



## RESEARCH ARTICLE

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### Key Points:

- Dissolved  $^{137}\text{Cs}$  in the Abukuma River displays significant seasonal fluctuations
- The main factors determining the seasonality of dissolved  $^{137}\text{Cs}$  activity concentrations are water temperature and  $\text{K}^+$
- The standard enthalpy of  $^{137}\text{Cs}$  desorption from sediments was determined to be approximately  $-19.3 \text{ kJ/mol}$

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## Factors Controlling the Dissolved $^{137}\text{Cs}$ Seasonal Fluctuations in the Abukuma River Under the Influence of the Fukushima Nuclear Power Plant Accident

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**Abstract** The 2011 Fukushima Daiichi Nuclear Power Plant (FDNPP) accident released large amounts of radioactive materials into the environment. River systems play an important role in the terrestrial redistribution of FDNPP-derived  $^{137}\text{Cs}$  in association with water and sediment movement. We examined the seasonal fluctuations in dissolved and particulate  $^{137}\text{Cs}$  activity concentrations and clarified the biological and physicochemical factors controlling  $^{137}\text{Cs}$  seasonality in the Abukuma River's middle course in the region affected by the FDNPP accident. The results showed seasonal fluctuations in the dissolved  $^{137}\text{Cs}$  activity concentration, with an increase in summer and a decrease in winter, although there was no clear seasonal change in the particulate  $^{137}\text{Cs}$  activity concentration. Water temperature and  $\text{K}^+$  concentration dominated the seasonality of the dissolved  $^{137}\text{Cs}$  activity concentration. The volumetric activity concentration of the organically bound  $^{137}\text{Cs}$  was found to be several orders of magnitude lower than that of the dissolved  $^{137}\text{Cs}$ . Therefore, we concluded that the  $^{137}\text{Cs}$  in organic matter is not a source of dissolved  $^{137}\text{Cs}$  in river water. The study also revealed the temperature dependence of  $K_d$  in riverine environments from a Van't Hoff equation. The standard reaction enthalpy of  $^{137}\text{Cs}$  in the Abukuma River was calculated to be approximately  $-19.3 \text{ kJ/mol}$ . This was the first study to clearly reveal the mechanisms by which the dissolved  $^{137}\text{Cs}$  activity concentration and  $K_d$  are influenced by chemical and thermodynamic processes in the middle course of a large river, and it is expected to lead to an improved model of  $^{137}\text{Cs}$  dynamics in rivers.

**Plain Language Summary** The 2011 Fukushima Daiichi Nuclear Power Plant (FDNPP) accident released large amounts of radioactive materials into the environment. River systems play an important role in the terrestrial redistribution of FDNPP-derived  $^{137}\text{Cs}$  in association with water and sediment movement. The dissolved  $^{137}\text{Cs}$  activity concentration in the Abukuma River showed clear seasonal fluctuations, with an increase in summer and a decrease in winter, although there was no clear seasonal change in the particulate  $^{137}\text{Cs}$  activity concentration. Water temperature and  $\text{K}^+$  concentration dominated the seasonality of the dissolved  $^{137}\text{Cs}$  activity concentration. Previously, decomposition of  $^{137}\text{Cs}$ -contaminated organic matter was thought to be the reason for the seasonality of the dissolved  $^{137}\text{Cs}$  activity concentration in rivers. However, in the middle course of the river, the organically bound  $^{137}\text{Cs}$  activity concentration is much lower than that of the dissolved  $^{137}\text{Cs}$  activity concentration, indicating that the decomposition of organic matter does not directly affect the dissolved  $^{137}\text{Cs}$  in the middle course. This study revealed that seasonal fluctuations in river temperature determine the seasonality of the dissolved  $^{137}\text{Cs}$  activity concentration in the middle course in the region affected by the FDNPP accident.

## 1. Introduction

The 2011 Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in Japan released large amounts of radionuclides. Among them,  $^{137}\text{Cs}$  has one of the most substantial long-term impacts on the terrestrial environment (Hirose, 2012; Steinhauser et al., 2014; Terada et al., 2020; Wada et al., 2016), because of its relatively long half-life (30.17 years). In fact,  $^{137}\text{Cs}$  remains a social concern at Chernobyl, even though more than 30 years have passed since the accident in 1986 (Beresford et al., 2016; Evangelou et al., 2016; Igarashi et al., 2020). Deposited  $^{137}\text{Cs}$  is strongly adsorbed by soils and is also present in environmental waters as dissolved ions. River systems play

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an important role in the terrestrial redistribution of FDNPP-derived  $^{137}\text{Cs}$  (so-called “ $^{137}\text{Cs}$  wash-off”) through water and sediment movement from forested upper course areas to middle and lower course areas in Fukushima Prefecture (Iwagami et al., 2017; Yoshimura et al., 2015). For instance, a total of 12 TBq of  $^{137}\text{Cs}$  was transported in the Abukuma River (the largest river system in the area contaminated by the FDNPP accident) to the ocean between June 2011 and August 2015 (Taniguchi et al., 2019).  $^{137}\text{Cs}$  wash-off mechanisms and factors controlling them are therefore the key to understanding  $^{137}\text{Cs}$  dynamics in the Fukushima region.

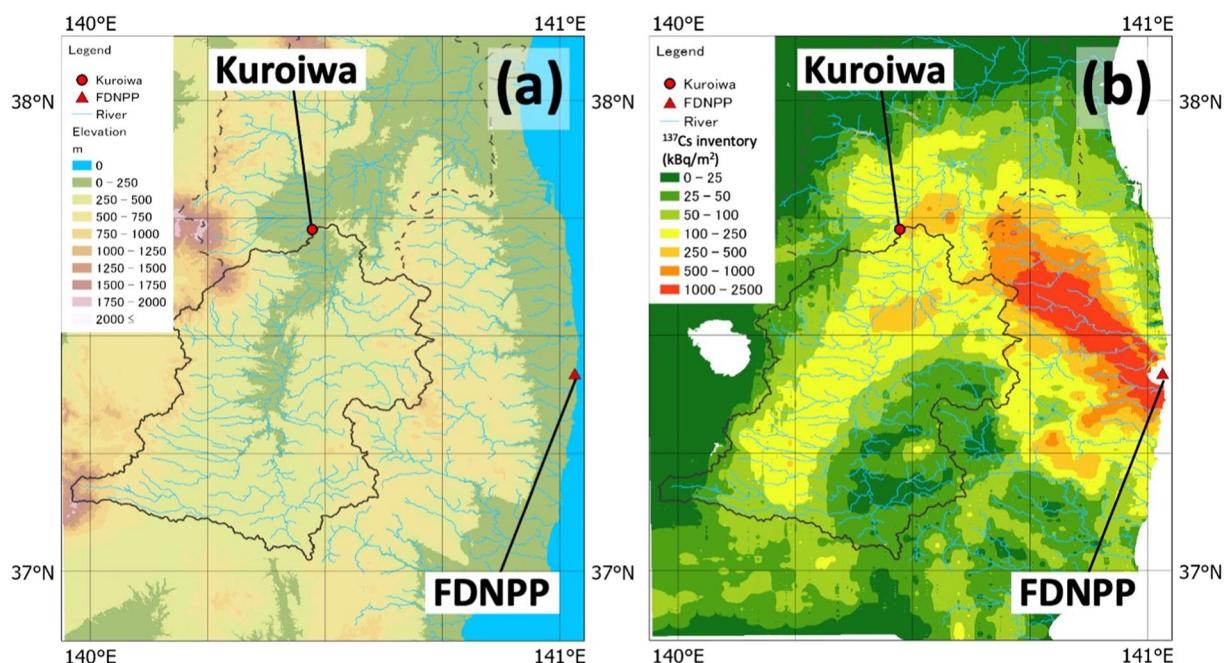
After the FDNPP accident, various studies were devoted to examining  $^{137}\text{Cs}$  dynamics in freshwater environments, including rivers and ponds. Previous studies have found that there are two types of trends in  $^{137}\text{Cs}$  activity concentrations in freshwater: a long-term trend and a seasonal trend. Both the dissolved and particulate  $^{137}\text{Cs}$  activity concentrations in rivers decreased rapidly during the first few years (up to 3 years), and have continued to decrease steadily since the initial decline began (Onda et al., 2020; Taniguchi et al., 2019). On this temporal trend over the first 10 years after the accident, seasonal fluctuations were also observed, which can be superimposed on this temporal trend as shown in Figures 2c and 2d.

The dissolved  $^{137}\text{Cs}$  activity concentrations in freshwater exhibited a peak in the summer, and then started to decrease toward the winter in rivers (Nakanishi et al., 2021; Nakanishi & Sakuma, 2019; Tsuji et al., 2016) and ponds (A. Konoplev, Wakiyama, et al., 2021; Matsuzaki et al., 2021). The former three studies, conducted in the upper courses of rivers, showed that the clear response of the dissolved  $^{137}\text{Cs}$  activity concentration to the ambient temperature can be attributed to the decomposition of  $^{137}\text{Cs}$ -contaminated organic matter under high-temperature conditions in summer. These studies were conducted in the upper courses of rivers and the hypothesis that organic matter could be a source of dissolved  $^{137}\text{Cs}$  in the upper courses was supported by the results of leaching tests using forest litter (Gomi et al., 2018; Sakuma et al., 2021). Thus, biological processes are considered to be an important source of dissolved  $^{137}\text{Cs}$  activity concentrations, at least in the upper courses of rivers flowing through mountainous forests in Japan.

