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Linking heterogeneous distribution of radiocaesium in soils and pond sediments in the Fukushima Daiichi exclusion zone to mobility and potential bioavailability

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ABSTRACT

During the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 significant amounts of radiocaesium were released into the atmosphere from the reactor units 1, 2 and 3. This caused a non-uniform deposition, in composition and direction, of ¹³⁴Cs and ¹³⁷Cs in the near field (<30 km) from the reactors. In this work, we elucidate the influence of speciation, including radioactive particles, on mobility and potential bioavailability of radiocaesium in soils and sediments from sites located in different directions and distances from the FDNPP. Samples collected in September 2016 were characterized and subjected to sequential chemical extractions and simulated gastrointestinal fluid leaching, and the ¹³⁷Cs and ¹³⁴Cs activities were determined in bulk, grain-size and extracted fractions. The results show that radiocaesium was mainly irreversibly bound and in an inert form. Combined, the two forms contained >90% of the activity present in soils and ~84% in sediments. Digital autoradiography revealed that the inert fraction was predominantly associated with heterogeneities, an indication of radioactive particles. The frequency of heterogeneities was correlated with ¹³⁷Cs activity concentrations, and both were in agreement with the ambient equivalent air doses measured *in situ* during sampling. Moreover, *in situ* gamma spectrometry measurements were used in the InSiCal software tool to derive ¹³⁴Cs and ¹³⁷Cs surface contamination. Soil activity concentrations and contamination density estimations, decay-corrected to the day of the FDNPP accident, resulted in ¹³⁴Cs/¹³⁷Cs ratios that match the reported release and deposition plumes from the reactor units. Overall, these results demonstrate the persistence of the particle contamination in the Fukushima near field and highlight the importance of including radioactive particles in environmental impact assessments.

1. Introduction

Following a severe nuclear event such as the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in March 2011, a significant portion of the released radionuclides is expected to be in the form of discrete radioactive particles of various sizes and compositions (Salbu et al., 2015), which may contribute to the inhomogeneous dispersal and distribution of contamination in the environment (IAEA, 2011). The total fission and activation products released from the FDNPP accident (mostly as aerosols or in a gaseous form) was estimated to be 9×10^{17} Bq

(UNSCEAR, 2014). The atmospheric releases occurred from reactor units 1, 2, and 3, of which 6 to 20×10^{15} Bq was estimated to be ¹³⁷Cs (UNSCEAR, 2014). The main deposition of radionuclides occurred via wet and dry processes during different phases of the accident, with ¹³⁷Cs levels of up to several MBq/m² measured in proximity to the FDNPP in the spring and summer of 2011 (IAEA, 2015). These release and deposition conditions resulted in a non-uniform radionuclide distribution, with regards to composition and direction, in the near field from the reactors (<30 km), but also in the contamination of large areas (50–70 × 20 km) in a north-western direction from the FDNPP (Hirose,

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2012; Saito et al., 2015). A variety of radioactive particles containing radioactive caesium isotopes, uranium, and a series of stable elements were formed during the accident under specific conditions involving interactions between volatile radionuclides and internal materials from inside the nuclear reactor containment (Abe et al., 2014; Adachi et al., 2013; Igarashi et al., 2019; Martin et al., 2019; Miyamoto et al., 2014; Ochiai et al., 2018; Salbu and Lind, 2016; Satou et al., 2016; Yamaguchi et al., 2018).

Formation of radionuclide containing particles in a major, accidental nuclear release can result from the destruction and liquefaction of the fuel matrix (occurring at high temperature and pressure) with a preferential release of volatile radionuclides such as Cs. This can be followed by clustering, condensation, and/or interactions with available surfaces upon cooling during dispersion (IAEA, 2011; Salbu et al., 2015). The source term and release scenario will define the particle's specific characteristics, such as elemental composition, particle size, structure, and oxidation state. These characteristics together with environmental conditions will control particle weathering. Moreover, these radioactive particles, which behave differently from ionic species, often carry a substantial fraction of radioactivity and can be subjected to re-suspension, atmospheric, and water transport, potentially leading to heterogeneous contamination. Failure to consider radioactive particles in environmental radioactivity calculations (which often assume that radionuclides are homogeneously distributed as simple atomic species) can lead to large uncertainties and significant errors in contamination risk and biological impact assessments (Salbu, 2009).

Deposited radioactive particles (i.e., entities in the size range 0.45 μm –2 mm) are usually considered inert under environmental conditions (Salbu et al., 2015) and can be retained in soils and sediments, acting as sinks that delay ecosystem transfer until particle weathering occurs. However, subsequent remobilisation processes may cause these contaminated soils and sediments to become a diffuse source of radionuclides (Salbu et al., 2015). Furthermore, radioactive particles can be taken up and retained by biota such as filter-feeders (e.g., blue mussels), soil dwelling organisms (e.g., snails), or grazing mammals (Salbu et al., 2018). In the latter case, the released radionuclides absorbed through the animal's gastro-intestinal tract can be further transported to muscle and milk, whereas particles retained in molluscs may be directly consumed. Both transfer scenarios can become a pathway by which humans can be exposed, for instance, to radiocaesium (Salbu, 2009). Therefore, a better knowledge and understanding of particle characteristics, weathering, uptake, remobilisation and bioavailability is essential to assess the long-term behaviour and impact of radioactive particles found within contaminated environments.

To elucidate the role of radioactive particles on mobility and potential bioavailability of radiocaesium in soils and sediments from the Fukushima Exclusion Zone (FEZ), we collected samples in September 2016 from highly contaminated locations south, northwest, and west of the FDNPP. Our aim was to evaluate the potential mobility and bioavailability of radiocaesium, determine the reversible and irreversible interactions of radiocaesium with soil and sediment components, and study the link between inhomogeneous radiocaesium distributions and the inert fraction in soils and sediments. To accomplish these aims, soil and sediment samples were characterised and leached following two different procedures: i) a simulated gastrointestinal tract fluid, and ii) a 6-step sequential chemical extraction. Digital autoradiography was used to study the presence and distribution of radiocaesium containing particles in bulk, particle-size fractions, and extracted residues, and to estimate the particle frequency at each sampling site. Additionally, radiocaesium activity concentration in soils and sediments were evaluated relative to field ambient dose rates, estimated surface contamination densities derived from laboratory measurements and *in situ* gamma spectrometry, and reported radiocaesium deposition.

