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Downward migration of ^{137}Cs within the humus layer under temperate coniferous stands in the Czech Republic --Manuscript Draft--

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Abstract:	<p>Abstract</p> <p>Purpose This study examined the current distribution and downward migration of ^{137}Cs in the humus horizon under temperate coniferous stands in the Czech Republic. Depth distribution profiles of lithogenic alkali metals (K, Rb and Cs) were also traced to find any indication regarding the ^{137}Cs dynamics within the humus horizon.</p> <p>Materials and methods Soil (bulk soil) samples were collected manually from the uppermost down to a depth of 20 cm at three points situated 10-20 m apart in three locations diversely affected by the Chernobyl accident in 1986. Humus samples (about 6 cm in thickness) were separately collected at three points adjacent to the bulk soil sampling. The humus samples were divided into three fractions (upper, middle and lower) denoted to Hu, Hm and Hl, respectively depending on their depths. Activity concentration of ^{137}Cs and the amount of alkali metals (K, Rb and Cs) in each humus fraction were determined with gamma spectrometry and ICP spectrometry, respectively. Some properties (pH, density, SOM and identification of clay minerals), of both bulk soils and humus horizons were also investigated.</p> <p>Results and discussion The highest activity concentration of ^{137}Cs (Bq kg⁻¹) appeared in the upper portion of the soil (mainly humus horizon) under three coniferous stands about 30 years after the Chernobyl accident. Increasing activity of ^{137}Cs (Bq) was found in the lower humus fraction (Hl, 4~6 cm depth range) with no appreciable amounts of clay minerals like illite and smectite in the investigated sites. The findings suggest that the fallout ^{137}Cs moves downward at a speed of 0.13~0.19 cm yr⁻¹ with degrading organic matter within the humus horizon. Possible association of ^{137}Cs with alkali metals (K, Rb and Cs) was suggested by depth distribution profiles of lithogenic</p>

	<p>alkali metals (K, Rb and Cs) in humus.</p> <p>Conclusion The humus horizon under temperate coniferous stands plays an important role in retaining fallout ^{137}Cs for a long time. Comparing the depth distributions of the fallout nuclide ^{137}Cs with the depth distributions of lithogenic alkali metals (K, Rb and Cs) gives valuable information for clarifying mechanism of ^{137}Cs movement in humus. Further investigation is needed to elucidate mechanism of ^{137}Cs migration within humus horizon by tracing ^{137}Cs speciation and decomposing soil organic matter simultaneously.</p> <p>Keywords Cesium-137 * Forest soil * Humus * Vertical migration rate, Alkali metals</p>
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SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES • RESEARCH ARTICLE

Downward migration of ^{137}Cs within the humus layer under temperate coniferous stands in the Czech Republic

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Abstract

Purpose This study examined the current distribution and downward migration of ^{137}Cs in the humus horizon under temperate coniferous stands in the Czech Republic. Depth distribution profiles of lithogenic alkali metals (K, Rb and Cs) were also traced to find any indication regarding the ^{137}Cs dynamics within the humus horizon.

Materials and methods Soil (bulk soil) samples were collected manually from the uppermost down to a depth of 20 cm at three points situated 10-20 m apart in three locations diversely affected by the Chernobyl accident in 1986. Humus samples (about 6 cm in thickness) were separately collected at three points adjacent to the bulk soil sampling. The humus samples were divided into three fractions (upper, middle and lower) denoted to H_u , H_m and H_l , respectively depending on their depths. Activity concentration of ^{137}Cs and the amount of alkali metals (K, Rb and Cs) in each humus fraction were determined with gamma spectrometry and ICP spectrometry, respectively. Some properties (pH, density, SOM and identification of clay minerals), of both bulk soils and humus horizons were also investigated.

Results and discussion The highest activity concentration of ^{137}Cs (Bq kg^{-1}) appeared in the upper portion of the soil (mainly humus horizon) under three coniferous stands about 30 years after the Chernobyl accident. Increasing activity of ^{137}Cs (Bq) was found in the lower humus fraction (H_l , 4~6 cm depth range) with no appreciable amounts of clay minerals like illite and smectite in the investigated sites. The findings

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3 36 suggest that the fallout ^{137}Cs moves downward at a speed of $0.13\sim 0.19\text{ cm yr}^{-1}$ with degrading organic
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6 37 matter within the humus horizon. Possible association of ^{137}Cs with alkali metals (K, Rb and Cs) was
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9 38 suggested by depth distribution profiles of lithogenic alkali metals (K, Rb and Cs) in humus.
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13 39 *Conclusion* The humus horizon under temperate coniferous stands plays an important role in retaining
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16 40 fallout ^{137}Cs for a long time. Comparing the depth distributions of the fallout radionuclide ^{137}Cs with the
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19 41 depth distributions of lithogenic alkali metals (K, Rb and Cs) gives valuable information for clarifying
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22 42 mechanism of ^{137}Cs movement in humus. Further investigation is needed to elucidate mechanism of ^{137}Cs
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25 43 migration within humus horizon by tracing ^{137}Cs speciation and decomposing soil organic matter
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28 44 simultaneously.
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33 45 **Keywords** Cesium-137 • Forest soil • Humus • Vertical migration rate, Alkali metals
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1 Introduction

Many highly-contaminated forest areas have been abandoned without any effective remediation in the thirty years since the Chernobyl accident (Beresford et al. 2016). Considerable amounts of ^{137}Cs still remain in the surface portion of forest soils (Winkelbauer et al. 2012; Szabó et al. 2012; Vahabi-Moghaddam and Khoshbinfar 2012; Petrovič et al. 2016). Transportation of deposited ^{137}Cs on the forest floor are affected by various environmental factors including surface runoff, microbial activity, root uptake and water movement in soil. Among the many studies that have focused on the dynamics of ^{137}Cs in forest ecosystems, clay mineralogy was found to be an important factor controlling the rather low mobility of ^{137}Cs caused by sorption and fixation by certain clay minerals (Sawhney 1972; Cornell 1993, Dołhańczuk-Śródka et al. 2006, Szabó et al. 2012). Recently, Fujii et al. (2016) investigated vertical migration of radiocesium (^{134}Cs and ^{137}Cs) deposited on several forest sites due to the accident of Fukushima Daiichi Nuclear Power Plant in Japan in 2011. They concluded that both organic components and clay minerals had enough capacities for retaining radiocesium in the surface soils during the initial stage of contamination.

