Discovery of radiocesium-bearing microparticles in river water and their influence on the solid-water distribution coefficient ($K_d$) of radiocesium in the Kuchibuto River in Fukushima

HIKARU MIURA,1 YUICHI KURIHARA,1 AYA SAKAGUCHI,2 KAZUYA TANAKA,3 NORIKO YAMAGUCHI,4 SHOGO HIGAKI5 and YOSHIO TAKAHASHI1*

1Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
2Center for Research in Isotopes and Environmental Dynamics, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan
3Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
4Institute for Agro-Environmental Sciences, NARO, 3-1-3, Kannondai, Tsukuba, Ibaraki 305-8604, Japan
5Isotope Science Center, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan

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We found four radiocesium-bearing microparticles (CsMPs) with high cesium (Cs) radioactivity in suspended particles collected from the Kuchibuto River in Fukushima by filtering water during 2011–2016. The CsMPs were identified by autoradiography and subsequently were separated from other suspended particles by the “multiple wet separation method” using a NaI scintillation counter. The present four CsMPs contained 0.426–2.827 Bq of $^{137}$Cs and had a chemical composition similar to that of particles released during the accident at the Fukushima Daiichi Nuclear Power Plant (FDNPP). The activity ratio of Cs ($^{134}$Cs/$^{137}$Cs) suggests that they originated from Unit 2 or 3 of the FDNPP. The ratio of the radioactivity of the separated CsMPs to the total radioactivity on the filters ranged from 0 to 46%. Moreover, we calculated the radioactivities of CsMPs with lower radioactivity (0.1 to 0.4 Bq $^{137}$Cs) determined by autoradiography. When smaller CsMPs were included, the ratio of the radioactivity of the CsMPs to the total radioactivity of radiocesium on the filters ranged from 1.3 to 67%. It has been previously suggested that the solid-water distribution coefficient ($K_d$) of radiocesium in rivers is apparently increased due to the possible presence of CsMPs in the solid phase because the water solubility of radiocesium in CsMPs is small. However, this study reveals that higher $K_d$ values in rivers in Fukushima compared with those in Chernobyl cannot be explained by the contribution of CsMPs alone. The temporal variation of the ratio of radioactivity of CsMPs to the total radioactivity of radiocesium in river water after the FDNPP accident is also discussed.

Keywords: radiocesium-bearing microparticle, solid-water distribution, Fukushima, river water, suspended particles

INTRODUCTION

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused by the Great East Japan Earthquake on 11th March 2011 led to the emission of a huge amount of fission products (e.g., $^{131}$I, $^{134}$Cs, and $^{137}$Cs) into the atmosphere (Yoshida and Takahashi, 2012). The released fission products included a large amount of cesium-137 ($^{137}$Cs) ($T_{1/2} = 30.2$ y) with a relatively long half-life (~1.3 $\times$ $10^{16}$ Bq; Chino et al., 2011; Kobayashi et al., 2013). Cesium-137 released into the atmosphere was deposited on the land surface by dry and wet deposition. It is discharged into rivers by erosion of surface soil and transported to the Pacific Ocean (e.g., Yamashiki et al., 2014). The migration processes of radiocesium (RCs; $^{134}$Cs and $^{137}$Cs) through rivers into the sea have been studied. The solid-water distribution of RCs in river water is important because hydrated RCs, which is not subject to flocculation and sedimentation processes in the estuary area, may be the main form of RCs transported into oceans. Takata et al. (2015) evaluated the flux of dissolved and particulate $^{137}$Cs from the river to the ocean to calculate the migration of $^{137}$Cs in the ocean. The solid-water distribution is also important in terms of the intake of organisms. Thus, the solid-water distribution of RCs has been intensively studied with respect to the emission of RCs associated with the FDNPP accident (Sakaguchi et al., 2015; Yoshimura et al., 2015; Kakehi et al., 2016; Konoplev et al., 2016; Fan and Takahashi, 2017).

