Applying an improved method to measure $^{134}\text{Cs}$, $^{135}\text{Cs}$, and $^{137}\text{Cs}$ activities and their atom ratios in marine sediments collected close to the Fukushima Daiichi Nuclear Power Plant

GUOSHENG YANG,$^{1,2}$ YOSHIHISA KATO,$^3$ HIROFUMI TAZOE$^1$ and MASATOSHI YAMADA$^{1,4}$

$^1$Department of Radiation Chemistry, Institute of Radiation Emergency Medicine, Hirosaki University, 66-1 Hon-cho, Hirosaki, Aomori 036-8564, Japan
$^2$Division of Nuclear Technology and Applications, Institute of High Energy Physics, Chinese Academy of Sciences; Beijing Engineering Research Center of Radiographic Techniques and Equipment, Beijing 100049, China
$^3$School of Marine Science and Technology, Tokai University, Orido 3-20-1, Shimizu, Shizuoka 424-8610, Japan

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The $^{135}\text{Cs}/^{137}\text{Cs}$ atom ratio has been proved to be a reliable tracer for radiocesium source identification in the studies on the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. However, due to the technical challenge to measure $^{135}\text{Cs}$, no $^{135}\text{Cs}$ data are available for Japanese river or ocean sediments. In the present study, the vertical distributions of $^{134}\text{Cs}$ and $^{137}\text{Cs}$ activities and their ratios in two marine sediment cores, collected offshore from the FDNPP site immediately after the accident, were measured by $\gamma$-spectrometry. A conventional introduction system was replaced by an APEX-Q system, by which it was possible to get 6.5 times higher Cs intensities and then $^{135}\text{Cs}$ was analyzed by triple-quadrupole inductively coupled plasma-mass spectrometry. From the vertical distributions, it was seen that the deposition of $^{134}\text{Cs}$ and $^{137}\text{Cs}$ presented an increasing trend, which indicated continuous radiocesium input into the ocean and deposition from sea water onto the sea floor up to the collection date. Therefore, the $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratios (0.866–1.16) and $^{135}\text{Cs}/^{137}\text{Cs}$ atom ratios (0.249–0.343) (all decay-corrected to March 11, 2011) in marine sediment core samples showed the fingerprints of radiocesium in the oceanic environment were mainly derived from the FDNPP.

Keywords: $^{135}\text{Cs}/^{137}\text{Cs}$ atom ratio, $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio, Fukushima Daiichi Nuclear Power Plant accident, marine sediment, triple-quadrupole inductively coupled plasma-mass spectrometry

INTRODUCTION

Volatile radiocesium was one of the major radionuclides released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 (Yoshida and Kanda, 2012; Merz et al., 2013; Kirchner et al., 2012; Steinhauser et al., 2014). According to the very recent study (Aoyama et al., 2016), the total atmospheric released amounts of $^{133}\text{Cs}$ were around 15–20 PBq, and most of the releases were dispersed over the North Pacific Ocean and then fell on the oceanic surface layer (12–15 PBq). In addition, there were direct releases and also discharges into the sea at the site, with the primary source of highly radioactive water being from a trench at the FDNPP (3.6 ± 0.7 PBq) (Tsumune et al., 2013). Furthermore, the released $^{134}\text{Cs}$ activity was almost the same as the $^{137}\text{Cs}$ activity (Yang et al., 2016a), and that of $^{135}\text{Cs}$ was estimated to be $6.74 \times 10^5$ PBq (Zheng et al., 2014a). Only a small portion of released radiocesium (3–6 PBq) was deposited in the terrestrial environment (Aoyama et al., 2016), from which it migrates downstream in rivers via attachment to suspended sediment and coarse organic matter, as well as being in a dissolved fraction, before finally accumulating in the ocean, especially in the marine sediment. This accumulation is possible because the major migration mode of radiocesium is on suspended sediment (96–99%) (Iwagami et al., 2017) and cesium can be selectively absorbed by clay minerals and subsequently deposited on the seafloor from sea water (Bu et al., 2014). Therefore, it is necessary to carry out long-term monitoring of radiocesium deposited in the marine sediment to obtain the fingerprints of radiocesium due to the FDNPP accident.