In our previous paper on ^{137}Cs retention with soil components under selected forest sites in the Czech Republic (Takahashi et al. 2017), the highest proportion of ^{137}Cs in soil was found in the organic horizons (O_f and O_h) under temperate coniferous stands diversely affected by the atmospheric fallout from the Chernobyl accident. We obtained relatively low apparent burial rate of ^{137}Cs ($0.04\text{--}0.08\text{ cm yr}^{-1}$) in the upper soil layer ($< 15\text{ cm depth}$), which contained no significant amounts of clay minerals, suggesting that

the ^{137}Cs may be associated with humic macromolecules in the upper soil layer down to a depth of about 15 cm. Humus has a much longer life span than any other organic materials among the various forest components. The “environmental memory” of an area can be traced back for at least the last 60-100 years (Sucharova et al. 2011). In a study of the interactions of radiocesium with humus in forest soils, Strebl et al. (1995) investigated distribution of ^{137}Cs in surface soils and found that the transfer rate of ^{137}Cs from forest soils to plants was much more strongly influenced by the quality of humus components rather than by their amounts. Kruse-Irmer and Gian (2003) reported that radiocesium would be involved in a shortcut element cycle in the system of humus layer-plant uptake-litter, considering the high bioavailability and low migration of radiocesium in the humus layers. High bioavailability and low migration rate of ^{137}Cs in humus obtained in their study suggested that ^{137}Cs may be rather strongly associated with humic components with appreciable amounts of ionic and/or exchangeable ^{137}Cs . Therefore, evaluating the distribution and mobility of ^{137}Cs in the humus layer in considerable detail is necessary for long-term fate of ^{137}Cs deposited in forest floors.

It is also important to consider the distribution of alkali metals (K, Rb and Cs) as well as ^{137}Cs in humus, because i) all belong to the alkali metal group with similar physicochemical properties, ii) stable alkali metals are from lithogenic (natural) source, whereas ^{137}Cs is originated from the atmosphere by accidental release (anthropogenic source), and iii) little is known about the distribution of the alkali metals as well as ^{137}Cs in forest humus. There are several papers describing analytical results of K, Rb and Cs in spruce

needles (*Picea abies* Karst.) and in the associated soils in Switzerland (Wyttenbach et al. 1995). Mean concentrations of these elements in soils were found in the order $K \gg Rb > Cs$, which were consistent with the average composition of the upper continental crust. They concluded that the change of the concentration with soil depth was completely explained by the dilution of the mineral soil with organic matter in near surface. Vinichuk et al. (2010) carried out a comparative study of accumulation of alkali metals (K, Rb, Cs) and ^{137}Cs in soil and fungi in a Swedish forest. They found a similar mechanism of Cs uptake by fungi to that of Rb, different with K uptake. These studies were aimed at understanding bioavailability of radionuclides to prevent ultimate exposure to living organisms.

The present study has especially focused on the current distribution and downward migration of ^{137}Cs in the humus horizon under the same stands as those previously investigated to elucidate site-specific and common properties of ^{137}Cs retention within the humus horizons. Depth distribution profiles of a lithogenic stable cesium (^{133}Cs) and other alkali metals (K and Rb) were also investigated to compare those of ^{137}Cs , and to find any relationships among them within the humus horizon 30 years after the Chernobyl accident.

2 Material and methods

2.1 Location, site description, and sample collection

The sites for investigation in this study were the same as those described in our previous paper (Takahashi et al. 2017), i.e. three temperate coniferous (*Picea abies*) stands with a mean stand age of 60-120 years in the Czech Republic. These sites were Přemyslov (50.101°N; 17.078°E), Opatovice (49.962°N; 15.196°E) and Průhonice (49.990°N; 14.543°E), as denoted sites I, II and III, respectively.

Soil (bulk soil) samples were manually collected every 2 cm from the uppermost down to a depth of 12 cm (6 subsamples), and one subsample each from 12 to 15 cm, and 15 to 20 cm in depth with a stainless frame (10 × 10 × 10 cm) at three points situated 10-20 m apart in each location in September 2014. Humus samples were separately collected at three points adjacent to bulk soil sampling. Mean thickness of the humus horizon was 6 cm, which was divided into three fractions of equal thickness (2 cm). The separated humus fractions were denoted by the upper (H_u) middle (H_m) and lower (H_l) depending on their depth.

2.2 Analytical procedures

All samples were air-dried and sieved with a 2-mm mesh filter in the laboratory. Soil pH (H_2O) was measured directly on each soil sample with a pH meter (HI-99121, Hanna Instruments, Ltd., Woonsocket, RI, USA). The amount of soil organic matter (SOM) was estimated by ignition weight loss (%) of each sample before and after heating at 500 °C for 2 hrs. Powder X-ray diffraction analyses (RINT-2000m, Rigaku, Tokyo, Japan) of all the samples investigated in this study were carried out under identical

116 experimental conditions (X-ray source; CuK α , applied voltage; 40 kV, maximum current; 30 mA,

117 diffraction angle 2 θ ; 3-40°).

118 The activity concentration of ^{137}Cs in each soil component was determined by gamma spectrometry with

119 a HPGe detector (GMX20P4-70; EG&G ORTEC, Oak Ridge, TN, USA). Acquisition time was set to be

120 144000 s for all measurements including a background check. Certified reference materials purchased from

121 the International Atomic Energy Agency (IAEA-372) and from the Japan Society for Analytical Chemistry

122 (JSAC0471, JSAC0472 and JSAC0473) to evaluate the ^{137}Cs activity concentration of individual samples

123 from count data obtained with the same geometry under identical operating conditions. The lowest limit of

124 detection was found to be 0.34 Bq kg $^{-1}$ with a confidence level of 95 % for ^{137}Cs activity concentration

125 under the experimental conditions in this study.

