



Simplified measurement method for dissolved radio-Cs in litter and soil seepage water using copper-substituted Prussian blue



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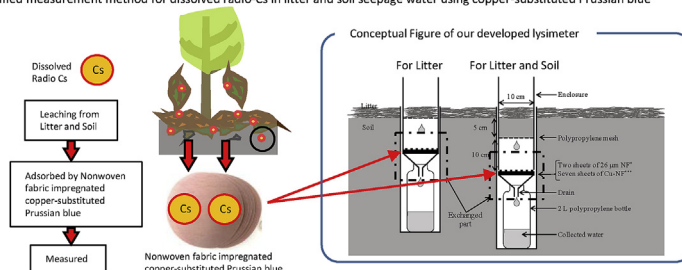
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HIGHLIGHTS

- We developed a simplified method for detecting dissolved radio-Cs in seepage water.
- 99% of dissolved ¹³⁷Cs from litter was collected in the field experiment.
- More than 90% of dissolved ¹³⁷Cs from soil seepage water was collected.
- This method reduces preparation time relative to conventional methods.
- The method can also separate the particulate and dissolved radio-Cs in situ.

GRAPHICAL ABSTRACT

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ABSTRACT

We developed a simple and rapid method for detecting dissolved radio-Cs in litter and/or soil seepage water using nonwoven fabrics impregnated with copper-substituted Prussian blue (Cu-NF). In laboratory and field experiments, litter and/or soil seepage water including dissolved radio-Cs were passed through traditional lysimeter systems combined with seven sheets of the Cu-NF. We then examined the recovery ratios of dissolved ¹³⁷Cs in the Cu-NF. In the laboratory experiments with faster flow rates (11–2200 mm h⁻¹), over 86% of the total dissolved ¹³⁷Cs in litter seepage water was detected in the Cu-NF and over 82% of the collected ¹³⁷Cs was present in the first three sheets. In the field experiments, 99% of the total dissolved ¹³⁷Cs litter seepage water was collected in the Cu-NF and more than 96% of the collected ¹³⁷Cs was present in the first three sheets. Furthermore, the recovery ratio of dissolved ¹³⁷Cs increased with increasing installation Cu-NF length, probably because the packed soil in the Cu-NF lysimeter become more stable over time. Finally, because only the Cu-NF is measured, it is not necessary to undertake traditional measurement preparations such as filtration to remove particulate radio-Cs materials and evaporative concentration for low concentration of radio-Cs. As a result, we can save time and effort in measurement preparation by using the Cu-NF lysimeter method.

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1. Introduction

Large amounts of radionuclides were released into the environment during the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 (Endo et al., 2012) and were widely

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dispersed on the surrounding terrain. As forest areas account for more than 70% of land in the Fukushima Prefecture, radioactive cesium (radio-Cs), especially ^{137}Cs , will remain in the areas for a considerable period of time because ^{137}Cs has the long half-life of 30.17 years. Therefore, the radioactive contamination of forests and forest products will be a matter of serious concern for some time to come (Kuroda et al., 2013).

Soon after the FDNPP accident, radio-Cs deposited on the forest floors was estimated to migrate into soil by becoming dissolved in water; however, the transported amounts of dissolved radio-Cs rapidly decreased with time after the accident (Matsunaga et al., 2013). Dissolved radio-Cs can move rapidly from the litter layer into soil and then from the soil to plants (Nakanishi et al., 2013). Therefore, studies of the migration of the radio-Cs among these components (e.g. plants, litter layer and soil) are important over the coming decades, rather than focusing only on radio-Cs accumulation within each component (Hashimoto et al., 2012). In addition, clarification of radio-Cs dynamics in forest ecosystems will play an important role in applications such as forest management and radiation protection, taking account of the various uses of forest resources (Fujii et al., 2014).

Two different methods have been employed to evaluate vertical migration of radio-Cs in forest soil: the soil profile method and the lysimeter method. Many studies have investigated vertical migration of radio-Cs by using the soil profile method (e.g. Straume et al., 2006; Takahashi et al., 2015), in which migration rates were estimated from changes of radio-Cs in soil depth profiles during periods from 1 year to several years. Although this method is relatively simple, sampling point must be shifted slightly at each sampling period. As it was well known that radio-Cs in forest soil shows extensive spatial heterogeneity (Onda et al., 2015), the soil profile results may be affected by the spatial variation of radio-Cs in soil. There is also a possibility that evaluation over short periods is associated with substantial uncertainty.

In contrast, a lysimeter method directly monitors migrating ions in the soil (Rasmussen et al., 1986). Several types of lysimeter, such as a zero-tension lysimeter (Giesler et al., 1996) and suction lysimeter (Kosugi and Katsuyama, 2004) stainless steel lysimeter (Tegen and Dörr, 1996), had been developed for forest soil monitoring. Although these methods were used after the Chernobyl accident in 1986 (Tegen and Dörr, 1996) and the FDNPP accident in 2011 (Nakanishi et al., 2014), it has not been widely adopted for radio-Cs monitoring because of its complex procedure and a huge amount of effort for pretreatment and analysis of collected drainage water. For example, to employ the lysimeter method, we need to excavate soil deeply (tens of centimeters) to install a large sized lysimeter. Therefore, multi-point monitoring with lysimeters in a forest ecosystem is not practical. In addition, using the lysimeter method, we need to collect drainage water once in several weeks or a month and bring the water sample to a laboratory for radio-Cs measurement because the activity concentration of radio-Cs is typically low (Nakanishi et al., 2014). Determination of the radio-Cs concentration in the water sample requires filtration and evaporative concentration prior to measurement or a long period for a small volume of collected water or a very low concentration of radio-Cs. Furthermore, the conventional lysimeter method separates dissolved radio-Cs from particulate radio-Cs not in-situ but in the laboratory by filtration. Therefore, development of a simple, rapid and easy monitoring method for radio-Cs in litter and soil seepage water is required to concentrate dissolved radio-Cs on-site to be easily measured.