2. Materials and methods

2.1. Site locations and sampling

Soil and sediment samples were collected between September 22nd and 27th, 2016 at 17 sampling sites within 8 different areas within the FEZ (ca. 30 km around the damaged FDNPP). These sites were located at different distances and directions from the FDNPP reactors within the main known plume directions towards the south and northwest (Table 1). The sampling site locations were plotted on a general high resolution satellite image map (sources: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN; accessed June 2018) and an image reflecting the situation at the time of fieldwork near the reactor (WorldView3, 10th September 2016, bands 5/3/2). In addition, ¹³⁷Cs deposition isolines were derived from region-wide surveys carried out after the FDNPP accident (UNSCEAR, 2014) and plotted on the same satellite image (Fig. 1).

At the soil sampling sites, the ground surface was surveyed with a hand-held dosimeter (Automess) to locate spots of activity significantly higher than the background in that area. In these "hot spots", soil samples were collected using either clean sample jars ($\varnothing$ 4.82 cm) as corers down to a depth of 3 or 6 cm, or a corer ($\varnothing$ 11 cm) to a 5 cm depth. In some cases, multiple cores of the same depth were taken, and the soil was mixed in clean zipped plastic bags. In other cases, a hand trowel was used to collect surface litter and the top soil layer, or the top 5 cm of a delimited 20 $\times$ 20 cm surface. Sediment samples were collected in two irrigation ponds within the FEZ, Inkyozaka (#16) and Suzuuchi (#18), and the Abukuma River in Fukushima City (control site, #19) using a 4.3 cm diameter corer. All samples were stored in zipped bags at 4 $^{\circ}\text{C}$ from the sampling day until the day of analysis.

2.2. Field dose rate measurements and *in situ* gamma spectrometry

Ambient equivalent dose rates for ¹³⁷Cs were obtained through various hand-held radiation dosimeters (Automess, Radiagem, FLIR) in $\mu\text{Sv/h}$ at the sampling sites (Table 1). The field (*in situ*) gamma spectrometry measurement system consisted of a GR1-A+ detector (1 cm^3 cadmium zinc telluride (CZT) crystal; Kromek, UK) mounted on an extendable rod protruding from a tripod at 1 m height above the ground surface and connected to a portable computer. This relatively small and light detector has semiconductor properties with a resolution of $\sim 1.8\%$ at 661.6 keV and 1% of the sensitivity of a typical 25% p-type HPGe detector. Spectra were acquired using Kromek's Multispect software such that a satisfactory number of net counts ($\sigma_A = (\sqrt{X})/t < 0.6$) were accumulated in the ¹³⁷Cs and ¹³⁴Cs energy peaks (661.6 and 796 keV, respectively). Subsequently, surface contamination densities of ¹³⁷Cs and ¹³⁴Cs were derived from the net counts of these photopicks using the software InSiCal (Mauring et al., 2018) for two groups of sampling sites categorised according to their proximity to one another (#1–5, within 120 m; and #9–12, within 20 m; Table 1). The range of soil densities measured across each group was combined with three source models (i.e., exponential distribution, 3 cm depth slab, 6 cm depth slab; based on measured ¹³⁷Cs activity concentrations, Table 1), and used in InSiCal to derive ¹³⁷Cs and ¹³⁴Cs contamination densities for individual sites within each site group. Additionally, the contamination inventory (kBq/m^2) was calculated in a "traditional" manner from soil measurements (i.e., activity, Bq/g; average density across the site group, g/cm^3 ; sample depth, taken as 6 cm) and compared to the three InSiCal model estimations. More details concerning the application of InSiCal in the derivation of contamination densities can be found in the Supporting Information.

2.3. Solid phase characterisation

Samples were thoroughly homogenized by manually mixing the content of the original sampling jar or bag and then a fraction was taken

Table 1
Sampling site details (site number - Fig. 1, location coordinates, distance and direction from FDNPP reactor, measured ambient equivalent dose rates), sample details (label number, sampling date, description and analyses performed), sample characterisation results and radiocaesium activity concentrations.

