Article

Fixed Point Observations and Characterization of Radioactive Caesium in Tama River

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Behavior of radioactive caesium, derived from Fukushima Dai-ichi Nuclear Power Plant Accident, in river water and sediment investigated during 2012–2016. Concentrations of radioactive caesium in river water and sediment were decreased with time exponentially. The residence half-life of radioactive caesium in the river water and sediment were 0.788–1.50 year for ¹³⁴Cs, 1.22–2.17 year for ¹³⁷Cs. Any decrease in radioactive caesium concentration in the Tama river is because of weathering effect than radioactive decay. Concentrations of suspended radioactive caesium temporarily increased when sediments were resuspended due to rain. On the other hand, dissolved radioactive caesium is not easily impacted by this factor. Radioactive caesium concentration in sediments was considerably higher than that in river water. It indicated that much of the radioactive caesium in the Tama river existed in the sediments. Sequential extraction, elemental and crystal phase analysis were performed on the sediments and examined the chemical state of radioactive caesium as well as the adsorption mechanism. Radioactive caesium in sediment was present in a stable chemical form, and there is possibility that radioactive caesium was incorporated in biotite.

Key Words: radioactive caesium, river water, sediment, fixed point observation, biotite, Fukushima Dai-ichi Nuclear Power Plant Accident

1. Introduction

Radioactive caesium (¹³⁴Cs and ¹³⁷Cs) was released into the environment contaminated rivers,^{1–4)} forests,^{5–7)} soils,^{8–11)} and oceans^{12–14)} by Fukushima Dai-ichi Nuclear Power Plant Accident in 2011. It is particularly important to analyze the radioactive caesium in rivers, as it has a major impact on humans and spreads radioactive contamination. Radioactive caesium in water exists as dissolved or suspended form,^{15–18)} and these behaviors are differently. Dissolved radioactive caesium exists as caesium ions and hydrated caesium ions,¹⁾ and gets transported

relatively rapidly through the water due to the speed of water flow, contaminating plants *via* root uptake.¹⁹⁾ While, suspended radioactive caesium is adsorbed onto suspended solids, where secondary contamination due to sediment runoff is a concern.²⁰⁾ If we can elucidate the transport and redistribution of radioactive caesium by understanding the behavior of radioactive caesium in water and sediments, it would aid in decontamination and rapid response efforts during radioactive accidents.

There have been many investigations for radioactive caesium in river water. In the Kuchibuto river (in Fukushima prefecture), the concentration of radioac-

tive caesium in water was found to be extremely high, *i.e.* 1470 Bq L^{-1} (as of 2011), where dissolved caesium concentration was 1 to 49% of the total concentration.²⁾ An investigation of the Abukuma river in Fukushima prefecture showed that the concentration of radioactive caesium in water was different in the upstream and downstream areas, and was highly correlated to the air dose rate.³⁾ In terms of sediments, it has been reported that finer particle sizes were associated with higher radioactive caesium concentrations, where radioactive caesium was adsorbed onto minerals such as smectite, mica, and illite.²¹⁾ However, these investigations were conducted in Fukushima prefecture, where the nuclear accident took place, and there have not been many long-term monitoring studies on the behavior of radioactive caesium in rivers in areas of Japan with lower doses. Therefore, we conducted a long-term monitoring study, from June 2012 to January 2016, of the behavior of radioactive caesium in the Tama river, located over 200 km from the Fukushima Daiichi nuclear power plant. We performed sequential extraction, as well as elemental and crystal phase analysis, on the sediments and examined the chemical state of radioactive caesium as well as the adsorption mechanism.

2. Experiment

2.1 Apparatus

γ -ray spectrometry was performed with a PGT HPGe detector, a high-purity germanium semiconductor detector, and radioactivity concentrations of ^{134}Cs and ^{137}Cs were calculated from γ -ray peaks at 604.7 keV and 661.7 keV, respectively. Detection efficiency was calculated with a sealed ^{152}Eu radioactive source (Japan Radioisotope Association) and KCl reagent.²²⁾ The radioactivity concentration of sample was corrected based on the sampling date.