After the FDNPP accident, a rapid method was developed for the detection of dissolved radio-Cs in fresh water using nonwoven fabric impregnated with Prussian blue (Yasutaka et al., 2013) or potassium zinc ferrocyanide (Yasutaka et al., 2015). Prussian blue

(potassium ferrocyanide (II) potassium oxide iron (II), $\text{KFe}[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$) is known to specifically adsorb dissolved radio-Cs (IAEA, 1997). Yasutaka et al. (2016) also developed the nonwoven fabrics impregnated with copper-substituted Prussian blue (hereafter, Cu-NF) for detecting radio-Cs in seawater. The Cu-NF can absorb the radio-Cs in the water sample with high concentration of co-existing ions.

In this study, we aimed to develop a simple, rapid and in-situ separation method for examining the migration of dissolved radio-Cs from soil and/or litter in forest using Cu-NF. We introduced the Cu-NF to a conventional lysimeter, which can adsorb dissolved radio-Cs in the seepage water in-situ. We also examined the recovery ratio of dissolved radio-Cs with the Cu-NF method in both laboratory and field experiments.

2. Materials and methods

We conducted two experiments using Cu-NF combined with a lysimeter (hereafter termed the Cu-NF lysimeter): laboratory experiments and field experiments. First, we confirmed the absorption ability of dissolved radio-Cs in litter seepage water using the Cu-NF in laboratory experiments. Next, we conducted field experiments to examine the applicability of this method to litter and/or soil seepage water in the forest environment.

2.1. Experimental materials

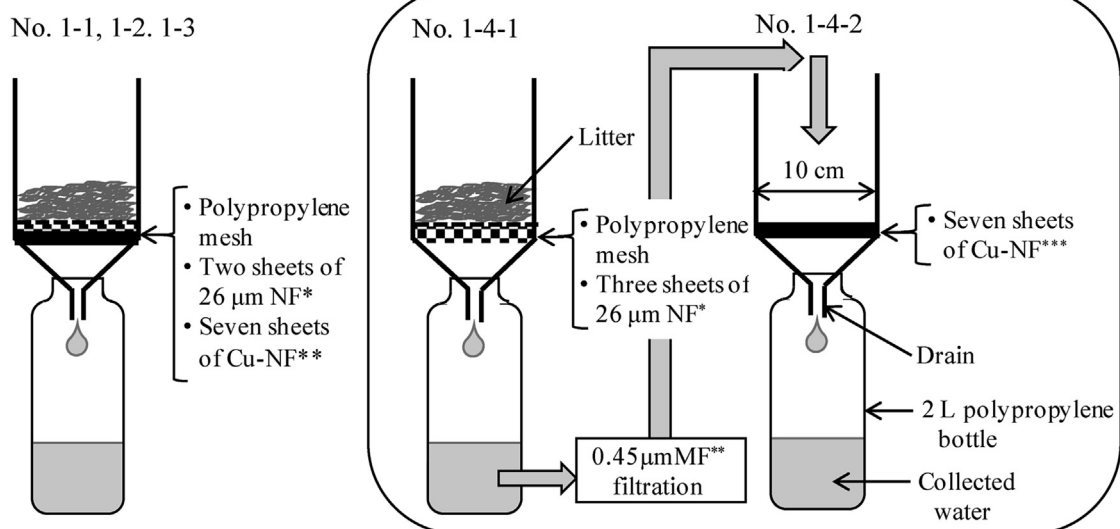
The Cu-NF lysimeters for the laboratory and the field experiments consisted of PVC pipes (90 cm²), nonwoven fabric filters and a polypropylene bottle (I-Boy, As ONE Corporation, Japan), as shown in Fig. 1. Litter and/or soil were packed as packing materials in the PVC pipes, followed by two or three sheets of 26 µm pore size nonwoven fabric sheets (ELV-130 for the laboratory experiment, H-8010 for the field experiment, Japan Vilene Co., Ltd., Japan) and seven sheets of Cu-NF (volumetric density 0.03 g cm⁻³, thickness 0.01 cm, Japan Vilene Co., Ltd., Japan). The 26 µm pore size nonwoven fabric sheets were used to collect soil particles to avoid contamination of the Cu-NF. Both the Cu-NF and the 26 µm pore size nonwoven fabric were cut to a diameter of 113 mm. The water, passed through litter and/or soil, the 26 µm pore size nonwoven fabric sheets and the Cu-NF, was collected with 2 L polypropylene bottles.