126 Inductively coupled plasma (ICP) analyses were carried out for all the samples to evaluate distribution

127 of some alkali metals (K, Rb and Cs) in humus and in bulk soils. Both Rb and Cs were determined with

128 ICP-mass spectrometry (ELAN 6000; Perkin Elmer Inc., Waltham, MA, USA), and K was analyzed with

129 ICP-atomic emission spectrometry (OPTIMA 5000; Perkin Elmer Inc., Waltham, MA, USA). Details of

130 the analytical procedures were described in our previous paper (Sucharová and Suchara 2006).

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132 2.3 Amount of alkali metals (K, Rb and Cs) and activity of ^{137}Cs in humus fraction

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134 Determination of the alkali metal in humus gives its concentration (C_X ; mg kg⁻¹). The amount (X_{hum} ; mg)
135 of an alkali metal (K, Rb or Cs) contained in humus fraction of a definite thickness (d ; cm) and dry density
136 (ρ ; g cm⁻³) could be calculated from the equation (1).

137

$$138 \quad X_{hum} = C_X \times \rho \times S \times d \times 10^{-3} \quad (1)$$

139

140 where S is the surface area of the humus fraction defined to be 100 cm² in this study.

141 Activity of ¹³⁷Cs (Bq) in humus fraction is also obtained from its activity concentration (Bq kg⁻¹) through
142 the equation (1).

143 The amount of an alkali metal (K, Rb Cs or ¹³⁷Cs) in the mineral component (X_{min}) of a humus fraction
144 could be estimated from the intercept of a linear relationship between SOM (%) and X_{hum} (mg, or Bq in the
145 case of ¹³⁷Cs), assuming that the forest humus is exclusively composed of organic (SOM) and mineral (min)
146 components.

147

$$148 \quad X_{hum} = a \cdot [SOM] + X_{min} \quad (2)$$

149

150 Where $X = K, Rb$ and Cs , and the subscripts of X , hum and min , denote humus and soil organic component,
151 respectively. A symbol a is the slope of the linear regression in the equation (2).

152

153 2.4 Vertical migration rate of ¹³⁷Cs

Vertical migration of ^{137}Cs in humus was investigated based on its depth distribution profiles obtained in this study at all three sites. Equation (3) was used to estimate a vertical migration rate of ^{137}Cs (Arapis and Karandinos 2004):

$$\bar{x} = \sum_i x_i g_i, \quad (3)$$

where $\bar{x}$ is the weighted mean depth (cm) of the vertical concentration distribution, x_i is the mean depth of the layer (cm), and g_i is the fraction of ^{137}Cs in the corresponding depth x_i .

The vertical migration rate of ^{137}Cs (R , cm yr^{-1}) was estimated from the mean depth values ($\bar{x}$, cm) divided by elapsed time (t , years) after the Chernobyl accident in 1986 ($R = \bar{x}/t$).

3 Results and discussion

3.1 Soil and site properties

Table 1 summarizes site-specific properties of soil including those (location, climate, soil type, forest type, stand age, ^{137}Cs inventory, apparent annual burial rate to mineral horizon and ecological half-life of ^{137}Cs) described in our previous paper (Takahashi et al. 2017). Among three sites investigated, soil and forest types are similar in properties, while other environmental factors are different, especially climatic conditions and stand age. The humus horizons in three sites (I, II and III) were selected to be similar

Table 1

170 thickness (~6 cm), which was further divided into three parts with equal thickness (2 cm); upper (H_u),
 171 middle (H_m) and lower (H_l). Moisture and the amount of soil organic matter (SOM) within each humus
 172 fraction decreased gradually to lower portion. Mean pH value was relatively constant ($3.4 \leq \text{pH} \leq 3.7$)
 173 independent of the sites with an exception in the site I (pH 4.5 at H_u). All the soils were classified into
 174 acidic Cambisol suggesting that the amounts of dissolved chemical species are relatively large in soil water.
 175 Gonet et al. (2008) investigated compositional and chemical changes of humus with depth in undisturbed
 176 forest soils in Slovakia. They showed that down the profile gave higher hydrophilic property of humus with
 177 higher carboxyl groups. Higher concentration of hydrophilic humic acids at deeper portion of the soil may
 178 result from increasing amount of decomposed SOM. Paul et al. (2015) investigated acidic and metal
 179 complexing properties of humic acids extracted from tea garden soils of different depths (surface, 15 and
 180 30 cm in depth) in India. They obtained different properties of the humic acids with depth, e.g. decreasing
 181 moisture content and increasing pKa values with depth. The pH value of each humus fraction was relatively
 182 low (pH; 3.4~4.5), which may result from pH buffer effects of hydrophilic humic acids with carboxylic and
 183 hydroxylic functional groups (Paul et al. 2015). Such low values are generally observed in humus layers of
 184 non-calcareous sandy soils summarized by De Vries and Leeters (2001) in forest stands in the Netherlands.
 185 These factors may facilitate dissociation of $^{137}\text{Cs}^+$ with anionic humus components at low pH in the lower
 186 humus horizon in our investigated sites.

3.2 Depth distribution profiles of alkali metals (K, Rb and Cs) in bulk soil and in humus horizon

Uptake of nutrients from soil is an important process in biological cycling in forest environment, in which radiocesium may be indiscriminately taken up by plant roots together with other alkaline elements such as rubidium (Rb) and stable cesium (Cs) as well as an essential nutrient potassium (K).

