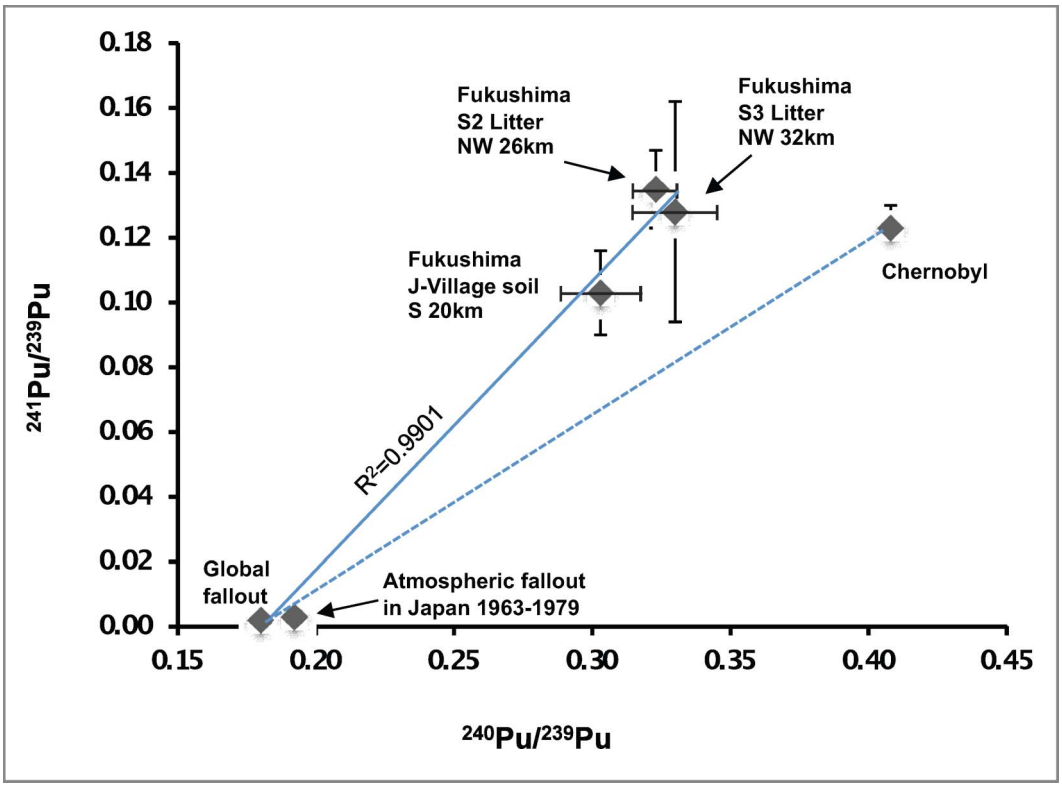

Figure 2 | Mixing plot of $^{241}Pu/^{239}Pu$ atom ratio vs. $^{240}Pu/^{239}Pu$ atom ratio for litter and surface soil samples collected in the 20-30 km zones of Fukushima prefecture, Japan, and a comparison of isotopic composition with those of the Chernobyl accident and the global fallout sources. Error bars are ± 1 standard deviation. Data on the Chernobyl accident are cited from Muramatsu et al.[14] and Ketterer et al.[15]. Data on the global fallout are cited from Kelley et al.[12]. Data on atmospheric fallout in Japan are cited from Zhang et al.[13]; these data were obtained from atmospheric fallout reference material prepared from samples collected at 14 stations through Japan in 1963-1979 by the Meteorological Research Institute (MRI), Japan.