A Thermo Scientific Niton XL3t was used for X-ray fluorescence analysis. The X-ray tube is a miniature Au tube, and the detector is a Si-PIN di-

ode. Measurements were taken for 90 s in the soil analysis mode.

A Rigaku RINT-2500 TTR-III was used for X-ray diffraction analysis. Cu was used for the X-ray tube, and the tube voltage and current for operation were 50 kV and 300 mA, respectively. Measurement conditions were continuous, with a step width of 0.01° , a measurement angle of $5\text{--}45^\circ$, and a scan speed of 5° min^{-1} .

To measure the conductivity, pH, oxidation-reduction potential, dissolved oxygen content, turbidity, and amount of dissolved solids of the river water samples, a HORIBA U-52 multiparameter water quality checker was used. Solid samples were dried using a Yamato DVS-402 Programmable gravity convection oven. For solid-liquid separation, a KOKUSAN H-103 N centrifuge was used.

2.2 Sediments and river water samples

River water and sediment samples were collected in Shukugawara, which is the mid-stream area of the Tama river (Fig. 1), between June 7, 2012, and January 26, 2016.

With a polyethylene container, 20 to 100 L of water was sampled directly from the surface of the river. Samples were filtered with ADVANTEC No. 5C filter paper with a retained particle size of $1 \mu\text{m}$, and suspended solids were captured. Subsequently, suspended solids were packed in a screw-top polystyrene container (height of 68 mm and inner diameter of 56 mm) with the filter paper, which was the suspended sample. To 5 L of filtrate, 30 mL of 12 mol L^{-1} HCl (extra pure grade, Junsei Kagaku) and 2 g of ammonium phosphomolybdate (AMP; 99% or more, Yoneyama Yakuhin Kogyo Co., Ltd.) were added, and the sample was then stirred for 1 h.²³⁾ After overnight incubation, this filtrate was filtered with ADVANTEC No. 5B, with a retained particle size of $4 \mu\text{m}$, to recover AMP with concentrated radioactive caesium. AMP was then packed

Fig. 1 Map of sampling point, Shukugawara (○). (A): Kanto region, Japan. (B): Tama river watershed. (a): Pacific ocean. (b): Tokyo bay. Black line: Tama river and tributary. Gray line: Prefectural border.

in a screw-top polystyrene container with the filter paper, as the dissolved sample. γ -ray spectrometry was performed for 48 h on each sample.

A sediment sample of about 1 kg was collected using a shovel from the sediment surface layer (less than 5 cm) at a water depth of 30 to 50 cm. Samples were dried for 24 h at 105°C in an oven. Subsequently, they were passed through a 2-mm sieve, reduced with the coning and quartering method, and then packed in screw-top polystyrene containers for measurement. γ -ray spectrometry was performed for 2 h on each sample.

2.3 Sequential extraction

The sequential extraction method, proposed by Tessier *et al.*,²⁴⁾ was applied to the sediment samples. This method fractionates and extracts trace metal elements in samples as ion-exchangeable (IE), bond to carbonates (CB), bond to Fe and Mn oxides (OX), bond to organics and sulfide compounds (OB), and residuals (RES). Further, 40 mL of 1 mol L⁻¹ MgCl₂ aqueous solution was added to 5 g of dried sediment and stirred for 1 h at room temperature with a magnetic stirrer (IE). After the IE extraction, 40 mL of 1 mol L⁻¹ CH₃COOH buffer solution, adjusted to a pH of 5, was added to the residue and stirred for 6 h at room temperature (CB). Subsequently, 100 mL of 0.04 mol L⁻¹ HONH₃Cl aqueous solution was added

to the residue, and the sample was heated and stirred for 6 h at 96°C (OX). Further, 15 mL of 0.02 mol L⁻¹ HNO₃ and 25 mL of 30% H₂O₂ aqueous solution was added to the residue after the OX extraction, and then heated and stirred for 3 h at 85°C. Then, 25 mL of 3.2 mol L⁻¹ CH₃COONH₄ aqueous solution, 15 mL of 0.02 mol L⁻¹ HNO₃, and 20 mL of pure water were added, and the sample was stirred for 3 h at room temperature (OB). The final residue was used as the RES sample and was dried for 24 h at 85°C. Each extraction liquid was stirred and centrifuged for 20 min at 3000 rpm to separate the eluate and residue. The extracted liquid and residue were placed in a screw-top polystyrene container, and γ -ray spectrometry was performed for 6 h.

