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1	Reactive transport of strontium in two laboratory-scale columns: experiments and modelling
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10 *Keywords:* illite; smectite; strontium; reactive transport; ion exchange model

#### 11 Abstract

To support the environmental monitoring of nuclear sites, reactive transport models used to predict the 12 13 migration of contaminants such as strontium-90 (<sup>90</sup>Sr) in soils, sediments and aquifers are developed, 14 continuously tested and improved. This study aims at assessing the adequacy of the multi-site ion exchanger model (MSIE) based on a component "additivity approach" and coupled to the advection-15 16 dispersion equation (ADE) to simulate Sr transport in a clayey sandstone and a Bt soil horizon. We have also compared the performance of the modelling approach with simulation results obtained by 17 considering a K<sub>d</sub> approach (constant K<sub>d</sub>). Transport experiments were performed in centimetre- and 18 decimetre-scale columns in order to test the model sensitivities to the mineral abundance and the 19 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 experimental data in the case of the clayey sandstone when a certain amount of uncertainty is 24 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<sub>d</sub> 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 breakthrough curve, especially through its low-capacity and high-selectivity site. This implies having 31 32 access to a robust and extensive set of retention parameters acquired on reference minerals. In this study, the results obtained for the clayey sandstone confirm the robustness of our selected parameters 33 when clay minerals have similar reactivity levels as the reference minerals. This set of parameters 34 appears more limited in the case of the Bt soil containing weathered or evolved minerals. The choice 35 36 of modelling approach is therefore crucial for accurately modelling and predicting Sr transport behaviour in porous media, as is the representativeness of the minerals in the database. 37

38

#### 39 **1. Introduction**

40 <sup>90</sup>Sr is a product of uranium and plutonium fission generated in nuclear reactors and is one of the most abundant radioisotopes released into the environment because of weapons testing and nuclear 41 accidents (Kashparov et al. 2003). 90Sr (29 years half-life) is highly soluble and its sorption is strongly 42 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 greater depths. To support the environmental monitoring of nuclear sites, reactive transport models are 45 being developed to simulate the migration of contaminants such as <sup>90</sup>Sr in soils, sediments and 46 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 approaches. The sorption of contaminants has been modelled using simple, empirical retention models 53 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, 2010). However, such models provide specific and contextual parameters determined in precise 56 physicochemical conditions and therefore often fail to be predictive. For instance, Szenknect et al. 57 (2008) simulated Sr transport through a sandy soil column using a constant K<sub>d</sub>. These authors 58 59 highlighted the fact that Sr reactive transport deviates from classical reactive transport including a retardation factor, although Sr sorption was described as instantaneous, reversible and with a linear 60 reaction at trace concentration (Szenknect et al. 2005, Wissocq et al., 2018). Moreover, to simulate Sr 61 transport in field experiments through aeolian sand sampled from the Chernobyl site, Bugai et al. 62 63 (2012) found  $K_d$  values to be the most sensitive parameter in the model. In this study, the  $K_d$  values obtained by laboratory batch tests (Szenknect et al., 2005) had to be adjusted to match the simulation 64 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 parameters acquired in dispersed multicomponent media (i.e. batch experiments) to compacted media 78 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 associated to specific sorption sites (Poinssot et al., 1999, Missana et al., 2008, 2014, Altmann et al., 84 2015, Wissocq et al., 2017, Martin et al., 2018, Latrille et al., 2019, Tournassat et al., 2013), which 85 86 are usually not differentiated in such a retention approach. By using a generalised composite approach, Voegelin et al. (2000) and Vulava et al. (2002) were able to use the same dataset in static and dynamic 87 conditions to reproduce the transport of major elements (Ca, Mg and Na) and Sr in trace form 88 (Szenknect et al., 2008). However, this approach is restricted to a specific context, which constrains its 89 90 extrapolation to other multi-component materials and extended environmental conditions. Vulava et al. (2002) compared various exchange models and evidenced a significant improvement was gained 91 92 with a multi-site cation exchange model to predict the transport behaviour of the major cations. Lu et

al. (2014) also made this assessment and used such a model to cover a large range of chemical 93 conditions without any adjustable parameters. Another approach is to resort to a multi-site ion 94 95 exchanger model using a component additivity approach, which takes into account the retention of contaminants on pure mineral phases (Peynet, 2003) so as to predict the retention of a multi-96 component assemblage. Wissocq et al. (2018) demonstrated its efficiency by predicting Sr retention 97 on a clayey sandstone without adjusting any of the parameters. Coupled with a transport model, this 98 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<sub>d</sub> approach, which is commonly used 107 in environmental impact calculations. The sensitivity of the additivity approach was tested by comparing Sr transport simulations carried out using data acquired by Latrille et al. (2017) with data 108 109 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 of these minerals, on the simulation results was evaluated. To do this, we used breakthrough curves 111 112 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

