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Articles

Pu Distribution in Seawater in the Near Coastal Area off Fukushima after the Fukushima Daiichi Nuclear Power Plant Accident

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The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident released large amount of radionuclides into the marine environment. Compared with the fission products, data on the distributions of Pu in the marine environment of the western North Pacific after the accident is limited. To better understand the Pu contamination in the marine environment after the accident, for the first time, we determined Pu isotope ratio ($^{240}Pu/^{239}Pu$) in addition to $^{239+240}Pu$ activity in seawater collected in the near coastal area (mostly within the 30 km zone) off the FDNPP site. The $^{239+240}Pu$ activities were 4.16-5.52 mBq/m^3 and the $^{240}Pu/^{239}Pu$ atom ratios varied from 0.221 to 0.295. These values were compared with the baseline data for Pu distribution in the near coast seawaters before the FDNPP accident (2008-2010). The results suggested that there is no significant Pu contamination in seawater in the near coastal area off the FDNPP site from the accident two years after the accident.

1. Introduction

Plutonium isotopes are normally produced in nuclear reactor fuel by neutron capture reactions. The predominant Pu isotope is ^{239}Pu produced by neutron capture of ^{238}U. When a fuel element containing ^{239}Pu is left in a reactor for any length of time further multiple neutron capture reactions can occur to yield higher Pu isotopes, such as ^{240}Pu, ^{241}Pu and ^{242}Pu. In addition, small quantities of ^{236}Pu and ^{238}Pu can be produced during the irradiation [1]. In Fukushima Daiichi Nuclear Power Plant (FDNPP) reactors, most of fuel used was UO_2, but in Unit 3 reactor, ca. 4% of the core loading was mixed-oxide fuel assemblies containing ~6% Pu [2]. Thus, after the FDNPP accident in March 2011, the release of Pu isotopes has attracted great public attention because they present a high risk for internal radiation exposure via ingestion of contaminated agricultural crops and marine products [3].

The FDNPP accident caused radioactive contamination in the environment through the deposition of the radionuclides released into the atmosphere as well as through the direct discharge of large amount of radioactive liquids [4,5]. In the terrestrial environment around the FDNPP site, the Pu isotopes released from the accident were characterized by high atom ratios of $^{240}Pu/^{239}Pu$ (0.30 – 0.33) and $^{241}Pu/^{239}Pu$ (0.103 – 0.135) [6], and were detected in various environmental samples, such as, soil, litter, dust (black substances) and aerosol samples and the total released amounts of Pu isotopes were estimated to be $1.0 – 3.5 \times 10^9$, $1.1 – 2.6 \times 10^{11}$ Bq, and $2.9 – 6.9 \times 10^9$ Bq for $^{239+240}Pu$, ^{241}Pu and ^{238}Pu, respectively [3,6-10]. 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 (ca. 10^{-3} Bq/mL) were detected [11]. These values were 6 to 7 orders of magnitudes higher than that of the seawater in the western North Pacific. In addition, a new study on Pu isotopes in recently deposited sediment found along rivers draining the regions of most contaminated by the inland radioactive plumes that were dispersed over Fukushima Prefecture suggested there was a potential sediment-borne Pu supply from Fukushima coastal rivers to the Pacific Ocean [12]. Thus more attention should be paid to the contamination situation of Pu isotopes in the marine environment off Fukushima since the FDNPP accident.

After the FDNPP accident, several studies reported the activity levels and isotopic compositions of Pu in the marine sediments of the western North Pacific [13-17]. Bu et al. also studied Pu distribution in seawater samples collected 30 km off the FDNPP site after the accident [18]. These studies suggested that the release of Pu isotopes from the FDNPP accident into the wider marine environment could be ignored. However, no data about Pu characterization in seawater within the 30 km zone around the FDNPP site was reported after the accident. Numerical modeling showed that the impact of Pu from the accident on the marine environment would mainly remain within the 30 km zone around FDNPP site considering the low mobility of Pu [19]. Therefore, Pu isotopes in seawater off the FDNPP site, especially within the 30 km zone, needs to be routinely investigated. In this study we analyzed the $^{239+240}Pu$ activities and $^{240}Pu/^{239}Pu$ atom ratios in seawater samples in the near coastal area off the FDNPP site (mostly within the 30 km zone) collected in May 2013, two years after the accident. A comparison was made between the obtained results and the baseline data of Pu information in seawater in the western North Pacific and its marginal seas, especially the near coast seawater before the accident (2008-2010) to identify the sources of Pu in the studied area and assess the possible Pu contamination to the marine environment due to the FDNPP accident.