2.2. Laboratory experiments

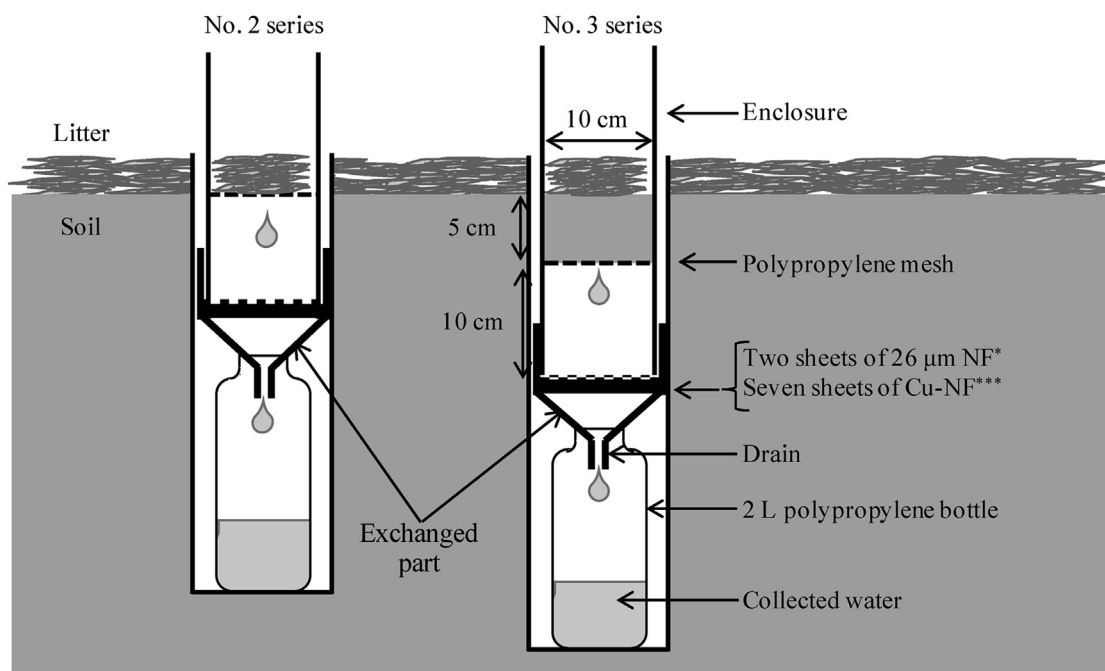
In the laboratory experiments, we evaluated the recovery ratio of dissolved radio-Cs in water passed through the litter in the Cu-NF lysimeter. The litter was separately collected from the L layer and F-H layer at a Japanese cedar forest (*Cryptomeria japonica*) in Kawamata, Yamakiya District, 40 km north-west of the FDNPP (37°36'29" N, 140°38'57" E; 583 m asl). Litter from the L layer (400 g) and the F-H layer (160 g) was mixed well after being cut to 2 cm in length. Next, the pipe was filled with litter (approximately 800 Bq/65 g wet weight) to a height of 5 cm in three of the Cu-NF lysimeters (Nos. 1-1, 1-2 and 1-3) and a control lysimeter (No. 1-4-1). In three of the Cu-NF lysimeters (Nos. 1-1, 1-2 and 1-3), two sheets of 26 µm pore size nonwoven fabric and seven sheets of Cu-NF were combined, and in the remaining lysimeter (No. 1-4-1), only three sheets of 26 µm pore size nonwoven fabric without Cu-NF was used as the control.

Table S1 and Fig. S1 show the experimental conditions and procedures. Ten liters of ion exchange water, which was approximately 1100 mm of throughfall volume and nearly the same as annual precipitation in Fukushima Prefecture (1166 mm, 1981–2010), was passed through each the Cu-NF lysimeter (Nos. 1-

(a) Laboratory experiment



(b) Field experiment



* nonwoven fabric sheets with 26 µm pore size

** 0.45 µm membrane filter

*** nonwoven fabrics impregnated copper-substituted Prussian blue

Fig. 1. Schematic of the Cu-NF lysimeter sets for the laboratory experiment (a) and field experiment (b).

1, 1-2, 1-3) and the control lysimeter (No.1-4-1; Fig. 1a). Water flow rates (L hour^{-1}) through the packing materials in the four lysimeters decreased with time because of the clogging of 26 µm pore size nonwoven fabric. The average flow rate was approximately 0.2 L h^{-1} (i.e. 22 mm h^{-1}), and initial and final rates were 8.0 and 0.1 L h^{-1} (i.e. 880 mm h^{-1} and 11 mm h^{-1}), respectively. Accordingly, flow rates of the water through the Cu-NF of No. 1-1, 1-2 and

1-3 agreed with the flow rates shown above.

For the control lysimeter (No. 1-4-2), the water passed through the lysimeter No. 1-4-1 was initially filtered with 0.45 µm membrane filters (mixed cellulose ester, Advantech, Tokyo, Japan) to remove particulate radio-Cs, and passed through seven sheets of Cu-NF (No. 1-4-2). The flow rate through No. 1-4-2 was constant, about 20 L h^{-1} (i.e. 2200 mm h^{-1}), which is rapid compared with

the other three Cu-NF lysimeters (No. 1-1, 1-2 and 1-3).

To measure the ^{137}Cs concentration in the water, the collected water passed through the Cu-NF lysimeter was first filtered using a $0.45\ \mu\text{m}$ membrane filter to remove suspended solids, except for the samples of No. 1-4-2. Next, 1 L of filtered water was evaporated on a Teflon sheet ($250 \times 250\ \text{mm}$) that was kept at $120\ ^\circ\text{C}$ by a hot plate. Thereafter, γ -ray measurements were performed with a low-background, well-type Ge detector (Seiko EG&G, GWL 120230-S, Shizuma et al., 2010). The measurement time for each sample was 10,000 s.