Throughout the experiment, extra pure grade reagents were used.

3. Results and discussion

3.1 Temporal changes in radioactive caesium concentration in river water

Table 1 and Table 2 show the activity concentrations of suspended and dissolved radioactive caesium in Tama river water sampled at Shukugawara during 2012–2015. The activity ratio of ¹³⁴Cs/¹³⁷Cs corrected at the time of March 15, 2011 was 1.04±0.15 and 0.99±0.14 for suspended and dissolved radioactive caesium, respectively, and it was confirmed that the

Table 1 Activity concentration of suspended radioactive caesium in river water sampled at Shukugawara

Sampling date	Activity concentration ($\pm 1\sigma$) / mBq L ⁻¹		¹³⁴ Cs/ ¹³⁷ Cs activity ratio*
	¹³⁴ Cs	¹³⁷ Cs	
2013.4.12	0.587 $\pm$ 0.091	0.961 $\pm$ 0.089	1.17
2013.5.14	0.844 $\pm$ 0.101	1.263 $\pm$ 0.094	1.32
2013.6.11	1.157 $\pm$ 0.110	1.818 $\pm$ 0.115	1.28
2013.7.11	0.595 $\pm$ 0.080	1.079 $\pm$ 0.081	1.14
2013.8.2	0.665 $\pm$ 0.100	1.654 $\pm$ 0.129	0.848
2013.9.27	0.337 $\pm$ 0.061	0.660 $\pm$ 0.062	1.13
2013.10.31	0.198 $\pm$ 0.048	0.552 $\pm$ 0.056	0.815
2013.11.7	0.226 $\pm$ 0.057	0.547 $\pm$ 0.063	0.945
2013.11.14	0.554 $\pm$ 0.075	1.463 $\pm$ 0.094	0.880
2013.11.21	0.329 $\pm$ 0.088	0.803 $\pm$ 0.098	0.950
2014.4.30	0.785 $\pm$ 0.106	2.110 $\pm$ 0.115	0.989
2014.5.30	0.335 $\pm$ 0.067	0.902 $\pm$ 0.071	1.01
2014.6.27	0.579 $\pm$ 0.091	1.397 $\pm$ 0.092	1.16
2014.7.29	0.454 $\pm$ 0.079	1.219 $\pm$ 0.084	1.07
2014.9.16	0.629 $\pm$ 0.093	1.704 $\pm$ 0.102	1.10
2015.1.29	0.169 $\pm$ 0.077	0.497 $\pm$ 0.078	1.14
2015.3.12	0.179 $\pm$ 0.055	0.675 $\pm$ 0.062	0.925
2015.5.22	0.350 $\pm$ 0.074	1.064 $\pm$ 0.070	1.22
2015.6.10	0.301 $\pm$ 0.084	1.088 $\pm$ 0.081	1.04
2015.7.14	0.232 $\pm$ 0.075	0.997 $\pm$ 0.077	0.904
2015.8.26	2.166 $\pm$ 0.234	9.959 $\pm$ 0.242	0.875
2015.9.12	0.179 $\pm$ 0.066	0.907 $\pm$ 0.071	0.806
2015.10.21	<0.03 ^a	0.071 $\pm$ 0.020	-
2015.11.25	<0.03 ^a	0.600 $\pm$ 0.059	-
2015.12.23	0.145 $\pm$ 0.026	0.523 $\pm$ 0.055	1.23

*Activity concentration was corrected at the time of March 15, 2011.