Terrestrial organic matter that enters aquatic ecosystems is exposed to in-river processes, such as metabolic decomposition (Battin et al., 2009) and downward transportation (Grace & Malhi, 2002), which, in turn, affect the dynamics of  $^{137}\text{Cs}$  that might have entered the river water. It has been well known that the majority of  $^{137}\text{Cs}$  is adsorbed onto frayed edge sites (FES) on suspended solids (SS). The selectivity of  $\text{Cs}^+$  by FES is approximately one thousand times higher than that of  $\text{K}^+$  and two hundred times higher than that of  $\text{NH}_4^+$  (Wauters et al., 1996). The FES constitute only a relatively small portion (0.001%–6%) of the cation exchange capacity (CEC) for most soils and sediments (e.g., Cremers et al., 1988; De Preter, 1990). At the same time, the amount of  $^{137}\text{Cs}$  in the environment is too small to occupy all the available FES. Also, SS, which are supplied from erosion processes and agricultural activity into the river along the way during the transport downstream, may provide adsorption sites for  $^{137}\text{Cs}$ . This phenomenon was confirmed by a laboratory study conducted in Fukushima, which demonstrated that radio cesium can be leached from contaminated litter into water and the leached radio cesium can subsequently be adsorbed onto minerals if there are mineral particles in the water (Sakai et al., 2015).

Biological processes are not the only factors that can change dissolved  $^{137}\text{Cs}$  activity concentrations. Dissolved  $^{137}\text{Cs}$  activity concentrations can also be changed by physicochemical processes, which are also affected by temperature. In particular, cation exchange kinetics at charged solid-liquid interfaces are influenced by temperature (e.g., Lee et al., 2017). It is empirically known that  $\text{Cs}^+$  adsorption on minerals decreases significantly with increasing temperature (Komarneni, 1979). Liu et al. (2003) studied  $\text{Cs}^+$  adsorption on high affinity sites (such as FES) and obtained a clear relationship between the solid-liquid distribution coefficient of  $^{137}\text{Cs}$  ( $K_d$ ) and temperature by conducting a laboratory experiment using  $^{137}\text{Cs}$ -contaminated sediments from the Hanford Nuclear Site in the United States. Tertre et al. (2005) reported that the thermodynamic temperature effect on  $\text{Cs}^+$  adsorption is visible only in cases of low-ionic-strength solutions and at neutral pH levels. Morel et al. (2007) showed that the reaction enthalpy changes in accordance with the progress of the ion exchange in which the tracer  $\text{Cs}^+$  is replaced with  $\text{Na}^+$ . These studies suggest that the adsorption of  $^{137}\text{Cs}$  on FES, which is a physicochemical process, is subject to a thermodynamic temperature effect. Therefore, seasonal fluctuations in  $^{137}\text{Cs}$  observed in rivers are not only due to the biological processes but also to the physicochemical processes.

During transport from the upper course to the middle and lower courses of rivers, the dissolved  $^{137}\text{Cs}$  activity concentration is changed by multiple biological and physicochemical processes. Thus, the biological processes that change the dissolved  $^{137}\text{Cs}$  activity concentration in the upper course may not apply in the middle and lower



**Figure 1.** (a) Main rivers and tributaries in the Abukuma River Basin; (b) the <sup>137</sup>Cs inventory from MEXT (2011).

courses. Moreover, biological and physicochemical process are both affected by temperature, but their response to temperature is completely different. The main objective of this study was to explore how these pathways separately or jointly impact the seasonality of <sup>137</sup>Cs dynamics in the middle course of the Abukuma River, which was affected by the FDNPP accident. To do this, we analyzed an 8-year record of dissolved and particulate <sup>137</sup>Cs measured by the “on-site-temperature” centrifuge method (Tsukada & Ohse, 2016), and complemented this with a thermodynamic analysis (e.g., Liu et al., 2003; Morel et al., 2007; Tertre et al., 2005). We also conducted analyses in order (a) to examine the seasonal fluctuations in the dissolved and particulate <sup>137</sup>Cs activity concentrations, and (b) to clarify the physicochemical and biological factors controlling <sup>137</sup>Cs seasonality in the middle course of the river. We envisaged that such analyses could be used to “pinpoint” the biological and physicochemical variables that mediate the temperature effect on <sup>137</sup>Cs, thereby assisting in the further development of models for simulating <sup>137</sup>Cs dynamics in the environment.

## 2. Material and Methods

### 2.1. Study Site

Our field observations were carried out at the Kuroiwa site ( $37^{\circ}43'37.05''\text{N}$ ,  $140^{\circ}28'23.42''\text{E}$ ; Figure 1a) in the middle part of the Abukuma River, Japan. The Kuroiwa site is approximately 80 km from the river mouth (the Pacific Ocean). The catchment above the Kuroiwa site covers an area of  $2,909 \text{ km}^2$ . The highest and lowest elevations lie at 1,835 m and 67 m, respectively. The <sup>137</sup>Cs-contaminated area in Abukuma River mainly extends over the upstream parts of the Kuroiwa site (Figure 1b). The average <sup>137</sup>Cs deposition in the basin was estimated to be  $103 \text{ kBq/m}^2$  (MEXT, 2011; Ochiai et al., 2015). Continuous river discharge rate ( $Q: \text{m}^3/\text{s}$ ) monitoring was conducted at the Kuroiwa site by the Japan Ministry of Land, Infrastructure, Transport and Tourism (MLIT, <http://www1.river.go.jp/cgi-bin/SiteInfo.exe?ID=302011282218150>).

### 2.2. Field Sampling

River water samples were collected at the Kuroiwa site from January 2012 to December 2019 at weekly intervals. To collect a large amount of particulate <sup>137</sup>Cs from suspended solids (SS), river water was pumped up using an electric pump, and a continuous high-speed centrifugation method (Tsukada & Ohse, 2016) was applied. A solid-retaining centrifuge (MAB 103B-24, Alfa Laval, Japan) was used at a flow rate of 12.5 L/min by filtering 2,000–4000 L

at 5,000 rpm to obtain SS. The particle size distribution in the recovered SS collected in 2019 was measured using a laser diffraction particle size analyzer (SALD-3100; Shimadzu Co., Ltd., Kyoto, Japan) with a measurement range from 0.01  $\mu\text{m}$  to 3.28 mm, and classified into 100 categories. A total of 37 samples were measured in 2019, and the minimum particle size of the recovered SS was  $0.50 \pm 0.03 \mu\text{m}$  (Ave  $\pm$  SD). Accordingly, it is possible that smaller particles of sizes below  $0.50 \mu\text{m}$  escaped from centrifugation. Considering the fact that the smallest particle size of the recovered SS was about  $0.50 \mu\text{m}$  when measured with a device capable of measuring particles as small as  $0.01 \mu\text{m}$ , we believe that almost all of the SS in the pumped water were collected through the centrifugation process. This can be supported by the finding from Sakaguchi et al. (2015) that the maximum concentration of  $^{137}\text{Cs}$  was found in the silt size fraction (3–63 mm) in the middle course of the Abukuma River (near the Kuroiwa site).

We collected dissolved  $^{137}\text{Cs}$  from the supernatant of the centrifuged water using a zeolite (SP-ZP-05, Tokyo Sincol Co., Ltd., Japan) during 2012, and subsequently using a nonwoven fabric cartridge filter impregnated with potassium zinc ferrocyanide (PB-C; CS-13ZN, Japan Vilene Co. Ltd., Japan; Yasutaka et al., 2013, 2015). A previous experiment (Tsuji et al., 2016) confirmed that the adsorption performance of  $^{137}\text{Cs}$  on PB-C is not temperature dependent. We also measured the river water temperature ( $T_w$ ), electrical conductivity (EC), and pH using a pH/EC meter (D-54, Horiba, Japan).

### 2.3. Laboratory Experiment

The SS samples obtained by continuous centrifugation were transferred to a Teflon beaker and dried in a dryer (MOV-212P, Sanyo Electric) at 50°C for at least 5 days. After drying, the samples were crushed into small pieces using a mortar and pestle to make them homogeneous and then transferred to a plastic container. The SS collected by continuous centrifugation contained organic matter. Using the method described by Tsukada et al. (2008), we separated the organically bound  $^{137}\text{Cs}$  from the recovered SS and measured its radioactivity according to the following procedure. First, 4 g of the SS sample was suspended in pure water, stirred and heated to 80°C. Then  $\text{H}_2\text{O}_2$  (35%), adjusted to pH 2 with  $\text{HNO}_3$ , was added slowly. In total, approximately 30 ml of  $\text{H}_2\text{O}_2$  per 4 g SS sample was added over the course of six hours. After cooling, 100 ml of 3.2 M  $\text{CH}_3\text{COONH}_4$  in 20%  $\text{HNO}_3$  was added, and the sample was agitated for 30 min.