To measure the ^{137}Cs concentration in the Cu-NF, the Cu-NF (seven sheets in total) was separated to the first three sheets and the latter four sheets, which were separately cut into 2-cm pieces. The Cu-NF were washed with an ultrasonic washing machine for 15 min before the radio-Cs measurement to remove particulate radio-Cs (under $26\ \mu\text{m}$ diameter) attached to the Cu-NF. We conducted preliminary repeated experiments of this washing process to check the effectiveness of this washing process. We found that the difference in the radio-Cs concentration between the Cu-NF after the 1st and 2nd washing process was negligible. Therefore, the Cu-NF was treated with ultrasonic washing for 15 min before measurements. The concentration of ^{137}Cs in the Cu-NF was determined by γ -ray spectrometry using a coaxial type, low background Ge detector (GEM Series HPGe Coaxial Detector System, GEM-110225, Seiko EG&G, Shizuma et al., 2016). The measurement time was 30,000 s.

2.3. Field experiments

Field experiments were conducted in a Japanese cedar forest (*Cryptomeria japonica*) in Kawamata, Yamakiya District ($37^\circ36'29''\text{N}$, $140^\circ38'57''\text{E}$; 583 m asl). Annual precipitation was 1342 mm (Tsushima weather station, Japan Meteorological Agency (JMA)) and average temperature was $11.9\ ^\circ\text{C}$ (Nihonmatsu weather station, JMA). The experimental site has not been subjected to any decontamination work. The thickness of the litter layer in the site was approximately 4 cm.

Six Cu-NF lysimeters were used in the field experiments (Fig. 1b). Three Cu-NF lysimeters were filled with 4 cm of litter, and installed under the litter layer (Nos. 2-1, 2-2 and 2-3), and three further Cu-NF lysimeters were filled with 4 cm of litter and 5 cm of soil, and installed at 5 cm depth below the soil surface (Nos. 3-1, 3-2 and 3-3). Intact litter and soil cores were collected by pounding a pipe with 10.7 cm diameter into the litter and soil to 5 cm depth and filled in Cu-NF lysimeters without further compaction. There were 10-cm blank/void spaces between the filled litter/soils and the Cu-NF (Fig. 1b). Seepage water was passed through the $26\ \mu\text{m}$ NF and the Cu-NF, and finally collected in 2 L polypropylene bottles. As the installation site was sloping, approximately 15 cm height of enclosures from the ground surface were combined with the Cu-NF lysimeters to avoid the direct influx of surface runoff into the Cu-NF lysimeters.

Lysimeters under the litter layer (Nos. 2-1, 2-2 and 2-3) were installed from 24 May to 27 August 2015, and those at 5 cm depth below the soil surface (Nos. 3-1, 3-2 and 3-3) from 3 July to 27 August 2015. Sample collection of the Cu-NF and water in the bottles was conducted three times for litter filled Cu-NF lysimeters (No. 2-1, 2-2 and 2-3 on 3 July, 30 July, and 27 August 2015) and twice for litter and soil filled Cu-NF lysimeters (Nos. 3-1, 3-2 and 3-3, on 30 July and 27 August 2015) during the experimental periods. The Cu-NF was exchanged without disturbance of litter/soils (Fig. 1b) because this equipment can be separate two parts, litter/soils with $26\ \mu\text{m}$ pore size nonwoven fabric sheet part and Cu-NF part. The volume of the collected water in the bottles was determined on each sample collection date. On the last sample collection

(27 August), the litter and soil in the Cu-NF lysimeters were also collected. The soil and litter in the Cu-NF lysimeters Nos. 3-1 and 3-2 were collected separately, but litter and soil of No. 3-3 could not be collected separately because the soil and litter had been disturbed and mixed together (probably by heavy precipitation events).

Measurement procedures for ^{137}Cs activities in collected water samples and the Cu-NF were the same as those in the laboratory experiments. The packing materials (litter and soil) were dried at $80\ ^\circ\text{C}$ for 48 h for analyzing ^{137}Cs activity. The samples were filled into 100 mL plastic polystyrene containers (U-8) and the concentrations of ^{137}Cs were determined by the low background Ge detector same as the measurement of Cu-NF (600 s of the measurement time).

3. Results and discussion

3.1. Laboratory experiments

Fig. 2 shows the results of the laboratory experiments. Approximately 86–93% of dissolved ^{137}Cs was collected in the Cu-NF and over 95% of the collected ^{137}Cs was present in the first three of the total seven sheets. This indicated that most of the dissolved radio-Cs was collected by the Cu-NF and 86–93% of dissolved radio-Cs in the seepage water was in ionic form.

The recovery ratio of dissolved ^{137}Cs in the Cu-NF for No. 1-4-2 (average flow rate: $2200\ \text{mm h}^{-1}$) presented the same pattern as those for No. 1-1, 1-2 and 1-3 (average flow rate $22\ \text{mm h}^{-1}$), even though the flow rate for No. 1-4 was 100 times faster than the others. The gravity-dependent flow rate range in the present study ($11\text{--}2200\ \text{mm h}^{-1}$) is thought to be acceptable for a good recovery rate, even though the recovery rate of ^{137}Cs in the Cu-NF decreases with the increasing flow rate (Yasutaka et al., 2016).