#### 2.1. Materials

121 The first material was a clayey sandstone (CS), which has already been described in detail by Wissocq et al. (2018). This clayey material was sampled from a depth of 31 metres in the Miocene geological 122 123 formation located at the Cadarache nuclear research centre (France). The rock sample was manually 124 crushed, air dried and sieved at  $300 \,\mu\text{m}$  and  $200 \,\mu\text{m}$ . 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 column. The  $< 25 \,\mu$ m fraction was isolated from the raw CS by dispersion in water followed by 126 127 sieving to 25 µm. The mineralogical composition was determined by X-ray diffraction (XRD) on airdried powder for the bulk material and on air-dried deposits and deposits saturated with ethylene 128 129 glycol for the  $< 25 \,\mu$ m fraction. Identification of crystallised phases was performed using the ClayXR software (Bouchet, 1992) and NEWMOD© software (Reynolds, 1985) was used for quantification. 130 131 The bulk material was mainly composed of quartz (75 wt%), clay minerals (20 wt%), carbonates (2.5 wt%) and iron oxides (2.5 wt%). The XRD mineralogical quantification of the < 25 µm fraction 132 133 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 (CEC) measurements on raw material, 300-200  $\mu$ m and < 25  $\mu$ m fractions were performed by K<sup>+</sup>/Cs<sup>+</sup> 135 136 cation exchange at pH 9. The resulting average value were respectively  $0.112 \pm 0.006$ ,  $0.064 \pm 0.020$ ,  $0.326 \pm 0.020$  eq/kg (Wissocq et al. (2017)). In our experimental chemical conditions (pH 6.5), 137 goethite remained positively charged (Hayes and Leckie, 1987; Villalobos and Leckie, 2000) and was 138 139 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 uncertainty (0.020 eq/kg, 6.3 % of material CEC). Consequently, smectite and illite were assumed to 141 142 govern the sorption processes. The reactive phases were therefore estimated equivalent to 27.7 % of illite and 26.7 % of smectite in the  $< 25 \,\mu m$  fraction. Illite and smectite content in the raw soil and in 143 144 the 300-200  $\mu$ m fraction are calculated by weighting their amount in the < 25  $\mu$ m fraction to the CEC 145 of the corresponding material.

The second material investigated in this study was a Bt horizon of a Luvisol (Bt) previously described 146 147 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% of organic matter. The < 2 mm air-dried soil was sieved at 300  $\mu$ m and 250  $\mu$ m to extract the material 149 used to fill the centimetre-scale column. The CEC was measured at  $0.13 \pm 0.01$  eq/kg (Lu *et al.*, 2014) 150 and this fraction contained 18 wt% of clay. The clay minerals identified by XRD were kaolinite, illite, 151 152 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<sup>©</sup> software developed by Chevron<sup>TM</sup> (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 smectite (36.4 %). For the purpose of modelling, the mineralogical composition of the clay size-156 fraction was therefore assimilated to 26.2 % of illite and 73.8 % of smectite. 157

2.2 Solutions and analytical methodsAll chemicals used were at least of analytical grade. CaCl<sub>2</sub>
(VWR Chemical) salt solutions and the Sr solutions were prepared with a SrCl<sub>2</sub> 6H<sub>2</sub>O salt (99.995%
trace metals basis, Sigma Aldrich) dissolved in Milli-Q water (Millipore®, 18.2 MΩ.cm<sup>2</sup>). Chemical
analyses were carried out by ionic chromatography (standards Chem-Lab) for Ca and by inductively
coupled plasma mass spectrometry (ICP-MS) (Plasma CAL standards) for Sr. The measurement
uncertainties were estimated at 2 %.

