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# Journal of Environmental Radioactivity Influence of non-equilibrium sorption on the vertical migration of 137Cs in forest mineral soils of Fukushima Prefecture --Manuscript Draft--

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Abstract:	Sorption hypotheses and models are required for the prediction of 137Cs migration in soils contaminated after nuclear reactor accidents and nuclear weapons tests. In assessment models, the Kd (distribution coefficient) hypothesis for sorption, which assumes that sorption is instantaneous, linear and reversible, has often been coupled with the convection-diffusion equation (CDE) to model 137Cs migration. However, it fails to describe 137Cs migration velocities which often decrease with time. Alternative equilibrium-kinetic (EK) hypotheses of 137Cs sorption/desorption have been suggested by laboratory experiments but have not been fully validated in field conditions. This work addressed the influence and magnitude of non-equilibrium 137Cs sorption in field conditions by reinterpreting, with an inverse approach, series of 137Cs profiles measured in mineral soils of forest plots located in Fukushima Prefecture (2013-2018). Our results show that the inclusion of non-equilibrium sorption significantly improves, compared to the equilibrium hypothesis, the realism of simulated 137Cs profiles. Fitted sorption parameters suggest a fast sorption kinetic (half-time of 1–7 hours) and a pseudo-irreversible desorption rate (half-time of 3.2 x 100 - 3.4 x 106 years), whereas equilibrium sorption (4.0 x 10-3 L kg-1 on average) only affects a negligible portion of 137Cs inventory. By June 2011, such EK parameters fitted on our plots realistically reproduced profiles measured in the same forest study site (Takahashi et al., 2015). Predictive modeling of 137Cs profiles in soil suggests a strong persistence of the surface 137Cs contamination by 2030, with exponential profiles consistent with those reported after the Chernobyl accident. This study demonstrates that hypotheses and parameters of 137Cs sorption can be partially inferred from in situ measurements. However, further experiments in controlled conditions are required to better estimate the sorption parameters and to identify the processes behind non-equilibrium sorption.						
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	Japan Atomic Energy Agency kurikami.hiroshi@jaea.go.jp Studies vertical migration of 137Cs						
	Our submission is very similar to their article in JER, but with improvements (data, models).						
	María Luciana Montes						

	Universidad Nacional de la Plata Imontes@fisica.unlp.edu.ar Works on vertical migration of 137Cs Proposed a non-equilibrium model of sorption
	Chuan-Pin Lee National Cheng Kung University cplee@mail.ncku.edu.tw Works on Cs sorption in soils Proposed a two-site sorption model
	James D. Begg Lawrence Livermore National Laboratory Begg2@llnl.gov Works on cesium sorption But more specifically on pure minerals
Opposed Reviewers:	
Response to Reviewers:	

# Highlights

- Equilibrium-kinetic model used to reproduce the vertical migration of <sup>137</sup>Cs in Fukushima soils.
- The inclusion of non-equilibrium improves the realism of simulated profiles.
- Fitted parameters suggest a fast and pseudo-irreversible sorption kinetic.
- Predictive modeling suggests a persistence of the contamination near the surface.

#### Abstract

Sorption hypotheses and models are required for the prediction of <sup>137</sup>Cs migration in soils contaminated after nuclear reactor accidents and nuclear weapons tests. In assessment models, the  $K_d$  (distribution coefficient) hypothesis for sorption, which assumes that sorption is instantaneous, linear and reversible, has often been coupled with the convection-diffusion equation (CDE) to model <sup>137</sup>Cs migration. However, it fails to describe <sup>137</sup>Cs migration velocities which often decrease with time. Alternative equilibrium-kinetic (EK) hypotheses of <sup>137</sup>Cs sorption/desorption have been suggested by laboratory experiments but have not been fully validated in field conditions. This work addressed the influence and magnitude of nonequilibrium <sup>137</sup>Cs sorption in field conditions by reinterpreting, with an inverse approach, series of <sup>137</sup>Cs profiles measured in mineral soils of forest plots located in Fukushima Prefecture (2013-2018). Our results show that the inclusion of non-equilibrium sorption significantly improves, compared to the equilibrium hypothesis, the realism of simulated <sup>137</sup>Cs profiles. Fitted sorption parameters suggest a fast sorption kinetic (half-time of 1–7 hours) and a pseudo-irreversible desorption rate (half-time of  $3.2 \times 10^{0}$ - $3.4 \times 10^{6}$  years), whereas equilibrium sorption (4.0 x  $10^{-3}$  L kg<sup>-1</sup> on average) only affects a negligible portion of  $^{137}$ Cs inventory. By June 2011, such EK parameters fitted on our plots realistically reproduced profiles measured in the same forest study site (Takahashi et al., 2015). Predictive modeling of <sup>137</sup>Cs profiles in soil suggests a strong persistence of the surface <sup>137</sup>Cs contamination by 2030, with exponential profiles consistent with those reported after the Chernobyl accident. This study demonstrates that hypotheses and parameters of <sup>137</sup>Cs sorption can be partially inferred from *in situ* measurements. However, further experiments in controlled conditions are required to better estimate the sorption parameters and to identify the processes behind nonequilibrium sorption.

**Keywords:** Kinetics, Inverse identification, Soil profile, modeling, Fukushima Dai-ichi Nuclear Power Plant accident, Cesium.



# Influence of non-equilibrium sorption on the vertical migration of <sup>137</sup>Cs in forest mineral soils of Fukushima Prefecture

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- 1 Influence of non-equilibrium sorption on the vertical migration of <sup>137</sup>Cs in forest mineral
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#### 3 Abstract

Sorption hypotheses and models are required for the prediction of <sup>137</sup>Cs migration in soils 4 contaminated after nuclear reactor accidents and nuclear weapons tests. In assessment models, 5 the  $K_d$  (distribution coefficient) hypothesis for sorption, which assumes that sorption is 6 instantaneous, linear and reversible, has often been coupled with the convection-diffusion 7 equation (CDE) to model <sup>137</sup>Cs migration. However, it fails to describe <sup>137</sup>Cs migration 8 velocities which often decrease with time. Alternative equilibrium-kinetic (EK) hypotheses of 9 <sup>137</sup>Cs sorption/desorption have been suggested by laboratory experiments but have not been 10 fully validated in field conditions. This work addressed the influence and magnitude of non-11 equilibrium <sup>137</sup>Cs sorption in field conditions by reinterpreting, with an inverse approach, series 12 of <sup>137</sup>Cs profiles measured in mineral soils of forest plots located in Fukushima Prefecture 13 (2013-2018). Our results show that the inclusion of non-equilibrium sorption significantly 14 improves, compared to the equilibrium hypothesis, the realism of simulated <sup>137</sup>Cs profiles. 15 Fitted sorption parameters suggest a fast sorption kinetic (half-time of 1-7 hours) and a pseudo-16 irreversible desorption rate (half-time of  $3.2 \times 10^{0}$ - $3.4 \times 10^{6}$  years), whereas equilibrium 17 sorption (4.0 x  $10^{-3}$  L kg<sup>-1</sup> on average) only affects a negligible portion of  $^{137}$ Cs inventory. By 18 June 2011, such EK parameters fitted on our plots realistically reproduced profiles measured in 19 the same forest study site (Takahashi et al., 2015). Predictive modeling of <sup>137</sup>Cs profiles in soil 20 suggests a strong persistence of the surface <sup>137</sup>Cs contamination by 2030, with exponential 21 profiles consistent with those reported after the Chernobyl accident. This study demonstrates 22 that hypotheses and parameters of <sup>137</sup>Cs sorption can be partially inferred from *in situ* 23 measurements. However, further experiments in controlled conditions are required to better 24 estimate the sorption parameters and to identify the processes behind non-equilibrium sorption. 25

26 Keywords: Kinetics, Inverse identification, Soil profile, modeling, Fukushima Dai-ichi

27 Nuclear Power Plant accident, Cesium.

#### 28 **1. Introduction**

Vertical migration of radiocesium is a key issue in soils impacted by Fukushima Dai-ichi 29 Nuclear Power Plant (FDNPP) accident. Among radioactive substances deposited on terrestrial 30 ecosystems, <sup>134</sup>Cs (with half-life 2.07 years) and <sup>137</sup>Cs (with half-life 30.2 years) were dominant 31 and have by far the most radiological significance (Saito et al., 2015). Contaminated territories 32 extend north-west of FDNPP and their most contaminated area, where initial <sup>137</sup>Cs density 33 exceeded 100 kBq/m<sup>2</sup>, covers approximately 3000 km<sup>2</sup> of essentially forested mountainous 34 environments (MEXT, 2013). Vertical migration of radiocesium determines its vertical 35 36 distribution in the soil, and thus controls its long-term environmental availability (e.g. to erosion, root uptake by plant, etc.) (Evrard et al., 2015; Konopleva et al., 2009; Rai and 37 Kawabata, 2020), its radiological impact by external radiation (Andersson and Roed, 1994), 38 39 and the efficiency of countermeasures (e.g. decontamination works) (Matsuda et al., 2015).

