Release of Pu Isotopes from the Fukushima Daiichi Nuclear Power Plant Accident to the Marine Environment Was Negligible

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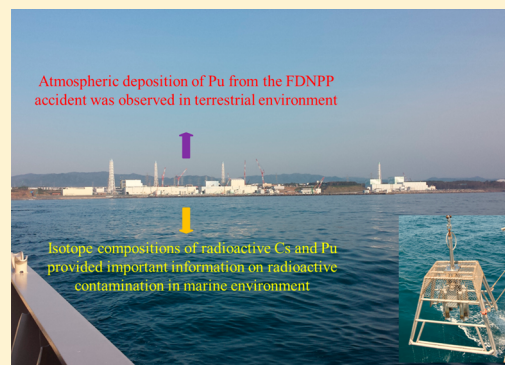
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Ⓢ *Supporting Information*

ABSTRACT: Atmospheric deposition of Pu isotopes from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident has been observed in the terrestrial environment around the FDNPP site; however, their deposition in the marine environment has not been studied. The possible contamination of Pu in the marine environment has attracted great scientific and public concern. To fully understand this possible contamination of Pu isotopes from the FDNPP accident to the marine environment, we collected marine sediment core samples within the 30 km zone around the FDNPP site in the western North Pacific about two years after the accident. Pu isotopes (^{239}Pu, ^{240}Pu, and ^{241}Pu) and radiocesium isotopes (^{134}Cs and ^{137}Cs) in the samples were determined. The high activities of radiocesium and the ^{134}Cs/^{137}Cs activity ratios with values around 1 (decay corrected to 15 March 2011) suggested that these samples were contaminated by the FDNPP accident-released radionuclides. However, the activities of $^{239+240}$Pu and ^{241}Pu were low compared with the background level before the FDNPP accident. The Pu atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) suggested that global fallout and the pacific proving ground (PPG) close-in fallout are the main sources for Pu contamination in the marine sediments. As Pu isotopes are particle-reactive and they can be easily incorporated with the marine sediments, we concluded that the release of Pu isotopes from the FDNPP accident to the marine environment was negligible.

Atmospheric deposition of Pu from the FDNPP accident was observed in terrestrial environment

Isotope compositions of radioactive Cs and Pu provided important information on radioactive contamination in marine environment

INTRODUCTION

On 11 March 2011, a massive earthquake with a magnitude of M 9.0 occurred in the western North Pacific about 180 km off the Fukushima Daiichi Nuclear Power Plant (FDNPP) in the northeast coast of Japan and it was followed by gigantic tsunami. As a result, power supplies were lost at the FDNPP and core cooling could not be carried out. This led to pressure buildups which were relieved in venting actions by operators and by hydrogen explosions. Consequently, large amounts of radionuclides were released into the environment. Extensive studies about the distributions and human health impacts of the volatile fission products, such as ^{90}Sr, ^{131}I, ^{134}Cs, and ^{137}Cs[1−5] in the environment after the accident have been conducted.[1−5] However, only limited studies have focused on the nonvolatile Pu isotopes in the environment. Pu isotopes present a high risk for internal radiation exposure via ingestion of contaminated agricultural crops and seafood products and are important for long-term dose assessment due to their long half-lives.[6,7] In the

FDNPP, Pu isotopes were produced in the reactor units which used uranium-based nuclear fuels and especially in the Unit 3 reactor, where 32 mixed-oxide fuel assemblies containing ∼6% Pu were initially loaded.[8] Thus, information about the release of Pu isotopes in the environment is also important to understand the reactor core damages.

The FDNPP accident introduced radioactive contamination into the marine environment through the deposition of the radionuclides released into the atmosphere as well as through the direct discharge of thousands of tons of radioactive liquid waste.[9,10] As marine products play an important role in the Japanese diet, seafood safety has attracted considerable public and scientific concern. In the terrestrial environment around
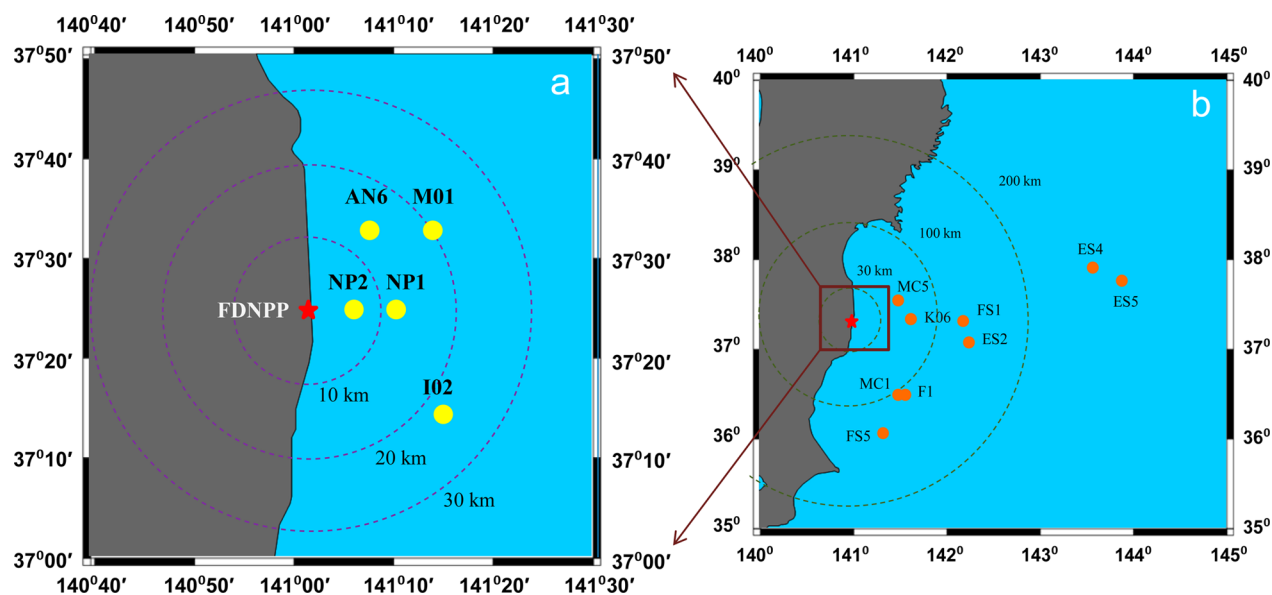
Figure 1. Map showing the locations for (a) sediment samples collected within the 30 km zone around the FDNPP site in this study and (b) sediment samples collected outside the 30 km zone around the FDNPP site in our previous studies (redrawn from Zheng et al.[16] and Bu et al.[17,18,20]).

