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1 **Reactive transport of strontium in two laboratory-scale columns: experiments and modelling**

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11 **Abstract**

12 To support the environmental monitoring of nuclear sites, reactive transport models used to predict the
13 migration of contaminants such as strontium-90 (⁹⁰Sr) in soils, sediments and aquifers are developed,
14 continuously tested and improved. This study aims at assessing the adequacy of the multi-site ion
15 exchanger model (MSIE) based on a component “additivity approach” and coupled to the advection-
16 dispersion equation (ADE) to simulate Sr transport in a clayey sandstone and a Bt soil horizon. We
17 have also compared the performance of the modelling approach with simulation results obtained by
18 considering a K_d approach (constant K_d). Transport experiments were performed in centimetre- and
19 decimetre-scale columns in order to test the model sensitivities to the mineral abundance and the
20 specificities of their reactive parameters. Non-reactive transport experiments with conservative tracers
21 allowed us to determine the transport parameters, such as porosity and dispersivity. In this paper, we
22 have compared the Sr transport simulation results with Sr experimental breakthrough curves acquired
23 at various flow velocities. The simulations results show that the K_d approach can reproduce
24 experimental data in the case of the clayey sandstone when a certain amount of uncertainty is
25 accepted, whereas the additivity approach better fits the Sr reactive transport in both columns

26 (especially the maximum value) without it being necessary to adjust the parameters. These results
27 advocate for more complex retention models than K_d to better understand and improve the robustness
28 of Sr transport predictions. The clay content, the relative abundance of illite and smectite, and the clay
29 mineral specificity, are all sensitive parameters when it comes to defining the reactive system involved
30 in Sr transport simulation. The results highlight the influence of illite in the spreading of the Sr
31 breakthrough curve, especially through its low-capacity and high-selectivity site. This implies having
32 access to a robust and extensive set of retention parameters acquired on reference minerals. In this
33 study, the results obtained for the clayey sandstone confirm the robustness of our selected parameters
34 when clay minerals have similar reactivity levels as the reference minerals. This set of parameters
35 appears more limited in the case of the Bt soil containing weathered or evolved minerals. The choice
36 of modelling approach is therefore crucial for accurately modelling and predicting Sr transport
37 behaviour in porous media, as is the representativeness of the minerals in the database.

38

39 1. Introduction

40 ^{90}Sr is a product of uranium and plutonium fission generated in nuclear reactors and is one of the most
41 abundant radioisotopes released into the environment because of weapons testing and nuclear
42 accidents (Kashparov *et al.* 2003). ^{90}Sr (29 years half-life) is highly soluble and its sorption is strongly
43 affected by competition with major cations in solution, i.e. with Ca and Mg. Moreover, it generally
44 does not remain on the soil surface like Cs (Berns *et al.*, 2018), which facilitates its migration to
45 greater depths. To support the environmental monitoring of nuclear sites, reactive transport models are
46 being developed to simulate the migration of contaminants such as ^{90}Sr in soils, sediments and
47 aquifers, the key requirement being a robust predictive performance.

48 Reactive transport processes, i.e. advection, dispersion and diffusion coupled with chemical reactions
49 involving precipitation, dissolution or adsorption-desorption, generally control contaminant migration
50 in natural environments. They result in retarded migration, often expressed by a delay with respect to
51 water tracers or by tails in the breakthrough curve (Liu *et al.*, 2017). The time dependence of reactive
52 transport requires examining both transport processes and reactivity formalisms used in the modelling
53 approaches. The sorption of contaminants has been modelled using simple, empirical retention models
54 such as linear (constant distribution coefficient K_d), Langmuir or Freundlich sorption isotherms
55 (Bachhuber *et al.*, 1982; Hölttä *et al.*, 1997, Cui *et al.*, 1998; Fesch *et al.*, 1998; Palagyi and Stamberg,
56 2010). However, such models provide specific and contextual parameters determined in precise
57 physicochemical conditions and therefore often fail to be predictive. For instance, Szenknect *et al.*
58 (2008) simulated Sr transport through a sandy soil column using a constant K_d . These authors
59 highlighted the fact that Sr reactive transport deviates from classical reactive transport including a
60 retardation factor, although Sr sorption was described as instantaneous, reversible and with a linear
61 reaction at trace concentration (Szenknect *et al.* 2005, Wissocq *et al.*, 2018). Moreover, to simulate Sr
62 transport in field experiments through aeolian sand sampled from the Chernobyl site, Bugai *et al.*
63 (2012) found K_d values to be the most sensitive parameter in the model. In this study, the K_d values
64 obtained by laboratory batch tests (Szenknect *et al.*, 2005) had to be adjusted to match the simulation
65 outcomes with the observed data. The mismatch was attributed to geochemical disturbances involving

66 changes in the competing cation (i.e. Ca) concentration in solution. Bugai *et al.* (2020) cautioned
67 against the concomitance of the adsorption/desorption reaction with other chemical processes in the
68 natural environment. Modelling on an aquifer scale can then be distorted by taking into account K_d
69 values measured in the laboratory that are not representative of the processes involved.

70 Another approach consists in coupling transport and thermodynamic retention models to account for
71 varying physicochemical conditions in the media. Ion-exchange models have often been retained for
72 multi-components materials (Vallochi *et al.*, 1981a and b; Schweich and Sardin, 1981; Appelo, 1994;
73 Vulava *et al.*, 2000; Steefel *et al.*, 2003; Lichtner *et al.*, 2004; Missana *et al.*, 2008; Tournassat *et al.*,
74 2013). Despite better consideration of the chemical reactions by these retention models, some authors
75 were required to adjust the sorption parameters obtained in batch experiments for trace elements (static
76 conditions) in order to reproduce reactive transport data (Steefel *et al.*, 2003; Szenknect *et al.*, 2005),
77 therefore diminishing the predictability of these reactive transport models. To apply the retention
78 parameters acquired in dispersed multicomponent media (i.e. batch experiments) to compacted media
79 (i.e. column or field experiment), it must be assumed that the entire solid is in contact with solution so
80 that all the sorption sites are called into play in the reactive process.

81 Among the tested approaches, the generalised composite approach consists in considering only one
82 ion-exchange site-bearing component to reflect the material's reactivity. However, it was previously
83 shown that the strongest affinity for trace elements (i.e. Sr, Zn, Tl, Cs...) on clay minerals is
84 associated to specific sorption sites (Poinssot *et al.*, 1999, Missana *et al.*, 2008, 2014, Altmann *et al.*,
85 2015, Wissocq *et al.*, 2017, Martin *et al.*, 2018, Latrille *et al.*, 2019, Tournassat *et al.*, 2013), which
86 are usually not differentiated in such a retention approach. By using a generalised composite approach,
87 Voegelin *et al.* (2000) and Vulava *et al.* (2002) were able to use the same dataset in static and dynamic
88 conditions to reproduce the transport of major elements (Ca, Mg and Na) and Sr in trace form
89 (Szenknect *et al.*, 2008). However, this approach is restricted to a specific context, which constrains its
90 extrapolation to other multi-component materials and extended environmental conditions. Vulava *et*
91 *al.* (2002) compared various exchange models and evidenced a significant improvement was gained
92 with a multi-site cation exchange model to predict the transport behaviour of the major cations. Lu *et*

93 *al.* (2014) also made this assessment and used such a model to cover a large range of chemical
94 conditions without any adjustable parameters. Another approach is to resort to a multi-site ion
95 exchanger model using a component additivity approach, which takes into account the retention of
96 contaminants on pure mineral phases (Peynet, 2003) so as to predict the retention of a multi-
97 component assemblage. Wissocq *et al.* (2018) demonstrated its efficiency by predicting Sr retention
98 on a clayey sandstone without adjusting any of the parameters. Coupled with a transport model, this
99 multi-site ion exchanger model has proved efficient in predicting the reactive transport of key
100 elements (Na and Ca) in a pure phase and a soil using the same dataset in static and dynamic
101 conditions (Tertre *et al.*, 2013; Lu *et al.*, 2014).

102 This study aims at assessing the adequacy of the multi-site ion exchanger model coupled with a
103 transport model to simulate Sr transport in natural materials. In this framework, the material retention
104 properties were taken into account by the additivity approach based on their mineralogical
105 compositions in reactive phases. Furthermore, the performance of our modelling approach was also
106 compared against simulation results obtained by considering a K_d approach, which is commonly used
107 in environmental impact calculations. The sensitivity of the additivity approach was tested by
108 comparing Sr transport simulations carried out using data acquired by Latrille *et al.* (2017) with data
109 from new experiments in a column filled with a clayey sandstone (on the scale of the centimetre and
110 decimetre). For this purpose, the influence of i) the mineral abundance and ii) the reactive parameters
111 of these minerals, on the simulation results was evaluated. To do this, we used breakthrough curves
112 established on the basis of two different length scales columns. In order to explore the scope of this
113 approach, a Bt soil horizon (Latrille *et al.*, 2017, Lu *et al.*, 2014) was chosen with relative abundances
114 of illite and smectite differing to those found in the clayey sandstone. The simulations were performed
115 by coupling the advection-dispersion equation (ADE) with the multi-site ion exchanger model (MSIE)
116 using both the sorption property database for illite and smectite recently established in batch
117 experiments by Wissocq *et al.* (2018), and the specific experimental input parameters relative to each
118 operating condition.