The activity concentration of  $^{137}\text{Cs}$  was measured in the following three phases; (a) the dissolved phase (zeolite and PB-C), (b) the particulate phase (SS obtained by continuous centrifugation), and (c) the organically bound phase (extracted liquid of decomposed organic matter), using a germanium semiconductor detector (Canberra GC4020, Canberra, USA) with a relative efficiency of 42.6% at the Institute of Environmental Radioactivity, Fukushima University. The radioactivity measurement time was adjusted for each sample so that the detection of dissolved and particulate  $^{137}\text{Cs}$  involved more than 100 counts and 400 counts, respectively. The radioactivity of  $^{137}\text{Cs}$  in the inorganically bound phase was calculated from the differences between (b) the particulate phase and (c) the organically bound phase.

A measured amount of collected SS were separated and baked at 500°C for five hours. Then, the amount of volatile suspended solids (VSS) was determined from the difference in weight before and after baking. In this study, we consider VSS to be the organic matter component of SS, containing particulate organic matter, organic matter in the form of colloids bound to mineral soils, and biological solids. It should be noted that the organically bound  $^{137}\text{Cs}$  activity concentrations were measured by extracting the recovered SS, not by measuring the activity concentration of VSS.

Major cations and anions were measured using ion chromatography (DIONEX 1100, Thermo Scientific, USA), after filtration by using 0.2  $\mu\text{m}$  cellulose acetate membrane filters (membrane filters, Advantec, Japan). The ammonia content was measured using the salicylic acid-hypochlorite method (Bower & Holm-Hansen, 1980).

## 3. Data Analysis

### 3.1. Empirical Equation for Expressing Temporal Trends

The long-term concentration of  $^{137}\text{Cs}$  in rivers is dominated by physical decay (half-life = 30.17 years) and diffusion in nature (A. Konoplev, Kanivets, et al., 2021; A. Konoplev, Wakiyama, et al., 2021; Smith et al., 2005).

Therefore, it was necessary to remove the effect of temporal changes on average concentrations in rivers in order to reveal the seasonality of radioactive concentrations in rivers over multiple years. By using the double exponential function that had been proposed in previous studies, we removed the long-term decay:

$$C_{\text{ref}}(t) = \alpha \exp[-(\lambda + k_1) \times t] + \beta \exp[-(\lambda + k_2) \times t] \quad (1)$$

where  $C_{\text{ref}}$  is the double exponential function for dissolved ( $d_{\text{ref}}$ : Bq/L), particulate ( $p_{\text{ref}}$ : Bq/kg), inorganic ( $i o_{\text{ref}}$ : Bq/kg) and organic ( $o_{\text{ref}}$ : Bq/kg)  $^{137}\text{Cs}$ ;  $t$  (days or years) is the time of interest after the FDNPP accident (13 March 2011);  $\lambda$  (1/yr) is the physical decay rate (=0.023) of  $^{137}\text{Cs}$ ; and  $\alpha, \beta$  (Bq/m<sup>3</sup>),  $k_1$ , and  $k_2$  (1/yr) are empirical fitting parameters for the double exponential empirical model. The constants  $\alpha, \beta, k_1$ , and  $k_2$  were fitted to minimize the root mean square error between the annual averaged values and the predicted values using the “optim” package in R 4.0.3 (R Core Team, 2020). The annual averaged values (obtained from the values measured from January to December for each year) were used as estimate parameters to avoid excessive fluctuations from non-averaged data (Igarashi et al., 2020).

To clarify the seasonal response of the dissolved and particulate  $^{137}\text{Cs}$  activity concentrations to changes in environmental factors, the temporal decreasing trend of  $^{137}\text{Cs}$  was removed using the results of Equation 1 as follows (Igarashi et al., 2020):

$$d_{\text{det}}(t) = c_d(t)/d_{\text{ref}}(t) \quad (2.1)$$

$$p_{\text{det}}(t) = c_p(t)/p_{\text{ref}}(t) \quad (2.2)$$

where  $c_d$  (Bq/L) and  $c_p$  (Bq/kg) are the dissolved and particulate  $^{137}\text{Cs}$  activity concentrations at time  $t$ , respectively, and  $d_{\text{det}}$  (unitless) and  $p_{\text{det}}$  (unitless) are the detrended dissolved and particulate  $^{137}\text{Cs}$  activity concentrations, respectively.

### 3.2. Solid-Liquid Distribution Coefficient and Thermodynamic Analysis

The  $^{137}\text{Cs}$  exchange between the dissolved and particulate phases of a soil-water system is characterized by the solid-liquid distribution coefficient  $K_d$ , which is an equilibrium constant between the particulate  $^{137}\text{Cs}$  activity concentration and the dissolved  $^{137}\text{Cs}$  activity concentration. In particular, the  $K_d$  obtained by the ratio of particulate and dissolved  $^{137}\text{Cs}$  activity concentration measured within a solid-liquid mixing is referred to as the apparent  $K_d$  (L/kg; e.g., Eyrolle-Boyer et al., 2016; A. Konoplev, 2020; A. Konoplev, Kanivets, et al., 2021; A. Konoplev, Wakiyama, et al., 2021) and calculated as follows:

$$K_d(t) = \frac{c_p(t)}{c_d(t)} \quad (3)$$

$K_d$  hereafter means apparent  $K_d$ . It is now generally accepted that the main mechanism for the solid-liquid reaction of  $^{137}\text{Cs}$  is ion exchange on FES (Cremers et al., 1988; A. Konoplev, 2020). For a “potassium scenario” (when  $\text{K}^+$  is the predominant competing cation for  $\text{Cs}^+$  including Cs isotopes), the ion-exchange equation can be written as follows:



where KX and CsX are species of  $\text{K}^+$  and  $\text{Cs}^+$  that are adsorbed by sediments, and  $\text{Cs}_{(\text{aq})}^+$  and  $\text{K}_{(\text{aq})}^+$  are their species in solution. The equilibrium exchange constant for CsK ( $K_c$ ) is defined as:

$$K_c(\text{Cs}/\text{K}) = \frac{[\text{K}_{(\text{aq})}^+][\text{CsX}]}{[\text{Cs}_{(\text{aq})}^+][\text{KX}]} \quad (5)$$

where  $[\text{CsX}]$  and  $[\text{KX}]$  are the mole fractions of exchangeable cations sorbed by sediments, and  $[\text{Cs}_{(\text{aq})}^+]$  and  $[\text{K}_{(\text{aq})}^+]$  are the dissolved concentrations for species  $\text{Cs}^+$  and  $\text{K}^+$ , respectively.

In the case of an “ammonium scenario,”  $\text{Cs-NH}_4$  cation exchange can be represented by a similar equation. Here, the temperature effect on the exchange constant  $K_c$  can be described by the Gibbs-Helmholtz equation as follows (Liu et al., 2003):

$$\frac{\partial \ln K_c}{\partial (1/T)} = -\frac{\Delta H}{R} \quad (6)$$

where  $\Delta H$  is the enthalpy change for Equation 4 at temperature ( $T$ ; K) and  $R$  (=8.314 J/mol K) is the gas constant. Assuming that the temperature effect on  $K_c$  (Equation 5) appears only for  $^{137}\text{Cs}$  and that  $K_c$  can be replaced with  $K_d$ , the reaction enthalpy can be obtained indirectly using the Van't Hoff equation as follows (Morel et al., 2007; Tertre et al., 2005):

$$\ln(K_d) = -\frac{\Delta H^\circ}{RT_w} + \text{const.} \quad (7)$$

where  $\Delta H^\circ$  (J/mol K) is the standard enthalpy change for Equation 5, and  $T_w$  (K) is the water temperature.

The most usual and conventional way of quantifying the temperature effect is to determine intrinsic thermodynamic properties such as enthalpy and entropy by a direct determination of the data, but this requires calorimetric studies (Angove et al., 1998; Echeverria et al., 2005; Karasyova et al., 1999). In the present study, the Van't Hoff equation can be used to calculate the enthalpy of the reaction based on the following assumptions: (a) the exchange between the dissolved and particulate phases of  $^{137}\text{Cs}$  is in a quasi-equilibrium state, because the dissolved  $^{137}\text{Cs}$  leached from forest litter in the upper course (Gomi et al., 2018; Sakai et al., 2015; Sakuma et al., 2021) is well-agitated with SS in the river water during transport to the middle and lower courses; and (b) the  $K_c(^{137}\text{Cs}/\text{K})$  in the quasi-equilibrium state is achieved through ion exchange between the FES and the solution, because the amount of  $^{137}\text{Cs}$  in the environment occupies only small portion of the FES (Cremers et al., 1988; A. Konoplev, 2020; A. Konoplev, Wakiyama, et al., 2021), and river water is in a low ionic strength condition and has a close-to-neutral pH (=6–8.3; Tertre et al., 2005).

### 3.3. Statistical Analyses

Statistical analyses were performed using R software (R Core Team, 2020). Since the  $^{137}\text{Cs}$  activity concentration in the environment is sometimes highly variable, statistical tests were conducted by excluding outliers (below the first quartile ( $Q_1$ ) –  $1.5 \times \text{IQR}$  or above the third quartile ( $Q_3$ ) +  $1.5 \times \text{IQR}$ ; here, the IQR (interquartile range) =  $Q_3 - Q_1$ ). Significant differences ( $p < 0.05$ ) in the  $^{137}\text{Cs}$  activity concentrations of each group were initially examined using ANOVA. Planned comparisons among the  $^{137}\text{Cs}$  activity concentrations were then conducted using a Tukey-Kramer test ( $p < 0.05$ ) to identify which of the  $^{137}\text{Cs}$  activity concentrations differed from each other.