the FDNPP site, the Pu isotopes released from the accident were detected in soil, litter, dust and aerosol samples after the accident and the total released amounts of Pu isotopes were estimated.[11−14] However, the amount of Pu isotopes directly released into the marine environment remains unknown. In the high level radioactive accumulated water collected at the FDNPP after the accident, high level radioactivities of Pu isotopes were detected ((5.8−13) × 10^{-2} Bq mL^{-1} for ^{238}Pu, (3.0−7.2) × 10^{-2} Bq mL^{-1} for $^{239+240}$Pu, (1.7−3.2) × 10^2 Bq mL^{-1} for ^{241}Pu; decay corrected to 19 January 2012).[15] These values were 6−7 orders of magnitude higher than that of the seawater in the western North Pacific. Thus, attention should be paid to the contamination situation of Pu isotopes in the marine environment off Fukushima since the FDNPP accident.

We previously studied Pu distributions in marine sediments and seawater samples collected in the western North Pacific 30 km off the FDNPP site within a few months to about two years after the accident and we observed no detectable Pu contamination from the FDNPP accident in the investigated areas.[16−20] Radiocesium isotopes from the accident have been widely observed in the marine sediments off Fukushima after the accident.[2,21,22] Pu isotopes are more particle-reactive than radiocesium and the sediment−water distribution coefficient (K_d) of Pu in the marine environment is 1×10^5, 2 orders of magnitude higher than that of Cs.[23,24] In Irish Sea, where has been contaminated by the discharged liquid radioactive waste from Sellafield nuclear fuel reprocessing plant, Mitchell et al.[25] found that the concentrations of Pu isotopes in the seawater and sediment declined with an availability time of ca. 100 years, which was at least 1 order of magnitude longer than that of ^{137}Cs. Thus, the possible FDNPP-released Pu isotopes in the marine environment could be more easily incorporated with the marine sediments and kept there for a long time. Recently Perianez et al.[26] modeled that if the discharge of Pu from the FDNPP accident occurred in the marine environment, it would remain within the 30 km zone around the FDNPP site. Therefore, the Pu isotopes in the marine sediments in the near coastal areas of Fukushima need to be investigated.

Pu atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) are used as powerful fingerprints for Pu source identification, as they are known to vary among different sources.[27] The Pu isotopes derived from the accident have been characterized by a high ^{240}Pu/^{239}Pu (>0.3) atom ratio,[11−14] which makes it easy to distinguish them from global fallout (^{240}Pu/^{239}Pu atom ratio = 0.18) in the terrestrial environment.[28] For the marine sediments, however, Pu isotopes around the FDNPP site could be attributed to global fallout and the Pacific Proving Ground (PPG) close-in fallout, which was transported by the oceanic currents from the nuclear weapon test sites in the Marshall Islands to the western North Pacific before the 2011 accident.[29,30] The FDNPP accident-derived ^{240}Pu/^{239}Pu atom ratio is higher than the global fallout ratio (0.18) but similar to that (0.30−0.36) of the PPG source.[11,14,29,31] Thus, the determination of another fingerprint ^{241}Pu/^{239}Pu atom ratio is strongly needed for distinguishing Pu sources in the marine sediments. The ^{241}Pu/^{239}Pu atom ratio (0.083−0.135)[11,14] of the FDNPP accident released Pu is almost 2 orders of magnitude higher than both the global fallout (0.0011)[28] and the PPG source (ca. 0.0020)[32,33] values (^{241}Pu decay corrected to 15 March 2011). However, the ^{241}Pu activity in the marine sediments is currently very low (<5 mBq g^{-1}) due to its short half-life (14.4 years), which makes it difficult to measure. Thanks to our established sensitive analytical methods based on anion-exchange chromatography and sector field ICP-MS, ^{241}Pu in the marine sediments can be accurately analyzed with sample amounts over 10 g.[18]

In this work, we collected marine sediment samples within the 30 km zone around the FDNPP site about two years after the accident to investigate the Pu distribution in the near coastal marine environment off Fukushima. Pu activities ($^{239+240}$Pu and ^{241}Pu) and atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) were determined to give a more comprehensive conclusion about the possible Pu contamination from the FDNPP accident. The radiocesium activities (^{134}Cs and ^{137}Cs) and ^{134}Cs/^{137}Cs activity ratio in these sediment samples were also measured.

