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# Influence of non-equilibrium and nonlinear sorption of $^{137}\text{Cs}$ in soils. Study with stirred flow-through reactor experiments and quantification with a nonlinear equilibrium-kinetic model

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1           **Influence of non-equilibrium and nonlinear sorption of  $^{137}\text{Cs}$  in soils.**  
2           **Study with stirred flow-through reactor experiments and quantification**  
3           **with a nonlinear equilibrium-kinetic model.**

4  
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11           **ABSTRACT**

12           This paper addresses the modelling of cesium sorption in non-equilibrium and nonlinear  
13 conditions with a two-site model. Compared to the classical  $K_d$  approach, the proposed model  
14 better reproduced the breakthrough curves observed during continuous-flow stirred tank  
15 reactor experiments conducted on two contrasted soils. Fitted parameters suggested contrasted  
16 conditions of cesium sorption between 1) equilibrium sites, with low affinity and high  
17 sorption capacity comparable to CEC and 2) non-equilibrium sites, with a fast sorption rate  
18 (half-time of 0.2-0.3 hours), a slow desorption rate (half-time of 3-9 days) and a very low  
19 sorption capacity (0.02-0.04% of CEC). Comparison of EK sites densities with sorption  
20 capacities derived from the literature suggests that the EK equilibrium and kinetic sites might  
21 correspond to ion exchange and surface complexation of soil clay minerals respectively. This  
22 work stresses the limits of the  $K_d$  model to predict  $^{137}\text{Cs}$  sorption in reactive transport  
23 conditions and supports an alternative non-equilibrium nonlinear approach.

24

## 25 **KEYWORDS**

26 cesium; sorption; soil; modelling; experiment; inverse modelling

27

## 28 **1. INTRODUCTION**

29 The various processes of solute retention on solid phases –referred to as *sorption* (Sposito,  
30 1984)– strongly govern the mobility, bioavailability and remediation of substances in the  
31 environment, and, in the case of radioactive substances, their radiological impact. They  
32 notably control the conditions of reactive transport of solutes occurring in solid-liquid systems  
33 such as rivers, soils and groundwater (Bouzidi et al., 2010; Fiengo Perez et al., 2015; Ilina et  
34 al., 2020; Limousin et al., 2007). A critical issue when assessing the reactive transport of  
35 solutes (such as radionuclides) in solid-liquid systems such as soils concerns the hypotheses  
36 and parameters modelling the rate of solute transfer between the solution and solid phases  
37 (Ardois and Szenknect, 2005; Chaif et al., 2021; Cherif et al., 2017; Limousin et al., 2007).

38 In impact assessment models, sorption is most commonly represented for a wide range of  
39 contaminants (including radionuclides) by an instantaneous, concentration-independent and  
40 completely reversible reaction, using an equilibrium coefficient also called distribution  
41 coefficient and noted  $K_d$  (IAEA, 2009). This model simply assumes a constant proportion ( $K_d$ )  
42 between concentrations in sorbed and soluble phases and, as a result, a constant proportion  
43 (called retardation factor) between water and solute fluxes (Bossew and Kirchner, 2004;  
44 Mishra et al., 2018; Szenknect et al., 2003). However, the  $K_d$  sorption model is not fully  
45 predictive. Deviations from its simplifying hypotheses have been reported for many solutes  
46 (including pesticides, radionuclides and notably cesium-137) and may result notably in earlier

47 solute arrival in groundwater and longer residence time in soils than the ideal  $K_d$  model (Bahr  
48 and Rubin, 1987; Schnaar and Brusseau, 2014). These deviations essentially result from:

49 1) Chemical non-equilibrium: sorption sites may differ in their reactivity with the solute,  
50 some reacting instantaneously and other slower than contact times with water (Chaif et al.,  
51 2021; Kurikami et al., 2017; Ota et al., 2016; Sardin et al., 1991). Important special cases are  
52 sorption irreversibility or pseudo-irreversibility: for a fraction of adsorbed solutes, the  
53 remobilization back into solution may be impossible or so slow that it can be considered as  
54 irreversible (Antonopoulos-Domis et al., 1995; Comans and Hockley, 1992; Montes et al.,  
55 2013; Toso and Velasco, 2001).

56 2) Physical non-equilibrium: some sorption sites may not be instantaneously accessible to  
57 the solute but limited by physical processes such as external and internal diffusion in solid  
58 particles (Chen et al., 2020; van Genuchten and Wagenet, 1989).

59 3) Sorption nonlinearity: sorption may vary with solute concentration if it involves  
60 multiple sorption sites having different densities and affinities for solute. For instance,  
61 sorption can be high at trace levels when selective sorption sites are concerned, and much  
62 lower when non-selective sorption sites also participate to solid-liquid exchanges (Cherif et  
63 al., 2017; Fesch et al., 1998; Wang et al., 1998).

64 For a better description of sorption, various multi-site equilibrium and/or kinetic (EK)  
65 models have been proposed. These empirical models, initially introduced for agrochemicals  
66 and heavy metals (Cameron and Klute, 1977; Selim and Mansell, 1976; van Genuchten and  
67 Wagenet, 1989), mitigate the  $K_d$  hypotheses by assuming that sorption occurs on 2–3 different  
68 types of solid sites, governed by equilibrium and/or kinetic rates. Depending on the modelled  
69 solutes, the existing variants combine multiple sorption properties such as equilibrium (e.g.  
70 linear isotherm), non-equilibrium (first order, second order sorption rates), non-linearity (e.g.

71 Langmuir, Freundlich isotherms) and sorption irreversibility. More recently, promising  
72 applications of EK models for radionuclide have been reported (Antonopoulos-Domis et al.,  
73 1995; Chaif et al., 2021; Garcia-Sanchez et al., 2014; Ota et al., 2016; Toso and Velasco,  
74 2001; Wang et al., 1998). However, the benefits of adopting equilibrium kinetic models of  
75 sorption have not been fully demonstrated. The process-based validation of these approaches  
76 still requires the interpretation of the different types of sorption sites in terms of real  
77 contamination pools and not hidden virtual compartments. Moreover, the scenarios of reactive  
78 transport for which EK hypotheses significantly improve the realism of predictions, compared  
79 to the simple  $K_d$  hypotheses, must be clarified.

80 Sorption reactions in soils have been studied both in the laboratory and in the field by  
81 complementary **experimental devices** that achieve different levels of representativity and  
82 bring different levels of information **about sorption reactions**. They usually consist in **batch**  
83 **experiments that allow a static study of sorption reactions in solid suspensions, or soil column**  
84 **experiments that allow the study of reactive transport in porous media**.

85 **An intermediate experimental device known as *stirred flow-through reactor experiments*,**  
86 **or continuous-flow stirred-tank reactor (CSTR) experiments, is particularly adapted to the**  
87 **study of rate-limited sorption under flowing conditions in disperse solid phases. This device**  
88 **consists in a well-mixed stirred cell, containing a known mass of solid and a known volume of**  
89 **solution (e.g. Garcia-Sanchez et al., 2014; Martin-Garin et al., 2003; Sparks et al., 1980; Van**  
90 **Cappellen and Qiu, 1997a,b) (Figure 1). During a classical reactor experiment, the injection**  
91 **flowrate is generally held constant ( $Q_i$ ) and the injected solute concentration consists in a**  
92 **finite step function (with value  $C_i$ ), while the dissolved concentration ( $C_w$ ) is monitored at the**  
93 **reactor outlet (Figure 2). Different reactor conditions allow then to test experimentally if**  
94 **solute reactions depend on solute-concentration ( $C_i$ ) and flowrate ( $Q$ ), and are thus nonlinear**  
95 **and not instantaneous (Bar-Tal et al., 1990).**

96 All these protocols require an inverse approach consisting in selecting a sorption model  
97 and estimating its parameters from observations by frequentist or bayesian calibration (e.g.  
98 Nicoulaud-Gouin et al., 2016; Toro and Padilla, 2017; van Genuchten et al., 2012). For model  
99 selection, varying contact times and influent concentrations have been recommended to test  
100 linearity and equilibrium hypotheses and reject improper models (e.g. Bar-Tal et al., 1990;  
101 Nicoulaud-Gouin et al., 2016). For parameter identification, the unicity of the sorption  
102 parameters derived from observations, also termed identifiability, must also be examined  
103 attentively to ensure that obtained parameter values are physically interpretable (Belsley et al.,  
104 1980; Brun et al., 2001; Stewart, 1987).

105 Large amounts of radionuclide have been released in the environment after the multiple  
106 nuclear weapons tests that took place from the 1950s to 1980 and the nuclear accidents of  
107 Chernobyl (1986) and Fukushima (2011) (Castrillejo et al., 2016; Klement, 1965; Steinhauser  
108 et al., 2015). Among these elements,  $^{137}\text{Cs}$  – due to its relatively long half-life ( $t_{1/2} = 30.2$   
109 years) – is considered the main source of radioactive soil contamination (Avery, 1996; Strebl  
110 et al., 1999) and the first source of nuclear waste in the first one hundred years after release.

111 Cesium sorption in soils is primarily governed by clay minerals (Bostick et al., 2002;  
112 Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Shenber and Eriksson, 1993;  
113 Wendling et al., 2005). In fact, radiocesium sorbs strongly and specifically on clay minerals  
114 (Cornell, 1993; Fuller et al., 2015; Okumura et al., 2019) but also less intensely on iron oxides  
115 and organic matter which often represent large sorption capacities (Rigol et al., 2002;  
116 Schwertmann and Taylor, 1989). On clay minerals, surface adsorption sites are very  
117 heterogeneous (Bradbury and Baeyens, 2000; Cornell, 1993; Eliason, 1966; Missana et al.,  
118 2004; Poinssot et al., 1999; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962). Five  
119 types of sorption sites are generally distinguished: basal surface sites, edge sites, hydrated  
120 interlayer sites, frayed edge sites (FES), and interlayer sites (Okumura et al., 2019). These

121 sites have contrasted densities and affinities to cesium. Hydrated interlayer, FES, and  
122 interlayer sites (that can be grouped under the term “interlayer sites”) have strong affinity to  
123 cesium but low density (Brouwer et al., 1983; Eberl, 1980; Francis and Brinkley, 1976;  
124 Jackson, 1962; Maes and Cremers, 1986; Poinssot et al., 1999; Rich and Black, 1964;  
125 Sawhney, 1972; Zachara et al., 2002). Planar sites have much lower affinity to cesium but  
126 represent most of the cation exchange capacity “CEC” and correspond to the basal surface  
127 and edge sites (Cornell, 1993; Rigol et al., 2002; Staunton and Roubaud, 1997; Zachara et al.,  
128 2002). Numerous laboratory studies indicate that Cs sorption is both time-dependent and  
129 concentration-dependent. Sorption experiments show that, although  $^{137}\text{Cs}$  sorption is initially  
130 rapid (minutes), it continues for months from non-selective to highly selective sorption sites  
131 (Konoplev et al., 1997). Desorption experiments also indicate that desorption of  $^{137}\text{Cs}$  is very  
132 slow (e.g.  $\sim 2$  years of half-life for Fukushima soils reported by Murota et al., 2016)  
133 particularly on clay minerals (Durrant et al., 2018). Moreover, many sorption isotherms  
134 indicate that affinity to cesium decrease when the concentration of soluble cesium ( $\text{Cs}^+$ ) and  
135 its competitors (mainly  $\text{K}^+$ ) increase in solution (Cherif, 2017; Siroux, 2017).

136 This work aimed at studying the hypotheses of non-equilibrium and non-linearity of  
137 cesium sorption in reactive transport conditions. Our specific objectives were to: (1) quantify  
138 the influence of cesium concentration and water transit time on sorption, (2) propose a simple  
139 sorption model taking into account these effects, (3) study the validity of this model and  
140 estimate its parameters, (4) relate the model compartments and parameters to measurable soil  
141 properties. For these purposes, flow-through reactor experiments were conducted on two  
142 contrasted soils under different conditions of injection concentration and flow rate. A 5-  
143 parameter equilibrium-kinetic model (EK5) including both sorption non-equilibrium and non-  
144 linearity was proposed to model cesium sorption and compared to a classical  $K_d$  approach. A

145 nonlinear regression approach was adopted to estimate  $K_d$  and EK5 parameters and to test  
146 EK5 vs  $K_d$  hypotheses.



## 147 **2. MATERIAL AND METHODS**

### 148 **2.1. Studied Soils**

149 Two soils, noted “Soil H” and “Soil S”, were selected for their contrasted physico-  
150 chemical and mineralogical properties (**Table 1**). Soil S was a calcareous sandy soil with pH  
151 = 9.32, 1.44‰ of organic matter, and CEC= 1.11 cmol<sup>+</sup>/kg. Soil H, on the other hand, had a  
152 loamy texture with pH = 5.5, 49.4‰ of organic matter, and CEC = 7.64 cmol<sup>+</sup>/kg. Soil  
153 samples were air dried and sieved (<2 mm) before use. For soil S, mineralogy of the fraction  
154 below 2µm was determined by ERM laboratory (Poitiers, France) using powder X-ray  
155 diffractometer (Bruker D8 Advance A25) with CuKα radiation at 40kV and 40 mA on  
156 oriented mounts. The same technique was used for soil H and the results were already  
157 published in a previous study (Siroux, 2017; Siroux et al., 2021). The detailed mineral  
158 composition of soils H and S is given in **Table S1** (in supplementary materials).

159

161 **Table 1.** Physico-chemical and mineralogical characteristics of soils H and S. Clay, silt and  
 162 sand percentages correspond to the granulometric classes of the international scale. Illite,  
 163 montmorillonite and kaolinite percentages correspond to mineralogical composition of the  
 164 fraction of the soils below 2  $\mu\text{m}$ , as determined by the X-Ray Diffractometry (XRD)  
 165 technique. Percentage intervals correspond to the range of realistic mineralogical  
 166 compositions compatible with the analytical results.

