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# Mineral Nanoparticle Aggregation Alters Contaminant Transport under Flow

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20 **Abstract**

21 Iron oxyhydroxide nanoparticle reactivity has been widely investigated, yet little is still  
22 known on how particle aggregation controls the mobility and transport of  
23 environmental compounds. Here, we examine how aggregates of goethite ( $\alpha$ -FeOOH)  
24 nanoparticle deposited on 100-300  $\mu\text{m}$  quartz particles ( $G_{\text{ag}}\text{CS}$ ), alter the transport of  
25 two emerging contaminants, and two naturally occurring inorganic ligands—silicates  
26 and phosphates. Bromide tracer experiments showed no water fractionation into mobile  
27 and immobile water zones in an individual goethite-coated sand (GCS) column,  
28 whereas around 10% of the total water was immobile in a  $G_{\text{ag}}\text{CS}$  column. Reactive  
29 compounds were, in contrast, considerably more mobile and affected by diffusion-  
30 limited processes. A new simulation approach coupling the mobile-immobile equation  
31 with surface complexation reactions to surface reactive sites suggests that ~90% of the  
32 binding sites were likely within the intra-aggregate zones, and that the mass transfer  
33 between mobile and immobile fractions was the rate-limited step. This diffusion-  
34 controlled process also affected synergetic and competitive binding, which have  
35 otherwise been observed for organic and inorganic compounds at goethite surfaces.  
36 These results thereby call for more attention on transport studies, where tracer or  
37 conservative tests are often used to describe the reactive transport of environmentally  
38 relevant molecules.

39

40 **Keywords:** nano-aggregates; reactivity; diffusion; mass transfer; immobile water;  
41 simulation.

42

## **Synopsis**

43 This work shows how diffusion-limited processes resulting from reactive nanoparticle  
44 aggregation alter binding dynamics and reactive transport in porous media.

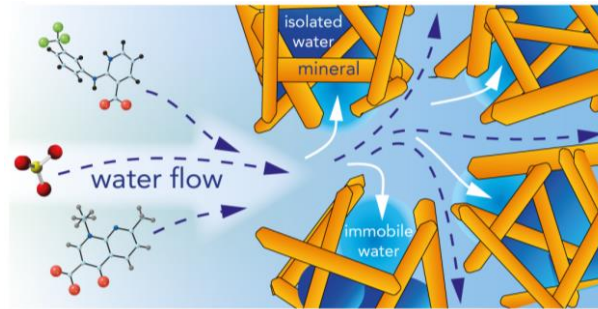
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## Graphical Abstract

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50

## 51 1. INTRODUCTION

52 Pedogenesis commonly produces (micro- and macro-) aggregates of reactive  
53 mineral particles.<sup>1-3</sup> As these aggregates are responsible for multi-modal pore size  
54 distributions, with small pores inside the aggregates and large inter-aggregate pores<sup>4</sup>,  
55 they have a propensity to alter solute transport.<sup>5</sup> The two-region two-porosity type  
56 model<sup>6</sup> is commonly used to describe such systems, and requires the assumption of two  
57 types of water fractions in the pore space—mobile water (inside macropores or inter-  
58 aggregate pores) and immobile water (inside micropores or intra-aggregate pores).  
59 Advection-dominated transport in the mobile water is accompanied by diffusive mass  
60 transfer of solutes between the mobile and immobile fractions.<sup>7,8</sup> In addition to physical  
61 processes, chemical interactions with environmental reactive surfaces, such as minerals,  
62 could also affect the mobility and fate of dissolved species.

63 Fe-oxyhydroxides are commonly found as minerals in environmental settings with  
64 different characteristics such as crystallinity, stability, specific surface area, and  
65 reactivity.<sup>9</sup> These characteristics influence the biogeochemical cycling and availability  
66 of elements and the transport and mobility of organic and inorganic compounds.  
67 Goethite ( $\alpha$ -FeOOH), the most abundant mineral of the iron oxide family, comes in a  
68 large variety of shapes and sizes.<sup>10</sup> Goethite generally does not occur as homogeneous  
69 assemblages, and frequently forms coatings on less soluble and less reactive soil  
70 particles, such as silica sand.<sup>11</sup> Moreover, Fe-oxyhydroxides may occur in homo-  
71 aggregate and/or hetero-aggregate structures in subsurface environments.<sup>11-14</sup> As most  
72 reactive (sorption and redox) surfaces are controlled kinetically by reaction steps on

73 oxide surfaces, mineral aggregates likely have a significantly different reactivity from  
74 their individual oxide counterparts. However, much of our knowledge concerning  
75 contaminant-mineral interactions at the molecular level is derived from extensive  
76 experimentation on pure mineral phases.<sup>15-17</sup> Although this literature provides a  
77 foundation for understanding reactive surface functional groups on individual mineral  
78 phases, chemical and physical phenomena in such homo-aggregated systems  
79 information cannot be readily extrapolated to those in complex hetero-aggregated  
80 mineral systems.

81 In this study, we examined how goethite aggregates obtained from freezing-thawing  
82 of fresh synthesized goethite particles<sup>18</sup> affect the adsorption dynamics and transport of  
83 reactive solutes in column experiments. Silicate and phosphate were chosen as they are  
84 two major oxyanions in soil-water systems,<sup>19</sup> and govern a wide range of  
85 biogeochemical processes such as contaminant fate and transport. Transport behaviors  
86 of nalidixic acid (NA), a quinolone antibiotic, and niflumic acid (NFA), an anti-  
87 inflammatory agent, were investigated because they are widely used in human and  
88 veterinary medicine, and are frequently detected in aquatic systems.<sup>20,21</sup> A better  
89 understanding of the molecular-level mechanisms of previously investigated<sup>17,22-25</sup>  
90 species binding to goethite surface sites could greatly improve our understanding of  
91 reactive transport behavior. Here, we focused on how the aggregates impact previously  
92 observed cooperative binding of NA/NFA, as well as competition adsorption of NA  
93 with dissolved phosphate (P) at goethite surfaces. Two kinds of coated sand were  
94 synthesized to mimic typical mineral coatings in environmental settings, goethite-

95 coated sand (GCS) and goethite aggregate-coated sand ( $G_{ag}CS$ ). After characterizing  
96 the hydrodynamic regime using a non-reactive bromide tracer and stop flow method,  
97 breakthrough curves (BTCs) of reactive solutes were determined with different inflow  
98 conditions. The BTCs of reactive solutes were then described by coupling mobile-  
99 immobile model with surface complexation reactions onto goethite surfaces using  
100 PHREEQC-2.