■ MATERIALS AND METHODS

Sediment Sampling. Sediment core sampling locations (NP2, 37°25.00′N 141°06.00′E; NP1, 37°25.00′N 141°10.70′E; AN6, 37°33.00′N 141°07.60′E; M01, 37°33.00′N 141°13.08′E; I02, 37°14.00′N 141°13.08′E) were in the western North Pacific within the 30 km zone around the FDNPP site. Collection was done with a sediment multiple corer during the UM 13−05 cruise (T/S Umitaka-maru, Tokyo University of Marine Science and Technology) in May 2013. The closest collection location (NP2) was ca. 5 km off the FDNPP site. The core samples were cut into 1 cm segments and stored in an on-board refrigerator until they were brought back to the land-based laboratory. The locations of the sampling sites within the 30 km zone around the FDNPP site of this study and of the sampling sites outside the 30 km zone in our previous studies[17,18,20] are shown in Figure 1.

Analytical Procedure for Radiocesium and Pu Isotopes. The sediment samples were first dried at 105 °C for 24 h. The activities of [134]Cs and ^{137}Cs were measured by gamma-ray spectrometry using an HPGe detector (GX-2019, Canberra) and the detection limit was ca. 1 mBq g^{-1}. The activities of radiocesium in the sediments were decay corrected to the sampling date. After the measurement of radiocesium, sediment samples were ashed in a microwave muffle furnace at 450 °C for 5 h to destroy the organic matter. The ignition losses of the samples were calculated from the weights before and after the ashing procedure.

About 2−40 g of dried sediment samples were weighed out for Pu analysis. The sample preparation procedures for Pu analysis were based on our previous work[18] and are illustrated in Supporting Information Figure S1. Briefly, a sediment sample and 20−40 mL concentrated HNO_3 were put in a Teflon vessel (120 mL) which was then tightly closed. Digestion was done on a hot plate at 160 °C for at least 4 h. Then the sample solution was filtered and its acidity was adjusted to that of 8 M HNO_3. $NaNO_2$ was added to the sample solution to a concentration of 0.2 M and the mixture was heated at 40 °C for 30 min to take Pu to the tetravalent state. After preconditioning the AG 1 × 8 resin column with 20 mL 8 M HNO_3-0.2 M $NaNO_2$, the sample solution was loaded onto the column. 50 mL 8 M HNO_3 was used for the washing of U, Pb, and Fe and 30 mL 10 M HCl was used for the washing of Th from the column and converting the resin back to the chloride form. Then Pu was eluted with 40 mL 0.1 M NH_4I-8.5 M HCl. The eluent was evaporated to near dryness in a 100 mL Teflon beaker. One mL *aqua regia* was added and the mixture was heated to dryness; this addition of acid and heating was repeated a second time to destroy the organic matter and remove the residual iodine. Then 2 mL concentrated HCl was added and the mixture was evaporated to dryness once more. After adding 4 mL of freshly prepared HCl-H_2O_2 and heating at 40 °C for 30 min, the sample solution was ready for loading onto the second AG MP-1 M resin column. The second resin column was preconditioned with 8 mL HCl-H_2O_2 and then the sample solution was loaded onto it. Twenty mL 8 M HNO_3 and 8 mL HCl were used for the further washing of U and Th, respectively. Pu was eluted from the AG MP-1 M resin with 16 mL concentrated HBr and the eluant was collected in a 30 mL Teflon beaker. After evaporating the sample solution to near dryness, 1 mL concentrated HNO_3 was added and this was heated to near dryness to remove HBr. The final residue was dissolved in 0.8 mL 4% HNO_3 in preparation for analysis. All

reagents were superpure grade and all the water that we used was treated with a Milli-Q water system (>18.0 MΩ).