	Soil H*	Soil S
Clay (%)	13.13	3.10
Silt (%)	54.05	0.70
Sand (%)	32.82	96.20
pH (H <sub>2</sub> O)	5.5	9.3
Organic matter (g/kg)	49.40	1.44
N (g/kg)	2.64	0.04
CaCO <sub>3</sub> (g/kg)	14	118
<b>Exchangeable cations (cmol<sup>+</sup>/kg)</b>		
CEC	7.64	1.11
CEC <2 $\mu\text{m}$	20.0	18.7
K <sup>+</sup>	0.32	0.23
Na <sup>+</sup>	0.20	0.14
Ca <sup>2+</sup>	3.23	31.20
Mg <sup>2+</sup>	0.60	0.72
<b>Mineralogy</b>		
Illite (%)	11 - 22	0 - 2

Montmorillonite (%)	43 - 56	23 - 27
Kaolinite (%)	14 - 23	4 - 9

167

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\* data from Siroux (2017)

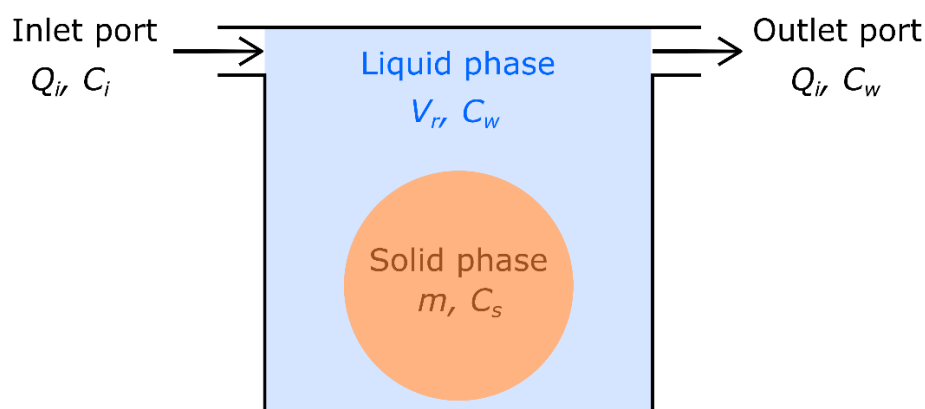
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169

## 170 2.2. Stirred flow-through reactor experiments

171 Principles of continuous-flow stirred tank reactor experiments are presented in  
172 introduction. Each experiment consisted in injecting an input solution into a chamber of  
173 volume  $V_r$  containing a known mass of soil  $m$ , and measuring  $^{137}\text{Cs}$  concentration ( $C_w$ ) at the  
174 output port of the chamber (Garcia-Sanchez et al., 2014; Martin-Garin et al., 2003; Van  
175 Cappellen and Qiu, 1997a,b) (**Figure 1**). The input and output ports were equipped with 0.45  
176  $\mu\text{m}$  pore size hydrofoil Teflon membranes (HVLP, Millipore). The input solution was injected  
177 at a constant flow rate in the reactor cell by a chromatography system (ÄKTA™ pure 25), and  
178 the direction of the flow was periodically reversed to avoid filter clogging. The continuous  
179 stirring was ensured by attaching the reactor to an external shaker. This method was preferred  
180 to a magnetic stir bar inside the cell to avoid destroying the solid particles. Samples were  
181 collected using a fraction collector and analyzed for  $^{137}\text{Cs}$  activity using a pure germanium  
182 gamma spectrometer (Camberra EGPC 42.190.R).

183



184

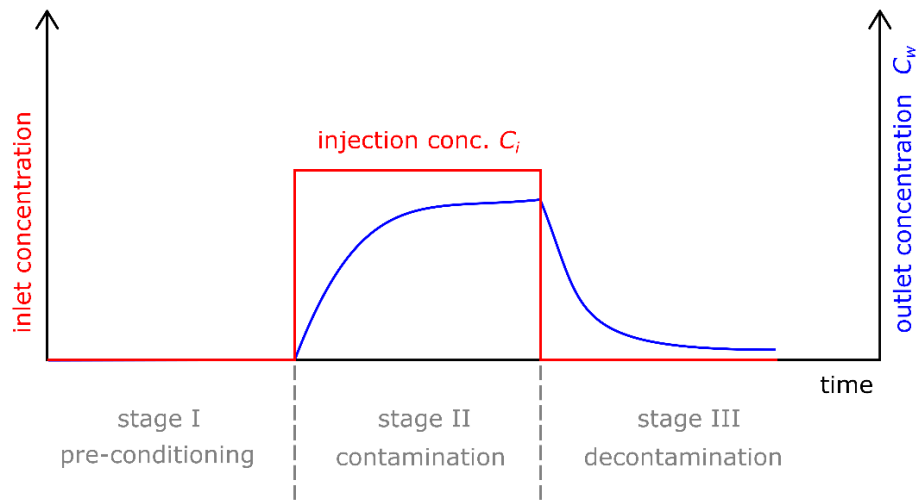
185 **Figure 1.** Principle of the continuous-flow stirred tank reactor (CSTR) experiments conducted  
186 in this study. A solution is injected into the reactor chamber (of volume  $V_r$ ) by its inlet port.

187 The solution is injected at a constant flow rate  $Q_i$  and is only contaminated during  
188 contamination stage (with concentration  $C_i$ ). Contaminant dilutes and interacts with the solid  
189 phase (with mass  $m$  and contamination concentration  $C_s$ ) inside the chamber. The reactor  
190 chamber is well-mixed and has a homogenous contaminant concentration in solution  $C_w$  that  
191 is monitored at the outlet port.

192

193 Each experiment consisted in a constant injection flow rate with three stages of  
194 contaminant injection (**Figure 2**): (1) a pre-contamination stage (noted stage I) during which a  
195 cesium-free solution was injected for at least 48 hours to allow the soil particles to reach a  
196 chemical equilibrium with the input solution; (2) A contamination stage (noted stage II),  
197 during which a cesium solution at a known concentration ( $C_i$ ) was injected until the  
198 normalized cesium concentration  $C_w/C_i$  either stabilized or reached 1; (3) A decontamination  
199 stage (noted stage III) during which the cesium-free solution was again injected until the  
200 normalized cesium concentration ( $C_w/C_i$ ) was below 4%.

201



202

203 **Figure 2.** The three stages of continuous-flow stirred tank reactor (CSTR) experiments  
204 conducted in this study. During each experiment, input solution was injected at a constant  
205 flow rate  $Q_i$  ( $\text{mL h}^{-1}$ ). During pre-conditioning (I) and decontamination (III) stages, input  
206 solution was a cesium-free solution. During contamination (II), input solution had a constant  
207 cesium concentration  $C_i$  ( $\text{mol L}^{-1}$ ).

208

### 209 **2.3. Input solutions**

210 Cesium-free input solutions (**Table 2**) were designed to mimic the soil solution in  
211 equilibrium with the soil. They were injected during the stages I and III of the experiments.  
212 For soil S, Ultrapure water ( $18 \text{ M}\Omega$  resistivity) was equilibrated with excessive amounts of  
213 calcite ( $\text{CaCO}_3$ ) and agitated in an open recipient to allow equilibrium with ambient air for at  
214 least 15 days. The solution was then filtered and spiked with sodium chloride. For soil H,  
215 Ultrapure pure water was directly spiked by a mixture of sodium chloride ( $\text{NaCl}$ ), calcium  
216 chloride ( $\text{CaCl}_2$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) and potassium chloride ( $\text{KCl}$ ).

217 Cesium input solutions were prepared by spiking cesium-free input solutions with  
218 approximate cesium concentrations of  $10^{-3}$  mol L<sup>-1</sup>,  $10^{-5}$  mol L<sup>-1</sup>, and  $10^{-8}$  mol L<sup>-1</sup> depending  
219 on the experiments (**Table 3**). These contaminated solutions were injected during the stages II  
220 of the experiments. This spiking was achieved by adding a mixture of stable (CsCl) and  
221 radioactive (<sup>137</sup>Cs) cesium and then solution pH was adjusted (to pH=8.3 and 5.1 for soils S  
222 and H, respectively) by adding a sodium hydroxide solution (NaOH). All cesium input  
223 solutions contained approximately 500 Bq mL<sup>-1</sup> of <sup>137</sup>Cs.

224

225 **Table 2.** Composition of the input solutions used for the stirred flow-through reactor  
226 experiments with the soils S and H. All concentrations are presented in mol L<sup>-1</sup>

Property	Soil S	Soil H
[Ca <sup>2+</sup> ]	5.00E-04	3.00E-04
[Na <sup>+</sup> ]	5.00E-03	1.40E-04
[Cl <sup>-</sup> ]	5.00E-03	3.43E-04
[NO <sup>3-</sup> ]	-	4.60E-04
[K <sup>+</sup> ]	-	6.30E-05
pH	8.3	5.1

227

## 228 2.4. Experimental design

229 In order to study the influence of non-equilibrium and non-linearity of cesium sorption,  
230 four stirred flow-through reactor experiments were conducted, for each soil, under different  
231 cesium input concentrations (C<sub>i</sub>) and flowrate (Q<sub>i</sub>) conditions (**Table 3**). In total, our  
232 experimental design combined three levels of cesium concentrations ( $10^{-3}$  mol L<sup>-1</sup>,  $10^{-5}$  mol L<sup>-1</sup>,  
233  $10^{-8}$  mol L<sup>-1</sup>) and two levels of flowrates (10 ml h<sup>-1</sup> and 35 ml h<sup>-1</sup>).

234

235 **Table 3.** Experimental conditions of the 4 stirred flow-through reactor experiments conducted  
 236 for soils S and H. The name of each experimental condition (e.g. “S8-10”) indicates the  
 237 combination of soil name (i.e. S or H), approximate cesium input concentration  $C_i$  (i.e.  $10^{-3}$ ,  
 238  $10^{-5}$  or  $10^{-8}$  mol L<sup>-1</sup>) and approximate flowrate  $Q_i$  (i.e. 10 or 35 mL h<sup>-1</sup>).

Properties	Experiments							
	S3-10	S5-35	S8-10	S8-35	H3-10	H5-35	H8-10	H8-35
Soil	S	S	S	S	H	H	H	H
$Q_i$ Average flow rate (mL h <sup>-1</sup> )	10.62	33.48	9.66	34.38	9.72	34.02	9.36	31.98
$C_i$ Cesium concentration (mol L <sup>-1</sup> )	9.97E-04	9.71E-06	6.57E-09	6.92E-09	1.04E-03	9.97E-06	1.21E-08	1.00E-08
$T_i$ Stage II duration (h)	141	92	262	194	140	71	671	294
Stage III duration (h)	263	192	938	602	338	195	1967	992
Stages II+III duration (h)	404	284	1200	796	478	266	2638	1286
m Soil mass (g)	3.70	3.78	3.78	3.57	2.83	3.12	3.06	3.09
$V_r$ Reactor water volume (mL)	33.5	33.5	33.5	33.5	33.5	33.5	33.5	33.5

239



## 240 2.5. Empirical model of cesium sorption in stirred flow-through reactors

241 The 5-parameter sorption model EK5 considered here is a generalized version of an  
242 empirical **linear non-equilibrium sorption** EK model (Chaif et al., 2021; Garcia-Sanchez et al.,  
243 2014; Nicoulaud-Gouin et al., 2016) that can include sorption nonlinearity (**Figure 3**). Sorbed  
244 concentrations are distributed between ‘fast’ sites ( $C_{s1}$ ) noted type-1 sites that are  
245 instantaneously in equilibrium with the aqueous phase –with an equilibrium constant noted  
246  $K_{d1}$  (L kg<sup>-1</sup>)– and ‘slow’ sites ( $C_{s2}$ ) noted type-2 sites that are governed by kinetic first order  
247 mass transfer –with sorption and desorption rates noted  $k^+$  (L kg<sup>-1</sup> s<sup>-1</sup>) and  $k^-$  (s<sup>-1</sup>) –. Type-1  
248 and type-2 sites are supposed to have maximum sorption capacities  $C_{s1}^{max}$  (mol kg<sup>-1</sup>) and  
249  $C_{s2}^{max}$  (mol kg<sup>-1</sup>), **as supported by experimental Cesium isotherms (e.g. Cherif et al., 2017 ;**  
250 **Siroux et al., 2021),** and their sorbed concentrations are modelled by a Langmuir isotherm and  
251 a Langmuir kinetic equation (e.g. Selim et al., 1976; Fukui, 1978):

$$252 \quad C_{s1} = \frac{K_{d1}}{1 + \frac{K_{d1}}{C_{s1}^{max}} C_w} C_w \quad (1)$$

$$253 \quad \frac{dC_{s2}}{dt} = k^+ \left(1 - \frac{C_{s2}}{C_{s2}^{max}}\right) C_w - k^- C_{s2} \quad (2)$$

254 The affinity to cesium is quantified by the solid/liquid concentration ratio at equilibrium in  
255 the absence of saturation ( $C_{s1} \ll C_{s1}^{max}$ ,  $C_{s2} \ll C_{s2}^{max}$ ). For type-1 sites, it corresponds by  
256 definition to the equilibrium constant  $K_{d1}$ . For type-2 sites, the solid/liquid concentration ratio  
257 tends to the equilibrium constant  $K_{d2}$  (L kg<sup>-1</sup>) defined by:

$$258 \quad K_{d2} = \frac{k^+}{k^-}$$

259 which thus defines their affinity to cesium.

260 This general formulation contains 3 model variants, noted  $K_d$ , EK3 and EK5, relying on  
 261 embedded hypotheses about type-1 and type-2 sorption sites (Table 4). The equations (1) and  
 262 (2) of EK5 model encompass the 3-parameter linear EK model (noted EK3), which  
 263 corresponds to the particular case of infinite sorption capacities  $C_{s1}^{max}$  and  $C_{s2}^{max}$ . They also  
 264 encompass the classical 1-parameter  $K_d$  approach, which only considers type-1 sites, and  
 265 corresponds to the particular case where  $k^+ = 0$  and  $k^- = 0$  and infinite  $C_{s1}^{max}$ .