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TABLE 1: Summary of distributions of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in surface seawater in the western North Pacific and its marginal seas

Study area	GPS location	Sampling date	$^{239+240}$Pu activity range (mBq/m^3)	^{240}Pu/^{239}Pu atom ratio range	Reference
Coastal Water off Aomori Prefecture	40-42ºN, 141-142ºE	1999-2000	4.6-8.8	ND	28
Coastal Water off Aomori Prefecture	40-42ºN, 141-143ºE	2001-2005	2.8-10	0.243-0.245	29
East China Sea	30-35ºN, 120-130ºE	1987	3.2-10[a]	0.199-0.246	32
East Sea/Japan Sea	35-43ºN, 130-138ºE	1993	6-10	ND	33
East Sea/Japan Sea	38-42ºN, 133-135ºE	1995	8-25	ND	34
East Sea/Japan Sea	35-41ºN, 129-137ºE	1993-1996	3.5-10.0	ND	35
East Sea/Japan Sea	35-41ºN, 129-137ºE	1993	3.4-20.8	ND	36
Japan Sea	38-39ºN, 132-136ºE	1984, 1993	6.7-9.5	0.233-0.235	37
Japan Sea	38-45ºN, 132-141ºE	1986-1997	3.0-14.0	ND	38
Sagami Bay	35º'N, 139º'E	1992	13.4	0.224	39
South China Sea	1-8ºN, 102-106ºE	2008	2.3-7.9	ND	40
Western North Pacific	14-32ºN, 128-138ºE	1996	1.52-1.87	0.199-0.224	41
Western North Pacific/Japan Sea	37-41ºN, 137-142ºE	1991-1993	4.9-7.8	0.221-0.235	42
Western North Pacific/Japan Sea	38-46ºN, 135-145ºE	1998	ND	0.204-0.225	43
Yellow Sea/Korea Strait/East Sea	33-39ºN, 124-132ºE	1999-2000	3.1-22.3	0.18-0.33	22

[a] Data that are apparently influenced by Changjiang River is not adopted there. "ND", stands for not detected.

2. Spatial and temporal distribution of Pu in seawater in the western North Pacific before the FDNPP accident

Before the FDNPP accident, Pu was deposited over the western North Pacific mainly as a result of global fallout following the atmospheric nuclear weapons tests about 50 years ago. Besides, the Pacific Proving Ground (PPG) close-in fallout is another important source other than global fallout, which made the $^{239+240}$Pu inventories in the seawater of the western North Pacific more than two times higher than those of the terrestrial environment at the same latitude [20,21]. The PPG sourced Pu was transported by ocean current to the western North Pacific and made the ^{240}Pu/^{239}Pu atom ratio in this sea area higher than that of global fallout [21-24]. Table 1 summarized the related studies on the distribution of Pu isotopes ($^{239+249}$Pu activity and ^{240}Pu/^{239}Pu atom ratio) in seawater of the western North Pacific conducted from 1984 to 2008.

Since the early 1970s, continuous investigation on the distribution of Pu activities in surface seawater showed a latitudinal distribution, with higher concentration in the mid-latitude region of the western North Pacific and relatively lower concentration in the equatorial region because the amount of radioactive deposition is controlled by the precipitation amount and stratosphere-troposphere air change [25-27]. For that reason, Pu activity in seawater of the western North Pacific took on a large variation (i.e. 1.52-22.3 mBq/m^3 as Table 1 shows) [22, 28-43].

Besides spatial distribution, temporal distribution of Pu in the North Pacific needs to be considered when we discuss the baseline data of Pu in seawater because $^{239+240}$Pu activities slowly decreased over time especially in surface seawater. Bowen et al. reported the $^{239+240}$Pu activities in central North Pacific seawater collected in 1974 and 1978 [20]. The results showed that Pu activities in the surface seawater decreased in 1978 compared with 1974. Hirose et al. estimated the $^{239+240}$Pu activities in the surface water of the Pacific ocean based on HAM database and obtained the temporal variation of $^{239+240}$Pu activities in the western North Pacific (25°N-40°N) from 1971 to 1998 and a clearly decrease of $^{239+240}$Pu activities with time was observed [26]. The $^{239+240}$Pu activities in the surface seawater of the western North Pacific decreased exponentially over recent decades. In the early 1970s, the $^{239+240}$Pu activities ranged from 8.1 to 35 mBq/m^3, while in 2000, they have been estimated to be 0.3-2.7 mBq/m^3 in the open ocean seawaters.