40 After accidental release in the atmosphere, vertical migration of radiocesium is forced initially by direct deposition and later by fluxes from contaminated canopy, and involves very distinct 41 42 processes in the upper litter layer and in the underlying mineral soil (Kruyts and Delvaux, 2002; 43 Thiry et al., 2000; Thiry and Myttenaere, 1993). Radiocesium, initially intercepted by the canopy, later reaches the ground by the action of precipitation (throughfall, stemflow) and the 44 fall of leaves (litterfall) (Goor and Thiry, 2004; Kato et al., 2017; Hoffman et al., 1995; Pröhl, 45 2009). In the litter layer, radiocesium is partly absorbed by organic matter (dead leaves and 46 branches) and is continuously transformed into mobile dissolved form by organic matter 47 degradation (Shcheglov, 1999). In the mineral soil, radiocesium sorbs strongly and specifically 48 49 on clay minerals (Fuller et al., 2015; Okumura et al., 2013) but also less intensely on iron oxides and organic matter which often represent large sorption capacities (Rigol et al., 1998; 50 51 Schwertmann and Taylor, 1989). Radiocesium can be transported in dissolved form by liquid advection with infiltrating water (Kurikami et al., 2017). It can also be transported in particulate 52

form by solid advection (e.g. by colloid and particle migration, bioturbation, soil tillage)
(Jagercikova et al., 2015; Jarvis et al., 2010).

Numerous <sup>137</sup>Cs depth profiles measured by soil sampling have documented the vertical 55 migration of <sup>137</sup>Cs originating from nuclear weapon fallout and Chernobyl and FDNPP accident 56 (Koarashi et al., 2012; Matisoff et al., 2011; Matsuda et al., 2015; Matsunaga et al., 2013; Rosén 57 et al., 1999; Takahashi et al., 2019). In undisturbed mineral soils, these authors indicate that 58 most of <sup>137</sup>Cs activity remains near the surface (e.g. 72% in 0-8 mm after 4 years reported by 59 Andersson and Roed, 1994) and then rapidly decreases with depth (Walling and He, 1999). At 60 a single date, in the first years after an accidental fallout, the depth variations of <sup>137</sup>Cs activity 61 are frequently reproduced empirically by a single exponential function (Matsuda et al., 2015; 62 Takahashi et al., 2019) that allows the calculation of the relaxation depth and the estimation of 63 dose conversion factors (Andersson and Roed, 1994; Likar et al., 1998; Saito et al., 2012). After 64 longer time periods, <sup>137</sup>Cs migration profiles are usually better described by Gaussian (Konshin, 65 66 1992; van Genuchten and Cleary, 1979), double exponential (Zombori et al., 1992), and polynomial (Van Siclen, 2011) functions. 67

In mineral soils, the vertical migration of  $^{137}$ Cs (and the dynamics of its depth profiles) has often 68 been modelled by the convection-diffusion equation (CDE) coupled with the  $K_d$  (distribution 69 coefficient) hypothesis for sorption (Kirchner et al., 2009). This approach assumes that <sup>137</sup>Cs 70 transport occurs only in dissolved form and is governed by convection (infiltration) and 71 diffusion (molecular diffusion and hydrodynamic dispersion). It also assumes that <sup>137</sup>Cs 72 73 interactions with the solid phase can be described by instantaneous, linear and reversible sorption processes, with an equilibrium coefficient noted  $K_d$  (IAEA, 2010). When fitted to 74 measured <sup>137</sup>Cs profiles with constant convection velocity and diffusion coefficient, this 75 approach leads to apparent migration velocities in the range 0.85 - 3.5 cm year<sup>-1</sup> for forest soils 76 impacted by the FDNPP accident (Mishra et al., 2018). 77

However, this approach is not fully predictive because  $K_d$  hypothesis fails to describe <sup>137</sup>Cs 78 migration velocities decreasing with time. Fast migration rates of <sup>137</sup>Cs have been reported in 79 the early phase after Chernobyl and Fukushima accidents (Bossew and Kirchner, 2004; 80 Schimmack et al., 1989; Shiozawa, 2013). On the contrary, an immobilization of <sup>137</sup>Cs in the 81 soil has been reported on the long term for fallout originating from nuclear weapon and 82 Chernobyl accident fallout (Andersson and Roed, 1994; Rosén et al., 1999; Toso and Velasco, 83 2001). These observations invalidate the time-independent sorption isotherm implied by the  $K_d$ 84 hypothesis. 85

Alternative equilibrium-kinetic (EK) hypotheses of  $^{137}$ Cs sorption/desorption have been suggested by laboratory experiments but have not been fully validated in field conditions. Long term laboratory experiments show that, although  $^{137}$ Cs sorption is initially rapid (minutes), it continues for months from non-selective to highly selective sorption sites (Konoplev et al., 1997). They also indicate that desorption of  $^{137}$ Cs is very slow (e.g. ~2 years of half-life for Fukushima soils reported by Murota et al., 2016) particularly on clay minerals (Durrant et al., 2018).

Other various multi-site equilibrium and/or kinetic models have been proposed (Antonopoulos-93 94 Domis et al., 1995; Montes et al., 2013; Nicoulaud-Gouin et al., 2016; Ota et al., 2016; Toso and Velasco, 2001), similarly to early formulations existing for agrochemicals (Cameron and 95 Klute, 1977; Selim and Mansell, 1976; van Genuchten and Wagenet, 1989). These empirical 96 models mitigate the  $K_d$  hypothesis by assuming that sorption occurs on 2–3 different types of 97 solid sites, governed by equilibrium and/or kinetic rates. In the laboratory, the EK approaches 98 better describe non-equilibrium <sup>137</sup>Cs sorption observed in batch sorption experiments (Lee et 99 100 al., 2013; Valcke and Cremers, 1994), stirred flow-through reactors, and soil columns (Ardois and Szenknect, 2005; Szenknect et al., 2003). However, in field conditions, evidences that 101 equilibrium-kinetic sorption explain observed <sup>137</sup>Cs migration are still limited. After Chernobyl 102

accident, <sup>137</sup>Cs depth profiles measured in 5 cm thick layers the first 6 years have been
reproduced by the convection-diffusion coupled with an EK sorption model (Toso and Velasco,
2001). After FDNPP accident, <sup>137</sup>Cs depth profiles measured in a bare soil over a 4.5 years
period have been convincingly simulated with sorption parameters derived from the literature
(Kurikami et al., 2017).

This work aimed at studying the importance of non-equilibrium sorption on the vertical 108 migration of <sup>137</sup>Cs in field conditions. Our objectives were to: (1) test its statistical significance, 109 (2) estimate its magnitude and (3) evaluate its influence on migration predictions. For these 110 purposes, the vertical distribution of <sup>137</sup>Cs was monitored at four dates (November 2013, 2014, 111 2016 and 2018) in four mineral soils from young cedar stands impacted by the Fukushima Dai-112 ichi Nuclear Power Plant accident in 2011, where <sup>137</sup>Cs input flux was not a pulse but was 113 affected by Cs cycling in the forest ecosystem. Equations coupling solute transport and  $K_d$ /EK 114 sorption were implemented to model the observed <sup>137</sup>Cs profiles. A nonlinear regression 115 approach was adopted to estimate  $K_d$  and EK parameters and test  $K_d$  vs EK hypotheses. 116

117

#### 2. Materials and Methods

#### 118 2.1. Modeling <sup>137</sup>Cs transport in the soil

119 Vertical distribution of <sup>137</sup>Cs in the mineral soil was considered to result from solute transport
120 and was modelled by a one-dimensional convection-dispersion equation coupled with an
121 Equilibrium-Kinetic model of sorption (EK).