119 **2. Materials and methods**

120 **2.1. Materials**

121 The first material was a clayey sandstone (CS), which has already been described in detail by Wissocq
122 *et al.* (2018). This clayey material was sampled from a depth of 31 metres in the Miocene geological
123 formation located at the Cadarache nuclear research centre (France). The rock sample was manually
124 crushed, air dried and sieved at 300 μm and 200 μm . The crushed bulk material was used to fill the
125 decimetre-scale column whereas a dried 300-200 μm fraction was selected for the centimetre-scale
126 column. The < 25 μm fraction was isolated from the raw CS by dispersion in water followed by
127 sieving to 25 μm . The mineralogical composition was determined by X-ray diffraction (XRD) on air-
128 dried powder for the bulk material and on air-dried deposits and deposits saturated with ethylene
129 glycol for the < 25 μm fraction. Identification of crystallised phases was performed using the ClayXR
130 software (Bouchet, 1992) and NEWMOD© software (Reynolds, 1985) was used for quantification.
131 The bulk material was mainly composed of quartz (75 wt%), clay minerals (20 wt%), carbonates
132 (2.5 wt%) and iron oxides (2.5 wt%). The XRD mineralogical quantification of the < 25 μm fraction
133 extracted from the raw material, revealed about 32 wt% of kaolinite, 20 wt% illite, 19 wt% smectite,
134 2 wt% chlorite, 17 wt% quartz and 10 wt% goethite, and no carbonates. Cation exchange capacity
135 (CEC) measurements on raw material, 300-200 μm and < 25 μm fractions were performed by K^+/Cs^+
136 cation exchange at pH 9. The resulting average value were respectively 0.112 ± 0.006 , 0.064 ± 0.020 ,
137 0.326 ± 0.020 eq/kg (Wissocq *et al.* (2017)). In our experimental chemical conditions (pH 6.5),
138 goethite remained positively charged (Hayes and Leckie, 1987; Villalobos and Leckie, 2000) and was
139 therefore considered as a non-reactive phase. Weighted by their relative abundance, chlorite and
140 kaolinite contributed to the material exchange capacity at a level equivalent to the CEC measurement
141 uncertainty (0.020 eq/kg, 6.3 % of material CEC). Consequently, smectite and illite were assumed to
142 govern the sorption processes. The reactive phases were therefore estimated equivalent to 27.7 % of
143 illite and 26.7 % of smectite in the < 25 μm fraction. Illite and smectite content in the raw soil and in
144 the 300-200 μm fraction are calculated by weighting their amount in the < 25 μm fraction to the CEC
145 of the corresponding material.

146 The second material investigated in this study was a Bt horizon of a Luvisol (Bt) previously described
147 and studied by Lamy *et al.* (2006) and Lu *et al.* (2014). The grain size distribution of this sandy clay
148 horizon was 70.7 wt% of sand, 8.9 wt% of silt and 20.4 wt% of clay, and it contained only 0.34 wt%
149 of organic matter. The < 2 mm air-dried soil was sieved at 300 μm and 250 μm to extract the material
150 used to fill the centimetre-scale column. The CEC was measured at 0.13 ± 0.01 eq/kg (Lu *et al.*, 2014)
151 and this fraction contained 18 wt% of clay. The clay minerals identified by XRD were kaolinite, illite,
152 and illite/smectite mixed layers. Clay minerals were quantified by modelling the X-ray diffraction
153 pattern in both air-dried and ethylene-glycol-solvated states, acquired on the clay size-fraction with the
154 Sybilla© software developed by Chevron™ (Aplin *et al.*, 2006). The assemblage consisted of discrete
155 illite (2.3 %), mixed-layers illite/smectite with 56.2 % IS (40/60) and 5.1% IS (29/71), and discrete
156 smectite (36.4 %). For the purpose of modelling, the mineralogical composition of the clay size-
157 fraction was therefore assimilated to 26.2 % of illite and 73.8 % of smectite.

158 **2.2 Solutions and analytical methods**All chemicals used were at least of analytical grade. CaCl_2
159 (VWR Chemical) salt solutions and the Sr solutions were prepared with a $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ salt (99.995%
160 trace metals basis, Sigma Aldrich) dissolved in Milli-Q water (Millipore®, 18.2 $\text{M}\Omega\cdot\text{cm}^2$). Chemical
161 analyses were carried out by ionic chromatography (standards Chem-Lab) for Ca and by inductively
162 coupled plasma mass spectrometry (ICP-MS) (Plasma CAL standards) for Sr. The measurement
163 uncertainties were estimated at 2 %.

164 Non-reactive tracers chosen for these experiments were ^2H ($^2\text{H}/^1\text{H} = 2000$), Cl^- in a CaCl_2 solution and
165 I^- in a CaI_2 solution (10^{-1} M). ^2H was mixed in a 10^{-2} M CaCl_2 solution. ^2H concentrations were
166 analysed with a deuterium analyser (Los Gatos Research Liquid-Water Stable Isotope Analyser). Cl^-
167 concentrations were measured by ionic chromatography. Cl^- and I^- concentrations were also directly
168 measured using an on-line electrical conductivity cell in the centimetre- and decimetre-column
169 devices.

170 The pH was measured using a combined glass pH electrode (Mettler Toledo) equipped with an
171 Ag/AgCl reference electrode. The electrode was calibrated with buffer solutions at pH 4, 7 and 12.

172 2.3 Column transport experiments

173 2.3.1 Experimental set-ups

174 Column transport experiments were performed on a centimetre- and a decimetre-scale column. Both
175 columns were placed in two adapted set-ups designed according to the same configuration shown in
176 Figure 1 and SI-1 (Latrille *et al.*, 2017).

177 This configuration included an HPLC pump (Hitachi LaChrom Elite L-2130) which regulated the flow
178 rate through the column. Two conductivity cells and pH electrodes (Amersham, Biosciences) were
179 placed on-line, arranged on each side of the column. Finally, a fraction collector (Omnicoil®, Lamda)
180 was used to receive and sequentially redistribute the outflowing solution in aliquots. Outflow tracer
181 concentrations were then analysed by ion chromatography (Cl⁻), electrical conductivity (CaI₂) and
182 ICP-MS (Sr).

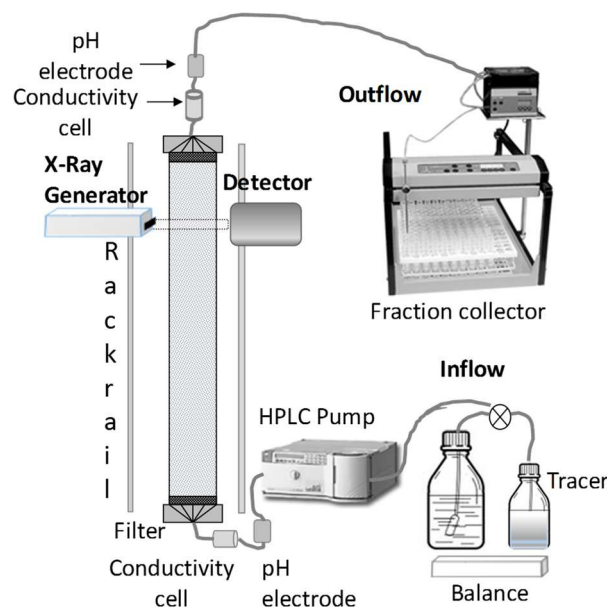
183 For the column experiments performed on a centimetre scale (SI-1), two glass chromatography
184 columns (Omnifit®) were filled by successively adding the material (respectively CS material in
185 column C1 and Bt material in column C3), compacted using a uniaxial press, to achieve a packed
186 length of 7.1 cm and a diameter 1 cm. Table 1 summarises the details of the packed columns according
187 to their geometric and physical features. The columns were saturated from the bottom with the
188 deaerated 10⁻² M CaCl₂ background solution and conditioned until equilibrium with this solution by
189 flowing ca. 500 pore volumes (v_p) through column C1 and 200 v_p through column C3.

Column	C1	C2	C3
Material	CS 300-200 μm	Bulk CS	Bt 300-250 μm
Length (cm)	7.1	35	7.1
Diameter (cm)	1	5	1
Porosity	0.362	0.326	0.518
Pore volume (cm ³)	2.02	225	2.85
Bulk density ^a (g.cm ⁻³)	1.69	1.79	1.65

190 ^a bulk density based on the dry solid mass introduced on filled volume ratio

191 Table 1: Geometric and physical properties of the three columns

192 At decimetre scale (Figure 1), the column experiments were performed by using the BEETI
 193 experimental device (Latrille and Cartalade, 2010). It was composed of a vertical polycarbonate
 194 column filled with bulk CS compacted in a uniaxial press, a controlled hydraulic circuit that enforced
 195 tracer migration, and a dichromatic X-ray spectrometer (DXS). Based on X-ray attenuation
 196 measurements, porous material properties (porosity, bulk density, water content and clay proportion)
 197 and resident concentrations of attenuating tracers can be quantified down the entire column (Figure 1).
 198 These measurements were used to evaluate the solid homogeneity and the water content in the
 199 compacted column. Moreover, depending on the calibration process, the clay proportion distribution
 200 along the column can also be estimated. Resident concentration profiles of the inert tracer CaI_2 were
 201 measured at eight specific locations down the column in order to determine the variability of
 202 dispersivity.