Oikawa et al. determined Pu isotopes in seawater collected off Rokkasho in northern Japan during 1991-2005 [29]. The $^{239+240}$Pu activities in surface seawater of this region varied from 2.8 to 10 mBq/m^3 with an average of 5.3 mBq/m^3. The estimated apparent half-life of Pu in the surface seawater was about 17.8 y at the end of the study period and it tended to gradually increase because the decrease rate of $^{239+240}$Pu in surface seawater would probably lessen with time. Recently, more comprehensive baseline data on $^{239+240}$Pu activities in near coastal seawaters collected off the sites of commercial nuclear power plants (including FDNPP and Fukushima Daini NPP) around the Japanese islands at 37 locations were summarized [30,31]. Based on this investigation, the $^{239+240}$Pu activity concentration in the surface water was independent of seawater properties, such as salinity and temperature, and the $^{239+240}$Pu activity ranged from 3.1 to 12 mBq/m^3 with the average of 5.2 ± 1.5 mBq/m^3 for the surface water samples collected during the 3 years (2008-2010) just before the FDNPP accident.

Although $^{239+240}$Pu activities in surface seawater slowly decrease with time, the ^{240}Pu/^{239}Pu atom ratio in seawater seems to be invariant with time. Yamada and Zheng determined the ^{240}Pu/^{239}Pu atom ratios in the water column of Japan Sea collected during 1984-1993, and no temporal variation was found [24]. After adequately mixing of seawater, ^{240}Pu/^{239}Pu atom ratio in seawater can be regarded as a consistent value if there isn't any other Pu source injection. As shown in Table 1, recent studies within 10 years showed a centralized ^{240}Pu/^{239}Pu atom ratio in seawater in the western North Pacific from 0.199 to 0.246 [32-43], with higher ratios (0.18-0.33) in the coastal waters of the Korean Peninsula [22]. These Korean Peninsula values are apparently higher than the characteristic ^{240}Pu/^{239}Pu atom ratio of 0.18 for global fallout and lower than the PPG derived Pu with a ^{240}Pu/^{239}Pu atom ratio of 0.36 [21,44,45], indicating a mix of Pu from these two sources in the western North Pacific. The baseline data on ^{240}Pu/^{239}Pu atom ratios compiled by Oikawa et al.[30], based on a ministry report on environmental radioactivity investigations that found the ^{240}Pu/^{239}Pu atom ratios ranged from 0.172 to 0.304, with the average of 0.234 ± 0.025 for the surface water samples collected during the 3 years (2008-2010) just before the FDNPP accident [31].

3. Materials and methods

3.1. Seawater sampling. Surface seawater (0-60 m) samples (20 L) were collected at the six locations described in

TABLE 2: Pu isotopes in surface seawater in the near coastal area off Fukushima after the FDNPP accident

Sample location ID	Sampling time	Water sampling depth (m)	GPS location	$^{239+240}$Pu activity (mBq/m^3)	^{240}Pu/^{239}Pu atom ratio
M01	2013/5/17	10	37°33'N, 141°13'E	4.36±0.57	0.221±0.040
M01	2013/5/17	50	37°33'N, 141°13'E	4.73±0.50	0.251±0.039
N01	2013/5/15	0	37°30'N, 141°30'E	4.23±0.48	0.295±0.048
N01	2013/5/15	20	37°30'N, 141°30'E	4.16±0.36	0.235±0.030
I02	2013/5/20	0	37°14'N, 141°14'E	4.23±0.34	0.242±0.037
NP1	2013/5/17	40	37°25'N, 141°11'E	5.30±0.42	0.249±0.034
NP1	2013/5/17	60	37°25'N, 141°11'E	5.52±0.43	0.293±0.038
AN6	2013/5/15	0	37°17'N, 141°05'E	4.56±0.44	0.286±0.056
AN6	2013/5/15	20	37°17'N, 141°05'E	4.55±0.74	0.227±0.041
NP2	2013/5/17	20	37°25'N, 141°06'E	4.73±0.45	0.278±0.040

Uncertainties are expressed as the expanded standard uncertainty with a coverage factor of 2.

