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1 **Retention and transport of PFOA and its fluorinated substitute,**
2 **GenX, through water-saturated soil columns**

3
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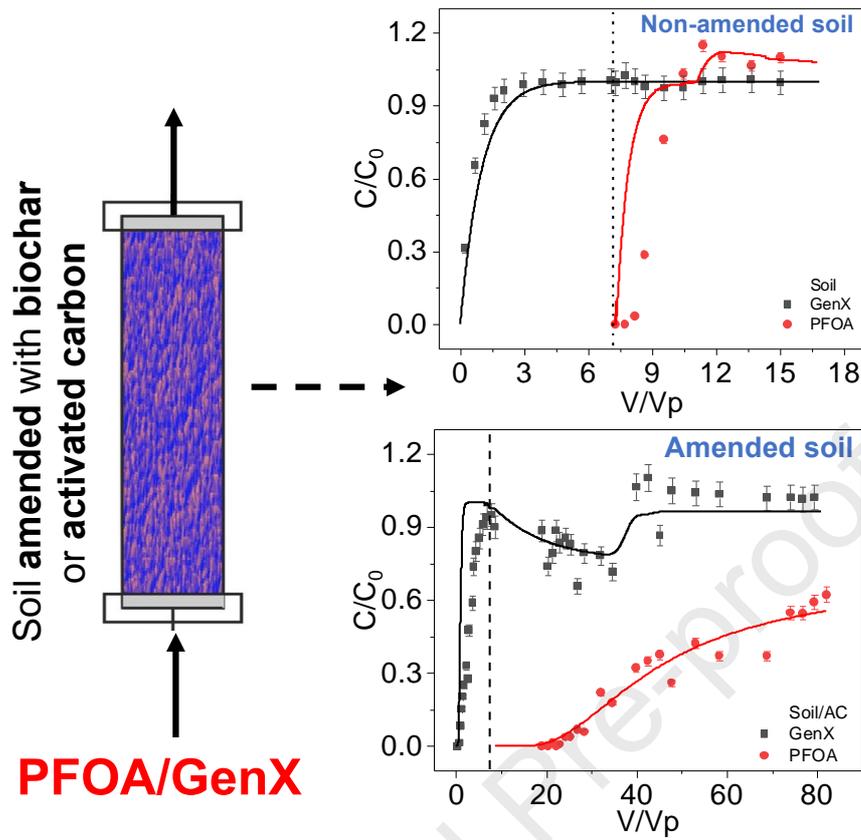
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Graphical abstract



Abstract

Perfluoro-2-propoxypropanoic acid (GenX) has emerged as a substitute for perfluorooctanoic acid (PFOA) especially since PFOA was listed among the persistent organic pollutants (POPs) by the Stockholm Convention in 2019. However, limited knowledge exists regarding the behavior and mobility of GenX in natural soils hindering the prediction of its environmental fate. This study investigated the mobility and retention of GenX and PFOA in soils under batch and water-saturated flow-through conditions. Batch experiments revealed that GenX has a lower binding affinity to soil than longer-chained PFOA, potentially threatening groundwater resources. Unlike metal-oxides/minerals (ferrihydrite, gibbsite and manganese dioxide), biochar (BC) and activated carbon (AC) amendments significantly enhanced the sorption of both GenX and PFOA in soil. Sorption data on minerals and carbonaceous materials implied that for shorter-chained GenX, the predominant mode of sorption was through electrostatic (ionic) interactions, while for longer-chained PFOA, hydrophobic interactions became progressively more important with increasing chain length. The dynamic flow experiments demonstrated that these soil amendments enhanced the retention of both compounds, thereby decreasing their mobility. Simultaneous injection of both compounds into columns pre-loaded with either PFOA or GenX increased their retardation. GenX sorption was more affected by pre-sorbed PFOA compared to the minimal impact of pre-loaded GenX on PFOA sorption. A newly developed reactive transport model, which incorporates a two-site sorption model and accounts for kinetic-limited processes, accurately predicted the sorption and transport of both compounds in single and binary contamination systems. These findings have important implications for predicting and assessing the fate and mobility of per- and polyfluoroalkyl substances (PFAS) in soils and groundwaters.

Keywords: PFAS; Soil; Mobility; Modeling; Groundwater.

44 **1. Introduction**

45 Per- and polyfluoroalkyl substances (PFAS) are a large group of highly stable chemicals
46 widely used in industry and consumer applications. Perfluorooctanoic acid (PFOA) is amongst
47 the most widespread and commonly studied PFAS known for its high toxicity and
48 environmental persistence. PFOA was added to the Stockholm Convention's list of persistent
49 organic pollutants in 2019, following perfluorooctanesulfonic acid (PFOS) in 2009 banning its
50 use and production (UNEP, 2009). To replace PFOA, a new fluorinated substitute called
51 perfluoro-2-propoxypropanoic acid (GenX) having a shorter carbon chain is being increasingly
52 used (Heidari et al., 2021; Li et al., 2021). While GenX may be considered as a safer
53 alternative to PFOA, there exists limited information about its fate and long-term effects on
54 human health and the environment. Therefore, it is important to monitor the fate and potential
55 impacts of these alternatives to ensure they do not pose similar risks. In March 2023, United
56 States Environmental Protection Agency (USEPA) announced a proposal for a National
57 Primary Drinking Water Regulation for six PFAS, including GenX chemicals (USEPA, 2023).
58 The agency aims to finalize the regulation by the end of 2023. The European Chemicals
59 Agency (ECHA) has also categorized GenX chemicals as substances of very high concern
60 (SVHCs) and is currently considering a ban on about 10,000 PFAS substances (ECHA, 2023;
61 Usman and Hanna, 2023).

62 Recent papers reported the existence of GenX in various environmental media, including
63 soil and water/wastewater (Heidari et al., 2021). For example, GenX was firstly detected in the
64 Xiaoqing River in China, the Rhine-Meuse delta in Netherlands and the Elbe and Rhine Rivers
65 in Germany (Heydebreck et al., 2015). According to Gebbink et al. (Gebbink et al., 2017), high

66 GenX concentrations have been found in the downstream area of a Dutch river, with values
67 ranging from 1.7 to 812 ng L⁻¹. High concentrations of GenX and related perfluoroalkyl ether
68 acids has also been reported in the Cape Fear River and in drinking water of more than
69 200,000 North Carolina residents (Hopkins et al., 2018). Similarly, Pike et al. (Pike et al., 2021)
70 found GenX in rainwater at all sites with a mean concentration of 0.8–2 ng L⁻¹ in their
71 investigations about PFAs in regional U.S. precipitation events.