The analysis of Pu isotopes was performed on a SF-ICP-MS (Element 2, Thermo Finnigan, Bremen, Germany). When combined with an APEX-Q high efficiency sample introduction system, the sensitivity of the SF-ICP-MS was between 1.0 and 1.5×10^7 cps ppb^{-1} for [238]U$^+$. The detailed operational setup and parameters of this analytical system were described elsewhere.[34] A certified Pu isotope standard solution (NBS-947) was used for mass bias correction and two marine sediment standard reference materials IAEA-368 and NIST-4357 were used for the analytical method validation. Figure 2
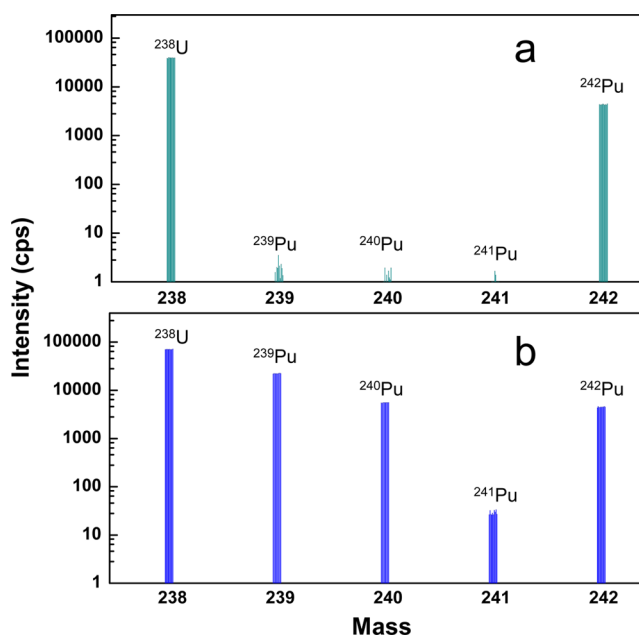
Figure 2. Typical mass spectra of (a) an operational blank and (b) a sediment sample analyzed by our method. [242]Pu was used as chemical yield tracer.

shows typical spectra of the marine sediments and the operational blank of the method. Using our Pu separation procedure and analysis system, we can sufficiently remove U interference from the sediment sample matrix and Pu isotopes can be reliably determined.[18]

■ RESULTS AND DISCUSSION

The results for Pu and radiocesium isotopes in the marine sediments within and outside the 30 km zone around the FDNPP site are summarized in Table 1. The vertical distributions of Pu and radiocesium isotopes and the ignition losses at sampling locations NP2, NP1, AN6, I02, and M01 are illustrated in Figure 3. More detailed analytical results are summarized in Supporting Information Tables S1 and S2.

Radiocesium contamination in the marine sediments. [134]Cs and ^{137}Cs are two of the major radionuclides released from the FDNPP accident into the environment. It has been estimated that the total atmospheric release of ^{137}Cs from the accident was 9.9−36 PBq and more than 70% was deposited in the ocean.[7,35−37] In addition, 2.3−27 PBq ^{137}Cs was directly released to the sea.[10,38,39] Although Cs is regarded as a "soluble" element in the marine environment, it can be selectively absorbed by clay minerals and subsequently deposited on the seafloor.

Table 1. Analytical Results for Pu Isotopes and Radiocesium in the Fukushima Sediment Samples[a]

sampling location	sampling date	location	water depth (m)	surface $^{239+240}$Pu activity (mBq g^{-1})	surface ^{241}Pu activity (mBq g^{-1})[b]	vertical ^{240}Pu/^{239}Pu atom ratio range	vertical ^{241}Pu/^{239}Pu atom ratio range[b]	vertical ^{134}Cs activity range (mBq g^{-1})[c]	vertical ^{137}Cs activity range (mBq g^{-1})[c]	vertical ^{134}Cs/^{137}Cs activity ratio range[b]
Within the 30 km Zone										
NP2	2013/5/17	37°25.00′N, 141°06.00′E	30	0.29 ± 0.01	0.39 ± 0.05	0.252–0.255	0.0012–0.0016	17.0–28.1	32.8–55.1	0.87–1.07
NP1	2013/5/17	37°25.00′N, 141°10.70′E	60	0.26 ± 0.01	0.31 ± 0.07	0.250–0.251	0.0014–0.0015	3.0–14.0	7.2–28.5	0.82–1.03
AN6	2013/5/15	37°33.00′N, 141°07.60′E	30	0.51 ± 0.01	0.65 ± 0.09	0.251–0.256	0.0015 ± 0.0002[d]	8.2–52.8	17.1–101.3	0.92–1.13
M01	2013/5/17	37°33.00′N, 141°13.08′E	60	0.34 ± 0.01	0.43 ± 0.04	0.235–0.258	0.0015 ± 0.0001[d]	3.4–11.1	8.3–24.9	0.85–1.24
I02	2013/5/20	37°14.00′N, 141°13.80′E	120	0.94 ± 0.01	1.12 ± 0.13	0.244–0.249	0.0013–0.0016	22.4–78.4	52.6–154.9	0.86–1.06
Outside the 30 km Zone										
MC1	2011/7/18	36°28.97′N, 141°29.93′E	1327	1.58 ± 0.03	1.49 ± 0.22	0.236–0.239	0.0015 ± 0.0002[d]			
MC5	2011/7/19	37°35.01′N, 141°30.95′E	141	0.48 ± 0.01	0.69 ± 0.10	0.201–0.255	0.0016 ± 0.0002[d]			
ES4	2011/7/18	37°51.96′N, 143°34.52′E	5253	1.23 ± 0.03	1.48 ± 0.26	0.188–0.212	0.0013 ± 0.0002[d]			
ES5	2011/7/18	37°47.69′N, 143°51.93′E	7047	1.08 ± 0.03	1.03 ± 0.16	0.189 ± 0.013[d]	0.0012 ± 0.0002[d]			
FS1	2011/8/2	37°19.97′N, 142°10.05′E	994	2.81 ± 0.04	3.13 ± 0.44	0.224–0.286	0.0014 ± 0.0000[d]	10.3	11.0	1.05
ES2	2011/8/2	37°03.98′N, 142°15.02′E	2138	3.09 ± 0.04	4.02 ± 0.27	0.216–0.247	0.0013 ± 0.0002[d]			
FS5	2011/8/3	36°00.00′N, 141°20.14′E	1198	3.53 ± 0.10		0.230 ± 0.015[d]		54.1	58.4	1.04
F1	2012/7/7	36°29.09′N, 141°30.01′E	1322	1.77 ± 0.05	1.49 ± 0.19	0.232–0.291	0.0014 ± 0.0002[d]			
K06	2013/1/13	37°20.00′N, 141°40.10′E	300	0.59 ± 0.02	0.93 ± 0.14	0.233–0.253	0.0015 ± 0.0002[d]			
FDNPP source						0.303–0.330	0.103–0.135			~1
global fallout (30–70° N)						0.180 ± 0.014	0.0011 ± 0.0002			
PPG close-in fallout						0.33–0.36	0.0018–0.0025			

