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Authors	Manabu Fujii, Keisuke Oono, Chihiro Yoshimura, Manami Miyamoto
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1 Title

2	The Role of Autochthonous Organic Matter in Radioactive Cesium
3	Accumulation to Riverine Fine Sediments
4	
5	Manabu Fujii ^{†,*} , Keisuke Ono [†] , Chihiro Yoshimura [†] , Manami Miyamoto [†]
6	
7	
8	† Department of Civil and Environmental Engineering, Tokyo Institute of Technology, 2-12-1-M1-4
9	Ookayama, Tokyo 152-8552, Japan
10	
11	
12	
13	* Corresponding author: <u>fujii.m.ah@m.titech.ac.jp</u>
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16 Abstract

Anthropogenically released radioactive cesium (RCs) poses serious ecological and 17 18 environmental concerns given its persistency in the environment. Although accumulation of RCs in aqueous and sedimentary environments is often reported to associate with organic matter (OM), the 19 mechanisms responsible remain unclear. Here, we investigated RCs in fine sediments along the 20 21 Abukuma River, the largest river near the Fukushima Daiichi Nuclear Power Plant, 1.5 to 4 years after 22 the accident. Measuring the density-separated sediment fractions with a broad range of OM content (%) indicated that the RCs concentration $(Bq kg^{-1})$ is positively correlated with OM content for 23 24 intermediate-density fractions in which OM is primarily characterized by autochthonous origin. This 25 relationship, however, did not hold for light-density fractions containing a high proportion of large-26 size allochthonous OM. Furthermore, H₂O₂-assisted OM digestion and amorphous material dissolution 27 treatments resulted in only a minor reduction in sedimentary RCs. These results along with the fact that sediments with high autochthonous OM content showed high specific surface area indicated that 28 29 RCs is tightly associated with finer-grained and chemically non-labile inorganic fractions concurrently 30 resident with autochthonous OM. Overall, our findings highlight that autochthonous OM exerts a 31 significant control on the accumulation, transport, and fate of RCs in aqueous and sedimentary 32 environments.

33

34

1. Introduction

36	The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident on March 11, 2011 resulted
37	in the tremendous release of a range of radionuclides, including 137-Cs, 134-Cs, 131-I, and 90-Sr into
38	the environment(Kinoshita et al. 2011, Kusakabe et al. 2013, Steinhauser et al. 2013, Yasunari et al.
39	2011). The leakage of radioactive cesium (RCs; 137-Cs and 134-Cs) was estimated to be on the order
40	of 10 ¹⁶ Bq(Nuclear Emergency Response Headquarters Government of Japan 2011). The long half-life
41	(~30 years for 137-Cs) and persistence of RCs in a range of aqueous and soil environments indicates
42	that contamination poses serious ecological, environmental, and social problems(Mizuno and Kubo
43	2013, Murakami et al. 2014, Nakai et al. 2015).
44	RCs has a high affinity for clay minerals, and thus the majority of RCs deposited on the
45	terrestrial surface environment in Fukushima Prefecture was retained in the upper layer of soil, within
46	a depth of ~5 cm for paddy field sites(Lepage et al. 2015, Matsuda et al. 2015) and in the surface litter
47	layer for forest soil(Koarashi et al. 2012). While a large portion of deposited RCs in the catchment
48	around FDNPP remains in the terrestrial environment (e.g., 1.6% wash-off in the Kuchibuto River
49	watershed by the end of 2014)(Wei et al. 2017b), terrestrial RCs has been gradually transported to
50	reservoirs, rivers, and environments further downstream(Wei et al. 2017a, Yamaguchi et al. 2012,
51	Yamashiki et al. 2014, Yoshimura et al. 2014). In freshwater affected by the FDNPP accident,
52	particulate RCs, such as that associated with fine suspended particles, was dominant in riverine RCs
53	transport according to field surveys performed several years after the accident(Nagao et al. 2013,

54	Sakaguchi et al. 2015, Tanaka et al. 2015, Yamashiki et al. 2014, Yoshimura et al. 2014), though
55	dissolved RCs has been also detected. In the river waters of the Abukuma River basin, for example,
56	dissolved RCs (<0.45 μ m, almost exclusively Cs ⁺) accounted for 1.2–49% of the total RCs with a
57	spatiotemporal average of 20% from June 2011 to December 2012(Sakaguchi et al. 2015).
58	After the global fallout due to the Chernobyl accident and nuclear weapons tests, a number of
59	studies on the environmental mobility, bioavailability, and fate of RCs, including adsorption and
60	fixation to clay minerals, have been published. Laboratory-based studies of the interaction of Cs with
61	clay minerals generally suggested that Cs is fixed in specific interlayers of minerals and in layer edge
62	sites, including frayed edge sites, and that it is also retained non-specifically on the surface of planar
63	sites(Bostick et al. 2002, Cornell 1993, Kim et al. 1996a, Kim et al. 1996b, Sawhney 1966). In
64	particular, Cs adsorption to micaceous minerals, such as illite(Comans et al. 1991, Comans and
65	Hockley 1992, Kim et al. 2007) and vermiculite(Bostick et al. 2002, Fan et al. 2014, Kogure et al.
66	2012), is highly selective, as dehydrated Cs ion is structurally fixed in the interlayers, with some studies
67	suggesting that this fixation reaction may be almost irreversible under specific conditions(Comans et
68	al. 1991, Mukai et al. 2016). Regarding the FDNPP-derived RCs, Mukai and co-workers found that
69	RCs were selectively and uniformly retained on porous weathered biotite (partially vermiculitized
70	biotite) in litter soil(Mukai et al. 2014).