^aNot detected.

radioactive caesium was derived from the Fukushima Dai-ichi Nuclear Power Plant Accident. The suspended concentration was lower than the dissolved concentration, indicating that radioactive caesium in Tama river water was mainly in a water-soluble state, such as ions. Fig. 2 shows the temporal changes in suspended radioactive caesium concentrations in river water. Fig. 3 shows the temporal changes in dissolved radioactive caesium concentrations at the same location. The suspended radioactive caesium concentration (C_{Cs}) decreased exponentially as a function of the days since the nuclear accident (d); $C_{Cs-134} = 1.67e^{-0.00126d}$ and $C_{Cs-137} = 2.53e^{-0.000874d}$. In the case of the dissolved one, $C_{Cs-134} = 22.9e^{-0.00204d}$ and $C_{Cs-137} = 20.4e^{-0.00104d}$. C_{Cs-134} and C_{Cs-137} are shown by solid and dashed lines, respectively in Figs. 2 and 3. We used Pearson's correlation coefficient (r) in the statistical analysis, which measures the strength and direction of a linear relationship

Table 2 Activity concentration of dissolved radioactive caesium in river water sampled at Shukugawara

Sampling date	Activity concentration ($\pm 1\sigma$) / mBq L ⁻¹		¹³⁴ Cs/ ¹³⁷ Cs activity ratio*
	¹³⁴ Cs	¹³⁷ Cs	
2012.6.7	14.03 $\pm$ 1.40	17.34 $\pm$ 1.16	1.19
2012.6.14	11.86 $\pm$ 1.75	15.38 $\pm$ 1.27	1.13
2012.6.29	8.30 $\pm$ 1.12	11.49 $\pm$ 0.99	1.08
2012.7.4	9.20 $\pm$ 0.92	12.25 $\pm$ 0.80	1.13
2012.7.26	10.45 $\pm$ 1.18	13.84 $\pm$ 1.03	1.16
2012.8.17	8.14 $\pm$ 0.82	12.34 $\pm$ 0.77	1.03
2012.8.29	7.98 $\pm$ 0.85	10.58 $\pm$ 0.75	1.19
2012.9.20	8.50 $\pm$ 0.71	12.20 $\pm$ 0.65	1.12
2012.10.10	9.02 $\pm$ 1.04	15.50 $\pm$ 1.06	0.953
2012.10.23	7.89 $\pm$ 0.95	11.81 $\pm$ 0.91	1.11
2012.11.13	4.24 $\pm$ 0.62	7.84 $\pm$ 0.66	0.911
2012.11.27	7.22 $\pm$ 0.60	11.26 $\pm$ 0.65	1.09
2012.12.18	9.73 $\pm$ 0.71	16.44 $\pm$ 0.80	1.03
2013.4.12	2.33 $\pm$ 0.13	5.15 $\pm$ 0.22	0.866
2013.5.14	5.49 $\pm$ 0.19	10.99 $\pm$ 0.30	0.982
2013.6.11	2.95 $\pm$ 0.13	6.67 $\pm$ 0.22	0.893
2013.7.11	6.00 $\pm$ 0.21	13.87 $\pm$ 0.36	0.896
2013.8.2	4.11 $\pm$ 0.17	8.73 $\pm$ 0.27	0.993
2013.9.27	2.02 $\pm$ 0.14	4.81 $\pm$ 0.23	0.929
2013.10.31	1.32 $\pm$ 0.09	3.48 $\pm$ 0.17	0.865
2013.11.7	1.80 $\pm$ 0.10	3.98 $\pm$ 0.17	1.03
2013.11.14	2.44 $\pm$ 0.13	5.29 $\pm$ 0.21	1.06
2013.11.21	3.08 $\pm$ 0.16	7.81 $\pm$ 0.27	0.915
2014.4.30	2.89 $\pm$ 0.15	8.06 $\pm$ 0.27	0.954
2014.5.30	3.51 $\pm$ 0.16	10.08 $\pm$ 0.29	0.951
2014.6.27	1.83 $\pm$ 0.12	5.37 $\pm$ 0.22	0.955
2014.7.29	1.62 $\pm$ 0.11	5.65 $\pm$ 0.22	0.823
2014.9.16	1.82 $\pm$ 0.12	6.61 $\pm$ 0.25	0.824
2015.1.29	1.19 $\pm$ 0.11	4.34 $\pm$ 0.24	0.924
2015.3.12	1.34 $\pm$ 0.10	5.19 $\pm$ 0.23	0.900
2015.5.22	0.77 $\pm$ 0.08	5.72 $\pm$ 0.25	0.497
2015.6.10	1.34 $\pm$ 0.12	4.83 $\pm$ 0.23	1.05
2015.7.14	0.93 $\pm$ 0.10	4.13 $\pm$ 0.21	0.878
2015.8.26	1.10 $\pm$ 0.10	4.01 $\pm$ 0.21	1.10
2015.9.12	0.26 $\pm$ 0.05	0.90 $\pm$ 0.10	1.20
2015.10.21	0.88 $\pm$ 0.09	3.29 $\pm$ 0.19	1.13
2015.11.25	0.87 $\pm$ 0.09	3.89 $\pm$ 0.21	0.967
2015.12.23	1.57 $\pm$ 0.12	8.05 $\pm$ 0.30	0.866