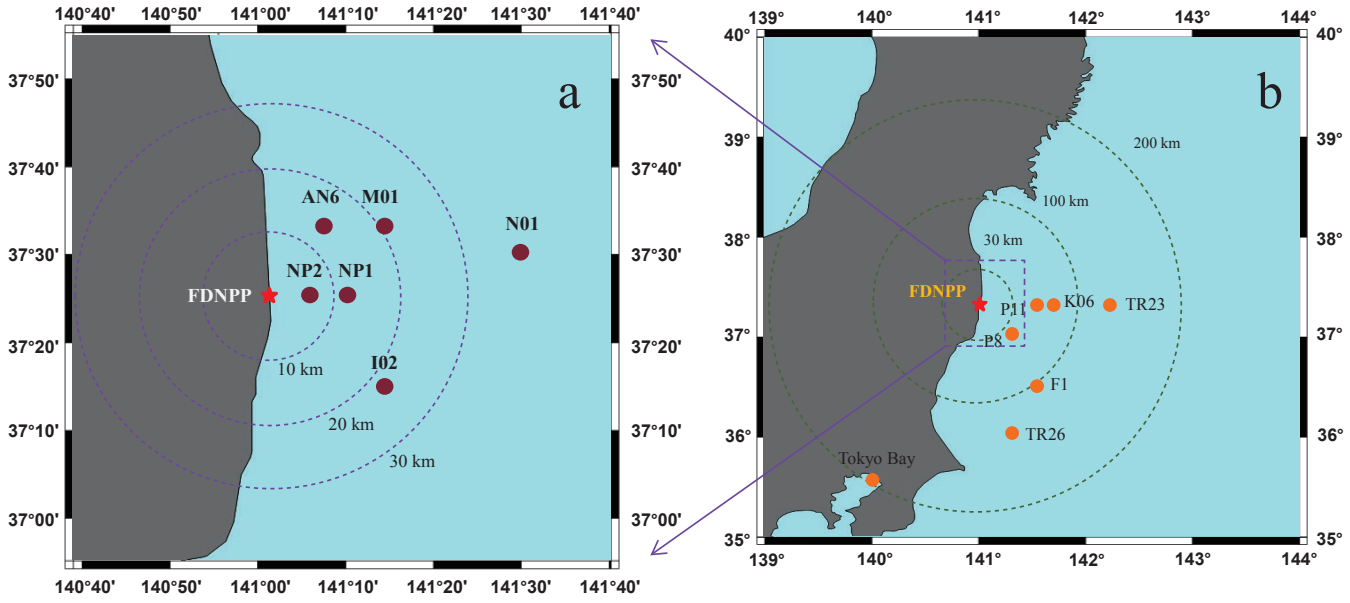

Figure 1. Map showing the locations for (a) seawater collected in the near coastal areas around the FDNPP site and (b) seawater collected outside the 30 km zone around the FDNPP site (redrawn from ref. 18). (The map is generated using Surfer 8.0)

Table 2 in the western North Pacific during the UM 13-05 cruise (T/S Umitaka-maru, Tokyo University of Marine Science and Technology) in May 2013. All the sampling locations were within the 30 km zone around the FDNPP site except N01, which was about 38 km away. Fig. 1 shows the seawater sampling locations in this study together with locations outside the 30 km zone off the FDNPP site which were investigated previously. The specific sampling date and water depth are given in Table 2.