While clay minerals are considered important carriers for RCs in natural aqueous systems,
 there are accumulated evidence that RCs concentrations in coastal marine (offshore region of FDNPP)

73	and Wuljin Nuclear Power Plant, Korea) and river sediments (six coastal river catchments close to
74	FDNPP) are positively related to organic matter (OM) content(Ambe et al. 2014, Kim et al. 2007,
75	Naulier et al. 2017, Ono et al. 2015). Since alkali metals, including Cs, negligibly form complexes
76	with OM due to the lack of coordination of these metal classes with acidic functional groups, the direct
77	association of RCs with metal binding sites in sedimentary OM is unlikely. Rather, the higher
78	accumulation of RCs in the OM-rich sediment may be related to the grain size and surface area of
79	sediment particles, mineral composition, or combinations of these factors (Ambe et al. 2014, Kim et
80	al. 2007), given that organic and mineral interactions in sediment have been elaborated by the OM-
81	mediated cross-linkage of fine particles(Bock and Mayer 2000) in addition to patch-type coverage of
82	OM primarily at the edge sites of minerals(Mayer 1999). Previous studies indicated the high
83	accumulation of RCs in the smaller size fractions of soil and suspended sediments(Ambe et al. 2014,
84	He and Walling 1996, Sakaguchi et al. 2015, Tanaka et al. 2015). In addition, organic carbon
85	concentrations in riverine and marine sediments are highly correlated with the unit mass-normalized
86	surface area of sediment determined by gas adsorption(Bergamaschi et al. 1997, Hedges and Keil 1995,
87	Keil et al. 1997).

However, the mechanisms behind the RCs accumulation in OM-rich particles remain unclear. Understanding the association of RCs with OM is of importance, given that presence of OM affects to the mobility and bioavailability of RCs in aqueous and sedimentary environments (e.g., Staunton et al., 2002). Since autochthonous OM is a major energy source for freshwater organisms such as grazing

92	fish, sedimentary RCs associated with autochthonous OM can be highly bioavailable and exhibit
93	dynamic behavior in freshwater environments and ecosystems (Fukushima and Arai 2014). In this
94	study, therefore, we investigated the interaction of FDNPP-derived RCs and riverine sediment with
95	particular attention given to the characterization of sedimentary OM including whether it is
96	allochthonous or autochthonous. Suspended and deposited fine sediments <2 mm in size were
97	collected at several sampling stations along the main stream of the largest river near the FDNPP, the
98	Abukuma River (Figure S1 in Supplementary Material SM 4), during summer and winter from 2012
99	to 2015. The dried sediment samples were then subjected to various physicochemical treatments (e.g.,
100	density-based separation, H2O2 treatment for OM digestion) and subsequent sediment property
101	analyses to examine the relationships among the RCs concentration, OM content, and other sediment
102	properties (e.g., specific surface area). In particular, the characteristics of density-fractionated
103	sediments with different degrees of OM proportions were extensively examined. Nitrogen-to-carbon
104	ratio (N/C ratio) analyses of the sediment samples and end-member samples from the Abukuma River
105	basin (e.g., terrestrial plants, soil OM and riverine algae) were used to identify the source of
106	sedimentary OM. Figure S2 shows an overview of this study, including sample collection, treatment
107	and analyses.

2. Materials and Methods

Detailed information on the general procedure, H₂O₂ treatment, sample analyses, statistical

analyses and fundamental water quality measurement is available in Supplementary Material (SM
1).

113

114 **2.1 Sample collection**

115	The Abukuma River has a basin area of approximately 5,400 km ² , a total main stream channel
116	length of ~240 km, and a flow rate of 117 m ³ ·s ⁻¹ (averaged over 1966–2009 at Tateyama observation
117	station). The river originates in Asahidake Mountain in the south of Fukushima Prefecture, passes
118	through Fukushima City which is approximately 60 km northwest of FDNPP and finally flows into the
119	Pacific Ocean in Watari City, Miyagi Prefecture.
120	Deposited fine sediments were collected at several sites in the main stream channel of
121	Abukuma River (St. 1 Watari, St. 2 Marumori, St. 3 Yahata, St. 4 Fukushima, St. 5 Nihonmatsu, and
122	St. 6 Akutsu; Figure S1). Samples were taken during stable water discharge periods in the summer
123	(July, 2012 and June 2015) and winter (January, 2013) 1.5 to 4 years after the accident. The lentic area
124	near the river bank (water depth of <20 cm) was selected as the main sampling site for deposited
125	sediment. In St. 4 Fukushima, deposited sediments were also collected from the river bank in the flood
126	plain. During sampling, sediments were carefully collected from the surface layer (layer depth of less
127	than 2-3 cm) in a 100 mL polystyrene container by using a plastic scoop and a gloved hand. The
128	sediment surface layer in the lentic areas was mostly composed of finer particles (<2 mm) compared

129 with those present in the bottom of lotic area. Indeed, the river bed in the lotic area of most sampling

130	sites consisted of large particles, including gravel and stones, and fine particles were neither observed
131	on the surface of river bed by visual inspection from river bank nor collected sufficiently with the
132	Ekman-Birge grab sediment sampler.

During the sample collection, water samples (40-100 L) were also collected in a 133 polypropylene container from either the river bank or top of a bridge by using plastic pump (Tempest 134135 DTW 60ft, Proactive). To investigate the origins of OM in the Abukuma River sediments, end-member samples, such as terrestrial soil, terrestrial plants, and riverine algae, were also collected along the 136 Abukuma River basin in December 2014 and June 2015 (in the vicinity of the sediment sampling 137 138 stations. The collected sediment, water, and end-member samples were transported to the experimental 139 laboratory immediately after the completion of the field survey. While the end-member and sediment 140 samples were collected from different multiple years, temporal trends of sample data were 141 indiscernible among the deposited and suspended sediments as well as the end-member samples, at 142 least, for a few years' data set investigated in this study, as discussed below.