*Activity concentration was corrected at the time of March 15, 2011.

between two variables (x, y) on a scatterplot, and is given by

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}}$$

where n refers to the number of data (x, y). In the case of the suspended radioactive caesium concentration, by inserting x as d and y as C_{Cs} , r was estimated -0.657 for C_{Cs-134} and -0.425 for C_{Cs-137} . On the other hand, in the case of the dissolved one, r was -0.910 for C_{Cs-134} and -0.746 for C_{Cs-137} which showed a strong correlation. Concentration of sus-

Fig. 2 Temporal changes of suspended ^{134}Cs (○) and ^{137}Cs (●) concentrations in Tama river water sampled at Shukugawara.
*: Sampled at August 26, 2015. Error bar: Standard deviation.

Fig. 3 Temporal changes of dissolved ^{134}Cs (○) and ^{137}Cs (●) concentrations in Tama river water sampled at Shukugawara.
Error bar: Standard deviation.

pendent radioactive caesium temporarily increases when sediments are resuspended due to rain (for example, at August 26, 2015) and there is an inflow of soil and suspended materials from the surrounding environment. This likely caused a little weak correlation with the number of days (since the nuclear accident). On the other hand, dissolved caesium is not easily impacted by these factors; thus, it had a strong correlation with the number of days (since the nuclear accident). According to the correlating equations between the concentrations of radioactive

caesium and the number of days (since the nuclear accident), the residence half-life of radioactive caesium in the river water were 1.50 year for suspended ^{134}Cs , 2.17 year for suspended ^{137}Cs , 0.931 year for dissolved ^{134}Cs , and 1.83 year for dissolved ^{137}Cs . Since the half-life of ^{134}Cs and ^{137}Cs are 2.06 and 30.1 years, respectively, any decrease in radioactive caesium concentration in the river water was because of weathering effect than radioactive decay.

Fig. 4 Relationship between dissolved ^{137}Cs concentrations with the conductivity, pH, oxidation-reduction potential, dissolved oxygen content, turbidity, and amount of dissolved solids in Tama river water.

3.2 The relationship between concentration of radioactive caesium in river water and water quality

Since the aquatic environment may have an impact on the dissolved radioactive caesium concentration, we investigated the relationship between dissolved caesium concentration and water quality. Fig. 4 shows the relationship between dissolved ^{137}Cs concentration with conductivity, pH, oxidation-reduction potential, dissolved oxygen content, turbidity, and amount of dissolved solids in the river water (from April 2013 to December 2015). The ^{137}Cs concentration showed weak correlations with conductivity, pH, turbidity, and amount of dissolved solids in the river water ($|r|=0.361\text{--}0.407$). While the correlation coefficients between ^{137}Cs concentration with oxidation-reduction potential and dissolved oxygen content were -0.119 and -0.164 , respectively, and there was no correlation between these.