3.2. Seawater sample analytical procedures. An analytical method based on anion-exchange chromatography using Dowex 1X8 resin and SF-ICP-MS for the determination of plutonium isotopes at ultra-trace level in seawater was established and validated in our previous work [18], and it was employed in this study to determine the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in the collected seawater samples. This method was characterized by a sufficiently low detection limit at sub-fg/mL level for ^{239}Pu and ^{240}Pu isotopes. About 0.57 pg ^{242}Pu was added to the seawater sample (pre-filtrated with an Advantec cartridge, 0.45 μm) as a yield tracer. $Fe(OH)_3$ was used for initial concentration to collect Pu by co-precipitation. After allowing the precipitate to settle, the sample supernatant was carefully siphoning away once and then again after a centrifuging step. The Fe precipitates together with Pu were dissolved in 8 M HNO_3. Then $NaNO_2$ was added to the sample solution and this was heated at 40°C to convert Pu to the tetravalent. Pretreated resin was packed in a 2.5 mL PTFE column and then preconditioned with 20 mL 8 M HNO_3–0.2 M $NaNO_2$ solution. The seawater sample (which now included the tetravalent Pu) was loaded onto the column and then the column was rinsed first with 50 mL 8 M HNO_3 and then with 30 mL 10 M HCl. Then 30 mL 0.1 M NH_4I–8.5 M HCl was loaded for Pu elution. The eluent was heated to dryness after adding 5 mL *conc.* HNO_3. Then 4 M CH_3COOH was added to dissolve the residue and the obtained solution was loaded to the second preconditioned resin column. Solution flowing through the resin was later mixed with the eluent of 20 mL *conc.* HBr. This solution was heated to dryness and 1 mL *conc.* HNO_3 was added and evaporated to dryness. After that, the final residue was dissolved in about 0.7 ml 4% HNO_3 for the SF-ICP-MS analysis. The information about the SF-ICP-MS analytical system and the detailed operation setup can be seen in another work [46].

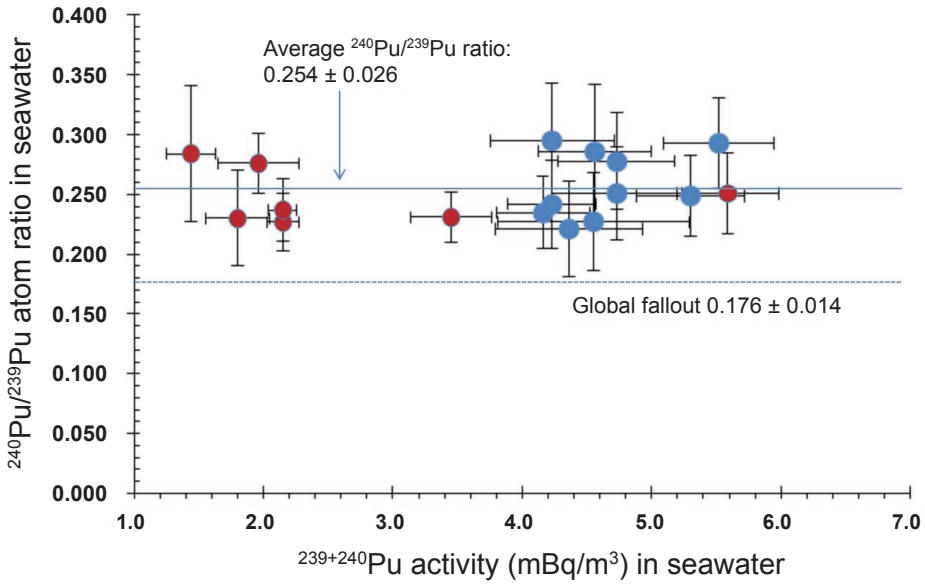

Figure 2. Relationship between $^{239+240}$Pu activity (mBq/m^3) and ^{240}Pu/^{239}Pu atom ratio found in the surface waters collected within the 30 km zone (blue circles) and in the zone of 30 km – 200 km (red circles). Data for 30 km – 200 km surface water were cited from Bu et al. [18].

4. Results and Discussion

The analytical results of Pu isotopes in the near coastal seawater samples off the FDNPP site were shown in Table 2. The $^{239+240}$Pu activities showed small variation with range from 4.16 to 5.52 mBq/m^3 in the surface seawaters collected within 30 km zone. The lower value of 4.16 mBq/m^3 was detected in sampling Station N01, located outside 30 km zone (ca. 38 km from the FDNPP). The ^{240}Pu/^{239}Pu atom ratios ranged from 0.221 to 0.295, with an average of 0.254 ± 0.026. Relationship between $^{239+240}$Pu activity (mBq/m^3) and ^{240}Pu/^{239}Pu atom ratio found in the surface waters collected within the 30 km zone and in the zone of 30 km – 200 km was plotted in Fig. 2. Data for 30 km – 200 km surface water were cited from Bu et al [18]. The ^{240}Pu/^{239}Pu atom ratios in the surface waters showed no significant difference and they were independent of sampling locations, and there was no clear relationship between the $^{239+240}$Pu activities and the ^{240}Pu/^{239}Pu atom ratios.