Figure 1 shows linear relationships between SOM and concentration of alkali metals (K, Rb and Cs) in bulk soil in the site III (Plühonice). The plots suggest that the concentrations of alkali metals increase linearly with increasing soil depth. The correlation coefficients between them were obtained for K ($R=0.998$, $n=8$, $p<0.01$), Rb ($R=0.994$, $n=8$, $p<0.01$) and Cs ($R=0.622$, $n=8$, $p<0.01$). Assuming that the soil is simply composed of organic and mineral components, the results in Fig. 1 indicate that these alkali metals are of lithogenic origin. There is scarce information available for comparing the amounts of alkali metals in humus. Among them Sucharova et al. (2011) conducted chemical analyses of 39 elements including alkali metals (K, Rb, Cs) in humus samples collected in coniferous forest sites across the Czech Republic. Median values in humus samples were reported as 3240, 19 and 2.2 mg Kg^{-1} for K, Rb and Cs, respectively. Using analytical data obtained on these elements, they investigated a trend analysis of the spatial distribution. They found that most anomalies of typical elements in the distribution could directly be linked to known industrial sites, mines, power plants or urbanization. Johanson et al. (2004) determined many chemical

Fig. 1

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205 elements including alkali metals (K, Rb and Cs) in forest soils close to the Nuclear Power Plant at Forsmark
206 in Sweden. They summarized concentrations (median values) of K, Rb and Cs in bulk soil to be 605 (370-
207 986), 2.52 (1.48-10.1) and 0.21 (0.080-0.68) mg kg⁻¹, respectively. They also showed two to five times
208 higher values of K and Rb concentrations in rhizosphere than those in bulk soil except for Cs which
209 remained at low levels independent of soil compartments. Vicichuk et al. (2010) investigated the
210 distribution of K, Rb and Cs in forest soil fractions including bulk soil and rhizosphere. Results in bulk soil
211 (mean ± standard deviation) were 642 ± 215, 3.9 ± 2.7 and 0.3 ± 0.2 (mg kg⁻¹) for K, Rb and Cs
212 concentrations, respectively. The similar trends appeared with higher K and Rb concentrations, and constant
213 Cs level in rhizosphere compared with those in bulk soil. All these results may partly support our finding
214 shown in Fig. 1, in which the alkali metal contents in soil vary at different soil compartments, probably
215 depending on the fraction of mineral components.

216 To estimate the amounts of alkali metals (K, Rb and Cs) contained in the mineral components (X_{min}; mg)
217 of a humus fraction of known thickness (d; cm), their amounts (x; mg), not concentration (mg kg⁻¹) were
218 calculated using the equations (1) and (2) explained in the Material and methods section. Table 2 lists the
219 results of regression analysis between SOM (%) and the amounts of alkali metals (mg) in each humus
220 fraction in three sites (Sites I, II and III), where the symbols r, n, p, a and X_{min} in the table denote Pearson's
221 correlation coefficient, number of data, probability, slope and intercept of the regression line, respectively.
222 As seen in Table 2, estimated amounts of K, Rb and Cs in mineral components (X_{min}, the value at the

Table 2

223 intercept) decreased in the order, Site II > Site I > Site III, suggesting that the underlying minerals in the
 224 Site II contain the highest amounts of the alkali metals among others. Another finding in Table 2 is that
 225 increasing ratios (the ratio of slopes) of Rb to K ($3\sim 4 \times 10^{-4}$), and of Cs to K ($1\sim 3 \times 10^{-4}$) against SOM
 226 resulted in similar values in all the investigated sites. Although there appeared some variability for Cs to K
 227 values, degradation and/or weathering mechanisms may play a role controlling the amounts of alkali metals
 228 in humus horizon. Regarding uptake of K and Rb by plants, Simonsson et al. (2016) investigated sources
 229 of K and its relation with K/Rb ratio in soil and biomass under a Norway spruce stand (*Picea abies* Karst.).
 230 They showed quite low K/Rb ratios in the forest floor as well as interlayers of 2:1 clay minerals and biomass
 231 to conclude the importance of clay minerals as fixing and releasing K and Rb in the cycling of nutrients in
 232 forest soil environment.

233 The results in Table 2 offer a new finding that concentration of alkali metals in humus varies at different
 234 depths (or with elapsed time after deposition of fresh soil organic matter) suggesting that the importance of
 235 humus fractions to be considered. The properties of humus components are supposed to change gradually,
 236 and to affect downward migration of ^{137}Cs in humus horizon. To elucidate a long-term behavior of ^{137}Cs in
 237 the forest ecosystem, Karadeniz and Yaprak 2007 investigated distribution of both ^{137}Cs and stable ^{133}Cs in
 238 forest ecosystems. They attributed observed higher concentration of Cs in O2 horizon to its possible
 239 bioaccumulation in the horizon. They suggested that differences in the ^{137}Cs and stable ^{133}Cs depth profiles
 240 reflect the latter being enclosed in bedrock particles in the mineral horizons.

3.3 Depth distribution profiles of ^{137}Cs in bulk soil and in humus horizon

Figure 2 shows the depth distribution profiles of ^{137}Cs activity concentration (Bq kg^{-1}) in bulk soil investigated in this study. Significant portion of ^{137}Cs was still found in the upper soil horizon (< 8 cm depth) 30 years after the Chernobyl accident in 1986, which had already been reported at different sampling points within the same sites in our previous paper (Takahashi et al. 2017). The highest activity concentration of ^{137}Cs were found to be $880 (\pm 5)$, $932 (\pm 6)$ and $240 (\pm 3)$ Bq kg^{-1} at 4-6 cm (Site I), 2-4 cm (Site II) and 6-8 cm (Site III), respectively. All these depths were included in humus horizon of soil, in which the site III of the oldest stand age (100-120 years) gave the lowest ^{137}Cs level among all. **Figure 3** shows distribution of mean ^{137}Cs activity concentration (Bq kg^{-1}) in each fraction (H_u ; 2-4 cm, H_m ; 4-6 cm, and H_l ; 6-8 cm in depth range) of humus horizon, in which the highest concentration of ^{137}Cs was found in the middle fraction (H_m) of humus in all the three sites.