The sorption model considered here is a modified version of the original EK model (van Genuchten et al., 1974; van Genuchten and Wagenet, 1989) that can cover not only equilibrium sorption, but also kinetic reversible/irreversible sorption (Garcia-Sanchez et al., 2014). Following this two-site concept (Fig. 1), sorbed concentrations (Bq kg<sup>-1</sup>) are distributed between type-1 'fast' sites that are at equilibrium with the aqueous phase ( $C_{sl}$ ) – with an equilibrium constant noted  $K_{dl}$  (L kg<sup>-1</sup>) – and type-2 'slow' sites that experience first-order mass transfer ( $C_{s2}$ ) with sorption and desorption rates noted  $k^+$  (L kg<sup>-1</sup> s<sup>-1</sup>) and  $k^-$  (s<sup>-1</sup>). Their governing equations are:

130 
$$C_{s1} = K_{d1}C_w$$
 (1)

131 
$$\frac{dC_{s2}}{dt} = k^+ C_w - k^- C_{s2}$$
(2)

where  $C_w$  (Bq L<sup>-1</sup>) is the soluble contaminant concentration in water. The EK sorption model encompasses the classical  $K_d$  approach, which only considers type-1 sites, and corresponds to the particular case where  $k^+=0$  and  $k^-=0$ .

The transient convective-dispersive transport of soluble <sup>137</sup>Cs in the soil system was modelled
by the following one-dimensional mass-balance equations:

137 
$$\frac{\partial(\partial(z)C_w + \rho(z)C_{s1})}{\partial t} = -k^+ \rho(z).C_w + k^- \rho(z).C_{s2} - \frac{\partial}{\partial z}(f_c + f_D)$$
(3)

138 
$$\frac{\partial(\rho(z)C_{s2})}{\partial t} = k^{+}\rho(z).C_{w} - k^{-}\rho(z).C_{s2}$$
(4)

139 where z (m) is depth in the soil,  $\theta$  (L L<sup>-1</sup>) is the volumetric water content and  $\rho$  (kg L<sup>-1</sup>) is the 140 soil bulk density. In Eq. (3),  $f_C$  and  $f_D$  correspond to the advection and dispersion flux densities 141 (Bq m<sup>-2</sup> s<sup>-1</sup>), defined as:

142 
$$f_C(z,t) = q(t).C_w$$
 (5)

143 
$$f_D(z,t) = -D\theta(z) \cdot \frac{\partial C_W}{\partial z}$$
(6)

144 where  $q (m^3 m^{-2} s^{-1})$  is the infiltration flux density and  $D (m^2 s^{-1})$  is the dispersion coefficient.

Half-times of sorption and desorption reactions  $T^+$  (s) and  $T^-$  (s) can be deduced from sorption parameters  $k^+$  and  $k^-$  respectively as follows:

147 
$$T^+ = \frac{\log(2).\theta}{\rho.k^+}$$
 (7)

148 
$$T^{-} = \frac{\log(2)}{k^{-}}$$
 (8)

In the model equations (1)-(2), sorption ( $K_{dl}$ ,  $k^+$ , and  $k^-$ ) and dispersion (D) parameters are considered constant in space (z) and time (t). However, in order to account for the complexity of the conditions of <sup>137</sup>Cs migration, the infiltration density q(t) was supposed transient. Moreover, volumetric water content  $\theta$  and bulk density  $\rho$  were supposed to vary with depth (z). The soil system was considered uncontaminated at initial time:

154 
$$C_w(z,0) = 0$$
 and  $C_{s1}(z,0) = C_{s2}(z,0) = 0$  (9)

and submitted to a total input  $I_0(t)$  (Bq m<sup>-2</sup> s<sup>-1</sup>) of dissolved <sup>137</sup>Cs at its top (z=0):

156 
$$f_{\mathcal{C}}(0,t) + f_{\mathcal{D}}(0,t) = I_0(t)$$
 (10)

and a no-diffusion condition at its bottom (z = L = 1m) (van Genuchten and Parker, 1984):

$$158 \quad \frac{\partial C_{W}(z,t)}{\partial z} \Big/_{L} = 0 \tag{11}$$

The system was solved numerically from March  $15^{\text{th}} 2011$  to November  $1^{\text{st}} 2018$  with variable time steps by an implicit finite-differences scheme. The soil was discretized into layers of depth 1 mm. Convection and dispersion terms  $f_C$  and  $f_D$  were spatially discretized with a first order centered scheme and second order centered scheme. The implicit Radau IIA scheme, available in the R package "deSolve" (Soetaert et al., 2010), was chosen for its stability, 5<sup>th</sup> order accuracy and tolerance to stiff equations.

165 *2.2. Study sites* 

Four mineral andosols plots of around 1 m<sup>2</sup> each, from a young cedar forest stand (noted YC1,
YC2, YC3, and YC4) impacted by the Fukushima Dai-ichi Nuclear Power Plant accident in

168 2011, were selected for application of our model. This monitoring site is located in Kawamata 169 Town (Yamakiya District) in the northern part of Fukushima Prefecture (e.g. Kato et al., 2019; 170 Takahashi et al., 2019), approximately 40 km northwest from FDNPP, where the total <sup>137</sup>Cs 171 fallout density was estimated to  $442 \pm 30$  kBq m<sup>-2</sup> (Loffredo et al., 2014) and the average annual 172 precipitation is 1271 mm year<sup>-1</sup> (Fig. 2).

The fluxes of <sup>137</sup>Cs to the forest floor were monitored monthly from 2011 to 2016 on this forest
stand (Kato et al., 2017; Loffredo et al., 2015; Loffredo et al., 2014).

Mineral soils of all plots had similar geochemical properties, with a fine silt texture, pH=5.7
and 10% of organic carbon (Teramage et al., 2018). Their main minerals were quartz, anorthite,
magnetite and kaolinite.

In each plot, soil cores (or profiles) were sampled in November of 2013, 2014, 2016, and 2018 178 from dug pits with open plastic boxes placed onto the undisturbed profile (Coppin et al., 2016). 179 180 At each sampling date, a new pit was dug close to previous ones (i.e. within a surface of  $1 \text{ m}^2$ ). Sampling depth was 8 cm in 2013 and was 20 cm thereafter. Samples were subdivided into 181 layers of 1 cm (0-6 cm depth range), 2 cm (6-20 cm depth range, except in 2014 where the 182 layers were 5 cm deep in 10–20 cm depth range) (Table S1 in supplementary materials). For 183 each layer, <sup>137</sup>Cs activity, water content and bulk density were measured with the same protocol, 184 as detailed by Coppin et al. (2016). Early measurements of <sup>134</sup>Cs/<sup>137</sup>Cs ratios were very close to 185 1 (reference date 2011/03/11) and supported the dominant contribution of FDNPP accidental 186 fallout to the measured <sup>137</sup>Cs activities. 187

#### 188 2.3. Transport parameters for the convection-dispersion model

Each sampled soil profile was modelled as a specific one dimensional soil system. Their transport parameters (Eq. (3)-(4)) were determined from site-specific information. As an exception, the dispersion coefficient D was fixed to  $10^{-8}$  m<sup>2</sup> s<sup>-1</sup> as a midway value between lower end value of  $2 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> for cesium diffusion in water (Sato et al., 1996) and higher end value of  $5 \times 10^{-8}$  m<sup>2</sup> s<sup>-1</sup> for effective dispersion coefficient proposed for Fukushima Prefecture soils (Kurikami et al., 2017). This constant dispersion coefficient value *D* was justified by preliminary simulations showing that simulated <sup>137</sup>Cs inventory profiles were not sensitive to diffusion uncertainty within this range.

#### 197 2.3.1. Solid and liquid volumetric content of the bulk mineral soil $(\rho, \theta)$

For each soil system, the profiles of humidity  $\theta(z)$  and density  $\rho(z)$  were supposed constant from initial time to measurement date (*Appendix B*). These values correspond to liquid/solid ratios ranging from 0.6 to 13.1 L kg<sup>-1</sup> depending on the depth and the plot.

#### 201 *2.3.2. Infiltration rate*

The infiltration flux density q(t) (mm s<sup>-1</sup>) was constructed as a monthly periodic step function derived from the simplified mass-balance:

$$204 \quad q = P - R - ETP_m \tag{12}$$

where *P* represented the monthly average precipitation of Kawamata region (Fig. 2). The runoff rate *R* was fixed at 5% of the precipitation rate (Mutreja, 1990; Subramanya, 2013), and monthly evapotranspiration  $ETP_m$  was calculated using a formula specific to Japanese forests (Komatsu et al., 2010) :

$$209 \quad ETP_m = 3.84T + 32.3 \tag{13}$$

with T (°C) corresponding to the mean monthly temperature. These approximate calculations lead to an annual infiltration of 294 mm year<sup>-1</sup> with maximum infiltration happening between June and October.