[a]Data for Pu isotopes in the sediment samples outside the 30 km zone around the FDNPP are cited from Zheng et al.[16] and Bu et al.[17,18,20]. Data for radiocesium of FS1 and FS5 (0–1 cm) are cited from Otosaka and Kato.[22]. Data for FDNPP source are cited from Zheng et al.[11]. Data for global fallout are results of litter and soil samples cited from Zheng et al.[11]. Data for global fallout in fallout are cited from Kelley et al.[28]. Data for the PPG close-in fallout are cited from Buesseler et al.[29] and Muramatsu et al.[31]. [b]Decay for ^{241}Pu and ^{134}Cs/^{137}Cs activity ratios corrected to 15 March 2011. [c]Decay for ^{134}Cs and ^{137}Cs activities corrected to the sampling date. [d]Only surface samples were measured.
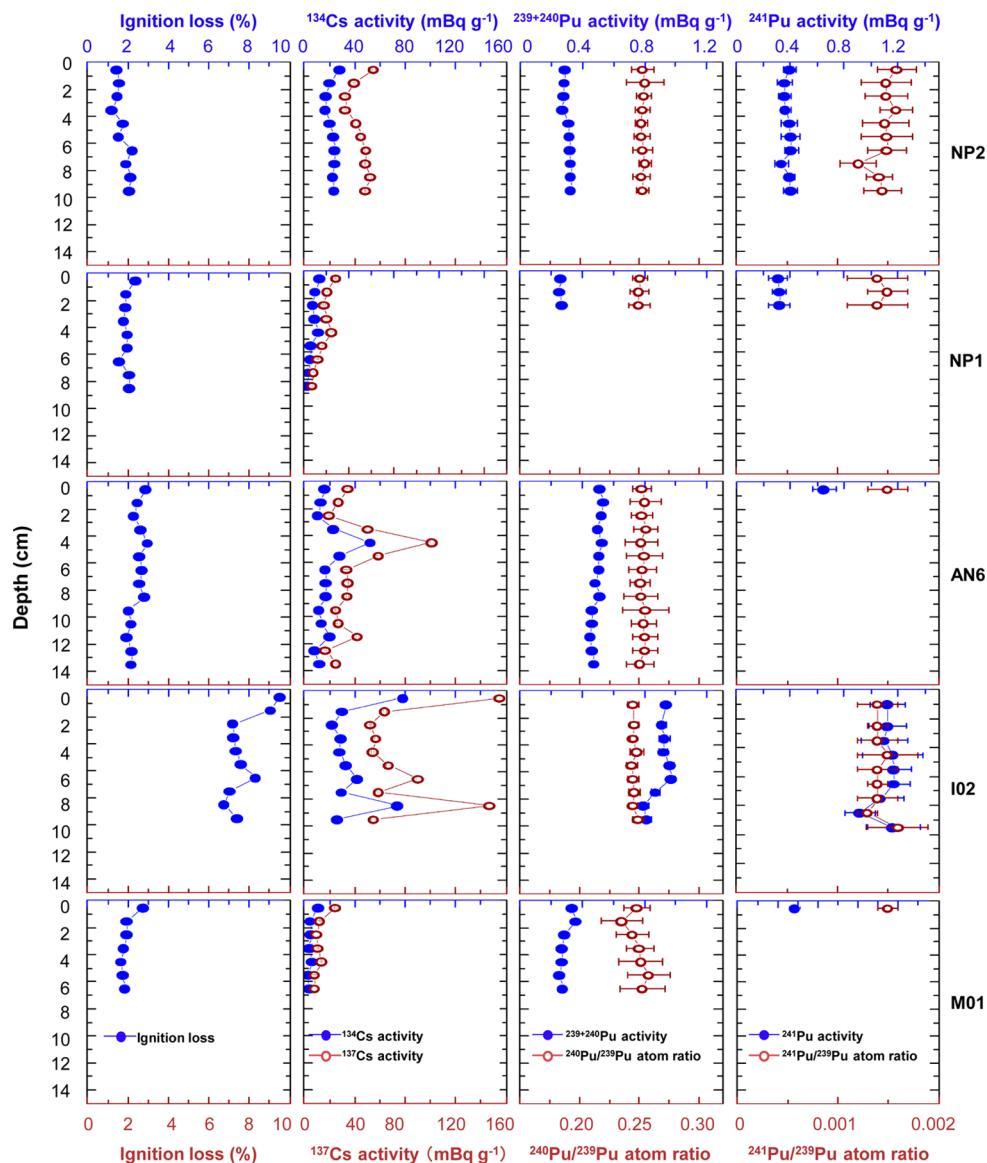
Figure 3. Vertical distributions of ^{137}Cs activities, $^{239+240}Pu$ activities, ^{241}Pu activities, $^{134}Cs/^{137}Cs$ activity ratios, $^{240}Pu/^{239}Pu$ atom ratios, and $^{241}Pu/^{239}Pu$ atom ratios in the sediment core samples.