Absolute activity (Bq) of ^{137}Cs was calculated using equation (1) in Material and methods to compare the amount of ^{137}Cs remaining in each humus fraction within 2 cm in thickness (200 cm^3 in volume). **Figure 4** summarizes the results on ^{137}Cs activity (Bq) as well as the amounts of alkali metals (K, Rb and Cs) in each humus fraction of in the three sites. Contrary to the results in **Fig. 3**, the ^{137}Cs activity clearly increased

Fig. 2

Fig. 3

Fig. 4

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3 258 towards deeper humus fraction to reach the maximum value at the deepest portion (H_i , 6-8 cm) in any sites.
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6 259 This fact confirms the ^{137}Cs deposited on the forest floor moved downward within humus horizon. The
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9 260 presence of a ^{137}Cs peak in organic (O_h , or O_f) horizons has been reported in the literature (e.g. Ylipietä et
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12 261 al. 2008; Karandeniz and Yaprak 2011; Alexery et al. 2014; Takahashi et al. 2017; Karandeniz et al. 2015a).
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15 262 However, few papers have addressed distribution of ^{137}Cs profile within humus horizon using sets of ^{137}Cs
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18 263 activity (Bq) data. The results must be the first finding to clarify the ^{137}Cs distribution in humus horizon.
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21 264 The same trend was observed on each alkali metal (K, Rb and Cs) distribution in humus fraction in Fig. 4,
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24 265 in which the amount of alkali metal increased towards deeper portion of humus fraction ($H_u < H_m < H_i$) as
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27 266 in the case of ^{137}Cs . Possible interactions of atmospheric ^{137}Cs with lithogenic alkali metals occur in
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30 267 biological uptake of nutrients in surface organic horizons. Chao et al. (2008) determined ^{137}Cs and alkali
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33 268 metals (K, Rb and K) in a perhumid montane forest ecosystem. They found that the $^{137}\text{Cs}/\text{Cs}$ ratio varied
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36 269 with soil horizons depending on the persistent supply of lithogenic Cs via weathering processes of minerals
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39 270 in deeper soil layers. They concluded that the $^{137}\text{Cs}/\text{Cs}$ ratio can be an indicator for monitoring the
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42 271 distribution and uptake of ^{137}Cs in the forest ecosystem.
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53 273 **3.4 Downward migration of ^{137}Cs in humus horizon**
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275 In the previous sections two important findings were obtained on **behavior** of ^{137}Cs and alkali metals (K,
 276 Rb and Cs) in humus, i) ^{137}Cs moved downward within humus horizon and its highest proportion was in
 277 the lowest fraction (H_l , 6-8 cm in depth range) at the sampling time in 2014, and ii) the amounts of alkali
 278 metals increased with increasing fraction of mineral components (or decreasing SOM) suggesting them as
 279 lithogenic origin.

280 The following two possibilities are now considered as explanations of the distribution of ^{137}Cs within humus
 281 horizon: 1) clay minerals such as illite and smectite fixing ^{137}Cs in their structures may be contained in the
 282 humus, and 2) downward movement of ^{137}Cs within humus horizon may be accompanied with degrading
 283 SOM. The first possibility came from the results in the literature that some clay minerals fix ^{137}Cs strongly
 284 within their layered structure, especially on micaceous clay minerals (Kruyts and Delvaux 2002; Nakao et
 285 al. 2014; Fuller et al. 2015).

286 No appreciable diffraction peaks corresponding to these clay minerals were detected in the lower range of
 287 diffraction angle ($3^\circ < 2\theta < 18^\circ$) on X ray diffraction (XRD) spectra of all the humus fractions (H_u , H_m and
 288 H_l) investigated in this study. An example of X ray diffraction pattern of a humus sample in the site I was
 289 shown in our previous paper (Takahashi et al. 2017). Table 3 lists major diffraction peaks (2θ , d-spacing)
 290 and assignment of the mineral in each humus fraction in the site III investigated in this study, in which only
 291 quartz was detected in all the cases. Amorphous materials, such as some alumino-silicates, hydrous iron

Table 3

292 oxides and strongly resistant organic residues may be contained in the lower portion of the humus horizon.
 293 All of them are supposed to be insignificant for the ^{137}Cs uptake (April and Deller 1990; Zhao et al. 2016).
 294 In our previous paper (Takahashi et al. 2017), the ecological half-life of ^{137}Cs in humus layer in the sites
 295 I, II and III were estimated to be 21.7, 19.8 and 24.8 years, respectively. A similar estimation reported by
 296 Alexey et al. (2014) gave values of the ^{137}Cs effective half-life in the fermentative forest litters to be 8-19
 297 years in Ukraine and Russian Federation forest sites. Several authors acknowledged that forest humus
 298 represents a sink for radiocesium recycling in a forest ecosystem, and that this sink for radiocesium will
 299 persist for many years (Melin et al. 1994; Bunzl et al. 1995; Schell et al. 1996). Furthermore, the time scale
 300 for this persistence will be decades rather than years (Rafferty et al. 2000).
 301 The mean depth of the humus layer was obtained in each site and ranged from 3.6 to 5.4 cm using Eq.
 302 (3). When considering the elapsed time after the Chernobyl accident in 1986 (28 years as of 2014), the
 303 ^{137}Cs vertical migration rate was estimated to be in the range of 0.13-0.19 cm yr^{-1} ($n=45$) in this study.
 304 Similar values have been reported in the literature (Belli et al. 1994; Arapis and Karandinos 2004;
 305 Almgren and Isaksson 2006; Karandeniz et al. 20015b) in other forest soils under different geological and
 306 climatic conditions. Takahashi et al. (2017) estimated apparent burial rate from humus to mineral soil
 307 horizon to be in the range of 0.04-0.08 cm yr^{-1} ($n=27$). Higher migration rate of ^{137}Cs within humus layer
 308 compared with that into mineral horizon supports previous findings in the literature in which humus does
 309 not strongly retain ^{137}Cs within its structure compared with weathered micaceous minerals (Rigol et al.

2002). Kruyts and Delvaux (2002) reviewed main processes and parameters controlling the mobility of radiocesium in semi-natural soils. They showed that thick humus facilitates transfer of ^{137}Cs from soil to plant (biorecycling), because of weak interaction between ^{137}Cs and soil organic matter. They further investigated mobility of radiocesium in forest floors with different humus types of different mixing of mineral and organic residues (Kruyts et al. 2004). They suggested that the mixing of organic residues with Cs-fixing minerals is a key process in ^{137}Cs mobility. Another important evidence for very low ^{137}Cs migration rate into mineral horizon was that there was a great gap in ^{137}Cs activity concentration between the lowest humus fraction (H_1) and the uppermost mineral phase as shown in Fig. 2. Further observations should be continued to elucidate dynamics of ^{137}Cs remaining in lower humus fraction.