143

144 **2.2 Pretreatment of sediment samples**

145 Sediment samples were pretreated according to the standard protocol for clay mineralogical 146 analyses(The Clay Science Society of Japan 2009). The deposited sediments were air-dried on a 147 ceramic plate at room temperature (25°C) for several days. The dried samples were then gently 148 homogenized with a mortar to break up the physically aggregated particles. The fine sediment particles

149	with size less than 2 mm were collected by a fractionation using 2 mm-pore size sieve. The
150	homogenization and sieving were repeated when small aggregates were still visible. Suspended
151	sediment samples were collected by vacuum filtration of the collected river water with 1 μm
152	hydrophilic polytetrafluoroethylene (PTFE) membrane filter (47 mm, Millipore, Japan). The dried
153	suspended sediments were finally obtained by resuspending the sediments on the filter in ultrapure
154	Milli-Q water (MQ; Millipore; 18.2 MΩ·cm resistivity at 25°C) and lyophilizing the suspension with
155	a vacuum freeze dryer (FDU-1200, EYELA, Japan) overnight. The deposited and suspended sediment
156	samples were stored in a desiccator in the dark condition when not in use.

158 **2.3 Density separation**

159 The density fractionation of sediment particles was performed based on the method used by 160 Arnarson and Keil(Arnarson and Keil 2001) with some modifications. Sodium polytungstate (SPT; Na₆[H₂W₁₂O₄₀], TC-Tungsten Compounds, Germany) was used as a heavy liquid. A solution of SPT 161 with a density of 2.8 g·cm⁻³ in MQ water was prepared, and dried sediments were added at a sediment 162 dry weight-to-solution volume (SDW/SV) ratio of 0.5 g·mL⁻¹. The sediment suspensions were 163 sonicated in a polypropylene container for 10 min followed by subsequent gentle agitation using a 164 shaker for 10 min to disperse aggregated particles loosely bound by cross-linkage via OM(Arnarson 165 and Keil 2001, Golchin et al. 1994). The suspension was then centrifuged for 20 min at 2,000 g at 166 room temperature. The heavier fraction pellet was resuspended in 2.8 g·cm⁻³ SPT, agitated and 167

168 centrifuged three times until no lighter particles were found to be suspended by visual inspection. At each step, supernatant containing the lighter fraction was carefully collected by pipette and stored for 169 the next separation treatment. To remove SPT, the pellet (density of $> 2.8 \text{ g} \cdot \text{cm}^{-3}$) was washed by 170 resuspending in MQ and centrifuging three times. After decanting, the pellet was lyophilized by the 171 vacuum freeze dryer and stored in a desiccator. 172 The supernatant in 2.8 g·cm⁻³ SPT was further diluted by adding MQ to adjust the SPT 173 solution density to 2.6 g·cm⁻³. By repeating the aforementioned processes, 2.6–2.8 and <2.6 g·cm⁻³ 174 sediment fractions were collected as a pellet and supernatant, respectively, after centrifugation. These 175 processes were repeated for the 2.4, 2.2, 2.0, 1.8 and 1.6 g·cm⁻³ SPT solutions to obtain sediments with 176 different densities. The lowest density (>1.6 $g \cdot cm^{-3}$) sediment fraction was collected by filtering the 177 supernatant in 1.6 g·cm⁻³ SPT with a 1 µm PTFE membrane filter, followed by washing, resuspension 178 179 in MQ and lyophilization. 180

181 **2.4 Hydrogen peroxide treatment**

Sediments were treated with H_2O_2 to remove the OM fraction (The Clay Science Society of Japan 2009). The dried sample was added to 8.6% H_2O_2 solution (Kanto Chemical, Japan) at a SDW/SV ratio of 0.14 g·mL⁻¹ and initially heated at 60 °C for 10 min. After bubbling ceased, the solution was heated for 1 h at 80 °C, at which disproportionation of H_2O_2 is promoted, to remove the remaining H_2O_2 . To minimize the readsorption of extracted RCs on the sediment particles, SCs (cesium

194	Supplementary Material SM 1.10 for details).
193	at 60 °C to examine the relationship between RCs removal with the degree of OM digestion (see
192	of dissociated RCs. H ₂ O ₂ treatment was conducted at different H ₂ O ₂ concentrations and digestion times
191	the sediments were calculated to be occupied and SCs adsorption was expected to prevent readsorption
190	Supplementary Material SM 2 for details). In this case, almost all (>99%) the Cs adsorption sites in
189	was greater than the Cs adsorption capacity for the selected samples (e.g., 0.38–1.2 μ mol \cdot g ⁻¹ ; see
188	of ~200 μ M. The ratio of SCs relative to SDW (SCs/SDW) was adjusted to 1.8–2.5 μ mol·g ⁻¹ , which
187	chloride, 133-Cs, Kanto Chemical) was added to the H ₂ O ₂ -sediment mixture at a final concentration

196 **2.5 Other chemical treatments**

197 Some deposited sediments were treated with the dithionite-citrate, acid ammonium oxalate, 198 and acid hydroxylamine methods to remove amorphous inorganic particles(Carter and Gregorich 199 2007). These treatments dissolve non-crystalline aluminosilicates, Fe oxides, and organically complexed metals, including Al, Fe, and Mn, via ligand- and reduction-promoted processes, although 200 the methods are much less effective in removing crystalline Al. The treatments were conducted by 201 using the standard protocol described elsewhere(Carter and Gregorich 2007), except that excess SCs 202 was amended in this study to the sample solution to prevent readsorption of dissociated RCs 203 (SCs/SDW of ~2.0 μ mol·g⁻¹ and SDW/SV of 0.14 g·mL⁻¹). 204

205

The dried sediments were treated at a SDW/SV ratio of ~0.75 g·mL⁻¹ with 1 M HCl (Kanto

206	Chemical), I M HNO ₃ (Kanto Chemical), I M NaOH (Kanto Chemical), I M ammonium acetate
207	(Kanto Chemical), and MQ water. Again, in all cases, the solution was amended with SCs at final
208	concentrations of ~200 μ M, corresponding to SCs/SDW of 1.6–2.1 μ mol \cdot g ⁻¹ . Sediment suspensions
209	were then incubated for an hour at 25 °C under gentle agitation. After centrifuging and decanting the
210	supernatant, the pellets were washed three times by resuspending in MQ and centrifuging. The washing
211	process was repeated for three times followed by the freeze drying.