72 Despite the widespread occurrence of GenX reported in many environmental media,
73 there exists limited information on the behavior and remediation of this new alternative
74 compound in geochemical settings. Yan et al. (2020) studied the transport of GenX in five
75 natural porous media with different geochemical properties. This group also conducted a study
76 to evaluate the ideal and non-ideal transport of GenX, PFOA and PFOS to evaluate the effect
77 of surfactant-induced flow and nonlinear air-water interfacial adsorption on PFAS transport
78 (Brusseau et al., 2021). Considering the widespread recognition of soil as an important
79 reservoir of PFAS contamination in soil (Lesmeister et al., 2021; Washington et al., 2019), it is
80 crucial to understand how these chemicals are transported in soils to enable their remediation.
81 Among the existing remediation strategies, soil immobilization is a cost-effective and
82 promising remediation approach for PFAS contaminated soils (Bolan et al., 2021; Mahinroosta
83 and Senevirathna, 2020). The use of suitable binding agents can reduce the pollutant mobility
84 and protect the water resources. Activated carbon (AC) or biochar (BC) are gaining attention
85 as environment-friendly and cost-effective alternative carbonaceous materials (Kupryianchyk
86 et al., 2016; Sørmo et al., 2021; Wang et al., 2019). However, there is a lack of research on
87 the transport and retention of GenX in the presence of soil immobilizing agents. Although

88 PFOA is being phased out, a significant amount of this pollutant is still present in environment
89 and is expected to remain for many years (ECHA, 2022). This study aims to enhance our
90 understanding of how GenX and PFOA behave and can be remediated in complex multi-
91 contaminated systems. Given the amphiphilic characteristic of GenX and PFOA, they may
92 interact competitively or synergistically with soil constituents, potentially affecting their
93 movement in the environment. Exploring these interactions can improve our understanding on
94 the fate of these compounds and develop effective remediation strategies.

95 For this, the present study has been performed to evaluate the transport and retention
96 behavior of PFOA and its substitute GenX in soil under saturated flow-through conditions. A
97 soil sampled from an agricultural area was used as a model natural material to emulate the
98 PFAS migration in natural environments. Dynamic column experiments are useful tools to
99 understand the transport of co-existing compounds and monitor the effect of non-equilibrium
100 sorption onto their mobility. The mobility of PFOA and GenX was evaluated in both pristine soil
101 and soil amended with carbonaceous adsorbents (AC and BC), in both single and binary
102 contamination systems, and in stagnant versus flowing groundwater settings. Breakthrough
103 curves (BTCs) of PFOA and GenX determined under different conditions were used to assess
104 their mobility in single and binary systems. Modeling of flow-through behavior of multiple
105 components using a two site sorption model with a kinetics term was investigated. This can
106 accurately describe the mobility of PFOA and GenX in the different scenarios considered in
107 this study. These efforts provide insights into the conditions under which GenX mobility can
108 be halted or retarded in soil columns. This will help to highlight the importance of soil
109 amendment and water chemistry in controlling the mobility of PFAS in complex soil systems.

110 2. Experimental section

111 2.1. Materials

112 Perfluoro-2-propoxypropanoic acid (GenX) and perfluorooctanoic acid (PFOA) were
113 purchased from Manchester Organics Limited and Sigma-Aldrich, respectively. Soil was
114 obtained from an agricultural field (Rennes, France). The soil was sieved multiple times until
115 achieving a particle size of 400-800 mesh, which was then used for the subsequent
116 experiments. The investigated soil was mainly composed of silt, sand and clay, with an
117 average total organic carbon (TOC) content of 2.2%. A detailed description of major
118 characteristics of the used soil are presented in the Supporting information (SI) (Table S1).
119 Four carbonaceous materials were used, including two biochars derived from coconut (BC1)
120 and beech (BC2), and two activated carbons obtained from coco (AC1) and wood (AC2). A
121 brief description of the synthesis and major properties of these carbonaceous materials is
122 provided in Table S2 and S3. The representative soil minerals including ferrihydrite, gibbsite
123 ($\text{Al}(\text{OH})_3$) and manganese dioxide (MnO_2) were synthesized using methods previously
124 published in the references (Hiemstra et al., 1999; Li et al., 2020; Schwertmann and Cornell,
125 2000; Usman et al., 2012) and detailed in the supporting information. Hydrochloric acid (HCl),
126 sodium hydroxide (NaOH) and sodium chloride (NaCl) were used to control the pH and ionic
127 strength of the solutions. Analytical grade potassium bromide (KBr), acetonitrile and
128 ammonium acetate were provided by Sigma Aldrich and used without further purification. All
129 solutions were prepared using deionized water (DI).

130

131

132 **2.2. Batch experiments**

133 A soil/solution ratio of 1 g/10 mL was maintained throughout the experimental process.
134 The initial pH of the soil slurry was kept constant at 7, by using 0.1 M HCl or NaOH during all
135 sorption experiments. 10 mM NaCl was used as the background electrolyte. All experiments
136 were conducted in 15 mL polypropylene tubes and placed on a shaker at 200 rpm. In batch
137 experiments, the kinetic sorption of PFOA and GenX was studied at different time intervals.
138 Aliquots were withdrawn and filtered through a 0.2 μm filter for the analysis of both compounds.
139 For the sorption isotherms of PFOA and GenX, a concentration range (0.05, 0.1, 0.2, 0.5, 1, 5
140 and 10 mg/L) was used to represent the approximate range of the miscible displacement
141 experiments. To test the sorption performance, sorbents were mixed to the soil (from 0 to 4%
142 w/w) followed by the addition of PFOA or GenX solution (1 mg L⁻¹ each). Reaction/contact
143 time was set as 24 h according to the results of kinetic sorption experiments. At the end of the
144 experiments, aliquots were withdrawn and filtered (0.2 μm) for further analysis. All these tests
145 were performed in triplicates. All results were expressed as a mean value of the replicates and
146 relative standard deviation (RSD) of the replicates was less than 5%.