It should be noted that all the fractions of humus horizon in this study did not contain appreciable amounts of clay minerals, especially illites and smectites as determined by X-ray diffraction analysis (Table 3). However, it is likely that mineral components of little or no ^{137}Cs retention, such as amorphous oxides (aluminum, iron and manganese) and quartz, were contained in each humus fraction, because the proportion of organic components was not higher than 90 % even in the upper-most fraction (H_u) of humus horizon as suggested in Fig. 1. The results, including the downward migration rate of ^{137}Cs , indicate that organic components of humus have certain capacity for retaining ^{137}Cs within each humus fraction (Fuller et al. 2015).

327 Although little is known about interaction of ^{137}Cs with SOM in humus horizon in the literature, possible
 328 role of organic matter in radiocesium adsorption in soils was reviewed by Staunton et al. (2002), focusing
 329 largely on their own results in the laboratory. They observed that soil organic matter appreciably reduced
 330 the ability to immobilize Cs (decreasing distribution coefficient of radiocesium) on reference clay minerals
 331 (illite and montmorillonite), despite the weak and non-specific interaction of Cs with soil organic matter.
 332 Regarding possible interactions of ^{137}Cs with SOM, soil microflora and microfauna may play a role in
 333 retaining radiocesium in their bodies (Kruse-Imer and Giani 2003; Karandeniz et al. 2015a).
 334 It is now speculated that radiocesium may be released from dead microorganisms, and then incorporated
 335 again into newborn organisms; that is, radiocesium is circulated within the surface soil including humus
 336 horizon. To elucidate the possible relationship between microbial activity and deposited radiocesium in the
 337 profiles of forest soil, a change in their population with depth needs to be considered. Susyan et al. (2006)
 338 investigated the state of the microbial community in forest soils in Russia by determining microbial biomass
 339 and respiration, and population densities of micro-organisms. They found that the microbial activity
 340 decreased with increasing soil depth. More than 50 % of microbial biomass in the entire soil profile was
 341 concentrated in the upper portion (0-24 cm in depth) of the soil (humus horizon).
 342 Decay of organic matter and nutrient cycling in forest soils are influenced by the interrelationships among
 343 climate, litter types and the variety and abundance of soil organisms. Regardless of considerable research

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3 344 on the effects of climate and litter quality, it is difficult to link the structure of soil communities to soil
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6 345 processes due to the lack of appropriate methods applicable to complex microbial communities (Leckie et
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9 346 al. 2004). To address this subject, they investigated the microbial communities (total microbial biomass
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12 347 and community composition) in forest floors of two forest sites **contrasting** in nitrogen availability in
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15 348 Canada. They found that bacterial and fungal communities were distinct in **the fermentation (F)**, upper
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18 349 humus and lower humus layers of the forest floor and total biomass decreased in deep layers. Their results
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21 350 may support the results obtained in this study that abiotic properties of humus horizon were changed
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24 351 between upper and lower fractions.

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29 352 A genetic technique on DNA and RNA quantification was applied to distinguish activity distribution of
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32 353 microbial biomass, especially bacterial and fungal biomass, in coniferous forest sites in the Czech Republic
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35 354 (Baldrian et al. 2012). They found that bacterial and fungal communities differ in their spatial distributions
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38 355 with fungal taxa more distinctly confined to either the litter of the organic horizon of soil and more
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41 356 heterogeneously distributed in the ecosystem. They also suggested that low abundance of several fungal
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44 357 taxa sometimes contributes to decomposition processed in soil. Several studies have indicated the
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47 358 importance of mycelia on the accumulation of radiocesium in surface soils (Guillitte et al. 1994; Brückmann
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50 359 and Woters 1994; Vinichuk and Johanson 2003; Yoshida et al. 2014). Regarding the distribution of fine
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53 360 roots in soils under coniferous stands (*Picea abies*), Børja et al. (2008) found that the highest root biomass
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56 361 was in the upper soil layers (humus layer and upper portion of mineral soil). Pertritan et al. (2011) also
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3 362 indicated that most fine roots were concentrated in the humus layer (more than 45 %) and in the top mineral
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6 363 soil (0-5 cm, about 15 %). This type of biological cycling is strongly associated with the downward
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9 364 movement of ^{137}Cs .

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13 365 Based on these findings and reports in the literature, various organic compounds of the humus layer are
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16 366 likely to retain ^{137}Cs within their structures. Decomposition of the organic matter in soil is largely a
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19 367 biological process that occurs naturally. Humus is regarded as successive decomposition products with
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22 368 complex chemical structures, remaining in soil for relatively long time. It is expected that properties of
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25 369 humus may change gradually with degrading organic matter, i.e. with depth, in undisturbed forest soil, and
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28 370 that the organic compounds in lower humus fraction (H_L) may be much more resistant to microbial oxidation
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31 371 than those in the upper fraction (H_u) (Gonet et al. 2008; Schaeffer et al. 2015). Dynamics of soil organic
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34 372 matter in humus could be considered with a parameter, mean residence time, of organic components.
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37 373 Different values of mean residence time and even different concept on humus formation were reported,
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40 374 which were inevitably caused by the complexity of organic matter in composition and structure,
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43 375 environmental parameters and separation techniques (Certini et al. 2004; Delula and Aplet 2008; Schmidt
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46 376 et al. 2011). Dynamics of soil humus should be investigated through carbon isotopes (^{13}C and ^{14}C) technique,
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49 377 which enables possible sources (and date) of carbon contained in the humus component (Paul et al. 1964;
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52 378 Fujiyoshi et al. 2010, 2012). Decomposition of soil organic matter therefore depends both on biotic and
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55 379 abiotic environment, thus ecosystem property (Lehmann and Kleber 2015).
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As shown in Fig. 4, the ^{137}Cs activity (Bq) remained in humus fraction decreased consistently in the order: $H_U < H_m < H_l$. The result together with those on ^{137}Cs mean downward migration rate (0.1-0.2 cm yr^{-1}) estimated in this study suggests that ^{137}Cs moved downward within humus horizon. Assuming that ^{137}Cs is released within a humus fraction due to the decomposition of host organic components, the downward migration of ^{137}Cs may depend on degradation rate of the organic components. If this assumption is appropriate, mean residence time of the host organic components may give similar mean residence time of ~30 (29~36) years to that of ^{137}Cs estimated from the ecological half-life of ^{137}Cs in humus horizon (Site I; 21.7, Site II; 19.8 and Site III; 24.8 years) estimated in our previous study (Takahashi et al. 2017). It is suggested that speciation of ^{137}Cs in humus fractions may be a potential approach to identify a target organic component, and that mean residence time of the humus components **should** be evaluated to assess a mechanism of downward migration of ^{137}Cs in humus horizon, while applying powerful tools like genetic and isotope (stable and radioactive) techniques.