Site details						Sample details				Solid phase characterisation ^b					Activity concentration (Bq/g) ^c	
#	latitude	longitude	distance (m)	direction	μSv/h	#	2016 date	Description	Analyses ^a	pH	Org. (%)	Sand (%)	Silt (%)	Clay (%)	¹³⁷ Cs	¹³⁴ Cs
1	37°25'29.4"N	141°01'0.11"E	1452	WNW	7.4	1a	25/9	Litter, surface	AR	–	–	–	–	–	–	–
						1b	25/9	Soil, 0–3 cm	AR	–	–	–	–	–	263 ± 7	23 ± 1
						1c	25/9	Soil, 0–6 cm	–	4.6	21	45	51	4.6	236 ± 6	22 ± 1
2	37°25'30.61"N	141°01'4.33"E	1411	WNW	5.0	2	25/9	Soil, 0–6 cm	SF, GI, AR	4.6	11	73	17	10	63 ± 11	5.2 ± 0.9
3	37°25'30"N	141°01'6"E	1375	WNW	7.4	3	25/9	Soil, 0–3 cm	–	4.9	33	90	8	2.4	389 ± 6	33 ± 0.8
4	37°25'31.01"N	141°01'07.67"E	1337	WNW	8.2	4a	25/9	Litter, surface	AR	–	–	–	–	–	–	–
						4b	25/9	Soil, 0–6 cm	AR	4.1	33	90	9	1.4	91 ± 3	7.9 ± 0.5
						5b	25/9	Soil, 0–6 cm	AR	4.6	22	43	41	16	308 ± 8	26 ± 1
5	37°25'33.77"N	141°01'09.53"E	1331	WNW	12.8	6a	27/9	Soil, 0–3 cm	SF, GI, AR	5.3	47	71	28	0.1	368 ± 9	33 ± 1
						6b	27/9	Soil, 0–6 cm	SF, GI, AR	5.3	48	42	53	4	298 ± 1	27 ± 1
						7a	27/9	Soil/gravel, 0–5 cm	SE, AR	7.4	5.0	63	27	10	349 ± 9	40 ± 1
6	37°23'58.32"N	141°02'0.31"E	2371	SSE	16.8	7b	27/9	Soil/gavel, 5–10 cm	SF, GI, AR	7.2	3.8	86	13.5	0.8	785 ± 20	103 ± 3
						7c	27/9	Soil/gravel, 10–15 cm	–	6.9	5.0	78	17	4.9	1321 ± 34	126 ± 3
						8	25/9	Soil, surface	SE, AR	6.6	15	84	12	4.1	224 ± 6	22 ± 1
7	37°24'25.25"N	141°41'59.89"E	1541	SSE	73.5	9a	24/9	Soil, 0–2.5 cm	AR	7.1	3.6	78	21	0.9	17.6 ± 0.7	1.9 ± 0.1
						9b	24/9	Soil, 0–5 cm	–	7.3	2.9	77	22	1.5	20.1 ± 0.5	2.0 ± 0.1
						10a	24/9	Soil, 0–2 cm	–	5.0	14	55	44	1.4	54.0 ± 2.4	5.4 ± 0.1
8	37°25'54"N	141°00'43"E	1452	WNW	62.0	10b	24/9	Soil, 0–3 cm	–	5.1	13	58	41	1.0	45.3 ± 0.9	4.3 ± 0.1
						10c	24/9	Soil, 0–6 cm	SE, AR	4.6	7.8	59	40	1.2	6.8 ± 0.2	0.6 ± 0.1
						11a	24/9	Soil, 0–3 cm	–	5.4	36	77	21	1.8	114 ± 25	9.4 ± 1.8
9	37°24'52"N	140°56'20"E	7842	WSW	1.7	11b	24/9	Soil, 0–6 cm	–	5.2	42	80	19	0.9	134 ± 2	11.6 ± 0.1
						12a	24/9	Soil, 0–3 cm	–	5.3	12	78	20	2.9	30 ± 1	2.6 ± 0.1
						12b	24/9	Soil, 0–6 cm	–	5.1	21	58	39	3.0	40 ± 1	3.3 ± 0.1
10	37°24'55"N	140°56'40"E	7834	WSW	2.2	13	27/9	Soil, surface	SE, AR	6.0	11	82.7	13.2	4.1	680 ± 17	–
11	37°24'58"N	140°56'39"E	7855	WSW	2.5	14	23/9	Soil, surface	–	–	–	–	–	–	3045 ± 78	256 ± 7
						16a	23/9	Soil, 0–5 cm	–	4.1	21	54	32	14	113 ± 9	11.1 ± 0.3
						16b	23/9	Sediment, surface	SE, AR	4.7	8.6	36	57	7.3	80 ± 2	7.6 ± 0.3
12	37°25'0.8"N	140°56'39.7"E	7842	WSW	1.9	16c	22/9	Soil, 0–5 cm	–	4.7	34	83	16	0.8	305 ± 15	26.8 ± 1.3
						16h	23/9	Soil, 0–5 cm	–	3.9	57	81	19	0.5	174 ± 5	14.1 ± 0.2
						16k	23/9	Soil, 0–5 cm	SF, GI, AR	5.2	20	76	23	0.4	142 ± 1	13.0 ± 0.7
13	37°24'33"N	141°01'44"E	1349	SSW	63.5	16n	23/9	Soil, 0–5 cm	SF, GI, SE, AR	4.3	8.1	92	8	0.04	41 ± 8	4.1 ± 0.6
						16o	23/9	Sediment, 0–1 cm	SF, GI, AR	4.8	7.7	87	13	0.01	94 ± 2	–
						16p	23/9	Sediment, 1–2 cm	SF	4.8	6.7	85	15	0.1	90 ± 2	–
14	37°24'33.18"N	141°01'43"E	1291	SSW	18.0	16q	23/9	Sediment, 2–3 cm	SF	4.8	5.1	91	9	0.05	66 ± 2	–
						17–3	25/9	Soil, 0–20 cm	–	4.9	50	78	20	2.0	1162 ± 26	106 ± 4
						17–cc	25/9	Soil, 0–20 cm	–	4.8	61	79	19	1.7	1244 ± 36	108 ± 3
15	37°25'30.58"N	141°01'2.07"E	1464	WNW	8.0	17–rr	25/9	Soil, 0–20 cm	–	4.8	63	77	21	2.1	1289 ± 10	114 ± 3
						17–t	25/9	Soil, 0–20 cm	SF, GI	5.2	47	83.8	15.8	0.4	1110 ± 29	105 ± 3
						17–v	25/9	Soil, 0–20 cm	AR	–	–	–	–	–	1263 ± 32	104 ± 3
16	37°24'33.18"N	141°01'43"E	1291	SSW	18.0	17–yy	25/9	Soil, 0–20 cm	SF, GI, AR	5.4	56	78.9	20.4	0.7	1069 ± 27	105 ± 3
						18b	22/9	Soil, surface	SE, AR	6.2	14	63	25	12	330 ± 1	31.7 ± 0.5
						18d	22/9	Soil, 0–5 cm	–	6.1	11	67	22	11	309 ± 4	31.8 ± 0.5
17	37°27'56"N	140°54'24"E	10561	WNW	19.2	18e	23/9	Sediment, 0–1 cm	SF, GI, AR	4.9	9.1	65	34	1.2	149 ± 4	–
						18f	23/9	Sediment, 1–2 cm	SF, GI	4.9	9.9	50	47	3.1	164 ± 4	–
						18g	23/9	Sediment, 2–3 cm	SF, GI, AR	4.9	9.7	51	46	3.1	172 ± 4	–
18	37°24'56.2"N	140°58'49.14"E	4690	WSW	d	19a	22/9	Sediment, 0–1 cm	SF, GI	6.3	8.8	57	42	0.4	1.73 ± 0.04	–
						19b	22/9	Sediment, 1–2 cm	SF, GI	6.2	11	54	46	0.5	2.73 ± 0.07	–
						19c	22/9	Sediment, 2–3 cm	SF, GI	6.1	7.2	74	26	0.3	1.23 ± 0.03	–

^a Type of analysis performed on samples: SF = activity concentration in size fractions, GI = simulated gastrointestinal fluid extractions, SE = sequential extractions, AR = autoradiography.

^b When organic matter content was >25%, the grain-size analysis was performed in ashed samples, thus results must be regarded as indicative.

^c Measured in November 2018.

^d No ambient dose rate measurements available.

Fig. 1. Location of sampling sites within the Fukushima exclusion zone (site numbers), ambient equivalent dose rate measurements in $\mu\text{Sv/h}$ at 1 m above ground (yellow circles; values in Table 1), and ^{137}Cs deposition in kBq/m^2 (colour isolines) derived from region-wide surveys carried out after the FDNPP accident (UNSCEAR, 2014). Sites #1–5 and #16 are by the Inkyozaka irrigation pond, and site #18 by the Suzuuchi irrigation pond. No ambient dose rate was available for site #18. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

to freeze-dry (20–90 h; Epsilon 2–4 LSCplus, Martin Christ). Dried samples were sieved to $<2\text{ mm}$ to discard stones and large pieces of debris, and subsamples were used for general characterisation and leaching experiments. Wet homogenized subsamples, taken before freeze drying, were used for sequential extraction experiments. Water content was determined by the weight difference before and after freeze-drying to correct wet masses.