## 4. Results

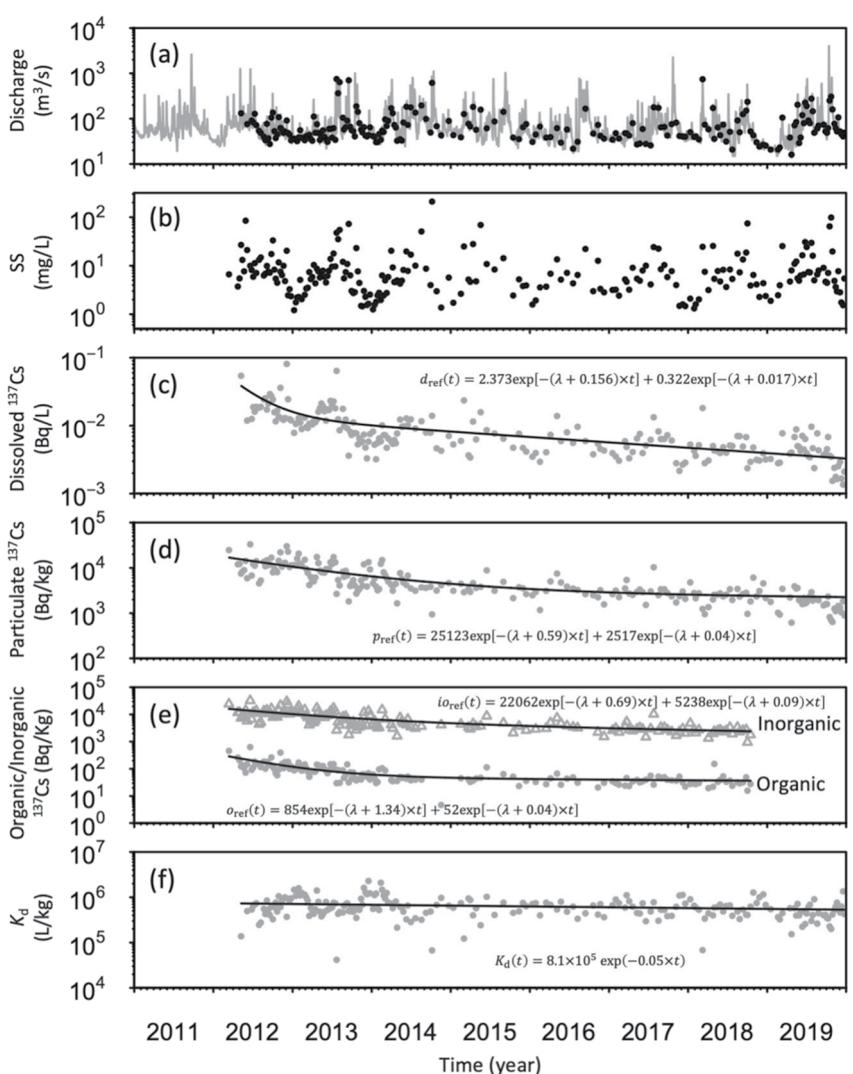
### 4.1. Temporal Changes of $^{137}\text{Cs}$ in the Abukuma River

The temporal changes of dissolved and particulate  $^{137}\text{Cs}$  and  $K_d$  from 2012 to 2019 are shown in Figure 2. Between 2012 and 2019, 221 observations were conducted. The discharge rates on the days when the observations were carried out were classified into three categories using a flow-duration curve, namely, high flow (57 times, 25.8%), medium flow (117 times, 52.9%), and low flow (47 times, 21.3%). The dates of observation were selected without any bias toward either high or low flow conditions. Figure 2a shows the time series of the river discharge ( $Q$ ) at the Kuroiwa site. River discharge amounts at each sampling time are indicated by solid circles. Figure 2b shows the time series of the suspended solids (SS) concentration. There is a clear seasonality in both the discharge rate and the SS concentration. The dissolved  $^{137}\text{Cs}$  activity concentration shows a decreasing trend over the observation period and can be fitted with an empirical double exponential model (Equation 1; Figure 2c). The highest and lowest dissolved  $^{137}\text{Cs}$  activity concentrations were  $8.1 \times 10^{-2}$  (Bq/L; on 5 December 2012) and  $1.3 \times 10^{-3}$  (Bq/L; on 17 December 2019), respectively. The particulate  $^{137}\text{Cs}$  activity concentration exhibits a decreasing trend similar to that of the dissolved phase (Figure 2d). Figure 2e shows the organically and inorganically bound  $^{137}\text{Cs}$  activity concentrations in SS. The organically bound  $^{137}\text{Cs}$  activity concentration, which was shown to constitute a few percent of the total particulate  $^{137}\text{Cs}$  activity concentration, is approximately two orders of magnitude lower than that of the inorganically bound  $^{137}\text{Cs}$  activity concentration. Figure 2f shows the temporal variation in  $K_d$  and the 8-year average of  $K_d$ , which is  $6.4 \times 10^5$  (L/kg). We were able to fit a single exponential function

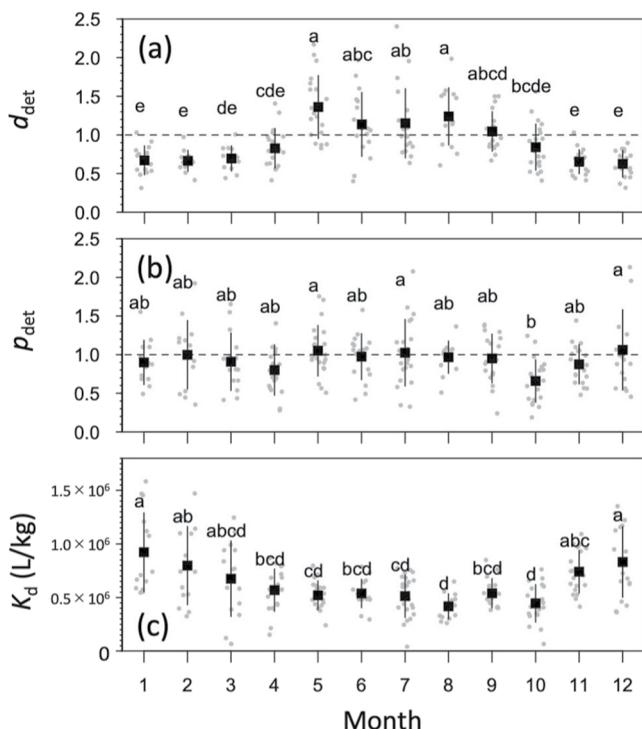
( $K_d = 8.1 \times 10^5 \exp(-0.05 \times t)$ ), which shows that the decreasing trend of  $K_d$  was not statistically significant (ANOVA;  $p = 0.30$ ).

#### 4.2. Seasonality of Detrended Dissolved and Particulate $^{137}\text{Cs}$ Activity Concentrations

To reveal the seasonal fluctuations in the temporal decreasing trend, trend removal (Equation 2) was applied. For the detrended dissolved  $^{137}\text{Cs}$  activity concentration ( $d_{\text{det}}$ ), our results show a clear seasonal fluctuation (Figure 3a; Tukey test,  $p < 0.05$ ), with the lowest values from November to February, an increase beginning in March and the highest values in May and August, followed by a decrease beginning in September. On the other hand, the particulate  $^{137}\text{Cs}$  activity concentration ( $p_{\text{det}}$ ) does not show a clear seasonal fluctuation (Figure 3b). Moreover, we could not identify a clear seasonal change in the detrended organically or inorganically bound  $^{137}\text{Cs}$  activity concentrations in SS (data not shown here). Figure 3c shows a significant seasonal change in  $K_d$ , which can be explained by changes in  $d_{\text{det}}$  and stability of  $p_{\text{det}}$ . It should also be noted that significant seasonality (ANOVA;  $p < 0.05$ ) was found for both monthly mean  $Q$  and SS concentrations (data not shown).  $Q$  and SS concentrations increased during summer and autumn when rainfall is higher. Despite the seasonality observed in  $Q$  and SS, no



**Figure 2.** Temporal changes in (a) river discharge\*, (b) suspended solids concentration, (c) dissolved  $^{137}\text{Cs}$  activity concentration, (d) particulate  $^{137}\text{Cs}$  activity concentration, (e) inorganic  $^{137}\text{Cs}$  (triangles) and organic  $^{137}\text{Cs}$  (solid circles) activity concentrations, and (f) solid-liquid distribution coefficient ( $K_d$ ). \*The gray line and solid circles indicate the observed river discharge rate at the Kuroiwa site and the river discharge rate on the sampling day, respectively.



**Figure 3.** Seasonal fluctuations of (a) detrended dissolved  $^{137}\text{Cs}$  activity concentration ( $d_{\text{det}}$ ), (b) detrended particulate  $^{137}\text{Cs}$  activity concentration ( $p_{\text{det}}$ ), and (c) solid-liquid distribution coefficient ( $K_d$ ). The gray dots, solid squares, and vertical bars in each panel represent the detrended values, averaged values, and the standard deviation for each month, respectively. The monthly averaged values and standard deviations were obtained after removing the outliers in each month (data points below the first quartile ( $Q_1$ ) –  $1.5 \times \text{IQR}$  or above the third quartile ( $Q_3$ ) +  $1.5 \times \text{IQR}$ ; here,  $\text{IQR} = Q_3 - Q_1$ ). Statistical tests were also conducted after removing outliers. Different letters indicate significant differences within each panel over the observation period ( $P < 0.05$ , Tukey's test).

concentrations in SS (Bq/L), but this is because the SS concentration (mg/L) itself exhibits seasonality. Again, it should be noted that the particulate, inorganically bound and organically bound  $^{137}\text{Cs}$  activity concentrations in SS (Bq/kg) do not exhibit seasonality.