4 Conclusions

Bulk soil and its humus horizon were separately collected from three coniferous forest sites in the Czech Republic in September 2014. The highest activity concentration of ^{137}Cs (Bq kg^{-1}) appeared in the upper portion of the soil (mainly in humus horizon) about 30 years after the Chernobyl accident. Increasing

activity of ^{137}Cs (Bq) was found in the lower humus horizon (H_1 , 4~6 cm depth range) in which no appreciable amounts of micaceous clay minerals like illite and smectite were detected in all the sites. Similar depth distribution profiles appeared for lithogenic alkali metals (K, Rb and Cs) in humus as in the case of fallout nuclide ^{137}Cs , suggesting that mineral components with little retention ability for ^{137}Cs increased at lower humus fraction. It is likely that organic components of humus layer have certain capacity of retaining ^{137}Cs in their structures. Downward migration rate of ^{137}Cs within the humus horizon (0.13-0.19 cm yr^{-1}) estimated in this study was about three times higher than those (0.04-0.06 cm yr^{-1}) previously obtained from the humus to mineral horizon. These findings suggest that ^{137}Cs moves downward with degrading organic matter within the humus horizon. Comparing depth distribution profiles between ^{137}Cs activity (Bq) and the amount (g) of alkali metals (K, Rb and Cs) may reflect possible association of ^{137}Cs with the alkali metals during biological activity within humus. Further investigation is needed to elucidate mechanism of ^{137}Cs migration within humus horizon, especially interactions of ^{137}Cs and degrading organic components.

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Fig. 1

Fig.2

Fig.3

Fig. 4

Figure caption

Figure. 1 Relationship between the amount of soil organic matter (SOM; %) and concentration of alkali metals (K; $\times 10^{-1}$ %, Rb; mg kg^{-1} , Cs; mg kg^{-1}) in surface soil down to a depth of 20 cm in the investigated sites (I, II, and III). Correlation coefficient of Cs with SOM was lower compared with those for K and Rb. Standard deviation (± 1 S.D.) of each data set was 1.8~4.8, 1.1~3.5 and 0.98~4.5 % for K, Rb and Cs, respectively.

Figure 2 Depth distribution profiles of ^{137}Cs activity concentration (Bq kg^{-1}) in surface soil (<20 cm depth) in the sites I, II and III. Most of the Chernobyl derived ^{137}Cs still existed in the upper portion (< 8 cm depth) of the soil. The site III showed the lowest activity concentration of ^{137}Cs among the three sites.

Figure 3 Depth distribution profiles of ^{137}Cs activity concentration (Bq kg^{-1}) in each humus fraction of 2 cm in mean thickness. The highest ^{137}Cs activity concentration was found in the middle fraction (H_m) of humus in all the sites investigated.

Figure 4 Depth distribution of ^{137}Cs activity (Bq) and of the alkali metals (K, Rb and Cs) in each humus fraction (H_u , H_m , and H_l) in the sites I, II and III. Both the ^{137}Cs activity and the amounts of alkali metals consistently increased to deeper fraction of humus horizon, in which the site III gave the lowest levels compared with other sites.

Table 1 Summary of the site-specific properties of soil including those (location, climate, soil type, tree type, stand age, ¹³⁷Cs inventory, annual apparent burial rate of ¹³⁷Cs to mineral horizon and ecological half-life) described in our previous study (Takahashi et al. 2017). Also included properties (mean thickness, pH, moisture SOM and density) of humus fractions (H_u, H_m, H_l) in humus horizon.

Properties	Site								
	I (Přemyslov)			II (Opatovice)			III (Průhonice)		
Location	50.111°N, 17.065 °E			49.962°N, 15.065 °E			49.986°N, 14.542 °E		
Altitude (m)	800			390			320		
Annual mean temperature (°C)	4-5			7-8			8-9		
Annual mean precipitation (°C)	800-1000			500-550			500-550		
Soil type	Mesobasic cambisol			Modal cambisol			Modal cambisol		
Tree type	<i>Picea abies</i>			<i>Picea abies</i>			<i>Picea abies</i>		
Stand age (y)	60-80			80-100			100-120		
¹³⁷ Cs inventory in 1986 (kBq m ⁻²)	9.46			1.16			5.56		
Annual apparent burial rate of ¹³⁷ Cs (cm y ⁻¹)	0.06 ± 0.01			0.04 ± 0.01			0.08 ± 0.01		
Ecological half-life of ¹³⁷ Cs (y) in humus	19.8			24.8			21.7		
Humus horizon*	H _u	H _m	H _l	H _u	H _m	H _l	H _u	H _m	H _l
Thickness (mean, cm)	2	2	2	2	2	2	2	2	2
pH (mean)	4.5	3.7	3.4	3.7	3.5	3.6	3.5	3.4	3.5
Moisture (mean, %)	55	40	30	42	30	27	39	37	22
SOM (mean, %)	81	56	50	83	77	68	81	66	33
Density (dry, mean, g cm ⁻³)	0.27	0.38	0.49	0.17	0.28	0.38	0.11	0.21	0.32

* Upper fraction (H_u), Middle fraction (H_m), Lower fraction (H_l)

Table 2 Results of the regression analysis between SOM (%) and the amounts of alkali metals (K, Rb and Cs) contained in each humus fraction in the sites I, II and III. The symbols r, n, p, a and $X_{\min}$ in the table denote Pearson's correlation coefficient, number of probability, slope and intercept of the regression line, respectively. The $X_{\min}$ value is the content (mg or g) of each alkali metal contained in mineral components of humus horizon with a thickness of 6 cm. Increasing ratio of ^{137}Cs (Bq) with decreasing SOM was also shown as a slope (a) in this table.