203

204 Figure 1. BEETI experimental set-up for transport column experiments at decimetre scale

205 X-ray attenuation measurements were performed using a dichromatic X-ray spectrometer (DXS)
 206 which combined an X-ray generator and a NaI detector (Latrille and Cartalade, 2010; Latrille and
 207 Néel, 2013). The X-ray beam was emitted in two energy ranges 20 – 40 keV and 50 – 75 keV. After
 208 crossing the column filled with the porous material, the NaI detector measured the beam count-rate.
 209 The source and detector were simultaneously moved up and down the column by a controlled rack rail

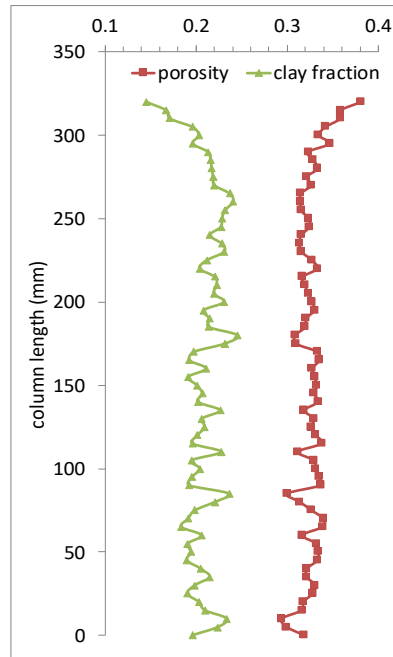
210 (Figure 1), and kept at specified locations ($0 < x < 32$ cm) during a set counting time (80 s). The X-ray
211 count-rate measured by the detector depended on the thickness and the type of the phases encountered
212 on the transmission path (fluid, bulk CS or clay and inert CaI_2 tracer), as well as on the counting time.
213 At each longitudinal location x on the column, the thickness of each phase was determined by solving
214 the Beer-Lambert's law (Eq. 1):

$$215 \quad I = I_0 \exp(-\sum_i \mu_i \rho_i z_i) \quad (\text{Eq. 1})$$

216 Where, I_0 is the count-rate emitted by the source; I is the count-rate detected per unit time for a given
217 X-ray energy range and transmitted throughout a column slice (5 mm x 20 mm); index i represents
218 each phase contained in the medium (clay or bulk CS, background solution, solute tracer); μ_i (m^2/kg) is
219 the mass attenuation coefficient, which depends on the phase composition and on the X-ray energy; ρ_i
220 (kg/m^3) is the density, and z_i (m) is the thickness of the phase. The mass attenuation coefficients of
221 clay, bulk CS, background solution (10^{-2} M CaCl_2) and tracer solution (CaI_2) were therefore
222 determined in this configuration using specific standards defined on the basis of the component
223 chemical composition. Calibration sequences were performed prior to experiments, as detailed in
224 Latrille and Néel (2013), to acquire the bulk CS standard and the clay standard. A specific calibration
225 allowed us to then determine the clay mineral attenuation by accounting for its chemical composition
226 acquired on the clay fraction extracted from bulk material. The clay mineral attenuation is
227 distinguished from that of sand in order to calculate the relative proportion of clay at each x position
228 along the column. The resident tracer concentration was calculable with the CaI_2 concentration
229 determined by converting the corrected count-rate of the low energy X-ray range using Eq. 1. During
230 the tracer experiment, at each selected x , measurements were repeated at a frequency of four to ten
231 minutes to yield the profiles of the resident tracer concentrations.

232 The porosity and clay proportion scanned along the column C2 are given in Figure 2. The porosity
233 appears to be relatively regular from the bottom up to 30 cm, with a value of 0.326 ± 0.015 . It then
234 increases to 0.38 for the last two centimetres. The clay fraction distribution followed the inverse trend
235 of porosity distribution, the material being less dense in the upper part of the column. The average clay

236 fraction was estimated at 0.208 ± 0.018 . Despite a lower compaction state limited to the upper part of
 237 the column, the standard deviation of the clay fraction and porosity remained small. Consequently, the
 238 material filling this column can be considered as sufficiently well compacted to assume a
 239 homogeneous column for the modelling approach.



240

241 Figure 2: Porosity and clay content distribution in the column C2: the clay fraction is expressed as the
 242 ratio between the clay surface mass ($\text{g}\cdot\text{cm}^{-2}$) and the sand surface mass ($\text{g}\cdot\text{cm}^{-2}$), considering $\rho_{\text{clay}} =$
 243 $\rho_{\text{sand}} \sim 2.65 \text{ g}\cdot\text{cm}^{-3}$. Porosity is calculated as $\theta = 1 - \frac{\rho_i}{\rho_{\text{CS}}}$ with ρ_i the solid density measured at x_i and ρ_{CS}
 244 the grain density of CS (ca. ρ_{sand})

245 Because Ca is the major exchangeable cation in the natural material, and in order to study competition
 246 between Sr and Ca only, all columns were then saturated and Ca-conditioned by injection in the
 247 upward direction of around $800 v_p$ of de-aerated $\text{CaCl}_2 10^{-2} \text{ M}$ solution (pH 6.5) at a constant flow rate
 248 ($6\text{-}10 \text{ cm}^3\cdot\text{h}^{-1}$). After saturation and conditioning, sorption sites of the clayey sandstone were mainly
 249 occupied by Ca^{2+} and H^+ .

250 2.3.2 Operating and experimental conditions

251 After the conditioning step, a de-aerated 10^{-2} M CaCl_2 background solution was injected at a constant
 252 flow rate through the column in an upward direction. As steady flow was achieved, a tracer solution
 253 was also injected at the same steady flow rate through the column inlet; this was done by either using
 254 an injection loop filled with a tracer solution (columns C1 and C3) or by switching to a tracer bottle
 255 (column C2). A loop volume of 20.8 cm^3 containing tracer solutions was injected into column C1 and
 256 C3, whereas a volume of 2500 cm^3 was injected into column C2. The outflowing solution was
 257 collected as aliquots every 10 or 15 minutes depending on the flow rate to be analysed. The flow rate
 258 was controlled by weighing the collected aliquots. Moreover, the flow rate in column C2 was also
 259 controlled by weighing the inflow bottle during the experimental time. The non-reactive tracers chosen
 260 for these experiments were ^2H ($^2\text{H}/^1\text{H} = 2000$), Cl^- and I^- (10^{-1} M) in the centimetre-scale columns and
 261 I^- in the decimetre-scale column. In case of the inert CaI_2 tracer, the pH and electrical conductivity
 262 were monitored at the column inlet and outlet and the tracer concentration was recorded. The initial
 263 tracer solution contained a mixture of $\text{ca.}10^{-4}$ M SrCl_2 and $\text{ca.}10^{-2}$ M CaCl_2 . The precise composition
 264 of the solutions used for each experiment was analytically controlled. No soluble natural Sr lixiviated
 265 from CS and Bt soil has been previously significantly measured by ICP/MS. Consequently, natural Sr
 266 was neglected in cation exchange process. The experimental parameters are summarised in Table 2.

Column	C1	C2	C3
Flow rate($\text{cm}^3 \cdot \text{h}^{-1}$) conservative tracer			
^2H	7.09 ± 0.68		7.21
	8.90 ± 0.36		8.43
	13.25 ± 0.29		
I^-	5.97 ± 0.20	51.93 ± 1.77	
		28.09 ± 1.79	
		27.28 ± 1.50	
		37.17 ± 1.60	
Cl^-	5.90 ± 0.34		
Flow rate($\text{cm}^3 \cdot \text{h}^{-1}$) Sr tracer	5.71 ± 0.18	19.86 ± 0.47	6.8 ± 0.22
	9.21 ± 0.28	27.21 ± 0.36	8.37 ± 0.49
	12.68 ± 0.21	38.24 ± 1.35	
	17.54 ± 0.31		
Dispersivity ^a (cm)	0.24	0.28	0.33
Injection volume (cm^3)	20.8	2500	20.8
Material CEC (eq/kg)	0.064 ± 0.003	0.112 ± 0.006	0.13 ± 0.01^b
% illite	5.84	10.14	4.73
%smectite	5.63	9.78	13.3

267 ^a Dispersivity determined from conservative tracer experiments

268 ^b Value provided by Lu *et al.* (2014)

269

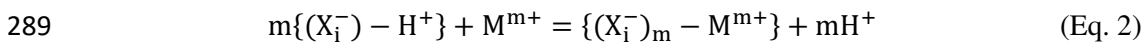
270 Table 2: Operating conditions for conservative tracers and Sr transport experiments

271 3. Reactive transport modelling

272 As mentioned above, the objectives of this study are to evaluate the additive approach so as to
273 simulate Sr transport in two-component materials. Thus, the experimental results were interpreted by
274 coupling the multi-site ion exchanger model with a transport model.

275 3.1. Sr sorption model: a multi-site ion exchanger model

276 The multi-site ion exchanger model (MSIE) used in this study has already been described in detail by
277 Motellier *et al.*, 2003; Jacquier *et al.*, 2004; Tertre *et al.*, 2009; Savoye *et al.*, 2012; Lu *et al.*, 2014,
278 Reinoso-Maset and Ly, 2014, Siroux *et al.*, 2017, 2018 and Wissocq *et al.*, 2018. In this model, the
279 ion-exchanger is composed of one or several negatively charged minerals. The latter typically have
280 their own negative sorption sites (called X_i^-) able to sorb cations. The ion exchange models initially
281 designed only allow the interpretation of ion exchange in terms of equilibrium and not reaction
282 mechanisms. Thus, they consider that all sites behave indistinctly in the same way. For clay minerals,
283 various adsorption sites result from isomorphic substitution of lattice cations and hydroxyl groups
284 sensitive to pH. The sorption sites are distinguished by their exchange capacities CE_i without any
285 structural assignment. Then, they are assumed as an intrinsic sorbent characteristic. Proton is the
286 reference competing cation, due to its small size and its occurrence in solution. In this approach, the
287 equilibrium expression below can be used to express the ion-exchange reaction related to the sorption
288 site X_i with cations (M^{m+}), including H^+ selected as the reference (Eq. 2):



290 with an associated apparent equilibrium constant (Eq. 3), the selectivity coefficient K^{i*} which includes
291 the unknown activity coefficient of the adsorbed species (see Wissocq *et al.*, 2018), as defined as
292 below:

$$293 \quad K_{mH^+/M^{m+}}^{i*} = \frac{[(X_i^-)_m - M^{m+}] [H^+]^m (\gamma_{H^+})^m}{[(X_i^-) - H^+]^m [M^{m+}] \gamma_{M^{m+}}} \quad (\text{Eq. 3})$$