3.3 Temporal changes in radioactive caesium concentration in sediments

Table 3 shows the activity concentrations of radioactive caesium in sediments sampled at Shukugawara during 2012–2016. Radioactive caesium concentration in sediments was considerably higher than that in river water, indicating that much of the radioactive caesium in the Tama river existed in the sediments. The activity ratio of $^{134}\text{Cs}/^{137}\text{Cs}$ corrected at the time of March 15, 2011 was 1.02 ± 0.13 . Fig. 5 shows temporal changes in the radioactive caesium concentration in sediments. As days passed after the nuclear accident, radioactive caesium concentration in the sediments decreased. This is likely due to weathering effect of the sediments, much like the radioactive caesium in river water. The concentration of radioactive caesium in sediments was expressed by the function of the days since the nuclear accident: $C_{\text{Cs-134}} = 214e^{-0.00241d}$ and $C_{\text{Cs-137}} = 215e^{-0.00156d}$, and the correlation coefficient r was estimated by

Table 3 Activity concentration of radioactive caesium in sediments sampled at Shukugawara

Sampling date	Activity concentration ($\pm 1\sigma$) / Bq kg ⁻¹		¹³⁴ Cs/ ¹³⁷ Cs activity ratio*
	¹³⁴ Cs	¹³⁷ Cs	
2012.6.7	171.6 $\pm$ 3.0	242.1 $\pm$ 5.5	1.04
2012.6.29	25.1 $\pm$ 1.3	39.4 $\pm$ 2.3	0.954
2012.7.4	131.5 $\pm$ 2.6	192.4 $\pm$ 4.8	1.03
2012.7.26	50.8 $\pm$ 1.8	77.3 $\pm$ 3.2	1.00
2012.8.17	24.4 $\pm$ 1.3	41.5 $\pm$ 2.4	0.919
2012.8.29	36.0 $\pm$ 1.5	54.6 $\pm$ 2.8	1.04
2012.9.20	51.2 $\pm$ 1.8	82.3 $\pm$ 3.2	1.00
2012.10.10	71.6 $\pm$ 2.4	97.6 $\pm$ 3.6	1.20
2012.10.23	97.8 $\pm$ 2.6	143.0 $\pm$ 4.7	1.13
2012.11.13	44.7 $\pm$ 1.8	72.4 $\pm$ 3.3	1.04
2012.11.27	29.8 $\pm$ 1.4	47.8 $\pm$ 2.5	1.06
2012.12.18	22.8 $\pm$ 1.3	42.3 $\pm$ 2.3	0.936
2013.4.12	41.2 $\pm$ 1.7	90.1 $\pm$ 3.5	0.876
2013.5.14	137.7 $\pm$ 2.9	264.4 $\pm$ 5.8	1.03
2013.6.11	29.7 $\pm$ 1.6	52.7 $\pm$ 2.9	1.14
2013.7.11	43.6 $\pm$ 2.0	77.9 $\pm$ 3.5	1.16
2013.8.2	35.4 $\pm$ 1.8	65.9 $\pm$ 3.2	1.13
2013.9.27	43.0 $\pm$ 2.4	108.0 $\pm$ 3.8	0.880
2013.10.31	15.9 $\pm$ 1.4	42.4 $\pm$ 2.2	0.871
2013.11.7	17.4 $\pm$ 1.5	38.2 $\pm$ 2.3	1.04
2013.11.14	18.0 $\pm$ 1.6	39.8 $\pm$ 2.4	1.05
2013.11.21	14.0 $\pm$ 1.2	38.2 $\pm$ 2.1	0.850
2014.4.30	13.5 $\pm$ 1.3	41.2 $\pm$ 2.4	0.870
2014.5.30	13.6 $\pm$ 1.3	38.9 $\pm$ 2.3	0.955
2014.6.27	12.6 $\pm$ 1.2	33.0 $\pm$ 2.2	1.07
2014.7.29	11.0 $\pm$ 1.1	34.4 $\pm$ 2.1	0.916
2014.9.16	10.5 $\pm$ 0.7	30.0 $\pm$ 1.4	1.05
2014.11.28	5.3 $\pm$ 0.6	21.2 $\pm$ 1.2	0.797
2015.1.29	6.4 $\pm$ 0.6	23.1 $\pm$ 1.3	0.938
2015.3.12	6.8 $\pm$ 0.8	21.3 $\pm$ 1.6	1.12
2015.5.22	5.1 $\pm$ 0.8	24.6 $\pm$ 1.8	0.772
2015.6.10	5.9 $\pm$ 0.8	18.6 $\pm$ 1.6	1.18
2015.7.14	5.5 $\pm$ 0.7	26.6 $\pm$ 1.6	0.798
2015.8.26	10.7 $\pm$ 1.2	46.6 $\pm$ 2.8	0.919
2015.9.12	5.8 $\pm$ 0.8	19.3 $\pm$ 1.7	1.23
2015.10.22	1.7 $\pm$ 0.5	5.85 $\pm$ 1.0	1.22
2015.11.2	1.0 $\pm$ 0.3	3.59 $\pm$ 0.6	1.19
2015.11.25	4.3 $\pm$ 0.7	15.1 $\pm$ 1.4	1.24
2015.12.23	3.3 $\pm$ 0.6	13.8 $\pm$ 1.3	1.05
2016.1.26	4.6 $\pm$ 0.7	22.4 $\pm$ 1.6	0.940