147 **2.3. Column experiments**

148 Briefly, 10 g soil was packed into a glass column with an internal diameter (D_{int}) of 1.6 cm
149 and a bed length (L) of 4.7 cm. The bulk density of the packed soil was 1.45 g/cm³. The pore
150 volume (PV = 7.5) was estimated by weight differences before and after the saturation of the
151 dry column. The column was firstly wetted upward with a background solution of 10 mM NaCl
152 at pH 7 with a constant flow rate of 0.5 mL min⁻¹ for 24 h until the column was saturated and
153 each parameter (pH, conductivity) became constant. Bromide tracer experiment was

154 performed using an input solution containing 10 mM NaBr in a solution of NaCl (10 mM) at pH
155 7. Br breakthrough curves for different columns (soil, soil amended with BC and soil amended
156 with AC) were obtained by analyzing the effluent solution with ion chromatography.

157 Following the pulse tracer experiments, six sets of column experiments were performed
158 by step-injection at a constant flow rate by injecting 1.0 mg L⁻¹ PFOA or GenX solution in 10
159 mM NaCl as the input solutions. A mixed solution of PFOA and GenX (1 mg L⁻¹) was injected
160 as well. Concerning the effect of BC or AC on the transport of PFOA and GenX, a certain
161 amount of BC or AC (0 to 4% w/w) was mixed with soil and then packed into the soil column.
162 The breakthrough column experiments were conducted under identical conditions as the pure
163 soil columns without sorbents. The pH of all input solutions was adjusted to a pH of 7 ± 0.1.
164 These solutions were injected with a constant flow rate of 0.5 mL min⁻¹ using an ÄKTA pure™
165 chromatography system equipped with a high precision pump with an integrated pressure
166 monitor. The effluent solutions were collected in tubes at 2.0 mL increments using a fractional
167 collector. The pH of the various solutions was determined by using an online pH meter. The
168 samples were then passed through a 0.2 µm filter. The concentrations of PFOA and GenX
169 were quantified using a high-performance liquid chromatography-tandem mass-spectrometry
170 (HPLC-MS/MS) system according to the reported method by Liu et al. (Liu et al., 2021). The
171 specific analytical method can be found in the SI. The column experiments were performed in
172 duplicates.

173 **2.4. Modeling**

174 First, the hydrodynamic parameters were obtained by fitting the breakthrough data of
175 a non-reactive tracer (bromide) using classical Advection Dispersion Equation (ADE)

176 (Šimůnek et al., 2003; Šimůnek and Van Genuchten, 2008):

$$177 \quad \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

178 where C is the concentration of solute (M/L^3), t represents the time (T), D is the dispersion
 179 coefficient (L^2/T), x is the spatial coordinate (L), and $v = q/\theta$ is the water velocity (L/T), where
 180 q is the Darcy velocity (L/T), θ is the volumetric water content (L^3/L^3). Breakthrough curves
 181 (BTC) for Br suggest the absence of great dispersion/diffusion or physical nonequilibrium
 182 effect (Fig. S1). Macroscopic dispersivity was obtained by the ratio of the dispersion coefficient
 183 (D) and of pore velocity (v). The Péclet number ($P_e = vL/D$) was high ($\sim 10^5$) in the column,
 184 suggesting the predominance of a convective regime, and the flow can be assumed to be
 185 homogeneous.

186 The reactive transport model is based on a two-site, advective-dispersive transport model
 187 with Freundlich-Langmuir kinetic sorption. The liquid and sorbed concentrations are ruled by
 188 the following differential equation that governs the chemical non-equilibrium transport for a
 189 homogeneous system under steady-state water flow (Šimůnek et al., 2003; Šimůnek and Van
 190 Genuchten, 2008):

$$191 \quad \frac{\partial C}{\partial t} + \frac{\rho \partial(S)}{\theta \partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2)$$

192 where ρ is solid bulk density and S is the sorbed concentration (M/M).

193 The BTCs for GenX, PFOA and PFOA/GenX transport under saturated-flow conditions
 194 were simulated assuming that sorption sites can be divided into two fractions, instantaneous
 195 (S^e), and kinetic (S^k) sorption sites.

$$196 \quad S = S^e + S^k \quad (3)$$

197 The instantaneous site term is expressed as:

198
$$S^e = fK \frac{C^\beta}{1+\eta C^\beta} \quad (4)$$

199 where f is the fraction of instantaneous sorption sites and K , β , and η are empirical coefficients.

200 The kinetic term is expressed as:

201
$$\frac{\partial S^k}{\partial t} = \alpha \left[(1-f)K \frac{C^\beta}{1+\eta C^\beta} - S^k \right] - \mu_s S^k \quad (5)$$

202 where α is a first-order kinetic rate coefficient (T^{-1}).

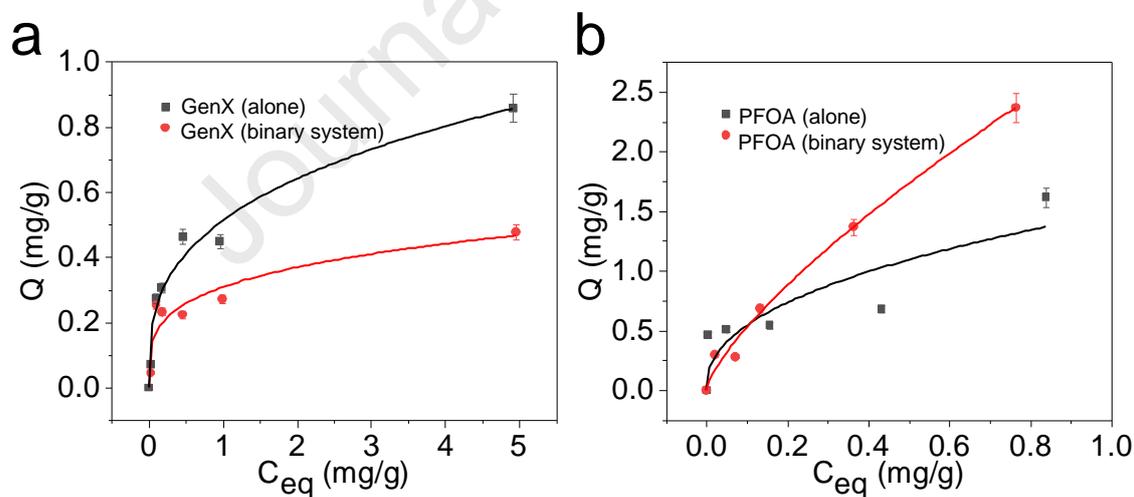
203 Transport modeling was performed with HYDRUS 1D. This code allows for the numerical
 204 resolution of equations 2-5 for several boundary and initial conditions: concentration flux at
 205 the inlet, zero concentration gradient at the outlet, and no solute at time zero. By using a least-
 206 squares optimization routine, HYDRUS 1D also allows inverse modeling to fit the model
 207 solution to the data to estimate fate and transport parameters. Values for the sorption
 208 parameter K , fraction of equilibrium sites f , kinetics adsorption α were determined through
 209 fitting the breakthrough curves and are reported in Tables S7-S8.