294 where i is the type of sorption site, $[]$ is the concentration of species in solution (mol.L^{-1}) or sorbed
 295 species (mol.kg^{-1} of dry solid), and γ is the activity coefficient of the species in solution. In this study,
 296 the selectivity coefficient of $\text{Sr}^{2+}/\text{Ca}^{2+}$ exchange is calculated for each site by combining $\text{Ca}^{2+}/2\text{H}^+$ and
 297 $\text{Sr}^{2+}/2\text{H}^+$ exchanges defined as follows:

$$298 \quad K_{\text{Ca}^{2+}/2\text{H}^+}^{*i} = \frac{[\text{X}_i^- - \text{H}^+]^2 [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}}}{[(\text{X}_i^-)_2 - \text{Ca}^{2+}] [\text{H}^+]^2 \gamma_{\text{H}^+}^2} \quad (\text{Eq. 4})$$

$$299 \quad K_{\text{Sr}^{2+}/2\text{H}^+}^{*i} = \frac{[\text{X}_i^- - \text{H}^+]^2 [\text{Sr}^{2+}] \gamma_{\text{Sr}^{2+}}}{[(\text{X}_i^-)_2 - \text{Sr}^{2+}] [\text{H}^+]^2 \gamma_{\text{H}^+}^2} \quad (\text{Eq. 5})$$

300 The site capacity, CE_i , is the sum of adsorbed species concentration per site (Eq. 6) and the sum of site
 301 capacities has to be equal to the CEC.

$$302 \quad \text{CE}_i = 2[(\text{X}_i^-)_2 - \text{Sr}^{2+}] + 2[(\text{X}_i^-)_2 - \text{Ca}^{2+}] + [\text{X}_i^- - \text{H}^+] \quad (\text{Eq. 6})$$

303 Ca^{2+} selectivity coefficients are estimated for illite and smectite from Ca saturation curves as a
 304 function of pH. Saturation curves permit to quantify experimentally the exchange capacity of major
 305 sites, depending on their saturation evidenced by $\text{Ca}^{2+}/2\text{H}^+$ exchange. They express the adsorbed
 306 species concentration (mol/kg of solid) versus pH. Similarly, the minor site capacity is estimated on
 307 the Sr^{2+} adsorbed concentration versus Sr concentration curve. Reversible Sr adsorption reactions on
 308 Ca-illite and Ca-smectite have been verified experimentally by desorption experiments performed
 309 respecting the physico-chemical conditions of each adsorption experiments. This validates the
 310 adsorption/desorption reaction by cation exchange. Then, Sr^{2+} selectivity coefficients are estimated for
 311 illite and smectite from both pH and concentration sorption curves (Wissocq *et al.*, 2018). Equations 4,
 312 5 and 6 are adjusted to the experimental adsorption isotherms by non-linear regression using Excel
 313 solver. Uncertainties on estimated selectivity coefficient were calculated by using the SolverAid macro
 314 De Levie (2004).

315 To apply this model on a natural soil or sediment by using a component additivity approach, it is
 316 assumed that the site capacities of the mineralogical assemblage are the sum of the site capacities of
 317 each reactive mineral component weighted by their relative abundance in the assemblage. In the two

318 mineralogical systems selected for this study, illite and smectite mainly govern the sorption properties
 319 by ion-exchange processes. Consequently, the CEC of each material results on the contribution of illite
 320 and smectite and can be expressed by equation (7):

$$321 \quad \text{CEC}_{\text{material}} = \sum_i (x_{\text{illite}} * \text{CE}_{i_{\text{illite}}} + x_{\text{smectite}} * \text{CE}_{i_{\text{smectite}}}) \quad (\text{Eq. 7})$$

322 Where x_{illite} and x_{smectite} are the illite and smectite abundance in the material, and $\text{CE}_{i_{\text{illite}}}$ and
 323 $\text{CE}_{i_{\text{smectite}}}$ represent the illite and smectite X_i^- site capacity respectively.

324 The selectivity coefficients of the mineralogical assemblage, restricted to a illite and smectite mixture,
 325 combine those which were determined on each site of pure illite and smectite in the batch experiments
 326 by Wissocq *et al.* (2018); they are summarised in Table 3. This multi-site ion exchanger model was
 327 implemented in the PHREEQC code using the EXCHANGE data block. Corrected selectivity
 328 coefficients obtained from the multi-site ion exchanger formalism were converted into the Gaines-
 329 Thomas formalism used by PHREEQC.

	Sites	CE _i (eq/kg)	$\text{Log}K_{2H^+/Ca^{2+}}^{*i}$	$\text{Log}K_{2H^+/Sr^{2+}}^{*i}$	$\text{Log}K_{Sr^{2+}/Ca^{2+}}^{*i}$
Illite	Xh	0.001	-0.403 ± 1.977	1.700 ± 1.823	-2.103 ± 2.181
	Xa	0.131	-2.166 ± 0.073	-2.435 ± 0.64	0.269 ± 0.644
	Xb	0.043	-4.311 ± 0.216	-3.685 ± 0.367	-0.626 ± 0.626
	Xc	0.074	-11.745 ± 0.205	-11.25 ± 0.713	-0.495 ± 0.742
Smectite	Xe	0.387	-0.491 ± 0.486	-0.310 ± 0.028	-0.181 ± 0.485
	Xf	0.361	-4.352 ± 0.032	-4.475 ± 0.081	0.123 ± 0.087
	Xg	0.136	-14.837 ± 0.063	-14.778 ± 0.201	-0.059 ± 0.211

330

331 Table 3: Site names, capacities CE_i and selectivity coefficients $K_{2H^+/Ca^{2+}}^{*i}$, $K_{2H^+/Sr^{2+}}^{*i}$ and $K_{Sr^{2+}/Ca^{2+}}^{*i}$ for
 332 Ca-illite and Ca-smectite (data acquired in batch experiments by Wissocq *et al.*, 2018).

333 The differences between $K_{2H^+/Ca^{2+}}^{*i}$ and $K_{2H^+/Sr^{2+}}^{*i}$ on the major illite sites are small given their
 334 uncertainties, only a significant difference is noticeable on the Xh site (Table 3). Consequently, the Sr
 335 selectivity compared to this of Ca is expressed by the negative value of $\text{Log}K_{Sr^{2+}/Ca^{2+}}^{*i}$. By neglecting

336 this minor site X_h , the reactivity of Sr is comparable to that of Ca, as it is classically done by
 337 considering one site (Wahlberg *et al.* 1965). For smectite, the differences are not very significant
 338 according to the uncertainties of the selectivity coefficients. Therefore, the small difference in affinity
 339 between Sr and Ca is mainly due to the reactivity on X_h site of illite. This suggests that smectite plays
 340 a secondary role in the global reactivity of materials towards Sr.

341 **3.2. Reactive transport model**

342 Transport processes are computed via the advection-dispersion equation (ADE):

$$343 \quad R_{(x)}\theta_{(x)}\partial_t C(x, t) = -\partial_x(q_{D(x)}C(x, t) - \theta_{(x)}D_{(x)}\partial_x C(x, t)) \quad (\text{Eq. 8})$$

344 With q_D representing the Darcy flow velocity ($\text{cm}\cdot\text{h}^{-1}$), θ representing the porosity (-), C the solute
 345 concentration ($\text{mol}\cdot\text{L}^{-1}$), R the retardation factor, and D the apparent dispersion coefficient (cm^2/h).

346 The retardation factor can be calculated by the following equation:

$$347 \quad R = 1 + \frac{\rho K_d}{\theta} \quad (\text{Eq. 9})$$

348 With ρ representing the mass density of solid and K_d the distribution coefficient.

349 R may depend on location x in the column when ρ and θ are spatially variable. However, in this study,
 350 we checked that the porous media were packed homogeneously and the transport parameters were
 351 considered uniform with x . Consequently, chemical retention can be expressed by Eq. 9 with a
 352 constant K_d . The retardation factor of a conservative tracer is equal to 1. The apparent dispersion
 353 coefficient is therefore calculated as follows:

$$354 \quad D = \tau D_0 + \lambda v_{(x)} \quad (\text{Eq. 10})$$

355 With D_0 being the molecular diffusion coefficient in free water (cm^2/h), τ the tortuosity (-), λ the
 356 dispersivity (cm), and v the pore velocity defined as $v(x) = \frac{q_D}{\theta(x)}$ (cm/h). The tortuosity was calculated
 357 following the Millington and Quirk (1961) equation.

358 The HYDRUS-1D code was used to simulate the conservative tracer experiments and the reactive
359 transport experiment considering the constant K_d approach. Reactive tracer experiments were also
360 simulated using the HP1 multicomponent transport module of HYDRUS-1D (Jacques and Simunek,
361 2010). This module couples HYDRUS-1D with the PHREEQC version 4 biogeochemical code
362 (Parkhurst and Appelo, 1999).

363 The column geometry was modelled using a 1D Cartesian domain; columns C1 and C3 were
364 discretized with 100 cells and column C2 with 350 cells. The columns were considered as physically
365 and chemically uniform soil profiles. The water flux was used for the flow boundary condition. For
366 conservative transport experiments and Sr transport in C1 and C3, the flow conditions imposed a
367 dispersive hydrodynamic regime. For experiments in the C2 column, the slow flow velocities required
368 taking into account a diffusion process. At the inlet, a constant tracer flux was imposed during the
369 injection time and a zero-concentration gradient was selected as the outlet condition.

370 The input parameters measured experimentally were: dispersivity, porosity, flow velocity, solution
371 compositions, and clay minerals characteristics relative to each material (site capacities, corrected
372 selectivity coefficients). The molecular diffusion coefficients for Sr, Ca and Cl were $7.91 \cdot 10^{-6}$, $7.92 \cdot 10^{-6}$
373 and $2.03 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ respectively (Mills and Lobo, 1989).

374 Dispersivity was estimated by using: dedicated deuterated water (^2H), the CaCl_2 and CaI_2 transport
375 experiment at centimetre scale (Table 2), and the CaI_2 transport experiment only at decimetre scale by
376 using the Inverse module of HYDRUS-1D (Simunek *et al.*, 2008). The Levenburg–Marquardt
377 algorithm was used to fit the nonlinear equations to experimental data.