213 **2.6 Sample analysis**

214 A full description of the sample analyses is provided in the Supplementary Material (SM 1). Briefly, the radioactivity concentrations ($Bq \cdot g^{-1}$) of 134-Cs and 137-Cs in the treated and untreated 215 216 dried sediments were determined by 604 and 661 keV gamma-rays using a germanium semiconductor 217 detector (SEGEMS GEM20-70, Seiko EG&G Co., Ltd., Japan). The decay of the activity was 218 corrected to the date of accident (March 14, 2011). Organic C and N contents and N/C ratio were measured by an elemental analyzer (Flash EA ConFlo III, Thermo Electron Corporation, USA) 219 220 equipped with an isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher Scientific, USA). Specific surface area of sediment was determined by the N₂ gas adsorption method using the automatic 221 222 surface area and porosimetry analyzer (TriStar II 3020, Micrometritics, USA). Prior to analyzing the 223 specific surface area, the H₂O₂-treated samples were heated at 350 °C for 5 h and evacuated with a 224 vacprep degasser (VacPrep 061LB, Micromeritics) to remove pre-adsorbed gases and water vapor from

the sample. Sediment particle size was determined by laser diffraction and scattering at 690 nm (SALD
3000S, Shimadzu, Japan). X-ray diffraction analysis of an oriented specimen was performed with an
X-ray diffractometer (X'pert-MPD-OEC, Philips). Microscope images of the sediment samples were
obtained by SEM (VE-9800, Keyence, Japan) and optical microscopy (TC5000, Meiji Techno, Japan).

230 **3. Results and Discussion**

231 **3.1 RCs concentrations in deposited and suspended sediments**

232 Concentrations of RCs (defined as the sum of radioactivity for 134-Cs and 137-Cs [Bq] per unit mass of dried sediment [kg]) ranged from 659 to 31,274 Bq·kg⁻¹ in air-dried or lyophilized samples 233 of deposited and suspended sediments (Table S1 and Figure S3). The average ratio of 134-Cs/137-Cs 234 235 was determined to be 0.99 for all the samples examined in this study (n = 87), consistent with the ratio 236 emitted from the FDNPP(Buesseler et al. 2011). The RCs concentrations of suspended sediment (8282–31,274 Bq·kg⁻¹, average of 16,834 Bq·kg⁻¹) were statistically greater than those for deposited 237 sediment (659–10,843 Bq·kg⁻¹, average of 4891 Bq·kg⁻¹) according to a single-tailed heteroscedastic 238 *t*-test ($p < 9.5 \times 10^{-5}$, n = 9-11) (Figure S3). For the sample set of suspended sediment, the RCs 239 concentration in winter 2013 (16,397-31,274 Bq·kg⁻¹, average of 20,500 Bq·kg⁻¹) was higher than 240 those collected in summer 2012 (8282–14,705 Bq·kg⁻¹, average of 12,253 Bq·kg⁻¹, p < 0.029, n = 4– 241 5), though these winter and summer samples were taken in different years. Spatial and seasonal trends 242 in RCs concentration were statistically indiscernible when deposited and suspended sediments were 243

244	pooled, even though the RCs deposition in the terrestrial environment varies substantially in the
245	Abukuma River catchment (Figure S1). Such a spatiotemporal variation in sedimentary RCs in rivers
246	may be reasonable, given that riverine sediments are a mixture of particles from a range of terrestrial
247	and aqueous sources in the catchment(Sakaguchi et al. 2015). Nonetheless, long-term monitoring with
248	higher sampling frequency would be important to understand the spatiotemporal mobility of RCs in
249	the riverine sediments and other aqueous environments in the catchment.
250	As a preliminary test to extract the factors relevant to sedimentary RCs concentration, a simple
251	correlation analysis was performed on RCs concentration and sediment properties, including organic
252	C and N content (%, defined as the mass of C or N per unit mass of dried sediment), N/C ratio, specific
253	surface area (m ² ·g ⁻¹), and sediment particle size (μ m). The Pearson's (<i>R</i>) correlation coefficients were
254	determined for all samples in addition to the subset of samples collected in 2012, 2013, and 2015
255	(Table S1). Statistically significant correlations were observed for some parameters associated with
256	OM except for the sample set for 2015. For example, C and N contents showed the highest positive
257	correlations with RCs concentration ($p < 0.01$, R and $\rho 0.69-0.72$ for all samples, Figures 1a and 1b),
258	and suspended sediment had higher C and N contents compared with deposited sediment. In addition,
259	specific surface area determined by the N2 adsorption BET method showed a significant correlation
260	with RCs concentration (Figure 1c). In addition, the specific surface area had a positive correlation
261	with organic C content (Figure 1d). In contrast to the specific surface area, neither sediment size nor
262	surface area determined by the laser diffraction/scattering method had a significant correlation with

263 sedimentary RCs concentration (Figures 1e and 1f).