266 In a stirred flow-through reactor with solid-liquid exchanges governed by the EK5 model,  
 267 conservation equations for the exchangeable stock  $S_{ex}$  (mol) in solution and on type-1 sites,  
 268 and for the fixed stock  $S_{fix}$  (mol) on type-2 sites, are then given by:

$$269 \quad \frac{dS_{ex}}{dt} = -k^+ m \left(1 - \frac{C_{s2}}{C_{s2}^{max}}\right) C_w + k^- S_{fix} + Q_i [C_i \delta(t) - C_w] \quad (3)$$

$$270 \quad \frac{dS_{fix}}{dt} = k^+ m \left(1 - \frac{C_{s2}}{C_{s2}^{max}}\right) C_w - k^- S_{fix} \quad (4)$$

271 where  $C_w$  (mol L<sup>-1</sup>) is the dissolved cesium concentration,  $Q_i$  (L s<sup>-1</sup>) is the flowrate,  $\delta(t)$  is  
 272 equal to 1 during contamination stage II and 0 otherwise,  $m$  is the soil mass. Exchangeable  
 273 ( $S_{ex}$ ) and fixed ( $S_{fix}$ ) stocks are related to sorbed concentrations as follows:

$$274 \quad S_{ex} = V_r C_w + m C_{s1} \quad (5)$$

$$275 \quad S_{fix} = m C_{s2} \quad (6)$$

276 The system of equations (3)-(6) was implemented within the R environment (R Core  
 277 Team, 2021) and was solved with the initial conditions  $C_w(0)=0$ ,  $C_{s1}(0)=0$  and  $C_{s2}(0)=0$ . In the  
 278 case of solid-liquid exchanges governed by the  $K_d$  approach, equations (3)-(6) result in the  
 279 following analytical solution for the breakthrough curve  $C_w(t)$ :

$$280 \quad C_w(t) = C_i \left(1 - e^{-\frac{Q}{R V_r} t}\right) \quad \text{if } t \leq T_i \quad (7)$$

281  $C_w(t) = C_w(T_i)e^{-\frac{Q}{RV_r}(t-T_i)}$  if  $t > T_i$  (8)

282 where the retardation factor  $R$  corresponds in this case to:

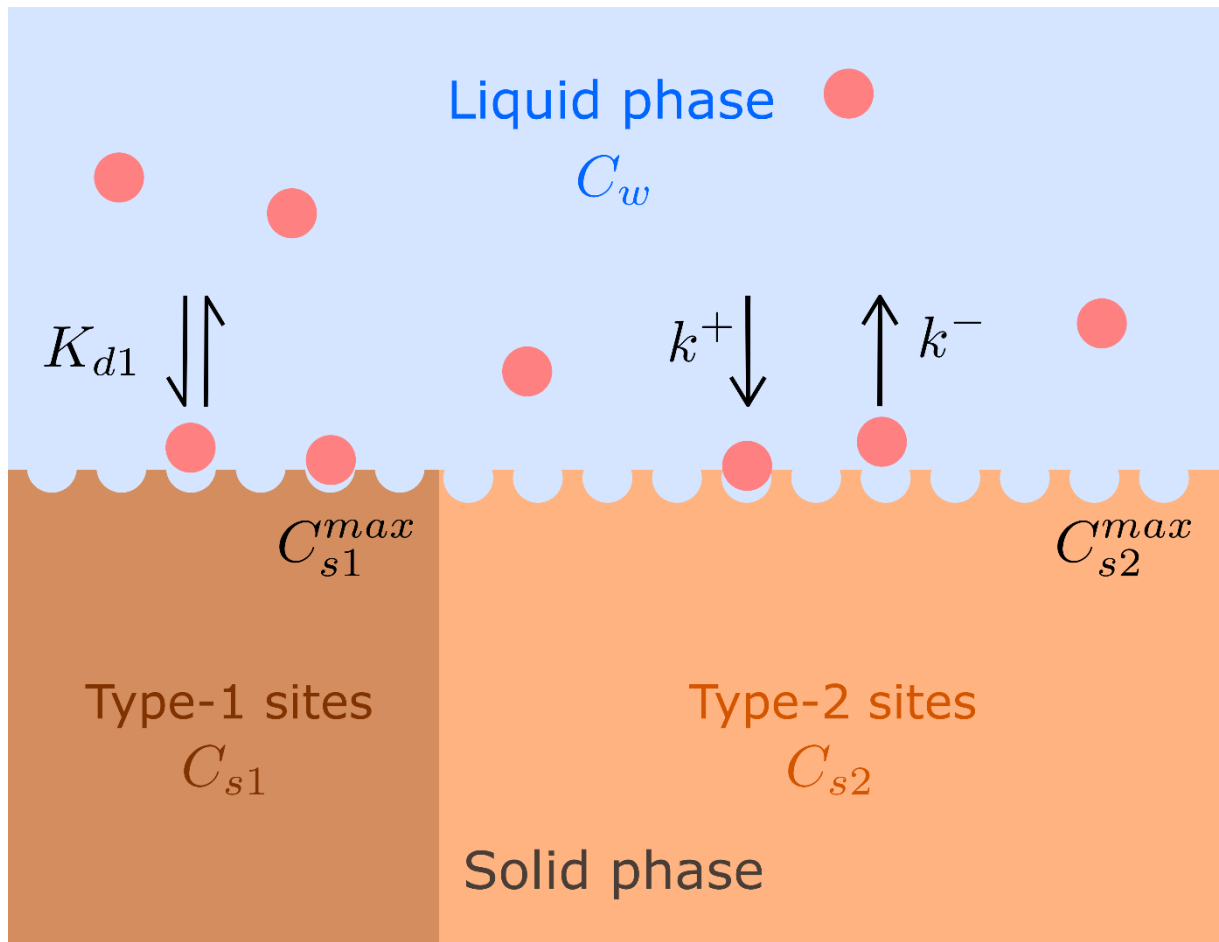
283  $R = 1 + \frac{m}{V_r}K_d$  (9)

284 In the general case, the system (3)-(6) was solved numerically with variable time steps by  
285 an implicit finite-differences scheme. The implicit Radau IIA scheme, available in the R  
286 package “deSolve” (Soetaert et al., 2010), was chosen for its stability, 5th order accuracy and  
287 tolerance to stiff equations.

288 As a consequence of the mass-balance equations (3)-(4) above, half-times of sorption and  
289 desorption reactions  $T^+$  (s) and  $T^-$  (s) in a stirred flow-through reactor can be defined as  
290 follows:

291  $T^+ = \frac{\log(2)V_r}{mk^+}$  (10)

292  $T^- = \frac{\log(2)}{k^-}$  (11)



293  
294

295 **Figure 3.** Compartment representation of the 5-parameter Equilibrium-Kinetic model EK5  
 296 applied to Cs sorption in this study. The model considers two types of solid sites for sorption.  
 297 Type-1 sites are governed by equilibrium parameter  $K_{d1}$  ( $\text{L kg}^{-1}$ ). Type-2 sites are controlled  
 298 sorption by first-order sorption and desorption constants  $k^+$  ( $\text{L kg}^{-1} \text{s}^{-1}$ ) and  $k^-$  ( $\text{s}^{-1}$ ).  $C_{s1}^{max}$  ( $\text{mol}$   
 299  $\text{kg}^{-1}$ ) and  $C_{s2}^{max}$  ( $\text{mol kg}^{-1}$ ) denote the sorption capacities of type-1 and type-2 sites.  
 300 Contaminant concentrations are denoted  $C_w$  ( $\text{mol L}^{-1}$ ) in water, and  $C_{s1}$ ,  $C_{s2}$  ( $\text{mol kg}^{-1}$ ) in the  
 301 solid phase.

302

303 **Table 4.** Parameters and hypotheses of the model variants  $K_d$ , EK3 and EK5 tested in this  
 304 study to model Cesium sorption. These 3 special formulations derive from equations (1) and  
 305 (2). EK5 corresponds to the full model, whereas  $K_d$  and EK3 introduce additional hypotheses  
 306 about sorption (the absence of nonlinearity and non-equilibrium) that numerically correspond  
 307 to particular fixed values for the sorption parameters  $k^+$ ,  $k^-$ ,  $C_{s1}^{max}$  and  $C_{s2}^{max}$ .

Model variant	Sorption hypotheses	Free parameters	Fixed parameters
<b><math>K_d</math></b>	Linear equilibrium (type-1)	$K_{d1}$	$k^+ = 0, k^- = 0$ $C_{s1}^{max} = \infty$
<b>EK3</b>	Linear equilibrium (type-1)+ Linear non-equilibrium (type-2)	$K_{d1}, k^+, k^-$	$C_{s1}^{max} = C_{s2}^{max} = \infty$
<b>EK5</b>	Nonlinear equilibrium (type-1) + Nonlinear non-equilibrium (type-2)	$K_{d1}, k^+, k^-, C_{s1}^{max}$ $C_{s2}^{max}$	-

308

## 309 2.6. Estimation of sorbed cesium stocks

310 Sorbed cesium stocks  $Q_s$  (mol) were estimated at the end of contamination and  
 311 decontamination stages II and III of each experiment in order to quantify cesium retention for  
 312 the different experimental conditions. Calculations were derived from a mass-balance  
 313 approach, and were based on the surface area separating breakthrough curves of cesium  $C(t)$   
 314 and of an inert tracer  $C^{tr}(t)$  submitted to the same experimental conditions (Limousin et al.,  
 315 2007; Martin-Garin et al., 2003). At any time  $t$  during the experiment, the sorbed cesium stock  
 316  $Q_s$  (mol) is governed by:

$$317 \quad Q_s(t) = V_r (C^{tr}(t) - C(t)) + \int_0^t Q(C^{tr}(\tau) - C(\tau)) d\tau \quad (12)$$

318 This formula was solved by numerical integration with the experimental concentrations  
 319  $C_w(t)$  for cesium (eq. 3) and the analytical solution  $C^{tr}(t)$  for the inert tracer, which is given  
 320 by:

$$321 \quad C^{tr}(t) = C_i \left(1 - e^{-\frac{Q}{V_r} t}\right) \quad \text{if } t \leq T_i \quad (13)$$

322 
$$C^{tr}(t) = C^{tr}(T_i)e^{-\frac{Q}{V_r}(t-T_i)} \quad \text{if } t > T_i \quad (14)$$

323 with the convention that  $t=0$  at the beginning of contamination stage II.

324 In equation (12),  $C_w/C_i$  values that were superior to 1 during stage II (and have no physical  
325 significance) were considered to be equal to 1 in order to avoid the underestimation of sorbed  
326 stocks.

327

## 328 **2.7. Model calibration and local identifiability**

329 Sorption parameters of models  $K_d$ , EK3 and EK5 were estimated by the least squares method,  
330 similarly to *in situ* calibrations detailed by Chaif et al. (2021). Briefly, the normalized  
331 dissolved concentration  $y_j=C_w/C_i$  was chosen as the observed variable in order to balance the  
332 weight of each experiment. To ensure the convergence to an absolute optimum, the sum of  
333 squares was minimized numerically from ten starting points by using the R routine “*optim*” (R  
334 Core Team, 2021). These starting points had the least sum of squares among a large set of  
335 candidate points evaluated in the parameters space (1000 for  $K_d$  model,  $12^3$  for EK3 model,  
336 and  $12^5$  for EK5 model). The likelihood ratio statistic (LR) was used to test hypotheses about  
337 sorption models (e.g.  $K_d$  vs EK3) (Huet et al., 2004). Confidence regions of estimated Cs  
338 sorption parameters  $\hat{\vartheta}$  for  $K_d$ , EK3 and EK5 models were approximated, at the level  $100*(1 -$   
339  $\alpha)\%$ , by the points in the parameters space satisfying the Beale’s condition (Beale, 1960;  
340 Seber and Wild, 1989). For each individual parameter  $\hat{\vartheta}_i$ , conservative confidence intervals  
341 were then defined as the upper/lower bounds for  $\vartheta_i$  in this region.

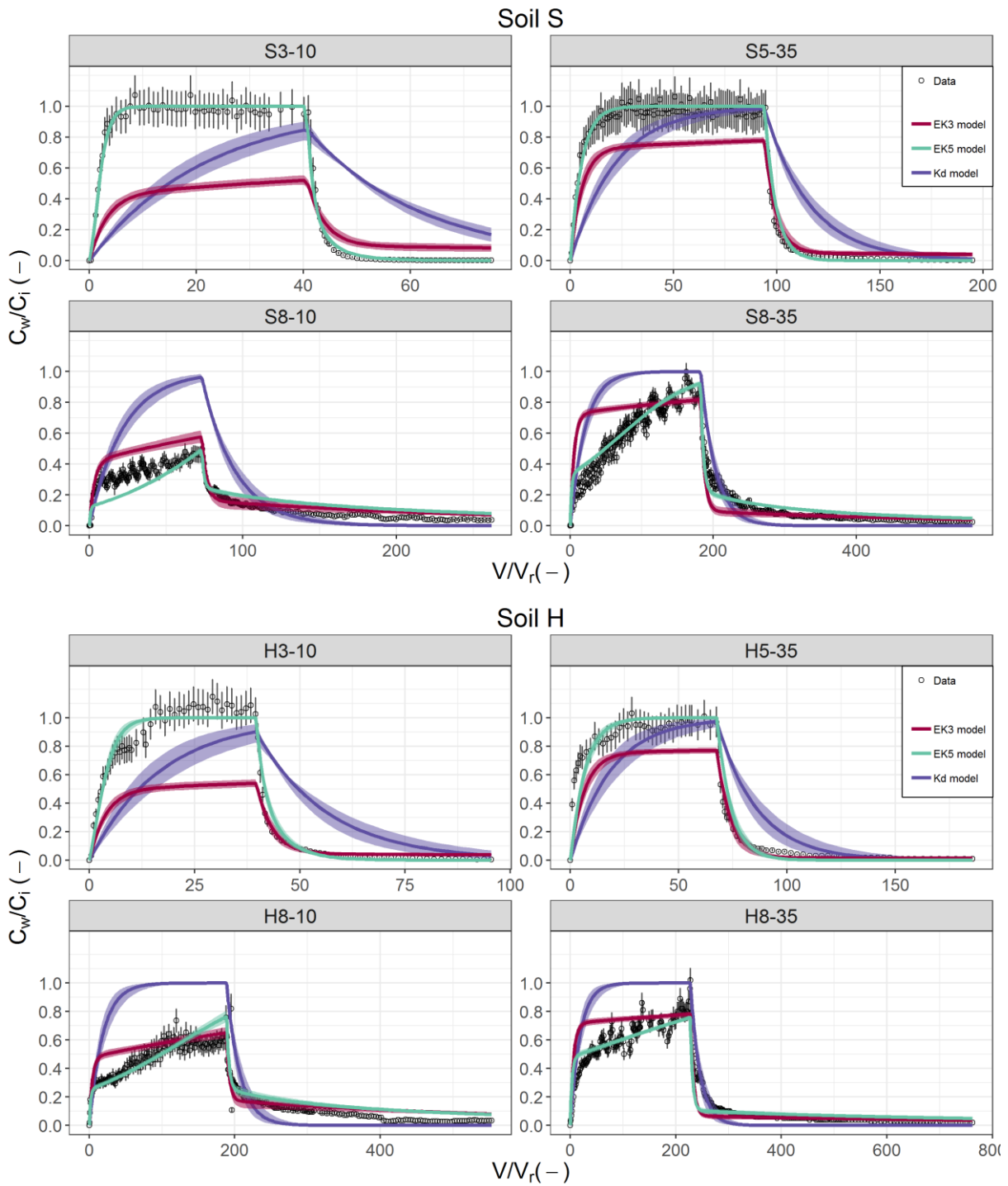
342 Identifiability, i.e. the unicity of the solution to the inverse problem, was diagnosed by the  
343 conditioning number  $\kappa$  of the sensitivity matrix (Belsley et al., 1980; Brun et al., 2001;  
344 Stewart, 1987), as fully described for reactor experiments by Nicoulaud-Gouin et al. (2016).