213 2.3.3. <sup>137</sup>Cs contamination input  $I_0(t)$ 

Total <sup>137</sup>Cs input  $I_0(t)$  (Bq m<sup>-2</sup> s<sup>-1</sup>) at the top of the mineral soil (Fig. 3) was derived from global 214 monitoring data from the forest stand (Fig. S1 in supplementary materials) and a first-order 215 compartment model for the organic layer (Fig. 4). The estimated <sup>137</sup>Cs input flux was a 216 continuous term for these forest mineral soils and reached a peak about 2 years after FDNPP 217 accident. Total <sup>137</sup>Cs input was supposed to have the same temporal pattern for all the plots, but 218 it was rescaled for each soil profile in order to make cumulated inputs equal to the total <sup>137</sup>Cs 219 inventory (Bq m<sup>-2</sup>) measured in the mineral soil at each sampling date. Total input  $I_0$  was 220 221 rescaled by a factor ranging from 0.17 to 2.34 compared to the average signal due to an initial fallout density of 442 kBq m<sup>-2</sup> in our young cedar stand. The variability of this scaling factor 222 stresses the spatial variability of initial fallout and fluxes of <sup>137</sup>Cs to forest floor in this young 223 cedar stand, as already reported by Kato et al. (2018). 224

Total <sup>137</sup>Cs input  $I_0(t)$  was considered to result from a direct deposit shortly after the accident and a slower input from the organic layer degradation. The calculations are briefly described here.

Cesium-137 fluxes of throughfall (TF), stemflow (SF) and litterfall (LF) were monitored in the young cedar stand since July 2011 and were modelled by double exponential equations (Kato et al., 2019). An initial deposit of 157 kBq m<sup>-2</sup> on the forest floor in March 2011 was calculated as the measured deposit on July 2011 (Kato et al., 2019) minus the extrapolated TF, SF and LF fluxes during the period March–July 2011. This value corresponds to an interception factor of 0.64 similar to the value 0.7 estimated by Kato et al. (2017).

The <sup>137</sup>Cs inventory of the organic layer was measured in November of 2013, 2014, 2016, and 2018. It was modelled by a single compartment submitted to initial deposit, SF, LF and TF inputs and releasing a <sup>137</sup>Cs flux to the underlying mineral soil with a first-order rate constant, estimated by the least squares method (Fig. 4). Cesium-137 root uptake was not considered in

this compartment approach because it had little influence on the dynamics of soil inventories in
Japanese cedar stands over the period 2011-2017 (Gonze et al., 2021).

The initial deposit on the forest floor was supposed to result from a constant flux density lasting for one day on March  $15^{\text{th}} 2011$ , which was supposed to be instantaneously partitioned between the mineral soil (10%) and the organic layer (90%). This configuration was one of many tested (20–80%, 30–70%) and was selected because it allowed the best reproduction of independent measurements of <sup>137</sup>Cs inventories of the organic layer and the mineral soil reported by Takahashi et al. (2019) just after the accident on the same forest site (Fig. S1).

#### 246 2.4. Statistical inference of sorption parameters ( $K_{dl}$ , k+, k-)

Sorption parameters were fitted on each plot (YC1 for example) at the four sampling dates simultaneously (2013, 2014, 2016, and 2018). This allowed the extraction of the set of parameters ( $K_d$  or EK) that best reproduced the contamination evolution from 2013 to 2018. An additional fitting was performed on all the plots at once.

251

#### 2.4.1. Parameter estimation

252 Cesium-137 sorption parameters of  $K_d$  and EK models, noted here ( $\vartheta$ ), were estimated by the 253 ordinary least-squares method (Seber and Wild, 1989), which consists in retaining the 254 parameter values  $\hat{\vartheta}$  that minimize the sum S( $\vartheta$ ) of squared differences between the *n* 255 observations y<sub>i</sub> and predictions f(x<sub>i</sub>,  $\vartheta$ ) of a variable y:

256 
$$S(\vartheta) = \sum_{i=1}^{n} (y_i - f(x_i, \vartheta))^2$$
(14)

where  $x_i$  denotes the experimental conditions (i.e. plot, time and depth of observation).

The normalized  ${}^{137}$ Cs inventory was selected as the fitted variable y in the sum of squares S (Eq. (14)) in order to balance the influence of years 2013, 2014, 2016, and 2018 in the fitting procedure. For each layer (e.g. 0–5 cm) of a given profile (e.g. November 2016), this variable was defined as the inventory of  $^{137}$ Cs (Bq) in the layer divided by the total  $^{137}$ Cs inventory (Bq) in this profile.

The minimization of S was performed numerically with gradient-free algorithms from a large set of starting points (1728) in the parameters' space with the R routine "*optim*" (R core Team, 2019). The algorithm of Brent (1971) was adopted for one-dimensional optimization (e.g.  $K_d$ model) and the algorithm of Nelder and Mead (1965) was adopted otherwise (e.g. EK model).

267 2.4.2. Testing sorption hypotheses

The likelihood ratio statistic (Huet et al., 2004) was used to test if supplementary nonequilibrium hypotheses can improve the classical K<sub>d</sub> approach (e.g.  $K_d$  vs EK). If  $\hat{\vartheta}_{K_d}$  and  $\hat{\vartheta}_{EK}$ denote the sorption parameters estimated under the null hypothesis  $K_d$  (p<sub>1</sub>=1 parameter) and the alternative hypothesis EK (p<sub>2</sub>=3 parameters) respectively, where  $K_d$  corresponds to a particular case of EK, then the likelihood ratio statistic *LR* (Eq. (15)) converges to a chi-squared distribution with (p<sub>2</sub>-p<sub>1</sub>) degrees of freedom.

274 
$$LR = n * \log S(\hat{\vartheta}_{K_d}) - n * \log S(\hat{\vartheta}_{EK})$$
(15)

The p-value of the *LR* statistic was used as a goodness-of-fit measure in replacement of the coefficient of determination  $R^2$  which is inadequate for nonlinear models (e.g. Spiess and Neumeyer, 2010).

278

#### 2.4.3. Confidence Regions

279 Confidence regions of estimated <sup>137</sup>Cs sorption parameters  $\hat{\vartheta}$  for  $K_d$  and EK models were 280 approximated, at the level 100\*(1 -  $\alpha$ )%, by the points  $\vartheta$  satisfying the Beale's condition (Beale, 281 1960; Seber and Wild, 1989):

282 
$$S(\vartheta) \le \left(1 + \frac{p}{n-p}F_{\alpha}(p, n-p)\right)S(\hat{\vartheta})$$
(16)

where p is the number of parameters and  $F_{\alpha}(p,n-p)$  is the quantile of level  $\alpha$  of the Fisher distribution with p and n-p degrees of freedom. This region was constructed numerically, for  $\alpha$ = 0.05, by randomly sampling points  $\vartheta$  in the neighborhood of  $\hat{\vartheta}$  and keeping the first 1000 satisfying the condition (Eq. (16)). For each estimated parameter  $\hat{\vartheta}_i$ , conservative confidence intervals were then defined as the upper/lower bounds for  $\vartheta_i$  in this region.

288

#### 289 **3. Results**

290

# 3.1. Temporal change in measured vertical distribution of <sup>137</sup>Cs

At all sampling dates, the total <sup>137</sup>Cs activity (kBq m<sup>-2</sup>) in the mineral soil was mostly fixed in the upper layers and rapidly decreased with depth (Fig. 5 for YC1 plot). For instance, 90% of the contamination was contained in the first 5 cm of the YC1 profile in 2018. The <sup>137</sup>Cs depth distribution seemed to mostly follow the exponential trend typically observed (Chamard et al., 1993; Kurikami et al., 2017; Matsuda et al., 2015).

In each layer, the total <sup>137</sup>Cs activity increased with time as a result of the continuous migration of the contamination from the organic layer to the mineral soil. In the case of the YC1 plot, the activity in the top layer (0-1 cm) increased from  $32.8 \pm 1.1$  kBq m<sup>-2</sup> in 2013 to  $142 \pm 28$  kBq m<sup>-2</sup> in 2018.