Soil and sediment pH was measured in 1:2 solid:solution volume ratio mixtures after overnight equilibration using a daily calibrated pH meter (WTW InoLab). Freeze-dried subsamples (1–5 g) were dried overnight at 105°C followed by equilibration in a desiccator and then ashed in a furnace (CWF 1200, Carbolite Gero) at 550°C for 20 h. Ashed samples were weighed and the percentage loss-on-ignition (LoI) provided the organic matter content. If this content was $<25\%$, grain-size distribution was determined with new freeze-dried subsamples (2–5 g) from which the organic matter was removed by heating with H_2O_2 until the end of reaction. Otherwise, the ashed samples were used to obtain indicative grain-size distributions only. The organic-free subsamples were wet sieved with MilliQ water to separate the sand fraction (2 mm – $63\text{ }\mu\text{m}$), and the resulting slurry was mixed again and allowed to settle. After 4 h, the top 5.18 cm was collected to separate the suspended clay ($<2\text{ }\mu\text{m}$) from the sedimented silt (63 – $2\text{ }\mu\text{m}$). This separation was repeated 4 times. Finally, the three fractions were dried in an oven at 105°C and the relative fractions (in %) were calculated from dry weights.

2.4. Leaching experiments

2.4.1. Simulated gastrointestinal fluid extractions

To estimate the bioavailable ^{137}Cs fraction in Fukushima soils and sediments respect to potential ingestion, leaching experiments simulating extractions occurring in human digestive systems were carried out with 12 samples from 6 sites (Table 1). Subsamples (ca. 1 g) were weighed into acid-washed centrifuged tubes (Nalgene) and reacted for

65 h with 10 mL of 0.16 M HCl, which simulates the extracting strength of human gastrointestinal tract fluid. These conditions mimic the maximum transit time through the intestines (Darley et al., 2003). Solution extract was separated from solids by centrifugation (10,000 g, 30 min; Beckman Coulter Allegra 64R centrifuge) and both were measured for ^{137}Cs activity by gamma spectrometry (section 2.5).

2.4.2. Sequential chemical extractions

To study the solid phase interactions of ^{137}Cs in the Fukushima soils, a modified 6-step sequential chemical extraction procedure based on Tessier’s methodology (Oughton et al., 1992) was applied to 7 samples from 6 sites (Table 1). Triplicate wet subsamples (2 g) were weighed into acid-washed centrifuge tubes (Nalgene) and measured on a NaI detector to determine the initial ^{137}Cs activity concentration (section 2.5). Then, and throughout the different extraction steps (Table 2), reagent solutions were added in a 1 g: 10 mL ratio and reacted at room temperature

Table 2
Experimental details (reaction solution, temperature and time) used at each step of the sequential chemical extractions and the associated compound fraction.

Step	Extraction solution	Temperature	Reaction time (h)	Associated fraction
1	H_2O	RT	1	water-soluble
2	1 M NH_4Ac (pH 7)	RT	2	exchangeable
3	1 M NH_4Ac (pH 5)	RT	2	pH sensitive
4	0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HAc (pH 3)	80°C	6	slightly reducible
5	30% H_2O_2 (pH 2)	80°C	5.5	oxidizable
	3.2 M NH_4Ac in 20% (v/v) HNO_3 , H_2O	RT	0.5	
6	7 M HNO_3	80°C	6	strongly oxidizable
Residue				non-soluble, inert

in a roller mixer (steps 1–3) or heated in a water bath (steps 4–6). After reaction, the suspensions were centrifuged at 10,000 g for 25 min. The supernatants were filtered by gravity through a 110 mm diameter filter paper (Whatman) and collected directly into 20 mL LSC polyethylene vials. In steps 3–6, the solid residues were additionally washed with 10 mL MilliQ water, hand-shook and centrifuged for 15 min, and the supernatants were filtered through the same filter paper and collected in a new LSC vial. The remaining solid residues and filter papers from step 6 were transferred to another LSC vial. Additionally, 3 method blanks were prepared in parallel by following the same sequential extraction procedure but without the solid phase. The ^{137}Cs and ^{134}Cs activity was determined in all fractions (i.e., supernatant extracts and solid residues of all samples and blanks; section 2.5) and its distribution was calculated with respect to the total activity (in %) as reversibly bound or bioavailable (steps 1–3), irreversibly bound (steps 4–6), and non-soluble or inert (residual fraction).

2.5. Radiocaesium activity concentration

The total ^{137}Cs and ^{134}Cs activities in bulk samples and associated leaching fractions were determined by gamma spectrometry using a well-type NaI detector (PerkinElmer Wizard2® 2480 automatic gamma counter). Solutions of known ^{137}Cs , ^{134}Cs , and $^{137}\text{Cs}+^{134}\text{Cs}$ activity were used as standards for quality control (energy peak, energy window, counting efficiency) of the instrument pre-set counting protocol. Samples were counted for 5 min (bulk samples) or 1–2 h (leaching experiment extracts), which provided an acceptable analytical precision of <1.5% (bulk) or <10% (extracts) counting uncertainty for activities >4 Bq, and ~25–30% (extracts) for lower activities. The background activity obtained from 3 to 10 empty vials measured on the same run as the samples was subtracted from the measured ^{137}Cs and ^{134}Cs counts per minute (cpm), followed by an efficiency correction of 30.2% and 17.4% ($\pm 0.2\%$; $n = 8$), respectively. The activity concentration (Bq/g) in each sample was calculated from corrected cpm with respect to dry mass. A certified reference material containing ^{137}Cs (IAEA-300 sediment) was measured with the same counting protocol as the samples to verify the counting accuracy and activity concentration calculations. The limit of quantification (LOQ) was calculated as 14.1 times the activity's uncertainty of background measurements ($\sigma_A = (\sqrt{X})/t$), resulting in ca. 0.04 Bq for both ^{137}Cs and ^{134}Cs .

Despite the lower measurement uncertainties (<3%) for similar counting times at low activities (<2 Bq) offered by a Ge-detector, a NaI detector with an automatic sampler was preferred here due to the high number of samples generated in the leaching experiments. Nonetheless, to further evaluate the accuracy of the NaI detector's measurements, $^{134}\text{Cs}+^{137}\text{Cs}$ standard solutions of two different activities (45 and 300 Bq) and 5 samples of 0.5–630 Bq were also measured in a Ge-detector (Canberra GL, 2020R LEGe coaxial detector equipped with Ortec GammaVision V7 software). Measurements of both standard solutions were always within $\pm 1\%$ between detectors, whereas results for samples of >1 Bq were within an acceptable error (<14%; slope of 1.11, $R^2 = 0.9987$). Activities <1 Bq were approaching the LOQ of the NaI detector and thus measurements presented a higher measuring uncertainty. In addition, these full γ -spectra also served to screen for other potential radionuclides present in the samples.