345 Conditioning numbers  $\kappa$  above 5 (resp. 10) were interpreted as moderately (resp. strongly)

346 non identifiable parameters (Belsley et al., 1980).

347

349 **3.1 Experimental breakthrough curves**



350

351

352 **Figure 4.** Curves of normalized concentrations  $C_w/C_i$  at reactor outlets as a function of  
 353 normalized volume passing through the reactor  $V/V_r$  (breakthrough curves, also noted BTC).



354 Dots correspond to observations and color lines correspond to least squares fits with the  $K_d$   
355 (purple), EK3 (red) and EK5 (green) models. Vertical bars correspond to the confidence  
356 intervals of the observations. Purple, red, and green shaded bands correspond to the 95%  
357 parametric uncertainty of fitted curves.

358

359 For both soils, our observations evidenced influences of flowrate and input concentrations  
360 on cesium sorption and thus support the non-equilibrium and nonlinear hypotheses (**Figure**  
361 **4**).

362 Cesium outlet concentrations  $C_w/C_i$  during contamination stage II systematically increased  
363 with flowrate. For instance, the input concentration was completely transmitted to the outlet  
364 ( $C_w/C_i = 1$ ) after a cumulated flowed volume  $V$  of around 200 reactor volumes ( $V_r$ ) at 35 mL  
365  $h^{-1}$  (experiments S8-35 and H8-35), whereas the breakthrough was still incomplete at 10 mL  
366  $h^{-1}$  at the end of contamination stage II ( $C_w/C_i$  below 0.6 for experiments S8-10 and H8-10).  
367 This trend indicates a smaller sorption when contact time with cesium decreases. These  
368 observations prove the influence of non-equilibrium in cesium sorption processes for the  
369 studied soils.

370 Cesium outlet concentrations  $C_w/C_i$  during contamination stage II systematically increased  
371 when input concentration increased. For high input concentrations ( $10^{-3}$  mol  $L^{-1}$ ), the  
372 equilibrium state, corresponding to  $C_w/C_i = 1$ , was reached after the injection of 10-25 reactor  
373 volumes  $V_r$  (S3-10 and H3-10) whereas for low concentrations ( $10^{-8}$  mol  $L^{-1}$ ) it was not  
374 achieved even after 80-200  $V_r$  ( $C_w/C_i = 0.46$  and  $C_w/C_i = 0.63$  for S8-10 and H8-10  
375 respectively). This trend indicates less soil capacity to fix cesium at higher dissolved  
376 concentrations. These observations prove the influence of nonlinearity on cesium sorption  
377 processes for the studied soils.

378 Cesium sorption was also affected by the nature of the soils. While similar input conditions  
379 provided similar BTC shapes for both soils, some differences in the equilibrium time were  
380 observed between the two soils. Convergence to equilibrium state was always faster for soil S  
381 than for H. For instance, outlet concentration was stabilized after the injection of 30  $V_r$  for S5-  
382 35 compared to 50  $V_r$  for H5-35.

383

### 384 **3.2. Sorbed concentrations and restitution**

385 Estimated sorbed stocks during contamination and decontamination stages II and III also  
386 revealed influences of flowrate and input concentrations on the reversibility of cesium  
387 sorption (**Table 5**).

388 Cesium desorption during decontamination stage III (termed here restitution) increased  
389 with injection concentration and indicated more reversible processes. For high injection  
390 concentration experiments (above  $10^{-5}$  mol L<sup>-1</sup>), restitution was always over 65% for both  
391 soils. At low injection concentrations ( $10^{-8}$  mol L<sup>-1</sup>), restitution did not exceed 50% and was  
392 around 34% (S8-10) at low flowrate and reached around 47% at high flowrate (S8-35).

393 Cesium restitution also increased with flowrate. For instance, restitution was around 35%  
394 for low flowrate experiments (S8-10 and H8-10) and reached around 45% with higher  
395 flowrate (S8-35 and H8-35).

396

397 **Table 5.** Experimental and EK5 simulated stocks of Cs at the end of contamination and  
 398 decontamination stages II and III as defined in equation (12). Restitution is defined at the ratio  
 399 of the desorbed and sorbed stocks of Cs.

Conditions	Calculation	Stock at end of stage II (mol)	Stock at end of stage III (mol)	Restitution (%)
S3-10	Experiment	6.38E-05	2.51E-05	61
	EK5	7.13E-05	7.46E-08	100
S5-35	Experiment	2.17E-06	7.70E-07	64
	EK5	1.77E-06	1.43E-08	99
S8-10	Experiment	1.02E-08	6.74E-09	34
	EK5	1.16E-08	6.66E-09	43
S8-35	Experiment	1.62E-08	8.54E-09	47
	EK5	1.47E-08	5.33E-09	64
H3-10	Experiment	1.32E-04	4.28E-05	68
	EK5	1.32E-04	5.76E-08	100
H5-35	Experiment	2.15E-06	4.49E-08	98
	EK5	2.24E-06	4.82E-08	98
H8-10	Experiment	3.95E-08	2.63E-08	33
	EK5	3.88E-08	1.79E-08	54
H8-35	Experiment	2.92E-08	1.70E-08	42
	EK5	2.93E-08	1.69E-08	42

400

### 401 3.3. Cesium sorption modelling

402 For both soils, EK5 model described significantly better the observed non-equilibrium and  
 403 nonlinear effects than EK3 and  $K_d$  models.

404 Qualitatively, the model EK5, with 5 degrees of freedom, better fitted the breakthrough  
 405 curves than EK3 and  $K_d$  models (3 and 1 degrees of freedom) (**Figure 4**). With a constant  
 406 retardation factor  $R$  (eq. 9) for all conditions, the  $K_d$  model underestimated  $C_w/C_i$  at high input  
 407 concentration values and overestimated them at low concentration values ( $C_w/C_i=1$  at the end  
 408 of stage II of all experiments). With kinetic rates of sorption and desorption allowing  
 409 asymmetry in the curves between stages II and III, EK3 model better fitted  $C_w/C_i$  during stage

410 III whereas it was still unrealistic during stage II (S5-35, H3-10, and H5-35 for example).  
411 With sorption capacities potentially limiting the sorption on type-1 and type-2 sites, EK5  
412 model better described the strong inflexions of  $C_w/C_i$  during stage II for all experiments with  
413 two exceptions being S8-10 where sorption was slightly overestimated at the start of stage II,  
414 and H8-10 where sorption was underestimated at the end of stage II.

415 Sorbed stocks predicted by the EK5 model showed two distinct behaviors depending on  
416 the input concentrations (Table 5). At high concentrations, sorption was completely reversible  
417 with restitution rates superior to 98% for both soils. At low concentrations, sorption was  
418 irreversible and restitution never exceeded 64%. These results suggest that EK5 model can  
419 reproduce both reversible and irreversible behaviors depending on the experimental  
420 conditions using the same set of parameters.

421 Quantitatively, the better performance of EK5 model vs EK3 and  $K_d$  was confirmed  
422 statistically for both soils by the likelihood ratio tests (Table 6). Even though the inclusion of  
423 non-equilibrium sorption significantly improved the fit (EK3 vs  $K_d$ ), the addition of nonlinear  
424 sorption made it even better, as indicated by p-values always under  $10^{-16}$  for the likelihood  
425 ratio test of model EK3 vs model EK5. These results prove that the formulation of sorption  
426 nonlinearity and non-equilibrium proposed by model EK5, although still very simple, brings a  
427 significant improvement to EK3 and  $K_d$  alternatives and suggest its applicability to various  
428 soils.

429

430 **Table 6.** Statistics summary of the fits of sorption models ( $K_d$ , EK3 and EK5). For each soil,  
 431 sorption models were fitted simultaneously on the 4 stirred flow-through reactor experiments.  
 432 Sum of squares S denotes the sum of squared errors between model predictions and  
 433 observations. The p-value of the Likelihood ratio (LR) statistic was derived from its  
 434 approximate chi-squared distribution, as detailed in Chaif et al. (2021).

Quantity		Soil S	Soil H
Sum of squares S	$K_d$ model	65.4	51.7
	EK3 model	29.6	17.4
	EK5 model	3.50	4.43
$K_d$ vs EK3	LR	665	786
	p-value	<1e-16	<1e-16
$K_d$ vs EK5	LR	2455	1771
	p-value	<1e-16	<1e-16
EK3 vs EK5	LR	1790	985
	p-value	<1e-16	<1e-16

435

### 436 3.4 Fitted parameters

437 For both soils, fitted EK5 parameters suggested very contrasted conditions of cesium  
 438 sorption between equilibrium and non-equilibrium sites in terms of characteristic sorption  
 439 times, affinity and sorption capacity (**Table 7**).

440 The type-1 equilibrium sites had a very high sorption capacity, as indicated by  $C_{sl}^{max}$   
 441 values comparable to soil CEC (**Table 1**), but had a non-specific affinity to cesium, as  
 442 indicated by low  $K_{d1}$  values (40 - 60 L kg<sup>-1</sup> depending on the soil).

443 The type-2 non-equilibrium sites had a fast sorption rate  $k^+$  and a slow desorption rate  $k^-$ .  
444 Sorption half-times  $T^+$  of less than one hour for both soils (0.2 and 0.3 hours on average for  
445 soils S and H respectively) were shorter than mean residence time of solution in the reactors  
446 (0.96 to 3.35 hours depending on the flowrate) and indicated a fast cesium sorption.  
447 Desorption half-times  $T^-$  were much longer (3 and 9 days on average for soils S and H  
448 respectively) and suggested a pseudo-irreversible cesium sorption.

449 The type-2 non-equilibrium sites had a very strong affinity to cesium but with a very  
450 limited sorption capacity. They had a specific affinity to cesium, as indicated by large values  
451 of their theoretical equilibrium ratio  $K_{d2} = k^+/k^-$  (3489 to 6171 L kg<sup>-1</sup> for soils S and H  
452 respectively). Their sorption capacity  $C_{s2}^{\max}$  was very small (0.04% and 0.02% of the CEC of  
453 soils S and H respectively) and indicated a very limited number of type-2 sites.

454 Soil H had a higher cesium sorption capacity than Soil S. Distribution coefficient of both  
455 equilibrium and kinetic sites  $K_{d1}$  and  $K_{d2}$  were respectively 51% and 77% higher in soil H  
456 than in S. Similarly, equilibrium and kinetics sites saturations  $C_{s1}^{\max}$  and  $C_{s2}^{\max}$  were 456%  
457 and 260% higher in H than S. These values are in line with the contrasted physiochemical and  
458 mineralogical properties of the two soils, notably the higher CEC and clay and organic matter  
459 content of soil H compared to S (**Table 1**).

460

461 **Table 7.** Fitted parameter values of the EK5 model. Values correspond to ordinary least-  
 462 squares estimations, and intervals correspond to conservative 95% confidence intervals.

<b>Parameter</b>	<b>Unit</b>	<b>Soil S</b>	<b>Soil H</b>
$K_{d1}$	$L\ kg^{-1}$	40 [34 ; 46]	60 [49 ; 74]
$k^+$	$L\ kg^{-1}\ s^{-1}$	4.71E-03 [4.27E-03 ; 5.24E-03]	2.45E-03 [2.20E-03 ; 2.73E-03]
$k^-$	$s^{-1}$	1.35E-06 [1.15E-06 ; 1.59E-06]	3.98E-07 [3.07E-07 ; 5.01E-07]
$C_{s1}^{max}$	$mol\ kg^{-1}$	1.38E-02 [1.01E-02 ; 1.92E-02]	7.67E-02 [4.94E-02 ; 1.39E-01]
$C_{s2}^{max}$	$mol\ kg^{-1}$	4.83E-06 [4.49E-06 ; 5.21E-06]	1.74E-05 [1.55E-05 ; 2.01E-05]

463

## 464 4. DISCUSSION

### 465 4.1. Experimental design

466 Our experimental design (combining 3 concentration levels and 2 flowrate levels in 4  
467 experiments) allowed to identify uniquely and accurately the EK5 parameters for both soils.  
468 The conditioning numbers  $\kappa$  (2.291 and 2.505) well below 5 indicated *a posteriori* that our  
469 experimental design constrained the fitted equations (3)-(4) to a unique set of parameter  
470 values (Table 8). The good identifiability of EK5 parameters was also confirmed numerically  
471 by the narrow confidence intervals of parameters, whose half-width did not exceed 16% for  
472 Soil S and 26% for Soil H (Table 7).

473 These numerical results suggest the adoption of our 4 reactor design for future CSTR  
474 experiments aiming at identifying EK5 parameters for other soils/radionuclides. They are  
475 complementary to more formal analyses recommending at least 2 experiments for the  
476 identification of the EK3 model (Nicoulaud-Gouin et al., 2016).

477 Considering that EK5 model well fitted the BTC curves, the EK5 parameters obtained in  
478 this study can be seen as simple but accurate indicators of sorption processes, and, as such,  
479 deserve further discussion about their physical interpretation.

480

481 Table 8. Local identifiability of EK5 parameters for soils S and H, as diagnosed from the  
482 conditioning number  $\kappa$  of the sensitivity matrix (Brun et al., 2001). The applied formulae are  
483 fully detailed in Nicoulaud-Gouin et al. (2016).

	Notation	Soil S					Soil H				
Eigenvalues	$\lambda_i$	2.079	1.155	0.862	0.508	0.396	2.025	1.398	0.724	0.530	0.323
Conditioning number	$\kappa$	2.291					2.505				



## 485 4.2. Physical nature of type-1 and type-2 sites

486 Since cesium sorption in soils is primarily governed by clay minerals (Bostick et al., 2002;  
487 Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Shenber and Eriksson, 1993;  
488 Wendling et al., 2005), it seems plausible that the equilibrium and kinetic sites postulated by  
489 the EK5 model are an empirical typology of the various clay sorption sites.