101

## 102 **2. MATERIALS AND METHODS**

103

104 **2.1. Materials.** All reagents were purchased from Sigma-Aldrich and used without  
105 further purification. All solutions were prepared with ultrapure water and no contact  
106 with glass surfaces during preparation to prevent silica contamination (see Supporting  
107 Information (SI) for more details). Quartz sand from Fontainebleau (100–300  $\mu\text{m}$ ) was  
108 purchased from VWR Prolabo (France). The sand was washed with HCl and  $\text{H}_2\text{O}_2$  and  
109 then with ultrapure water several times to remove impurities.

110 **2.2 Synthesis of goethite and goethite aggregates.** Goethite was synthesized as  
111 described in previous studies<sup>26–28</sup> (see SI for more details). The purity of goethite was  
112 confirmed by X-ray diffraction (XRD). The Brunauer, Emmett, and Teller (BET)  
113 specific surface area of the synthetic goethite was  $91 \pm 1 \text{ m}^2/\text{g}$ , determined by multipoint  
114 adsorption isotherm of  $\text{N}_2$  (g) onto goethite. The point of zero charge (PZC) of goethite,  
115 determined at 298 K in 0.01, 0.1, and 1 M NaCl solutions by the potentiometric titration



116 method, was 9.1. Our previous TEM investigations showed that goethite particles were  
117 acicular in shape, with lengths in the 200-400 nm and widths in the 10-20 nm range.

118 Goethite aggregates were synthesized using a previously established freezing-  
119 thawing method<sup>18</sup>, as described in the SI. XRD and BET data showed that freezing-  
120 thawing and drying did not affect the crystal structure or the specific surface area of  
121 goethite. The size distribution of pores (Figure S1) in goethite aggregates was evaluated  
122 by applying the Barrett–Joyner–Halenda (BJH) method (assuming cylindrical pore  
123 shape) to the N<sub>2</sub> gas desorption isotherm data.

124 Water vapor adsorption and desorption measurements were conducted to check the  
125 effects of aggregation on the distribution of hydroxo-groups of the goethite surface. The  
126 results (Figure S2) confirmed no modification of the distribution of hydroxo groups  
127 between unaggregated and aggregated goethite. More information about  
128 characterization is given in the SI. Details about the synthesis of individual goethite-  
129 coated sand (GCS) and aggregated goethite-coated sand (G<sub>ag</sub>CS) are also reported in  
130 the SI. According to iron measurements, the goethite content in GCS and G<sub>ag</sub>CS was 1  
131  $\pm 0.02$  wt%.

132 **2.3. Column experiments.** Continuous flow-through experiments were conducted at  
133 room temperature and under water-saturated conditions. Columns (1.6 cm internal  
134 diameter) were packed with 15 g of GCS or G<sub>ag</sub>CS, which provided the same bed length  
135 ( $4.9 \pm 0.1$  cm) and the same bulk density ( $1.55 \pm 0.05$  g/cm<sup>3</sup>). The columns were wetted  
136 upward with a 0.01 M NaCl background electrolyte solution at a flow rate of 0.5  
137 mL/min (Darcian velocity of 14.92 cm/h) for 24 h to reach water-saturated conditions.

138 Pore volume (PV) for GCS and G<sub>ag</sub>CS columns was determined by weighing and was  
139  $4.3 \pm 0.1$  mL and  $4.1 \pm 0.1$  mL, respectively. Once the columns were saturated, flow  
140 characteristics of the porous bed were determined by injecting a 2-mL pulse of tracer  
141 solution (0.05 M NaBr) followed by 10 PV of 0.01 M NaCl at a flow rate of 0.5 mL/min.  
142 Solutions of 0.05 M NaBr were prepared with 0.01-M NaCl background electrolyte. In  
143 addition, two independent sets of flow-interruption experiments with step-injection of  
144 tracer solution (0.05 M NaBr) were performed for GCS and G<sub>ag</sub>CS columns. The  
145 duration of flow-interruption was set to 12 hours. For all tracer experiments, the tracer  
146 experimental BTC in each experiment was determined by continuously measuring  
147 effluent conductivity.

148 After tracer experiments, reactive transport experiments were first conducted with  
149 a step injection of 10- $\mu$ M NA solution (0.01-M NaCl and at pH 5) into GCS and G<sub>ag</sub>CS  
150 columns at constant flow rate of 0.5 mL/min. In addition to the organic ligand, two sets  
151 of column experiments were performed for dissolved silicate (Si), which followed the  
152 step-injection of two concentrations of Si solutions (1000- and 2000- $\mu$ M Si in 0.01 M  
153 NaCl at pH 5) into GCS and G<sub>ag</sub>CS columns at the same flow rate. Furthermore,  
154 synergistic adsorption of NA/NFA and competitive adsorption of NA/P on goethite  
155 were investigated by injecting 10- $\mu$ M NA with 10- $\mu$ M NFA or 10- $\mu$ M NA with 100-  
156  $\mu$ M P into both columns at a constant flow rate of 0.5 mL/min. The background  
157 electrolyte concentration of the injected solution was 0.01-M NaCl at pH 5. Continuous  
158 on-line pH measurements were performed using pre-calibrated pH flow through a  
159 sensor in all breakthrough experiments. In addition, the pH of collected fractions was

160 routinely checked using a pH meter. Each column experiment has been duplicated  
161 (regardless of injection with single or multiple compounds), i.e. two new packed  
162 columns within two independent sets of flow-through experiments. In addition, tracer  
163 experiments have been conducted for each new column. As such, the discrepancy in  
164  $G_{agCS}$  vs  $GCS$  was systematically confirmed through different columns tests in several  
165 independent sets and using various kinds of solutes.