In contrast, about 7–14% of ^{137}Cs was also detected in the water passed through the Cu-NF and the $0.45\ \mu\text{m}$ membrane filter. Cu-NF adsorbed only ionic radio-Cs. As mentioned in the laboratory test, over 95% of the collected ^{137}Cs was present in the first three of the

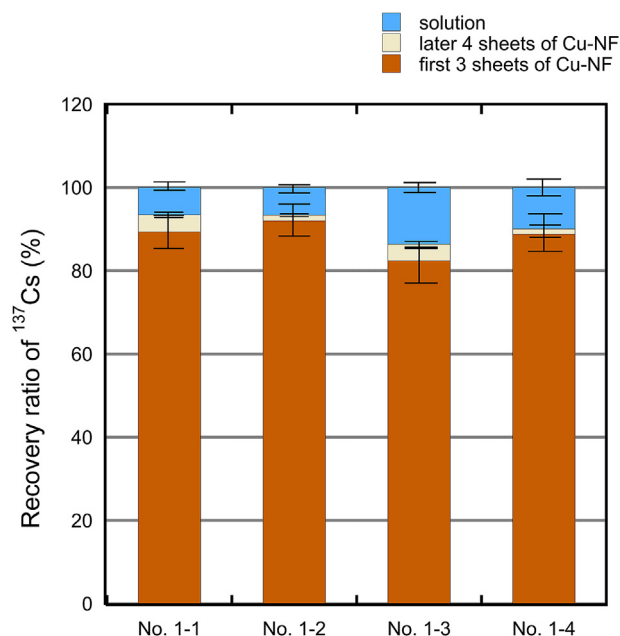


Fig. 2. Recovery ratios of ^{137}Cs detected in the Cu-NF and the water passed through the Cu-NF. The ^{137}Cs concentrations in the water are shown after filtration with $0.45\ \mu\text{m}$ membrane filters. The error bars indicate the measurement error.

Table 1
Collecting volume of the water samples during monitoring period.

Monitoring period (year/ month/day)	Days	Collecting water volume (ml) (calculated precipitation [mm])						^a Precipitation (mm) (maximum [mm h ⁻¹])
		No. 2-1	No. 2-2	No. 2-3	No. 3-1	No. 3-2	No. 3-3	
1st 2015/5/24–2015/7/2	40	353 (39)	510 (57)	620 (69)	—	—	—	144 (29)
2nd 2015/7/3–2015/7/29	27	615 (68)	480 (53)	969 (108)	637 (71)	814 (90)	722 (80)	148 (15)
3rd 2015/7/30–2015/8/27	28	620 (69)	522 (58)	967 (107)	748 (83)	927 (103)	836 (93)	137 (13)

^a Data at Tsushima meteorological station, 10 km south-east of the monitoring site (Japan Meteorological Agency database, <http://www.jma.go.jp/jma/index.html>).

total seven sheets and under 5% of ¹³⁷Cs was remain later four sheets. This result indicated that almost all ionic radio-Cs were adsorbed Cu-NF.

In this term, there is the possibility that other existing forms of the radio-Cs (except for the dissolved form in the water; particulate radio-Cs with radius of less than 0.45 μm and/or colloid radio-Cs), may pass through 0.45 μm membrane filters but not become adsorbed to the Cu-NF. The contribution of the undetermined forms of radio-Cs is estimated at about 7–14% in our laboratory experiments and thus clearly cannot be ignored. However, the flow rates (No.1-1 – No.1-3 initial 2200 mm h⁻¹, average 22 mm h⁻¹ and No.1-4-2 initial 2200 mm h⁻¹, average 22 mm h⁻¹) in the laboratory experiments are far higher than those encountered when precipitation penetrates into forest soil in the environment. This flow condition may cause that some radio-Cs, which adsorbed soil particle, organic matter, dissolve organic carbon and/or colloid with radius of less than 0.45 μm, were drove in the collected water because of these abnormally high flow rates. As a result, 7–14% of the undetermined forms of radio-Cs may be measured. This hypothesis will reinforcement at the result of field experiment.

3.2. Field experiments

3.2.1. ¹³⁷Cs activity of the packing materials and collected water volume

Table S2 shows the ¹³⁷Cs activities in the packing materials in each Cu-NF lysimeter. The average ¹³⁷Cs activities of the lysimeters installed under litter layer and in soil at 5 cm depth were 779–1006 and 1665–2181 Bq, respectively, which is consistent with the results of spatial heterogeneity of radio-Cs in forest soil after the FDNPP accident (Onda et al., 2015).

Table 1 shows the collected volumes of water samples of the Cu-NF lysimeters and precipitation (mm) with hourly maximum precipitation (mm h⁻¹) at the Tsushima weather station (JMA), the nearest meteorological station, during the experimental periods. Monitored precipitations by the JMA during three experimental periods were 137–148 mm, while the collected water were 39–108 mm (77 mm on average, calculated by collected water volumes). The difference between the lowest and highest volumes of the collected water depended on neither the installed depths of the Cu-NF lysimeters nor the location of installation in the forest stand. Our results were consistent with a previous study on large spatial variation in throughfall and soil water (Kobayashi et al., 2000).

3.2.2. Recovery ratios of dissolved ¹³⁷Cs with the Cu-NF

Table 2 shows the results from the lysimeters filled with litter (Nos. 2-1, 2-2 and 2-3). More than 99% of the total dissolved ¹³⁷Cs was collected by the Cu-NF, and 96% of the collected ¹³⁷Cs was located in the first three sheets (Table 2). Dissolved ¹³⁷Cs was detected in the collected water but the ratio is much lower (under 1%). This result may be mainly owing to the slow flow rate (maximum 29 mm h⁻¹) compared with the laboratory experiments (11–2200 mm h⁻¹). However, the high concentration of ¹³⁷Cs in the Cu-NF also indicates that the radio-Cs in the seepage water was mainly in an ionic form. Based on these results, we conclude that the Cu-NF lysimeter method is suitable for detecting dissolved radio-Cs in litter seepage water in the forest environment in place of traditional lysimeter methods.

The recovery ratios of dissolved radio-Cs in the litter and soil seepage water (Nos. 3-1, 3-2 and 3-3) were over 90% for the second experimental period, and were over 97% for the third experimental

Table 2
Recovery ratios of dissolved ¹³⁷Cs with the Cu-NF and ¹³⁷Cs activities of the collected water.