## 300 *3.2. Kinetic vs equilibrium modeling of*<sup>137</sup>Cs transfer in mineral soil

The EK model fitted the measured contamination profiles slightly better than the  $K_d$  model (Fig. 5 for plot YC1 and Fig. S2-S4 in supplementary materials for the remaining plots). While both models globally reproduced the decrease of contamination with depth for all the profiles, the EK model better reproduced the contamination persistence at the soil surface. For instance, for the first layer (0–1 cm) in 2013, EK and  $K_d$  estimated an inventory of  $38 \pm 6$  kBq m<sup>-2</sup> and  $48 \pm$ 8 kBq m<sup>-2</sup>, respectively, whereas the measured value was  $33 \pm 1$  kBq m<sup>-2</sup>. On the contrary, the  $K_d$  model underestimated the contamination remaining at the soil surface, and particularly

significantly starting from 2016 where it estimated  $63 \pm 15$  kBq m<sup>-2</sup> in the first layer ( $93 \pm 18$ 308 kBq m<sup>-2</sup> measured and 77  $\pm$  15 kBq m<sup>-2</sup> with EK). In 2018, the gap became clearer with  $K_d$ 309 estimating a surface inventory of  $82 \pm 21$  kBq m<sup>-2</sup> compared to the measured value of  $142 \pm 28$ 310 kBq m<sup>-2</sup> and 133  $\pm$  28 kBq m<sup>-2</sup> estimated with EK. As a consequence, the  $K_d$  model also 311 overestimated the contamination into deeper layers and thus overestimated the migration 312 velocity of <sup>137</sup>Cs. For example, the relaxation mass depth  $\beta$  (g cm<sup>-2</sup>), which quantifies the mass 313 depth at which the  $^{137}$ Cs concentration reduces to 1/e of the concentration at the ground surface 314 315 (Matsuda et al., 2015), calculated with the  $K_d$  model in 2018 (1.1 ± 0.2 g cm<sup>-2</sup>) was more than two times higher than the measured value  $(0.44 \pm 0.10 \text{ g cm}^{-2})$ , while the EK derived value was 316 considerably closer to it  $(0.59 \pm 0.08 \text{ g cm}^{-2})$  (Table S2 in supplementary materials). 317

Quantitatively, the better performance of EK model vs  $K_d$  model was confirmed statistically for 318 all plots YC1-YC4 by the analysis of the sum of squares (Table 1). For the fits conducted 319 separately on each plot, but also simultaneously on all plots, EK model fits had significantly 320 lower sum of squares, as indicated by p-values ranging from  $1.8 \times 10^{-13}$  to  $8.1 \times 10^{-3}$  (the highest 321 value corresponding to YC4 plot) for the likelihood ratio test of model  $K_d$  vs model EK. Varying 322 p-values between plots resulted from the spatial variability of <sup>137</sup>Cs migration observed in the 323 4 plots belonging to the same forest stand. These results show that, all other hypotheses being 324 equal, the inclusion of rate-limited sorption sites significantly improve the realism of simulated 325 <sup>137</sup>Cs profiles. 326

#### 327 *3.3. Fitted parameters*

For the  $K_d$  model, fitted values of partition coefficient of <sup>137</sup>Cs were physically sound but in the high range for loamy soils (Table 2). Fitted values of the partition coefficient (corresponding here to  $K_d$ ) varied between 8.8 x 10<sup>2</sup> L kg<sup>-1</sup> and 4.1 x 10<sup>3</sup> L kg<sup>-1</sup> depending on the plot. As expected, fitted  $K_d$  values were highest in parcels YC1 (2.4 x 10<sup>3</sup> L kg<sup>-1</sup>) and YC3 (4.1 x 10<sup>3</sup> L kg<sup>-1</sup>) where observed vertical migration rates of <sup>137</sup>Cs were slower (Table S2), and thus
 observed <sup>137</sup>Cs retention was higher.

For the EK model, fitted parameter values suggested a limited influence of equilibrium sorption and a dominant role of rate-limited sorption sites with poorly reversible sorption due to short sorption times (half-time of 1–7 hours) and very long desorption times (half-time of  $3.2 \times 10^{0}$ –  $3.4 \times 10^{6}$  years) (Table 2). Simulated profiles of type-1 and type-2 sites inventories for the period 2013-2018 indicated that, for all dates and depths, the contribution of the equilibrium sites to the sorption of <sup>137</sup>Cs is practically negligible compared to the kinetic sites with more than 99.9% of the contamination sorbed on the kinetic sites in YC1.

- Fitted values of partition coefficient  $K_{dl}$  were almost equal to zero for all parcels (4.0 x 10<sup>-3</sup> L
- $kg^{-1}$  on average) and their associated confidence regions were below 2400 L kg<sup>-1</sup>, which suggest
- a negligible contribution of equilibrium sorption sites to the retention of  $^{137}$ Cs in the soil.
- Fitted values of kinetic desorption rate k had wide confidence intervals between  $1.0 \ge 10^{-17}$  and 2.0  $\ge 10^{-8}$  s<sup>-1</sup>, which corresponded to desorption half-time T of 6.1  $\ge 10^{-2} - 9.5 \ge 10^{8}$  years. These results suggest pseudo-irreversible sorption of <sup>137</sup>Cs in the studied soil.
- Fitted values of kinetic sorption rate  $k^+$  were around 10<sup>-5</sup> L kg<sup>-1</sup> s<sup>-1</sup> and corresponded to sorption half-time  $T^+$  ranging from 1 to 7 hours, which suggest short sorption times compared to residence time of infiltrating water (around 12 days cm<sup>-1</sup> on average).

#### 350 4. Discussion

351

#### 4.1. Kinetic vs equilibrium modeling of <sup>137</sup>Cs transfer in mineral soil

Our results show that the inclusion of rate-limited sorption sites significantly improve the realism of simulated <sup>137</sup>Cs profiles. They suggest that <sup>137</sup>Cs persistence at the soil surface may result from non-equilibrium sorption. However, for both approaches, our simulated profiles did not fully reproduce the observed inventories in deeper layers (Fig. 5). This also suggests that our modeling hypotheses, and notably that <sup>137</sup>Cs migration in the soil is solely governed by transient convective-dispersive transport of soluble <sup>137</sup>Cs, may ignore other processes including but not limited to colloid migration, bioturbation, preferential flows, and root uptake (Jagercikova et al., 2015; Jarvis et al., 2010; Konoplev et al., 2015; Miyahara et al., 2015).

This conclusion confirms the simulations of *in situ* observations made on bare soils impacted by the FDNPP accident with a two-site equilibrium-kinetic model of sorption (Kurikami et al., 2017). Our elements of evidence are here based on a more extensive dataset (four dates, four plots, and a reconstructed continuous supply of <sup>137</sup>Cs to the mineral soil) and on a nonregression analysis including parameter estimation and hypothesis testing.

The EK hypothesis better reproduced the observed profiles than the  $K_d$  hypothesis because nonequilibrium-kinetic sorption allows the advection velocity v (m s<sup>-1</sup>) (Eq. (17)) of <sup>137</sup>Cs contamination, not only to increase with water flux density q (m s<sup>-1</sup>), but also to decrease with sorption onto type-2 sites.

369 
$$v = q \frac{C_W}{\theta C_W + \rho C_{s1} + \rho C_{s2}}$$
 (17)

370 This behavior is consistent with migration velocities reported in the literature. Two months after the FDNPP accident, the recorded migration rates were two to three orders of magnitude greater 371 372 than those calculated using a  $K_d$  value derived from soils of Japanese paddy fields (Shiozawa et al., 2011). Similarly, 11–24% of the total <sup>137</sup>Cs inventory was already beyond the first 5 cm 373 layer just three months after the FDNPP accident (Koarashi et al., 2012). This fast migration of 374 <sup>137</sup>Cs seems to only take place in the first months after the deposition and the migration rates 375 quickly start to decrease. This phenomenon is mainly due to the high content of organic matter 376 in the firsts cm of soil that inhibits sorption on mineral surface by coating, leading to a deeper 377 migration due to the weak and highly reversible <sup>137</sup>Cs retention on organic matter (Koarashi et 378

al., 2012). For instance, the migration rates measured two months after the accident dropped by
a factor of 10 to 20 after 6 to 12 months (Shiozawa, 2013). Similar trends were observed after
the Chernobyl accident with a clear distinction between a faster short term migration rate and a
slower long term one (Chibowski et al., 1999; Schimmack et al., 1989). For instance, migration
rates dropped from 0.5–1.0 cm year<sup>-1</sup> in the first year to 0.2–0.6 cm year<sup>-1</sup> thereafter (Kirchner
et al., 2009; Rosén et al., 1999).

This analysis prompts the rejection of the  $K_d$  hypothesis but does not fully validate the compartments (type-1 and type-2 sites) and processes introduced by the EK hypothesis.