*Activity concentration was corrected at the time of March 15, 2011.

$r = -0.784$ and $r = -0.757$. This results a high degree of correlation between the concentration of radioactive caesium in sediments and the number of days since the nuclear accident. Furthermore, there was a temporary increase in radioactive caesium concentration in the sediments during rainfall events (August 26, 2015) as with suspended radioactive caesium. However, the influence of rainfall for radioactive caesium in the sediments was smaller than that for suspended radioactive caesium.

The residence half-life of radioactive caesium in

sediment were 0.788 and 1.22 years for ¹³⁴Cs and ¹³⁷Cs, respectively, and these are shorter than the residence half-life of radioactive caesium in the river water.

3.4 Chemical analysis of radioactive caesium in sediments

At the beginning of the monitoring, radioactive caesium concentration in sediments changed drastically but became stable with time. This indicates that radioactive caesium is incorporated into sediments in a stable form. Therefore, in order to survey the chemical state of radioactive caesium in sediments, the sequential extraction was employed on the sediments. Table 4 shows the sequential extraction result of sediments sampled in May 2013 and August 2015. Here, IE is a fraction in which metallic elements exist as water-soluble compounds, and metallic elements are easily released from samples into the water. CB is a fraction in which metallic elements are bonded with carbonate ions, where metallic elements are released to the environment by mild acids such as rainwater. OX is a fraction in which metallic elements are incorporated in Fe and Mn oxides, and metallic elements are eluted in a reducing atmosphere in which the structures of Fe and Mn oxides are destroyed. OB is a fraction in which metallic elements bond with organic materials and sulfide compounds, where metallic elements are chemically stable but gradually eluted under an oxidizing atmosphere. RES is a fraction where metallic elements are chemically stable, and it is not likely that metallic elements are released and dispersed into the environment. Radioactive caesium was detected in the OX, OB, and RES fractions in both samples, but not in the IE and CB fractions. In other words, radioactive caesium was found in sediments in a state that is not easily dissolved in water. This result was similar to extraction result by adsorption experiment.²⁵⁾ With increased days, radioactive caesium concentrations

Fig. 5 Temporal changes of ^{134}Cs (○) and ^{137}Cs (●) concentrations in sediment sampled at Shukugawara. *: Sampled at August 26, 2015. Error bar: Standard deviation.

Table 4 Chemical form of ^{137}Cs in sediment sampled at Shukugawara

Sampling date	Elution ratio, %				
	IE	CB	OX	OB	RES
May 14, 2013	0	0	24.4	12.5	63.1
August 26, 2015	0	0	20.1	3.0	76.9

IE: Ion-exchangeable, CB: bond to carbonates, OX: bond to Fe and Mn oxides, OB: bond to organics and sulfide compounds, RES: residuals.

of OX and OB fractions decreased, while radioactive caesium concentration in the RES fraction increased. Radioactive caesium in the soil tended to increase with the number of days (since the nuclear accident) in the insoluble RES fraction.¹¹⁾ We guess that the radioactive caesium in the RES fraction of sediment sample is chemically stable with lapse of time.