Lysimeter no. and monitoring period		Cu-NF ^a (%)			Collected water ^b (%)
		First three sheets	Latter four sheets	Total	
2-1	1st 2015/5/24–7/2	98.9	0.7	99.6	0.4
	2nd 2015/7/3–7/29	99.6	0.3	99.9	0.1
	3rd 2015/7/30–8/27	96.1	3.4	99.5	0.5
2-2	1st 2015/5/24–7/2	97.6	2.2	99.8	0.2
	2nd 2015/7/3–7/29	98.6	0.8	99.3	0.7
	3rd 2015/7/30–8/27	99.2	0.5	99.7	0.3
2-3	1st 2015/5/24–7/2	98.6	1.2	99.8	0.2
	2nd 2015/7/3–7/29	99.4	0.4	99.7	0.3
	3rd 2015/7/30–8/27	98.2	1.4	99.5	0.5
3-1	2nd 2015/7/3–7/29	74.9	19.2	94.1	5.9
	3rd 2015/7/30–8/27	95.9	2.8	98.8	1.2
3-2	2nd 2015/7/3–7/29	80.7	10.0	90.7	9.3
	3rd 2015/7/30–8/27	94.9	2.8	97.7	2.3
3-3	2nd 2015/7/3–7/29	89.3	5.7	95.0	5.0
	3rd 2015/7/30–8/27	98.4	0.9	99.3	0.7

^a ¹³⁷Cs activity after ultrasonic washing.

^b ¹³⁷Cs activity after filtration with 0.45 μm membrane filters.

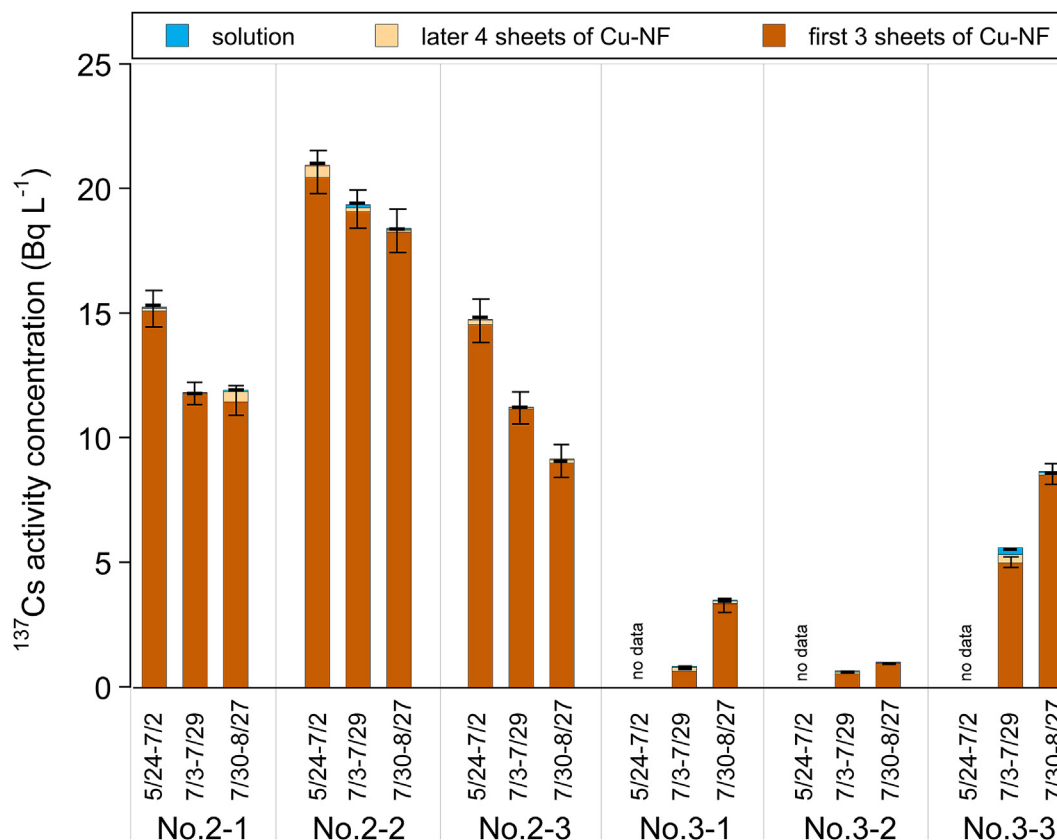


Fig. 3. Dissolved ^{137}Cs concentrations in litter and soil seepage water (^{137}Cs in Cu-NF and collected water after 0.45 μm MF filtration) during the monitoring periods. Cu-NF lysimeter Nos. 2-1, 2-2 and 2-3 were installed under the litter layer, and Nos. 3-1, 3-2 and 3-3 were installed at 5 cm soil depth. The error bars indicate the measurement error.

period (Table 2; note that no data of Nos. 3-1, 3-2 and 3-3). The recovery ratio in the second experimental period was lower than that in the third experimental period for all three samples. In addition, the recovery ratio of ^{137}Cs in the first three sheets of the Cu-NF in the secondary experimental period (74.9–89.3%) was lower than that in the third experimental period (94.9–98.9%). In both laboratory and field experiments, the precipitation volume, maximum precipitation rate, collected volume and the radioactivity of soil and litter in the second experimental period were the same as those in the third experimental period (Table 1 and Fig. 3).