Primarily because our statistical tests only indicate that the EK hypothesis is more plausible but do not prove that it is the only possible explanation. Several models have focused instead on the nonlinearity of sorption reactions. It is the case, for instance, of the mechanistic models that describe the interactions of <sup>137</sup>Cs with the different soil reactive components taking place in one or multiple sites (Bradbury and Baeyens, 2000; Cherif et al., 2017; Poinssot et al., 1999; Tournassat et al., 2013).

Secondly, because our nonlinear regressions were performed on observed total inventory (Bq 393 m<sup>-2</sup>) where the nature of type-1 and type-2 sites were neither known nor measured. Our 394 hypothesis states that type-2 sites correspond to sorption sites fully in contact with water but in 395 chemical non-equilibrium. They can, however, also correspond to regions of the soil where 396 water is less mobile and is therefore in physical non-equilibrium with the mobile water 397 (Brusseau et al., 1989). The chemical non-equilibrium interpretation of type-2 sites seems to be 398 supported by batch observations in Fukushima soils, where non-exchangeable <sup>137</sup>Cs has been 399 reported to increase with time (Murota et al., 2016), but needs to be confirmed in real porous 400 media where immobile regions may also exist. 401

402 *4.2. Fitted parameters* 

For the  $K_d$  model, fitted values of partition coefficient of <sup>137</sup>Cs were mostly in the range of values found in the literature. For instance, the *IAEA* reports a range of [39–55 000 L kg<sup>-1</sup>] for loamy soils with a mean value of 3500 L kg<sup>-1</sup> (IAEA, 2009).  $K_d$  values for Japanese andosol soils were also reported [217–8490 L kg<sup>-1</sup>] with a mean value of 1560 L kg<sup>-1</sup> extracted from 7day sorption experiments (Nakamaru et al., 2007).

For the EK model, the contribution of the kinetic sites to the sorption was dominant and seemed 408 to be governed by a fast sorption (half-time of 1–7 hours) and an almost irreversible desorption 409 (half-time of  $3.2 \times 10^{0}$ - $3.4 \times 10^{6}$  years) whereas the contribution of the equilibrium sites was 410 negligible. Qualitatively, contrasted characteristic times of sorption have already been 411 qualitatively evidenced in batch experiments (Comans and Hockley, 1992; Durrant et al., 2018; 412 Konoplev et al., 1997; Murota et al., 2016). Quantitatively, our confidence regions for  $K_{dl}$  (1.0 413  $x 10^{-6} - 2.4 \times 10^{3} \text{ L kg}^{-1}$ ,  $k^{+} (1.0 \times 10^{-6} - 2 \times 10^{-4} \text{ L kg}^{-1} \text{ s}^{-1})$  and  $k^{-} (1.0 \times 10^{-17} - 1.6 \times 10^{-7} \text{ s}^{-1})$ 414 were mostly consistent with values derived from other equilibrium-kinetic models proposed in 415 416 the literature (Table 3). However, our *in situ* values are not directly comparable to the literature due to differences in the studied sites, the origin of the contamination (weapon tests, Chernobyl 417 accident or FDNPP fallout) and the formulation of the model (e.g. lack of equilibrium sites 418 and/or desorption kinetics). 419

Half-times of sorption and desorption reactions  $T^+$  and T need to be interpreted with care since 420 their confidence intervals covered 2 and 10 orders of magnitude respectively and their values 421 lied outside the time scales of observations ( $\sim 2-7$  years after the accident). Their large 422 423 variability, illustrated in Table 2, may result from their non-identifiability with our set of observations. Their values may also be biased by our uniformity hypotheses concerning 424 425 sorption parameter and water transit times in the mineral soil. The contribution of equilibrium constant  $K_{dl}$  and desorption kinetic rate k on observed total inventory was not statistically 426 significant (Tables S3-S5 in supplementary materials). Thus, the distribution of <sup>137</sup>Cs in the 427

studies site seems to be mainly governed by a fast kinetic sorption. Moreover, with almost 428 identical sum of squared errors than the EK model, the sorption model based only on an 429 irreversible kinetic sorption rate  $(k^+)$  appears as the optimal formulation for this study. 430 However, these parameters and their associated compartment and processes need to be 431 confirmed and refined in controlled conditions such as stirred flow-through reactors (for 432 chemical non-equilibrium sorption) (Martin-Garin et al., 2003) and in soil columns (for 433 chemical and physical non-equilibrium sorption) where dissolved and sorbed inventories are 434 distinguished. 435

Water available <sup>137</sup>Cs fractions predicted with fitted EK parameters seemed consistent with the 436 low values of extractable fractions reported on andosols of Japanese cedar stands, although 437 these quantities are not exactly equivalent. Indeed, simulated profiles at all dates and depths 438 indicated that 99.9% of <sup>137</sup>Cs inventory was on type-2 sites, which corresponds to an available 439 fraction with water of 0.1% on type-1 sites. In the laboratory for the same mineral soil, 440 extractable <sup>137</sup>Cs fraction with water was less than 1% and reached 0.2% one year after 441 contamination when <sup>137</sup>Cs was added to the soil in soluble form, and was below detection limit 442 when <sup>137</sup>Cs was added in solid litter form (Teramage et al., 2018). In the same laboratory study, 443 the extractable <sup>137</sup>Cs fraction with ammonium acetate varied from 36 to 55% when <sup>137</sup>Cs was 444 added in soluble form, whereas it was only around 3 % when the contamination was added in 445 solid litter form. In a similar mineral soil of Japanese cedar stand, extracted <sup>137</sup>Cs fraction with 446 ammonium acetate from in situ samples decreased from 6.1% to 3% during the period 2011-447 2015 (Manaka et al., 2019). 448

### 449 4.3. Implications for the assessment of $^{137}$ Cs profiles

Even if EK is statistically preferable to  $K_d$ , the choice of  $K_d$  vs EK hypothesis seems visually to have a minor influence on <sup>137</sup>Cs vertical migration during the period 2013-2018 (Fig. 5). However, deviations from the equilibrium hypothesis (fast sorption, slow desorption) appear
much critical for environmental impact assessments at shorter and longer time scales.

On the short term, the EK hypothesis induced a faster migration of <sup>137</sup>Cs with simulated profiles 454 analog to those reported early after the Fukushima accident (Fig. 6, YC2011). In June 2011, EK 455 parameters fitted on plot YC1 realistically reproduced the profiles measured in the forest study 456 site (Takahashi et al., 2015) and notably the early progression of <sup>137</sup>Cs to the 3–4 cm layer. On 457 the other hand,  $K_d$  parameter fitted on plot YC1 predicted that <sup>137</sup>Cs was almost exclusively 458 retained in the 0-1 cm layer.  $L_{1/10}$ , which indicates the depth (cm) at which the soil contains 459 90% of the contamination inventory (Matsuda et al., 2015), was around 0.5 cm for  $K_d$ 460 simulations whereas it was equal to 2.5 cm for observations and EK simulations. A fast 461 establishment of extended <sup>137</sup>Cs profiles, which is in line with the EK hypothesis, was also 462 observed in similar forest soils of Fukushima Prefecture in June-July 2011, where up to 90% of 463 the <sup>137</sup>Cs was retained in the first 5 cm layer (Koarashi et al., 2012; Matsunaga et al., 2013). 464

On the long term, the EK hypothesis induced a stronger persistence of the surface <sup>137</sup>Cs 465 contamination with exponential profiles consistent with those reported after the Chernobyl 466 accident (Fig. 6, YC2030). In November 2030, simulated  $L_{1/10}$  was around 4.5 cm with EK 467 hypothesis and 8 cm with  $K_d$  hypothesis. The EK parameterization simulated exponential 468 profiles similar to those observed from 2013 to 2018 due to the dominant pseudo-irreversible 469 sorption of  $^{137}$ Cs on type-2 sites. On the other hand, the  $K_d$  parameterization predicted Gaussian-470 shaped profiles due to continuous desorption of <sup>137</sup>Cs from equilibrium type-1 sites. The 471 472 exponential shape predicted by EK hypothesis seems to be in line with the long term behavior of radiocesium observed following the Chernobyl accident. For instance, measurements 473 474 conducted in Sweden from 1987 to 2007 showed that the profiles conserve the exponential form (Jarvis et al., 2010). A similar profile shape was measured in German forest soils with more 475 than 50% of the <sup>137</sup>Cs activity still remaining in the upper 10 cm soil layer 19 years after the 476

477 accident and a peak of the activity concentration in the first soil horizon (Konopleva et al.,478 2009).