For long-term monitoring and source identification, the $^{134}\text{Cs}/^{137}\text{Cs}$ atom ratio instead of the $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio has been proved to be a powerful geochemical tracer since $^{135}\text{Cs}$ has a longer half-life ($t_{1/2} = 2.3 \times 10^6$ y) than that of $^{134}\text{Cs}$ ($t_{1/2} = 2.06$ y) (Zheng et al., 2014a, b; Bu et al., 2016; Yang et al., 2016a, b). However, meas-
urement of $^{135}$Cs encounters a great technical challenge, and there were no $^{135}$Cs data available in Japanese environmental samples before the FDNPP accident. Therefore, in terms of source term attribution for the FDNPP accident, several novel methods have been developed recently to measure trace $^{135}$Cs and thus to obtain the $^{135}$Cs/$^{137}$Cs atom ratio in different environmental matrices (Zheng et al., 2014a, 2014b, 2016; Cao et al., 2016; Yang et al., 2016a, b). Furthermore, the arithmetic means of the $^{134}$Cs/$^{137}$Cs activity ratio (1.033 ± 0.006) and $^{135}$Cs/$^{137}$Cs atom ratio (0.334 ± 0.005) (decay-corrected to March 11, 2011), from leaves of plants collected immediately after the FDNPP accident, were confirmed to represent the FDNPP derived radiocesium signature (Yang et al., 2016a). However, no data for the $^{135}$Cs/$^{137}$Cs atom ratio were available in the Japanese marine sediment up to date. Therefore, to widen the application of the $^{135}$Cs/$^{137}$Cs atom ratio as a tracer of radiocesium, obtaining this ratio in samples of marine sediment collected close to the FDNPP site is desirable, because it not only provides information apart from the $^{134}$Cs/$^{137}$Cs activity ratio, but it can also overcome the application limit of the $^{134}$Cs/$^{137}$Cs activity ratio due to the short half-life of $^{134}$Cs.

In the present study, marine sediment core samples collected offshore from the FDNPP site immediately after the FDNPP accident, were used. Firstly, the introduction system for triple-quadrupole inductively coupled plasma-mass spectrometry (ICP-QQQ) was changed from a conventional double pass Scott type spray chamber to the APEX-Q system in order to increase the signal intensities of Cs. Subsequently, conventional γ spectrometry was combined with ICP-QQQ to measure the vertical distributions of $^{134}$Cs, $^{135}$Cs, and $^{137}$Cs activities to study the deposition of radiocesium from seawater to marine sediment. Finally, $^{134}$Cs/$^{137}$Cs activity ratios and $^{135}$Cs/$^{137}$Cs atom ratios were also obtained to gain new knowledge on the fingerprints of radiocesium in the oceanic environment that were mainly derived from the FDNPP accident.

**SAMPLES AND EXPERIMENTAL PROCEDURES**

**Sampling**

The details of procedures for sampling from ship and pretreating marine sediment samples have been described elsewhere (JAMSTEC, 2011). In order to measure artificial radioactive nuclides emitted in the FDNPP accident for verification of the mechanism of transport and circulation of artificial radioactive nuclides in the ocean, surface sediment was sampled by using a multiple core sampler. This core sampler had 6 sub-core samplers (I.D., 74 mm; length, 60 cm) and a main body weight of 620 kg. Sediment samples for the radionuclide analysis were collected at two stations, D1 and D2 (Fig. 1), during the MR11-05 Cruise of the R/V Mirai. The same designations are used for the stations and the cores themselves. On board the ship, each sediment core sample was extruded at 0.5-cm intervals in the top 2 cm-layer and at the 1.0-cm intervals in the depth from 2 to 10 cm, as shown in Supplementary Tables S1 and S2.