166 Soluble Si and P were determined by molybdenum blue spectrophotometric  
167 methods.<sup>29</sup> The measurement error of this method was no more than 3%.  
168 Concentrations of NA and NFA in the collected fractions were determined by a high-  
169 performance liquid chromatography (HPLC) system equipped with an auto sampler  
170 (Waters 717 plus) using a C18 column (250 mm×4.6 mm i.d., 5 μm) and a UV detector.  
171 The mobile phase was a mixture of water/acetonitrile (60:40 v/v) containing 0.1% of  
172 formic acid. The flow rate of the mobile phase was set at 1 mL/min in isocratic mode  
173 for the HPLC analysis. The UV detector was set to 258 nm for NA and 283 nm for  
174 NFA. The estimated error for NA and NFA was 5%. Solute elution was characterized  
175 by the BTC, namely through relative concentration ( $C/C_0$ ) vs. injected PV. All column  
176 experiments were terminated when the effluent concentration reached a steady-state  
177 value.

178 **2.4. Surface complexation modeling.** Surface complexation modeling was done with  
179 geochemical speciation code PHREEQC-2.<sup>30</sup> The charge-distribution multisite  
180 complexation (CD-MUSIC) model<sup>31</sup> was used to calculate surface species of two  
181 organic ligands (NA and NFA) and two oxyanions (Si and P) on goethite. More details

182 are reported in the SI, and the surface complexation reactions of all surface species as  
183 well as the protonation constants of surface groups are reported in Table S1.

184 **2.5. Surface complexation modeling combined with kinetics.** Prevailing non-  
185 equilibrium conditions required implementation of kinetics in surface complexation  
186 reactions. NA can form metal-bonded (MB), (hydrogen-bonded) HB, and outer-sphere  
187 (OS) complexes,<sup>17</sup> a result confirmed by our ATR-FTIR data (Figure S3). To describe  
188 adsorption kinetics of Si and P on goethite, we propose a multiple-site  
189 equilibrium/kinetic surface reaction expression, which was modified from a two-site  
190 equilibrium/kinetic sorption model<sup>32</sup> and a multi-rate surface reaction expression.<sup>33</sup> All  
191 details about the modeling approach are reported in the SI.

192 **2.6. Reactive transport modeling.** To model reactive solute transfer under dynamic  
193 conditions, we coupled the transport module with surface complexation model  
194 considering both equilibrium and non-equilibrium reactions in PHREEQC-2. The  
195 transport module allows the simulation of advection and dispersion in relation with  
196 either advection-dispersion equation (ADE) or mobile-immobile model (MIM)  
197 approaches. More details including used equations, transport parameters and sensitivity  
198 analysis are reported in the SI.

199

200

### 201 3. RESULTS AND DISCUSSION

202 First, analysis of bromide BTCs with the moment method was performed as  
203 described in previous studies<sup>34,35</sup> (see SI for more details). In both GCS and  $G_{ag}CS$   
204 columns, mass balance ratios estimated by the zero-order moment were close to unity,  
205 and retardation factors estimated by the first-order moment were slightly below 100%.  
206 These results revealed the presence of completely isolated water in both types of  
207 columns. Modeling with ADE for nonreactive tracer (equation S2.3) accurately  
208 reproduced bromide BTCs in GCS columns, and provided all the hydrodynamic  
209 parameters (isolated water fraction and dispersivity) needed for modeling. These  
210 parameters suggested that 15.3% of the total water volume was completely isolated,  
211 and that the immobile water fraction can be ignored. Flow in the  $G_{ag}CS$  columns was,  
212 in contrast to GCS columns, heterogeneous because of water fractionation. MIM fitting  
213 (equations S2.4a-S2.4c, Figure S4 and Table S2), showed that 76.0% of the total water  
214 was free flowing, while the rest was either immobile (9.8%) or completely isolated  
215 (14.2%). The determined mass transfer rate constant  $\omega$  is  $1.48 \times 10^{-3} \text{ min}^{-1}$  ( $0.089 \text{ h}^{-1}$ ),  
216 and this falls within in the typical range ( $\sim 0.03\text{--}0.09 \text{ h}^{-1}$ )<sup>33,36</sup> at similar scales and under  
217 similar injection conditions. The determined hydrodynamic parameters in both GCS  
218 and  $G_{ag}CS$  columns were further validated by independent tracer experiments (Figure  
219 S5) conducted using flow-interruption method.

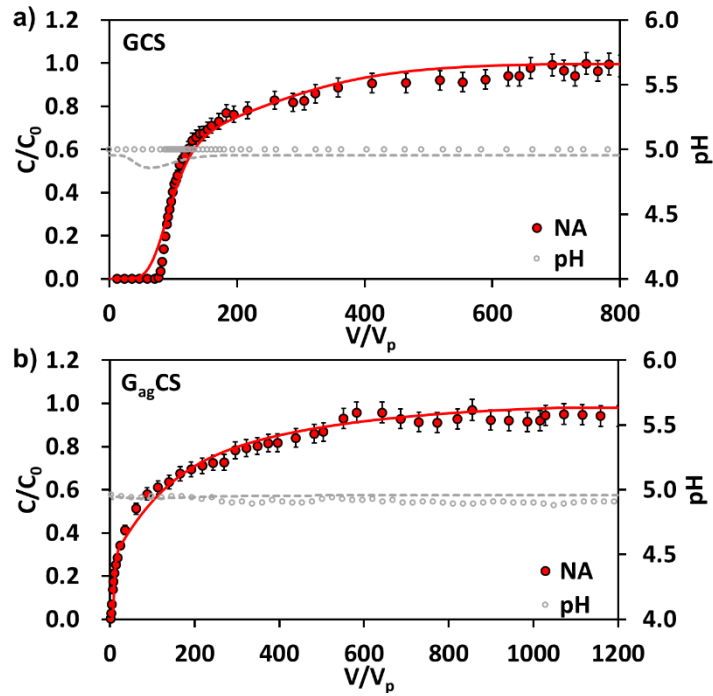
220 From these hydrodynamic parameters (Table S2), we could also estimate the  
221 characteristic times relative to advective and dispersive solute transport between the