at site S2 and S3, relative to the total amount of ^{137}Cs releases, 1.5×10^{16} Bq and 3.58×10^{16} Bq, estimated by METI (Ministry of Economy, Trade and Industry, Japan)[20] and Stohl et al.[3], respectively, assuming ^{137}Cs and Pu isotopes followed same deposition mechanism, and no significant variation of ^{137}Cs/$^{239+240}$Pu activity ratio during the release and deposition. It should be noted that there is no attempt to make an accurate estimation on the release of Pu from the Fukushima DNPP accident due to the limited data on the deposition of Pu, but rather a rough estimation to obtain the information on the order of magnitude of Pu release from the accident. As shown in Table 2, the amounts of released $^{239+240}$Pu and ^{241}Pu were $1.0\times10^{9}-2.4\times10^{9}$ Bq, and $1.1\times10^{11}-2.6\times10^{11}$ Bq, respectively. These values are very close to those estimated by METI[20], and about 4 orders of magnitude lower than those of the Chernobyl accident.[17,18,21] Kirchner et al.[22] recently calculated the mean fuel inventory of Pu isotopes in the Fukushima DNPP reactors using ORIGEN-ARP module of the SCALE-5.1 code system, this made it possible to estimate the percentages of the amounts of released Pu isotopes to core inventory with the information of fuel load in Unit 1, Unit 2 and Unit 3 reactors (in total 250 t). It was found that although the inventories of Pu isotopes in the reactors in the Fukushima DNPP were ca. 3.5 times those in the Chernobyl No. 4 reactor[23], the percentages of core inventory released for both $^{239+240}$Pu and ^{241}Pu were about 5 orders of magnitude lower than those of the Chernobyl accident. These results suggested that for the Fukushima DNPP accident, the plutonium emitted into the environment was mainly due to the release of Pu associated with fuel fragments as a consequence of the hydrogen explosions, as suggested by Kirchner et al.[22].

MEXT has estimated the $^{239+240}$Pu dose of external exposure and inhalation from resuspension as 0.12 mSv for a person living for 50 years in the contaminated area[8]. On the other hand, the ^{241}Pu/$^{239+240}$Pu activity ratio of the Fukushima-derived Pu was found to be higher than 100. The additional dose contribution from ^{241}Pu has to be estimated. As an example, assuming a similar contamination of ^{241}Pu in the surface soil as that in the litter layer and using the method of IAEA-TECDOC-955[24], we estimated the ^{241}Pu dose for a person living for 50 years in the vicinity of S2 site to be 0.44 mSv, about 4 times the $^{239+240}$Pu dose.

^{241}Pu is a beta-emitting isotope, as a result of ^{241}Pu decay the increase of ^{241}Am may significantly enhance the alpha-activity level in the contaminated area for a certain period of time. Using the ^{241}Pu/$^{239+240}$Pu activity ratio of the Fukushima-derived Pu (107.8), we made a prognostic prediction on the ingrowth of ^{241}Am (Fig. 3). Details of the theoretical calculation on the decay of ^{241}Pu and ingrowth of ^{241}Am are described in Methods Section. The result showed that the ^{241}Am/$^{239+240}$Pu activity ratio would increase quickly reaching a value of 1 in the year 2018 and it would reach a maximum value of 3.12 in the year 2081, followed by a gradual decrease. This calculated maximum value of 3.12 is almost one order of magnitude higher than that of the expected global fallout ^{241}Am/$^{239+240}$Pu in the year 2042[25]. Furthermore, the increased amount of ^{241}Am may remain in the surface soil for decades together with Pu isotopes. In our previous study on the migration of ^{241}Am and Pu released from the atomic bomb detonation in Nagasaki[26], we found that the ^{241}Am/$^{239+240}$Pu activity ratio (0.036 ± 0.006) detected in a soil core (0–15 cm) in Nishiyama area, Nagasaki, Japan in 2008 approached the expected maximum value[27], indicating that ^{241}Am and Pu were still together in the soils after six decades and showing no significant difference regarding their downward migration behavior (Fig. 3). In addition, a more efficient transfer of ^{241}Am into plants may be expected. A recent study showed that the coefficients of ^{241}Am transfer from soil to wild plants[28], particularly to legumes, are 3–5 times higher than those of ^{239,240}Pu. Therefore, it is highly necessary to investigate the distribution and surface activity of ^{241}Pu inside the 20 km zone, where much higher ^{241}Pu could be expected. This is important for the long-term dose assessment of actinides, and will have important implications in the strategy for decontamination procedures.

For soil samples collected in Mito, Chiba, and Kamagaya Cities, although ^{137}Cs activities were significantly higher than the activity level before the accident (Table 1), for example, the Kamagaya soil sample 2 (0–2 cm) collected on the grounds of a Japanese shrine, near the drain pipes from a building roof, had a ^{137}Cs activity of 11429 ± 88 mBq/g, the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios were the typical values of the global fallout and no ^{241}Pu could be detected. We concluded this Pu was consistent with global fallout origin. If any, the Fukushima source contribution to the total Pu activity was negligible.