The solid-water distribution coefficient ($K_d$), which is often used to discuss the adsorption reaction of RCs in natural water, is calculated using the following equation:

$$K_d (L/g) = \left[ {^{137}Cs}_{\text{solid}} (Bq/g) / {^{137}Cs}_{\text{water}} (Bq/L) \right].$$

*Corresponding author (e-mail: ytakah@eps.s.u-tokyo.ac.jp)
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Among various studies, Kakehi et al. (2016) analyzed suspended particles and water at an estuary, which showed that the $K_d$ value decreases with increasing salinity. Yoshimura et al. (2015) showed that the regional variation in the $K_d$ value is affected by the mineral composition. In particular, Konoplev et al. (2016) suggested that (i) the $K_d$ values in rivers in Fukushima are 1–2 orders of magnitude higher than those in Chernobyl, and (ii) this is partly due to radiocesium-bearing microparticles (CsMPs) that might be present in solid phases in rivers in the Fukushima area.

Radiocesium-bearing microparticles are $\sim 1–10 \mu m$ in size. The matrix is SiO$_2$ glass, which contains Cs and many other elements such as iron, zinc, chlorine, and potassium (Adachi et al., 2013; Abe et al., 2014; Kogure et al., 2016; Yamaguchi et al., 2016; Satou et al., 2016; Furuki et al., 2017; Higaki et al., 2017; Imoto et al., 2017). However, in most of the studies, CsMPs were collected before they were deposited on the ground such as from aerosol filters (Adachi et al., 2013; Abe et al., 2014) and nonwoven fabric used as ground cover material for vegetable cultivation (Kogure et al., 2016; Yamaguchi et al., 2016), which can be collected more easily than those in soils and sediments. None of these studies focused on CsMPs in suspended particles in river water, which is focused in this study.

Cesium in CsMPs incorporated in SiO$_2$ glass is generally water-insoluble (Adachi et al., 2013). Thus, Cs in CsMPs is independent of the mineral-water distribution of Cs based on adsorption-desorption reactions. When the contribution of $^{137}$Cs in CsMPs is not negligible compared with the total $^{137}$Cs in suspended particles, the apparent $K_d$ value will be higher than the intrinsic $K_d$ value related to the adsorption-desorption reaction of phyllosilicate minerals in suspended particles (Qin et al., 2012; Mukai et al., 2014). Hence, we separated CsMPs from suspended particles in the Kuchibuto River that flows through heavily RCs-contaminated areas in Fukushima, Japan (Yoshida and Takahashi, 2012). The isolation of CsMPs from suspended particles enabled us to estimate the contribution of $^{137}$Cs in CsMPs to the $K_d$ value in the river, which helps to better understand the solid-water distribution of $^{137}$Cs in rivers. This information, in turn, may be important for the discussion of the RCs intake of organisms, which depends on the chemical species of RCs such as dissolved RCs, RCs adsorbed on particulate matter, or RCs in CsMPs.

Aerosol filters collected soon after the accident contained both water-insoluble and -soluble RCs (Tanaka et al., 2013). The former is regarded as CsMPs, while the latter can be water-soluble species such as sulfate aerosols (Kaneyasu et al., 2012). The former can remain in CsMPs for a relatively long time in the environment, that is, several years to several decades, due to its insoluble nature (Yamaguchi et al., 2016; Satou et al., 2018), whereas the latter is involved in the solid-water reaction in soil and aquatic systems. Thus, the type of deposition, that is, as water-insoluble or -soluble RCs, is very important to understanding the migration of RCs in Fukushima. However, there are few data on the ratio of water-insoluble and -soluble RCs in the environment. Note that the latter includes RCs that was strongly adsorbed on phyllosilicate minerals after the deposition in this study. Suspended particles in river water originate from wide areas in the watershed of the river. Thus, it is expected that the RCs fraction in CsMPs in suspended particles represents average RCs fractions in the CsMPs (=water-insoluble) and water-soluble species in the watershed.

Hence, the purpose of this study is to determine the influence of CsMPs on the $K_d$ value in the river by calculating the ratio of $^{137}$Cs in CsMPs to the total $^{137}$Cs in suspended particles, which is also related to initial Cs species (water-soluble or -insoluble) at the time of deposition in March 2011.