#### 479 **5.** Conclusions

Our study demonstrated that an equilibrium-kinetic parameterization of sorption may improve 480 the assessment of <sup>137</sup>Cs migration in post-accidental situations. From an extensive dataset 481 covering 4 plots over 5 years (2013-2018), an inverse analysis of the vertical migration of  $^{137}$ Cs 482 in the mineral layers of Japanese cedar soils allowed us to reach several conclusions. Firstly, 483 <sup>137</sup>Cs dissolved transfer may take place in chemical non-equilibrium conditions. Secondly, 484 485 fitted sorption parameters suggest a fast sorption kinetic (half-time of 1-7 hours) and pseudoirreversible desorption rate (half-time of  $3.2 \times 10^{\circ} - 3.4 \times 10^{\circ}$  years). Equilibrium sites ( $K_{dl} =$ 486 4.0 x 10<sup>-3</sup> L kg<sup>-1</sup> on average) only describe a negligible portion of <sup>137</sup>Cs sorption. Finally, 487 predictive short term (June 2011) and long term (November 2030) simulations are coherent 488 with literature with a fast initial migration (3 months after the deposition) and a long term 489 490 persistence of the contamination near the surface (at least 20 years after the deposition).

From a methodological standpoint, this study also demonstrated that hypotheses and parameters of  $^{137}$ Cs sorption can be partially inferred from profiles measured *in situ*. The EK hypotheses and parameters could be tested on other  $^{137}$ Cs profiles datasets. However, the monitoring strategy has to cover short (< 1 year) and long (> 5 years) term periods, and provide enough information about hydrology and  $^{137}$ Cs source term.

Some questions concerning the EK hypothesis/model still need to be addressed. Further complementary experiments in controlled conditions of water flow, <sup>137</sup>Cs input and solute transport (such as continuously stirred flow through reactors and soil columns) are necessary to more accurately identify the sorption parameters. These experiments could also allow a clearer distinction between type-1 and type-2 sorption sites and the identification of the processes of
non-equilibrium sorption (e.g. chemical *vs* physical non-equilibrium).

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#### **806 FIGURE CAPTIONS**

Figure 1: Compartment representation of the Equilibrium-Kinetic (EK) model (Garcia-Sanchez et al., 2014) applied to <sup>137</sup>Cs sorption in the mineral soil. This model introduces type-1 sites with instantaneous sorption (with equilibrium parameter  $K_{dl}$ ), and type-2 sites with kinetically controlled sorption (with first-order sorption and desorption rates  $k^+$  and  $k^-$ ). Cesium-137 concentrations are denoted  $C_w$  (Bq L<sup>-1</sup>) in water, and  $C_{sl}$ ,  $C_{s2}$  (Bq kg<sup>-1</sup>) in the solid phase.

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Figure 2: Average monthly hydro-climatic conditions of the studied plots. Light blue bars correspond to precipitation rates P (mm), and solid lines correspond to average monthly temperatures T (°C) measured at Kawamata during the period 1982-2012 (, 2020). Dark blue bars represent the estimated monthly infiltration rates q (mm) by application of Eq. (10).

- Figure 3: Instantaneous and cumulated  $^{137}$ Cs input flux at the top of the mineral soil. This signal, resulting from a compartment model of the organic layer fitted to monitoring data, is here
- represented in the case of a unit contamination of  $^{137}$ Cs (1 Bq m<sup>-2</sup>) at the date of the accident.
- be represented in the case of a diff containing of the CS (1 bq in ) at the date of the accidence

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Figure 4: Total <sup>137</sup>Cs input  $I_0$  (Bq m<sup>-2</sup> s<sup>-1</sup>) at the top of the mineral soil was reconstructed as a direct deposit shortly after the accident and a slower input from the organic layer degradation. The initial deposit on the forest floor was supposed to last for one day on March 15th 2011, and

- to be instantaneously partitioned between the mineral soil (10%) and the organic layer (90%).
- The release flux of  $^{137}$ Cs from the organic layer was modelled by a first-order rate constant.
- 827

Figure 5: Profiles of <sup>137</sup>Cs total inventory (kBq m<sup>-2</sup>) observed (grey) and simulated with the 828 fitted sorption parameters of  $K_d$  model (red) and EK model (blue) for plot YC1. Zero depth 829 corresponds by convention to the organic layer/mineral soil interface. Activities are decav-830 corrected to the accident date (March 15<sup>th</sup> 2011). Each measurement is represented by a vertical 831 line that indicates the thickness of the sampled layer. Areas shaded in grey correspond to the 832 95% confidence intervals of the measurements. Red and blue shaded bands correspond to the 833 uncertainty of simulated profiles resulting from the 95% uncertainty of fitted parameters of Kd 834 and EK models respectively. 835

836

Figure 6: Profiles of <sup>137</sup>Cs total inventory (kBq m<sup>-2</sup>) simulated with the fitted sorption parameters of  $K_d$  model (red) and EK model (blue) in June 2011 (YC2011) and November 2030 (YC2030). Profiles are presented with the same conventions as in Fig. 5. Data for June 2011 were reported by Takahashi et al. (2015).

841

# 842 **TABLE CAPTIONS**

Table 1: Statistics summary of  $K_d$  and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot (columns YC1, YC2, YC3, and YC4) or simultaneously on all plots (column YC). Sum of squares denotes the sum of squared errors between model predictions and observations (Eq. (14)). Likelihood ratio (*LR*) statistic was calculated with Eq. (15). Its associated p-value was derived from the approximate chisquared distribution for *LR* as described in section 2.4.2.

849

Table 2: Parameter values of  $K_d$  and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot separately (YC1, YC2, YC3 and YC4) or simultaneously on all plots (YC). Min and Max represent the limits of the 95% confidence interval, as defined by the Beale method (described in section 2.4).  $T^+$  and  $T^-$  respectively denote the half-times of sorption and desorption reactions and SS denotes the sum of squared errors.

855

Table 3: Equilibrium and kinetic sorption parameters of <sup>137</sup>Cs derived from the literature. Values were recalculated using site specific parameters of this study  $(D, \theta, \rho,...)$  to follow the model formulation adopted in this study.

### 860 SUPPLEMENTARY MATERIALS

#### 861 File AppendixA.doc

862

863	Figure S1 : Evolution of <sup>137</sup> Cs distribution between the organic and mineral compartments of
864	the soil simulated by considering that 10% of <sup>137</sup> Cs total fallout reached the mineral soil in the
865	first day after the accident.

866

Figure S2 : Profiles of <sup>137</sup>Cs total inventory (kBq/m<sup>2</sup>) simulated with the fitted sorption parameters of  $K_d$  model (red) and EK model (blue) for plot YC2.

869

Figure S3 : Profiles of <sup>137</sup>Cs total inventory (kBq/m<sup>2</sup>) simulated with the fitted sorption parameters of  $K_d$  model (red) and EK model (blue) for plot YC3.

872

Figure S4 : Profiles of <sup>137</sup>Cs total inventory (kBq/m<sup>2</sup>) simulated with the fitted sorption parameters of  $K_d$  model (red) and EK model (blue) for plot YC4.

875

- Table S2 : Relaxation mass depth  $\beta$  (g cm<sup>-2</sup>) calculated on the profiles of <sup>137</sup>Cs total inventory
- $(kBq m^{-2})$  in the sampled layers of each plot. β was derived either from measured profiles
- 878 (column Data) or from profiles simulated with the fitted parameters of  $K_d$  and EK models.

879

Table S3 : Statistics summary of kinetic only and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot (columns YC1, YC2, YC3, and YC4) or simultaneously on all plots (column YC). Sum of squares denotes the sum of squared errors between model predictions and observations (Eq. 14). Likelihood ratio (*LR*) statistic was calculated with Eq. (15). Its p-value was derived from the approximate chi-squared distribution for *LR* as described in section 2.4.2.

886

Table S4 : Statistics summary of no kinetic desorption ( $k^-=0$ ) and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot (columns YC1, YC2, YC3, and YC4) or simultaneously on all plots (column YC). Sum of squares denotes the sum of squared errors between model predictions and observations (Eq. 14). Likelihood ratio (*LR*) statistic was calculated with Eq. (15). Its p-value was derived from the approximate chi-squared distribution for *LR* as described in section 2.4.2.

- Table S5 : Statistics summary of kinetic sorption only ( $k=0, K_{dl}=0$ ) and EK model fitted on
- normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot
- (columns YC1, YC2, YC3, and YC4) or simultaneously on all plots (column YC). Sum of
- squares denotes the sum of squared errors between model predictions and observations (Eq.
- 898 14). Likelihood ratio (LR) statistic was calculated with Eq. (15). Its p-value was derived from
- the approximate chi-squared distribution for LR as described in section 2.4.2.
- 900

## 901 File AppendixB.xlsx

- 902
- Table S1. Measured depth profiles of dry density, water content and <sup>137</sup>Cs activity on plots
   YC1-YC4 (2013-2018).