264

265 **3.2 RCs distribution in density-separated sediments**

Sediment fractions with a wide spectrum of OM contents (0.15-24%, Table S2) were 266 obtained by separating deposited sediment samples collected at three sampling stations (St. 1 Watari, 267 268 St. 2 Marumori, and St. 4 Fukushima) into eight fractions with the density-based method. Hereafter, sample fractions with densities of >2.4, 1.8–2.4, and <1.8 g \cdot cm⁻³ are referred to as heavy, intermediate, 269 and light fractions, respectively. The organic C measurement undoubtedly indicated gradual increase 270 in OM content with decreasing sediment density (Table S2). The scanning electron microscopy (SEM) 271 272 images demonstrated a gradient in the fractionated sediment morphology from crystalline particles for 273 heavy fractions to amorphous aggregate for light fractions (Figure S4). The X-ray diffraction (XRD) 274 analysis were consistent with the SEM observations. Distinct peaks corresponding to the crystalline 275 structure of clay minerals, such as mica and amphibole that appear in the lower angle region ($<10^{\circ}$), were found for the heavy fractions, whereas such peaks became indiscernible for the intermediate and 276 light fractions (Figure S5). The peaks associated with quartz also decreased with decreasing density 277278 and only a few small peaks were seen for the light fractions, indicating the dominance of the amorphous 279 structure in the light fractions.

For the deposited sediments, the RCs concentrations in the light and intermediate fractions (1527–19,288 Bq·kg⁻¹, n = 24) were greater than those in the heavy fractions (148–8150 Bq·kg⁻¹, n = 24)

8) at a statistically significant level ($p < 2.4 \times 10^{-3}$ according to a single-tailed heteroscedastic *t*-test) 282 (Figure S6a). The deposited sediments from St. 1 Watari in 2012 and St. 4 Fukushima in 2015 had the 283 highest RCs concentrations in the lowest density fraction (<1.6 g·cm⁻³, 17,123–19,288 Bq·kg⁻¹), 284whereas the highest RCs concentrations were found in fractions with densities of 1.6-1.8 g·cm⁻³ 285 (14,356 Bq·kg⁻¹) and 2.0–2.2 g·cm⁻³ (12,105 Bq·kg⁻¹) for the sediments from St. 2 Marumori and St. 286 287 4 Fukushima in 2013, respectively. The RCs concentrations for the light fraction were larger than those for the parent unseparated sediment samples. For the suspended sediments, the highest RCs 288 concentrations were also observed in the light and intermediate fractions (<2.4 $g \cdot cm^{-3}$) for the all 289 290 sampling stations examined (Figure S7a). In contrast to the RCs concentrations, the proportion of RCs 291 activity in each fraction (%, defined as the ratio of RCs activity for each fraction [Bq] relative to the 292 sum of RCs activity for all fractions [Bq]) was always highest in the intermediate fractions because the majority of sediment weight was accounted for by the density fractions of 1.8-2.4 g·cm⁻³ (Figures 293 S6b, S6c, S7b and S7c). 294

For the density-separated sediment, the RCs concentration was positively correlated with organic C content (Figure 2), consistent with the results for the unseparated sediments. In particular, heavy and intermediate fractions with a C content less than 6% showed a linear relationship (R=0.90, $p=1.6 \times 10^{-9}$, n=24, Figure 2a). In contrast, for the light fractions with a high organic C content (>7%), the RCs concentrations were relatively constant or even dropped as the organic C content increased. Thus, correlation between RCs and organic C contents became relatively week when all data were

pooled (i.e., R=0.61, p=2.0 x 10⁻⁴, n=32). Likewise, RCs concentrations for suspended sediment 301 302 substantially fluctuated at higher organic C contents (R=0.61, p=0.10, n=8, Figure 2b). Visual 303 inspection with an optical microscope indicated that the lightest fraction with lower RCs concentrations (i.e., outlier data) contained relatively large amount of large-size terrestrial OM, such 304 as wood debris and leaves, in contrast to the heavy and intermediate fractions which mainly contained 305 306 fine particles (Figures 3 and S8). This microscopic observation invokes the notion that lower RCs concentrations arose from the smaller surface area. Indeed, the positive correlations were also found 307 308 for RCs versus specific surface area as well as organic C content versus specific surface area for the density-separated samples (Figures 2c and 2d). The former plot demonstrated positive linear 309 310 relationship with no outlier data for the samples examined, which is further discussed in detail as noted 311 below.

312

313 **3.3 Source of sedimentary OM**

The N/C ratio was analyzed to investigate the source of OM present in sediment samples. The parameters were compared with those for the end-member samples collected along the Abukuma River basin (e.g., terrestrial plants, soil OM, and riverine microalgae [periphyton]; **Table S3**). The endmember samples were selected according to the land use coverage in the Abukuma River catchment (**Figure S1**).

319

The N/C ratios for the riverine and terrestrial OM showed distinct variation (p < 0.05; Tukey's

320	test; Figure 4). For example, N/C for riverine algae (0.10–0.14) was higher than for terrestrial plants
321	and soil OM (0.01–0.09), which consist of OM with low N/C ratios such as lignin and cellulose(Sato
322	et al. 2006). The ranges for these end-members samples were consistent with previous reports for
323	terrestrial C ₃ higher plants (less than ~0.05)(Hedges et al. 1986) and phytoplankton (0.09–0.2)(Finkel
324	et al. 2010). The N/C ratios for unseparated suspended and deposited sediments (0.09-0.14) were
325	comparable to those for riverine algae. Although some of the deposited sediments showed lower N/C
326	ratios (0.07-0.14) than those for the suspended sediments, the N/C ratios for deposited sediments were
327	still statistically higher than those for the terrestrial plants and soil OM ($p < 0.05$; Tukey's test).
328	In the density-separated samples, N/C ratios for the heavy and intermediate fractions (0.07-
329	0.13) were comparable to suspended sediment and riverine algae. In contrast, light fractions showed
330	lower N/C ratios (0.04–0.09), which were similar to the N/C ratios for terrestrially derived soil OM
331	(0.04–0.09). It should be noted that terrestrial plant has a relatively lower N/C ratio due to the presence
332	of carbon rich components such as lignin and cellulose (Hedges et al. 1986). these results suggested
333	that OM present in the light density fractions is mainly accounted for by allochthonous OM (i.e.,
334	terrestrial origin), whereas the intermediate fractions likely contained autochthonous OM at relatively
335	higher proportion.