2.6. Radioactivity distribution and particle identification

Digital autoradiography was used as an imaging technique for the identification of inhomogeneous radioactivity distributions and radioactive particles in 18 samples from 13 sites before and/or after leaching (Table 1). Known amounts of dry samples (0.5–2 g) were thinly spread on 20×10 cm double-sided adhesive pieces, which were then fixed on white cardboard sheets and wrapped with commercial cling film to avoid sample displacement and cross contamination. The samples were then exposed to radiation sensitive films (digital phosphor imaging

plate, Molecular Dynamics, Amersham Pharmacia Biotech) inside a sealed exposure cassette, which was placed between lead sheets in a dark room to reduce external interferences. Exposure time was 3 days, except for low activity samples, which were exposed for 1 week. The photo-stimulated luminescence (PSL) signals (autoradiography images or autoradiograms) were obtained by scanning the exposed plates on a portable imaging plate scanner (HD-CR 35 NDT, Dürr NDT, Germany) with a $50 \mu\text{m}$ pixel size resolution. Autoradiography images were analysed using an imaging software (ImageJ 1.52h; open source, <http://imagej.nih.gov/ij/>). Images were inverted and the background signal was removed by manually setting an intensity threshold. High PSL intensity spots were associated to radioactive particles by applying a further threshold based on a 25–5000 pixel area and a 0.1–1 sphericity requirement. Subsequently, spots within these criteria were counted automatically by the software. Intensity surface plots showing the relative PSL intensity (energy deposited per unit area) over the sample area were used to visually identify the radioactive particles.

3. Results

3.1. Dose rates and contamination densities

The highest ambient equivalent dose rates (>60 $\mu\text{Sv/h}$) were measured at sites located south and northwest of the FDNPP, whereas remote sites towards the west were associated with levels lower than 2.5 $\mu\text{Sv/h}$ (Fig. 1, Table 1). It is worth noting that site #17, located 10.5 km on a northwest direction from the reactor, was characterised by an intermediate dose rate of ~20 $\mu\text{Sv/h}$.

Contamination densities for ^{137}Cs derived from the three InSiCal models were similar (Table S1 in SI), and thus the calculations were insensitive to whether a slab of contamination or exponential distribution was assumed or whether the slab thickness estimation varied within a few centimetres. These ^{137}Cs , as well as ^{134}Cs , contamination densities were in good agreement with the “traditional” method calculations when the contamination density was lower than ~1200 kBq/m². However, at higher values, they differed by a factor of 1.9–4.5. This direct comparison was regarded as indicative only since the soil density data was limited and no uncertainty estimate was made (Table S1 in SI).

3.2. Soil and sediment characterisation

Characterisation analyses (Table 1, Fig. 2) showed that the pH ranged between 3.9 and 7.4 for soils, whereas sediments exhibited a pH of 4.8 ± 0.1 . The organic matter content was in general lower for the sediments ($8 \pm 2\%$, $n = 10$) than the soils, which ranged from 3 to 33% ($n = 33$) with samples from sites #6 and #17 containing up to 50–60% organic matter. The main grain-size fractions in both soils and sediments were sand (42–92%) and silt (8–57%), with a very low content of clay (0.02–16%; median = 1.5%, $n = 43$). The total ^{137}Cs activity concentrations were comparable among samples taken at the same site area, but varied over 3 orders of magnitude across sites, with the highest activity concentrations (700–3000 Bq/g) measured in samples from site #17 (10.5 km northwest) and hot-spots found in sites #7, #13 and #14 (1.5 km south). Soils from 1 km further south (#6) were characterised by lower activities, similar to the 40–400 Bq/g measured in soils and sediments taken as near as 1.5 km northwest (#1–5, #8, #16) and as far as 4.5 km west (#18) from the reactor. The most western sites (#9–12) presented even lower activity concentrations (10–140 Bq/g). For all sites, the average sample activity concentration was 20–500 times higher than the <3 Bq/g measured in the river sediments taken outside the FEZ, 63 km northwest from the reactor (site #19).

The distribution of ^{137}Cs activity (Bq/sample) according to grain-size exhibited a general trend for soils from different sites (Fig. 2 A), with the ^{137}Cs activity almost equally distributed between sand and silt fractions (median of ca. 50 and 45%, respectively) despite the significantly higher sand fraction (>75% vs. 10–25%). The sediment collected in site #16

Fig. 2. Distribution of grain-size fractions (sand, 2 mm–63 μm ; silt, 63–2 μm ; clay, <2 μm) and their associated ^{137}Cs activity for: (A) soils samples #2 (0–6 cm), #6a and #6b (0–3 and 0–6 cm), #7b (5–10 cm), #16k and #16n (0–5 cm), and #17-t and #17-yy (0–20 cm), (B) sediments (0–1, 1–2 and 2–3 cm) from sites #16 and #18 (samples #16o, 16p, 16q and #18e, 18f, 18g, respectively). Initial total ^{137}Cs activity concentrations are reported in Table 1.

exhibited a similar grain-size distribution to the soils (85% sand, 15% silt), but the ^{137}Cs activity was mainly present in the sand fraction (~80%; Fig. 2 B). In contrast, site #18's sediment activity was almost equally distributed between sand and silt (similar to the soil samples) and so were the sand and silt fractions (55 and 40%, respectively; Fig. 2 B). Since the clay fraction mass was very small (0.3–30 mg), the associated activity concentration was relatively high in some cases (197–12,870 Bq/g). However, in all cases, the ^{137}Cs activity associated with the clay fraction (1–103 Bq) represented <5% of the total activity in a given soil or sediment sample.

The ^{137}Cs activity measurements for soil samples corresponding to 5–6 cm depth were generally similar to those obtained for the top 2.5–3 cm (sites #1–5 and #16, #6, #9–12), as well as to the first 3 cm of the sediment profiles collected at sites #16 and #18 (Table 1). Only site #7 presented a 3.5-fold increase in activity in the 15 cm depth profile.

3.3. Leaching experiments

Leaching with simulated gastrointestinal fluid during 65 h extracted <3% of the total ^{137}Cs activity in any of the 12 soils and sediments. For the most radioactive samples (e.g., #17), this represented ca. 35 Bq. The total amount of ^{137}Cs leached from any of the soils and sediment (Fig. 3 A) was also low (1–15% of total activity) after sequentially applying water (step 1), exchangeable (step 2), pH sensitive (step 3), and slightly reductive (step 4) extractions. A similarly low fraction (1–8%) was recovered in the oxidizable extraction (step 5). Only treatment with 7 M HNO_3 at 80 $^\circ\text{C}$ (step 6) resulted in a higher extraction of ^{137}Cs from the soils (43–87%). Yet, a significant amount remained in the residual fraction (10–56%). According to these extracted fractions, Cs in soils was thus mainly irreversibly bound (44–89%) or found in an inert form (Fig. 3 B). In contrast, the reversibly- and irreversibly-bound ^{137}Cs fractions of site #16's sediment was significantly lower (11% and 23%, respectively), and most of the activity was measured in the residual fraction (~65%). Overall for the Fukushima soils and sediments, the reversibly-bound fraction was minimal (0.4–11%).