**Reagents and materials**

Reagents were of analytical grade, including HCl, HNO$_3$, and NH$_3$·H$_2$O. Ultrapure grade HNO$_3$ obtained from Tama Chemicals (Tokyo, Japan), and Milli-Q water (>18.2 M$_{\Omega}$ cm$^{-1}$) were used for preparation of the final sample solution prior to ICP-QQQ measurement. Single-element standard solutions (1000 mg L$^{-1}$) of Cs, Ba, Mo, Sn, and Sb were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). A 10 mg L$^{-1}$ multi-element standard stock solution (SPEX-XSTC 622), containing Cs, Ba, Mo, Sn, and Sb in 5% HNO$_3$, was purchased from SPEX CertiPrep (Metuchen, NJ, USA). High purity N$_2$O, He and Ar (>99.999%), were obtained from Sumitomo Seika Chemicals Co., Ltd. (Tokyo, Japan) and Taiyo Nippon Sanso Corp. (Tokyo, Japan). A 0.45 μm syringe filter
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(Minisart RC15, Sartorius Stedim Biotech, Goettingen, Germany) was employed to separate the ammonium molybdophosphate (AMP, Nacalai Tesque, Inc., Kyoto, Japan)—adsorbed Cs precipitate from a prepared sediment sample solution. Then, the AMP-adsorbed Cs was dissolved and released from the syringe filter by NH$_3$·H$_2$O. A 2 mL amount of cation-exchange resin, AG 50W-X8 (200–400 mesh, hydrogen form) obtained from Bio-Rad (Hercules, CA, USA), was packed in a Muromac mini-column (M type, 6.5–8.5 mm (i.d.) ¥ 45 mm (H), Fukuoka, Japan) for Cs separation and purification. Soil (IAEA-375) certified reference material was used to validate the developed method.

**Measurement of isotopes and treatment of sediment samples**

Activities of $^{134}$Cs and $^{137}$Cs were measured using an EG&G Ortec model GWL-120230 well-type HPGe detector. The specific gamma rays at 604.7 keV and 795.9 keV for $^{134}$Cs and 661.7 keV for $^{137}$Cs were counted for 48 h using a Seiko EG&G model 7800 multi-channel analyzer. The efficiencies were calibrated using a house reference material for $^{137}$Cs (45 Bq kg$^{-1}$) prepared by adsorption of a known activity $^{137}$Cs standard solution (Japan Radioisotope Association) to a known amount of Uranium-Thorium Ore DL-1a for use as the reference material of $^{210}$Pb (provided by Canada Center for Mineral and Energy Technology).

For measurement of $^{135}$Cs, the sediment core sample slice was put in a muffle oven and dried, and its organic matter was decomposed at 450°C for 2 h. Then the solid sample material was put into PFA jar with a lid (Savillex, Eden Prairie, MN, USA) and leached with 20 mL of concentrated HNO$_3$ while heating on a hot plate at 180°C for 2 h. After filtration, the sample solution was adjusted to 4 M HNO$_3$ by adding Milli-Q water. The separation of Cs was conducted according to the literature as described in Supplementary Fig. S1 (Yang et al., 2016b). The Agilent 8800 (ICP-QQQ, Agilent Technologies, Santa Clara, CA, USA) featuring an octopole collision/reaction cell situated between two quadrupole mass filters (first, Q1; second, Q2) was employed for analysis of $^{134}$Cs/$^{137}$Cs activity ratios and $^{135}$Cs/$^{137}$Cs atom ratios. Finally, $^{135}$Cs activity could be obtained by combining the data from $\gamma$ spectrometry and ICP-QQQ.

**RESULTS AND DISCUSSION**

**Improvement of sensitivity by using the APEX-Q introduction system**

In the authors’ previous study (Yang et al., 2016b), leached Cs from soil and sediment samples was selectively adsorbed by AMP as a precipitate. After dissolving the precipitate in NH$_3$·H$_2$O solution, that solution was purified via single cation-exchange chromatography to remove the majority of isobaric and polyatomic interference elements. Then, the final Cs solution was measured by ICP-QQQ, coupled with the conventional introduction
A system of a double pass Scott type spray chamber with PFA MicroFlow nebulizer. This gave low detection limits of $2.59 \times 10^{-5}$ Bq kg$^{-1}$ and $3.28$ Bq kg$^{-1}$ for $^{137}$Cs and $^{135}$Cs, respectively, that made it possible to carry out $^{135}$Cs/$^{137}$Cs atom ratio analysis in environmental samples. In the present study, in order to further increase the signal intensities of Cs, the conventional introduction system was replaced by a high efficiency sample introduction system (APEX-Q, Elemental Scientific, Omaha, NE, USA) equipped with a PFA MicroFlow nebulizer. As shown in Fig. 2, the signal intensities of Ba were suppressed sharply when in-

Fig. 3. Signal intensities of $^{119}$Sn$^{18}$O$^+$ in ICP-QQQ obtained with the double pass Scott type spray chamber with PFA MicroFlow nebulizer and (solid circles) the APEX-Q introduction system (solid squares).