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

The pH was measured using a combined glass pH electrode (Mettler Toledo) equipped with anAg/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).

This configuration included an HPLC pump (Hitachi LaChrom Elite L-2130) which regulated the flow rate through the column. Two conductivity cells and pH electrodes (Amersham, Biosciences) were placed on-line, arranged on each side of the column. Finally, a fraction collector (Omnicoll<sup>®</sup>, Lamda) was used to receive and sequentially redistribute the outflowing solution in aliquots. Outflow tracer concentrations were then analysed by ion chromatography (Cl<sup>-</sup>), electrical conductivity (CaI<sub>2</sub>) and ICP-MS (Sr).

For the column experiments performed on a centimetre scale (SI-1), two glass chromatography columns (Omnifit®) were filled by successively adding the material (respectively CS material in column C1 and Bt material in column C3), compacted using a uniaxial press, to achieve a packed length of 7.1 cm and a diameter 1 cm. Table 1 summarises the details of the packed columns according to their geometric and physical features. The columns were saturated from the bottom with the deaerated  $10^{-2}$  M CaCl<sub>2</sub> background solution and conditioned until equilibrium with this solution by flowing ca. 500 pore volumes (v<sub>p</sub>) through column C1 and 200 v<sub>p</sub> 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 <sup>3</sup> )	2.02	225	2.85
Bulk density <sup>a</sup> (g.cm <sup>-3</sup> )	1.69	1.79	1.65

<sup>a</sup> bulk density based on the dry solid mass introduced on filled volume ratio

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

At decimetre scale (Figure 1), the column experiments were performed by using the BEETI 192 experimental device (Latrille and Cartalade, 2010). It was composed of a vertical polycarbonate 193 194 column filled with bulk CS compacted in a uniaxial press, a controlled hydraulic circuit that enforced tracer migration, and a dichromatic X-ray spectrometer (DXS). Based on X-ray attenuation 195 measurements, porous material properties (porosity, bulk density, water content and clay proportion) 196 197 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

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

X-ray attenuation measurements were performed using a dichromatic X-ray spectrometer (DXS)
which combined an X-ray generator and a NaI detector (Latrille and Cartalade, 2010; Latrille and
Néel, 2013). The X-ray beam was emitted in two energy ranges 20 – 40 keV and 50 – 75 keV. After
crossing the column filled with the porous material, the NaI detector measured the beam count-rate.
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 ( $0 \le x \le 32$  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<sub>2</sub> 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 
$$I = I_0 exp(-\sum_i \mu_i \rho_i z_i)$$
(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);  $\mu_i$  (m<sup>2</sup>/kg) is 219 the mass attenuation coefficient, which depends on the phase composition and on the X-ray energy;  $\rho_i$ 220  $(kg/m^3)$  is the density, and  $z_i$  (m) is the thickness of the phase. The mass attenuation coefficients of clay, bulk CS, background solution (10<sup>-2</sup> M CaCl<sub>2</sub>) and tracer solution (CaI<sub>2</sub>) were therefore 221 222 determined in this configuration using specific standards defined on the basis of the component chemical composition. Calibration sequences were performed prior to experiments, as detailed in 223 Latrille and Néel (2013), to acquire the bulk CS standard and the clay standard. A specific calibration 224 allowed us to then determine the clay mineral attenuation by accounting for its chemical composition 225 acquired on the clay fraction extracted from bulk material. The clay mineral attenuation is 226 227 distinguished from that of sand in order to calculate the relative proportion of clay at each x position along the column. The resident tracer concentration was calculable with the CaI<sub>2</sub> concentration 228 determined by converting the corrected count-rate of the low energy X-ray range using Eq. 1. During 229 230 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.

The porosity and clay proportion scanned along the column C2 are given in Figure 2. The porosity appears to be relatively regular from the bottom up to 30 cm, with a value of  $0.326 \pm 0.015$ . It then increases to 0.38 for the last two centimetres. The clay fraction distribution followed the inverse trend of porosity distribution, the material being less dense in the upper part of the column. The average clay fraction was estimated at  $0.208 \pm 0.018$ . Despite a lower compaction state limited to the upper part of the column, the standard deviation of the clay fraction and porosity remained small. Consequently, the material filling this column can be considered as sufficiently well compacted to assume a homogeneous column for the modelling approach.