490 The non-linearity of Cs sorption is mainly due to the heterogeneity of the surface  
491 adsorption sites (Bradbury and Baeyens, 2000; Cornell, 1993; Eliason, 1966; Missana et al.,  
492 2004; Poinssot et al., 1999; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962)  
493 which, as reviewed in introduction, broadly includes interlayer sites with low density strong  
494 affinity to cesium but and planar sites with higher densities but lower affinity cesium. These  
495 observations have been summarized quantitatively with a simplified two-site thermodynamic  
496 model of Cs sorption on clay noted 1-pK DL/IE (Cherif et al., 2017). The first sites are  
497 governed by an ion exchange (IE) model which simulates the adsorption of Cs on negatively  
498 charged sites of planar surface of clay minerals, including outer-basal and interlayers sites  
499 ( $\equiv X^-$ ). The second sites are governed by a surface complexation (SC) model used to describe  
500 the adsorption of cations on a single FES site ( $\equiv S O^{-0.5}$ ) (Cherif et al., 2017 and references  
501 therein). A database of these sites densities is available for illite, montmorillonite and  
502 kaolinite minerals. Therefore, for a given soil, knowing its mineralogical composition allows  
503 the estimation of IE and surface complexation sites densities (Table 9).

504 The densities of type-1 equilibrium sites (given by  $C_{s1}^{\max}$ ) and type-2 kinetic sites (given  
505 by  $C_{s2}^{\max}$ ) of EK5 model seem to correspond to those of IE and SC sites of clay minerals of  
506 both soils respectively (Table 9). On one hand, IE sites densities were almost identical to  
507  $C_{s1}^{\max}$  for soil S (relative error of 5%) and around two times higher for soil H. On the other

508 hand, the offset between  $C_{s2}^{\max}$  and surface complexation sites densities was of a similar  
509 magnitude for both soils (relative error of 80% and 52% for S and H respectively). These  
510 differences can be explained by : (1) the presence of other sites, mainly organic matter, that  
511 can contribute to cesium sorption (Nakamaru et al., 2007; Rigol et al., 2002; Valcke and  
512 Cremers, 1994); (2) The uncertainty related to the estimation of proportions of the clay  
513 minerals (illite, montmorillonite and kaolinite available in the soils). In fact, the XRD method  
514 used to estimate these proportions is semi-quantitative and only provides a gross estimation of  
515 these proportions (Table 1).

516 With parameters values of  $C_{s1}^{\max}$  and  $C_{s2}^{\max}$  fixed to Exchange and surface complexation  
517 sites densities of the studied soils (Table 9), the model EK5 yielded satisfactory predictions of  
518 BTC (Figure 5). The model EK5 satisfactorily reproduced all the experimental breakthrough  
519 curves except for experiments S8-10 and S8-35, where predicted concentrations  $C_w/C_i$   
520 increased towards unity earlier than observed. This is mainly due to the surface complexation  
521 sites density being slightly lower than  $C_{s2}^{\max}$  which lead to a premature saturation of kinetic  
522 sites at the end of stage II of experiment S8-10. The exchange and surface complexation sites  
523 densities seem to provide a good first indicator of the sorption capacities of equilibrium and  
524 kinetic sites. However, the uncertainties associated with the proportions of minerals and their  
525 IE and SC densities may explain the imprecise estimation of the  $C_{s1}^{\max}$  and  $C_{s2}^{\max}$  parameters.

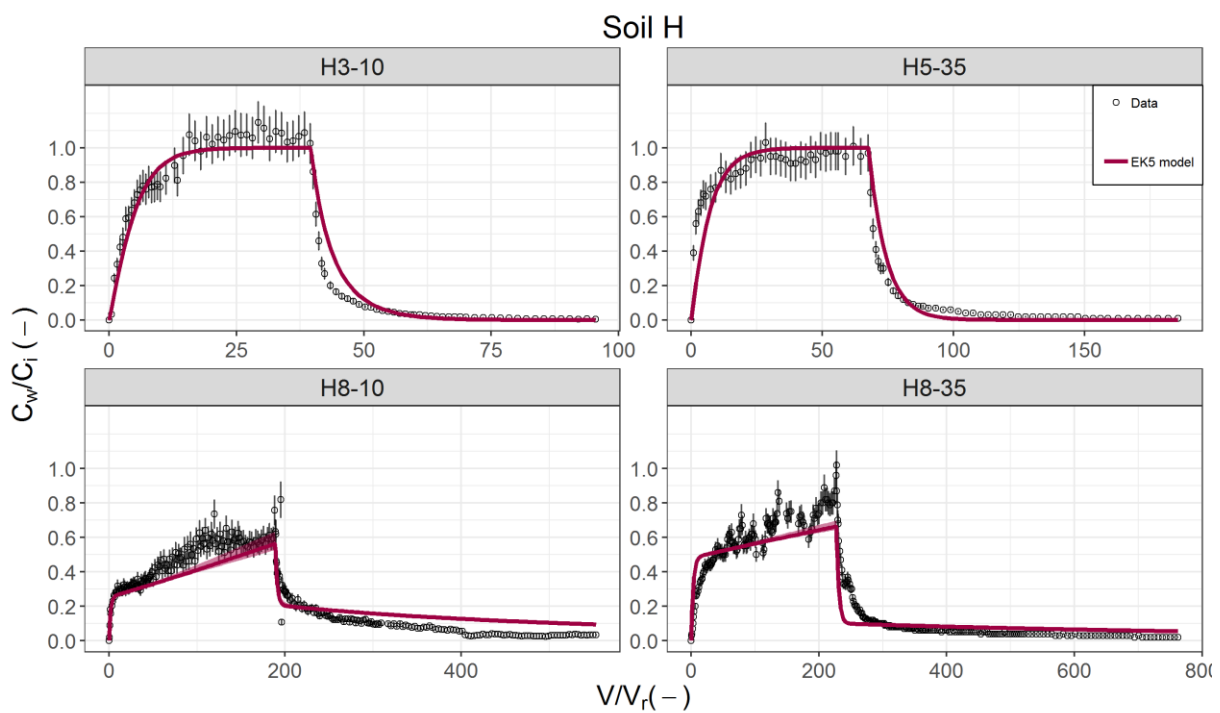
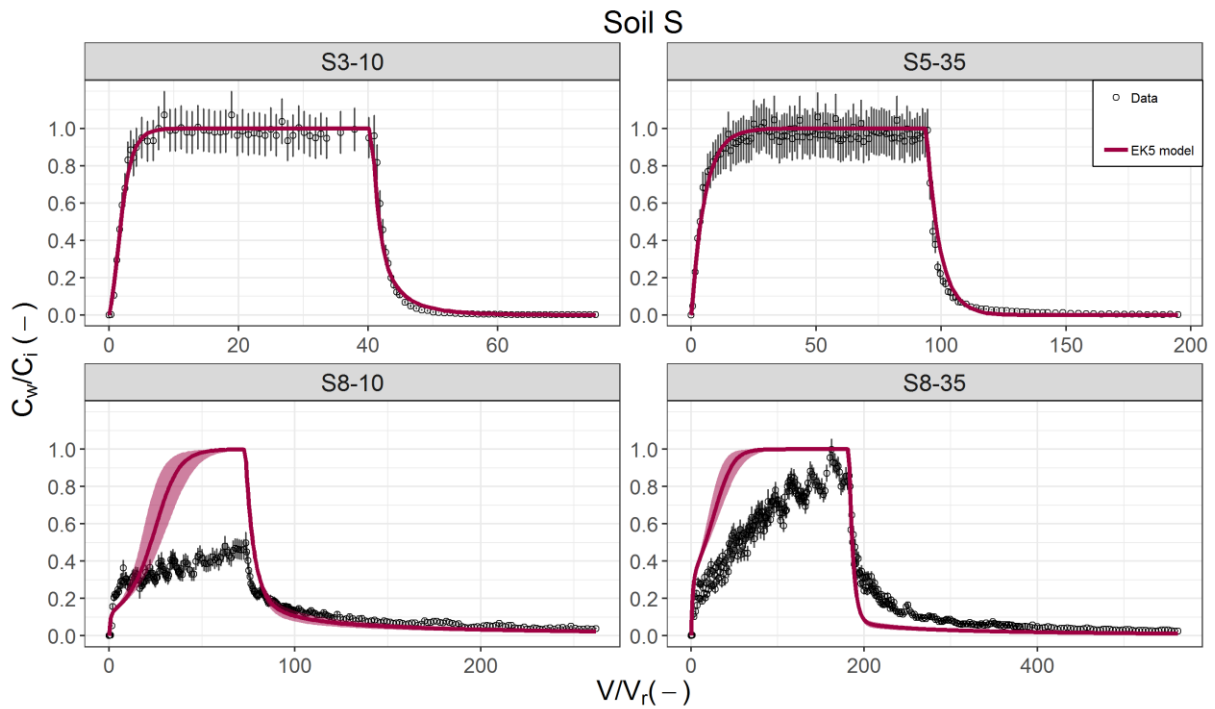
526

527 **Table 9.** Exchange and surface complexation sites densities derived from the mineralogical  
 528 properties of the studied soils and the properties of illite, montmorillonite and kaolinite  
 529 compiled by Cherif et al. (2017). Cation exchange capacity (CEC) (from **Table 1**) and fitted  
 530 sorption capacities  $C_{s1}^{\max}$  and  $C_{s2}^{\max}$  (from **Table 7**) are recalled here to support the  
 531 comparisons given in the text.

	Soil S			Soil H		
	Min	Mean	Max	Min	Mean	Max
<b>Ion Exchange “IE” sites density (mol kg<sup>-1</sup>)</b>	1.19E-02	1.31E-02	1.43E-02	1.53E-01	1.80E-01	2.07E-01
<b>CEC (mol kg<sup>-1</sup>)</b>	1.11E-02			7.64E-02		
<b><math>C_{s1}^{\max}</math> (mol kg<sup>-1</sup>)</b>	1.01E-02	1.38E-02	1.92E-02	4.94E-02	7.67E-02	1.39E-01
<b>Surface complexation sites density (mol kg<sup>-1</sup>)</b>	6.59E-07	9.77E-07	1.30E-06	2.63E-05	3.66E-05	4.70E-05
<b><math>C_{s2}^{\max}</math> (mol kg<sup>-1</sup>)</b>	4.49E-06	4.83E-06	5.21E-06	1.55E-05	1.74E-05	2.01E-05

532

533



537 **Figure 5.** Cs breakthrough curves simulated by the EK5 model with  $C_{s1}^{\max}$  (resp.  $C_{s2}^{\max}$ )  
 538 equal to the ion exchange (resp. surface complexation) sites densities (**Table 9**). Other  
 539 parameters ( $K_{d1}$ ,  $k^+$ , and  $k^-$ ) were at fitted values (**Table 7**).

### 540 **4.3. Cesium sorption and reversibility on equilibrium and kinetic sites**

541 The EK5 hypothesis better reproduced the experimental results by considering that  
542 sorption sites act differently at low, intermediate and high concentrations of cesium (**Figure**  
543 **6**).

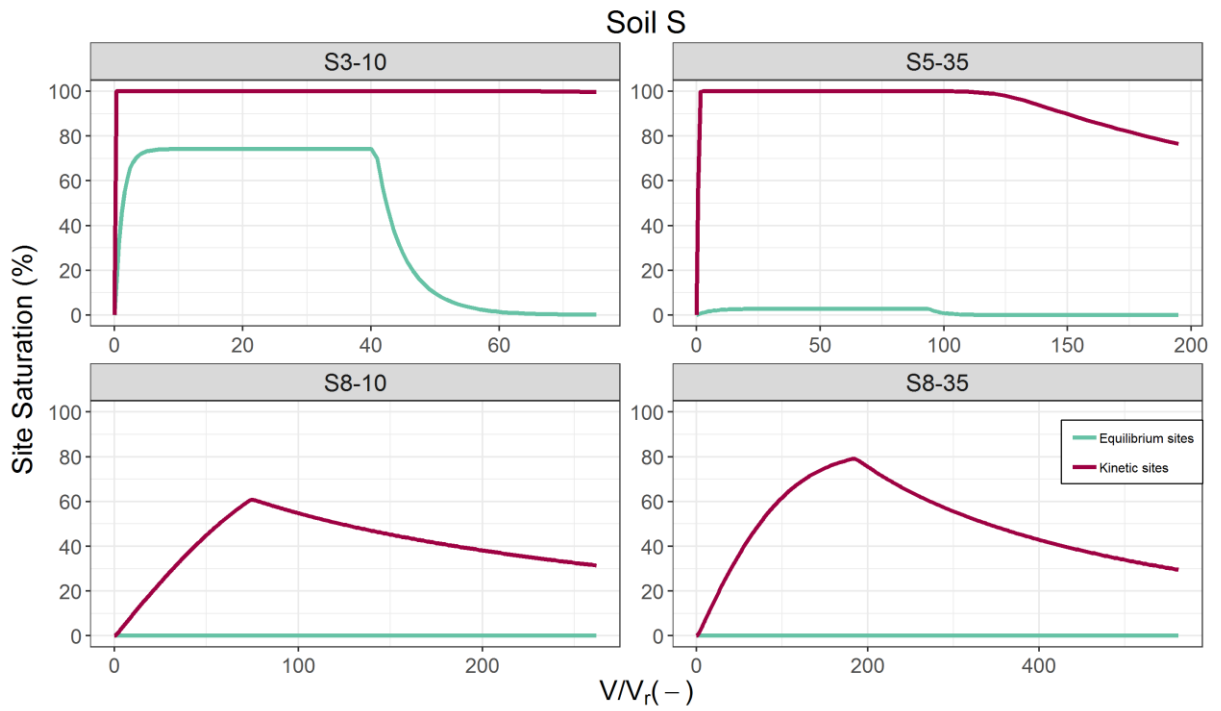
544 At low input concentrations ( $10^{-8}$  mol L<sup>-1</sup>), simulated Cs sorbed on type-2 sites without  
545 saturation of sorption capacity at the end of contamination stage II (e.g. 60% for S8-10 and  
546 80% for S8-35). Simulated Cs sorption on type-1 sites was virtually inexistent (with  
547 saturation index almost at 0%) due to their much lower affinity to Cs. As a consequence,  
548 simulated Cs desorption during decontamination stage III resulted only from type-2 sites.

549 At high input concentrations ( $10^{-3}$  mol L<sup>-1</sup>), simulated Cs also initially sorbed on type-2  
550 sites. However, type-2 sites rapidly reached saturation (less than one hour), and simulated Cs  
551 continued to sorb on type-1 sites without saturation at the end of contamination stage II (e.g.  
552 around 75% for S3-10 and 45% H3-10). Considering that type-1 sites held almost all the  
553 sorbed inventory, simulated Cs desorption during decontamination stage III resulted only  
554 from type-1 sites.