Fig. 4. Signal intensities of $^{121}$Sb$^{18}$O$^+$ in ICP-QQQ obtained with the double pass Scott type spray chamber with PFA MicroFlow nebulizer and (solid circles) the APEX-Q introduction system (solid squares).
creasing the N₂O gas flow rate, due to the formation of BaO+ via O-atom transfer and BaOH+ via the reaction of BaO+ with H₂O (Granet et al., 2008; Zheng et al., 2014b; Bu et al., 2016; Yang et al., 2016b). When increasing the N₂O flow rate from 0.04 to 0.54 mL min⁻¹ for the conventional introduction system and from 0.04 to 0.61 mL min⁻¹ for the APEX-Q introduction system, a more than 10⁴-fold increase of the 133Cs/138Ba atom ratio was observed for both introduction systems. In addition, for 1 ng mL⁻¹ of 133Cs, the intensities for the APEX-Q system were 6.2–9.6 times higher than that of the conventional introduction system. Since the maximum 133Cs/138Ba atom ratio was observed at 0.54 mL min⁻¹ N₂O for the conventional introduction system and 0.61 mL min⁻¹ for the APEX-Q system, for further comparison, 0.54 and 0.61 mL min⁻¹ N₂O flow rates were selected to evaluate the performance of these two systems, respectively. Under the optimal situations, the 133Cs intensity for the APEX-Q system was 6.5 times higher than that of the conventional introduction system.

The isobaric interference of 135Ba and polyatomic interferences of 97Mo⁴₀Ar⁺ and 11⁷Sn⁴₀O⁺ influence the 133Cs analysis by ICP-MS. In addition, the isobaric interference of 13⁷Ba and polyatomic interferences of 9⁵Mo⁴₀Ar⁺ and 12¹Sb⁴₀O⁺ influence the 13⁷Cs analysis by ICP-MS. Therefore, for the samples and certified reference material, the concentrations of Ba, Mo, Sb, and Sn were also analyzed. As show in Figs. 3 and 4, the signal intensities for Ba, Mo, Sb, and Sn in the ICP-QQQ with the conventional introduction system were almost the same.

Fig. 5. Vertical distributions of 134Cs and 137Cs activities (decay-corrected to collection date), and 13⁴Cs/13⁷Cs activity ratios (decay-corrected to March 11, 2011) in two marine sediment cores (all errors in the present study were shown as 1σ).
same as those with the APEX-Q system. The signal intensity of $^{138}$Ba in the Cs fraction was close to 1 cps, indicating there was almost no signal contribution from $^{135}$Ba and $^{137}$Ba for the signal intensity at $m/z$ 135 and 137, since the relative abundances of $^{135}$Ba, $^{137}$Ba and $^{138}$Ba are 6.59%, 11.23% and 71.70%, respectively. Furthermore, the final Sn and Sb concentrations after AMP adsorption and cation-exchange chromatographic separation were <0.50 and <0.05 ng mL$^{-1}$, respectively, which demonstrated that signal intensity contributions of $^{119}$Sn$^{16}$O$^+$ and $^{121}$Sb$^{16}$O$^+$ were less than 1 cps for the signal intensity at $m/z$ 135 (Fig. 3) and 137 (Fig. 4), respectively. Molybdenum in the Cs eluate was generally below 30 ng mL$^{-1}$, however, in some cases, up to 50 ng mL$^{-1}$ of Mo was observed. There was no signal at $m/z$ 135 or 137 even for 100 ng mL$^{-1}$ of Mo, which demonstrated that the signal intensity contributions from $^{95}$Mo$^{40}$Ar$^+$ and $^{97}$Mo$^{40}$Ar$^+$ could be ignored during environmental samples analysis. Therefore, the APEX-Q system was suitable for the detailed $^{135}$Cs analysis.

Radiocesium isotopes

Most of the radionuclides released into the atmosphere by the FDNPP accident, were deposited in the Pacific Ocean (Aoyama et al., 2016). Radiocesium deposited in the terrestrial environment migrates downstream in rivers adsorbed on suspended sediment and coarse organic matter, as well as in a dissolved fraction, before finally accumulating in the ocean (Iwagami et al., 2017). Although Cs is regarded as a “soluble” element in the marine environment, it can also be selectively absorbed by clay minerals and subsequently deposited on the seafloor (Bu et al., 2014). Therefore, the radiocesium fingerprints due to the FDNPP accident may be obtained in the marine sediment in the offshore from the FDNPP.