378 The illite and montmorillonite characteristic inputs for simulations performed with HP1 take into
379 account the respective site densities and selectivity coefficients weighted by the amount of every phase
380 in each column. The solution compositions were: 10^{-2} M CaCl_2 as the background solution, and 10^{-4} M
381 SrCl_2 and 10^{-2} M CaCl_2 for the tracer solution with a pH 7 (C3) or 6.5 (C1 and C2). The precise
382 measured concentrations in each solution were implemented in the code for each experiment.

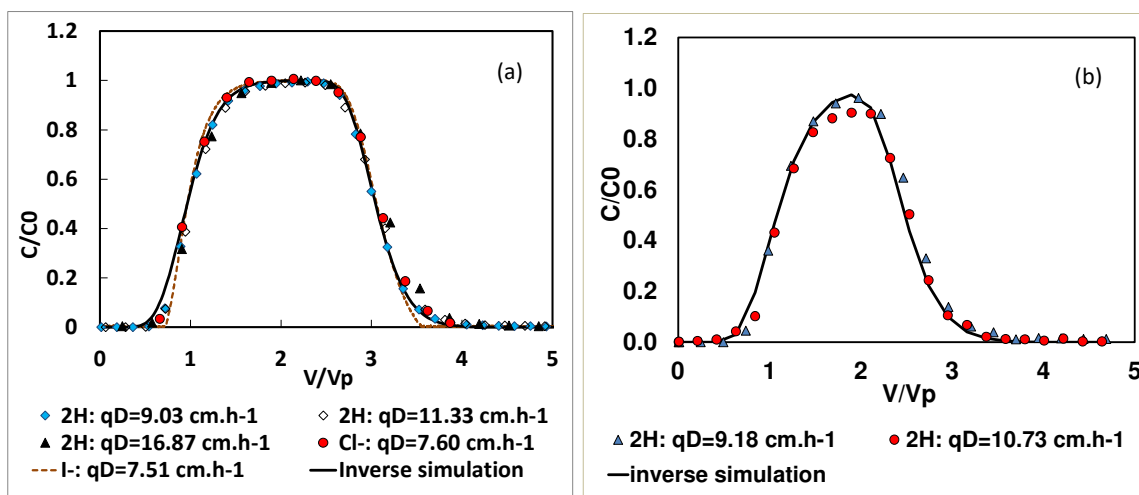
383 **4 Results and discussion**

384 **4.1 Conservative transport**

385 Non-reactive transport experiments were performed on the three columns before the Sr transport
 386 experiment to estimate the effective porosity available for transport and to determine the dispersivity
 387 independently from chemical retention.

388 **4.1.1 Conservative transport at centimetre scale**

389 The breakthrough curves (BTCs) of conservative, charged and neutral, tracers were acquired at
 390 varying flow rates in order to verify the flow independence towards preferential paths in the
 391 centimetre-scale columns C1 and C3. Figure 3 shows the BTCs as concentrations normalised to the
 392 injected concentration (C_0) versus volume of solution flowing through the column normalised to the
 393 column pore volume (v_p). In this way, it is possible to compare the results on a single plot. In the case
 394 of column C1, the BTCs resulting from the three conservative tracers overlap with one another (Figure
 395 3a). Anion exclusion process and dual porosity can therefore be excluded, and the accessible porosity
 396 can be assimilated to the total porosity. Similarly for column C3 (Figure 3b), the ^2H BTCs are
 397 superimposed for both flow velocity. This justifies considering the total porosity to describe transport
 398 in the centimetre-scale Bt soil column (C3) and the CS column (C1).

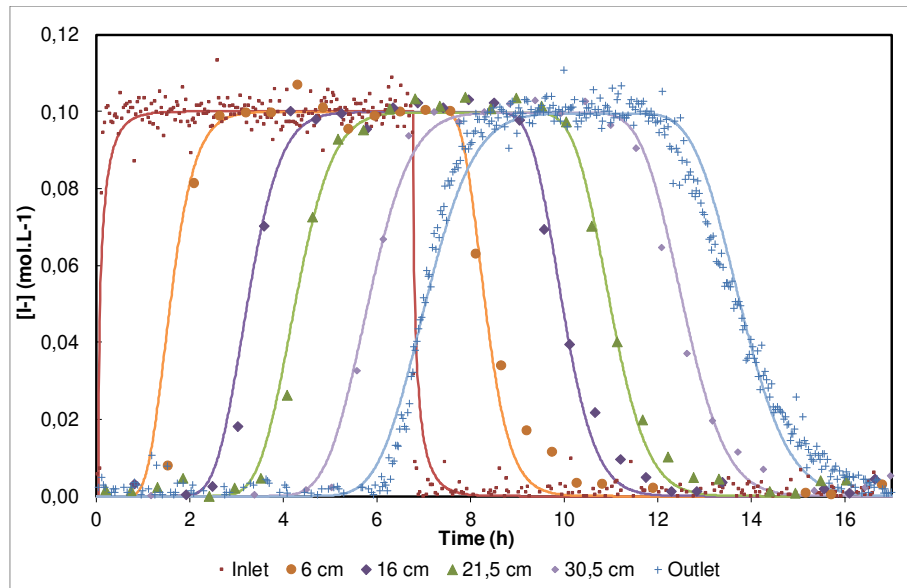


399
 400 Figure 3: Conservative transport in (a) column C1 and (b) column C3. The inverse simulation results
 401 are displayed with a black line.

402 The total porosity and experimental flow velocity were used in the inverse module of Hydrus-1D to
403 calculate the longitudinal dispersivity by way of adjustment with the experimental BTCs. The
404 dispersivity values obtained were 0.24 ± 0.01 and 0.33 ± 0.02 cm for column C1 and C3 respectively
405 ($R^2 = 0.998$).

406 **4.1.2 Conservative transport at decimetre scale**

407 Conservative transport experiments were performed with a CaI_2 tracer in column C2. Four tracer
408 injections were conducted at various flow velocities to acquire the CaI_2 concentration curves at eight
409 locations along the column and the BTCs at the column inlet and outlet (Figure 4). As in the
410 centimetre-scale columns, the total porosity and measured flow velocities were chosen as input
411 parameters for the inverse modelling on the complete set of resident concentration curves,
412 simultaneously. The dispersivity was then estimated by inverse modelling. Finally, the resulting
413 simulations show good agreement with the resident concentration curves. A slightly larger dispersion
414 can be observed in the curve at the outlet, which is attributable to extra-column artefacts due to the
415 presence of the filter with different transport properties. The average dispersivity was estimated at
416 0.323 ± 0.014 cm ($R^2 = 0.975$) in the decimetre-scale column considering the four experiments. By
417 overlapping the simulations with data, it becomes evident that a unique set of total porosity, flow rate
418 and dispersivity values are necessary to successfully simulate the resident concentration curves
419 simultaneously at the eight locations along column C2. These results support the assumption of a
420 continuous and homogeneously packed medium.



421

422 Figure 4: Experimental iodide concentration versus time recorded at 4 of the 8 locations ($x = 6$ cm, 16
 423 cm, 21.5 cm and 30.5 cm from the column bottom) along column C2; inlet (red) and outlet (blue)
 424 BTCs of the CaI_2 tracer. The solid lines indicate the simulation curves

425 4.2 Sr reactive transport in a clayey sand

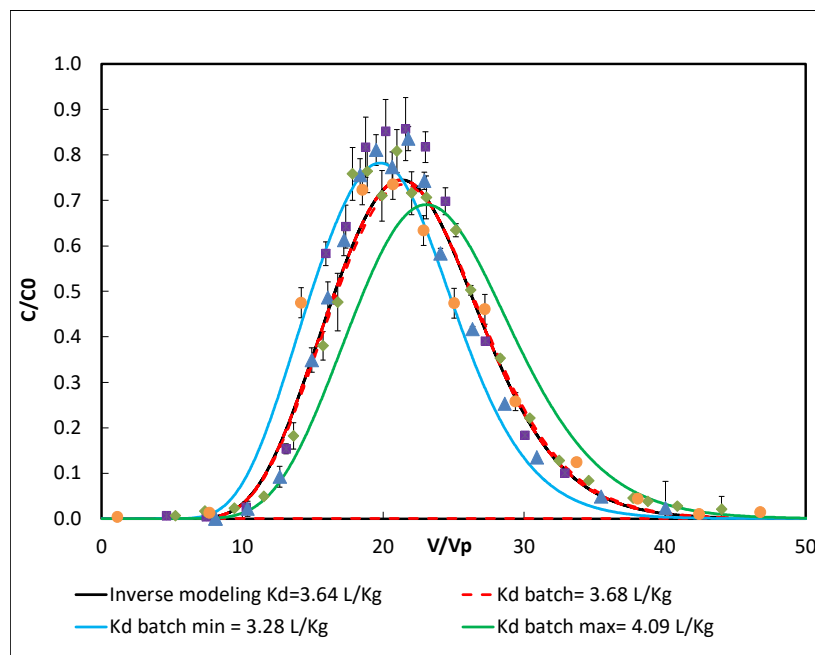
426 In order to compare the additivity approach with the commonly used K_d approach, simulations were
 427 carried out to interpret the experimental BTCs acquired on the CS material in the centimetre-scale
 428 column.