210 3. Results and discussion

211 3.1. Batch sorption experiments on pristine soil

212 The sorption isotherms of GenX and PFOA in soil were determined in both single (GenX
 213 or PFOA tested alone) and binary systems (mixed contamination of GenX and PFOA) (Figure
 214 1). Preliminary sorption tests conducted over a reaction time of 24 h indicated that the sorption
 215 equilibrium was not attained (Figure S2). As reported in previous batch studies, equilibrium
 216 times between PFAS and some soils/sorbents may be as long as 3 weeks and thus true
 217 equilibrium will be unlikely considering the retention time in real settings (Parker et al., 2023;
 218 Xiao et al., 2017). Thus, 24 h was selected as a representative reaction time point. In both
 219 single and mixed contamination systems, PFOA showed higher sorption than GenX. Moreover,

220 PFOA sorption further increased in the presence of GenX in mixed contamination system while,
 221 GenX sorption was reduced in the mixed system (Figure 1). This synergistic effect was
 222 confirmed by determining the sorption constants. The sorption isotherms of GenX and PFOA
 223 were best described using Freundlich equation (Figure 1). The lower K value of GenX
 224 suggests higher mobility and lower retention in the soil, likely due to its lower hydrophobicity
 225 compared to longer-chained PFOA (Table S4). This suggests that PFOA could have a higher
 226 affinity towards soil in the presence of GenX. No plateau in sorption isotherm was observed
 227 over the tested concentration range. The higher and quicker sorption of PFOA than GenX can
 228 be attributed to the presence of a longer and consecutive carbon chain and an additional C-F
 229 unit in the perfluorinated structure, thereby providing PFOA with a lower water solubility and a
 230 higher hydrophobicity (Sasi et al., 2021).



231
 232 **Figure 1:** Sorption isotherm curves of GenX (a) and PFOA (b) in single (pollutant alone) and
 233 binary contamination systems (GenX and PFOA) in pristine soil. (Soil to solution ratio = 1 g/10
 234 mL, pH = 7, reaction time = 24 h). Solid lines represent the sorption model.

235

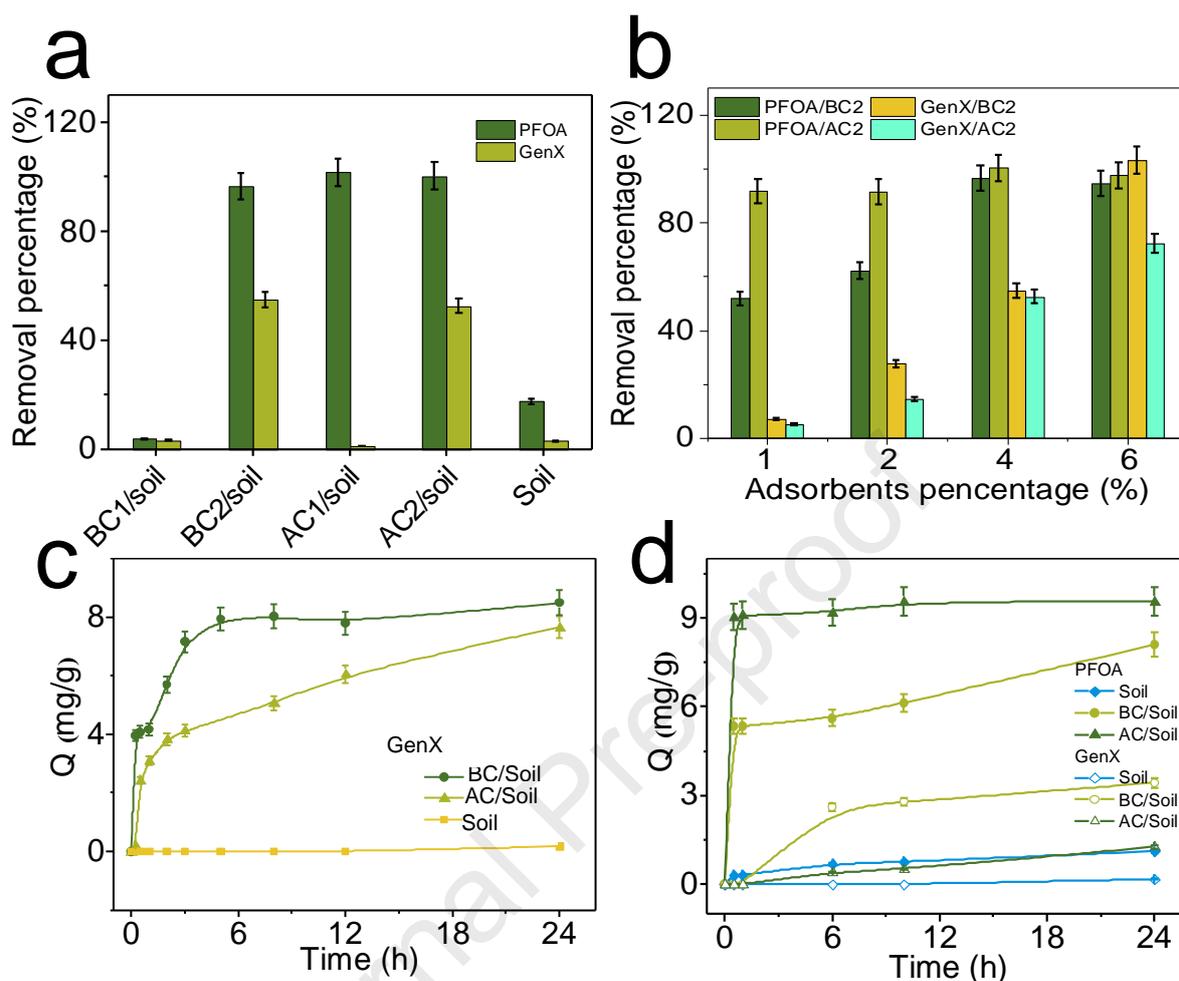
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237 **3.2. Batch sorption experiments on soil amended with BC and AC**