222 mobile and immobile water. We find that exchange between these two water fractions  
223 was not instantaneous insofar as the mass transfer time ( $T_{\omega} = 31.4$  min) was longer than  
224 the advection time ( $T_{adv} = 6.2$  min). Using these hydrodynamic parameters (Table S2),  
225 we explored the mobility in non-aggregated and aggregated goethite-bearing columns  
226 of single compounds (Section 3.1) and of mixed compounds (Section 3.2).

227

### 228 **3.1. Mobility of single compounds in GCS and $G_{ag}$ CS columns**

229 The experimental BTCs for NA obtained from GCS and  $G_{ag}$ CS columns had  
230 asymmetrical shapes (Figure 1), suggesting significant influence of rate-limited  
231 sorption process. The long tails observed in the BTC for NA in the GCS column was  
232 likely caused by chemical kinetic limitations. This was supported further by the  
233 mitigated tail of the NA BTC, obtained at a lower flow rate (0.1 mL/min) (Figure S6).  
234 Accordingly, our previous spectroscopic work<sup>17</sup> showed that NA binds to reactive  
235  $\equiv\text{FeOH}^{-0.5}$  sites via hydrogen bonding and metal–carboxylate interactions, and MB  
236 formation is generally considered the rate-determining step.<sup>37</sup> In the  $G_{ag}$ CS column, the  
237 BTC for NA exhibited an early breakthrough (starting at around 3 PV), and had an  
238 extremely extended tail.



239

240 **Figure 1.** Experimental and modeled BTCs for NA and pH in GCS and  $G_{ag}CS$  columns. Influent

241 solutions of 10- $\mu$ M NA were injected in step-type concentration boundary condition. Inflow

242 conditions: flow rate 0.5 mL/min, 10-mM NaCl background electrolyte inflow pH  $5.0 \pm 0.1$ . Pore

243 volumes of GCS columns and  $G_{ag}CS$  columns are  $4.3 \pm 0.1$  mL and  $4.1 \pm 0.1$  mL, respectively. The

244 solid and dashed lines are modeled BTCs for NA and pH obtained using PHREEQC-2, respectively.

245

The points correspond to the experimental data.

246

Due to the presence of immobile water fraction, this mobility behavior could be

247

attributed to both chemical and physical non-equilibria through distribution of reactive

248

sites in the intra-aggregate zones. Despite the observed discrepancy in breakthrough

249

behavior in the GCS and  $G_{ag}CS$  columns, NA surface loadings (estimated by zeroth

250

moment analysis of the experimental BTC) was  $0.28 \text{ NA/nm}^2$  in both columns when

251

experiments were terminated. For GCS, the BTC for NA was well described by

252

combining the classical ADE and two-step kinetic expression of surface complexation

253 reactions of NA onto goethite<sup>38</sup> (Figure 1). The macroscopic forward and backward  
254 kinetic rate constants in the column were 0.050 h<sup>-1</sup> and 0.009 h<sup>-1</sup>, respectively.

255 To account for the physical non-equilibrium in G<sub>ag</sub>CS column, the MIM transport  
256 module was coupled to the same two-step kinetic expression to simulate the NA  
257 transport behavior in G<sub>ag</sub>CS column. This approach was based on four hypotheses: i)  
258 NA adsorption in the mobile domain was mainly controlled by rate-determining  
259 chemical kinetics; ii) NA adsorption in the immobile domain was kinetically governed  
260 by diffusion at the interface between the mobile and immobile water fraction, diffusion  
261 into the immobile water fraction, and chemically rate-limited adsorption; iii) diffusion  
262 at the interface between the mobile and immobile water fractions and diffusion into the  
263 immobile water fraction was one integrated process and can be described with a  
264 constant first-order mass transfer coefficient  $\omega$  (T<sup>-1</sup>); and iv) chemical kinetics for NA  
265 adsorption followed the same kinetic laws regardless of the location (at the surface of  
266 aggregates or inside the aggregates).

267 In the constructed model, the mass transfer coefficient  $\omega$  (T<sup>-1</sup>) and fraction  $f$  (%)  
268 were the only two optimizable parameters by fitting the experimental data. The other  
269 hydrodynamic parameters (mobile water content, the water content visited by the  
270 solutes, and the hydrodynamic dispersion coefficient) were fixed at the same values for  
271 all solutes, and derived from fitting the tracer BTCs. To investigate how these two  
272 parameters affected the shape of BTCs for NA, sensitivity analyses of parameter  $\omega$   
273 and  $f$  were performed (see SI for more details). Based on the results from sensitivity  
274 analyses (Figure S7), we found that parameters  $\omega$  and  $f$  could be independently