 $C_{s1}$ 

Type-2 sites  $C_{s2}$ 

# Solid phase



<sup>137</sup>Cs input flux I<sub>0</sub> (Bq m<sup>-2</sup> d<sup>-1</sup>)









Table 1 : Statistics summary of  $K_d$  and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot (columns YC1, YC2, YC3, and YC4) or simultaneously on all plots (column YC). Sum of squares denotes the sum of squared errors between model predictions and observations (Eq. (14)). Likelihood ratio (*LR*) statistic was calculated with Eq. (15). Its associated p-value was derived from the approximate chi-squared distribution for *LR* as described in section 2.4.2.

				Dataset		
Quantity		YC1	YC2	YC3	YC4	YC
Sum of	<i>K<sub>d</sub></i> model (1 parameter)	0.22	0.30	0.10	0.44	1.21
squares	EK model (3 parameters)	0.12	0.21	0.053	0.35	0.86
Number o	fobservations	44	44	44	44	176
Likelihood	l ratio ( <i>LR</i> )	26	15	28	9.6	59
Approx. p	-value	2.4 x 10 <sup>-6</sup>	5.4 x 10 <sup>-4</sup>	6.5 x 10 <sup>-7</sup>	8.1 x 10 <sup>-3</sup>	1.8 x 10 <sup>-13</sup>

Table 2 : Parameter values of  $K_d$  and EK model fitted on normalized profiles of <sup>137</sup>Cs inventory. Fits were conducted either separately on each plot separately (YC1, YC2, YC3 and YC4) or simultaneously on all plots (YC). Min and Max represent the limits of the 95% confidence interval, as defined by the Beale method (described in section 2.4).  $T^+$  and  $T^-$  respectively denote the half-times of sorption and desorption reactions and *SS* denotes the sum of squares.

	EK model						K <sub>d</sub> m	odel	
Dataset	Quantity	K <sub>d1</sub> (L kg <sup>-</sup>	$k^{+}$ (L kg <sup>-1</sup> s <sup>-1</sup> )	<i>k</i> <sup>-</sup> (s <sup>-1</sup> )	<i>T</i> <sup>+</sup> (h)	<i>T</i> <sup>-</sup> (y)	SS	$K_d (L \text{ kg}^{-1})$	SS
		1)							
	Value	8.1 x 10 <sup>-4</sup>	2.4 x 10 <sup>-5</sup>	3.1 x 10 <sup>-15</sup>	2.5	3.1 x 10 <sup>6</sup>	1.2 x 10 <sup>-1</sup>	2.4 x 10 <sup>3</sup>	2.2 x 10 <sup>-1</sup>
YC1	Min	1.0 x 10 <sup>-6</sup>	1.4 x 10 <sup>-5</sup>	1.0 x 10 <sup>-17</sup>	1.1	1.2		1.6 x 10 <sup>3</sup>	
	Max	1.4 x 10 <sup>3</sup>	5.3 x 10 <sup>-5</sup>	8.0 x 10 <sup>-9</sup>	4.6	9.5 x 10 <sup>8</sup>		3.7 x 10 <sup>3</sup>	
	Value	<b>8.8</b> x 10 <sup>-4</sup>	1.6 x 10 <sup>-5</sup>	2.8 x 10 <sup>-15</sup>	3.7	3.4 x 10 <sup>6</sup>	2.1 x 10 <sup>-1</sup>	1.5 x 10 <sup>3</sup>	3.0 x 10 <sup>-1</sup>
YC2	Min	1.0 x 10 <sup>-6</sup>	6.7 x 10 <sup>-6</sup>	1.0 x 10 <sup>-17</sup>	0.9	4.9 x 10 <sup>-1</sup>		8.5 x 10 <sup>2</sup>	
	Max	1.5 x 10 <sup>3</sup>	6.7 x 10 <sup>-5</sup>	2.0 x 10 <sup>-8</sup>	9.1	9.4 x 10 <sup>8</sup>		2.7 x 10 <sup>3</sup>	
	Value	9.6 x 10 <sup>-3</sup>	4.8 x 10 <sup>-5</sup>	3.0 x 10 <sup>-9</sup>	1.3	3.2	5.3 x 10 <sup>-2</sup>	4.1 x 10 <sup>3</sup>	1.0 x 10 <sup>-1</sup>
YC3	Min	1.0 x 10 <sup>-6</sup>	2.1 x 10 <sup>-5</sup>	1.0 x 10 <sup>-17</sup>	0.6	6.3 x 10 <sup>-1</sup>		3.1 x 10 <sup>3</sup>	
	Max	2.4 x 10 <sup>3</sup>	1.0 x 10 <sup>-4</sup>	1.5 x 10 <sup>-8</sup>	2.9	9.5 x 10 <sup>8</sup>		5.2 x 10 <sup>3</sup>	
	Value	6.8 x 10 <sup>-3</sup>	<b>8</b> .9 x 10 <sup>-6</sup>	5.0 x 10 <sup>-14</sup>	6.9	1.9 x 10 <sup>5</sup>	3.5 x 10 <sup>-1</sup>	<b>8.8</b> x 10 <sup>2</sup>	4.4 x 10 <sup>-1</sup>
YC4	Min	1.0 x 10 <sup>-6</sup>	1.1 x 10 <sup>-6</sup>	1.0 x 10 <sup>-17</sup>	0.3	6.1 x 10 <sup>-2</sup>		$4.2 \ge 10^2$	
	Max	1.2 x 10 <sup>3</sup>	2.1 x 10 <sup>-4</sup>	1. 6 x 10 <sup>-7</sup>	0.6	9.4 x 10 <sup>8</sup>		1.6 x 10 <sup>3</sup>	
YC	Value	2.0 x 10 <sup>-3</sup>	1.9 x 10 <sup>-5</sup>	1.1 x 10 <sup>-15</sup>	3.3	8.5 x 10 <sup>6</sup>	8.7 x 10 <sup>-1</sup>	1.9 x 10 <sup>3</sup>	1.2

Μ	lin	1.0 x 10 <sup>-5</sup>	1.4 x 10 <sup>-5</sup>	1.0 x 10 <sup>-17</sup>	1.8	1.6	$1.5 \ge 10^3$
М	lax	$5.6 \ge 10^2$	3.3 x 10 <sup>-5</sup>	6.1 x 10 <sup>-9</sup>	4.5	9.4 x 10 <sup>8</sup>	2.5 x 10 <sup>3</sup>

	Sorption parameters						
Reference	$K_{dl}$ (L kg <sup>-1</sup> )	$k^+$ (L kg <sup>-1</sup> s <sup>-1</sup> )	<i>k</i> <sup>-</sup> (s <sup>-1</sup> )	$T^{+}$ (h)	<i>T</i> (d)		
Toso and Velasco (2001)	$7.9 \ge 10^2 - 1.5 \ge 10^3$	6.3 x 10 <sup>-6</sup> -8.7 x 10 <sup>-8</sup>	-	27 - 38	-		
Montes et al. (2013)	$2.1 \ge 10^4 - 4.4 \ge 10^4$	7.2 x 10 <sup>-6</sup> -7.3 x 10 <sup>-5</sup>	-	3 – 33	-		
Antonopoulos-Domis et al. (1995)	-	1.6 x 10 <sup>-5</sup>	-	15	-		
Ota et al. (2016)	$1.8 \ge 10^2 - 2.3 \ge 10^3$	3.2 x 10 <sup>-8</sup> -1.5 x 10 <sup>-7</sup>	4.2 x 10 <sup>-9</sup> –1.8 x 10 <sup>-8</sup>	1.6 x 10 <sup>3</sup> -7.4 10 <sup>3</sup>	1.9 x 10 <sup>2</sup> -8.3 x 10 <sup>2</sup>		
IAEA (2009)	-	8.8 x 10 <sup>-7</sup> –4.2 x 10 <sup>-6</sup>	2.4 x 10 <sup>-8</sup> –9.8 x 10 <sup>-8</sup>	17-80	11 – 43		

Table 3 : Equilibrium and kinetic sorption parameters of <sup>137</sup>Cs derived from the literature. Values were recalculated using site specific parameters of this study  $(D, \theta, \rho, ...)$  to follow the model formulation adopted in this study.

#### **Declaration of interests**

 $\boxtimes$  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.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Supplementary Material 1

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