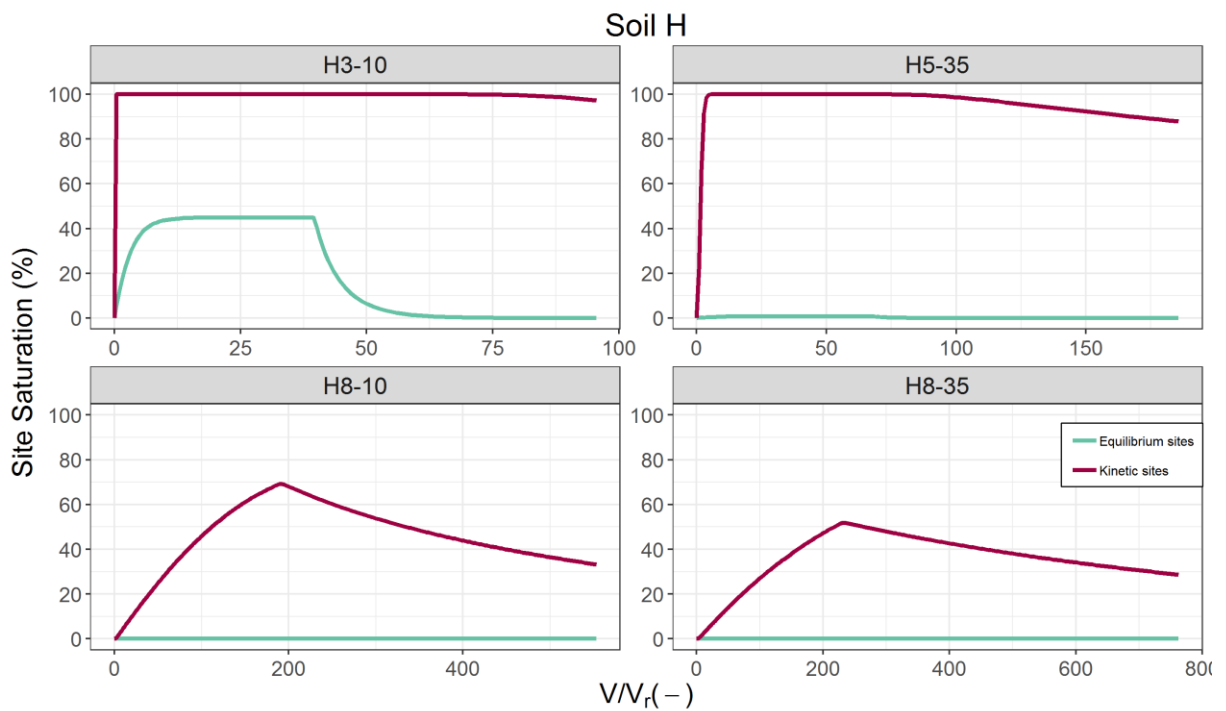
555 At intermediate input concentrations ( $10^{-5}$  mol L<sup>-1</sup>), simulated Cs initially sorbed on type-2  
556 sites (at short times) and on type-1 sites during contamination stage II. During  
557 decontamination stage III, type-1 and type-2 sites both contributed to desorption in the  
558 opposite order. Indeed, simulated Cs initially desorbed exclusively from low affinity type-1  
559 sites. After type-1 sites were rapidly decontaminated (less than 6 hours), simulated Cs  
560 continued to desorb from high affinity type-2 sites and this process was much slower.

561 This behavior of the EK5 model is consistent with studies evidencing specific and non-  
562 specific cesium sorption in soils. In fact, several studies conducted on clay minerals (illite,

563 montmorillonite and kaolinite) have shown that cesium sorption takes place on two distinct  
564 sites with different affinities (Benedicto et al., 2014; Brouwer et al., 1983; Missana et al.,  
565 2014b; Poinssot et al., 1999; Staunton and Roubaud, 1997). The sorption isotherms obtained  
566 in these studies showed that cesium sorption depended on the cesium concentration in the  
567 solution. At low concentrations, cesium sorption was the highest and decreased when cesium  
568 concentrations increased.



570



571

572 **Figure 5.** Percentage of occupied sites for type-1 equilibrium (green) and type-2 kinetic (red)  
 573 sites, as simulated by the EK5 model with fitted parameters (**Table 7**). Cumulated flowed  
 574 volume at the reactor outlet  $V$  is normalized by the volume  $V_r$  of the reactor chamber.

#### 575 4.4. Domains of sorption nonlinearity and non-equilibrium

576 Rewriting the equations of reactive transport (3)-(4) can reveal when nonlinear and non-  
 577 equilibrium effects are significant (and the full EK5 model is required) and when linearity or  
 578 equilibrium hypotheses are appropriate (and  $K_d$  or EK3 models can be used).

579 In the case of the EK3 model, the reactive transport equations (3) and (4) have been  
 580 rewritten in a simplified form by introducing the following transformations (Nicoulaud-Gouin  
 581 et al., 2016):

$$C_w^* = \frac{C_w}{C_i}; \quad C_{s2}^* = \frac{m C_{s2}}{V_r C_i}; \quad t^* = \frac{Q_i t}{V_r}; \quad D_{a1} = \frac{mk^+}{Q_i}; \quad D_{a2} = \frac{V_r k^-}{Q_i}; \quad K_{d1}^* = \frac{m}{V_r} K_{d1}$$

582 where  $C_w^*$  and  $C_{s2}^*$  are dimensionless concentrations in solution and on type-2 sites,  $t^*$  is  
 583 dimensionless time,  $D_{a1}$  and  $D_{a2}$  are ratios of sorption and desorption times to water residence  
 584 time, also known as Damköhler numbers (Bahr and Rubin, 1987). In the case of the full EK5  
 585 model, reactor equations (3) and (4) here write:

$$586 \quad \frac{dC_w^*}{dt^*} = -\frac{1+D_{a1}(1-\tau_2)}{R(C_w^*)} C_w^* + \frac{D_{a2}}{R(C_w^*)} C_{s2}^* + \frac{\delta}{R(C_w^*)} \quad (15)$$

$$587 \quad \frac{dC_{s2}^*}{dt^*} = D_{a1}(1-\tau_2)C_w^* - D_{a2}C_{s2}^* \quad (16)$$

$$588 \quad R(C_w^*) = 1 + \frac{K_{d1}^*}{\left(1 + \frac{K_{d1}^*}{C_{s1}^{max*}} C_w^*\right)^2} \quad (17)$$

589 where  $R$  is the retardation factor due to type-1 sites. The dimensionless sorption capacity  
 590  $C_{s1}^{max*}$  of type-1 sites and the rate of occupied type-2 sites  $\tau_2$  are defined by:

$$C_{s1}^{max*} = \frac{m C_{s1}^{max}}{V_r C_i}; \quad \tau_2 = \frac{C_{s2}}{C_{s2}^{max}}$$



591 In equation (15), type-2 sorption of a contaminant is significant if  $D_{a1} > 1$ , or equivalently  
592 if the half-time of the sorption reaction  $T^+$  is shorter than water residence time ( $T^+ < T_w$ ).  
593 Similarly, type-2 desorption of a contaminant can occur significantly if  $D_{a2} > 1$ , or  
594 equivalently if the half-time of the desorption reaction  $T^-$  is shorter than water residence time  
595 ( $T^- < T_w$ ). As a consequence, the condition ( $T_w < T^+$  or  $T_w < T^-$ ) corresponds to the non-  
596 equilibrium sorption domain, and in particular, the domain  $T_w \ll T^-$  corresponds to pseudo-  
597 irreversible sorption (**Figure 7**).

598 Type-1 sorption is governed by a Langmuir isotherm (eq. 1) and tends to saturate when  
599  $K_{d1}C_w/C_{s1}^{\max}$  exceeds 1, which corresponds to  $C_w$  greater than  $C_{s1}^{\max}/K_{d1}$ . Quantitatively,  
600 type-1 sites are saturated at 50% when  $C_w$  is equal to  $C_{s1}^{\max}/K_{d1}$ , and are saturated at 99%  
601 when  $C_w$  is approximately  $100 C_{s1}^{\max}/K_{d1}$ . Similarly, from equation (2), type-2 sorption tends  
602 at equilibrium to a Langmuir isotherm, which saturates when  $C_w$  is greater than  $C_{s2}^{\max}/K_{d2}$ .  
603 As a consequence, dissolved cesium concentrations  $C_w$  lying in the intervals  
604  $[1,100]*C_{s1}^{\max}/K_{d1}$  or  $[1,100]*C_{s2}^{\max}/K_{d2}$  correspond to the domain of nonlinear sorption  
605 (**Figure 7**).

606 This analysis thus shows that the minimal sorption model depends on the residence time of  
607 water ( $T_w$ ) and the dissolved cesium concentration in water ( $C_w$ ). Three broad sorption  
608 domains can be defined and distinguished in the plane ( $T_w, C_w$ ) (**Figure 7**): the equilibrium  
609 domain (where sorption can be described by an isotherm model, including the  $K_d$  model at  
610 trace concentrations), the linear equilibrium (where the linear kinetic approximation EK3  
611 applies) and the nonlinear non-equilibrium domain (where the full EK5 cannot be simplified).  
612 The nonlinear non-equilibrium domain indicates the reactive transport scenarios for which the  
613 EK5 model can improve the realism of predictions.

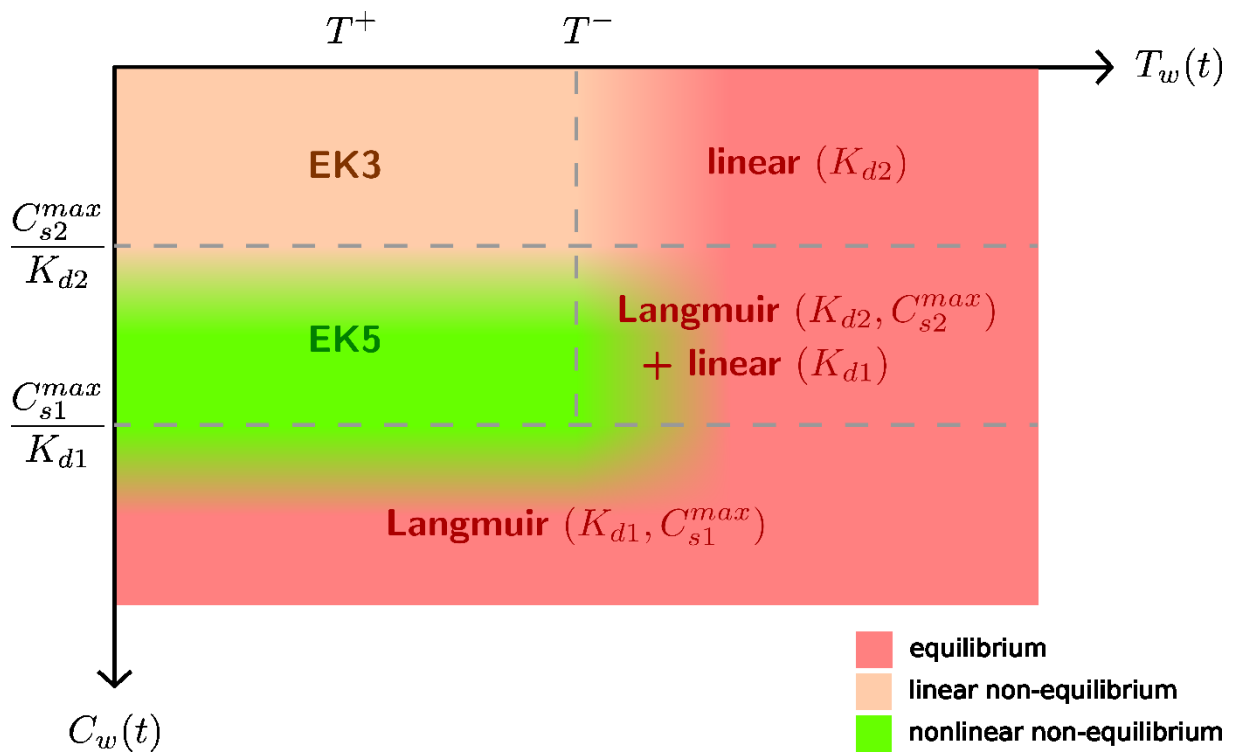
614 For scenarios of radiocesium release in the environment, the influence of sorption  
615 nonlinearity may not be significant on reactive transport and the approximations of models  $K_d$   
616 or EK3 may be valid. Indeed, the linear domain corresponds to dissolved concentrations  
617 below  $C_{s2}^{\max}/K_{d2}$ , i.e. approximately below  $1.4 \cdot 10^{-9}$  and  $2.8 \cdot 10^{-9}$  mol L<sup>-1</sup> for the studied soils S  
618 and H. In the case of <sup>137</sup>Cs (with mass activity  $3.22 \cdot 10^{12}$  Bq g<sup>-1</sup>), this would correspond to  
619 maximum concentrations of 71 and 146 kBq L<sup>-1</sup>. However, nonlinear sorption may occur at  
620 much lower concentrations  $C_w$  in the presence of stable cesium in the soil and more  
621 competing cations in the solution (e.g. Fukui, 1978; Saiers and Hornberger, 1996; Flury et al.,  
622 2004).

623 On the contrary, the influence of non-equilibrium sorption on reactive transport may be  
624 critical for common hydrological conditions. In a porous medium of characteristic length  $L$   
625 (m) and humidity  $\theta$  (-), a characteristic water flux density  $q_i$  (m<sup>3</sup> s<sup>-1</sup> m<sup>-2</sup>) corresponds to a  
626 water residence time:

$$T_w = \frac{q_i}{L \theta}$$

627 Sorption and desorption can generally be considered instantaneous for Damköhler numbers  
628  $Da_1 = T_w/T^+$  and  $Da_2 = T_w/T^-$  higher than 100 (e.g. Bahr and Rubin, 1987). For soils S and H,  
629 sorption had very short half-lives  $T^+$  (0.2 and 0.3 h) and can be considered much faster than  
630 water residence time in a soil column for common hydrological situations. However,  
631 desorption has much longer half-lives  $T^-$  (3 and 9 days) and may be often comparable to water  
632 residence time. As a result, the equilibrium model  $K_d$  may be appropriate for very slow water  
633 flows as observed in underground or deep geological nuclear waste repositories  
634 (Grigaliūnienė et al., 2020; Medved' and Černý, 2019; Yim and Simonson, 2000). But non-  
635 equilibrium model EK3 model seems better appropriate for the fast transient contamination

636 and infiltration conditions occurring in the unsaturated zone (Ardois and Szenknect, 2005;  
 637 Brusseau et al., 1989; Maraqa et al., 1999; Testoni et al., 2017).