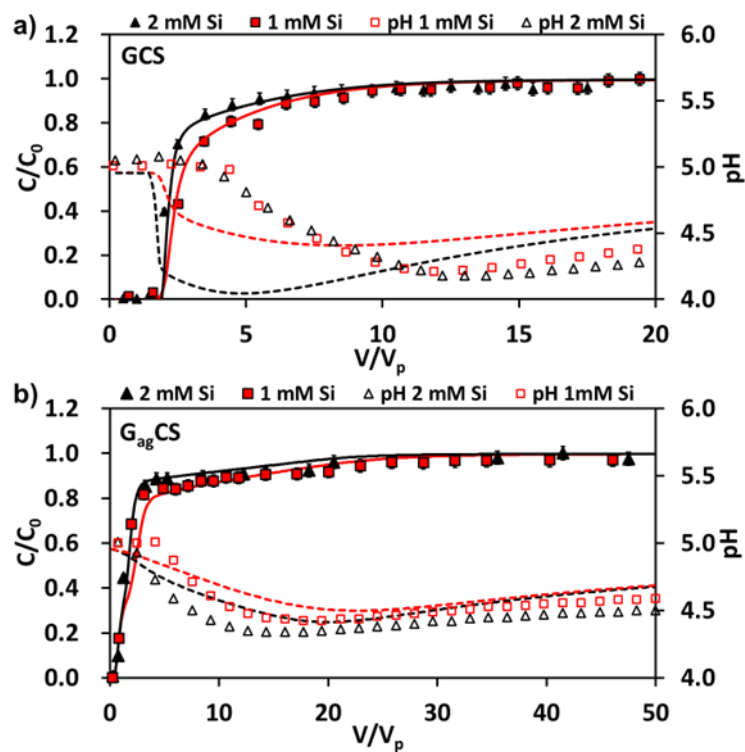
275 determined by curve-fitting:  $f$  mainly governed the position of initial breakthrough  
276 point, whereas  $\omega$  determined the turning point of relative concentration where the  
277 tailing starts. This ensures confidence for their estimates and proves that there is no  
278 concern about equifinality and non-uniqueness.

279 The best fit of the experimental BTC for NA in  $G_{ag}CS$  column was obtained  
280 (Figure 1) when we considered the distribution of the sorption sites between mobile and  
281 immobile fraction, with around 10% sorption sites in contact with the mobile ( $f = 10\%$ )  
282 water fraction and the rest (90%) in contact with the immobile water fraction. The mass  
283 transfer coefficient ( $\omega = 4.32 \text{ h}^{-1}$ ) relates to the diffusion from the mobile to the immobile  
284 water fractions and diffusion from the immobile water to sorption sites.

285 In conclusion, the transport behavior of NA through the aggregated  $G_{ag}CS$  system  
286 was governed by a combination of two different processes. Adsorption first proceeded  
287 onto the most accessible surface sites, followed by adsorption to sites located within  
288 aggregates, and thus coupled to physical (*e.g.* diffusion within the intra-aggregate zones)  
289 and chemical non-equilibrium processes. Similar experimental phenomena were also  
290 reported in a previous study<sup>39</sup> where coupled mass transport and reactions in both  
291 intragranular and inter-granular domains described the spatial and temporal dependence  
292 of uranyl surface complexation rates in sediments.

293 To further validate the influence of aggregated systems on reactive solute transport  
294 and the distribution of reactive sites of goethite in  $G_{ag}CS$  columns, we performed  
295 column experiments for silicate solutions in both GCS and  $G_{ag}CS$  columns under  
296 similar flow-through conditions. Like NA, BTC for Si exhibited discrepancy between

297 the two types of columns (Figure 2). The shape of the experimental BTC for silicate  
 298 was more asymmetrical in the  $G_{ag}CS$  column as it has an earlier breakthrough point and  
 299 extended tailing (Figure 2b). This essentially points to physical limitations within  
 300 aggregated porous media. In GCS columns, silicate surface loadings, estimated by  
 301 integrating the area above the BTC, were  $\sim 0.58 \text{ Si/nm}^2$  at 1 mM and  $\sim 0.78 \text{ Si/nm}^2$  at  
 302 2 mM. Only a slight increase of silicate surface loadings was found in  $G_{ag}CS$  column,  
 303 reaching  $\sim 0.62 \text{ Si/nm}^2$  at 1 mM and  $\sim 0.85 \text{ Si/nm}^2$  at 2 mM. As oligomerization and  
 304 polymerization reactions only occurred when monomer silicates attach to existing MB  
 305 Si species at high Si surface loading ( $\sim 1 \text{ Si/nm}^2$ ),<sup>25</sup> no oligomerization and  
 306 polymerization reactions were expected in these two columns.



307  
 308 **Figure 2.** Experimental and modeled BTCs for Si and pH in GCS (a) and  $G_{ag}CS$  columns (b). Influent  
 309 solutions of 1-mM and 2-mM Si were injected in step-type concentration boundary condition. Inflow

310 conditions: flow rate 0.5 mL/min, 10-mM NaCl background electrolyte inflow pH  $5.0 \pm 0.1$ . Pore  
311 volumes of GCS columns and  $G_{ag}CS$  columns are  $4.3 \pm 0.1$  mL and  $4.1 \pm 0.1$  mL, respectively. The  
312 solid and dashed lines are modeled BTCs for Si and pH, respectively. The points correspond to the  
313 experimental data.

314 Incorporating the concept of two-site equilibrium/kinetic sorption<sup>32</sup> into the multi-  
315 rate surface reaction expression, the BTCs for Si in GCS columns were well described  
316 by combining surface complexation parameters with only Si monodentate species (Si  
317 surface loadings below  $\sim 1$  Si/nm<sup>2</sup>) and ADE transport parameters. In this model setup,  
318 the ratio between equilibrium sorption sites and kinetic sorption sites was set to equal  
319 1:1 (Table S3), a ratio also used in a previous study.<sup>38</sup> Because this semi-empirical  
320 model describes a chemical nonequilibrium, pH variation was not well captured (Figure  
321 2a).