238 Lower sorption and higher mobility of GenX could be threatening due to increased risks
239 of its transfer to groundwater systems. The risks can be even higher in mixed-contamination
240 systems. Therefore, in the following studies, the role of soil amendments (BC1, BC2, AC1,
241 and AC2) was tested to improve the sorption of GenX and PFOA in soil system. The obtained
242 results indicate that soil amendments enhanced the sorption capacity for both GenX and
243 PFOA (Figure 2a). Among the tested amendments, BC2 and AC2 showed higher sorption
244 efficiency for both GenX and PFOA. Owing to their high sorption efficiency, the role of BC2
245 and AC2 was further evaluated at various amounts (1, 2, 4 and 6% w/w). The results presented
246 in Figure 2b show that an increase in the amount of soil amendments favoured the sorption of
247 both pollutants, with a more significant increase in the case of GenX. Compared to less than
248 10% of GenX sorption in the presence of 1% w/w amendments, the retention of GenX was
249 enhanced up to 95% and 68% after the addition of 6% w/w BC2 and AC2 to soil, respectively.
250 Similarly, amending soils with 1% w/w AC2 or BC2 retained PFOA up to 62% and 92%,
251 respectively. Soils containing 4% w/w of amendment sorbed about 100% and 55% of PFOA
252 and GenX, respectively. The sorption amounts of GenX in soils with 4% w/w of amendments
253 as a function of time are shown in Figure 2c. The results indicate that GenX sorption amounts
254 on soil with BC2 or AC2 were 8.1 mg g^{-1} and 7.5 mg g^{-1} , respectively. About half of this amount
255 was sorbed within the first hour. Despite having a lower surface area, BC2 exhibited slightly
256 higher affinity for GenX in soil compared to AC2. To gain further insight into the material
257 reactivity, TEM (Figure S3) and EDS-mapping (Figure S4 and S5) were used to analyze BC2
258 and AC2. EDS mapping results showed a notable difference, with the presence of carbon,

259 oxygen and phosphorus on the surface of AC2, while a variety of metal ions were observed
260 on the surface of BC2. As a result, the higher GenX sorption to BC2 may be due to the surface
261 characteristics of BC2, which may promote a combination of electrostatic interactions,
262 hydrophobic forces and surface complexation mechanisms.

263 The sorption of GenX and PFOA soil amended with 1% w/w AC2 or BC2 was also
264 investigated in binary systems (Figure 2d). The sorbed amount of PFOA increased to 9.5 mg
265 g⁻¹ and 7.6 mg g⁻¹, respectively, while the values of GenX were 1.2 mg g⁻¹ and 2.7 mg g⁻¹,
266 respectively. A slight decrease was noted with respect to single systems due to the competitive
267 sorption in mixture systems. As demonstrated above, AC2 exhibited higher sorption capacity
268 for PFOA than GenX. A two-step sorption was observed which could be explained by rapid
269 sorption through surface interaction between the carboxyl group of GenX and surface sites
270 followed by an intra-particle diffusion limited process (Li et al., 2018; Nguyen et al., 2020).

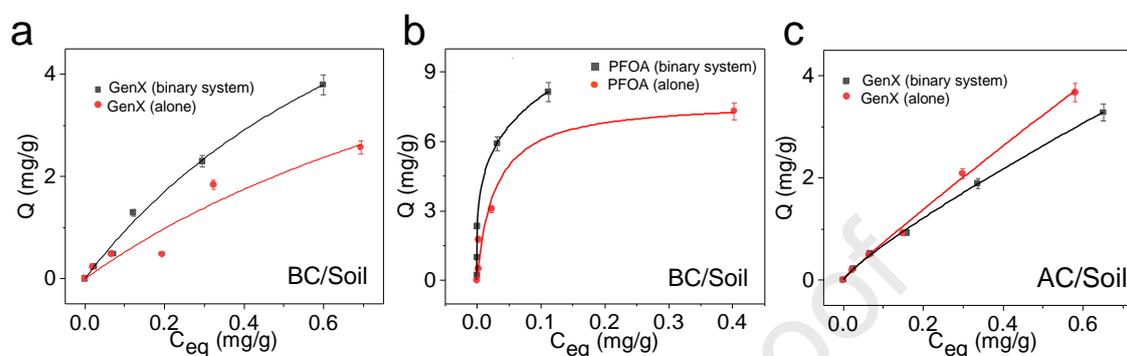


271
 272 **Figure 2:** Sorption efficiency of PFOA and GenX in soil in the presence of 4% different bio-
 273 chars (BC1 and BC2) and activated carbons (AC1 and AC2), respectively (a). Removal
 274 percentage of PFOA and GenX with various amounts of sorbents (w/w) in soil amended with
 275 AC2 and BC2 (b). Sorption kinetics of GenX onto soil with and without 4% w/w AC2 and BC2
 276 (c). Comparison of the sorption amounts of PFOA and GenX in the mixed solution in soil with
 277 1% w/w sorbents (d). ($C_{\text{GenX}0} = C_{\text{PFOA}0} = 1 \text{ mg L}^{-1}$, soil to solution ratio = 1 g/10 mL, pH = 7,
 278 reaction time = 24 h). Lines in these figures are only visual guides.

279

280 The sorption isotherms were also determined in soil amended with 4 % w/w of AC2 or
 281 BC2 (Figure 3). For GenX or PFOA sorption on amended soil, isotherms were better described
 282 by a Freundlich model, suggesting heterogeneous binding sites and a lack of saturable sites
 283 on the surface of tested sorbents. The sorption amounts of GenX or PFOA were found higher

284 in mixed systems as compared to tests with single-compounds for BC2 (Figure 3a and 3b).
 285 However, for AC2, the sorption of GenX was slightly reduced in mixed systems which could
 286 be linked to higher affinity of PFOA towards AC2 as shown above (Figure 3c).