**EXPERIMENTAL**

Suspended particles and river water samples (<0.45 μm) were collected from the Kuchibuto River by filtering water (volume: 44–100 L) during 2011–2016 (Fig. 1). Suspended particles were first collected with a 3 μm pore size membrane filter; subsequently, a 0.45 μm pore size membrane filter was used. However, no CsMPs were found in the 0.45–3 μm fraction of the suspended particles. Thus, we collected CsMPs mainly from suspended particles (3–63 μm) collected on the 3 μm pore size membrane filter. After the filters were dried at 60°C for 12 h, they were placed into a plastic container and the total radioactivities of $^{137}$Cs were measured with a high-purity germanium semiconductor detector (HPGe; GX4018, CANBERRA Industries Inc., USA). The radioactivities are decay-corrected values as to 11th March 2011. The RCs in the filtered water samples (20 L) was measured after RCs was preconcentrated in the water samples using ammonium molybdophosphate (Sakaguchi et al., 2012), which was applied to the measurement of RCs using the HPGe. More details about the sampling sites, sampling methods, and radioactivity measurement of the filters and water samples are provided in Sakaguchi et al. (2015). The radioactivity data of suspended particles and water in 2011 and 2012 were taken from Sakaguchi et al. (2015), while those for 2014–2016 were determined in this study.

The distribution of RCs on the filter samples was measured by autoradiography with imaging plates (IP; BAS-MS 2040, Fujifilm Corp., Japan) and an IP reader (FLA-9000, FujiFilm Corp., Japan). The IP was exposed to the filter samples for 20 min. The IP reader quantifies...
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The radiation intensity as photo stimulated luminescence (PSL). Four CsMPs with known $^{137}$Cs amount (0.64 Bq, 1.36 Bq, 1.45 Bq, and 4.6 Bq) were in contact with the IP for 20 minutes to yield PSL values in four areas measured by the IP reader. We calculated the sum of PSL in each spot based on which we determined the relationship between the PSL and $^{137}$Cs radioactivity.

We calculated $^{137}$Cs of each spot on the filter by PSL based on which we could distinguish CsMPs containing more than 0.4 Bq $^{137}$Cs from suspended particles. In our wet separation method, the separation of CsMP was always successful when the CsMPs contained more than 0.4 Bq $^{137}$Cs. Motai et al. (2016) separated soil particles containing $^{137}$Cs from soils in Fukushima and measured the $^{137}$Cs radioactivity in such soil particles. Their results showed that weathered biotite contains ~0.01 Bq $^{137}$Cs and organic matter-bearing particles contain ~0.05 Bq $^{137}$Cs. Thus, we assume that any particles containing more than 0.1 Bq $^{137}$Cs are CsMPs because the radioactivity of 0.1 Bq $^{137}$Cs per one particle is much larger than that of organic matter-bearing particles, which have the highest radioactivity among any soil particles (Motai et al., 2016).

It is possible that CsMPs containing less than 0.1 Bq of $^{137}$Cs are also present, but the distinction between CsMPs, weathered biotite, and organic matter-bearing particles based on the difference in the radioactivity is difficult. Further separation of CsMPs containing less than 0.4 Bq $^{137}$Cs after the identification of smaller CsMPs by autoradiography is also difficult. Thus, the $^{137}$Cs radioactivity in CsMPs containing 0.1 to 0.4 Bq $^{137}$Cs was calculated using PSL without wet separation.

With respect to the identification of CsMPs on the filters, any particles with high radioactivity were found on the filters. A portion (approximately 5 mm x 5 mm) of the filter including the CsMP was cut and placed into a plastic tube with water. The CsMP was separated from the filter to water by ultrasonic agitation. At this point, the CsMP was transferred to the water phase as suspended particulate matter along with many other particles. The water containing the CsMP was divided into two tubes; one of the two exhibited higher $^{137}$Cs radioactivity due to the presence of CsMP, which can be identified with the

Fig. 1. Map of the sampling site (Kuchibuto River Downstream) in the Fukushima area. The inventory map of $^{137}$Cs from MEXT (2011) is cited.