429 4.2.1 Tentative interpretation using a constant K_d

430 A retardation factor based on a constant K_d was tested to interpret Sr reactivity, specifically on the CS
 431 material. It is generally admitted that Sr is characterized by a linear isotherm (Wissocq et al., 2018,
 432 Rafferty et al., 1981). Wissocq *et al.* (2018) evidenced constant K_d values for Sr concentrations in
 433 solution up to 10^{-3} M in the case of Sr sorption on the CS material. Moreover, Szenknect *et al.* (2005)
 434 pointed out that, based on the flow-through reactor study, the K_d value was constant for Sr
 435 concentrations below 10^{-6} mol.L $^{-1}$. The isotherm described by the Langmuir model shows that a
 436 nonlinear, instantaneous and reversible sorption process controls Sr chemical reactivity. The Sr
 437 adsorption kinetics studied by Galambos *et al.* (2013) on clay mixtures evidenced an adsorption

438 equilibrium achieved in one minute. The Sr adsorption reaction can be considered faster than the
439 contact time in our transport experiments.

440 Four Sr BTCs were acquired on column C1 at varying flow velocities (Table 3). In Figure 5, the four
441 normalised BTCs overlap with each other, indicating that Sr transport is independent from the flow
442 rate in this context. The symmetric BTCs confirm the absence of a sorption kinetic effect on Sr
443 transport in these experimental conditions. Direct simulations were conducted using the K_d based on
444 batch sorption experiments (Wissocq *et al.*, 2018) and the K_d estimated from inverse modelling. Both
445 simulation curves reproduced the BTCs experimental shapes well. This indicates that Sr and
446 conservative tracers migrate through the material using the total porosity and the same transport
447 pathways (i.e. same dispersivity as for the tracers). The K_d fitted on the experimental data was 3.64
448 $L.Kg^{-1}$, similar to the mean K_d estimated by batch experiments ($3.68 \pm 0.4 L.Kg^{-1}$). Hence, site
449 availability in compacted media remains the same as in dispersed material. The simulated curves
450 overlap the data although the maximum intensity of the peak was not reached. Maximum and
451 minimum batch K_d values (3.28 and 4.09 $L.Kg^{-1}$ respectively) were also tested to estimate the K_d
452 variability on the simulation results. The experimental data lie well between the two curves, except for
453 a few points at the maximum concentration. When considering the minimum batch K_d , the simulated
454 curve recorded an earlier arrival and higher intensity than the curve obtained by inverse modelling.
455 Accordingly, the simulated curve with the maximum batch K_d revealed a lower intensity and a longer
456 residence time in the column. This confirms that K_d is a highly sensitive parameter when it comes to
457 simulating reactive transport in columns. Consequently, K_d determined in static conditions may be
458 used to describe Sr transport in the CS material if uncertainties can be tolerated (safety criteria for
459 instance).



460

461 Figure 5: Sr breakthrough curves acquired at different flow velocities in column C1 (data points:
 462 purple squares at 7.27 cm.h⁻¹, blue triangle at 11.73 cm.h⁻¹, green diamonds at 16.14 cm.h⁻¹ and orange
 463 circles at 22.33 cm.h⁻¹) and compared with direct modelling results obtained with the batch K_d (solid
 464 and dashed lines).

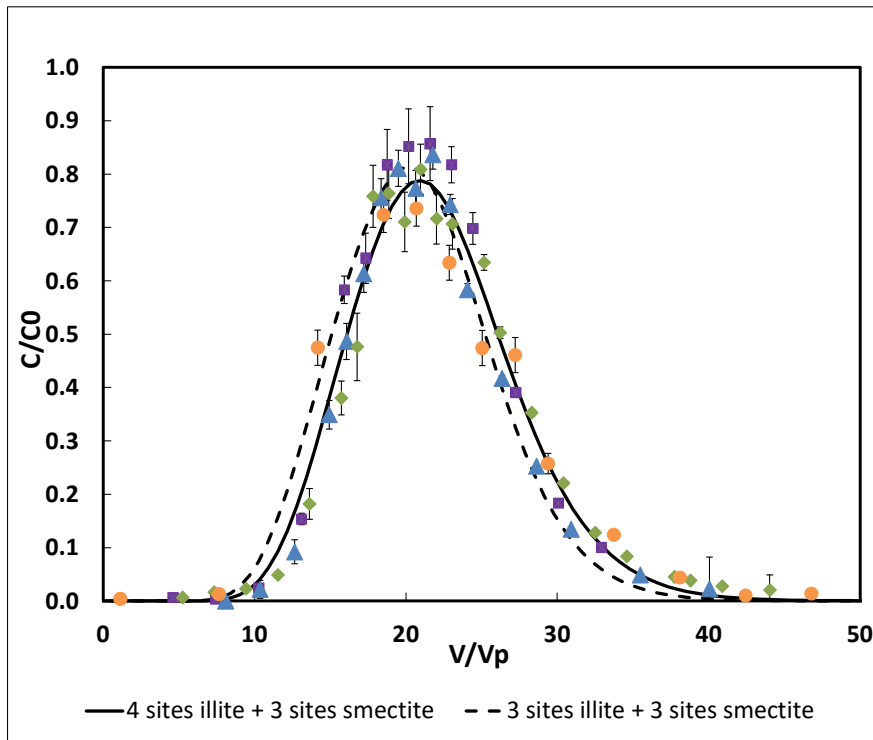
465 4.2.2 Additivity approach using a multi-site cation exchanger model

466 In order to explain the role of the different clay minerals in Sr transport, simulations were conducted
 467 using the additivity of the illite and smectite sorption properties and considering their relative
 468 abundances in porous media. Wissocq *et al.* (2018) successfully applied an additivity approach with a
 469 multi-site ion exchanger model (MSIE) based on a mixture of pure mineral phases (illite and smectite)
 470 to simulate Sr sorption on the CS material in batch experiments. This approach was therefore adopted
 471 in our work to simulate Sr transport through CS columns by coupling the MSIE model with the
 472 transport model (ADE). Transport parameters such as total porosity and dispersivity deduced from
 473 transport experiments using conservative tracers, were once again used for the simulations. The
 474 sorption properties of reactive phase-type (illite or smectite) and their abundance in the material are
 475 hence two determining parameters. In the centimetre scale column, the clayey sandstone was assumed
 476 to behave like a homogeneous media. Therefore, our approach first focuses on the mineral specificity.

477 For this purpose, it is generally admitted that three major sorption sites are necessary to describe the
478 illite and smectite exchange capacity (Nolin, 1997, Tertre *et al.*, 2009, Wissocq *et al.*, 2017). The
479 sorption properties of CS are assumed analogue to those of an illite and a smectite phases mixture.
480 However, Wissocq *et al.* (2018) obtained a better interpretation of the Sr sorption curves on pure illite
481 in batch experiments by considering a fourth site: a low-capacity and high-affinity site. Such low-
482 capacity sites are recognised to act principally at low concentration and represent less than 0.5 % of
483 the total exchange capacity of the clay mineral (Brouwer *et al.*, 1983; Baeyens and Bradbury, 1997;
484 Poinssot *et al.*, 1999; Missana *et al.*, 2004, 2008; Tertre *et al.*, 2009, Martin *et al.*, 2018, Latrille *et al.*,
485 2019). On another hand, Sr sorption isotherms on smectite did not reveal the contribution of this kind
486 of site. The significance of X_h site on Sr transport is therefore investigated by comparing simulation
487 including or not the X_h site.

488 Following the literature, the simulations were firstly carried out with the three major sites for illite (X_a ,
489 X_b , X_c) and smectite (X_e , X_f , X_g). Their specific features are given in Table 3. Simulations results
490 obtained on column C1 are shown in Figure 6. Compared with experimental BTCs, the simulated
491 curve indicates a slightly earlier arrival time in column C1 conserving the BTCs' rather symmetrical
492 shape and fit in the experimental data range.

493



494

495 Figure 6: Sr breakthrough curves acquired at different flow velocities (points) in column C1 compared
 496 with direct modelling results. Simulation considers three sites for smectite and three (dashed curve) or
 497 four sites for illite (solid black line).

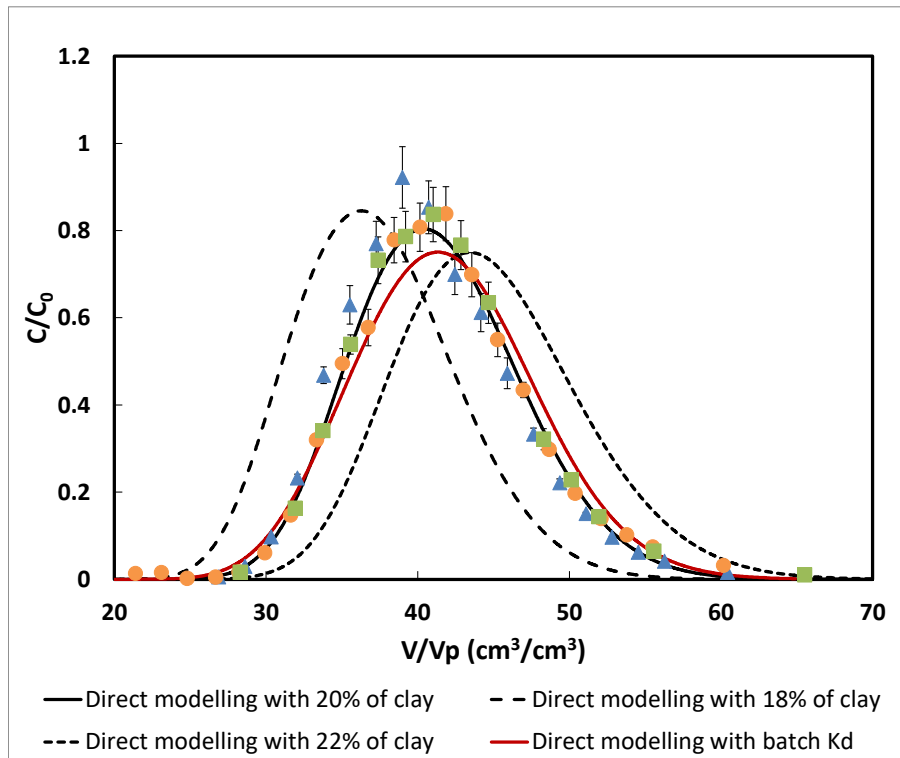
498 To assess the influence of the minor site in Sr transport, sensitivity calculations were performed
 499 including the fourth site (X_h) on illite (Figure 6). Again, the simulated curve was correctly
 500 superimposed on the Sr breakthrough curve in the CS column and reproduced the BTCs' shape,
 501 leading to a slightly better fit with respect to the maximal intensity and the short tail.