322 To simulate the BTCs for silicate in  $G_{ag}CS$  columns, multi-site equilibrium/kinetic  
323 sorption was merged into the multi-rate surface reaction expression to consider the  
324 distribution of sorption sites in the mobile/immobile water fractions. Coupling SCM,  
325 including surface reactions of silicate monodentate species with MIM transport model  
326 (same transport parameters for NA were used, including  $f = 10\%$  and  $\omega = 4.32$  h<sup>-1</sup>),  
327 adequately reproduced the breakthrough behaviors of Si at two influent concentrations  
328 (Figure 2b). The need to couple multi-site equilibrium/kinetic sorption with MIM  
329 model suggests a combined chemical and physical non-equilibria. The quality of fitting  
330 between the modeled and experimental BTCs for pH was also improved in comparison  
331 to the case of GCS columns (Figures 2b vs. 2a, pH). The best fitting and related

332 optimized parameters (Table S3) suggest that all sorption sites located in the mobile  
333 domain are kinetically-limited. Moreover, the ratio between equilibrium and kinetic  
334 sorption sites located in the immobile domain was 1:9.

335 Model validation confirmed around 10% sorption sites were in contact with the  
336 mobile water fraction at the column scale, leaving the rest (90%) in contact with the  
337 immobile water fraction. Moreover, the mass transfer coefficients of reactive solutes  
338 (NA or silicate) were 2 orders of magnitude higher than nonreactive solute Br<sup>-</sup>. This  
339 disparity may be explained by the difference in concentration gradient within the  
340 internal pores and the coupling between physical (flow field) and chemical (solute ionic  
341 radius, molecular diffusion, etc.) processes. Similar results have been reported in a  
342 previous study,<sup>40</sup> which showed that diffusion-controlled adsorption rate of arsenate  
343 onto porous ferric hydroxide depends on particle size.

344 Since the coupled processes of physical and chemical nonequilibria appeared to  
345 control the breakthrough behavior of reactive solutes in G<sub>ag</sub>CS columns, we checked  
346 whether a simplified model could be developed to simulate the breakthrough behaviors  
347 using an overall rate of both of the processes. This approach required that assumption  
348 that the combined processes of physical non-equilibrium and chemical kinetics  
349 occurring within the internal pores of aggregates (immobile domain) follow a first-order  
350 kinetic law, and can be described by a single mass transfer coefficient as required in  
351 MIM. In other words, physical and chemical non-equilibria are lumped into physical  
352 non-equilibrium, an “implicit” approach with respect to the “explicit” one previously  
353 mentioned.

354 We applied this implicit approach to model the reactive transport of silicate and NA  
355 in  $G_{ag}CS$  columns. Considering the fast adsorption onto most accessible surface sites  
356 located in the mobile domain, this process can be considered instantaneous and can be  
357 described using an equilibrium-based SCM. The modeling results (Figures S8 and S9a)  
358 showed that the breakthrough behavior of silicate can be captured using this approach  
359 provided that the mass transfer coefficient  $\omega$  is optimized and set to  $0.05 \text{ h}^{-1}$ . However,  
360 this approach did not fit well with the time evolution of pH. We named this coefficient  
361  $\omega_{overall}$  since the optimized value of  $\omega$  can be considered an overall mass transfer  
362 coefficient, which may be affected by various chemical and physical factors in the  
363 immobile water fraction. Our parameter  $\omega_{overall}$  was used not only for silicate but also  
364 for  $H^+$  with the “implicit” physical/chemical nonequilibrium, as the “explicit”  
365 physical/chemical nonequilibrium decouples the kinetics for pH and silicate. The  
366 failure to capture pH variation underestimated the mass transfer rate constant of protons  
367 when using the “implicit” physical/chemical nonequilibrium. This also suggested that  
368 variations in pH could be a proxy for investigating the rate of processes governed by  
369 the physical nonequilibrium. For NA, the overall breakthrough behavior of NA and pH  
370 was well described when  $\omega_{overall}$  is set to  $2.35 \text{ h}^{-1}$ , yet the pH time evolution showed no  
371 proton release during the transport experiment (Figure S9b). Parameters used in the  
372 “implicit” approach were summarized in Table S4.

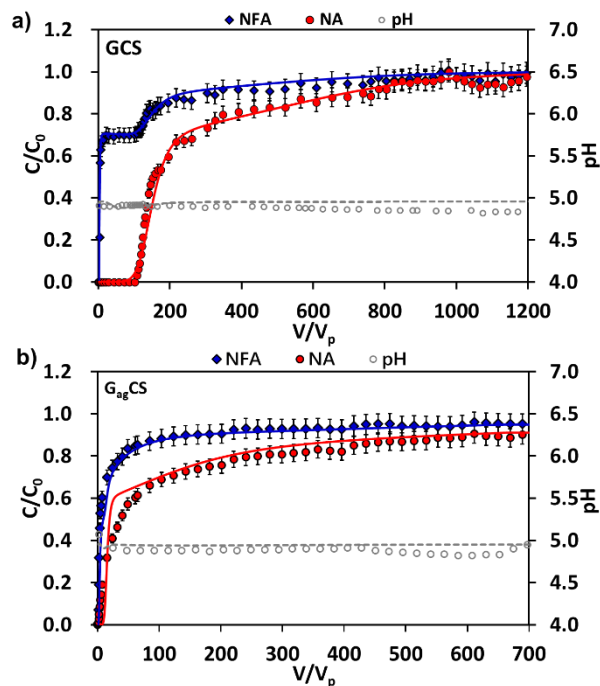
373 Overall, this implicit model approach could be used as a simplified method to  
374 describe the mobility of reactive compounds, although variations in pH could not be  
375 systematically predicted. This can be a benefit when reaction rate constants are difficult

376 to acquire, and the internal pores of mineral assemblages host a significant proportion  
377 of reactive surface sites.