3.5 The relationship between radioactive caesium in sediments and sediment components

Since certain sediment components might contribute to maintenance of radioactive caesium, we investigated the relationship between dissolved caesium concentrations with constituent elements and crystal phase. First, we analyzed the constituent elements of sediments using X-ray fluorescence analysis. Fig. 6 shows the relationship between ^{137}Cs concentration in sediments and K, Ti, Mn, Fe, Zn,

Rb, Sr, and Zr concentrations. The concentration of ^{137}Cs showed a negative strong correlation with alkali metals (K and Rb) concentration ($r_K = -0.724$ and $r_{\text{Rb}} = -0.767$), and a positive strong correlation with Mn, Fe and Zn concentration ($r_{\text{Mn}} = 0.906$, $r_{\text{Fe}} = 0.932$ and $r_{\text{Zn}} = 0.854$). Sediments mainly consist of minerals and organic materials. Since K, Mn, Fe, Zn, and Rb are commonly contained in minerals, adsorption of radioactive caesium to sediments is highly influenced by the mineral species that constitute the sediments. Therefore, we conducted a crystal phase analysis of sediments. Fig. 7 shows X-ray diffraction patterns of sediment samples collected in November 2013. Quartz (SiO_2), plagioclase ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$), halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), biotite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH},\text{F})$ - $\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH},\text{F})_2$ - $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH},\text{F})_2$), muscovite ($\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$), and kaolinite ($\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$) were detected. Minerals that contain K and Fe were detected, but minerals containing Mn, Zn, and Rb were not detected. This is because those concentration was extremely low. Biotite is a mineral that contains both K and Fe, and radioactive caesium is easily adsorbed onto this mineral.²⁶⁾ Since ^{137}Cs concentration had a negative correlation with K concentration and a positive correlation with Fe

Fig. 6 Relationship between ^{137}Cs concentrations with K, Ti, Mn, Fe, Zn, Rb, Sr, and Zr concentrations in sediment. Error bar: Standard deviation.

Fig. 7 X-ray diffraction pattern of sediment sampled at Shukugawara, Tama river. Bi: Biotite, Hal: Halloysite, Ka: Kaolinite, Mus: muscovite, Pl: Plagioclase, Qtz: Quartz.

concentration, it is likely that radioactive caesium substitutes for the K ions in biotite or is adsorbed *via* lattice defects. It is considered that because of magnetic interaction with Fe, radioactive caesium is first adsorbed onto the sediment's surface and then gradually incorporated into the crystal lattice of minerals and becomes stable.

4. Conclusions

We conducted monitoring of radioactive cae-

sium in the Tama river, which is a low-dose area, to track the behavior of radioactive caesium. The concentration of radioactive caesium in river water and sediment decreased exponentially in a short period of time less than half-life. Radioactive caesium concentration was found to be highest in sediments, followed by the dissolved and then suspended state. When sequential extraction analysis was performed on the sediments, radioactive caesium was present in a stable chemical form but not in a water-soluble

form. As a result of elemental analysis, concentration of radioactive caesium in sediment had strong correlations with K, Mn, Fe, Zn, and Rb concentration. In addition to this, from the results of crystal phase analysis, there is possibility that radioactive caesium was incorporated in biotite.

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要 旨

多摩川における放射性セシウムの定点観測とキャラクタリゼーション

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多摩川中流域で定点観測を実施し、河川水及び底質中の放射性セシウムの挙動を2012年から2016年にかけて調査した。河川水及び底質中の放射性セシウム濃度は、時間とともに減少した。これらの放射性セシウムの滞留半減期は¹³⁴Csで0.778–1.50年、¹³⁷Csで1.22–2.17年であり、放射性セシウムの風化現象が確認された。雨により水中が懸濁すると、懸濁態放射性セシウム濃度が一時的に増加した。一方、溶存態放射性セシウムはこの影響を受けなかった。放射性セシウム濃度は河川水よりも底質の方がかなり高く、多摩川の放射性セシウムの多くが底質に存在していた。底質に関して逐次抽出、元素および結晶相分析を行い、放射性セシウムの化学状態と底質への吸着メカニズムを調査した。底質中の放射性セシウムは安定した化学形態で存在しており、バイオタイトが放射性セシウムを取り込んでいる可能性があった。