As summarized Table 1, there was a large variation of $^{239+240}$Pu activities in seawater in the western North Pacific due to the latitudinal dispersion, the influence of oceanographic processes, and the temporal variation [27]. The $^{239+240}$Pu activities in 1990s varied from 3.1 mBq/m^3 to 22.3 mBq/m^3. If we suppose that the apparent half-residence time of Pu still remained to at 17.8 y during the past two decades, from that viewpoint, $^{239+240}$Pu activities in the seawater in 2011 could be less than 10 mBq/m^3.

Compared with the $^{239+240}$Pu activities in the western North Pacific in the 1990s, $^{239+240}$Pu after 2000 varies in a relatively smaller range (i.e. 2.8 mBq/m^3-10 mBq/m^3). As mentioned before, $^{239+240}$Pu activities in the surface seawater slowly decrease with time and the decrease rate is getting slower. During 2008 to 2010, just before the FDNPP accident, $^{239+240}$Pu activities in near coastal seawaters collected off the sites of commercial nuclear power plants around the Japanese islands ranged from 3.1 to 12 mBq/m^3 with the average of 5.2 ± 1.5 mBq/m^3. These data provided reliable baseline of $^{239+240}$Pu activities before the accident.

The comparison of the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater before and after the accident in the western North Pacific and the near coastal waters was illustrated in Fig. 3. The $^{239+240}$Pu activities of 4.16 mBq/m^3 to 5.52 mBq/m^3 observed in surface seawaters within the 30 km zone off the FDNPP site are within the range of baseline data even when we take account of the temporal distribution of baseline data. Furthermore, these results are also comparable to the results of Oikawa et al. (3.1-12 mBq/m^3) for the near coastal seawaters off the sites of commercial nuclear power plants during 2008 to 2010 [30]. In a previous study [18], we analyzed Pu isotopes in seawater samples collected in the western North Pacific 30 - 200 km off the FDNPP site after the accident and found that the $^{239+240}$Pu activities were 0.43-5.59 mBq/m^3. The $^{239+240}$Pu activities in the near coastal seawater showed a smaller variation compared with that in seawater 30 - 200 km off the FDNPP site. This is because in the near coastal area, the strong coastal current made the efficient mixing of Pu of different water masses, and also the vertical mixing with Pu originated from bottom sediment taking into account the shallow water depth of several tens meters. All the observed $^{239+240}$Pu activities in the Fukushima seawater samples were consistent with the background data before the accident, suggesting no significant extra injection of Pu into the marine environment after the accident. In the Nuclear Regulation Authority (NRA) report [47], there are two sampling sites close to the FDNPP: T-1 was located 30 m north from the mouth of the discharge canal for reactors 5 and 6, and T-2-1 was 1.3 km south from the discharge canal for reactors 1 to 4. In these sampling sites, $^{239+240}$Pu concentrations in seawater were reported in 2012-2014 and the range was from detection limit to 14 mBq/m^3 except 31 mBq/m^3 observed at T-2-1 site on 10 April 2014. Thus most data were within the range of $^{239+240}$Pu activity data before the accident as reported above. However, in the NRA report [47], there was no additional information such as ^{240}Pu/^{239}Pu atom ratio, therefore, further discussion is not available.

The particle scavenging and upwelling processes may have less influence on the ^{240}Pu/^{239}Pu atom ratio than on the $^{239+240}$Pu activity in seawater samples because the ^{240}Pu/^{239}Pu atom ratio in seawater distributed homogenously with water depth and this ratio in seawater column also doesn't vary with time [20,22,37]. Thus, compared with $^{239+240}$Pu activity, ^{240}Pu/^{239}Pu atom ratio could provide further information for source identification.