The reason for the relatively low recovery ratio of Nos. 3-1, 3-2 and 3-3 in the second monitoring period is not clear. However, soil disturbance probably occurred in the second experimental period, perhaps because of the soil packing in the Cu-NF lysimeters and/or spaces between the packed soil and the PVC pipes. After a certain amount of time (~approximately one month), spaces among the soil particles are infilled and soil cores gradually became stable. In the third measurement period, over 98% of the dissolved ^{137}Cs was collected in the Cu-NF and over 95% of the ^{137}Cs was present in the

first three sheets, showing a similar pattern to the results of the litter seepage water. The Cu-NF lysimeter can be considered suitable for soil seepage water; however, we suggest that sample collection to be conducted after the lysimeter has been installed for a certain amount of time (~approximately one month).

3.2.3. Concentration and migration rate of radio-Cs from litter or soil

Fig. 3 shows the ^{137}Cs concentrations in litter and/or soil seepage water in the Cu-NF and collected water in each Cu-NF lysimeter during the experimental periods. Average ^{137}Cs concentration collected under litter layer (Nos. 2-1, 2-2, 2-3) was approximately 15 Bq L⁻¹, while that in soil at 5 cm depth (Nos. 3-1, 3-2, 3-3) was 1.5 Bq L⁻¹. The ^{137}Cs concentration in seepage water from each Cu-NF lysimeter showed temporal variation. Although the temporal variation was observed, the range of in ^{137}Cs migration among lysimeters were larger than the temporal variation in each Cu-NF lysimeter. Longer monitoring period (e.g. one year) than that of the present study is required to discuss a temporal trend of ^{137}Cs

Table 3
Flux and migration rate of dissolved ^{137}Cs during the monitoring period.

Lysimeter no.	^{137}Cs flux (Bq m ⁻² day ⁻¹)			Migration rate of investigated period (% day ⁻¹)
	2015/5/24–2015/7/2	2015/7/3–2015/7/29	2015/7/30–2015/8/27	
S2-1	14.9	29.9	29.1	0.023
2-2	29.6	38.0	38.0	0.027
2-3	25.4	44.7	35.0	0.034
3-1	–	2.1	10.2	0.001
3-2	–	2.0	3.6	0.001
3-3	–	15.8	28.5	0.006

migration.

Table 3 shows the ^{137}Cs fluxes during the experimental periods. Daily migration rates of ^{137}Cs at 5 cm depth in litter or soil were also calculated. We observed that approximately 0.03% of ^{137}Cs in the litter layer migrated to the surface soil over a day in the dissolved form, while annual ^{137}Cs migration at 5 cm depth accounted for approximately 0.003%. This indicates that radio-Cs migrating from the litter layer to the soil remains in the surface layer of soil (<5 cm), which is consistent with previous studies in the Fukushima region (Takahashi et al., 2015).

However, the migration of ^{137}Cs at 5 cm depth for lysimeter No. 3-3 was larger than those of the other two Cu-NF lysimeters, probably because of the disturbed packing material in No. 3-3. For lysimeter Nos. 3-1 and 3-2, dissolved ^{137}Cs leached from litter layer stopped at the surface part of soils, while for lysimeter No. 3-3, dissolved ^{137}Cs may be leached from litter mixed in soils located near Cu-NF, the and dissolved ^{137}Cs was collected by Cu-NF. Although the water volumes collected and the ^{137}Cs concentration varied between Cu-NF lysimeters and sampling periods (Table 1 and Fig. 3), the annual ^{137}Cs flux and the migration rates were spatially homogeneous. Based on these results, we can also use the Cu-NF lysimeter to calculate the flux of dissolved ^{137}Cs only by measuring the radio-Cs activity of the Cu-NF without water sample collection, and to monitor radio-Cs in the field over the long term.

4. Conclusion

In this study, we developed a simple, rapid and easy install and monitoring method for radio-Cs in litter and/or soil seepage water. The Cu-NF lysimeter method was showed to be able to collect dissolved radio-Cs in seepage water. By introducing the Cu-NF to a traditional lysimeter method, the concentration of dissolved radio-Cs in litter or soil seepage water can be evaluated by measuring the Cu-NF after ultrasonic washing. Accordingly, this method can reduce the time required for measurement preparation.

Furthermore, this method also has potentials of several advantages for the long-term monitoring. If we only focus on ^{137}Cs fluxes, bottles for water collection need not be prepared, and consequently we do not pay attention to the overflowing of seepage water from water bottles. Although the Cu-NF lysimeters were installed for up to 40 days in the environment, seven sheets of Cu-NF collected dissolved radio-Cs in 10 L (annual throughfall in Fukushima region) of litter passed water in the laboratory experiment. This means that Cu-NF have a potential adsorption ability of radio-Cs and stable-Cs, which exist higher concentration compared with radio-Cs in the environment. In addition, the Cu-NF lysimeter can be installed at a shallower position below the soil surface than traditional lysimeters. However, this research does not confirm the durability of Cu-NF and condition of clogging of 26 μm -NF in the long-term monitoring. For using long term-monitoring over 3 months, further researches such as actual long term experiment are needed. However, this method have a potential that can be monitored radio-Cs in seepage water by not only the one month but also long-term installation (e.g. several months ~ a year) of the Cu-NF lysimeters, and thus reduce the time and effort needed to collect sample water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.08.010>.