638

639 **Figure 6.** Applicability domains of the models  $K_d$  (linear), EK3 and EK5 at a given time  $t$  of a  
 640 reactive transport scenario with mean residence time of water  $T_w(t)$  and dissolved cesium  
 641 concentration  $C_w(t)$ . This representation is specific to this study, where it was observed that  
 642 type-2 sorption time  $T^+$  was shorter than desorption time  $T^-$ , and that the density of type-2  
 643 sorption sites ( $C_{s2}^{max}$ ) was much lower than the density of type-1 sites ( $C_{s1}^{max}$ ).

## 644 5. CONCLUSIONS

645 This work demonstrated that non-equilibrium and non-linear processes can influence  
646 cesium sorption in conditions of reactive transport.

647 For each studied soil, the 4 stirred flow-through reactor experiments indicated that cesium  
648 was less retarded when injected concentrations and/or flow rate increased. The proposed  
649 sorption model EK5 reproduced significantly better the experimental observations compared  
650 to simpler sorption models ( $K_d$  and EK3). It could well reproduce, with a single set of  
651 parameters, the four breakthrough curves of cesium observed for both soils in the range 10-35  
652 mL h<sup>-1</sup> for flow rate and 10<sup>-8</sup>-10<sup>-3</sup> mol L<sup>-1</sup> for injection concentration. For both soils, the fitted  
653 EK5 parameters suggested contrasted conditions of cesium sorption between equilibrium and  
654 non-equilibrium sites. The equilibrium sites had a sorption capacity comparable to soil CEC,  
655 but had a low affinity to cesium (40-60 L kg<sup>-1</sup>). The non-equilibrium sites had a much shorter  
656 sorption half-time (0.2-0.3 hours) compared to half-time of desorption (3-9 days), which  
657 allows pseudo-irreversible cesium sorption at high flow rates. The non-equilibrium sites had a  
658 strong affinity to cesium (3489-6171 L kg<sup>-1</sup>) but their sorption capacity only represented 0.02-  
659 0.04% of the CEC. The type-1 equilibrium and type-2 kinetic sites postulated by the EK5  
660 model are an empirical representation of soil sorption sites that seems physically sound. They  
661 seem to correspond respectively to ion-exchange and surface complexation sites of clay  
662 minerals, as suggested by the similarity between their fitted and measured sorption capacities.

663 From a methodological standpoint, this study also showed that an experimental design  
664 combining four flow-through reactor experiments with different conditions of flow rate and  
665 injection concentration allows a precise identification of the 5 parameters of the proposed  
666 EK5 model. This study also suggested the conditions of Cs reactive transport for which non-  
667 equilibrium and nonlinear effects are important and thus variants of the EK5 model may be

668 more realistic than the  $K_d$  model. Non-equilibrium sorption effects increase when water  
669 residence time decreases and becomes comparable to the half times of sorption and desorption  
670 reactions (respectively 1 hour and 6-20 days for the studied soils). Non-linear sorption effects  
671 emerge when sorbed Cs concentration is close to sorption capacity limits of type-2 and type-1  
672 sites (approximately 1% and 99% of CEC for the studied soils). However, the applicability of  
673 proposed EK model calibrated in the laboratory for predicting the reactor transport of Cs *in*  
674 *situ* on contaminated soils has not been fully demonstrated yet. The validity and parameter  
675 values of the EK5 model derived here from stirred flow-through reactor experiments concern  
676 small representative elementary volumes and may no longer apply for complex flows in  
677 porous media where other processes of nonlinear and non-equilibrium sorption may emerge.  
678 Further experiments on soils with more contrasted physico-chemical properties (e.g. content  
679 in clay minerals) and on systems of different levels of complexity (from batch reactors to soil  
680 columns) are necessary to generalize the findings of this work.

681

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685 **REFERENCES**

686 Antonopoulos-Domis M., Clouvas A., Hiladakis A., Kadi S., 1995. Radiocesium distribution  
687 in undisturbed soil: measurements and diffusion-advection model. *Health Physics* 1995; 69:  
688 949-953. <https://doi.org/10.1097/00004032-199512000-00009>.

689 Ardois C., Szenknect S., 2005. Capability of the Kd model to predict radionuclides behaviour  
690 and transport in unsaturated columns under steady flow conditions. *Radioprotection* 40, S53–  
691 S59. <https://doi.org/10.1051/radiopro:2005s1-009>. Vol 40, 2005.

692 Avery S.V., 1996. Fate of caesium in the environment: distribution between the abiotic and  
693 biotic components of aquatic and terrestrial ecosystems. *Journal of Environmental*  
694 *Radioactivity* 30: 139-171.

695 Bahr J.M., Rubin J., 1987. Direct comparison of kinetic and local equilibrium formulations  
696 for solute transport affected by surface reactions. *Water Resources Research* 23: 438-452.

697 Bar- Tal A., Feigenbaum S., Sparks D.L., Pesek J.D., 1990. Analyses of Adsorption Kinetics  
698 Using a Stirred- Flow Chamber: I. Theory and Critical Tests. *Soil Science Society of*  
699 *America Journal* 54: 1273-1278.

700 Beale E.M.L., 1960. Confidence Regions in Non-Linear Estimation. *Journal of the Royal*  
701 *Statistical Society. Series B (Methodological)* 22: 41-88.

702 Belsley D.A., Kuh E., Welsch R.E., 1980. *Regression diagnostics : identifying influential data*  
703 *and sources of collinearity*. John Wiley and sons, Hoboken, New Jersey.  
704 <http://doi.org/10.1002/0471725153>

705 Benedicto A., Missana T., Fernández A.M., 2014. Interlayer collapse affects on cesium  
706 adsorption onto illite. *Environmental Science & Technology* 48: 4909-4915.

707 Bossew P., Kirchner G., 2004. Modelling the vertical distribution of radionuclides in soil. Part  
708 1: the convection–dispersion equation revisited. *Journal of Environmental Radioactivity* 73:  
709 127-150.

710 Bostick B.C., Vairavamurthy M.A., Karthikeyan K., Chorover J., 2002. Cesium adsorption on  
711 clay minerals: An EXAFS spectroscopic investigation. *Environmental Science & Technology*  
712 36: 2670-2676.

713 Bouzidi A., Souahi F., Hanini S., 2010. Sorption behavior of cesium on Ain Oussera soil  
714 under different physicochemical conditions. *Journal of Hazardous Materials* 184: 640-646.

715 Bradbury M.H., Baeyens B., 2000. A generalised sorption model for the concentration  
716 dependent uptake of caesium by argillaceous rocks. *Journal of Contaminant Hydrology* 42:  
717 141-163.

718 Brouwer E., Baeyens B., Maes A., Cremers A., 1983. Cesium and rubidium ion equilibriums  
719 in illite clay. *The Journal of Physical Chemistry* 87: 1213-1219. Brun R., Reichert P., Künsch  
720 H.R., 2001. Practical identifiability analysis of large environmental simulation models. *Water*  
721 *Resources Research* 37: 1015-1030.

722 Brusseau M.L., Jessup R.E., Rao P.S.C., 1989. Modeling the transport of solutes influenced  
723 by multiprocess nonequilibrium. *Water Resources Research* 25: 1971-1988.

724 Cameron D., Klute A., 1977. Convective- dispersive solute transport with a combined  
725 equilibrium and kinetic adsorption model. *Water Resources Research* 13: 183-188.

726 Castrillejo M., Casacuberta N., Breier C.F., Pike S.M., Masqué P., Buesseler K.O., 2016.  
727 Reassessment of <sup>90</sup>Sr, <sup>137</sup>Cs, and <sup>134</sup>Cs in the coast off Japan derived from the Fukushima  
728 Dai-ichi nuclear accident. *Environmental Science & Technology* 50: 173-180.

729 Chaif H., Coppin F., Bahi A., Garcia-Sanchez L., 2021. Influence of non-equilibrium sorption  
730 on the vertical migration of <sup>137</sup>Cs in forest mineral soils of Fukushima Prefecture. *Journal of*  
731 *Environmental Radioactivity* 232: 106567.

732 Chen G.-N., Li Y.-C., Zuo X.-R., Ke H., Chen Y.-M., 2020. Comparison of Adsorption  
733 Behaviors of Kaolin from Column and Batch Tests: Concept of Dual Porosity. *Journal of*  
734 *Environmental Engineering* 146: 04020102.

735 Cherif M.A., 2017. Dynamic modeling of the (bio)availability of radionuclides in soils: a  
736 comparative model-experiment approach applied to the transfer of Cs (I) in the rhizosphere  
737 (in french). PhD thesis, Aix-Marseille Université, 2017.  
738 <http://www.theses.fr/2017AIXM0547>.

739 Cherif M.A., Martin-Garin A., Gérard F., Bildstein O., 2017. A robust and parsimonious  
740 model for caesium sorption on clay minerals and natural clay materials. *Applied*  
741 *Geochemistry* 87: 22-37.

742 Chorover J., Choi S., Amistadi M.K., Karthikeyan K., Crosson G., Mueller K.T., 2003.  
743 Linking cesium and strontium uptake to kaolinite weathering in simulated tank waste  
744 leachate. *Environmental Science & Technology* 37: 2200-2208.

745 Comans R.N.J., Hockley D.E., 1992. Kinetics of cesium sorption on illite. *Geochimica et*  
746 *Cosmochimica Acta* 56: 1157-1164.

747 Cornell R.M., 1993. Adsorption of cesium on minerals: A review. *Journal of Radioanalytical*  
748 *and Nuclear Chemistry* 171: 483-500.

749 Durrant C.B., Begg J.D., Kersting A.B., Zavarin M., 2018. Cesium sorption reversibility and  
750 kinetics on illite, montmorillonite, and kaolinite. *Science of The Total Environment* 610-611:  
751 511-520.



752 Eberl D.D., 1980. Alkali cation selectivity and fixation by clay minerals. *Clays and clay*  
753 *minerals* 28: 161-172.

754 Eliason J., 1966. Montmorillonite exchange equilibria with strontium-sodium-cesium.  
755 *American Mineralogist: Journal of Earth and Planetary Materials* 51: 324-335.

756 Fesch C., Simon W., Haderlein S.B., Reichert P., Schwarzenbach R.P., 1998. Nonlinear  
757 sorption and nonequilibrium solute transport in aggregated porous media: Experiments,  
758 process identification and modeling. *Journal of Contaminant Hydrology* 31: 373-407.

759 Fiengo Perez F., Sweeck L., Bauwens W., Van Hees M., Elskens M., 2015. Adsorption and  
760 desorption kinetics of <sup>60</sup>Co and <sup>137</sup>Cs in freshwater rivers. *Journal of Environmental*  
761 *Radioactivity* 149:81-89. <https://doi.org/10.1016/j.jenvrad.2015.07.010>

762 Flury M., Czigány S., Chen G., Harsh J.B., 2004. Cesium migration in saturated silica sand  
763 and Hanford sediments as impacted by ionic strength. *Journal of Contaminant Hydrology* 71:  
764 111-126.

765 Francis C., Brinkley F., 1976. Preferential adsorption of <sup>137</sup>Cs to micaceous minerals in  
766 contaminated freshwater sediment. *Nature* 260: 511-513.

767 Fukui M., 1978. Evaluation of a Combined Sorption Model for Describing Cesium Transport  
768 in a Soil. *Health Physics* 35: 552-562.

769 Fuller A.J., Shaw S., Ward M.B., Haigh S.J., Mosselmans J.F.W., Peacock C.L., Stackhouse  
770 S., Dent A.J., Trivedi D., Burke I.T., 2015. Caesium incorporation and retention in illite  
771 interlayers. *Applied Clay Science* 108: 128-134.

772 Garcia-Sanchez L., Loffredo N., Mounier S., Martin-Garin A., Coppin F., 2014. Kinetics of  
773 selenate sorption in soil as influenced by biotic and abiotic conditions: a stirred flow-through  
774 reactor study. *Journal of Environmental Radioactivity* 138: 38-49.

775 Gil-García C., Rigol A., Vidal M., 2009. New best estimates for radionuclide solid–liquid  
776 distribution coefficients in soils, Part 1: radiostrontium and radiocaesium. *Journal of*  
777 *Environmental Radioactivity* 100: 690-696.

778 Grigaliūnienė D., Poškas R., Kilda R., Jouhara H., Poškas P., 2020. Modeling radionuclide  
779 migration from activated metallic waste disposal in a generic geological repository in  
780 Lithuania. *Nuclear Engineering and Design* 370: 110885.

781 Huet S., Bouvier A., Poursat M.-A., Jolivet E., 2004. Accuracy of estimators, confidence  
782 intervals and tests. *Statistical Tools for Nonlinear Regression: A Practical Guide With S-*  
783 *PLUS and R Examples*. Springer Verlag, New York. <https://doi.org/10.1007/b97288>.

784 IAEA, 2009. Quantification of Radionuclide Transfer in Terrestrial and Freshwater  
785 Environments for Radiological Assessments. Report IAEA-TECDOC-1616. International  
786 Atomic Energy Agency, Vienna.

787 Iliina S.M., Marang L., Lourino-Cabana B., Eyrolle F., Boyer P., Coppin F., Sivry Y. Gélabert  
788 A., Benedetti M.F., 2020. Solid/liquid ratios of trace elements and radionuclides during a  
789 Nuclear Power Plant liquid discharge in the Seine River: Field measurements vs geochemical  
790 modeling. *Journal of Environmental Radioactivity* 220-221: 106317.

791 Jackson M., 1962. Interlayering of expansible layer silicates in soils by chemical weathering.  
792 *Clays and clay minerals* 11: 29-46.

793 Jagercikova M., Cornu S., Le Bas C., Evrard O., 2015. Vertical distributions of <sup>137</sup>Cs in  
794 soils: a meta-analysis. *Journal of Soils and Sediments* 15: 81-95.

795 Jarvis N.J., Taylor A., Larsbo M., Etana A., Rosén K., 2010. Modelling the effects of  
796 bioturbation on the re-distribution of <sup>137</sup>Cs in an undisturbed grassland soil. *European*  
797 *Journal of Soil Science* 61: 24-34.