240

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

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

250 2.3.2 Operating and experimental conditions

251	After the conditioning step, a de-aerated 10 <sup>-2</sup> M CaCl <sub>2</sub> 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 <sup>3</sup> containing tracer solutions was injected into column C1 and
256	C3, whereas a volume of 2500 cm <sup>3</sup> 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 ${}^{2}H$ ( ${}^{2}H/{}^{1}H$ = 2000), Cl <sup>-</sup> and I <sup>-</sup> (10 <sup>-1</sup> M) in the centimetre-scale columns and
261	I in the decimetre-scale column. In case of the inert CaI <sub>2</sub> 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 ca.10 <sup>-4</sup> M SrCl <sub>2</sub> and ca.10 <sup>-2</sup> M CaCl <sub>2</sub> . 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(cm <sup>3</sup> .h <sup>-1</sup> ) conservative tracer			
$^{2}H$	$7.09 \pm 0.68$		7.21
	$8.90 \pm 0.36$		8.43
	$13.25 \pm 0.29$		
I-	$5.97 \pm 0.20$	$51.93 \pm 1.77$	
		$28.09 \pm 1.79$	
		$27.28 \pm 1.50$	
		$37.17 \pm 1.60$	
Cl	$5.90 \pm 0.34$		
Flow rate(cm <sup>3</sup> .h <sup>-1</sup> ) Sr tracer	$5.71 \pm 0.18$	$19.86 \pm 0.47$	$6.8 \pm 0.22$
	$9.21 \pm 0.28$	$27.21 \pm 0.36$	$8.37 \pm 0.49$
	$12.68 \pm 0.21$	$38.24 \pm 1.35$	
	$17.54 \pm 0.31$		
Dispersivity <sup>a</sup> (cm)	0.24	0.28	0.33
Injection volume (cm <sup>3</sup> )	20.8	2500	20.8
Material CEC (eq/kg)	$0.064 \pm 0.003$	$0.112 \pm 0.006$	$0.13 \pm 0.01^{b}$
% illite	5.84	10.14	4.73
%smectite	5.63	9.78	13.3

<sup>&</sup>lt;sup>a</sup> Dispersivity determined from conservative tracer experiments

268 269 <sup>b</sup> Value provided by Lu *et al.* (2014)

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

271

# 3. Reactive transport modelling

As mentioned above, the objectives of this study are to evaluate the additive approach so as to
simulate Sr transport in two-component materials. Thus, the experimental results were interpreted by
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 their own negative sorption sites (called Xi) able to sorb cations. The ion exchange models initially 280 281 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 sensitive to pH. The sorption sites are distinguished by their exchange capacities CE<sub>i</sub> without any 284 structural assignment. Then, they are assumed as an intrinsic sorbent characteristic. Proton is the 285 286 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 site  $X_i$  with cations (M<sup>m+</sup>), including H<sup>+</sup> selected as the reference (Eq. 2): 288

289 
$$m\{(X_i^-) - H^+\} + M^{m+} = \{(X_i^-)_m - M^{m+}\} + mH^+$$
 (Eq. 2)

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

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

where *i* is the type of sorption site, [] is the concentration of species in solution (mol.L<sup>-1</sup>) or sorbed species (mol.kg<sup>-1</sup> of dry solid), and  $\gamma$  is the activity coefficient of the species in solution. In this study, the selectivity coefficient of Sr<sup>2+</sup>/Ca<sup>2+</sup> exchange is calculated for each site by combining Ca<sup>2+</sup>/2H<sup>+</sup> and Sr<sup>2+</sup>/2H<sup>+</sup> exchanges defined as follows:

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

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

300 The site capacity, CEi, is the sum of adsorbed species concentration per site (Eq. 6) and the sum of site301 capacities has to be equal to the CEC.