References

- Endo, S., Kimura, S., Takatsui, T., Nanasawa, K., Imanaka, T., Shizuma, K., 2012. Measurement of soil contamination by radionuclides due to the Fukushima Dai-ichi Nuclear Power Plant accident and associated estimated cumulative external dose estimation. *J. Environ. Radioact.* 111, 18–27.
- Fujii, K., Ikeda, S., Akama, A., Komatsu, M., Takahashi, M., Kaneko, S., 2014. Vertical migration of radiocesium and clay mineral composition in five forest soils contaminated by the Fukushima nuclear accident. *Soil Sci. Plant Nutr.* 60, 751–764.
- Giesler, R., Lundström, U.S., Grip, H., 1996. Comparison of soil solution chemistry assessment using zero-tension lysimeters or centrifugation. *Eur. J. Soil Sci.* 47, 395–405.
- Hashimoto, S., Ugawa, S., Nanko, K., Shichi, K., 2012. The Total Amount of Radioactivity Contaminated Materials in Forests in Fukushima, Japan, vol. 2, p. 416. Scientific Reports.
- IAEA, 1997. The Use of Prussian Blue to Reduce Radioaesium Contamination of Milk and Meat Produced on Territories Affected by the Chernobyl Accident. IAEA-TECDOC-926.
- Kobayashi, M., Onodera, S., Kato, M., 2000. Effect of a tree on water movement in a forest soil. *J. Jpn. For. Soc.* 82, 287–294.
- Kosugi, K., Katsuyama, M., 2004. Controlled-suction period lysimeter for measuring vertical water flux and convective chemical fluxes. *Soil Sci. Soc. Am. J.* 68, 371–382.
- Kuroda, K., Kagawa, A., Tonosaki, M., 2013. Radiocesium concentrations in the bark, sapwood and hardwood of three species collected at Fukushima forests half a year after the Fukushima Dai-ichi nuclear accident. *J. Environ. Radioact.* 122, 37–42.
- Matsunaga, T., Koarashi, J., Atarashi-Andoh, M., Nagao, S., Sato, T., Nagai, H., 2013. Comparison of the vertical distributions of Fukushima nuclear accident radiocesium in soil before and after the first rainy season, with physicochemical and mineralogical interpretations. *Sci. Total Environ.* 447, 301–314.
- Nakanishi, T., Matsunaga, T., Koarashi, J., Atarashi-Andoh, M., 2014. ^{137}Cs vertical migration in a deciduous forest soil following the Fukushima Dai-ichi Nuclear Power Plant accident. *J. Environ. Radioact.* 128, 9–14.
- Nakanishi, T.M., Kobayashi, N.I., Tanoi, K., 2013. Radioactive cesium deposition on rice, wheat, peach tree and soil after nuclear accident in Fukushima. *J. Radioanal. Nucl. Chem.* 296, 985–989.
- Onda, Y., Kato, H., Hoshi, M., Takahashi, Y., Nguyen, M.L., 2015. Soil sampling and analytical strategies for mapping fallout in nuclear emergencies based on the Fukushima Dai-ichi Nuclear Power Plant accident. *J. Environ. Radioact.* 139, 300–307.
- Rasmussen, L., Jørgensen, P., Kruse, S., 1986. Soil water samplers in ion balance studies on acidic forest soils. *Environ. Contam. Toxicol.* 36, 563–570.
- Shizuma, K., Oba, Y., Takada, M., 2016. A Practical Method for Determining γ -ray Full-energy Peak Efficiency Considering Coincidence-summing and Self-absorption Corrections for the Measurement of Environmental Samples after the Fukushima Reactor Accident (Nuclear Instruments and Methods in Physics Research Sect B accepted).
- Shizuma, K., Takatori, H., Takenaka, K., Murataka, A., Kojima, Y., Endo, S., 2010. Measurement of uranium, radium and radon concentration in ground water sampled over Hiroshima Prefecture, Japan. *Radioisotopes* 59, 163–171.
- Straume, T., Anspaugh, L.R., Marchetti, A.A., Voigt, G., Minenko, V., Gu, F., Men, P., Trofimik, S., Tertyalevich, S., Drozdovitch, V., Shagalova, E., Zhukova, O., Germenchuk, M., Berlovich, S., 2006. Measurement of ^{129}I and ^{137}Cs in soils from Belarus and reconstruction of ^{131}I deposition from the Chernobyl accident. *Health Phys.* 91, 7–19.
- Takahashi, J., Tamura, K., Suda, T., Matsumura, R., Onda, Y., 2015. Vertical distribution and temporal changes of ^{137}Cs in soil profiles under various land uses after the Fukushima Dai-ichi Nuclear Power Plant accident. *J. Environ. Radioact.* 139, 351–361.
- Tegen, I., Dörr, H., 1996. Mobilization of cesium in organic rich soils: correlation with production of dissolved organic carbon. *Water, Air, & Soil Pollut.* 88, 133–144.
- Yasutaka, T., Miyazu, S., Kondo, Y., Tsuji, H., Arita, K., Hayashi, S., Takahashi, A., Kawamoto, T., Aoyama, M., 2016. Development of a copper-substituted, Prussian

- blue-impregnated, nonwoven cartridge filter to rapidly measure radiocesium in seawater. *J. Nucl. Sci. Technol.* 53, 1243–1250.
- Yasutaka, T., Kawamoto, T., Kawabe, Y., Sato, T., Sato, M., Suzuki, Y., Nakamura, K., Komai, T., 2013. Rapid measurement of radiocesium in water using a Prussian blue impregnated nonwoven fabric. *J. Nucl. Sci. Technol.* 50, 674–681.
- Yasutaka, T., Tsuji, H., Kondo, Y., Suzuki, Y., Takahashi, A., Kawamoto, T., 2015. Rapid quantification of radiocesium dissolved in water by using nonwoven fabric cartridge filters impregnated with potassium zinc ferrocyanide. *J. Nucl. Sci. Technol.* 52, 792–800.