In addition to the atmospheric releases, the cooling of the reactors with fresh water and seawater, and the release of highly contaminated water from the damaged reactor buildings resulted in the direct discharges of radionuclides into the Pacific Ocean[29,30]. The water-soluble ^{137}Cs released from the atmospheric fallout and the directly discharged radioactive waste water caused serious contamination in the marine environment[31]. However, information on the distribution of plutonium in the marine environment is very limited. It remains unknown if there was a Pu contamination derived from the release of radioactive waste water. Starting from May, 2011, MEXT monthly reported the monitoring results of $^{239+240}$Pu and ^{238}Pu activities in seawater and sediments in the 15 km zone in the Pacific off Fukushima[32]. As the monitoring was conducted using the analytical methods for emergency monitoring, the reported activities of $^{239+240}$Pu and ^{238}Pu in seawater were always lower than the detection limits (<0.55 mBq/L for $^{239+240}$Pu, and <0.61 mBq/L for ^{238}Pu). Although the $^{239+240}$Pu activities in sediments ranged from 0.015 to 0.97 mBq/g, were within the range of $^{239+240}$Pu activities observed in

Table 2 | Comparison of Pu releases during the Fukushima DNPP accident and the Chernobyl accident

		Fukushima DNPP		
	Chernobyl*	METI calculated	Estimation of this study	Remarks
Amount of released (Bq)				A rough estimation on the amounts of atmospheric release of Pu isotopes based on the ^{137}Cs/$^{239+240}$Pu activity ratio observed in litter samples in 20–30 km zones relative to the total amount of ^{137}Cs released estimated by METI[20] and Stohl et al.[3]
$^{239+240}$Pu	8.7×10^{13}	6.4×10^{9}	$1.0\times10^{9}-2.4\times10^{9}$	
^{241}Pu	7.2×10^{15}	1.2×10^{12}	$1.1\times10^{11}-2.6\times10^{11}$	
Pu inventories at reactors (Bq) at the time of accident initiation				Estimated based on the calculated mean inventory (Bq/t) by Kirchner et al.[22], assuming that Pu isotopes were released from Unit 1 (70 t fuel), Unit 2 (90 t fuel) and Unit 3 (90 t fuel) reactors with a total fuel load of 250 t
$^{239+240}$Pu	2.4×10^{15}	–	8.3×10^{15}	
^{241}Pu	1.9×10^{17}	–	7.0×10^{17}	
Percentage of core inventory released (%)				Although the inventories of Pu isotopes in reactors in the Fukushima DNPP are *ca.* 3.5 times those in the Chernobyl accident, the percentages of core inventory released are *ca.* 5 orders of magnitude lower than those of the Chernobyl accident
$^{239+240}$Pu	3.5	–	$1.2\times10^{-5}-2.9\times10^{-5}$	
^{241}Pu	3.5	–	$1.6\times10^{-5}-3.7\times10^{-5}$	

*Data on the Chernobyl accident are cited from Kruger et al.[17], IAEA (1986)[18], Harrison et al.[21], and Devell et al.[23].

