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# The role of autochthonous organic matter in radioactive cesium accumulation to riverine fine sediments

Manabu Fujii*, Keisuke Ono, Chihiro Yoshimura, Manami Miyamoto

*Department of Civil and Environmental Engineering, Tokyo Institute of Technology, 2-12-1-M1-4 Ookayama, Tokyo 152-8552, Japan*

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ABSTRACT

Anthropogenically released radioactive cesium (RCs) poses serious ecological and 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 mechanisms responsible remain unclear. Here, we investigated RCs in fine sediments along the Abukuma River, the largest river near the Fukushima Daiichi Nuclear Power Plant, 1.5–4 years after the accident. Measuring the density-separated sediment fractions with a broad range of OM content (%) indicated that the RCs concentration ($\mathrm{Bq \cdot kg^{-1}}$) is positively correlated with OM content for intermediate-density fractions in which OM is primarily characterized by autochthonous origin. This relationship, however, did not hold for light-density fractions containing a high proportion of large-size allochthonous OM. Furthermore, $H_2O_2$-assisted OM digestion and amorphous material dissolution 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 RCs is tightly associated with finer-grained and chemically non-labile inorganic fractions concurrently resident with autochthonous OM. Overall, our findings highlight that autochthonous OM exerts a significant control on the accumulation, transport, and fate of RCs in aqueous and sedimentary environments.

## 1. Introduction

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident on March 11, 2011 resulted in the tremendous release of a range of radionuclides, including 137-Cs, 134-Cs, 131-I, and 90-Sr into the environment (Kinoshita et al., 2011; Kusakabe et al., 2013; Steinhauser et al., 2013; Yasunari et al., 2011). The leakage of radioactive cesium (RCs; 137-Cs and 134-Cs) was estimated to be on the order of $10^{16}$ Bq (Nuclear Emergency Response Headquarters Government of Japan, 2011). The long half-life (~30 years for 137-Cs) and persistence of RCs in a range of aqueous and soil environments indicates that contamination poses serious ecological, environmental, and social problems (Mizuno and Kubo, 2013; Murakami et al., 2014; Nakai et al., 2015).

RCs has a high affinity for clay minerals, and thus the majority of RCs deposited on the terrestrial surface environment in Fukushima Prefecture was retained in the upper layer of soil, within a depth of ~5 cm for paddy field sites (Lepage et al., 2015; Matsuda et al., 2015) and in the surface litter layer for forest soil (Koarashi et al., 2012). While a large portion of deposited RCs in the catchment around FDNPP remains in the terrestrial environment (e.g., 1.6% wash-off in the Kuchibuto River watershed by the end of 2014) (Wei et al., 2017b), terrestrial RCs has been gradually transported to reservoirs, rivers, and environments further downstream (Wei et al., 2017a; Yamaguchi et al., 2012; Yamashiki et al., 2014; Yoshimura et al., 2014). In freshwater affected by the FDNPP accident, particulate RCs, such as that associated with fine suspended particles, was dominant in riverine RCs transport according to field surveys performed several years after the accident (Nagao et al., 2013; Sakaguchi et al., 2015; Tanaka et al., 2015; Yamashiki et al., 2014; Yoshimura et al., 2014), though dissolved RCs has been also detected. In the river waters of the Abukuma River basin, for example, dissolved RCs ($<0.45\ \mu$m, almost exclusively $Cs^+$) accounted for 1.2–49% of the total RCs with a spatiotemporal average of 20% from June 2011 to December 2012 (Sakaguchi et al., 2015).

After the global fallout due to the Chernobyl accident and nuclear weapons tests, a number of studies on the environmental mobility, bioavailability, and fate of RCs, including adsorption and

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* Corresponding author.
*E-mail address:* fujii.m.ah@m.titech.ac.jp (M. Fujii).