The activities of ^{134}Cs and ^{137}Cs in the sediments investigated in this study ranged from 3.0 to 78.4 mBq g^{-1} and from 7.2 to 154.9 mBq g^{-1}, respectively (decay corrected to the sampling date). These values are significantly higher than that of the background level (0−2 mBq g^{-1} for ^{137}Cs in the surface sediments off Fukushima in 2010) before the FDNPP accident.[40] Kusakabe et al.[2] studied the distribution of radiocesium in marine sediments collected 30 km off Fukushima in 2011 and 2012, and they found that the activities of ^{137}Cs in the surface sediments ranged from 1.7 to 580 mBq g^{-1}. Our results for the sediments within the 30 km zone around the FDNPP site were within their reported concentration range. The highest activity of radiocesium in the sediment cores was observed at location I02 southeast of the FDNPP site. It has been simulated that the contaminated water released from the FDNPP accident had generally flowed southward from the adjacent area of the FDNPP site in March and April 2011,[10] which could lead to higher deposition of radiocesium at location I02 than at other locations even though I02 was the furthest from the FDNPP site among all the

sampling locations in this study. Moreover, the sediments collected at I02 had a higher percentage of silt and contained a higher amount of organic matter than sediments collected at the other locations, which would lead to them incorporating more radiocesium from the seawater.

The FDNPP-released radiocesium was characterized by a $^{134}Cs/^{137}Cs$ activity ratio of 1 on 15 March 2011.[37,41] In our study, the $^{134}Cs/^{137}Cs$ activity ratios for the sediments ranged from 0.82 to 1.24 with an average of 0.99 ± 0.07 (Figure 4), clearly indicating that these sediments were contaminated with radiocesium from the FDNPP accident. The inventories of radiocesium in the sediment core samples were shown in SI Table S1. The inventories (0−10 cm) of ^{134}Cs and ^{137}Cs ranged from 743 to 11162 Bq m^{-2} and from 1663 to 18867 Bq m^{-2}, respectively, not significantly higher than that reported for the sediments collected 30 km off the FDNPP site.[2,21,22] The ratios of radiocesium inventories in the surface layers (0−3 cm) to that in the whole sediment cores (0−10 cm) (F_{0-3}) ranged from 0.19 to 0.54. Otosaka et al.[21,22] also reported that for the sediments in the shallow depth of 100 m in the coastal areas of

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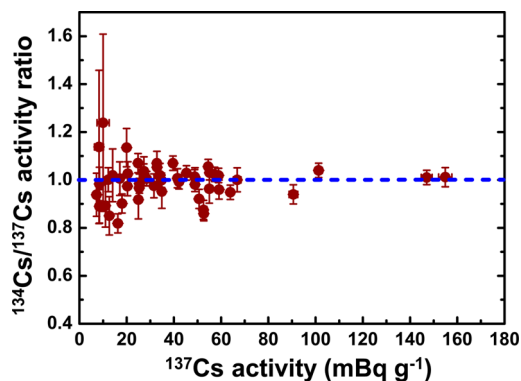
Figure 4. Results of ^{137}Cs activities and ^{134}Cs/^{137}Cs activity ratios in the marine sediments (decay corrected to 15 March 2011). The blue dashed line represents the ^{134}Cs/^{137}Cs activity ratio fingerprint of the FDNPP accident released radiocesium.

Ibaraki and Fukushima, the F_{0-3} values of radiocesium were less than 0.5.

Vertical Distribution of Pu Activities and Inventories. In previous studies,[17,18,20] we determined the distribution of Pu isotopes in the marine sediments collected 30 km off Fukushima and we found that there was no detectable Pu contamination originating from the FDNPP accident. The $^{239+240}$Pu and ^{241}Pu activities in the sediment cores within the 30 km zone around the FDNPP site ranged from 0.25 to 0.97 mBq g^{-1} and from 0.31 to 1.12 mBq g^{-1}, respectively (Supporting Information Table S2), typically lower than that of the sediments collected outside the 30 km zone as summarized in Table 1. The $^{239+240}$Pu activities were comparable with the values (0.7–1.0 mBq g^{-1}) observed in the surface marine sediments off Fukushima in 2008–2010 before the accident.[42] ^{241}Pu is regarded as a more sensitive indicator for the recently released Pu as the background level of ^{241}Pu in the environment is currently very low due to its short half-life (14.4 years). In a location (37°12′N, 141°20′E) close to I02, a ^{241}Pu activity of 0.99 mBq g^{-1} was reported in the surface sediment in 2008, which was similar to the results we found at location I02 and higher than that observed at other locations.[42] These results suggested that there were no abnormal values for Pu concentration in the sediments collected within the 30 km zone around the FDNPP site.