378

### 379 **3.2. Effect of diffusion-controlled mass transfer on synergistic or competitive** 380 **binding**

381 As reported in previous work,<sup>41</sup> NA and NFA exerted a mutual effect on their  
382 breakthrough behavior under flow. Indeed, the experimental BTC for NFA exhibited a  
383 two-step behavior in GCS column, whereas the BTC for NA tailed extensively before  
384 reaching a total breakthrough (Figure 3a). This behavior was explained to result from  
385 NA-NFA dimer formation on goethite, and stabilized by hydrogen bonding and van der  
386 Waals interactions.<sup>17,22</sup> These interactions effectively enhanced the NFA binding,  
387 which is otherwise low. We applied the previously published approach<sup>41</sup> by combining  
388 co-binding reactions and NA adsorption kinetics without modifying the forward and  
389 backward kinetic rate constants of NA. Here, occurrence of co-binding reactions was  
390 assumed to be instantaneous at the molecular reaction scale and the apparent reaction  
391 rates were assumed to be limited by adsorption kinetics of NA. The modeled BTCs  
392 captured the mobility behavior of both NFA and NA (Figure 3a).



393

394

395 **Figure 3.** Experimental and modeled BTCs for NA and NFA in GCS (a) and  $G_{ag}CS$  columns (b).

396 Inflow conditions:  $[NA] = 10 \mu M$ ,  $[NFA] = 10 \mu M$ , flow rate = 0.5 mL/min, 10-mM NaCl background

397 electrolyte, inflow pH  $5.0 \pm 0.1$ . Pore volumes of GCS columns and  $G_{ag}CS$  columns are  $4.3 \pm 0.1$  mL

398 and  $4.1 \pm 0.1$  mL, respectively. Solid lines and dashed lines are modeled BTCs obtained using

399 PHREEQC-2. Points represent the experimental data points.

400

401 Surprisingly, in the  $G_{ag}CS$  system the experimental BTCs for NFA adopted a

402 classical sigmoidal shape (i.e., one step behavior akin to that of NA) and both

403 compounds underwent faster breakthrough and extended long tailing. After  $\sim 550$  PV,

404 the experimental BTCs for NA and NFA reached a plateau at relative concentrations of

405  $\sim 0.9$  and  $\sim 0.95$ , respectively. This finding suggests that the NFA breakthrough

406 behaviors of NA are the result of by co-binding. Here, the physical non-equilibrium led

407 to slower NA adsorption onto goethite and therefore limited the occurrence of co-  
408 binding reactions. This finding may also explain why the observed two-step behavior  
409 of NFA in GCS column disappeared in the  $G_{ag}CS$  column.

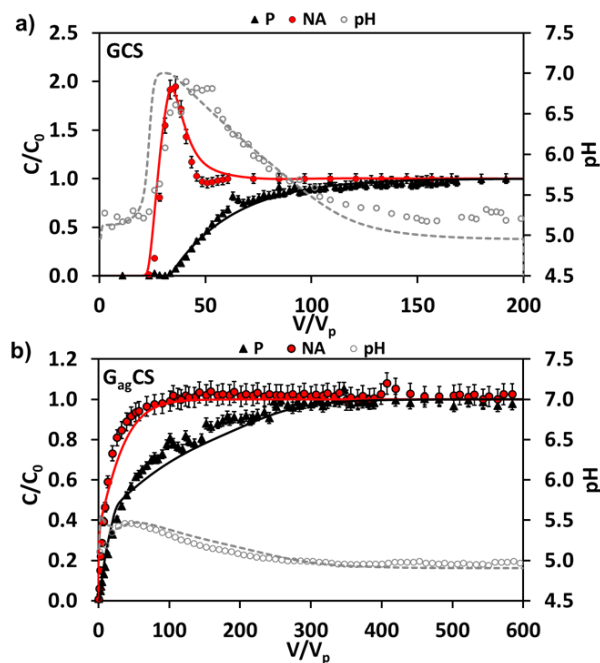
410 Attempts were made to simulate the transport of NA and NFA in  $G_{ag}CS$  column via  
411 both explicit model (Fig. S10) and implicit model (Fig. 3b) approaches. The occurrence  
412 of co-binding reactions was assumed to be instantaneous, and thus was rate-limited by  
413 NA adsorption kinetics. An overall mass transfer coefficient  $\omega_{overall}$  of  $1.44 \text{ h}^{-1}$  was also  
414 used to describe the apparent sorption dynamic of NA and NFA. For both modeling  
415 approaches we found that the modeled BTCs were relatively in good agreement with  
416 experimental BTCs (Figure S10 and Figure 3b). With the assistance of these modeling  
417 results, we suggest that coupled processes of physical and chemical nonequilibria may  
418 explain the concomitancy of earlier breakthrough and very long tailing. This would  
419 consequently explain the discrepancy in the transport behavior of NFA and NA in GCS  
420 vs.  $G_{ag}CS$  systems. The modeling results also support the occurrence of NA/NFA co-  
421 binding reactions in  $G_{ag}CS$  columns.

422 We also compared the co-transport of NA and P in GCS and  $G_{ag}CS$  columns (Figure  
423 4). In the GCS column, the experimental BTC for P exhibited a sigmoidal-like shape,  
424 whereas the experimental BTC for NA was characterized by a prominent desorption  
425 front in the range of  $\sim 25\text{--}65 \text{ PV}$  after a short adsorption front and before reaching a  
426 plateau at  $C/C_0 = 1$  (Figure 4a). A significant extent of NA desorption was observed for  
427 P adsorption, as NA surface loadings in the GCS column decreased from the maximum



428 at  $\sim 0.05 \text{ NA/nm}^2$  at the middle of the breakthrough experiment to  $\sim 0.03 \text{ NA/nm}^2$  at the  
 429 end of the breakthrough experiment.

430 In  $G_{\text{ag}}\text{CS}$  column, the experimental BTC of P was characterized by a regular  
 431 asymmetrical shape, whereas that of NA exhibited faster breakthrough (Figure 4b).  
 432 Unlike the GCS column, there was no significant desorption front of NA in  $G_{\text{ag}}\text{CS}$   
 433 column, but similar total surface loadings were observed for P ( $\sim 1.10 \text{ P/nm}^2$ ) and NA  
 434 ( $\sim 0.02 \text{ NA/nm}^2$ ) in both columns.