302 
$$CE_i = 2[(X_i^-)_2 - Sr^{2+}] + 2[(X_i^-)_2 - Ca^{2+}] + [X_i^- - H^+]$$
 (Eq. 6)

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

To apply this model on a natural soil or sediment by using a component additivity approach, it is assumed that the site capacities of the mineralogical assemblage are the sum of the site capacities of each reactive mineral component weighted by their relative abundance in the assemblage. In the two mineralogical systems selected for this study, illite and smectite mainly govern the sorption properties
by ion-exchange processes. Consequently, the CEC of each material results on the contribution of illite
and smectite and can be expressed by equation (7):

321 
$$CEC_{material} = \sum_{i} (x_{illite} * CE_{i_{illite}} + x_{smectite} * CE_{i_{smectite}})$$
 (Eq. 7)

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

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

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

330

Table 3: Site names, capacities  $CE_i$  and selectivity coefficients  $K^{*i}_{2H+/Ca2+}$ ,  $K^{*i}_{2H+/Sr2+}$  and  $K^{*i}_{Sr2+/Ca2+}$  for Ca-illite and Ca-smectite (data acquired in batch experiments by Wissocq *et al.*, 2018).

The differences between  $K_{2H^+/Ca^{2+}}^{*i}$  and  $K_{2H^+/Sr^{2+}}^{*i}$  on the major illite sites are small given their uncertainties, only a significant difference is noticeable on the Xh site (Table 3). Consequently, the Sr selectivity compared to this of Ca is expressed by the negative value of  $LogK_{Sr^{2+}/Ca^{2+}}^{*i}$ . By neglecting this minor site  $X_h$ , the reactivity of Sr is comparable to that of Ca, as it is classically done by considering one site (Wahlberg *et al.* 1965). For smectite, the differences are not very significant according to the uncertainties of the selectivity coefficients. Therefore, the small difference in affinity between Sr and Ca is mainly due to the reactivity on  $X_h$  site of illite. This suggests that smectite plays 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 
$$R_{(x)}\theta_{(x)}\partial_t C(x,t) = -\partial_x (q_{D(x)}C(x,t) - \theta_{(x)}D_{(x)}\partial_x C(x,t))$$
(Eq. 8)

With q<sub>D</sub> representing the Darcy flow velocity (cm.h<sup>-1</sup>), θ representing the porosity (-), C the solute
concentration (mol.L<sup>-1</sup>), R the retardation factor, and D the apparent dispersion coefficient (cm<sup>2</sup>/h).
The retardation factor can be calculated by the following equation:

$$R = 1 + \frac{\rho K d}{\theta} \tag{Eq. 9}$$

348 With  $\rho$  representing the mass density of solid and K<sub>d</sub> the distribution coefficient.

R may depend on location *x* in the column when  $\rho$  and  $\theta$  are spatially variable. However, in this study, we checked that the porous media were packed homogeneously and the transport parameters were considered uniform with *x*. Consequently, chemical retention can be expressed by Eq. 9 with a constant K<sub>d</sub>. The retardation factor of a conservative tracer is equal to 1. The apparent dispersion coefficient is therefore calculated as follows:

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

With  $D_o$  being the molecular diffusion coefficient in free water (cm<sup>2</sup>/h),  $\tau$  the tortuosity (-),  $\lambda$  the dispersivity (cm), and *v* the pore velocity defined as  $v(x) = \frac{q_D}{\theta(x)}$  (cm/h). The tortuosity was calculated following the Millington and Quirk (1961) equation. The HYDRUS-1D code was used to simulate the conservative tracer experiments and the reactive transport experiment considering the constant K<sub>d</sub> approach. Reactive tracer experiments were also simulated using the HP1 multicomponent transport module of HYDRUS-1D (Jacques and Simunek, 2010). This module couples HYDRUS-1D with the PHREEQC version 4 biogeochemical code (Parkhurst and Appelo, 1999).

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

The input parameters measured experimentally were: dispersivity, porosity, flow velocity, solution compositions, and clay minerals characteristics relative to each material (site capacities, corrected selectivity coefficients). The molecular diffusion coefficients for Sr, Ca and Cl were 7.91 10<sup>-6</sup>, 7.92 10<sup>-6</sup> and 2.03 10<sup>-5</sup> cm<sup>2</sup>.s<sup>-1</sup> respectively (Mills and Lobo, 1989).

Dispersivity was estimated by using: dedicated deuterated water (<sup>2</sup>H), the CaCl<sub>2</sub> and CaI<sub>2</sub> transport experiment at centimetre scale (Table 2), and the CaI<sub>2</sub> transport experiment only at decimetre scale by using the Inverse module of HYDRUS-1D (Simunek *et al.*, 2008). The Levenburg–Marquardt algorithm was used to fit the nonlinear equations to experimental data.