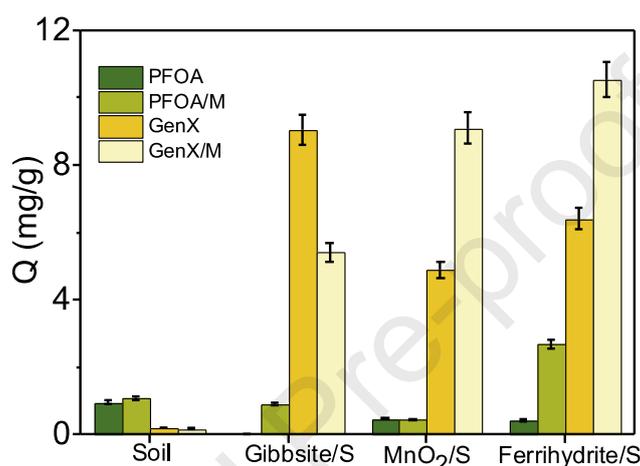
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 288

289 **Figure 3:** Sorption isotherms of GenX (a) and PFOA (b) on soil with 4% w/w of BC2 in single
 290 and binary contamination systems (GenX + PFOA). Sorption isotherms of GenX in soil with
 291 4% w/w of AC2 in single and mixed-contamination systems (c). The sorption of PFOA on AC2
 292 is not shown because all C_{eq} values were below the detection limit, likely due to the strong
 293 sorption of PFOA onto AC.

294

295 Given that BC2, having more metal ions on its surface (Table S3), exhibited higher
 296 sorption, the sorption capacities of three common and naturally occurring metal-oxides,
 297 including ferrihydrite, gibbsite and manganese dioxide, were also investigated (Figure 4). The
 298 sorption capacity for GenX alone was in the following order: gibbsite > ferrihydrite > MnO₂. In
 299 the binary system, the presence of PFOA promoted the sorption capacities of ferrihydrite and
 300 MnO₂ for GenX. However, the sorption amounts were significantly lower compared to those of
 301 carbonaceous amendments, AC2 or BC2 (Table S5). While carbonaceous materials with a
 302 hydrophobic surface can attract more hydrophobic compounds, minerals, typically have
 303 hydrophilic surfaces that attract more hydrophilic compound. These results suggest that

304 hydrophobicity is still the main driving force for sorption of PFOA and GenX (Li et al., 2023),
 305 followed by electrostatic interactions, surface complexation and hydrogen bonding (Li et al.,
 306 2023; McGarr et al., 2023). Therefore, AC2 and BC2 were further used in dynamic column
 307 experiments to investigate the immobilization of GenX and PFOA in soil and their transport
 308 under flow-through conditions.



309
 310 **Figure 4:** The sorption amount of PFOA and GenX onto soil with 2% w/w of ferrihydrite,
 311 gibbsite and MnO₂, respectively, in which S represents soil. ($C_{\text{GenX}0}=C_{\text{PFOA}0}=1.0 \text{ mg L}^{-1}$, the
 312 ratio of soil and solution is 1g/10 mL, pH = 7, reaction time: 24 h).

313 3.3. GenX and PFOA mobility in soil columns

314 The transport process of GenX and PFOA in soil columns were investigated under three
 315 different conditions: pristine soil, soil with 2% and 4% w/w of each BC2 or AC2 in soil. To
 316 examine the co-mobility of PFOA and GenX in soil, continuous flow experiments were
 317 conducted using two approaches. The first approach involved injecting 1 mg L⁻¹ of GenX first,
 318 followed by a mixture of 1 mg L⁻¹ GenX + PFOA when the total breakthrough of GenX was
 319 achieved (GenX/(GenX+PFOA)). The second approach involved injecting 1 mg L⁻¹ of PFOA
 320 first, followed by a mixture of 1 mg L⁻¹ PFOA + GenX when the total breakthrough of PFOA
 321 was achieved (PFOA/(PFOA+GenX)).

322 In the pristine soil columns, the total breakthrough of GenX and PFOA was achieved at 2
323 PV and 3.4 PV, respectively, when GenX was injected first followed by the injection of the
324 mixture (Figure 5a). On the other hand, when PFOA was injected first followed by the injection
325 of the mixture, the total breakthrough of PFOA and GenX occurred at 2.7 PV and 5 PV,
326 respectively (Figure 5b). These results indicate that pre-loaded columns with either GenX or
327 PFOA can reduce the mobility of the other pollutant in soil. It is important to note that the
328 presence of GenX solution resulted in a relative outlet concentration of PFOA beyond 1 (C/C_0).
329 However, this does not necessarily imply that the affinity of GenX towards soil is higher than
330 PFOA. Typically, non-ideal behavior including early breakthrough and concentration
331 fluctuation, is often recognized as sign of non-equilibrium and/or rate-limited transport,
332 especially for longer-chain PFASs in simulations (Brusseau et al., 1989; Šimůnek and Van
333 Genuchten, 2008). Given the heterogeneous nature of soil as a matrix and the complex
334 chemistry of PFOA binding involving both hydrophobic and electrostatic interactions, its non-
335 ideal behavior is expected.