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fixation to clay minerals, have been published. Laboratory-based studies of the interaction of Cs with clay minerals generally suggested that Cs is fixed in specific interlayers of minerals and in layer edge sites, including frayed edge sites, and that it is also retained non-specifically on the surface of planar sites (Bostick et al., 2002; Cornell, 1993; Kim et al., 1996a, 1996b; Sawhney, 1966). In particular, Cs adsorption to micaceous minerals, such as illite (Comans et al., 1991; Comans and Hockley, 1992; Kim et al., 2007) and vermiculite (Bostick et al., 2002; Fan et al., 2014; Kogure et al., 2012), is highly selective, as dehydrated Cs ion is structurally fixed in the interlayers, with some studies suggesting that this fixation reaction may be almost irreversible under specific conditions (Comans et al., 1991; Mukai et al., 2016). Regarding the FDNPP-derived RCs, Mukai and co-workers found that RCs were selectively and uniformly retained on porous weathered biotite (partially vermiculitized 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 and Wuljin Nuclear Power Plant, Korea) and river sediments (six coastal river catchments close to FDNPP) are positively related to organic matter (OM) content (Ambe et al., 2014; Kim et al., 2007; Naulier et al., 2017; Ono et al., 2015). Since alkali metals, including Cs, negligibly form complexes with OM due to the lack of coordination of these metal classes with acidic functional groups, the direct association of RCs with metal binding sites in sedimentary OM is unlikely. Rather, the higher accumulation of RCs in the OM-rich sediment may be related to the grain size and surface area of sediment particles, mineral composition, or combinations of these factors (Ambe et al., 2014; Kim et al., 2007), given that organic and mineral interactions in sediment have been elaborated by the OM-mediated cross-linkage of fine particles (Bock and Mayer, 2000) in addition to patch-type coverage of OM primarily at the edge sites of minerals (Mayer, 1999). Previous studies indicated the high accumulation of RCs in the smaller size fractions of soil and suspended sediments (Ambe et al., 2014; He and Walling, 1996; Sakaguchi et al., 2015; Tanaka et al., 2015). In addition, organic carbon concentrations in riverine and marine sediments are highly correlated with the unit mass-normalized surface area of sediment determined by gas adsorption (Bergamaschi et al., 1997; Hedges and Keil, 1995; 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). For example, autochthonous OM is a major energy source for freshwater organisms such as grazing fish; thus sedimentary RCs associated with autochthonous OM can be highly bioavailable and exhibit dynamic behavior in freshwater environments and ecosystems (Fukushima and Arai, 2014). In this study, therefore, we investigated the interaction of FDNPP-derived RCs and riverine sediment with particular attention given to the characterization of sedimentary OM including whether it is allochthonous or autochthonous. Suspended and deposited fine sediments <2 mm in size were collected at several sampling stations along the main stream of the largest river near the FDNPP, the Abukuma River (Fig. S1 in Supplementary Material SM 1), during summer and winter from 2012 to 2015. The dried sediment samples were then subjected to various physicochemical treatments (e.g., density-based separation, $H_2O_2$ treatment for OM digestion) and subsequent sediment property analyses to examine the relationships among the RCs concentration, OM content, and other sediment properties (e.g., specific surface area). In particular, the characteristics of density-fractionated sediments with different degrees of OM proportions were extensively examined. Nitrogen-to-carbon ratio (N/C ratio) analyses of the sediment samples and end-member samples from the Abukuma River basin (e.g., terrestrial plants, soil OM and riverine algae) were used to identify the source of sedimentary OM. Fig. S2 shows an overview of this study, including sample collection, treatment and analyses.

## 2. Materials and methods

Detailed information on the general procedure, $H_2O_2$ treatment, sample analyses, statistical analyses and fundamental water quality measurement is available in Supplementary Material (SM 2).

### 2.1. Sample collection

The Abukuma River has a basin area of approximately 5400 $km^2$, a total main stream channel length of ~240 km, and a flow rate of 117 $m^3 s^{-1}$ (averaged over 1966–2009 at Tateyama observation station). The river originates in Asahidake Mountain in the south of Fukushima Prefecture, passes through Fukushima City which is approximately 60 km northwest of FDNPP and finally flows into the Pacific Ocean in Watari City, Miyagi Prefecture.

Deposited fine sediments were collected at several sites in the main stream channel of Abukuma River (St. 1 Watari, St. 2 Marumori, St. 3 Yahata, St. 4 Fukushima, St. 5 Nihonmatsu, and St. 6 Akutsu; Fig. S1). Samples were taken during stable water discharge periods in the summer (July, 2012 and June 2015) and winter (January, 2013) 1.5–4 years after the accident. The lentic area near the river bank (water depth of <20 cm) was selected as the main sampling site for deposited sediment. In St. 4 Fukushima, deposited sediments were also collected from the river bank in the flood plain. During sampling, sediments were carefully collected from the surface layer (layer depth of less than 2–3 cm) in a 100 mL polystyrene container by using a plastic scoop and a gloved hand. The sediment surface layer in the lentic areas was mostly composed of finer particles (<2 mm) compared with those present in the bottom of lotic area. Indeed, the river bed in the lotic area of most sampling sites consisted of large particles, including gravel and stones, and fine particles were neither observed on the surface of river bed by visual inspection from river bank nor collected sufficiently with the Ekman-Birge grab sediment sampler.

During the sample collection, water samples (40–100 L) were also collected in a polypropylene container from either the river bank or top of a bridge by using plastic pump (Tempest DTW 60 ft, 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 Abukuma River basin in December 2014 and June 2015 (in the vicinity of the sediment sampling stations). The collected sediment, water, and end-member samples were transported to the experimental laboratory immediately after the completion of the field survey. While the end-member and sediment samples were collected from different multiple years, temporal trends of sample data were indiscernible for the deposited and suspended sediments as well as the end-member samples, at least, for a few years' data set investigated in this study (as discussed below).

### 2.2. Pretreatment of sediment samples

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