3.4 Effects of chemical treatments on radioactive Cs removal 337

338

To examine the role of OM in RCs accumulation, the unseparated deposited sediment samples

339	were further subjected to a range of chemical treatments. The H ₂ O ₂ treatment removed substantial
340	portion of sedimentary OM (e.g., 60–86% and 65–77% of organic C and N, respectively) (Figure S9).
341	Consistently, the SEM images demonstrated the removal of amorphous aggregates after the H ₂ O ₂
342	treatment (Figure S4). In contrast to OM removal, the residual rates of RCs, defined as the ratio of
343	residual RCs concentration after treatment to initial RCs concentration, were greater than 0.60 with an
344	average \pm standard deviation of 1.0 ± 0.20 for the samples examined ($n = 12$, Figure S9 and Table
345	S4). This result indicated that RCs concentrations were stable against to H ₂ O ₂ -assisted OM digestion.
346	We speculated that a significant amount of RCs had been released into the water column
347	during the H ₂ O ₂ digestion: yet, most of the RCs was detected in the particulate fraction owing to
348	readsorption onto the sediment surface. Therefore, we conducted the H ₂ O ₂ treatment using a solution
349	amended with a high concentration of stable Cs (SCs; 133-Cs) to mask the sites potentially available
350	for readsorption of dissociated RCs. The ratio of SCs to sediment dry weight was adjusted to values
351	greater than the Cs adsorption capacity per unit mass of sediment (see Supplementary Material SM
352	2 for details). However, the observed insignificant removal of RCs in the presence of excess SCs
353	(Figure S9) suggests that the dissociation of RCs from the sediment particles to the water column was
354	negligible during the digestion treatment. Thus, our data indicates that little RCs was accumulated in
355	or directly associated with the organic compounds in the sediments examined, unless otherwise RCs
356	was specifically and locally accumulated in the fraction of H ₂ O ₂ -recalcitrant OM, such as pyrogenic
357	materials, aliphatic compounds, or other organic constituents like lignin-derived and N-containing

358	compounds(Mikutta et al. 2005). Nonetheless, the modified H ₂ O ₂ treatments yielding higher removal
359	rates of OM (up to 96%) also resulted in insignificant reduction of RCs (Supplementary Material
360	SM 1.10), indicating that the accumulation of RCs in refractory organic compounds is less likely.
361	To investigate the nature of sedimentary RCs further, we conducted treatments using various
362	chemicals such as strong acid (HNO3 and HCl), alkaline (NaOH) and ammonium acetate solutions in
363	addition to digestion of non-crystalline minerals using dithionite-citrate, acid ammonium oxalate and
364	acid hydroxylamine methods (Figure S10). However, all the treatments resulted in either a negligible
365	or small reduction of RCs concentration (residual rates greater than 0.70). Given that soil OM has been
366	reported to be highly stabilized by non-crystalline minerals(Torn et al. 1997), amorphous inorganic
367	and organic mixtures were also suspected to be the candidates of RCs carriers. However, little RCs
368	was extracted by the dithionite-citrate, acid ammonium oxalate, and acid hydroxylamine methods,
369	which are capable of extracting organically complexed metals (Al, Fe, Mn), amorphous inorganic Al,
370	Fe and Mn forms and non-crystalline aluminosilicates (e.g., allophane and imogolite)(Carter and
371	Gregorich 2007). Note that these methods are less effective in removing crystalline oxides and
372	hydroxides of Al and virtually no metals from crystalline silicate minerals(Carter and Gregorich 2007).
373	The results generally suggested that the RCs present in our sediments is chemically non-labile and
374	perhaps fixed by micaceous or other clay minerals in a relatively stable manner.

3.5 Correlation of RCs and sediment specific surface area

377	The apparent correlation of RCs and OM contents is likely attributed to the relationship
378	between OM and specific surface area. Our data indicated that the organic C content is significantly
379	and positively correlated with the specific surface area for the unseparated and density-fractionated
380	sediments (Figures 1d and 2d). The previous findings also indicated that the OM content are highly
381	correlated with particle surface area determined by gas adsorption in the majority of soils and river
382	and coastal sediments(Bergamaschi et al. 1997, Keil et al. 1997, Mayer 1994, 1999). In addition, the
383	particulate organic C-to-surface area ratios (OC/SA) for our unseparated samples ($0.24-1.4 \text{ mg-C} \cdot \text{m}^2$)
384	were comparable to those determined for river sediments in previous work (0.43–0.91 mg-C \cdot m ²) (Keil
385	et al. 1997).

The OC/SA (36.6 mg- $C \cdot m^2$) for the density-separated outlier sample with a low RCs 386 387 concentration at high organic C content was an order of magnitude greater than the unseparated 388 samples, indicating extremely low surface area per unit mass of organic C most likely due to the 389 significant participation of large-size allochthonous OM (e.g., woody debris or leaf fragments; Figure 390 3). In such case, RCs concentration did not necessarily increase with increasing OM content, which is 391 in contrast to the positive correlation between specific surface area and RCs concentration for the all samples (Figure 5). The linear relationship between RCs concentration and specific surface area 392 393 suggests that RCs carrying capacity per unit of sediment surface area is relatively constant and irrespective of OM source. The adsorption process of RCs and clay minerals (e.g., illite and biotite) 394 395 are well documented in literature and the RCs adsorption is in many cases related to the particle size