435

436

437 **Figure 4.** Experimental and modeled BTCs for NA and P in GCS (a) and  $G_{\text{ag}}\text{CS}$  columns (b). Inflow

438 conditions:  $[\text{NA}] = 10 \mu\text{M}$ ,  $[\text{P}] = 100 \mu\text{M}$ , flow rate = 0.5 mL/min, 10-mM NaCl background

439 electrolyte, inflow pH  $5.0 \pm 0.1$ . Pore volumes of GCS columns and  $G_{\text{ag}}\text{CS}$  columns are  $4.3 \pm 0.1 \text{ mL}$

440 and  $4.1 \pm 0.1 \text{ mL}$ , respectively. Solid lines and dashed lines are modeled BTCs obtained using

441 PHREEQC-2. The points represent the experimental data points.

442

443 To describe the co-mobility of NA and P in GCS column, surface complexation  
444 reactions of NA and P (considering both monodentate and bidentate complexes), two-  
445 step kinetic surface reaction expression of NA, and a single-rate surface reaction  
446 expression of P were combined with ADE transport module. The calculated BTCs for  
447 NA, P, and pH fitted the experimental results (Figure 4a) with a kinetic rate constant of  
448 P sorption of  $0.24 \text{ h}^{-1}$ , and using all previously obtained parameters for NA (Table S1  
449 and S3).

450 In the  $G_{\text{ag}}\text{CS}$  column, surface complexation parameters of P were integrated into the  
451 previously developed MIM transport model for NA without modifying the forward and  
452 backward kinetic rate constants of NA as well as the mass transfer coefficient  $\omega$ . As  
453 shown in Figure S11, the calculations describe the BTCs for P and pH, but not for NA.  
454 Another possibility to improve the modeling is to consider first the P adsorption—i.e.,  
455 most surface hydroxo groups of goethite are likely first occupied by P before injection  
456 of NA and P. This assumption, motivated by the greater affinity of P to goethite,<sup>42</sup> has  
457 allowed for a better fitting of the BTC for NA as shown in Figure 4b.

458 Collectively, these results show that a diffusion-controlled process within particle  
459 aggregates alters cooperative or competitive binding and the mobility of reactive solutes.  
460 As the co-interactions at the surface generally depend on the local concentration of each  
461 species, decreasing the solute mass transported into the intra-aggregate zones per time  
462 unit may change the surface speciation. In other words, the immobile water located at

463 intra-aggregate zones can act as a buffer zone, and this can slow down the mass transfer  
464 of solutes to reactive sorption sites located within the intra-aggregate zones.

465

### 466 **3.3. Implications for the diffusion-controlled transport of environmental** 467 **compounds in nature**

468

469 Reactive mineral nanoparticle aggregation alters the mobility of the reactive  
470 solutes, yet it still allows a homogeneous flow. Aggregation favors the early  
471 breakthrough of NA and Si and extensive tailing in columns. This can be explained by  
472 a combination of physical and chemical non-equilibria. The solutes are subjected to  
473 physical non-equilibrium, restricting access to the immobile water fraction where the  
474 majority of sorption sites is present. As such, only a small number of reactive sites are  
475 in contact with the mobile water fraction. Under this condition, some solutes remain  
476 only in the mobile water fraction and may quickly go through the column. Other solutes  
477 diffuse from the mobile to the immobile water fraction, gaining access to more sorption  
478 sites. This may explain the concomitancy of the earlier breakthrough and the very long  
479 tailing, a phenomenon more pronounced in strongly sorbing solutes.

480 Small amounts of immobile water (~ 10% of the total porosity) did not drastically  
481 impact tracer transport, yet they had a great impact on reactive solute transport,  
482 especially when a significant portion of the sorption sites was located in the immobile  
483 water fraction (intra-aggregate zones). In these zones, diffusion from the mobile to the  
484 immobile water fractions, coupled with surface reactions, governed overall reaction

485 rates. We therefore conclude that sorption site localization and related local hydraulic  
486 conditions at pore-scale are the prevailing factors controlling contaminant transport,  
487 even under conditions of homogenous flow. To this, we add that water fractionation  
488 can also change competitive (desorption peaks above  $C/C_0 = 1$ ) or synergistic (two-  
489 plateaus curves) shapes for BTCs into regular S-shaped BTCs.

490 This study also raised the importance of a consistent use of tracers for  
491 characterizing flow patterns and predicting reactive solute transfer. Nonreactive tracers  
492 reveal the main pattern of flow at the column scale but lack information on the local  
493 hydrodynamic conditions in the vicinity of sorption sites. Consequently, the injection  
494 of nonreactive tracers at the column scale may not be necessarily appropriate for  
495 characterizing local hydrodynamic conditions at the interface scale. Conversely, the use  
496 of reactive solutes, with a well-known chemistry and reactivity, could help probe  
497 changes in local hydrodynamic conditions. As such, by revealing difference in non-  
498 reactive and reactive solute transport through aggregated nanominerals, we expect that  
499 our work will help improve accurate characterization of flow within porous media, and  
500 even pave the way for designing better engineered reactive tracers.

501

## 502 **Supporting Information**

503 Synthesis of goethite, goethite aggregates and coatings materials; Control tests with the  
504 bare sand and reactivity and stability assessments with uncoated and coated sands;  
505 ATR-FTIR investigations and surface complexation modeling; Surface complexation  
506 modeling combined with kinetics and modeling parameters; Analysis and modeling of

507 tracer breakthrough curves (BTCs), pulse and step injection, with and without stop flow;  
508 Reactive transport modeling (PHREEQC2); Sensitivity analysis of mass transfer  
509 coefficient  $\omega$  and fraction of sorption sites in contact with mobile water,  $f$ ; Experimental  
510 and modeled BTCs for NA, Si and P in GCS and  $G_{ag}CS$  columns.

511

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516

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