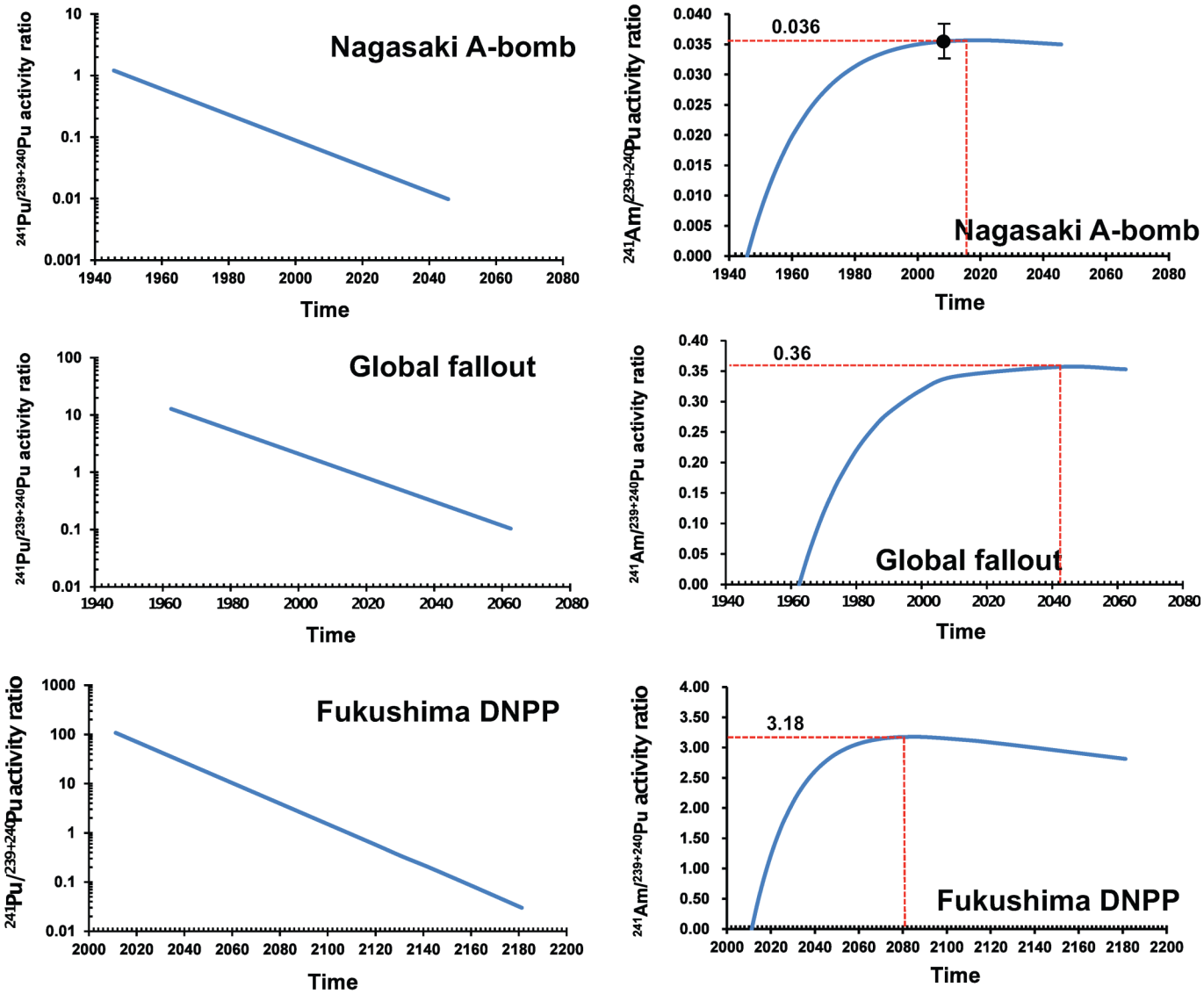

Figure 3 | Curves of the calculated activity ratios of $^{241}Pu/^{239+240}Pu$ and $^{241}Am/^{239+240}Pu$ from the Nagasaki atomic bomb Pu, the global fallout Pu and the Fukushima DNPP accident Pu with elapsed time. The ^{241}Am ingrowth from the Nagasaki atomic bomb detonation was based on the initial $^{241}Pu/^{239+240}Pu$ activity ratio estimated by Yamamoto et al.[27]. The $^{241}Am/^{239+240}Pu$ activity ratio (0.036 ±0.006) detected in a soil core collected in Nishiyama area, Nagasaki, Japan in 2008 approached the calculated maximum value, indicating that ^{241}Am and Pu were still together in the soils after 6 decades. ^{241}Am from the global fallout source was expected to reach the maximum $^{241}Am/^{239+240}Pu$ activity ratio of 0.36 in the year 2042[25]. The theoretic calculation indicated that $^{241}Am/^{239+240}Pu$ activity ratio would quickly approach the value of 1 by 7 years after the Fukushima DNPP accident and it would reach a maximum value of 3.18 in the year 2081.

sediments in the Japanese coastal area before the Fukushima DNPP accident[33], no information on the Pu isotopic composition is available for source identification. Obviously, the possible release of Pu isotopes and their impact on the marine environment need further studies.