In the marine environment with a high sedimentation rate, usually a subsurface Pu activity maximum corresponding to the year of 1963, when the largest global fallout Pu occurred, can be observed.[43] However, in Figure 3, both the $^{239+240}$Pu and ^{241}Pu activities were almost constant in each sediment core from the surface to the investigated depth and no distribution peaks could be found. As most of the sediments were sandy with low organic matter content, the bioturbation effect in the sediments was low. Thus, the strong coastal current and the earthquake and tsunami happened in March 2011 could be the main reasons that led to the sufficient mixing of Pu in these sediments. The inventories of $^{239+240}$Pu at NP2 (0–10 cm), NP1 (0–3 cm), AN6 (0–14 cm), M01 (0–7 cm), and I02 (0–10 cm) were calculated to be 52.3, 13.7, 119.3, 37.3, and 102.6 Bq m^{-2}, respectively, and they were comparable with that of the sediments outside the 30 km zone around the FDNPP site observed in our previous study.[17] The inventories of ^{241}Pu at NP2 (0–10 cm), NP1 (0–3 cm) and I02 (0–10 cm) were 66.0, 16.6, and 126.4 Bq m^{-2}, respectively. These values are the first reports for vertical distributions of ^{241}Pu in the marine sediments in the western North Pacific.

Distribution of Pu Atom Ratios and Pu Source Identification. Pu atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) have been regarded as powerful fingerprints for Pu source identification. In soil and litter samples obtained around the FDNPP site, Zheng et al.[11] observed that the accident-released Pu isotopes were characterized by high ^{240}Pu/^{239}Pu (0.30–0.33) and ^{241}Pu/^{239}Pu (0.103–0.135) atom ratios. Shinonaga et al.[14] determined Pu isotopes in aerosol samples collected 120 km from the plant site a few days after the accident and they found similar Pu atom ratios (0.32 ± 0.10 for ^{240}Pu/^{239}Pu and 0.117 ± 0.032 for ^{241}Pu/^{239}Pu) in these samples. These Pu isotopic composition values could be considered as the indicator for the FDNPP-derived Pu. The ^{240}Pu/^{239}Pu and
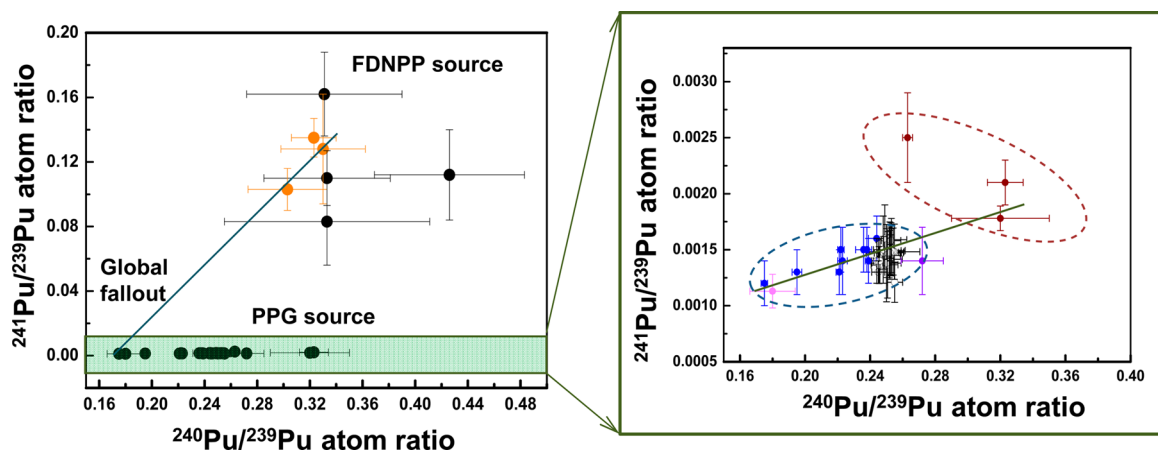
Figure 5. Mixing plot of ^{241}Pu/^{239}Pu atom ratio vs ^{240}Pu/^{239}Pu atom ratio in the Fukushima sediments, comparison with the Pu compositions of global fallout, FDNPP release, and the PPG close-in fallout. The closed orange circles (soil and litter samples, cited from Zheng et al.[11]) and closed black circles (aerosol samples, cited from Shinonaga et al.[14]) represent the FDNPP source; the closed pink circle represents the global fallout (cited from Kelley et al.[28]); the closed blue circles represent the surface sediment samples collected outside the 30 km zone (cited from Bu et al.[18]); the open black circles represent the vertical distributed sediment samples within the 30 km zone; the closed violet circle represents the Sagami Bay sediment sample (cited from Zheng and Yamada[48]); the closed wine circles represent the PPG source (cited from Yamamoto et al.[32] and Lachner et al.[33]).