Since the half-life of $^{134}$Cs is short ($t_{1/2} = 2.06$ y), the environmental $^{134}$Cs contamination before the FDNPP accident was negligible. Therefore, the environmental $^{134}$Cs activities (decay-corrected to the collection date, July 19, 2011) in the sediment cores D1 (MC05) (0–650 Bq kg$^{-1}$) and D2 (MC04) (0–560 Bq kg$^{-1}$) obtained after the FDNPP accident, would indicate the contamination level due to this accident (Fig. 5). At the same time, the $^{137}$Cs activities (decay-corrected to the collection date) observed in the sediment cores D1 (MC05) (0.5–629 Bq kg$^{-1}$) and D2 (MC04) (1.0–681 Bq kg$^{-1}$) were significantly higher than that of the background level (0–2 Bq kg$^{-1}$ in the surface sediments collected off Fukushima Prefecture in 2010) before the FDNPP accident (MEXT, 2010). Furthermore, as shown in Fig. 5, the vertical distributions presented an increasing trend for the deposition of $^{134}$Cs and $^{137}$Cs, which indicated continuous radiocesium input into the ocean and deposition from sea water to the sea floor up to the collection date (July 19, 2011). In the region adjacent to the FDNPP, existence of a small but persistent leak of radiocesium has also been pointed out (Kanda, 2013). Furthermore, transport processes of particulate radiocesium were investigated using a sediment trap deployed at about 100 km east of the FDNPP from August 2011 to June 2013, where the observed $^{137}$Cs flux was highest in September 2011 and decreased over time with seasonal fluctuations (Otosaka et al., 2014). Therefore, the $^{134}$Cs/$^{137}$Cs activity ratios in the marine sediment core samples could show one fingerprint of radiocesium in the seawater that had been released by the FDNPP.

<table>
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<tr>
<th>Reactor Unit No.</th>
<th>1</th>
<th>2</th>
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<td>1.046</td>
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<td>0.647</td>
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<td>0.348</td>
<td>0.380</td>
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<td>Core 4 SFP-4</td>
<td>0.315</td>
<td>0.484</td>
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<td>0.414</td>
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<tr>
<th>Marine sediment Station No. (Core ID)</th>
<th>D1 (MC05)</th>
<th>D2 (MC04)</th>
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<tbody>
<tr>
<td>$^{134}$Cs/$^{137}$Cs*</td>
<td>0.692–1.16</td>
<td>0.707–0.993</td>
</tr>
<tr>
<td>$^{135}$Cs/$^{137}$Cs**</td>
<td>0.343 ± 0.132</td>
<td>0.249 ± 0.141</td>
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</table>

$^{134}$Cs/$^{137}$Cs was shown as activity ratio; $^{135}$Cs/$^{137}$Cs was shown as atom ratio. $^{134}$Cs and $^{137}$Cs activities were decay-corrected to March 11, 2011.

*Values in all sediment layers.

**Values in the upper layer. All errors in the present study were shown as 1σ.
cores of the damaged Units 1–3 and in the spent fuel pools (SFPs) have been frequently employed (Table 1) (Nishihara et al., 2012). As shown in Fig. 5, $^{134}$Cs penetrated down to the 6–7 cm sediment sample slice of D1 (MC05) and the 5–6 cm sediment sample slice of D2 (MC04), however, their $^{134}$Cs/$^{137}$Cs activity ratios were lower with larger errors in these slices (0.692 ± 0.664 for D1) were observed, 0.707 ± 0.154 (4.1) for D2 (MC04)). These may be due to the significant influence of global fallout in the beginning of the FDNPP accident. Apart from these two layers, the $^{134}$Cs/$^{137}$Cs activity ratios in D1 (MC05) and D2 (MC04) cores ranged from 0.866 to 1.16 and from 0.870 to 0.993 with small errors (decay-corrected to March 11, 2011). Therefore, the release of radiocesium from the SFPs can be excluded due to their lower $^{134}$Cs/$^{137}$Cs activity ratios (0.536–0.742), as shown in Table 1.