396	and surface area of sediment (e.g., Mukai et al., 2014; Yoshimura et al., 2014). Mukai et al. (2014), for
397	example, reported that RCs adsorption to the finer biotite was greater for the RCs-contaminated soil
398	particles in Fukushima indicating the importance of surface are of minerals to the RCs adsorption.
399	Because the majority of RCs activity in sediment occurred in the intermediate density
400	fractions (1.8–2.4 g·cm ⁻³ , Figures S6 and S7), where OM is mainly characterized by autochthonous
401	origin (according to the N/C ratio analysis), the RCs concentration in the riverine deposited and
402	suspended sediments is mostly related with the autochthonous OM. The monolayer hypothesis
403	proposes that sedimentary OM does not equally cover the particle surface. Rather, OM occurs in a
404	patch manner(Mayer 1999) and play important role in cross-linkage of organic and mineral
405	aggregates(Bock and Mayer 2000). As noted below in more detail, such role of autochthonous OM is
406	likely important in the accumulation of the RCs-contaminated inorganic mineral particles in riverine
407	sediments. A previous study also indicated that most fluvial particulate OM is closely associated with
408	suspended minerals(Keil et al. 1997), though some portions of particulate OM may occur as discrete
409	large-size organic particles (fragments) with this type of OM most likely to be allochthonous
410	origin(Keil et al. 1997).In contrast to the specific surface area, the particle diameter and surface area
411	determined by the laser scattering technique did not have a significant relationship with RCs or OM
412	(Table S1). In addition, the surface area calculated with this technique was smaller than the BET
413	specific surface area by one or two orders of magnitude. The lack of significant correlation suggests
414	that the laser scattering technique is insufficient to quantify, with high accuracy, the microstructure of

415 fine particulate surface including RCs fixing and adsorption sites.

416

417 **3.6** Potential mechanism behind the correlation of RCs and autochthonous OM

418 Given the chemically inert nature of sedimentary RCs observed in this and previous studies, the results from this study indicate that RCs in riverine sediment is fixed by the clay minerals (e.g., 419 420 biotite) most likely via irreversible process (Mukai et al., 2014). While aqueous and sedimentary fine particles are generally composed of various components such as organisms (e.g., phytoplankton, 421 422 terrestrial plant fragments, other organisms), detritus (e.g., fecal pellet) and inorganic matters, fine clay 423 minerals can form microaggregates with autochthonous OM including phytoplankton (Alldredge and 424 Silver, 1988; De La Rocha et al., 2008). However, it should be noted that previous studies consistently 425 indicated that direct association of mineral particles and phytoplankton is unlikely (Ransom et 426 al.,1999). Rather, extracellular polymeric substances such as polysaccharides are recognized to play a 427 role in the formation of organic and inorganic miroaggregates. Such polymeric substances are most 428 likely secreted by surrounding microorganisms such as bacteria and phytoplankton and contribute to 429 the stabilization of organic and inorganic aggregates via cation-mediated cross-linkage (Verdugo et al., 2004; Hamm 2002; Kovac et al., 2014; Deng et al., 2015). Therefore, it is likely that such polymeric 430 431 substances acted as a glue of clay minerals and autochthonous OM forming the microaggregates in our riverine fine sediments. 432

433

Given that microorganisms and polymeric organic substances preferentially sequesters the

434	fine particles with high surface area (primarily clay minerals) in marine sediments (Ransom et al.,
435	1998), specific surface area of sediment is more likely controlled by the fine inorganic particles rather
436	than organic matters. It would be reasonable, therefore, to conclude that the observed correlations
437	among RCs, autochthonous OM and specific surface area of sediment is due to the accumulation of
438	RCs-contaminated fine minerals in the OM-rich sediment. Indeed, in the specific surface area analysis,
439	we removed sedimentary organic matters prior to the BET measurement via combustion treatment, as
440	such the BET measurement in this study represents the surface area of inorganic fraction of sediment.
441	It has been well recognized that soil OM such as humic substances can adsorb onto the surface
442	of clay minerals and such soil OM exerts a hindering effect on Cs adsorption to clay minerals via
443	covering or blocking the specific adsorption site (e.g., FES). Thus, Cs mobility and bioavailability are
444	enhanced in the presence of soil OM (Staunton et al., 2002). However, possible differences in the role
445	of soil and aqueous OM in terms of RCs interaction is, at least partially, related to timing of Cs
446	adsorption to clay minerals during the longitudinal transport from terrestrial runoff to downstream
447	river systems. In contrast to soil OM, interaction of autochthonous OM with RCs in aqueous sediment
448	occurs in the river systems. In such case, RCs is already carried by the fine minerals, and dissolution
449	of RCs from minerals to aqueous phase and subsequent steric hindrance of aqueous RCs re-adsorption
450	to minerals by autochthonous OM are less likely to occur simply because of the irreversible nature of
451	RCs fixation to the minerals.

453 **4. Conclusions**

The present study investigated the characteristics of fine sediments and FDNPP-derived RCs 454 455 in the Abukuma River, Japan with emphasis on the association of RCs with sedimentary OM. Comprehensive analyses of the RCs concentration and physicochemical properties of sediments 456 indicated strong relationship between RCs concentration and OM contents for the suspended and 457 458 deposited sediments and the density-separated samples. In particular, the significant correlation between OM and RCs was observed for the intermediate density sediments where the highest 459 460 proportion of RCs activity was found and autochthonous OM dominantly occurs. The correlation did 461 not hold for some light density fractions due to the presence of large-size allochthonous OM. 462 Despite the correlation of RCs concentration and OM content, removing the majority of 463 sedimentary OM by H₂O₂ treatment resulted in the small reduction of RCs concentration, indicating 464 that the direct association of RCs with sedimentary OM is less likely. The BET specific surface area was correlated with sedimentary RCs concentration, and this variable could explain the outlier sample, 465 466 which showed relatively low RCs concentration at high OM content. These results combined with the 467 fact that sedimentary RCs was not extractable in a series of chemical digestion assays indicated that 468 finer-grained and chemically non-labile inorganic minerals associated with autochthonous OM are an 469 important carrier of RCs.