^{241}Pu/^{239}Pu atom ratios in the marine sediments within the 30 km zone around the FDNPP site showed very small variations, ranging from 0.233 to 0.258 and from 0.0012 to 0.0016, respectively. In Figure 5, we plotted the Pu atom ratios in the sediments within 30 km zone around the FDNPP site, in the surface sediments outside the 30 km zone and in other sources. The values for Pu isotopes in the Fukushima marine sediments within the 30 km zone around the FDNPP site were far from the mixing line between global fallout and the FDNPP source but along the mixing line between global fallout and the PPG source. This result suggested that global fallout and the PPG close-in fallout were still the two main sources for Pu contamination in the marine sediments in the near coastal areas of Fukushima after the accident.

The Fukushima accident-derived Pu isotopes were evidenced in the terrestrial environment. The total amount of $^{239+240}$Pu released into the atmosphere was estimated to be $1.0–3.5 \times 10^9$ Bq, which was 4 orders of magnitude lower than that of the Chernobyl accident.[6,13] If we assume that half of these Pu isotopes deposited in the sea around the FDNPP site in a circle with a radius of 100 km and all finally incorporated into the corresponding marine sediments. We can estimate that the extra inventory of $^{239+240}$Pu was ca. 0.1 Bq m^{-2}; this amount of $^{239+240}$Pu input was negligible compared to the inventory of $^{239+240}$Pu (around 100 Bq m^{-2}) in the marine sediments before the accident. Therefore, the contamination of Pu isotopes in the marine environment from the FDNPP accident through atmospheric deposition could be small considering the dilution effect of seawater. The direct discharge of radioactive liquid waste should be the main way for possible Pu contamination from the FDNPP accident to the marine environment. However, very limited information is available regarding Pu concentration in the directly discharged radioactive liquid waste from the accident. In our previous study,[19] we investigated the Pu distribution in seawater samples (collected from May 2011 to January 2013) in the western North Pacific after the FDNPP accident and found that both the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios were in the range of the background values before the accident. As the Pu isotopes are particle-reactive and they can be easily incorporated by sinking particles, Pu distribution in the near coastal marine sediments can give direct information about Pu contamination in the marine environment. As no detectable Pu isotopes from the FDNPP accident could be identified in the marine sediments within the 30 km zone in this study, we concluded that the release of Pu isotopes from the FDNPP accident to the marine environment was negligible compared with the background levels. Global fallout and the PPG close-in fallout are the two main sources for Pu contamination in the marine environment before and after the FDNPP accident.

It can be seen in Figure 5, the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios in the surface marine sediments collected outside the 30 km zone around the FDNPP site were slightly lower than that of the sediments collected within the 30 km zone around the FDNPP site. However, high Pu atom ratios (^{240}Pu/^{239}Pu > 0.27) have been commonly observed in the deeper layer sediments outside the 30 km zone due to the direct deposition of the PPG close-in fallout.[17] As discussed before, the strong physical sedimentation mixing process in the near coastal marine environment resulted in the constant distribution of Pu atom ratios in the marine sediments within the 30 km zone around the FDNPP site. Based on a simple

two-end-member mixing model,[44] we calculated the inventory-weighted contributions of these two sources for Pu distribution in the marine sediments investigated in this study. Global fallout and the PPG close-in fallout contributed $47 \pm 3\%$ and $53 \pm 3\%$, respectively to the Pu contamination in the marine sediments within the 30 km zone around the FDNPP site. The results were similar to the results (38–43% for the PPG close-in fallout and 62–57% for global fallout) we observed in the western North Pacific outside the 30 km zone around the FDNPP site.[20]

In this study, for the first time, we investigated the distribution of Pu activities ($^{239+240}$Pu and ^{214}Pu) and Pu atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) in sediment core samples collected in the western North Pacific within the 30 km zone around the FDNPP site after the March 2011 accident. We provided new information for a better understanding of the influence of the FDNPP accident on Pu contamination in the marine environment. We found that the release of Pu isotopes from the accident to the marine environment was negligible to date. Pu isotopes in the marine sediments originated from global fallout and PPG close-in fallout. However, in the water intake position of the reactor unit 1, ^{238}Pu and $^{239+240}$Pu activities were found to be 0.21 mBq g^{-1} and 1.2 mBq g^{-1} in the surface sediment in July 2011, respectively, two to three times higher than those in the sediment before the accident.[45] The ^{238}Pu/$^{239+240}$Pu activity ratio of 0.175 was also higher than that (0.037) of the global fallout material in Japan.[46] These results revealed the local deposition of the FDNPP derived Pu in that region although the Pu activities were still relatively low. Presently, 270 000 tons of radioactive liquid waste are stored in large tanks within the FDNPP site boundary and the total amounts of ^{238}Pu, $^{239+240}$Pu, and ^{241}Pu contained in this were estimated to be 3×10^8 Bq, 1×10^8 Bq, and 1×10^{10} Bq, respectively.[47] Future earthquakes and other unexpected events could cause leakage of this stored liquid waste and introduce new Pu contamination into the sea. Therefore, Pu isotopes in the marine environment, especially in the trench or very local coastal site near the FDNPP site should be continuously investigated.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Table S1. Activities and inventories of radiocesium in the sediment samples. Table S2. Analytical results of Pu isotopes in the marone sediments within the 30 km zone around the FDNPP site. Figure S1. Analytical procedure for the determination of Pu isotopes in marine sediments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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