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NaI scintillation counter (Packard Cobra 5003, GMI, USA) in a relatively short time compared with the detection using the HPGe. This separation process using water was adopted assuming that CsMPs are water-insoluble. The separation process was repeated approximately 30 times (Kurihara et al., in preparation). After the final separation, the CsMP with water was loaded on carbon tape and air-dried. More details about this wet separation method are given in Kurihara et al. (in preparation). This method can separate CsMPs more quickly and efficiently than previous methods (Adachi et al., 2013; Yamaguchi et al., 2016). In addition, it is easier to identify CsMPs separated by this method using scanning electron microscope (SEM; S-4500, Hitachi, Japan) because the method does not use any adhesive tapes that can incorporate CsMPs. In other methods, CsMP can be loaded on the carbon tape with many other particles, which makes it relatively difficult to identify CsMP with SEM.

The elemental composition of CsMPs was measured with energy dispersive X-ray spectroscopy (EDS; Sigma, Kevex, USA). Subsequently, the $^{134}$Cs and $^{137}$Cs radioactivities in the CsMPs were measured with the HPGe. Radioactivity standard solutions for $^{134}$Cs (0.182 Bq on 25th November, 2016, Japan Radioisotope Association, CZ-010) and $^{137}$Cs (1.40 Bq on 25th November, 2016, Japan Radioisotope Association, CS-005) on a 1 mm square filter were used. These radioactivity standard solutions were calibrated by the Japan Calibration Service System (JCSS; http://www.nite.go.jp/en/jajapan/jcss/index.html). We calculated the radioactivities of the CsMPs based on the standards.

**RESULTS AND DISCUSSION**

**Separation and characterization of CsMPs in suspended particles**

Filters containing suspended particles in the downstream of the Kuchibuto River (N 37°34′52″, E 140°32′21″) were collected during six sampling campaigns (Table 1). The $^{137}$Cs radioactivity of suspended particles on the filters and filtered waters were measured based on which apparent $K_d$ values were calculated. The data for 2011 and 2012 are from Sakaguchi et al. (2015). More information (sampling date, weight of suspended particles, and volume of filtered water) and the location are shown in Table 1 and Fig. 1, respectively.

To separate CsMPs from suspended particles, we first used autoradiography to find the CsMPs on the filters. The PSL intensity was calibrated to $^{137}$Cs radioactivity using a known amount of $^{137}$Cs in CsMPs (Fig. 2), which enabled us to calculate the radioactivity of $^{137}$Cs in CsMPs by PSL.

Table 1. Information of suspended particles (SPs) (Sakaguchi et al., 2015)

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Date</th>
<th>Suspended particles weight (g)</th>
<th>$^{137}$Cs on filter (Bq/g)</th>
<th>Filtered water volume (L)</th>
<th>$^{137}$Cs in water (mBq/L) ($&lt;0.45 , \mu m$)</th>
<th>Log($K_d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuchibuto River (downstream)</td>
<td>31-Jul-2011</td>
<td>0.855</td>
<td>34.8 ± 1</td>
<td>50</td>
<td>21 ± 1</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td>3-Aug-2012</td>
<td>0.426</td>
<td>18.1 ± 0.8</td>
<td>100</td>
<td>9.4 ± 0.8</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td>3-May-2016</td>
<td>0.920</td>
<td>12.6 ± 0.1</td>
<td>90</td>
<td>7.6 ± 0.2</td>
<td>3.22</td>
</tr>
<tr>
<td>Location</td>
<td>22-Nov-2014</td>
<td>0.0684</td>
<td>16.7 ± 0.3</td>
<td>60</td>
<td>1.2 ± 0.2</td>
<td>4.15</td>
</tr>
<tr>
<td>N</td>
<td>22-Nov-2015</td>
<td>0.139</td>
<td>25.2 ± 1</td>
<td>81</td>
<td>2.7 ± 0.3</td>
<td>3.97</td>
</tr>
<tr>
<td>37°34′52″, 140°32′21″</td>
<td>1-Apr-2016</td>
<td>0.483</td>
<td>2.74 ± 0.1</td>
<td>44</td>
<td>2.1 ± 0.2</td>
<td>3.12</td>
</tr>
</tbody>
</table>