We also examined the impact of physicochemical processes, which is influenced by the thermodynamic effect. The reaction enthalpy was obtained indirectly using the Van't Hoff equation (Equation 7; Figure 6). There was a good correlation between the inverse water temperature and  $\ln(K_d)$  ( $R^2 = 0.81$ ). The linear relationship allowed us to approximate  $\Delta H^\circ$  as a constant, which we estimated to be  $-19.3$  (kJ/mol) at the Kuroiwa site in the middle course of the Abukuma River.

## 5. Discussion

In order to address the objectives of this study, this discussion is divided into three sections. The first reports on the temporal changes and seasonality of the  $^{137}\text{Cs}$  activity concentrations in each phase and  $K_d$  in the middle course of the river environment, using observational data collected over 8 years. The second presents the factors controlling the detrended dissolved and particulate  $^{137}\text{Cs}$  activity concentrations. And the third considers how water temperature is associated with solid-liquid distribution in the middle course, as well as how biological and physicochemical processes affect the dissolved  $^{137}\text{Cs}$  activity concentration and the seasonal fluctuations of  $K_d$ .

significant seasonal change was observed in  $p_{\text{det}}$  in the middle course of the river, which may be the result of the sediment that is the origin of SS being averaged out due to mixing during transport to the middle course.

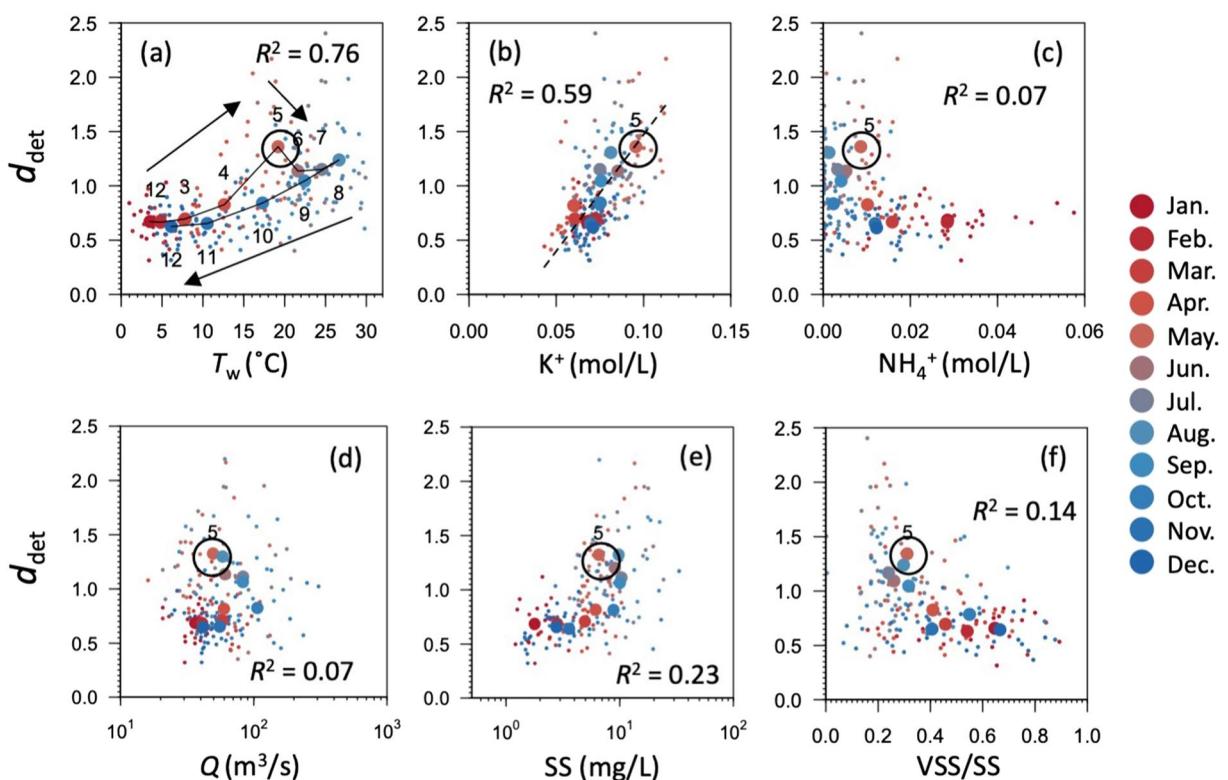
### 4.3. Potential Factors Determining the Seasonality of the Dissolved $^{137}\text{Cs}$ Activity Concentration

Since  $p_{\text{det}}$  did not show a clear seasonal fluctuation, the seasonal fluctuation in  $d_{\text{det}}$  was considered to be determined by factors other than the temporal variation in particulate  $^{137}\text{Cs}$  activity concentration. The response of  $d_{\text{det}}$  to water temperature and  $\text{K}^+$  is shown in Figures 4a and 4b.  $d_{\text{det}}$  increased with increasing water temperature ( $R^2 = 0.76$ ; Figure 4a). Moreover, a hysteresis relationship with water temperature was observed. The hysteresis was at its most pronounced in May. The value of  $d_{\text{det}}$  corresponded closely to the water temperature, even when the hysteresis relationship was taken into account. Moreover,  $d_{\text{det}}$  was highly correlated with  $\text{K}^+$  ( $R^2 = 0.59$ ), which reached its highest value in May, when  $d_{\text{det}}$  was also at its maximum value. Thus, the observed hysteresis relationship between  $d_{\text{det}}$  and water temperature can be explained by  $\text{K}^+$  (Figure 4b). However, we were unable to detect a clear response of  $d_{\text{det}}$  to  $\text{NH}_4^+$  ( $R^2 = 0.07$ ; Figure 4c), the river discharge rate ( $R^2 = 0.01$ ; Figure 4d), the SS ( $R^2 = 0.17$ ; Figure 4e), or the ratio of VSS to SS ( $R^2 = 0.14$ ; Figure 4f).

### 4.4. Biological and Physicochemical Factors Controlling Dissolved $^{137}\text{Cs}$ Seasonality

We attempted to clarify the relationship between the organically bound and dissolved  $^{137}\text{Cs}$  activity concentrations. The organically bound  $^{137}\text{Cs}$  volumetric activity concentration in the river water was approximately one to three orders of magnitude lower than that of the dissolved  $^{137}\text{Cs}$  activity concentration at the Kuroiwa site (Figure 5). The  $^{137}\text{Cs}$  contained in the organic matter may have already been fully leached out. Therefore, biological processes may not be involved in the increase in the dissolved  $^{137}\text{Cs}$  activity concentration in summer in the middle course. Here, there appears to be seasonality in the particulate, inorganically bound and organically bound  $^{137}\text{Cs}$  activity concentrations.

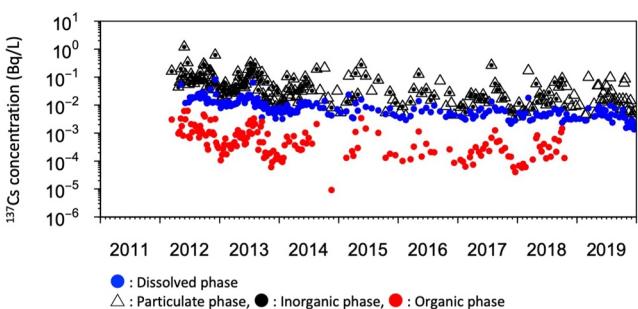
We also attempted to clarify the relationship between the organically bound and dissolved  $^{137}\text{Cs}$  activity concentrations. The organically bound  $^{137}\text{Cs}$  volumetric activity concentration in the river water was approximately one to three orders of magnitude lower than that of the dissolved  $^{137}\text{Cs}$  activity concentration at the Kuroiwa site (Figure 5). The  $^{137}\text{Cs}$  contained in the organic matter may have already been fully leached out. Therefore, biological processes may not be involved in the increase in the dissolved  $^{137}\text{Cs}$  activity concentration in summer in the middle course. Here, there appears to be seasonality in the particulate, inorganically bound and organically bound  $^{137}\text{Cs}$  activity concentrations.



**Figure 4.** Responses of the detrended dissolved  $^{137}\text{Cs}$  activity concentration ( $d_{\text{det}}$ ) to (a) water temperature, (b)  $\text{K}^+$  concentration, (c)  $\text{NH}_4^+$  concentration, (d) specific river discharge, (e) suspended solids concentration, and (f) the ratio of volatile suspended solids to suspended solids. Each color represents the values from January to December, as shown in the legend to the right of the figure. The difference between the light and solid colors indicates the detrended values and their monthly averaged values. The numbers in each panel indicate the months. The monthly averaged values were calculated after removing outliers (data points below the first quartile ( $Q_1$ ) –  $1.5 \times \text{IQR}$  or above third quartile ( $Q_3$ ) +  $1.5 \times \text{IQR}$ ; here,  $\text{IQR} = Q_3 - Q_1$ ).