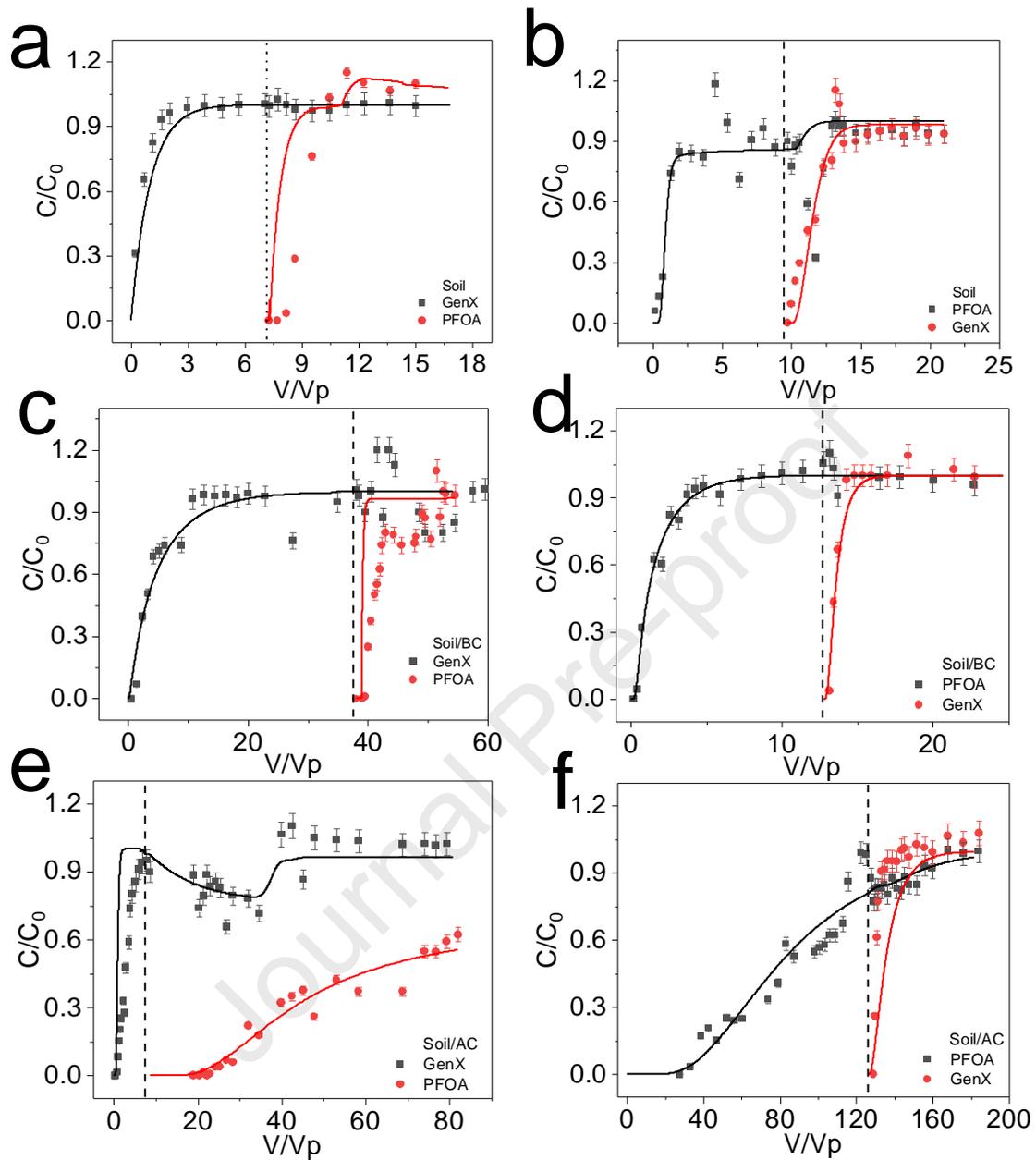
336 The introduction of BC in soil column slightly enhanced the sorption of GenX or PFOA in
337 stage 1 compared to pristine soil column, resulting in the total breakthrough of GenX and
338 PFOA at 16.27 and 8.63 V/V_p , respectively (Figure 5c and 5d). However contrary to the pristine
339 soil column, the sequential injection (stage 2) of the mixed GenX+PFOA solution in the GenX-
340 preloaded BC2-amended soil column caused the competitive desorption of GenX resulting in
341 a relative outlet concentration beyond 1 (Fig. 5c), while enhanced PFOA sorption was
342 observed under such condition (the total breakthrough could not reach 1). This is likely caused
343 by the replacement of GenX by more hydrophobic PFOA on the sorption sites of BC2/soil

344 indicating the higher affinity of active sites on adsorbents for more hydrophobic compounds
345 (Wang et al., 2019). Similarly, after PFOA sorption reached equilibrium in the BC2-amended
346 soil, GenX sorption was affected (the total breakthrough lies at 14.79 V/V_p) in the following
347 injection of mixed solution. However, no obvious observation of enhanced PFOA sorption
348 could be made due to extremely low GenX sorption in the column.

349 In soil columns amended with AC2 or BC2, both compounds exhibit similar affinity for
350 GenX in stage 1, with a total breakthrough achieved at around 10 PV (Figs. 5c and 5e).
351 However, in AC2-amended soil column, PFOA sorption was greatly improved but complete
352 breakthrough (i.e. $C/C_0 = 1$) was not attained until breakthrough point was at 180 V/V_p. This is
353 much slower than the first two scenarios and can be attributed to higher affinity of PFOA
354 towards PFOA as noted above. As shown in Figure 5e, injecting a mixture of PFOA+GenX
355 after total breakthrough of GenX decreased GenX outlet concentrations. This breakthrough
356 started at 18.95 V/V_p, and gradually reached a complete breakthrough at 39.86 V/V_p. In
357 contrast, injecting a mixed solution of PFOA+GenX after total breakthrough of PFOA (Figure
358 5f) delayed the breakthrough point of GenX to 14.6 V/V_p compared to 8.5 V/V_p in the single
359 system (stage 1, Figure 5e). This is likely because the PFOA sorbed on AC2 can act as the
360 new sorption sites of GenX. However, preloaded GenX cannot act as new sorption sites for
361 PFOA sorption because it competes with PFOA for sorption sites of AC2. This competition can
362 promote the mobility of PFOA in AC2-amended soil column (the breakthrough point of PFOA
363 in single system decrease from 83 V/V_p to 63 V/V_p in binary system). Furthermore, when PFOA
364 was pre-sorbed, the retardation of GenX was hindered due to the obstructed contact surfaces
365 of soils and sorbents by the long-chained PFOA.

366 The affinity of GenX or PFOA towards pristine soil, AC2-amended soil, and BC2-amended
367 soil and the interactions between GenX and PFOA were quantitatively assessed based on
368 their loading amounts and the results are summarized in Table S6 and Table S7. With the
369 addition of BC2 and AC2, the loading amounts of GenX on soil reached 0.0154 mmol g⁻¹ and
370 0.0072 mmol g⁻¹, respectively which represent an increase of more than 15.8 times and 7.2
371 times than pristine soil. Meanwhile, with the following injection of GenX/PFOA solution, the
372 loading amounts of PFOA on soil were enhanced with the addition of BC2 and AC2 as well,
373 which were approximately 4.1 times and 26.8 times higher than in pristine soil, respectively.
374 Then, the loading amounts of PFOA on soil were greatly enhanced with the addition of BC2
375 and AC2, by a factor of 1.86 (0.00853 - 0.00459 mmol g⁻¹) and 31.2 (0.14 - 0.00459 mmol g⁻¹),
376 respectively. These findings suggest a pronounced sorption effect of AC2 for PFOA in the
377 soil.

378



379

380 **Figure 5:** The breakthrough curves of GenX and PFOA in pristine soil column (a and b), in
 381 soil column packed with BC2 (c and d) and in soil column packed with AC2 (e and f) ($C_{\text{GenX}0} =$
 382 $C_{\text{PFOA}0} = C_{\text{GenX/PFOA}0} = 1.0$ mg/L). Among them, the injection sequence of a, c and e is GenX
 383 prior to PFOA/GenX solution, and the injection sequence of b, d and f is PFOA prior to the
 384 mixed solution. Inflow conditions: flow rate = 0.5 mL min^{-1} , 10 mM NaCl background electrolyte,
 385 pore volume of soil, soil with BC2 and soil with AC2 are 6.5 ± 0.1 mL, 8.0 ± 0.1 mL and 7.6 ± 0.1
 386 mL, respectively, inflow pH 7.0 ± 0.1 . Solid lines are calculated breakthrough curves for GenX
 387 and PFOA using Hydrus-1D.