Methods

Soil and litter sampling. Soil samples (0–2, 5–7, and 10–12 cm) were collected in the Evacuation-Prepared Area (J-Village, 20 km south of Fukushima DNPP) in April, 2011. The soil samples from J-Village were collected in a flower garden. The collection of the organic layer and soil samples in a forest floor was carried out in a deciduous broad-leaved forest at 3 sampling locations differing in distance and direction from the nuclear power plant in the Deliberate Evacuation Area (S1, in Katsurao Village, 25 km WNW of Fukushima DNPP, N37°29′02.8″ E140°45′46.4″; S2, in Namie Town, 26 km NW of Fukushima DNPP, N37°34′17.1″ E140°47′39.9″; and S3, in Iitate Village, 32 km NW of Fukushima DNPP, N37°36′20.0″ E140°45′17.1″) in May, 2011. For each location, 3 samples were collected several meters apart for organic layer and soil samples. The organic layer samples were divided into 2 parts, the upper litter layer (AOL) and the lower fermentation + humus layer (AOF, AOH). From under the organic layer, a 5-cm soil core was taken at 0–5 cm depth. The soil cores were sliced into 1–5 cm thick slices using a spatula. The upper litter layer and surface soil sample (0–1 cm) were analyzed for Pu isotopes.

Soil samples, including a core sample down to 13 cm (0–1, 1–3, 3–5, and 5–13 cm were collected on the campus of the National Institute of Radiological Sciences (NIRS) in Chiba City in April, 2011. The surface soil samples from Mito City (0–1 cm) were collected in the playground of a public park, and the those from Kamagaya City (0–2, 2–5 cm) were collected in the garden of a private residence and the grounds of a Japanese shrine in August, 2011.

All samples were oven dried at 80°C overnight and passed through a 2 mm mesh sieve. The soil from the flower garden had no large stones and almost all the fraction could pass through the sieve. All samples were measured for ^{137}Cs activity after passing the 2 mm mesh sieve. For Pu isotope analysis, organic matter in the samples was decomposed by heating in a Muffle oven at 450°C for 6 hours.

Analytical procedures for ^{137}Cs and Pu isotopes. ^{137}Cs activity was determined using a Ge detection system (Seiko EG&G) for 3600 s for most cases. The ^{137}Cs activity was determined using its peak at 661.6 KeV. A mixed gamma standard solution

(Amersham, QCY-46) was used for an efficiency correction and reference standard materials IAEA-156, 373 and 375 were used for an accuracy check[11]. Pu isotope separation and purification were done using a modified method based on the MEXT method for Pu analysis in environmental samples[34]. Briefly, 3.0–7.0 g samples (soil and litter) were mixed with 1 pg ^{242}Pu tracer, and digested by heating on a hot-plate using 10 $MHNO_3$-1 M HF. After the digestion, the solution was heated to dryness, and the residues were dissolved in 30 ml 8 M HNO_3. $NaNO_2$ was added to adjust the Pu oxidation state, and then 0.3 g boric acid was added to convert unreacted HF to BF_4^-. Dowex 1×8 anion resins were used in the separation and purification processes. After loading the sample solution on the first Dowex 1×8 column (2 ml), sequential elution of U, Th and Pu was conducted using 35 ml 8 M HNO_3, 35 ml 10 M HCl, and 35 ml NH_4I-HCl solution, respectively. The obtained Pu fraction was heated to dryness after adding 5 ml HNO_3. The residue was dissolved in 10 ml 4 M acetic acid, and this solution was loaded onto the second Dowex 1×8 column (2 ml). Then 20 ml 4 M acetic acid was used to wash the column and all the eluted solution was collected for Pu analysis. The collected acetic acid solution (30 ml) was heated to dryness, and the residue was dissolved in 0.7 ml 4% HNO_3 for Pu isotope analysis using a highly sensitive APEX/SF-ICP-MS analytical system[10]. Sediment standard reference materials IAEA-368 (marine sediment standards, International Atomic Energy Agency) and SRM-4354 (freshwater lake sediment standards, American National Standards Institute of Technology) were used for analytical method validation[13,35].