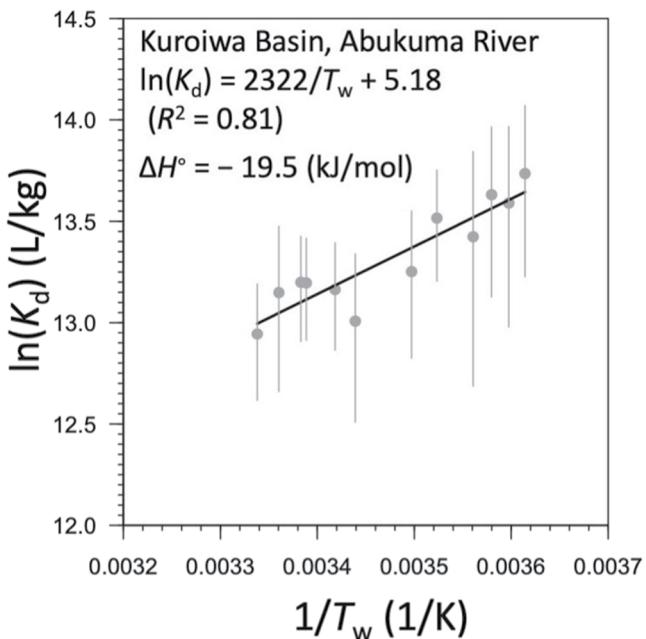
### 5.1. Temporal Changes of $^{137}\text{Cs}$ Activity Concentrations in the River Environment

Previous studies have reported that the particulate  $^{137}\text{Cs}$  activity concentration exhibits an exponential decline beginning immediately after the accident based on a regression analysis conducted across the Fukushima rivers (Onda et al., 2020; Taniguchi et al., 2019). The temporal decreasing trend in the dissolved  $^{137}\text{Cs}$  activity concentration have also been monitored, but precisely how much the dissolved  $^{137}\text{Cs}$  activity concentration will decrease remains unclear due to the limited number of observations (Taniguchi et al., 2019). We examined the temporal changes for both the dissolved and particulate  $^{137}\text{Cs}$  activity concentrations from data covering 8 years of observation. Both the dissolved and particulate  $^{137}\text{Cs}$  activity concentrations exhibited a rapidly decreasing trend during the first few years, followed by a more gradually decreasing trend thereafter (Figures 2c and 2d).



**Figure 5.** Temporal changes in the dissolved  $^{137}\text{Cs}$  activity concentration (solid blue circles), particulate  $^{137}\text{Cs}$  volumetric activity concentration (triangles), inorganically bound  $^{137}\text{Cs}$  volumetric activity concentration (solid black circles), and organically bound  $^{137}\text{Cs}$  volumetric activity concentration (solid red circles). In all cases, the unit is  $\text{Bq/L}$ .

Taniguchi et al. (2019) showed that the speed of the decline in  $^{137}\text{Cs}$  activity concentrations during the initial period immediately following the accident in the upper course of the Abukuma River was  $0.92\text{--}2.11 \text{ years}^{-1}$ , and that thereafter the decline slowed to  $0.37\text{--}0.75 \text{ years}^{-1}$  until the fifth year. The estimated  $k_1$  ( $=0.59 \text{ years}^{-1}$ ) of the particulate  $^{137}\text{Cs}$  activity concentration in this study was in the range of the values reported by Taniguchi et al. (2019) until the fifth year. As shown in Figure 2d, the current diminishing trend of the particulate  $^{137}\text{Cs}$  activity concentration in the Abukuma River was estimated to be  $0.04 \text{ years}^{-1}$ , and this decline is expected to become more gradual in the future. The temporal diminishing trend of the dissolved  $^{137}\text{Cs}$  activity concentration decreased from  $0.156$  to  $0.017 \text{ years}^{-1}$  from 2012 to 2019. The



**Figure 6.** Relationship of the log-scale solid-liquid distribution coefficient ( $K_d$ ) to inverse water temperature ( $1/T_w$ ). Gray dots indicate the observed values. Black dots and bars represent the averages and the standard deviation for monthly  $K_d$ . The solid line ( $\ln(K_d) = 2,322/T_w + 5.18; R^2 = 0.81$ ) expresses the linear regression line of best fit.

current diminishing trend in the Abukuma River is close to that of the long-term component parameter proposed ( $=0.02 \text{ years}^{-1}$ ) by Smith et al. (2004). It is expected that the dissolved  $^{137}\text{Cs}$  activity concentration will continue to decay at a slow rate.

We also found that both the organically and inorganically bound  $^{137}\text{Cs}$  activity concentrations can be also expressed by a double exponential equation (Figure 2e). These are caused by physical decay and natural attenuation processes, including advection, diffusion and dispersion, but these processes do not reduce the total amount of radionuclides; rather, they affect radionuclide distribution over space and time, and may dilute radionuclides in the environment or partially remove/relocate and spread them (A. Konoplev, Kanivets, et al., 2021; A. Konoplev, Wakiyama, et al., 2021; Smith et al., 2005).

Regarding  $K_d$ , we could not identify a clear decreasing trend from the annual average of  $K_d$  (ANOVA;  $p = 0.30$ ). The 8-year averaged  $K_d$  ( $=8.1 \times 10^5 \text{ L/kg}$ ) in this study is similar to the values that were observed elsewhere in Fukushima (Nakanishi & Sakuma, 2019; Taniguchi et al., 2019; Yoshimura et al., 2015). In the early stage of the accident, highly radioactive Cs-rich microparticles (CsMPs) were widely dispersed and were observed at the Tsukuba, Japan (~170 km to the south of the FDNPP). Thus, the trend of decline in  $K_d$  ( $=-0.05 \text{ years}^{-1}$  in Figure 2f) could be associated with  $^{137}\text{Cs}$  leaching from CsMPs (e.g., Ikehara et al., 2020; A. Konoplev, Wakiyama, et al., 2021). However, as the Abukuma River, including the Kuroiwa site, is a considerable distance away from the FDNPP (Figure 1a), it remains unclear whether CsMPs contribute to the temporal decrease in  $K_d$ , and accordingly, this phenomenon requires further investigation.

Previous studies estimated the  $^{137}\text{Cs}$  activity concentrations in particulate organic matter (POM) from the  $^{137}\text{Cs}$  activity concentrations in SS in river water, but did not directly measure any actual  $^{137}\text{Cs}$  activity concentrations in POM (Naulier et al., 2017). In this study, we centrifuged 2,000–4,000 L of river water and recovered few grams of SS in order to directly measure the radioactivity of the  $^{137}\text{Cs}$  contained as organically bound in SS. Although the supernatant liquid after centrifugation and the solution after a PB-C may have contained dissolved phase, POM, and organic matter in colloids bound to mineral soils, and so on, we did not measure the mass balance of the recovered  $^{137}\text{Cs}$ . This was because we assumed that the amount of the collected samples was too small to allow us to accurately measure the radioactivity of the  $^{137}\text{Cs}$  that they contained. In addition, as mentioned above, we think that most of the SS contained in the river water pumped into the centrifuge was successfully collected after centrifugation (the minimum particle size of the recovered SS was  $0.50 \pm 0.03 \mu\text{m}$ ; Ave  $\pm$  SD). We did not measure the organic carbon content of the bulk, dissolved, and particulate phases, or of the residues (effluent after extraction with ferrocyanide cartridges). Sakaguchi et al. (2015) reported that the filtered colloidal fractions,  $<100$  and  $<10 \text{ kDa}$ , have nearly the same concentrations as those of the filtered ( $0.45 \mu\text{m}$ ) water. This result indicated that the  $^{137}\text{Cs}$  in the dissolved fraction was truly dissolved rather than present in a colloidal form that can pass through a  $0.45 \text{ mm}$  filter. The radioactivity of  $^{137}\text{Cs}$  in various forms in supernatant liquid after centrifugation will be the subject of future studies.

Our results showed that clear seasonal fluctuations  $d_{\text{det}}$  were observed within the temporal decreasing trend over the 9 years following the accident (Figure 3a). As mentioned in 4.2,  $d_{\text{det}}$  exhibits a clear seasonal fluctuation reaching low levels in winter and high levels in summer, and has two distinct peak values that appear in May and August, respectively. This result suggests that the seasonal fluctuation of detrended dissolved  $^{137}\text{Cs}$  activity concentrations includes a component with a 1-year time scale due to temperature changes and a component with a shorter time scale due to changes in one or more other factors. A detailed discussion of this finding is provided in Section 5.2. However, no clear seasonality was observed in  $p_{\text{det}}$  (Figure 3b). Thus, it can be concluded that the seasonal fluctuation of  $K_d$  (Figure 3c) is associated with dissolved  $^{137}\text{Cs}$  activity concentrations and not with particulate  $^{137}\text{Cs}$  activity concentrations.

Regarding particulate  $^{137}\text{Cs}$ , we examined organically and inorganically bound  $^{137}\text{Cs}$  activity concentrations separately and found that neither exhibited clear seasonality. River sediment transport in the middle and lower courses of the Abukuma River changes over a span of several years to several decades due to the impact of erosion processes such as landslides and large typhoon events (Togashi & Mano, 2004). For this reason, we consider that particulate  $^{137}\text{Cs}$ , either organic or inorganic, at the Kuroiwa site is incorporated into the sediment production and transport processes over a long time scale throughout the entire basin, and this is why it does not exhibit any clear seasonal fluctuation.