![Fig. 2. Calibration of photo stimulated luminescence (PLS) by $^{137}$Cs radioactivity in CsMPs.](image-url)
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Separate the CsMPs with more than 0.4 Bq $^{137}$Cs using our method. Based on the criteria, we identified four CsMPs from filters collected in six sampling campaigns, which were subsequently separated by the wet separation method. Consequently, one, two, and one CsMPs were separated from the filters collected on 31st July 2011, 3rd May 2014, and 11th Nov. 2015, respectively. This is the first study in which CsMPs transported into river water were successfully discovered. The presence of CsMPs in the river water is consistent with the insoluble nature of CsMPs reported in the literature such as Adachi et al. (2013).

After the separation of the material with high specific radioactivity by the wet separation method, we identified CsMPs by SEM and EDS. The results of SEM (Fig. 3) and EDS (Fig. 4) show that (i) the sizes of the almost spherical particles were 1.3, 1.6, 1.8, and 2.8 μm, and (ii) the chemical composition of these particles containing Si, Cs, Fe, and Zn was similar to that reported for other spherical CsMPs (Adachi et al., 2013; Abe et al., 2014; Kogure et al., 2016; Yamaguchi et al., 2016; Satou et al., 2016; Furuki et al., 2017; Higaki et al., 2017; Imoto et al., 2017). The radioactivities of CsMPs were 0.426 ± 0.008, 0.680 ± 0.011, 1.617 ± 0.012, and 2.827 ± 0.024 Bq. The radioactivity of 0.426 Bq $^{137}$Cs is the lowest radioactivity reported for CsMPs so far. Adachi et al. (2013) reported CsMP containing 0.66 Bq $^{137}$Cs.

The activity ratios of radionuclides at the accident were calculated for Units 1, 2, and 3 of the FDNPP using the information from Nishihara et al. (2012). The activity ratios of $^{134}$Cs/$^{137}$Cs as to 11th March 2011 in the CsMP samples found in this study were 1.084 ± 0.098, 1.096 ± 0.107, 1.085 ± 0.056, and 1.096 ± 0.049, similar to the values calculated for Unit 2 or 3 but higher than that of Unit 1 (Fig. 5). These results show that the CsMPs found in suspended particles in the river originated from Units 2 and/or 3 of the FDNPP.

Satou et al. (2016) reported the relationship between the apparent volume of CsMPs estimated by SEM images and $^{137}$Cs in the CsMPs from Unit 2 or 3 (Fig. 6). Our CsMP data plotted in Fig. 6 are consistent with that of Satou et al. (2016), which suggests that these CsMPs collected from suspended particles in the river were due to the FDNPP accident. Ono et al. (2017) suggested that nonspherical larger CsMPs originate from Unit 1 and deposited relatively closer to the FDNPP. The source of the Kuchibuto River is in the Yamakiya District with high RCs deposition but sufficiently distant from the FDNPP (~40 km); therefore, CsMPs from Unit 1 may not have reached this area. The fact that we could only recover almost spherical and small CsMPs likely reflects that nonspherical and large CsMPs were not deposited in the watershed of the Kuchibuto River.

**Influence of CsMP on the $K_d$ value**

The total radioactivities of the suspended particles on the filters ($= A_{(Total)}$) used for the filtration of the river...
Radioactivities of $^{137}$Cs in separated CsMPs ($=A(\text{CsMPs})$) are shown in Table 2. These values allowed us to calculate the ratio of $^{137}$Cs in separated CsMPs ($=R(\text{CsMPs})$) based on $A(\text{CsMPs})$ and $A(\text{Total})$:

$$R(\text{CsMPs}) (\%) = \frac{A(\text{CsMPs})}{A(\text{Total})} \times 100.$$  

The $R(\text{CsMPs})$ was 1.4%, 30%, and 46% of the total $^{137}$Cs in suspended particles collected on 31st July 2011, 3rd May 2014, and 11th Nov. 2015, respectively (Table 2). The $R(\text{CsMPs})$ was 0% on other days because the CsMPs were not separated. Radiocesium-bearing microparticles with low radioactivity are often too small to be found with SEM. However, it is possible that smaller CsMPs with lower radioactivities contribute to the increase of $R(\text{CsMPs})$. Thus, particles containing 0.1 to 0.4 Bq $^{137}$Cs were identified based on the autoradiography analysis, but they are not separated by the wet separation method as shown in Section “Experimental”. As discussed in Section “Experimental”, the particles with more than 0.1 Bq $^{137}$Cs are considered to be CsMPs because the radioactivities of the soil particles are less than 0.05 Bq (Motai et al., 2016). The $^{137}$Cs radioactivities in the unseparated smaller CsMPs ($=a(\text{CsMPs})$) were calculated by PSL. The ratio of $^{137}$Cs in separated and unseparated CsMPs to the total $^{137}$Cs in suspended particles ($=r(\text{CsMPs})$) was calculated based on $a(\text{CsMPs})$, $A(\text{CsMPs})$, and $A(\text{Total})$ (Table 3):

$$r(\text{CsMPs}) (\%) = \left[ \frac{a(\text{CsMPs}) + A(\text{CsMPs})}{A(\text{Total})} \right] \times 100.$$  

The $r(\text{CsMPs})$ was 15%, 1.3%, 36%, 67%, 66%, and 36% of the total $^{137}$Cs in suspended particles collected on 31st July 2011, 3rd Aug. 2012, 3rd May 2014, 22nd Nov. 2014, 22nd Nov. 2015, and 1st Apr. 2016, respectively (Table 3). The number of CsMPs in each $^{137}$Cs radioactivity range is shown in Fig. 7. Seventeen CsMPs were found on the filter on 31st July 2011 (Table 3). Figure 7 suggests the presence of CsMPs containing less than 0.1 Bq $^{137}$Cs; however, the distinction between CsMPs, weathered biotite, and organic matter particles based on the different radioactivity is difficult. It is most likely that $^{137}$Cs in CsMPs cannot be readily
leached by water due to its insoluble nature (Adachi et al., 2013), which is independent of the solid-water adsorption-desorption reaction of Cs in river water quantified using the $K_d$ value. The adsorption-desorption reaction of $^{137}$Cs in river and estuary areas has been discussed in various studies in Fukushima based on the $^{137}$Cs radioactivity in water and solid phases separated by filtration or sedimentation (Sakaguchi et al., 2015; Kakehi et al., 2016). If the $K_d$ values are calculated applying radioactivities of these filters including CsMPs as $^{137}$Cs in the solid phase, the $K_d$ values will be overestimated. If the effect of the CsMPs on the $K_d$ is large, this factor should be corrected when the adsorption-desorption reaction is discussed based on $K_d$ value. According to Konoplev et al. (2016), the $K_d$ values in rivers in Fukushima are 1–2 orders of magnitude higher than those in Chernobyl, partly because the CsMPs are present in the solid phase in Fukushima. However, our results show that at most 67% of $^{137}$Cs were from CsMPs, which increases the log$K_d$ value by only 0.49 (Fig. 8), showing that the higher $K_d$ values in Fukushima compared with Chernobyl cannot be explained with the presence of CsMPs only. Konoplev et al. (2016) also suggested that soils in Fukushima have a higher Radiocesium Interception Potential (RIP; Cremers et al., 1988; Wauters et al., 1996; Bradbury and Baeyens, 2000; Fan et al., 2014; Uematsu et al., 2015) than in Chernobyl, possibly due to the different mineral composition of suspended particles in the two areas. In addition, the presence of high concentrations of organic matter (>10 mgC/L) in Chernobyl (Pripyat River) inhibits a strong association of RCs with phyllosilicate minerals, which is not the case in Fukushima (Takahashi et al., 2017). Thus, factors such as mineralogy and organic matter content are mainly responsible for the higher $K_d$ value in Fukushima relative to Chernobyl, even when taking the presence of CsMPs in Fukushima into account.