502 4.2.3 Sr reactive transport on a decimetre scale

503 The effect of the mineral abundance on the Sr transport results was tested on a larger column scale.
 504 Local stacking heterogeneities of small extent ($\pm 2\%$ of clay content) were recorded during the
 505 decimetre-column filling process (Figure 2). They express the clay fraction variability along the
 506 column. The grain-size fractionation uncertainty was around 2%. This implies a CEC variation in the
 507 filling material of $\pm 0.012 \text{ eq.kg}^{-1}$, which equates to a variability in sorption capacity (i.e. in number of
 508 site). Only the cumulative effect of variations in the clay fraction could be tested, given that Sr BTCs
 509 were only available at the column outlet. Simulations were therefore carried out at various averaged

510 clay fraction contents and then compared with the experimental data in order to test the sensitivity of
511 simulation outcomes to CEC variability.

512 Sr transport experiments were also performed on decimetre-scale columns (C2) filled with same
513 material and applying three different flow rates (Figure 7). The resulting BTCs are well superimposed,
514 as in the case of the centimetre-scale column. In the modelling, we considered that the porous medium
515 was homogeneous, even though small-scale heterogeneities were detected on the porosity and clay
516 proportion distribution (Figure 2). The measured flow rate, an averaged total porosity and dispersivity
517 were used as input parameters for simulations with the HP1 and HYDRUS 1D codes. As for column
518 C1, direct simulations with HYDRUS 1D were conducted using the K_d value based on batch sorption
519 experiments ($K_d = 6.44 \text{ L/kg}$), in Fig. 7. The simulated curve with K_d overlaps well with the data in
520 terms of arrival time and tail, but not so well with the maximal intensity of the peak. Then, MSIE
521 model was tested to improve the simulation outcomes. The C2 column reactivity was simulated using
522 the sorption parameters relative to illite and smectite, weighted by their relative abundance in the
523 material. The average clay proportion, estimated at ca. 20% by dichromatic X-ray spectrometry
524 (Figure 2), was taken into account to calculate the sorption parameters of the CS material by
525 considering three sites for smectite and four sites for illite with HP1. The simulation results in Figure 7
526 are in good agreement with the experimental Sr BTCs. As observed in the C1 column, there was no
527 visible broadening of the Sr tracer curve. Theoretically, upscaling the column size has no impact on
528 the Sr transport in the case of a homogeneous porous medium containing easily accessible sorption
529 sites.



530

531 Figure 7: Sr breakthrough curves acquired in the decimetre column (C2) at flow rates of 1.95 $\text{cm}\cdot\text{h}^{-1}$
 532 (orange circles), 1.39 $\text{cm}\cdot\text{h}^{-1}$ (green squares) and 1.01 $\text{cm}\cdot\text{h}^{-1}$ (blue triangles). The simulation results
 533 obtained with 22 % of clay (dotted line), 20 % of clay (solid line) and 18 % of clay (dashed line) by
 534 considering three sites for smectite and four sites for illite. Direct modelling results with the batch K_d
 535 value at 6.44 $\text{L}\cdot\text{Kg}^{-1}$ (red line).

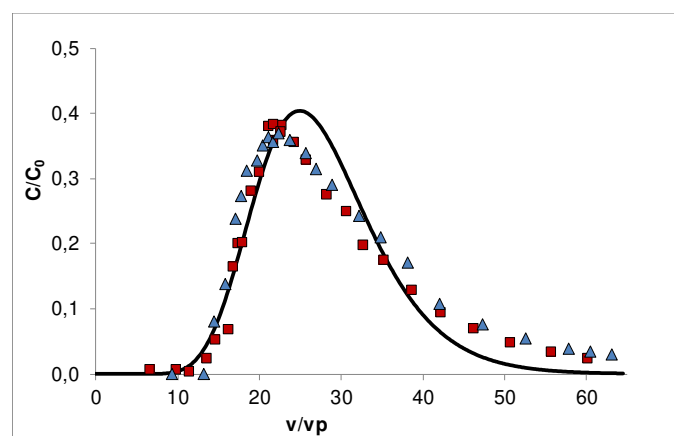
536 To assess the sensitivity of clay content variability, two additional simulations were performed
 537 considering 18% and 22% clay fractions (Figure 7) with HP1. The results indicate an earlier arrival
 538 and retardation of the front respectively, the whole curves being shifted in time. This small uncertainty
 539 was also sensitive for the arrival time of the front. Overall, the reactive transport model successfully
 540 predicts the Sr reactive transport through the clayey sandstone on a decimetre scale with transport
 541 parameters and chemical retention based on clay mineral contributions that have been determined
 542 experimentally. Independently from the relative abundance of the clay minerals, the clay fraction in
 543 each column appears to have a strong impact on the modelling outcome. This may explain the
 544 difficulty of simulating transport on a field scale where the heterogeneity of porous media can be more
 545 marked.

546 **4.3 Sr reactive transport in a Bt soil horizon**

547 In order to explore the scope of this approach, a similar study was replicated in another column filled
548 with a different material. Two Sr BTCs were acquired on the Bt soil horizon (column C3, Latrille *et*
549 *al.*, 2017) under operating conditions comparable to those of column C1. Expressed in normalised
550 concentration vs. normalised flowing volume over pore volume, the data obtained with two different
551 flow velocities once again overlapped each other (Figure 8) and show spreading curves with a larger
552 tail than the Sr BTCs for CS material (Figure 6). The BTCs indicate the same relative arrival time as
553 that of column C1, corresponding to the injection of ten pore volumes (v_p), but they differ in intensity
554 and tail length. The geometrical features of both columns are comparable and cannot be invoked to
555 explain the difference in the intensity of the BTCs. Nonetheless, both materials have a distinct CEC:
556 0.064 eq/kg in column C1 compared with 0.13 eq/kg in column C3. These CEC values represent the
557 respective illite and smectite contributions in each porous medium. As detailed in Table 2, the illite
558 and smectite contents are similar in the CS material, whereas the illite-to-smectite ratio is 0.35 in the
559 Bt soil.

560 **4.3.1 K_d and MSIE modelling results**

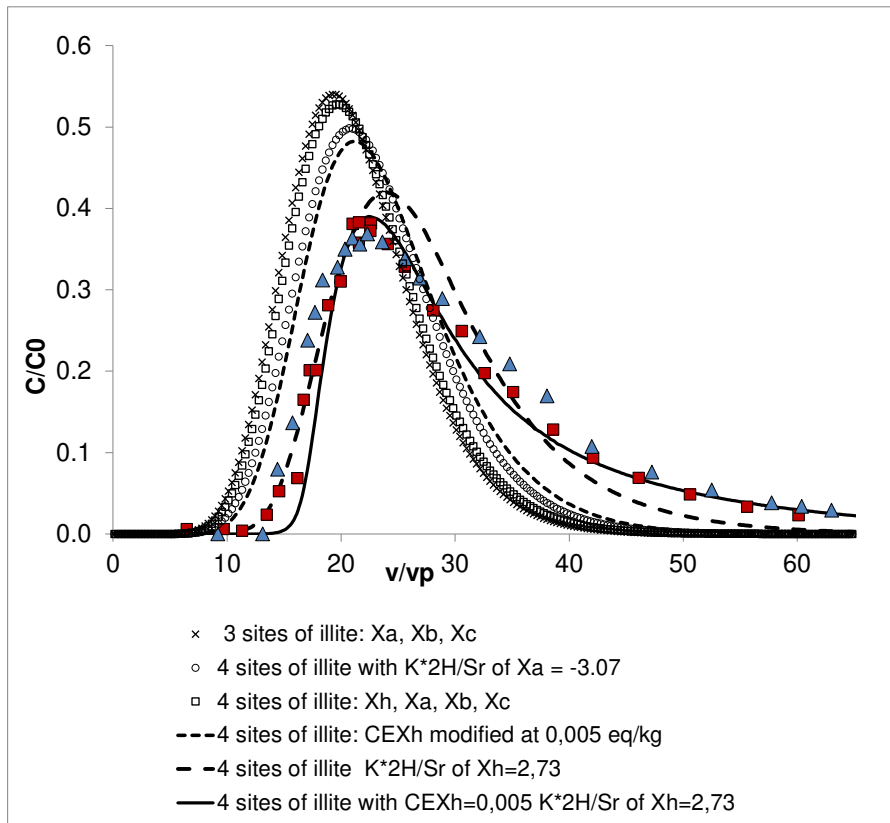
561 In Figure 8, the simulated curve (black solid line) was obtained by inverse modelling using the
562 experimental flow velocities, total porosity and dispersivity. The optimized K_d was found to be
563 7.5 L.Kg^{-1} ($R^2 = 0.949$). This curve does not fit the experimental data satisfactorily, showing a delayed
564 maximum value and a shorter tail.