3.4. Activity and particle distribution

Digital autoradiography of soils and sediments before and after sequential extraction experiments revealed clear spots of high intensity PSL signal, potentially associated with radioactive particles (Figs. 4 and 5). Other radionuclides, such as ^{40}K , U, Th or Pu, can also excite imaging plates (Mukai et al., 2014), therefore several full γ -spectra (section 2.5, data not shown) were collected and screened to confirm that no other

Fig. 3. (A) ^{137}Cs activity fractions extracted from 6 soils and 1 sediment (#16b) for each sequential extraction step (S1-6) and the remaining residuals (Rsd). Details of extracting solutions are presented in Table 2. Error bars represent 1 σ of triplicate samples. (B) Distribution of ^{137}Cs (as %) in soils and sediment based on the sequential extraction fractions. Initial total ^{137}Cs activity concentrations are reported in Table 1. Inset numbers represent the $^{134}\text{Cs}/^{137}\text{Cs}$ decay-corrected activity ratio of the inert fraction (as the average (1 σ) of triplicate samples). *Total ^{134}Cs activity for sample #10c was reaching the LOQ.

radionuclides besides ^{134}Cs and ^{137}Cs were at a detectable activity level. Consequently, the PSL signals were associated with radiocaesium.

The autoradiograms showed a distribution of the signal intensity in the different grain-size fractions (Fig. 4) that were in good agreement

Fig. 4. Autoradiography images of bulk and associated sand-, silt- and clay-size fractions of representative soils (#6b, #7b, #16k, #17-yy) and sediments (#16o, #18g) after characterisation analyses. Colour scale represents photo-stimulated luminescence (PSL) signal intensity. Not enough clay fraction sample material was available for sample #7b. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

with the measured activity concentrations, i.e., a slightly higher activity in the silt than in the sand fraction of soils, and *vice versa* in the case of sediments (Fig. 2). All fractions, including the very limited clay fraction, presented high intensity spots, strongly indicating the presence of radioactive particles. Converting the autoradiograms of bulk and residual samples to relative PSL intensity surface plots (Fig. 5) visually demonstrated the presence of heterogeneities as particles. Moreover, the systematic analysis of the autoradiograms showed that bulk samples contained a relatively high particle content (>19 particles/g), with samples of highest activity (e.g., #17-v) featuring the highest number of particles (Table 3). In a few cases for the bulk samples, aggregates of soil and sediments were observed as high PSL intensity spots, which resulted in a higher variability on the particle count (e.g., #4b, #7a, #9a, #14). Remarkably, sequential extraction residuals exhibited between 2.5 and 13.5 times lower particle frequency (2–12 particles/g) than the corresponding untreated bulk samples.

4. Discussion

The ambient equivalent dose rate measurements (5–73 $\mu\text{Sv/h}$ for SSW/SSE and WNW locations and 1.7–2.5 $\mu\text{Sv/h}$ for WSW sites) were in good agreement with the >19 $\mu\text{Sv/h}$ recorded in the south and north-west vicinity of the FDNPP and the lower dose rates (3.8–19 $\mu\text{Sv/h}$) in western locations reported for July 2011 (Saito et al., 2015). These authors showed that air dose rate in the FEZ is largely correlated with the ^{137}Cs deposition density ($R^2 = 0.73$), and that the main contribution

to the effective dose in June 2011 was due to radiocaesium (ca. 71% ^{134}Cs and 28% ^{137}Cs). The ^{137}Cs density calculations from our *in situ* gamma spectrometry measurements resulted in ^{137}Cs levels of a few MBq/m^2 for the locations closest to the FDNPP (sites #1–5), approaching the levels reported for areas in proximity to the accident site shortly after the main radionuclide deposition (IAEA, 2015). Hence, the InSiCal software appeared to provide reliable determinations of contamination level, supporting earlier studies wherein robust estimates of contamination densities from *in situ* gamma ray measurements were made (Mauring et al., 2018).

Additionally, the total ^{137}Cs activity concentrations measured in surface samples (Table 1) and the calculated ^{137}Cs inventories based on their characteristics (Table S1 in SI) fitted reasonably well with the air measurements and surface estimations, and were consistent with the contamination densities mapped from soil measurements reported after the accident (isolines in Fig. 1) (UNSCEAR, 2014). In general, higher ambient dose rate locations were characterised with higher radiocaesium activity, e.g. site #13 or #17, with the exception of forestry sites such as #8. In this site, the ambient dose rate was among the highest (62 $\mu\text{Sv/h}$), yet the surface soil exhibited a moderately low ^{137}Cs activity concentration (~ 225 Bq/g) compared to soils from other sites. This anomaly may be explained by the incorporation of radioactivity above ground within the canopies and trunk of trees and consequent transfer attenuation to the forest floor (Kato et al., 2012a).

The $^{134}\text{Cs}/^{137}\text{Cs}$ deposition density ratio based on a large-scale soil sampling and measurements ($n = 2168$, 100 km radius from FDNPP) was almost constant at 0.91 regardless of the location (Saito et al., 2015). However, the $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratios (decay corrected to the time of the accident) of all our samples varied from 0.90 to 1.45 (Fig. 6 A1). The average ratio of 1.02 ± 0.08 ($n = 33$, excluding site #7) was within the error of 0.97 ± 0.09 obtained in the InSiCal surface estimations (Table S1 in SI), and both are consistent with reported information on released airborne $^{134}\text{Cs}/^{137}\text{Cs}$ (IAEA, 2015) and the estimated inventory released from reactor units 1, 2 and 3 of 0.94, 1.08 and 1.05, respectively (Miyamoto et al., 2014). Air surveys in a <5 km radius from the FDNPP reported isotopic ratios of the radiocaesium deposition of <1.00 (unit 1) in a northwest direction, whereas west and south directions had a combination of 1.00–1.06 (unit 3) and >1.06 (unit 2) (Chino et al., 2016). In our study, activity ratios of bulk samples from sites in both WNW and WSW directions were within error of the reactor unit 1, 2 and 3 inventory ratios (Fig. 6 A1). Only the deeper layers (5–10 and 10–15 cm) of site #7 soil sample, located in a SSE direction, were characterised by a ratio of >1.2 . Thus, overall, there was not a clear trend relating isotopic ratio to direction from FDNPP. It is worth mentioning that the ^{134}Cs activity measurements were carried out after ~ 3.8 ^{134}Cs half-lives since the FDNPP accident, thus the isotopic ratio calculations have a greater associated uncertainty than individual ^{137}Cs activity measurements, especially in the less contaminated sites.