If an equilibrium of the adsorption-desorption reaction between water and phyllosilicate minerals in the river is established, $K_d$ values will be constant. However, we often observe a large variation of $K_d$ values over a period of time at the same site in the Kuchibuto River. Figure 8 shows the large variation in apparent $K_d$ values among
Table 3. Information of radiocesium-bearing microparticles (CsMPs) with $^{137}\text{Cs}$ above 0.1 Bq including smaller particles that cannot be separated

<table>
<thead>
<tr>
<th>Date</th>
<th>$^{137}\text{Cs}$ in CsMPs (Bq)</th>
<th>The number of CsMPs (Bq)</th>
<th>$^{137}\text{Cs}$ on filter (%)</th>
<th>Log$_{10}[(K_d/Lg^{1/10})]$ without CsMPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>31-Jul-2011</td>
<td>4.32</td>
<td>17</td>
<td>14.5</td>
<td>3.15</td>
</tr>
<tr>
<td>3-Aug-2012</td>
<td>0.11</td>
<td>1</td>
<td>1.30</td>
<td>3.28</td>
</tr>
<tr>
<td>3-May-2014</td>
<td>4.12</td>
<td>6</td>
<td>35.5</td>
<td>3.03</td>
</tr>
<tr>
<td>22-Nov-2014</td>
<td>0.77</td>
<td>4</td>
<td>67.4</td>
<td>3.66</td>
</tr>
<tr>
<td>22-Nov-2015</td>
<td>2.33</td>
<td>5</td>
<td>66.1</td>
<td>3.50</td>
</tr>
<tr>
<td>1-Apr-2016</td>
<td>0.48</td>
<td>3</td>
<td>36.3</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Implications for the contribution of RCs in CsMPs to the total RCs

Finally, it is suggested that r(CsMPs) reflects the water-insoluble fraction of RCs because CsMPs were deposited over a wide area in the watershed of the river. The fact that the r(CsMPs) is 14.5% and 1.30% in 2011 and 2012, respectively, indicates that the main RCs emitted from FDNPP must have been water-soluble in the watershed of the Kuchibuto River. It initially was subject to dissolution in water and subsequently to adsorption reactions to minerals, in particular phyllosilicate minerals in the surface environment of the area (Qin et al., 2012; Mukai et al., 2014). These results are consistent with several previous studies: (i) more than 50% of RCs in aerosols collected during the FDNPP accident were water soluble (Tanaka et al., 2013) and (ii) the main Cs species in soil and river systems is Cs adsorbed on phyllosilicate minerals (Qin et al., 2012; Mukai et al., 2014).

The ratio of $^{137}\text{Cs}$ in CsMPs to total $^{137}\text{Cs}$ in the river water has increased in 2014–2016 compared with that in 2011–2012. It is known that the radioactivity of RCs in the Kuchibuto River has decreased with time after the accident (Sakaguchi et al., 2015). The rate of the decline of total $^{137}\text{Cs}$, including both dissolved and particulate phases, has been interpreted by two or three exponential terms (Smith et al., 2004; Smith and Beresford, 2005),
where the second and third terms are related to (i) its fixation in soil and redistribution process and (ii) long-term equilibrium condition. The first term reflecting fast decline is related to the rapid wash-off process from the soil surface to river water, mainly due to the flushing of soluble RCs. A similar temporal variation has been observed in soil water (Iwagami et al., 2017) and the Kuchibuto River (Nuclear Regulation Authority, 2015) in the Fukushima area; a contribution of the first term showing rapid decrease has been observed during 2011 to 2012. On the other hand, the ratio of $^{137}$Cs to CsMPs to total $^{137}$Cs in CsMPs to total $^{137}$Cs in the river water has increased with the increase of the elapsed time, which is possibly related to the rapid decrease of the wash-off fraction in the river. Thus, we suggest that the $r$(CsMPs) was smaller in 2011 and 2012 but increased during 2014–2016. Based on these results, it is possible that the CsMPs fraction of $^{137}$Cs in various rivers will increase in future. The fraction should be continuously measured in future to understand the dependence of $r$(CsMP) on the area and the elapsed time and its influence on $K_d$.

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