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

## 383 4 Results and discussion

#### **384 4.1 Conservative transport**

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

#### 388 4.1.1 Conservative transport at centimetre scale

The breakthrough curves (BTCs) of conservative, charged and neutral, tracers were acquired at 389 390 varying flow rates in order to verify the flow independence towards preferential paths in the centimetre-scale columns C1 and C3. Figure 3 shows the BTCs as concentrations normalised to the 391 injected concentration (C<sub>0</sub>) versus volume of solution flowing through the column normalised to the 392 column pore volume  $(v_p)$ . In this way, it is possible to compare the results on a single plot. In the case 393 394 of column C1, the BTCs resulting from the three conservative tracers overlap with one another (Figure 3a). Anion exclusion process and dual porosity can therefore be excluded, and the accessible porosity 395 can be assimilated to the total porosity. Similarly for column C3 (Figure 3b), the <sup>2</sup>H BTCs are 396 superimposed for both flow velocity. This justifies considering the total porosity to describe transport 397 398 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 results401 are displayed with a black line.

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

### 406 4.1.2 Conservative transport at decimetre scale

Conservative transport experiments were performed with a CaI<sub>2</sub> tracer in column C2. Four tracer 407 injections were conducted at various flow velocities to acquire the CaI<sub>2</sub> concentration curves at eight 408 locations along the column and the BTCs at the column inlet and outlet (Figure 4). As in the 409 410 centimetre-scale columns, the total porosity and measured flow velocities were chosen as input parameters for the inverse modelling on the complete set of resident concentration curves, 411 simultaneously. The dispersivity was then estimated by inverse modelling. Finally, the resulting 412 413 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 presence of the filter with different transport properties. The average dispersivity was estimated at 415  $0.323 \pm 0.014$  cm (R<sup>2</sup> = 0.975) in the decimetre-scale column considering the four experiments. By 416 417 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 simultaneously at the eight locations along column C2. These results support the assumption of a 419 420 continuous and homogeneously packed medium.



#### 421

Figure 4: Experimental iodide concentration versus time recorded at 4 of the 8 locations (x = 6 cm, 16
cm, 21.5 cm and 30.5 cm from the column bottom) along column C2; inlet (red) and outlet (blue)
BTCs of the CaI<sub>2</sub> 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<sub>d</sub>

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

438 equilibrium achieved in one minute. The Sr adsorption reaction can be considered faster than the439 contact time in our transport experiments.

Four Sr BTCs were acquired on column C1 at varying flow velocities (Table 3). In Figure 5, the four 440 normalised BTCs overlap with each other, indicating that Sr transport is independent from the flow 441 442 rate in this context. The symmetric BTCs confirm the absence of a sorption kinetic effect on Sr transport in these experimental conditions. Direct simulations were conducted using the K<sub>d</sub> based on 443 batch sorption experiments (Wissocq *et al.*, 2018) and the  $K_d$  estimated from inverse modelling. Both 444 445 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 L.Kg<sup>-1</sup>, similar to the mean K<sub>d</sub> estimated by batch experiments  $(3.68 \pm 0.4 \text{ L.Kg}^{-1})$ . Hence, site 448 449 availability in compacted media remains the same as in dispersed material. The simulated curves overlap the data although the maximum intensity of the peak was not reached. Maximum and 450 minimum batch  $K_d$  values (3.28 and 4.09 L.Kg<sup>-1</sup> respectively) were also tested to estimate the  $K_d$ 451 variability on the simulation results. The experimental data lie well between the two curves, except for 452 a few points at the maximum concentration. When considering the minimum batch K<sub>d</sub>, the simulated 453 curve recorded an earlier arrival and higher intensity than the curve obtained by inverse modelling. 454 455 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<sub>d</sub> is a highly sensitive parameter when it comes to 457 simulating reactive transport in columns. Consequently, K<sub>d</sub> 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).