The results for different soils depths showed that the ^{137}Cs activity was, in general, homogeneously distributed in the first centimetres of the soil surface (i.e., 0–6 cm). This is consistent with previous studies showing that 86–90% of the radiocaesium inventory was contained in the upper 2–4 cm of soil sample profiles taken across the Fukushima prefecture within the first 2 years after the FDNPP accident (Kaneko et al., 2015; Kato et al., 2012b; Matsuda et al., 2015). In some exceptional cases, no substantial decrease in the surficial 10 cm was reported despite that ^{137}Cs often exhibited a rapid exponential decrease with depth (Rosenberg et al., 2017). Similar activity profiles were recorded for our urban soils collected near the FDNPP (e.g., #7), which contained higher activity 10–15 cm deeper in the soil (also higher ^{134}Cs activity respect to ^{137}Cs). Similarly, high ambient dose rates were consistently measured from 0 down to 20 cm when sampling in the most distant site (#17, near Omaru Shrine), and for which soil samples contained comparable activity concentrations (1189 ± 89 Bq/g, $n = 6$; Table 1).

This predominance of top surface contamination may favour physical transport and, in turn, result in deposition and accumulation in

Fig. 5. Autoradiography images and associated relative intensity surface plots (3D graphs) of representative “urban” soil (#7a), natural soil (#17-v) and pond sediment (#16b) before (bulk) and after (residual) sequential extraction experiments. Colour scale and surface plots’ z-axis represent photo-stimulated luminescence (PSL) signal intensity. Surface plots’ x-y axes are in pixels with 50 $\mu\text{m}/\text{pixel}$ autoradiography image resolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Number of particles per g of dried mass of bulk and sequential extraction residuals of litter, soils and sediments obtained from autoradiograms analysis. Errors represent 1σ of replicate measurements (bulk) or samples (residuals).

Sample	Particles/g	
#	bulk	residuals
1a ^a	42 $\pm$ 15	–
1b	52 $\pm$ 3	–
2	70 $\pm$ 7	–
4a ^a	28 $\pm$ 3	–
4b	41 $\pm$ 16	–
5b	33 $\pm$ 8	–
6a	46 $\pm$ 6	–
7a	68 $\pm$ 10	9 $\pm$ 2
7b	59 $\pm$ 4	–
8	81 $\pm$ 7	6 $\pm$ 0
9a	19 $\pm$ 8	–
10c	–	2 $\pm$ 1
13	77 $\pm$ 4	11 $\pm$ 4
16b ^b	32 $\pm$ 1	12 $\pm$ 3
16n	53 $\pm$ 3	7 $\pm$ 1
17-v	136 $\pm$ 2	–
18b	–	8 $\pm$ 5
18e ^b	69 $\pm$ 1	–

^a Litter.

^b Sediment.

water catchments. Wakiyama et al. (2017) observed a higher contamination density in the bottom sediments than those in the soils of Suzuuchi and Funasawa reservoir ponds (<4 km from FDNPP on a west direction), suggesting that radiocaesium was transported from the bank and accumulated in the pond. In our study, the sediments at sites #16 and #18 (Inkyozaka and Suzuuchi ponds, respectively) contained comparable levels of ^{137}Cs activity concentrations to those reported by Wakiyama et al. (2017). However, those were of lower activity concentration than the site’s corresponding soils. These differences between studies, together with the variability in depth profiles among the sampling locations, suggests that the local geography and erodibility over time play a role in the distribution of the radiocaesium contamination in subsurface environments.

Retention of radiocaesium contamination will also be affected by characteristics of the soil and sediment. Tanaka et al. (2018) demonstrated that ^{137}Cs presented an equally strong retention in all the different fractions of Fukushima riverbed sediments. Samples analysed in this work were characterised by very low activity associated to clay (Fig. 2), most likely due to the low clay fraction (<5% in 36 out of 43 samples). This grain-size distribution differs from the relatively higher clay content (12–42%) reported for soils of sites at 40–200 km from the FDNPP (Itoh et al., 2014), but is in better agreement to the fractions (8–14% clay, 14–33% silt) reported for 11 soils collected within a 12 km radius from the FDNPP (Saito et al., 2014). The organic content, on the other hand, varied greatly among sites, and urban samples from areas

Fig. 6. Decay-corrected $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratio (A1) and number of particles per g of dry mass (A2) of bulk samples as a function of sampling site's distance from the FDNPP reactor. Samples have been grouped by the site's direction respect to the reactor (symbol colours). Error bars represent 1σ of replicate measurements. Dashed lines in A1 represent activity ratio of FDNPP reactor units' inventory. (B) ^{137}Cs activity concentration as a function of particles per gram of dry mass in bulk and sequential extraction residuals. Full and dashed lines represent the best linear fit to all the data points and its associated 95% confidence level bands, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

near the FDNPP (e.g., sites #7, #13, #14) contained, as expected, a much lower organic content than samples from areas in, or near, forests (e.g., #6, #17). These forest sites were characterised by the presence of a litter layer, which consequently contained a significant fraction of the activity. In fact, over 90% the ^{137}Cs activity in our samples was measured in the larger-sized fractions (i.e., $>2\mu\text{m}$; Fig. 2), which is in agreement with the 80–88% measured in the $>48\mu\text{m}$ fraction reported by Kaneko et al. (2015).

Besides the association of radionuclides with various grain-size fractions, it is also essential to determine solid speciation and reactivity for elucidating radiocaesium behaviour and long-term bioavailability. Previous studies have showed that radiocaesium in Fukushima aerosols, weathered rock, soil and river suspended sediments was of rather low solubility in water over a wide pH range ($<0.8\%$ leached) (Tanaka et al., 2013). The simulated gastrointestinal juice applied to our soils and sediments is a stronger extractant than water, but still resulted in a very low remobilisation of radiocaesium ($<3\%$). Also, small fractions ($<11\%$) were leached during the first sequential extraction steps (using 1 M ammonium acetate), suggesting a low ion exchange of NH_4^+ with sorbed Cs. This is in good agreement with the 10–17% ^{137}Cs associated to the exchangeable fraction in Fukushima soils and sediments reported by other authors and the hypothesis that radiocaesium is largely irreversibly sorbed (Kaneko et al., 2015; Saito et al., 2014; Tanaka et al., 2018). These authors also reported a significant fraction of ^{137}Cs in the corresponding geochemical phases ($>75\%$ in sediments, $>63\%$ in soils), which is in good agreement with our sequential extractions, where $\sim 80\%$ ^{137}Cs for sediments and 89–99% ^{137}Cs for soils was associated with the strongly oxidizable and extraction residue fractions. These results demonstrated that the radiocaesium in the FEZ soils and sediments is mainly irreversibly bound or in an inert form and has a very low bioavailability in the case of ingestion or retention in biota.