The ^{240}Pu/^{239}Pu atom ratio in seawater in the western North Pacific before the FDNPP accident ranged widely from 0.18 to 0.33 as presented in Table 1, suggesting a mixing of global fallout Pu and the PPG derived Pu. More recently, the ^{240}Pu/^{239}Pu atom ratios in seawater collected off the coastal area of Japan from 2008 to 2010 ranged from 0.173 to 0.304

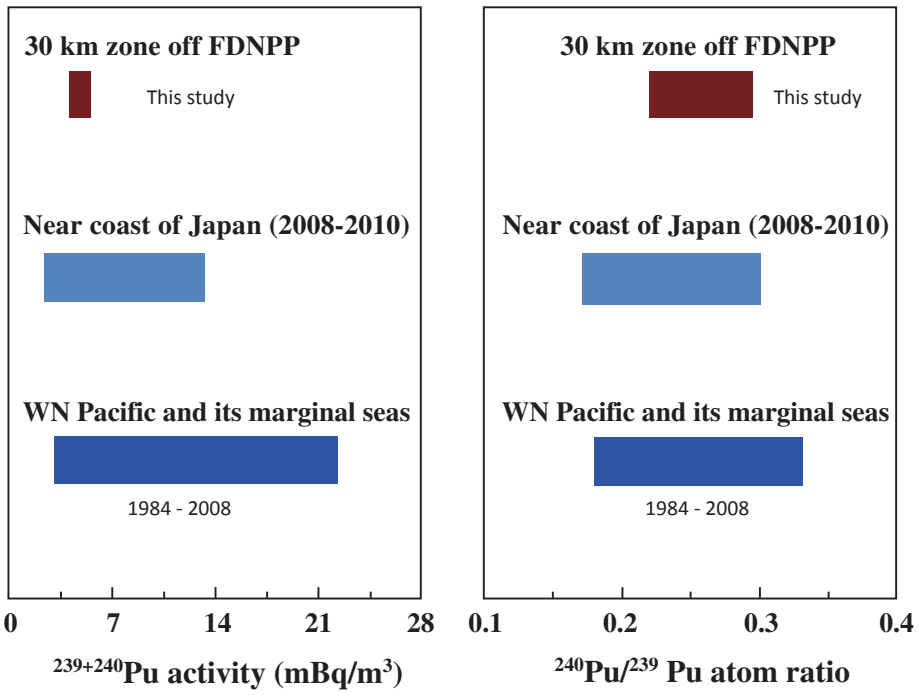

Figure 3. Comparison of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater samples within the 30 km zone off the FDNPP site with the background level in near coast of Japan [30,31] and in the western North Pacific and its marginal seas (Summarized from data in Table 1).

[30,31]. Our determined ^{240}Pu/^{239}Pu atom ratios in the surface seawater within the 30 km zone off the FDNPP after the accident were 0.221-0.295, typically in the range of the background data in the western North Pacific before the accident. Oikawa et al. reported the ^{240}Pu/^{239}Pu atom ratios of surface seawater collected off the FDNPP and Fukushima Daini NPP (about 10 km south of the FDNPP) ranged from 0.195 to 0.259 during the period of 2008 to 2010 [30]. In addition, among the studies listed in Table 1, the sample locations in the work of Yamada and Zheng [42] and of Oikawa et al. [29] were relatively closer to the FDNPP site than others. The ^{240}Pu/^{239}Pu atom ratios in these two studies were 0.221-0.235, and 0.243-0.245, respectively, similar to the data obtained in our study. These results suggested that the sources of Pu in the marine environment in the near coastal area off the FDNPP site were the same before and after the nuclear accident. In our previous work [16], we determined the Pu distribution in sediment samples collected within the 30 km zone around the FDNPP site. The obtained isotopic ratios of Pu (^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu) were found to be different from those of the FDNPP accident released Pu [6,16], and showed that global fallout and the PPG close-in fallout were still the two main sources for Pu contamination in the sediments. Based on the seawater results obtained in the present study, we can reach the same conclusion that there was no significant Pu contamination derived from the FDNPP accident in the marine environment two years after the its occurrence.

5. Conclusions

In this study we analyzed the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater samples collected in the near coastal area off the FDNPP site (mostly within the 30 km zone) two years after the nuclear accident. The $^{239+240}$Pu activities in the seawater samples ranged from 4.16-5.52 mBq/m^3, while the ^{240}Pu/^{239}Pu atom ratios were 0.221-0.295. Our results agreed well with the baseline data before the accident, revealing that no significant Pu was released into the marine environment from the FDNPP accident. Global fallout and the PPG close-in fallout are still the two main sources for Pu contamination in the western North Pacific. Considering that the seawater samples in this study were collected 2 years after the FDNPP accident, we couldn't conclude whether Pu was discharged into the marine environment during the accident. This remains to be clarified by analyzing the seawater samples collected in April or May of 2011, the period of heaviest radioactive contamination in the ocean after the accident.

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