565

566 Figure 8: Sr breakthrough curves in Bt soil in column C3 obtained with flow velocities of 8.66 cm.h⁻¹
567 (red squares) and 10.66 cm.h⁻¹ (blue triangles) and the dispersivity determined with a conservative
568 tracer at 0.33 cm. Inverse modelling simulation given a K_d optimised at 7.50 L.Kg⁻¹ (black line)

569 The presence of a tail in the BTC could be attributable to transport mechanisms (double porosity or
570 intra-particle diffusion) or chemical mechanisms (kinetic control of sorption/desorption, sorption site
571 parameters). We discarded transport based on the results obtained with conservative tracers (single
572 porosity), which show no such tail in the BTCs. Based on Galambos *et al.* (2013) and Siroux *et al.*
573 (2017), kinetic effects may also be excluded. Indeed, the results of these studies evidenced Sr sorption
574 achieved at shorter time (about seconds to hours, respectively) than the experimental time scale of our
575 study. In order to reduce the mismatch between simulation and experimental data and to explain the
576 dissymmetry of the BTC, additional simulations were therefore conducted to test the additivity
577 approach with the MSIE model. The simulation results (Figure 9) obtained with the parameters
578 described above (three or four sorption sites on Ca-illite) do not improve the mismatch. They show an
579 early arrival time, a larger intensity and a depleted tail (small squares and crosses in Figure 9). Further
580 sensitivity calculations on the variability of the clay fraction (in the uncertainty range, i.e. 17 % to
581 19.4 % of < 2 μm) indicate a significant shift in time towards an earlier breakthrough, a higher
582 maximal value, and symmetrical curves without any tail (SI2). As a result, the clay mineral amount
583 does not explain the late arrival and length of the tail. The relative abundance of illite and smectite was
584 also tested in the range of uncertainties observed by the CEC and XRD quantifications. Obviously, the
585 relative proportions of illite and smectite are so strongly constrained that the simulation results reveal
586 no significant enhancement (SI3).



587

588 Figure 9: Sr breakthrough curves acquired on the Bt soil (column C3) at two different flow velocities
 589 (blue and red points). The simulation considers the dispersivity determined with a conservative tracer
 590 at 0.33 cm and 18 % of clay content.

591 The sensitivity calculations were therefore extended to the parameters of sorption sites, focusing on
 592 the illite, to investigate their influence on Sr transport (considering the lower uncertainty on site
 593 selectivity coefficients of montmorillonite) (Table 3). The additional simulations involved the
 594 selectivity coefficient of the major site X_a for Ca-illite, which shows the largest uncertainty, as well as
 595 both the selectivity coefficient and exchange capacity, which are characteristics of the highest
 596 selective site X_h (Figure 9). When the selectivity coefficient of X_a is increased to the highest eligible
 597 value in the uncertainty range, $K^{*X_a}_{2H+/Sr2+} = -3.075$, the curve shows a slight shift in time and the
 598 intensity decreases, but not enough to match the experimental data (circles in Figure 9). A similar
 599 result was obtained when the CE_{X_h} value was increased to 0.005 eq/kg (dotted line in Figure 9). This
 600 shows that the major site selectivity coefficient and the CE_{X_h} values are not solely responsible for the
 601 large tail. When the simulation was conducted with an increased selectivity coefficient (representing

602 0.5σ), $K^{*Xh}_{2H+/Sr2+} = 2.73$ (Table 3), a slight improvement could be observed with a breakthrough time
603 closer to the observations, but still not matching the tail (dashed line in Figure 9). It is only by
604 increasing both the site capacity CE_{Xh} to 0.005 eq/kg and the selectivity coefficient from 0.5σ that the
605 simulated curve adequately superimposes with the experimental data (solid line in Figure 9). It appears
606 that the low-capacity and high-affinity sites of illite are key to widespread dispersion and tailing
607 during Sr transport in this soil column.

608 **4.3.2 Discussion on the Bt soil results**

609 The overall results suggest that Sr transport in these experiments occurs without limitation imposed by
610 site accessibility as suggested by the superimposed BTCs for the two flow velocities and the matching
611 arrival time of the simulated curve with the K_d approach. In the case of the Bt soil, the BTC curves
612 show a marked tail that is more difficult to capture with the models. As suggested by Bugai *et al.*,
613 (2012, 2020), a K_d approach is unable to predict the impact of chemical disturbances in case of mixed
614 cation competition. In the same way, Vulava *et al.* (2000) have already studied cation exchange
615 equilibria between the two major cations in a natural soil material by assimilating its retention
616 properties to one-site. They evidenced that classical one-site cation exchange equations do not
617 accurately describe cation exchange isotherms over a wide range of concentrations. In the same line,
618 Missana *et al.* (2008) recommended the description of radionuclide retention by a mechanistic
619 approach rather than distribution coefficient. Another hypothesis is that other minor reactive
620 components in the soil may influence the sorption of Sr.

621 The low soil organic matter content in this soil sample (0.34 %) and its small influence on Sr
622 adsorption (Samadfam *et al.*, 2000) lead us to disregard its contribution to Sr transport in the Bt soil
623 column.

624 Ferrihydrite is also frequently encountered in this type of soil. Hofmann *et al.* (2005) noticed
625 significant Sr adsorption on ferrihydrite at pH 7 (conditions close to our experiment pH~7), i.e. $4.5 \cdot 10^{-6}$
626 mol of Sr per gram of ferrihydrite. Considering the 2.27% of iron of the Bt soil horizon (Lamy *et al.*,
627 2006) attributed to iron oxide, it can be converted into 3.6 wt% of ferrihydrite (Lu, 2015). The ability

628 of this oxide to capture Sr in the column C3 (i.e.; 0.32 g of ferrihydrite) yields $1.46 \cdot 10^{-6}$ mol of Sr
629 compared with $5.2 \cdot 10^{-2}$ mol of Sr introduced, which is equivalent to a capture rate of 0.03 for one
630 thousand. Despite the negligible contribution of this minor mineral on Sr sorption, our modelling
631 approach will gain from being refined with available data that can be interpreted using our formalism.

632 The simulation results obtained by coupling the MSIE model with ADE therefore focused on the
633 sorption on clay minerals. These results reinforce the robustness of the additivity approach and the
634 parameters for the sedimentary rock (CS material), but are limited in the predictive capacity of the
635 modelling for the Bt soil. One of the sorption properties of the illite site needed to be adjusted in order
636 to simulate Sr transport behaviour in the soil. This highlights the difficulty of assimilating the sorption
637 properties of soil clay minerals (illite from the Bt soil) with respect to those of sedimentary clay
638 minerals (illite from the Puy region). Several explanations can be proposed for this behaviour. Firstly,
639 the exchange capacity of the low-capacity and high-affinity sites of illite (denoted here CE_{xh}) was
640 previously estimated by other authors with various trace elements (Poinssot *et al.*, 1999, Missana *et al.*
641 2008, 2014, Altmann *et al.*, 2015, Martin *et al.*, 2018, Latrille *et al.*, 2019). This value was found only
642 by adjusting the Sr sorption curves to 0.005 eq/kg in Wissocq *et al.*, (2017) and 0.002 eq/kg in
643 Altmann *et al.* (2014) and 0.0027 eq/kg in Latrille *et al.*, 2019 to model Zn sorption on Na-illite and
644 Ca-illite respectively. Lower values were also found by Poinssot *et al.* (1999), i.e., 0.0005 eq/kg for Cs
645 sorption on Na-illite, which is close to that determined by Missana *et al.* (2014) for Cs sorption on Ca-
646 illite (i.e. 0.0003 eq/kg) and Martin *et al.* (2018) for Tl sorption on Ca-illite (i.e. 0.00025 eq/kg). Such
647 differences evidence the difficulty of constraining this low-capacity site with good accuracy.
648 Secondly, clay minerals in soil are commonly encountered in a wide range of particle sizes from
649 50 nm to 5 μ m (Hubert et al, 2012), i.e. a finer size than in sedimentary clay. Inherent to their high
650 specific surface and CEC (Reinholdt *et al.*, 2013), the finest particles have a larger ability to adsorb. In
651 this respect, we know that illite can be weathered or micro-divided due to pedogenic processes. In soil
652 environments, illite may contain a larger amount of low-capacity and high-selectivity sites (commonly
653 referred to as frayed edge sites) attributed to particle edges (Sawhney, 1972), and fewer sites located
654 on the basal surface and in the interlayer space. As a result, the reactivity of soil illites is enhanced

655 compared with sedimentary clay mineral like illite du Puy and illite contained in the CS material. This
656 assumption is consistent with the simulation results obtained by adjusting the capacity and affinity of
657 the fourth site on illite in the Bt soil.

658 **4. Conclusion**

659 In this study, we coupled the multi-site ion exchanger model (MSIE) based on a component additive
660 approach, with the advection-dispersion equation (ADE). We did this to assess how well it would be
661 able to simulate Sr reactive transport in two materials, a clayey sandstone and a Bt soil. Non-reactive
662 transport experiments performed with conservative tracers were first used to determine the transport
663 parameters, such as porosity and dispersivity. This reactive transport model was tested to simulate Sr
664 transport data acquired in a centimetre- and a decimetre-scale column. Although the K_d approach is
665 able to describe Sr sorption in static conditions (batch) and remains applicable in dynamic conditions
666 for the CS material (given the K_d value uncertainty), it is less efficient at reproducing experimental
667 data in the column for the Bt soil. Using the additivity approach and considering components
668 described by multi-sorption sites, the reactive transport of Sr in the clayey material CS can be
669 successfully predicted on a centimetre- and decimetre-scale without adjusting any of the parameters
670 (those measured in batch experiments). Sensitivity parameter tests revealed the noticeable impact of
671 the clay content and mineralogical characteristics on Sr transport simulations. These results highlight
672 the influence of illite on Sr BTC spreading, especially through its low-capacity and high-selectivity
673 site. This implies having access to a robust and extensive database established with reference minerals.
674 The results of this study confirm the robustness of our database when clay minerals have reactivity
675 properties similar to those of the reference minerals employed to build the database. In the case of the
676 Bt soil containing weathered mineral or evolved minerals, this database appears more limited and
677 needs to be perfected. The choice of modelling approach is therefore crucial when modelling and
678 predicting the behaviour of Sr transport in porous media. To consolidate the robustness of this
679 approach, it would be relevant to test it on heterogeneous media and to acquire retention properties of
680 weathered illite. Moreover, a systematic sensitivity analysis would also be interesting, potentially
681 unraveling a combined effect of different parameters.

682

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