## 5.2. Factors Controlling Detrended Dissolved and Particulate $^{137}\text{Cs}$ Activity Concentrations

Since the FDNPP accident, studies in the upper courses of rivers have reported on the seasonal fluctuations of the dissolved  $^{137}\text{Cs}$  activity concentration (Nakanishi & Sakuma, 2019; Tsuji et al., 2016), and the major factor governing this seasonality is considered to be temperature changes over the course of a year. In addition, it was clarified that changes in  $\text{K}^+$  concentrations in river water in the Fukushima area affect dissolved  $^{137}\text{Cs}$  and  $K_d$  (Tsuji et al., 2016). Previous studies also reported on the role of the main competing ions  $\text{K}^+$  and  $\text{NH}_4^+$  in  $^{137}\text{Cs}$  desorption from solid particles into solution for ponds located close to the FDNPP (A. A. Konoplev et al., 2018; Matsuzaki et al., 2021). This competition between cations could also be a factor in the seasonal changes of  $K_d$ .

The present study also found that the  $d_{\text{det}}$  value corresponds well to the water temperature (Figure 4a;  $R^2 = 0.76$ ), and  $\text{K}^+$  concentration (Figure 4b;  $R^2 = 0.59$ ). This result supports those of previous studies that indicated a correspondence between the dissolved  $^{137}\text{Cs}$  activity concentration and the water temperature in Fukushima rivers (Nakanishi et al., 2021; Nakanishi & Sakuma, 2019; Tsuji et al., 2016). A novel finding from our study is that the relationship between temperature and  $d_{\text{det}}$  follows a pattern of hysteresis, which can be explained by the  $\text{K}^+$  concentration.

The  $\text{K}^+$  concentration in the middle and lower courses of rivers changes due to seasonal agricultural activities. It is historically known that water contamination by SS load and fertilizer runoff is high during the period from the puddling of paddy fields (*shiro-kaki* work) to the transplanting of rice seedlings in May (Harada et al., 2011; Suzuki & Tabuchi, 1984; and Yamashiki et al., 2006). Hence, the high  $\text{K}^+$  concentration in May due to seasonal agricultural activities may be the reason why  $d_{\text{det}}$  is higher in May than in June and September, despite the water temperature being lower in May than in the latter months. In addition, the monthly mean SS concentration reached its maximum in May (Figure 4e). This could also be due to seasonal SS loading from farmland due to agricultural activities. On the assumption that ion-exchange (the influence of competing cations) is a factor affecting seasonal fluctuations in the dissolved  $^{137}\text{Cs}$  activity concentration and  $K_d$ , we examined the relationship between the  $^{137}\text{Cs}$  concentration and the  $\text{NH}_4^+$  and  $\text{K}^+$  concentrations as  $\text{NH}_4^+$  competes with  $^{137}\text{Cs}$  as well as with  $\text{K}^+$  (Wauters et al., 1996). Observational data showed a decrease in the  $\text{NH}_4^+$  concentration during the summer months when  $d_{\text{det}}$  was high. The  $\text{NH}_4^+$  concentration in the Abukuma River was lower than that measured in ponds in Fukushima (A. A. Konoplev et al., 2018). Thus, the influence of  $\text{NH}_4^+$  changes on  $d_{\text{det}}$  at the Kuroiwa site is thought to be more limited than that observed in ponds in Fukushima.

Studies at Fukushima (e.g., Sakuma et al., 2019; Tsuji et al., 2016) and at Chernobyl (Voitsekhovitch et al., 1993) showed that the river flow is responsible for an increase in the dissolved concentrations of radionuclides such as  $^{137}\text{Cs}$  in river water. This is because, the contribution of surface runoff from the contaminated topsoil layer is relatively large, and that from the less-contaminated deep soil later is relatively small, when river flows increase with rainfall and snowmelt events. We conducted our field sampling under a wide range of flow conditions, but no clear response of  $d_{\text{det}}$  to river discharge was observed (Figure 4d). As in other rivers, the contribution of surface water to groundwater is considered to be higher during periods of high flow than of low flow. However, the influence of surface runoff and groundwater mixing on the formation of dissolved  $^{137}\text{Cs}$  activity concentrations is unclear. Our sampling was conducted at about 1-week intervals, which may have been insufficient to capture the relationship between the discharge rate ( $Q$ ) and dissolved  $^{137}\text{Cs}$  activity concentrations. As shown in Figure 2a, the daily  $Q$  fluctuates greatly within the sampling period and, therefore, the relationship between  $Q$  and dissolved  $^{137}\text{Cs}$  activity concentrations should be discussed on a shorter time scale, which is a future challenge.

Takata et al. (2020) pointed out a negative relationship between sediment concentrations and dissolved  $^{137}\text{Cs}$  activity concentrations in rivers. This is natural because the total number of  $^{137}\text{Cs}$  adsorption sites increases when the sediment concentration is high. In contrast to this, we observed a positive relationship between  $d_{\text{det}}$

and SS, and the coefficient of determination was not high (Figure 4e). Therefore, we do not consider the input of sediments to be the main mechanism for determining the dissolved  $^{137}\text{Cs}$  activity concentration, although we do not overlook the processes taking place between the sediment concentration and the dissolved  $^{137}\text{Cs}$  activity concentration.

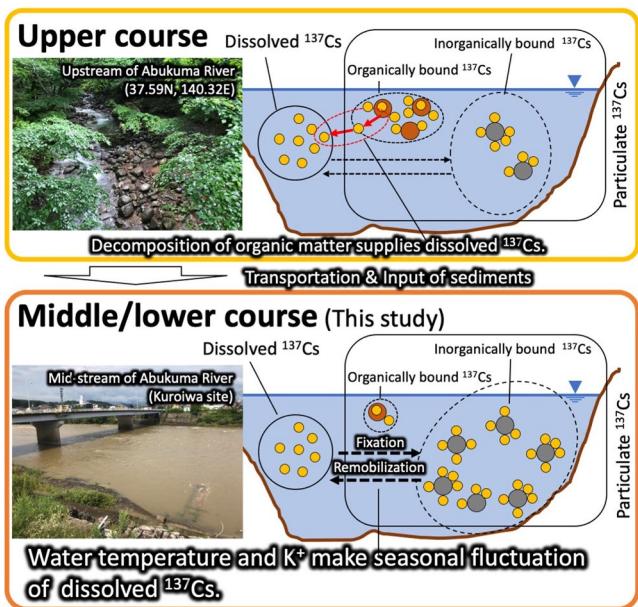
Recently, it has been suggested that the increase in dissolved  $^{137}\text{Cs}$  activity concentrations during the summer months is due to decomposition of  $^{137}\text{Cs}$ -contaminated organic matter as a result of temperature increase (e.g., Nakanishi & Sakuma, 2019; Sakai et al., 2015; Tsuji et al., 2016). In order to examine this possibility, we assumed that volatile suspended solids (VSS) comprise the organic matter content of the SS. If  $d_{\text{det}}$  corresponds to the organic matter content in the SS (VSS/SS), this implies that the organic matter content may be the source of the dissolved  $^{137}\text{Cs}$  activity concentration. However, the monthly average values of  $d_{\text{det}}$  decreased in line with the increase in VSS/SS. The dissolved  $^{137}\text{Cs}$  activity concentration does not correspond with the organic matter content in the SS ( $R^2 = 0.14$ ; Figure 4f), which is different from what had been assumed in previous studies (Tsuji et al., 2016). Terrestrial organic matter may be changed through decomposition by metabolic processes (Battin et al., 2009) and by transport to the middle and lower courses (Grace & Malhi, 2002). These in-river processes may also affect the dissolved  $^{137}\text{Cs}$  activity concentration in the middle and lower courses.

### 5.3. Water Temperature Determines Solid-Liquid Distribution in the Middle Courses

Studies conducted after the FDNPP have shown that the upper courses of rivers, which flow through largely forested areas, organic matter plays an important role as a source of dissolved  $^{137}\text{Cs}$  in river waters (Kurikami et al., 2019; Sakuma et al., 2021). It was also reported that a significant relationship existed between the temperature and the dissolved  $^{137}\text{Cs}$  activity concentration (Tsuji et al., 2016), resulting in clear seasonality in the dissolved  $^{137}\text{Cs}$  activity concentration, with high summer values and low winter values, while particulate  $^{137}\text{Cs}$  activity concentration does not correspond closely to temperature (Nakanishi et al., 2021; Nakanishi & Sakuma, 2019). From these studies, it can be concluded that the increase in the dissolved  $^{137}\text{Cs}$  activity concentration in summer is due to biological processes through which high summer temperatures accelerate the decomposition of  $^{137}\text{Cs}$ -contaminated organic matter.