The lower chemical reactivity of RCs in riverine sediment is consistent with the short biological decay of grazing fish (e.g., *Plecoglossus altivelis*) in the Abukuma River after the FDNPP

472	accident (half-life of ~39 days)(Iguchi et al. 2013). Given that the major pathway of RCs contamination
473	in such grazing fish species is via intake of autochthonous OM, the short retention time of RCs is at
474	least partially associated with the lower digestibility of the contaminated inorganic sediment in the fish
475	body. Furthermore, the longer decay of RCs for fish species in freshwater lakes with longer hydraulic
476	time may be relevant to the greater autochthonous OM production and RCs retention in ecosystems
477	after the FDNPP accident(Fukushima and Arai 2014). Finally, autochthonous OM in the water bodies
478	can be an important carrier and sink for terrestrially derived RCs-contaminated soil particles. This
479	notion, for example, implies that algal pond may be useful for the remediation of contaminated aqueous
480	environment and higher priority for decontamination may be given to the fine sediment in lentic areas
481	where autochthonous OM dominates. Therefore, autochthonous OM is of great concern in view of the
482	mobility, bioavailability, and fate of FDNPP-derived RCs in aqueous and sedimentary environments.
483	

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- 653 **Figure Captions**
- 654

655 Figure 1. Relationships among RCs concentration and parameters related to sediment quality for 656 unseparated samples: (a) RCs concentration and organic C content, (b) RCs concentration and organic 657 N content, (c) RCs concentration and specific surface area (determined by the N₂ adsorption method), (d) organic C content and specific surface area (determined by the N₂ adsorption method), (e) RCs 658 concentration and particle diameter (median value determined by the laser diffraction and scattering 659 660 method) and (f) RCs concentration and surface area calculated from particle diameter. The data and error bars represent average and standard deviation from the measurement. Regarding the symbols, 661 662 DS and SS represent deposited and suspended sediments and the numbers 2012, 2013 and 2015 663 indicate the sampling year. Linear regression line (solid line) and 95% confidence interval (dashed line) are shown when the regression analysis is statistically significant (p < 0.05). Detailed values for 664 the data used in Figure 1 are listed in Table S1. 665

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667 Figure 2. Relationships among RCs concentration and sediment qualities for the density-separated sediments. (a) RCs and organic C content for deposited sediment (DS: St. 1 Watari in 2012, St. 2 668 669 Marumori in 2013, St. 4 Fukuhima in 2013 and 2015), (b) RCs and organic C content for suspended sediment (SS: St. 1 Watari in 2012, St. 2 Marumori in 2013 and St. 4 Fukushima in 2013), (c) RCs and 670 671 specific surface area for deposited sediment (St. 2 Marumori in 2013) and (d) organic carbon C and 672 specific surface area for deposited sediment (St. 2 Marumori in 2013). In the panels (a) an (b), data for each density fraction is shown using different type of symbol. Data for the unseparated deposited 673 674 sediment samples were plotted together in the panels (c) and (d). The data and error bars represent 675 average and standard deviation from the measurement. Linear regression line (solid line) and 95% 676 confidence interval (dashed line) are shown in the panels (c) and (d). In the panel (d), outlier data (light 677 fraction) is shown in the bracket. Detailed values for the data used in Figure 2 are listed in Tables S1 678 and S2.

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Figure 3. Images from optical microscopic observation for four types of density separated deposited sediment collected at St. 2 Marumori in 2013 (a_2 : < 1.6 g/cm³, b_1 : 1.6-1.8 g/cm³, d_1 : 2.0-2.2 g/cm³ and g_1 : 2.6-2.8 g/cm³. The arrows in the right bottom figure (plot of RCs versus organic C content) represent the samples a_2 , b_1 , d_1 and g_1 with sample a_2 being considered as outlier. Microscopic images for the density separated sediment collected from other sampling stations are also shown in the in Supplementary Material Figure S8.

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Figure 4. Box plot of N/C ratio for deposited and suspended sediments (DS and SS), density-separated sediment and end-member samples collected along the Abukuma River basin (i.e., terrestrial soils and plants and riverine algae). Top, middle and bottom horizontal lines represent third quartile, median and first quartile, respectively. Upper and lower whiskers represent maximum and minimum values,

- respectively. The different letters (i.e., a, b, c and d) indicate significant difference at 5% level
 according to Tukey's test. Detailed values for the data used in Figure 4 are listed in Tables S1, S2 and
 S3.
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Figure 5. Relations between (a) organic C content and RCs concentration and (b) specific surface area 695 and RCs concentration for unseparated and density-separated samples. Unseparated samples are from 696 deposited sediment in 2012 and 2013 (DS2012 and DS2013) and density-separated samples are from 697 698 St. 2 Marumori in 2013. Symbols represent open circles for unseparated samples, gray diamonds for density-separated heavy (>2.4 g.cm³) and intermediate $(1.8 - 2.4 \text{ g.cm}^3)$ fractions and closed diamond 699 for density-separated light fraction (<1.8 g.cm³). Values of R² and p and regression equation from 700 linear regression analysis (for all data [n= 19]) were also provided. The data in this figure were 701 702 reproduced by using the data from Figure 1 (for unseparated samples) and Figure 2 (for density-703 separated samples).





200 μm 200 μm

b1. Marumori 2013: 1.6-1.8g/cm³

a2. Marumori 2013: <1.6g/cm³



d1. Marumori 2013: 2.0-2.2g/cm³



g1. Marumori 2013: 2.6-2.8g/cm³





Figure 4