388

389

390 In overall column experiments, BC2 showed a greater affinity for GenX, while AC2
391 revealed a stronger preference for PFOA as exhibited in the batch experiments. However, the
392 sorption of both shorter-chained GenX and longer-chained PFOA in amended soil columns
393 were subject to the competition effect when present together. The pre-sorbed GenX would be
394 desorbed due to the existence of PFOA while the sorption of PFOA would be decreased due
395 to the occupied sorption sites. In a reversed injection sequence, the pre-sorbed PFOA would
396 hinder the retardation and sequestration of GenX in soil. Interestingly, GenX was significantly
397 influenced by the presence of PFOA while PFOA was only minimally affected by GenX in the
398 amended soil columns.

399

400 **3.4. Reactive transport simulation of PFOA and GenX in soil columns**

401 The two-site chemical nonequilibrium model was used to describe the BTCs of both
402 compounds in the three scenarios using Hydrus-1D. Modeling parameters of different stages
403 and scenarios are presented in Table S7 and Table S8. First, the equilibrium model failed to
404 accurately predict the mobilization of both GenX and PFOA in stage 1, indicating the presence
405 of nonequilibrium sorption in all scenarios. However, in stage 2, the mobilization of GenX and
406 PFOA could be well predicted by the equilibrium model when complete breakthrough ($C/C_0 =$
407 1) was attained and no further sorption occurred in pristine soil columns. For AC2 or BC2
408 amended soil columns, PFOA and GenX in stage 2 were still well predicted by the model but
409 with extremely low input K values.

410 The K values were significantly different between the pristine soil columns and the BC2
411 or AC2 amended soil columns. The simulated K values of PFOA and GenX in AC2 or BC2

412 amended soil columns were 20 times higher than those in pristine soil columns. The lower
413 immobilization of GenX when injected in PFOA pre-loaded soil columns may result from
414 saturation of sorption sites and steric hindrance caused by PFOA.

415 In all simulations for GenX and PFOA, the percentage of instantaneous sorption (f values)
416 varied. GenX had f values of approximately 50-87 % while these values were around 32-63%
417 for PFOA, despite having a higher molecular weight. As reported elsewhere (Xiao et al., 2019),
418 the characteristic time of electrostatic interaction is relatively faster than hydrophobic-related
419 interaction. Compared to the f values of PFOA, the higher fraction of instantaneous sorption
420 of GenX suggested that retention of GenX may have been primarily driven by electrostatic
421 interaction rather than by hydrophobic interactions. Similarly, the f values of GenX in BC2 or
422 AC2 amended soil columns were higher than those in pristine soils, which can be attributed to
423 electrostatic interactions due to the presence of extra metal ions and organic matters. Despite
424 no diffusion-limited process was integrated in the modeling approach, the obtained results
425 effectively predicted the solutes transport in the soil with or without amendments, and thus
426 supports the underlying sorption mechanisms.

427 **4. Conclusions**

428 GenX has become a major focus of scientific research due to its use as an alternative for
429 PFOA. Due to its huge production, usage and environmental discharge, a substantial amount
430 of Genx may accumulate in soil, together with PFOA which still persists in the environment. In
431 this study, batch results showed that the sorption of GenX, which is already small, is further
432 decreased in the presence of PFOA, consistent with their respective molecular structures.
433 Amending soils with carbonaceous amendments (BC or AC) was found to effectively reduce

434 the transport and mobility of GenX. The sorption of GenX by pure minerals (ferrihydrite,
435 gibbsite and manganese dioxide) was significantly lower than those of carbonaceous
436 materials. This suggests that hydrophobic interactions play a crucial role in controlling the
437 retention and transport of GenX and PFOA in soils, followed by electrostatic interaction and
438 surface complexation mechanism. Furthermore, breakthrough curves (BTCs) were obtained
439 from various soil columns using two injection sequences, and the experimental results showed
440 good agreement with the BTC simulated using HYDRUS-1D. The pre-sorption of GenX or
441 PFOA in soil column was found to retard the subsequent transportation of PFOA or GenX due
442 to the co-binding and hydrophobic effects. In contrast, soil columns amended with BC2 or AC2
443 showed obvious retardation of the BTCs of GenX or PFOA with an efficient enhancement of
444 their loading amounts in column. However, the subsequent injection of a mixture of PFOA and
445 GenX resulted in lower loadings PFOA and GenX due to the competition for the limited
446 sorption sites. Particularly, the sorption of GenX was significantly influenced by PFOA, while
447 PFOA was less affected by the presence of GenX in the amended soil columns. Lower binding
448 affinity and higher mobility of GenX could potentially threaten the groundwater resources
449 which should be further evaluated in environmentally-relevant scenarios under real field
450 conditions. The risks of pollution transfer can be even higher in mixed-contamination scenarios.
451 An increased release of GenX into the environment can occur when both PFOA and GenX
452 are treated collectively or individually by similar sorption strategies. A thorough
453 characterization of the type of the existing contamination is needed before implementing a
454 remediation strategy. Although no transformation of GenX or PFOA was observed in amended
455 soil columns, abiotic and/or biotic transformation may take place in soils depending on

456 hydrological and biogeochemical conditions. Therefore, further studies should be conducted
457 to assess the impact of physical and (bio)chemical factors on the fate and mobility of PFAS in
458 soil columns. Finally, though these amendments (e.g., biochar and activated carbon) were
459 effective at immobilizing GenX and PFOA, the long-term effects of these amendments on the
460 pollutant availability and mobility require further investigations.

461

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- 577

Highlights

- Higher mobility of PFOA and its alternative, GenX, in pristine soil columns.
- GenX showed lower binding affinity to soil than PFOA, threatening groundwater.
- Soil amendments enhanced retention of both compounds through different mechanisms.
- Simultaneous injection of both compounds increased their retardation in pre-loaded columns.
- New model well predicts GenX & PFOA transport in single/binary contaminations.

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Credit Author Statement

G. Liu: Data curation; Formal analysis; Conceptualization, Writing - Original draft preparation.

M. Usman: Writing - Original draft preparation, Writing - Review & Editing. **T. Luo:** Writing-

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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

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