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

#### 465

460

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

In order to explain the role of the different clay minerals in Sr transport, simulations were conducted 466 467 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 transport experiments using conservative tracers, were once again used for the simulations. The 473 sorption properties of reactive phase-type (illite or smectite) and their abundance in the material are 474 475 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 in batch experiments by considering a fourth site: a low-capacity and high-affinity site. Such low-481 capacity sites are recognised to act principally at low concentration and represent less than 0.5 % of 482 483 the total exchange capacity of the clay mineral (Brouwer et al., 1983; Baeyens and Bradbury, 1997; Poinssot et al., 1999; Missana et al., 2004, 2008; Tertre et al., 2009, Martin et al., 2018, Latrille et al., 484 485 2019). On another hand, Sr sorption isotherms on smectite did not reveal the contribution of this kind of site. The significance of X<sub>h</sub> site on Sr transport is therefore investigated by comparing simulation 486 487 including or not the X<sub>h</sub> site.

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

493





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

The effect of the mineral abundance on the Sr transport results was tested on a larger column scale. Local stacking heterogeneities of small extent ( $\pm 2\%$  of clay content) were recorded during the decimetre-column filling process (Figure 2). They express the clay fraction variability along the column. The grain-size fractionation uncertainty was around 2%. This implies a CEC variation in the filling material of  $\pm 0.012$  eq.kq<sup>-1</sup>, which equates to a variability in sorption capacity (i.e. in number of site). Only the cumulative effect of variations in the clay fraction could be tested, given that Sr BTCs were only available at the column outlet. Simulations were therefore carried out at various averaged clay fraction contents and then compared with the experimental data in order to test the sensitivity ofsimulation 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, as in the case of the centimetre-scale column. In the modelling, we considered that the porous medium 514 515 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 were used as input parameters for simulations with the HP1 and HYDRUS 1D codes. As for column 517 518 C1, direct simulations with HYDRUS 1D were conducted using the Kd value based on batch sorption 519 experiments (Kd = 6.44 L/kg), in Fig. 7. The simulated curve with Kd 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 material. The average clay proportion, estimated at ca. 20% by dichromatic X-ray spectrometry 523 524 (Figure 2), was taken into account to calculate the sorption parameters of the CS material by considering three sites for smectite and four sites for illite with HP1. The simulation results in Figure 7 525 are in good agreement with the experimental Sr BTCs. As observed in the C1 column, there was no 526 527 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.



Figure 7: Sr breakthrough curves acquired in the decimetre column (C2) at flow rates of 1.95 cm.h<sup>-1</sup> (orange circles), 1.39 cm.h<sup>-1</sup> (green squares) and 1.01 cm.h<sup>-1</sup> (blue triangles). The simulation results obtained with 22 % of clay (dotted line), 20 % of clay (solid line) and 18 % of clay (dashed line) by considering three sites for smectite and four sites for illite. Direct modelling results with the batch K<sub>d</sub> value at 6.44 L.Kg<sup>-1</sup> (red line).

530

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 parameters and chemical retention based on clay mineral contributions that have been determined 541 542 experimentally. Independently from the relative abundance of the clay minerals, the clay fraction in each column appears to have a strong impact on the modelling outcome. This may explain the 543 difficulty of simulating transport on a field scale where the heterogeneity of porous media can be more 544 545 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 with a different material. Two Sr BTCs were acquired on the Bt soil horizon (column C3, Latrille et 548 549 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 tail than the Sr BTCs for CS material (Figure 6). The BTCs indicate the same relative arrival time as 552 that of column C1, corresponding to the injection of ten pore volumes  $(v_p)$ , but they differ in intensity 553 and tail length. The geometrical features of both columns are comparable and cannot be invoked to 554 555 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 and smectite contents are similar in the CS material, whereas the illite-to-smectite ratio is 0.35 in the 558 559 Bt soil.

#### 560

# 4.3.1 Kd and MSIE modelling results

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



565

Figure 8: Sr breakthrough curves in Bt soil in column C3 obtained with flow velocities of 8.66 cm.h<sup>-1</sup> (red squares) and 10.66 cm.h<sup>-1</sup> (blue triangles) and the dispersivity determined with a conservative tracer at 0.33 cm. Inverse modelling simulation given a  $K_d$  optimised at 7.50 L.Kg<sup>-1</sup> (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 described above (three or four sorption sites on Ca-illite) do not improve the mismatch. They show an 578 early arrival time, a larger intensity and a depleted tail (small squares and crosses in Figure 9). Further 579 sensitivity calculations on the variability of the clay fraction (in the uncertainty range, i.e. 17% to 580 581 19.4 % of  $< 2 \mu m$ ) indicate a significant shift in time towards an earlier breakthrough, a higher maximal value, and symmetrical curves without any tail (SI2). As a result, the clay mineral amount 582 does not explain the late arrival and length of the tail. The relative abundance of illite and smectite was 583 584 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).