Two end-member mixing model for source apportionment of the Fukushima DNPP accident source Pu. Since two isotopically distinctive Pu sources, global fallout and the Fukushima DNPP accident fallout, were identified in this study, it is possible to evaluate the individual relative contribution from global and the Fukushima DNPP accident Pu based on ^{240}Pu/^{239}Pu ratios. We used a simple two end-member mixing model, which is similar to the one described by Krey[19], to calculate the relative contribution of the Fukushima DNPP accident source Pu:

$$Y = \frac{(Pu)_F}{(Pu)_G} = \frac{(R_G - R_S)(1 + 3.674R_F)}{(R_S - R_F)(1 + 3.674R_G)} \quad (1)$$

where (Pu) = activity of $^{239+240}$Pu; R=^{240}Pu/^{239}Pu atom ratio; and subscripts F, G, and S refer to Fukushima DNPP accident, global fallout, and the soil sample in J-Village, respectively. This equation converts ^{240}Pu/^{239}Pu atom ratio data to activity ratios of $^{239+240}$Pu from two sources. The constant 3.674 is the ratio of the specific activities of ^{240}Pu to ^{239}Pu obtained from IAEA-recommended half-lives of 24110±30 and 6563±7 years for ^{239}Pu and ^{240}Pu, respectively. We defined

$$(Pu)_T = (Pu)_F + (Pu)_G \quad (2)$$

where $(Pu)_T$ is the total activity of $^{239+240}$Pu in the sample, and $(Pu)_G$ consists of the global fallout. Hence, the percentage of the Fukushima DNPP accident source Pu could be obtained from the following equation:

$$\frac{(Pu)_F}{(Pu)_T} = \frac{Y}{1+Y} \quad (3)$$

Kelley et al.[12] reported the mass ratio of ^{240}Pu/^{239}Pu in global fallout to be 0.180 ± 0.007, based on a world-wide program of sampling conducted at 21 sites in 1970 and 1971 between 30°N and 70°N. The ^{240}Pu/^{239}Pu ratio of the Fukushima DNPP accident obtained in this study was 0.327. Therefore, the percentage of the Fukushima DNPP accident source Pu could be calculated using the ^{240}Pu/^{239}Pu atom ratio of 0.303 in the surface soil in the J-Village to be 87%.

Theoretical calculation of the decrease of ^{241}Pu/$^{239+240}$Pu activity ratio and the increase of ^{241}Am/$^{239+240}$Pu activity ratio with time. We calculated the decrease of ^{241}Pu/$^{239+240}$Pu activity ratio with time using the equation given below:

$$\frac{A_{241Pu(t)}}{A_{239+240Pu(t)}} = \frac{A_{241Pu(0)}}{A_{239+240Pu(0)}} \times e^{(-\lambda_{241Pu}t)} \quad (4)$$

where A means the activity and the subscripts t and 0 mean the values at time t and t_0, respectively. It is assumed that $A_{239+240Pu}(t) \approx A_{239+240Pu}(0)$. λ_{241Pu}=0.0483 y^{-1}.

For the calculation of the increase of ^{241}Am/$^{239+240}$Pu activity ratio with time, we used the following equation:

$$\frac{A_{241Am(t)}}{A_{239+240Pu(t)}} = \frac{A_{241Pu(0)}}{A_{239+240Pu(0)}} \times \frac{\lambda_{241Am}}{(\lambda_{241Am} - \lambda_{241Pu})}\left[e^{(-\lambda_{241Pu}t)} - e^{(-\lambda_{241Am}t)}\right] \quad (5)$$

where A means the activity and the subscripts t and 0 mean the values at time t and t_0, respectively. It is assumed that $A_{239+240Pu}(t) \approx A_{239+240Pu}(0)$. λ_{241Pu}=0.0483 y^{-1}, and λ_{241Am}=0.0016 y^{-1}. The activity ratios of ^{241}Pu/$^{239+240}$Pu at t=0 for Nagasaki atomic bomb, the global fallout and the Fukushima DNPP accident were 1.21[27], 12.8[25] and 107.8 (this study), respectively.

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Author contributions

J. Z., K. T., Y. W., and S. U. designed the study. J. Z. conducted Pu isotope analyses and wrote the manuscript. K. T., T. A., Y. W. and N. I. analysed ^{137}Cs activity. Y. K., S. F., S. Y., and S. I. participated in the soil sampling, discussed the results and commented on the manuscript.

Additional information

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