It is interesting to note that although the clay fraction was relatively low and there was no clear correlation between clay content and activity concentration of strongly oxidizable and residual fractions ($R^2 \sim 0.15\text{--}0.36$), a high ^{137}Cs activity fraction was present in the irreversibly-bound and inert phases. A relatively small fraction of clay may lead to significant Cs binding to soils and sediments due to the strong adsorption affinity of clays, e.g., submicron-size sheet aluminosilicates forming Fukushima soils (Kaneko et al., 2015). These have been shown to have minimum solubility in water and persist over a long period of time (Itoh et al., 2014; Satou et al., 2016) but can be dissolved with a strong acid and high temperature (Saito et al., 2014), as used in the last step of the sequential extraction procedure. In our samples, there was however a high activity concentration remaining in the residual fraction. Moreover, the decay-corrected activity ratio of the irreversibly bound fractions was <0.85 , whereas the residuals were within the inventory values for reactor units 2 and 3 (1.00–1.08, Fig. 3). Therefore, sorption onto clay minerals was not considered the main process governing the retention of radiocaesium, and the ^{137}Cs activity was associated with particles $>2\mu\text{m}$.

The role of particles as the main radiocaesium carrier, and the spatial variability of radioactivity in Fukushima's surface environments, has already been demonstrated by other authors (Tanaka et al., 2013; Wakiyama et al., 2017). In our study, the significant number of particles identified with digital autoradiography (Figs. 4 and 5, Table 3) confirmed the presence of radioactive heterogeneities in Fukushima soils and sediments, including litter layers and residual fractions. Although this technique does not determine the particle source (i.e., it only provides the location of a given particle), it has already been used to successfully identify and isolate Cs containing particles in Fukushima aerosols, soils, rocks, sediments and biota for further characterisation (Adachi et al., 2013; Miura et al., 2018; Mukai et al., 2014; Niimura et al., 2015; Satou et al., 2016; Tanaka et al., 2013). More recently, it has also been used to quantify the number of particles and their associated activity by calibrating the PSL response of the autoradiography system

using micrometre sized radiocaesium particles with known activities (Ikehara et al., 2018; Itoh et al., 2014; Miura et al., 2018). In the present work, although the PSL intensity was not calibrated to emission activity, automatically counting Cs particles from autoradiograms allowed us to easily compare between samples of different sites, including before and after sequential extractions.

The number of radioactive particles differed among bulk samples (Table 3) but appeared to be associated with the direction and distance from the FDNPP reactors (Fig. 6 A2). Between ca. 30 to 80 particles/g were counted for sites <2.5 km, either in a SSE/SSW or WNW direction. A similar number was seen for the sediment sample at Suzuuchi pond, ~4.5 km west from the reactor (site #18), probably due to transport from the pond's bank and subsequent deposition. The number decreased to <20 particles/g at sites located 4 km further west (site #9), an area whose soils also contained the lowest activity concentration. The highest number of hot spots (ca. 135 particles/g) was found at site #17, the furthest away on a WNW direction. Bulk samples from this site were characterized by many, relatively small and well-defined spherical high PSL intensity spots in the autoradiograms (Fig. 5) and showed no heterogeneity in the moderated ^{137}Cs activity concentration measured among a large number of aliquots (Table 1). This suggests that a high number of small-sized, low activity particles are rather evenly distributed at site #17. Overall, the spatial distribution of particles (Fig. 6 A2) correlates with the ambient equivalent dose rate measurements (Fig. 1) and ^{137}Cs surface contamination density estimates (Table S1 in SI), and consequently with the reported deposition pattern (Chino et al., 2016).

The significant decrease in particle number after the sequential extractions (Table 3) suggests that radiocaesium was lost during the leaching process due to either dissolution of the particles or disintegration of aggregates. Yet, the remaining particles carried a considerable fraction of the ^{137}Cs activity (Fig. 3). Moreover, the higher the particle frequency, the higher the ^{137}Cs activity concentration (Fig. 6 B). This correlation was less clear among the bulk samples, probably due to soil aggregates or non-spherical particles. A wide variety of shapes and forms have already been identified and found in soils, including amorphous, non-spherical particles (Higaki et al., 2017; Satou et al., 2016; Yamaguchi et al., 2018) and clay minerals and organic matter aggregates (Mukai et al., 2014). In our study, dried soil and sediments were only spread thinly over a surface, without the grinding, ultrasonic bathing, sieving or filtration steps used by other authors, and which probably counteracted agglomeration of soil and sediment particles (Ikehara et al., 2018; Itoh et al., 2014; Miura et al., 2018). The presence of soil and sediment aggregates in our samples may have affected the PSL signal shape and thus the counting by the imaging software, where a certain sphericity was set. Nevertheless, analysing the samples after the sequential extractions, where aggregates dissolved and thus the counting variability was reduced, allowed us to unambiguously identify inert particles in the investigated Fukushima soils and sediments collected 5 years after the accident. These particles, which represented 25–65% of the total ^{137}Cs activity, will exhibit low weathering rates and low potential bioavailability.

5. Conclusions

Results from our leaching experiments and digital autoradiography analyses demonstrated that the radioactive contamination in soils and sediments from the FEZ was sparingly soluble under environmentally relevant conditions (i.e. water, exchangeable and pH sensitive extractions), and was dominated by inert heterogeneities in the form of radiocaesium containing particles. The majority of the radioactivity was generally found in the upper layer of soils and sediments (<5–6 cm) and distributed evenly among the sand- and silt-size fractions. Moreover, the activity concentration of soils or sediments was positively correlated with the particle frequency and in good agreement with ambient equivalent dose rates measured at the associated sites. The spatial distribution of particle frequency over the FEZ area was also dependent on

distance and direction from the FDNPP, as expected from the reported directions of the main deposition plumes that occurred during the accident. The geomorphology and land use may have played an important role in certain areas by enhancing deposition and accumulation of radiocaesium containing particles.

Overall, the radiocaesium in the contaminated soils and sediments studied here showed relatively low bioavailability and weathering. However, mobility and remobilisation of the particles could occur by physical transport. Indeed, relatively large (6–12 μm) non-spherical radiocaesium bearing particles were found 5 years after the accident inside houses located ~2 km WNW from the FDNPP (Higaki et al., 2017), suggesting particle resuspension and/or long-term environmental mobility. Our results demonstrate that radiocaesium containing particles are still an existing problem in the Fukushima area and should not be omitted when environmental impact is assessed.

Declaration of competing InterestCOI

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvrad.2019.106080>.

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