798 Klement A.W. Jr, 1965. Radioactive fallout phenomena and mechanisms. *Health Physics* 11:  
799 1265-1274.

800 Konoplev A, Bulgakov A, Hilton J, Comans R, Popov V., 1997. Long-term kinetics of  
801 radiocesium fixation by soils. In: G. Desmet et al. (Eds), *Freshwater and Estuarine*  
802 *Radioecology*, Elsevier, pp.173-182.

803 Kurikami H., Malins A., Takeishi M., Saito K., Iijima K., 2017. Coupling the advection-  
804 dispersion equation with fully kinetic reversible/irreversible sorption terms to model  
805 radiocesium soil profiles in Fukushima Prefecture. *Journal of Environmental Radioactivity*  
806 171: 99-109.

807 Limousin G., Gaudet J.P., Charlet L., Szenknect S., Barthès V., Krimissa M., 2007. Sorption  
808 isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry*  
809 22: 249-275.

810 Maes A., Cremers A., 1986. Highly selective ion exchange in clay minerals and zeolites. In:  
811 *Geochemical Processes at Mineral Surfaces*, Chapter 13, pp 254-295. ACS Symposium Series  
812 Vol. 323. <https://doi.org/10.1021/bk-1987-0323.ch013>.

813 Maraqa M.A., Wallace R.B., Voice T.C., 1999. Effects of residence time and degree of water  
814 saturation on sorption nonequilibrium parameters. *Journal of Contaminant Hydrology* 36: 53-  
815 72.

816 Martin-Garin A., Van Cappellen P., Charlet L., 2003. Aqueous cadmium uptake by calcite: a  
817 stirred flow-through reactor study. *Geochimica et Cosmochimica Acta* 67: 2763-2774.

818 Mazet P., 2008. Influence of transient flow on the mobility of strontium in unsaturated sand  
819 columns (in french). PhD thesis, Université Joseph Fourier, Grenoble.

820 Medved' I., Černý R., 2019. Modeling of radionuclide transport in porous media: A review of  
821 recent studies. *Journal of Nuclear Materials* 526: 151765.

822 Mishra S., Sahoo S.K., Bossew P., Sorimachi A., Tokonami S., 2018. Reprint of “Vertical  
823 migration of radio-caesium derived from the Fukushima Dai-ichi Nuclear Power Plant  
824 accident in undisturbed soils of grassland and forest?”. *Journal of Geochemical Exploration*  
825 184: 271-295. <https://doi.org/10.1016/j.gexplo.2016.07.027>

826 Missana T., Benedicto A., García-Gutiérrez M., Alonso U., 2014a. Modeling cesium retention  
827 onto Na-, K- and Ca-smectite: Effects of ionic strength, exchange and competing cations on  
828 the determination of selectivity coefficients. *Geochimica et Cosmochimica Acta* 128: 266-  
829 277.

830 Missana T., García-Gutiérrez M., Alonso U., 2004. Kinetics and irreversibility of cesium and  
831 uranium sorption onto bentonite colloids in a deep granitic environment. *Applied Clay*  
832 *Science* 26: 137-150.

833 Missana T., García-Gutiérrez M., Benedicto A., Ayora C., De-Pourcq K., 2014b. Modelling  
834 of Cs sorption in natural mixed-clays and the effects of ion competition. *Applied*  
835 *Geochemistry* 49: 95-102.

836 Montes M.L., Silva L.M.S., Sá C.S.A., Runco J., Taylor M.A., Desimoni J., 2013. Inventories  
837 and concentration profiles of <sup>137</sup>Cs in undisturbed soils in the northeast of Buenos Aires  
838 Province, Argentina. *Journal of Environmental Radioactivity* 116: 133-140.

839 Murota K., Saito T., Tanaka S., 2016. Desorption kinetics of cesium from Fukushima soils.  
840 *Journal of Environmental Radioactivity* 153: 134-140.

841 Nakamaru Y., Ishikawa N., Tagami K., Uchida S., 2007. Role of soil organic matter in the  
842 mobility of radiocesium in agricultural soils common in Japan. *Colloids and Surfaces A:  
843 Physicochemical and Engineering Aspects* 306: 111-117.

844 Nicoulaud-Gouin V., Garcia-Sanchez L., Giacalone M., Attard J.C., Martin-Garin A., Bois  
845 F.Y., 2016. Identifiability of sorption parameters in stirred flow-through reactor experiments  
846 and their identification with a Bayesian approach. *Journal of Environmental Radioactivity*  
847 162-163: 328-339.

848 Okumura M., Kerisit S., Bourg I.C., Lammers L.N., Ikeda T., Sassi M., Rosso K.M., Machida  
849 M. 2019. Radiocesium interaction with clay minerals: Theory and simulation advances Post-  
850 Fukushima. *Journal of Environmental Radioactivity* 89: 135-145.

851 Ota M., Nagai H., Koarashi J., 2016. Modeling dynamics of <sup>137</sup>Cs in forest surface  
852 environments: Application to a contaminated forest site near Fukushima and assessment of  
853 potential impacts of soil organic matter interactions. *Science of The Total Environment* 551-  
854 552: 590-604.

855 Poinssot C., Baeyens B., Bradbury M.H., 1999. Experimental and modelling studies of  
856 caesium sorption on illite. *Geochimica et Cosmochimica Acta* 63: 3217-3227.

857 Porro I., Newman M.E., Dunnivant F.M., 2000. Comparison of batch and column methods for  
858 determining strontium distribution coefficients for unsaturated transport in basalt.  
859 *Environmental Science & Technology* 34: 1679-1686.

860 R Core Team, 2021. R: A Language and Environment for Statistical Computing. R  
861 Foundation for Statistical Computing, Vienna, Austria. <https://www.R-project.org/>

862 Rich C., Black W., 1964. Potassium exchange as affected by cation size, pH, and mineral  
863 structure. *Soil Science* 97: 384-390.

864 Rigol A., Vidal M., Rauret G., 2002. An overview of the effect of organic matter on soil–  
865 radiocaesium interaction: implications in root uptake. *Journal of Environmental Radioactivity*  
866 58: 191-216.

867 Rosén K., Öborn I., Lönsjö H., 1999. Migration of radiocaesium in Swedish soil profiles after  
868 the Chernobyl accident, 1987–1995. *Journal of Environmental Radioactivity* 46: 45-66.

869 Saiers J.E., Hornberger G.M., 1996. Migration of <sup>137</sup>Cs through quartz sand: experimental  
870 results and modeling approaches. *Journal of Contaminant Hydrology* 22: 255-270.

871 Sardin M., Schweich D., Leij F.J., van Genuchten M.Th., 1991. Modeling the Nonequilibrium  
872 Transport of Linearly Interacting Solutes in Porous Media: A Review. *Water Resources*  
873 *Research* 27: 2287-2307.

874 Savoye S., Beaucaire C., Fayette A., Herbette M., Coelho D., 2012. Mobility of cesium  
875 through the callovo-oxfordian claystones under partially saturated conditions. *Environmental*  
876 *Science & Technology* 46: 2633-2641.

877 Sawhney B., 1972. Selective sorption and fixation of cations by clay minerals: a review.  
878 *Clays and clay minerals* 20: 93-100.

879 Schnaar G., Brusseau M.L., 2014. Nonideal Transport of Contaminants in Heterogeneous  
880 Porous Media: 11. Testing the Experiment Condition Dependency of the Continuous-  
881 Distribution Rate Model for Sorption-Desorption. *Water, Air and Soil Pollution* 225: 2136.

882 Schwertmann U., Taylor R.M., 1989. Iron oxides. In: Dixon, J.B. and Weed S.B. (Eds.),  
883 *Minerals in Soil Environments*, 2nd Edition, Soil Science Society of America, Inc., Madison,  
884 pp.379-438. <https://doi.org/10.2136/sssabookser1.2ed.c8>.

885 Seber G.A.F., Wild C.J., 1989. Nonlinear regression. John Wiley, New York.  
886 <https://doi.org/10.1002/0471725315>.

887 Selim H., Mansell R., 1976. Analytical solution of the equation for transport of reactive  
888 solutes through soils. *Water Resources Research* 12: 528-532.

889 Selim, H.M., Davidson J.M., Mansell R.S., 1976. Evaluation of a two-site adsorption–  
890 desorption model for describing solute transport in soil. p. 444–448. In *Proc. Summer*  
891 *Computer Simulation Conf.*, Washington, DC. 12–14 July 1976. Simulation Councils, La  
892 Jolla, CA.

893 Shenber M., Eriksson Å., 1993. Sorption behaviour of caesium in various soils. *Journal of*  
894 *Environmental Radioactivity* 19: 41-51.

895 Siroux B., 2017. Interactions in a cesium, strontium/natural organic matter and soil clays  
896 system. From decontamination to remediation (in french). PhD thesis. Université Sorbonne  
897 Paris Cité. <https://tel.archives-ouvertes.fr/tel-02083966>

898 Siroux B., Latrille C., Beaucaire C., Petcut C., Tabarant M., Benedetti M.F., Reiller P.E.,  
899 2021. On the use of a multi-site ion-exchange model to predictively simulate the adsorption  
900 behaviour of strontium and caesium onto French agricultural soils, *Applied Geochemistry*  
901 132, 105052. <https://doi.org/10.1016/j.apgeochem.2021.105052>.

902 Sparks D., Zelazny L., Martens D., 1980. Kinetics of potassium desorption in soil using  
903 miscible displacement. *Soil Science Society of America Journal* 44: 1205-1208.

904 Sposito G., 1984. *The surface chemistry of soils*. Oxford University Press, New York.

905 Staunton S., Roubaud M., 1997. Adsorption of  $^{137}\text{Cs}$  on montmorillonite and illite: effect of  
906 charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid. *Clays and*  
907 *clay minerals* 45: 251-260.

908 Steinhauser G., Niisoe T., Harada K.H., Shozugawa K., Schneider S., Synal H.-A., Walther  
909 C., Christl M., Nanba K., Ishikawa H., Koizumi A., 2015. Post-accident sporadic releases of  
910 airborne radionuclides from the Fukushima Daiichi nuclear power plant site. *Environmental*  
911 *Science & Technology* 49: 14028-14035.

912 Stewart G.W., 1987. Collinearity and least squares regression (with discussion). *Statistical*  
913 *Science* 2: 68-100.

914 Strebl F., Gerzabek M., Bossew P., Kienzl K., 1999 Distribution of radiocaesium in an  
915 Austrian forest stand. *Science of The Total Environment* 226: 75-83.

916 Szenknect S., 2003. Radionuclides migration in the unsaturated zone: experimental study and  
917 modeling applied to the Chernobyl pilot site (in french). PhD thesis. Université Joseph  
918 Fourier, Grenoble.

919 Szenknect S., Gaudet J.-P., Dewiere L., 2003. Evaluation of distribution coefficients for the  
920 prediction of strontium and cesium migration in a natural sand at different water contents.  
921 *Journal de Physique IV (Proceedings)* 107(1): 1279-1282.  
922 <https://doi.org/10.1051/jp4:20020534>

923 Takahashi J., Onda Y., Hihara D., Tamura K., 2019. Six-year monitoring of the vertical  
924 distribution of radiocesium in three forest soils after the Fukushima Dai-ichi Nuclear Power  
925 Plant accident. *Journal of Environmental Radioactivity* 210: 105811.

926 Testoni R., Levizzari R., De Salve M., 2017. Coupling of unsaturated zone and saturated zone  
927 in radionuclide transport simulations. *Progress in Nuclear Energy* 95: 84-95.



928 Toro J., Padilla I.Y., 2017. Spatial Distribution of Fate and Transport Parameters Using  
929 CXTFIT in a Karstified Limestone Model. American Geophysical Union, Fall Meeting 2017,  
930 abstract H51C-1288.

931 Toso J., Velasco R., 2001. Describing the observed vertical transport of radiocesium in  
932 specific soils with three time-dependent models. *Journal of Environmental Radioactivity* 53:  
933 133-144.

934 Soetaert, K., Petzoldt, T., Setzer, R.W., 2010. Solving differential equations in R: package  
935 deSolve. *J. Stat. Software* 33 (9), 1-25. <https://doi.org/10.18637/JSS.V033.I09>.

936 Valcke E., Cremers A., 1994. Sorption-desorption dynamics of radiocaesium in organic  
937 matter soils. *Science of The Total Environment* 157: 275-283.

938 Van Cappellen P., Qiu, L., 1997a. Biogenic silica dissolution in sediments of the Southern  
939 Ocean. I. Solubility. *Deep-Sea Res. Part II* 1997; 44: 1109-1128.

940 Van Cappellen P., Qiu L., 1997b. Biogenic silica dissolution in sediments of the Southern  
941 Ocean. II. Kinetics. *Deep Sea Research Part II: Topical Studies in Oceanography* 1997; 44:  
942 1129-1149.

943 van Genuchten M.Th., Simunek J.J., Leij F.J., Toride N., Šejna M., 2012. STANMOD: Model  
944 Use, Calibration, and Validation. *Transactions of the ASAE* 55:1353-1366.  
945 <https://doi.org/10.13031/2013.42247>.

946 van Genuchten M.Th., Wagenet R.J., 1989. Two-Site/Two-Region Models for Pesticide  
947 Transport and Degradation: Theoretical Development and Analytical Solutions. *Soil Science*  
948 *Society of America Journal* 53: 1303-1310.

949 Wahlberg J., Fishman M.J., 1962. Adsorption of cesium on clay minerals. Geological Survey  
950 Bulletin 1140-A, US Government Printing Office. <https://doi.org/10.3133/b1140A>.

951 Wang W.-Z., Brusseau M.L., Artiola J.F., 1998. Nonequilibrium and nonlinear sorption  
952 during transport of cadmium, nickel, and strontium through subsurface soils. In: Jenne E.A.  
953 (Ed.), Adsorption of Metals by Geomedia, Academic Press, pp. 427-443.  
954 <https://doi.org/10.1016/B978-012384245-9/50021-9>.

955 Wendling L.A., Harsh J.B., Ward T.E., Palmer C.D., Hamilton M.A., Boyle J.S., Flury M.,  
956 2005. Cesium desorption from illite as affected by exudates from rhizosphere bacteria.  
957 Environmental Science & Technology 39: 4505-4512.

958 Yim M.-S., Simonson S.A., 2000. Performance assessment models for low level radioactive  
959 waste disposal facilities: A review. Progress in Nuclear Energy 36: 1-38.

960 Zachara J.M., Smith S.C., Liu C., McKinley J.P., Serne R.J., Gassman P.L., 2002. Sorption of  
961 Cs<sup>+</sup> to micaceous subsurface sediments from the Hanford site, USA. Geochimica et  
962 Cosmochimica Acta 66: 193-211.