Figure 9: Sr breakthrough curves acquired on the Bt soil (column C3) at two different flow velocities
(blue and red points). The simulation considers the dispersivity determined with a conservative tracer
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 selectivity coefficient of the major site X<sub>a</sub> for Ca-illite, which shows the largest uncertainty, as well as 594 both the selectivity coefficient and exchange capacity, which are characteristics of the highest 595 selective site X<sub>h</sub> (Figure 9). When the selectivity coefficient of X<sub>a</sub> is increased to the highest eligible 596 value in the uncertainty range,  $K^{*Xa}_{2H+/Sr2+} = -3.075$ , the curve shows a slight shift in time and the 597 intensity decreases, but not enough to match the experimental data (circles in Figure 9). A similar 598 599 result was obtained when the  $CE_{Xh}$  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<sub>Xh</sub> values are not solely responsible for the 601 large tail. When the simulation was conducted with an increased selectivity coefficient (representing 602  $0.5 \sigma$ ), K<sup>\*Xh</sup><sub>2H+/Sr2+</sub> = 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<sub>Xh</sub> to 0.005 eq/kg and the selectivity coefficient from 0.5  $\sigma$  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<sub>d</sub> approach. In the case of the Bt soil, the BTC curves show a marked tail that is more difficult to capture with the models. As suggested by Bugai et al., 612 613 (2012, 2020), a Kd approach is unable to predict the impact of chemical disturbances in case of mixed cation competition. In the same way, Vulava et al. (2000) have already studied cation exchange 614 equilibria between the two major cations in a natural soil material by assimilating its retention 615 properties to one-site. They evidenced that classical one-site cation exchange equations do not 616 617 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 approach rather than distribution coefficient. Another hypothesis is that other minor reactive 619 620 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.

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

of this oxide to capture Sr in the column C3 (i.e.; 0.32 g of ferrihydrite) yields 1.46  $10^{-6}$  mol of Sr compared with 5.2  $10^{-2}$  mol of Sr introduced, which is equivalent to a capture rate of 0.03 for one thousand. Despite the negligible contribution of this minor mineral on Sr sorption, our modelling 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 Caillite (i.e. 0.0003 eq/kg) and Martin et al. (2018) for Tl sorption on Ca-illite (i.e. 0.00025 eq/kg). Such 646 differences evidence the difficulty of constraining this low-capacity site with good accuracy. 647 Secondly, clay minerals in soil are commonly encountered in a wide range of particle sizes from 648 649 50 nm to  $5 \mu \text{m}$  (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 compared with sedimentary clay mineral like illite du Puy and illite contained in the CS material. This
assumption is consistent with the simulation results obtained by adjusting the capacity and affinity of
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 approach, with the advection-dispersion equation (ADE). We did this to assess how well it would be 660 able to simulate Sr reactive transport in two materials, a clayey sandstone and a Bt soil. Non-reactive 661 662 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 transport data acquired in a centimetre- and a decimetre-scale column. Although the K<sub>d</sub> approach is 664 able to describe Sr sorption in static conditions (batch) and remains applicable in dynamic conditions 665 666 for the CS material (given the  $K_d$  value uncertainty), it is less efficient at reproducing experimental data in the column for the Bt soil. Using the additivity approach and considering components 667 668 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 site. This implies having access to a robust and extensive database established with reference minerals. 673 The results of this study confirm the robustness of our database when clay minerals have reactivity 674 675 properties similar to those of the reference minerals employed to build the database. In the case of the Bt soil containing weathered mineral or evolved minerals, this database appears more limited and 676 needs to be perfected. The choice of modelling approach is therefore crucial when modelling and 677 predicting the behaviour of Sr transport in porous media. To consolidate the robustness of this 678 679 approach, it would be relevant to test it on heterogeneous media and to acquire retention properties of weathered illite. Moreover, a systematic sensitivity analysis would also be interesting, potentially 680 681 unraveling a combined effect of different parameters.

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