Recent studies have also reported that organic matter acts as a major carrier for radiocesium transfer from contaminated forest areas to the ocean in the case of Fukushima (Eyrolle-Boyer et al., 2016). Naulier et al. (2017) found that the organic fraction in SS was the main phase that carries radiocesium, especially during the early autumn season. Evidence of organically bound  $^{137}\text{Cs}$  being decomposed in river water is provided by radiocesium leaching experiments on contaminated litter (Nakanishi et al., 2014; Sakuma et al., 2021). Sakai et al. (2015) showed that the average  $^{137}\text{Cs}$  activity concentration in litter decreases to 71% on day 1, 66% on day 7, and 56% on day 30. Gomi et al. (2018) demonstrated that the residual  $^{137}\text{Cs}$  in litter decreases significantly after about 150 days in both riffles and pools in the upper courses of rivers. These results further support that the  $^{137}\text{Cs}$ -contaminated organic matter supplied from the forest to the river during the autumn is leached into the dissolved phase within a few months during the winter, before the beginning of spring.

Biological processes such as decomposition of organic matter may be further advanced during transport from the upper courses to the middle and lower courses of rivers (Battin et al., 2009; Grace & Malhi, 2002). Previous studies were mainly focused on upper course areas flowing through forests (Tsuji et al., 2019) or rivers close to nuclear power plants facing the sea and with only a short distance from the mountains to the sea (Nakanishi et al., 2021; Nakanishi & Sakuma, 2019). Their catchment areas were rather small and the river lengths were too short to be taken into consideration. On the other hand, the Abukuma River is a large river that runs the length of Fukushima Prefecture from south to north, with the catchment area at the Kuroiwa site being 2,909 km<sup>2</sup>, which is between one and two orders of magnitude larger than that of the upper course portion of the Ota River (21 km<sup>2</sup>; Tsuji et al., 2016) or the mouths of the Ukedo and Ota Rivers (151 and 57 km<sup>2</sup>, respectively; Nakanishi & Sakuma, 2019). It is supposed that the organic matter observed at the Kuroiwa site has been exposed to cumulative biological processes during its long transport from the upper course. Our results showed that the organically bound  $^{137}\text{Cs}$  volumetric activity concentration in river water was approximately one to three orders of magnitude lower than that of the dissolved  $^{137}\text{Cs}$  activity concentration at the Kuroiwa site (Figure 5). Fick's laws suggest that dissolved  $^{137}\text{Cs}$  can be taken up by organic matter in SS, but organically bound  $^{137}\text{Cs}$  does not leach into solutions containing a high concentration of dissolved  $^{137}\text{Cs}$ . One interesting study reported a significant negative correlation between the size of a forest area and the SS concentration in rivers in eastern Japan (including the Abukuma



**Figure 7.** Schematic diagram of  $^{137}\text{Cs}$  dynamics and factors controlling seasonal fluctuations in the middle course of the Abukuma River.

River; Tsuji et al., 2019). It mentions that in upper courses with a large portion of forest area, there are relatively few mineral particles onto which  $^{137}\text{Cs}$  can be adsorbed, but SS, which are supplied from agricultural land and other land use types into the river along the way during transport downstream, do provide adsorption sites for  $^{137}\text{Cs}$ . In fact, the forest cover area and SS concentration in the Ota River are 96% and  $2.1\text{ g/m}^3$ , respectively, while in the middle course of the Abukuma River, the forest coverage and SS concentration are 59% and  $13\text{ g/m}^3$ , respectively (Tsuji et al., 2019). These results suggest that the  $^{137}\text{Cs}$ -contaminated litter supplied to the river in autumn is leached out before spring, and  $^{137}\text{Cs}$  is adsorbed to SS (minerals) supplied from land uses other than forests while being transported downstream.

Then, what determines the dissolved  $^{137}\text{Cs}$  activity concentration in the middle course? The answer can be derived from previous studies. Liu et al. (2003), Tertre et al. (2005), and Morel et al. (2007) revealed that the temperature affects the adsorption and desorption of  $^{137}\text{Cs}$  between the solution and high-affinity sites, such FES. The Van't Hoff equation allows us to estimate  $\Delta H^\circ = -19.3\text{ kJ/mol}$  at the Kuroiwa site (Figure 6). This value is in agreement with results obtained using the Van't Hoff equation from ponds in Fukushima (Suzuuchi, Funasawa, and Inkyozaka;  $\Delta H^\circ = -19.0\text{ kJ/mol}$ ; A. Konoplev, Wakiyama, et al., 2021). The results of laboratory experiments calculated  $\Delta H^\circ = -18.2\text{ kJ/mol}$  using the Van't Hoff equation with  $^{137}\text{Cs}$ -contaminated sediments at the Hanford Nuclear Site in the United States (Liu et al., 2003). Interestingly, the results of direct enthalpy measurements from microcalorimetric studies also showed similar values of  $\Delta H^\circ = -19\text{ kJ/mol}$

(Tertre et al., 2005) and  $\Delta H^\circ = -15\text{ kJ/mol}$  (Morel et al., 2007). As previously confirmed in the laboratory, our results demonstrated that a major portion of the  $^{137}\text{Cs}$  in the river environment is selectively adsorbed by the FES in SS, and that the dissolved  $^{137}\text{Cs}$  activity concentration can change due to a physical process that is temperature dependent. From the above, we concluded that (a) biological processes cannot be contributing to the increase in dissolved  $^{137}\text{Cs}$  activity concentrations during the summer in the middle course of the Abukuma River; (b) the largest fraction of the particulate  $^{137}\text{Cs}$  observed at the Kuroiwa site is retained by minerals (such as FES), and therefore, (c) the dissolved  $^{137}\text{Cs}$  activity concentration is determined by physicochemical processes between FES and the solution, which are affected by changes in water temperature and  $\text{K}^+$  (Figure 7).

We wish to emphasize that the most important aspect of these results is the water temperature at which the solids are separated from the liquids. In general, when quantifying the  $^{137}\text{Cs}$  activity concentrations in dissolved and particulate forms in environmental waters, water samples are collected in the field, but solid-liquid separation is conducted in the laboratory. In principle, however, the solid-liquid distribution is influenced by the temperature. Therefore, solid-liquid separation in the laboratory needs to be conducted not at room temperature but at the temperature of the water at the time the sample was collected. We have successfully explained the temperature effect on  $K_d$  from a thermodynamic standpoint because we conducted the solid-liquid separation by continuous centrifugation at the local water temperature in the field. In this context, it should be noted that the x-axis of the Van't Hoff plot is the inverse of absolute temperature, so the impact of temperature on  $K_d$  is larger at lower temperatures. For instance, the  $K_d$  value of a sample obtained at a water temperature of  $5^\circ\text{C}$  is  $8.0 \times 10^5\text{ (L/kg)}$ , but when that sample is separated at  $15^\circ\text{C}$ , the  $K_d$  value is  $6.0 \times 10^5\text{ (L/kg)}$ , and when it is separated at  $25^\circ\text{C}$ , the  $K_d$  value is  $4.6 \times 10^5\text{ (L/kg)}$ . As mentioned above,  $\text{K}^+$  concentration may also play a role in dissolved  $^{137}\text{Cs}$  activity concentration and  $K_d$ . Therefore, it is necessary to experimentally verify the  $\text{K}^+ - K_d$  relationship under various water temperature conditions. This study is the first to explain the temperature effect on  $K_d$  in the middle course of the Abukuma River by combining physicochemical and biological processes. Finally, we strongly recommend that solid-liquid separation of environmental water be conducted at the same water temperature as that at the time the sample was collected.

## 6. Conclusion

Our investigation of dissolved and particulate  $^{137}\text{Cs}$  activity concentrations in river water from the middle course of the Abukuma River revealed the following:

1. The dissolved and particulate  $^{137}\text{Cs}$  activity concentrations in river water exhibited a temporal decreasing trend. However, the decreasing trend of  $K_d$  was not statistically significant.
2. The detrended dissolved  $^{137}\text{Cs}$  concentration in river water exhibited clear seasonal changes, but no clear seasonal change was detected in the detrended particulate  $^{137}\text{Cs}$  activity concentration or in the detrended organic and inorganic  $^{137}\text{Cs}$  activity concentrations in suspended solids.
3. The detrended dissolved  $^{137}\text{Cs}$  activity concentration increased with increasing water temperature, and the relationship exhibited hysteresis, which is explained by the  $\text{K}^+$  content. Therefore, we consider that physicochemical processes, such as the water temperature and the  $\text{K}^+$  concentration, are the dominant factors in determining the seasonal fluctuations in the dissolved  $^{137}\text{C}$  activity concentration.
4. This is the first study to show that the volumetric activity concentration of the organically bound  $^{137}\text{Cs}$  was one to three orders of magnitude lower than that of the dissolved  $^{137}\text{Cs}$  activity concentration over the study period, which led us to the conclusion that  $^{137}\text{Cs}$  bound to organic matter in suspended solids cannot be a substantial source of the dissolved  $^{137}\text{Cs}$  in the river water in the middle course of the Abukuma River.
5. The temperature dependence of  $K_d$  follows the Van't Hoff equation, and the standard enthalpy of the water in the Abukuma River was estimated from the plot to be approximately  $-19$  (kJ/mol).
6. As previous studies have pointed out, in situ solid-liquid separation at the river water temperature is necessary in order to accurately measure the  $^{137}\text{Cs}$  activity concentrations in environmental waters.

## Data Availability Statement

All data used in the analyses are available from the following repository: (Igarashi\_Nanba\_2021\_abukuma\_river\_2012\_2019; <https://osf.io/vr94g/>).

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