For comparison with other studies, the inventory data, $F_{0.3}$, values, defined as the proportion of $^{134}$Cs inventory in the upper 3 cm to the cumulative inventory in the sediment core, were found to be 0.70 ± 0.01 in D1 (MC05) (water depth: 141 m) and 0.76 ± 0.01 in D2 (MC04) (water depth: 158 m). Similar values were observed in the offshore (0.78 ± 0.16, water depth: 100–400 m) and hemipelagic (0.93 ± 0.14, water depth > 400 m) regions (Otosaka and Kato, 2014). On the other hand, $F_{0.3}$ values for the sediment samples in the near-shore regions (water depth < 100 m) in the coastal areas of Ibaraki and Fukushima were below 0.5 (Otosaka and Kobayashi, 2013; Otosaka and Kato, 2014).

In terms of $^{135}$Cs, no data had been available in the marine sediment core to date. Low $^{135}$Cs activities in the upper sediment layers of D1 (MC05) and D2 (MC04) core samples were found: (2.86 ± 1.10) × 10$^{-3}$ Bq kg$^{-1}$ and (2.24 ± 1.27) × 10$^{-3}$ Bq kg$^{-1}$, respectively. When decay-corrected to March 11, 2011, the $^{135}$Cs/$^{137}$Cs atom ratios were observed to be 0.343 ± 0.132 and 0.249 ± 0.141, respectively in the upper sediment layers of D1 (MC05) and D2 (MC04) samples. Although a narrower variation in the $^{135}$Cs/$^{137}$Cs atom ratio (0.334 ± 0.005) was observed in leaves of plants collected immediately after the FDNPP accident (Yang et al., 2016a), wider ranges of 0.315–0.419 in soil samples (Yang et al., 2016a; Zheng et al., 2014a) and 0.329–0.391 in river suspended particles (Cao et al., 2016) were observed for $^{134}$Cs/$^{137}$Cs atom ratios. The reasons are that leaves of plants have less global fallout depletion than that soil has and plant leaves generally have no-acumulating characteristics for Cs via soil-to-plant transfer (IAEA, 2010). It should be noted that the $^{135}$Cs/$^{137}$Cs atom ratios with larger errors in the present study were due to the extremely low $^{135}$Cs activities in these two marine sediment cores. In any case, this study is the first time to show $^{135}$Cs activities and $^{134}$Cs/$^{137}$Cs atom ratios in the marine sediment collected offshore from the FDNPP following the FDNPP accident.

**CONCLUSION**

In order to measure trace $^{134}$Cs in marine sediment, the conventional introduction system was replaced by a high efficiency sample introduction system (APEX-Q) to increase the signal intensities of Cs in the ICP-QQQ system used for this study. After this replacement, the $^{133}$Cs intensity obtained for the APEX-Q system was 6.5 times higher than that of the conventional introduction system, while, the signal intensities for matrix elements, Ba, Mo, Sb, and Sn in the ICP-QQQ remained in the same low level, indicating no influence on the analysis of $^{134}$Cs. Subsequently, higher $^{134}$Cs activities (decay-corrected to the collection date) in the sediment cores D1 (MC05) (0–650 Bq kg$^{-1}$) and D2 (MC04) (0–560 Bq kg$^{-1}$) and higher $^{137}$Cs activities (decay-corrected to the collection date) in the sediment cores D1 (MC05) (0.5–629 Bq kg$^{-1}$) and D2 (MC04) (1.0–681 Bq kg$^{-1}$) were observed, indicating the release of radiocesium from the FDNPP accident. Finally, for the first time, low $^{139}$Cs activities (2.24–2.86) × 10$^{-3}$ Bq kg$^{-1}$ in marine sediment samples were found, indicating the release amount of $^{135}$Cs was trace, if at all. In addition, the obtained $^{135}$Cs/$^{137}$Cs atom ratio of 0.249–0.343 may indicate one radiocesium fingerprint in marine sediment derived from the FDNPP accident. The study points out the need to analyze more samples to depict the effect of the FDNPP accident to the oceanic environment.

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**REFERENCES**


SUPPLEMENTARY MATERIALS

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/52/MS484.pdf) Figure S1 Tables S1 and S2

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