Element (radionuclide)	Site														
	I (Přemyslov)					II (Opatovice)					III (Průhonice)				
	r	n	p	a	$X_{\min}$	r	n	p	a	$X_{\min}$	r	n	p	a	$X_{\min}$
K (g)	0.95	9	<0.01	0.29 (0.06)	2.6	0.99	9	<0.01	0.71 (0.14)	6.25	0.99	9	<0.01	0.05 (0.01)	0.44
Rb (mg)	0.96	9	<0.01	0.09 (0.02)	0.8	0.99	9	<0.01	0.25 (0.05)	2.20	0.99	9	<0.01	0.02 (0.01)	0.22
Cs (mg)	0.96	9	<0.01	3.58 (0.77)	0.35	0.96	9	<0.01	6.77 (1.33)	0.62	1.0	9	<0.01	1.67 (0.32)	0.16
^{137}Cs (Bq)	1.0	9	<0.01	1.75 (0.33)	-	0.93	9	<0.01	5.35 (0.66)	-	0.97	9	<0.01	0.20 (0.04)	-

Table 3 Major diffraction peaks (2θ and d-spacing) and assignment of the mineral observed in each humus fraction (H_u , H_m and H_l) in the site III ($3^\circ < 2\theta < 38^\circ$).

Site III	2θ ($^\circ$ CuK α)	d ($\text{\AA}$)	Assignment
H_u	20.88	4.26	Quartz
	26.62	3.34	Quartz
	36.54	2.46	Quartz
H_m	20.88	4.26	Quartz
	26.61	3.34	Quartz
	36.57	2.46	Quartz
H_l	20.82	4.26	Quartz
	26.66	3.34	Quartz
	36.54	2.46	Quartz

Reply to the reviewer's comments and advices

We would greatly appreciate your help to refine our current revised manuscript. Reading the general comments of yours, we reconsidered the important findings obtained in the present study to shorten the extra discussion. We also thank you for suggesting many mistakes in English. We checked all of them to be revised as shown in red in the text (The corrected parts in blue were undertaken by the authors themselves). The followings were the reply to the reviewer's comments.

General comments

Page 21, lines 354-360

We erased whole the paragraph on biotic and abiotic effects on the sorption of stable cesium and strontium in soil components conducted in the laboratory (Seeprasert et al. 2016). As the reviewer suggested, this part was not directly connected to our results.

Page 22, lines 374-402

This part, concerned with “mean residence time” of soil organic components, may beyond the scope of this paper. We decided to shorten this part, and only to add a potential usefulness of carbon (^{13}C and ^{14}C) isotope technique to elucidate the source and date of soil organic components obtained in our previous studies (Fujiyoshi et al. 2010, 2012) as well as a work in the literature (Paul et al. 1964).

Typographical corrections

We corrected all the suggestions by the reviewer (as shown in red in the text), except for one:

Page 9, line 138

Unit of dry density is $[\text{g cm}^{-3}]$. The value 10^{-3} is multiplied to the right side in the equation (1).

The corresponding author, Ryoko FUJIYOSHI (July 25 2017)

July 26 2017

List of changes

The table below lists changes in the previous manuscript, according to the comments given by the Editor and Reviewer. All the corrections were written in red in the text of the revised manuscript.

Line(s)	Line(s) revised	Comment	Response	Note
		Correct numbering of Figures (Figs. 2, 3 and 4)	Done	Editor
Abstract				
20	20	Change the word	Done	Reviewer
21	21-22	Delete dangling phrases	Done	Reviewer
35	34	Delete dangling phrases	Done	Reviewer
41	39	Add “The”	Done	Reviewer
41	39	Change the phrase	Done	Reviewer
42	40-41	Re-write the phrase	Done	Reviewer
Introduction				
48	46-47	Revise the sentence	Done	Reviewer
53	51	Re-write the phrase	Done	Reviewer
59	56-57	Replace the words	Done	Reviewer
64	61	Replace the word	Done	Reviewer
65	62	Re-write the phrase	Done	Reviewer
79	76	Add “the”	Done	Reviewer
80	77	Re-write the phrase	Done	Reviewer
82	79	Add “the”	Done	Reviewer
92	89	Change the word	Done	Reviewer
96	93	Add “the”	Done	Also line 91
Material and methods				
99	96	Replace the phrase	Done	
138	135	Unit of dry density	Unit of dry density is $[g\ cm^{-3}]$. The value 10^{-3} is multiplied to the right hand side of the equation (1).	Explanation
Results and discussion				

166	163	Replace subsection title	Done	Reviewer
187-188	184	Replace the phrase	Done	Reviewer
210	208	Re-write the phrase	Done	Reviewer
211	208	Add “the”	Done	Reviewer
214	211	Replace the word	Done	Reviewer
277	274	Replace the word	Done	Reviewer
319	316	Replace the word	Done	Reviewer
324	321	Add “the”	Done	Reviewer
326	323-324	Re-write the sentence	Done	Reviewer
349	346	Move the word	Done	Reviewer
350	347	Define the word	Added the full spelling	Reviewer
354-360		Not directly connected to the present study	The whole paragraph on biotic and abiotic effects on the sorption of stable cesium and strontium in soil components conducted in the laboratory (Seeprasert et al. 2016).	Reviewer (Authors)
374-402	375-377	Beyond the scope of this study	This part was shortened, and added a potential usefulness of carbon (¹³ C and ¹⁴ C) isotope technique to elucidate the source and date of soil organic components obtained in our	Reviewer (Authors)

			studies (Fujiyoshi et al. 2010, 2012) as well as a work in the literature (Paul et al. 1964).	
411	387	Delete “then” and “highly”	Done	Reviewer
412	388	Replace the word	Done	Reviewer
413	390	Delete the phrase	Done	Reviewer
Conclusion				
423	399	Replace the word	Done	Reviewer
430	406	Adjust the style	Done	Reviewer
431	407	Delete the phrase	Done	Reviewer