

Supplementary Information

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

Guanhong Liu^{a,b}, Muhammad Usman^a, Tao Luo^a, Pierre-François Biard^a, Kuangfei Lin^b, H. Chris Greenwell^c, Khalil Hanna^{a,c,*}

^a Université de Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS,
ISCR-UMR 6226, F-35000, Rennes, France

^b State Environmental Protection Key Laboratory of Environmental Risk Assessment and
Control on Chemical Process, School of Resource and Environmental Engineering, East
China University of Science and Technology, Shanghai 200237, China

^c Department of Chemistry, Durham University, Mountjoy Site, South Road, Durham
DH1 3LE, UK

*For correspondence: khalil.hanna@ensc-rennes.fr

Materials synthesis

Preparation of AC and BC

The activated carbons used in this study were produced by pyrolyzing coconut and wood materials at 800 °C. Biochars were obtained by burning cocoa and beech waste in tubular furnaces under nitrogen at temperatures above 250 °C for 2 hours. The resulting materials were manually ground into powders and sieved (250 µm) for further use.

Preparation of ferrihydrite

Ferrihydrite was synthesized in the laboratory as described by Schwertmann and Cornell (Schwertmann and Cornell 2000). It was prepared by neutralizing a 0.2 M ferric chloride solution with 1 M NaOH to a pH of around 7.5 as reported in our previous study (Usman et al. 2012).

Preparation of gibbsite

Synthetic gibbsite was prepared using the method described by Hiemstra et al. (Hiemstra et al. 1999). In this procedure, an amorphous aluminum hydroxide suspension is produced, followed by a dialysis at a certain temperature. The amorphous aluminum hydroxide suspensions were obtained by titrating 2 L of an aluminum nitrate solution (1 M) with 4 M NaOH in a plastic vessel to a pH of 4.5 under a nitrogen gas atmosphere to eliminate CO₂. The titrant was added at a constant rate of about 10 mL/min. All chemicals were of analytical reagent grade, and fresh double-distilled water was used. Then, the amorphous aluminum hydroxide suspensions were dialyzed against double-distilled water at 70 °C for 4 weeks with daily refreshing of the solution, resulting in gibbsites.

Preparation of acid birnessite

Acid birnessite was prepared following the procedure of Li et al. (Li et al. 2020). For this, 166 mL of concentrated HCl was added dropwise to 2.5 L of 0.4 M KMnO_4 . The suspension was stirred vigorously and kept at 90 °C during the HCl addition. The reaction was maintained at 90 °C for a further 10 min. Then, the obtained slurry was stirred vigorously at room temperature for 15 h. The precipitate was collected by centrifugation and washed with ultrapure water repeatedly until a conductivity nearing $0.6 \mu\text{S cm}^{-1}$ was measured. The suspensions were stored in polypropylene containers at 4 °C until further use

Analyses of PFOA and GenX

The concentrations of PFOA and GenX were determined according to the reported method by Liu et al. (Liu et al. 2021). HPLC-MS/MS was equipped with a Zorbax eclipse plus a C18 column (2.1 mm × 100 mm × 3.5 μm). A mixture of acetonitrile (A)/5 mM ammonium acetate (B) was used as the mobile phase with a flow rate of 0.3 mL/min. The eluent gradient was set with the following adjustments: started with 40 % A, increased linearly to 90 % in 5 min, and then back to 40 % and held for 3 min. Products were identified in negative ESI multiple reaction monitoring (MRM) mode.

Table S1. The properties of the soil used in this study.

Soil property		
pH		6.9
Sand (wt %)		20.5
Silt (wt %)		59.8
Clay (wt %)		19.7
Humidity (%)		1.4
CEC (meq/100g)		13.4
OC (%)		2.2
TN (g/kg N)		2.3
Exchangeable elements (mg/kg)	P ₂ O ₅	241
	CaO	3243
	MgO	321
	K ₂ O	529
Total elements (mg/kg)	Cd	< 0.5
	Al	21000
	Co	13
	Cu	37
	Fe	35182
	Mn	593
	Zn	128

Table S2. The major characteristics of soil and tested carbonaceous adsorbents.

Adsorbent	SSA (m ² /g)	Total pore volume (cm ³ /g)
Soil	13 ±1	-
BC1	190 ± 5	0.17
BC2	388 ±10	0.42
AC1	1138 ± 20	0.68
AC2	1350 ± 20	0.83

Table S3. The element content in AC2 and BC2.

Elemental content	Element (Atomic %)	AC2	BC2
	C	83.78	70.84
	O	15.80	21.70
	Mg	-	3.58
	Al	-	0.33
	Ca	-	2.09
	Fe	-	1.33

	K	-	0.04
	Na	-	0.03
	P	0.41	-

Table S4. The first order adsorption rate coefficient of GenX and PFOA in single and mixed (binary) systems.

	Single system		Mixed system	
	GenX	PFOA	GenX	PFOA
K	0.1388	1.488	0.070	2.9902
R ²	0.7039	0.8239	0.5717	0.9754

Table S5. The comparison of adsorption amount of PFOA and GenX with 2% amendment in soil.

Compounds	Ferrihydrite	Gibbsite	MnO ₂	AC2	BC2
Adsorption amount (mg/g)					
PFOA	0.42	0	0.47	45.67	31.14
GenX	6.411	9.054	4.89	7.19	13.77

Table S6. Changes of GenX and PFOA loadings in different scenarios when GenX was injected firstly and then the mixture of PFOA and GenX and changes of PFOA and GenX loadings in different scenarios when PFOA injected firstly and then the mixture of GenX and PFOA.

Loading (mmol/g)	Soil	Soil/BC	Soil/AC
GenX Phase1	0.000641	0.0154	0.0072
GenX Phase1+2	0.000575	0.0174	0.00264
PFOA	0.0019	0.00169	0.051
PFOA Phase1	0.000807	0.00853	0.143
PFOA Phase1+2	0.00297	0.00105	0.155
GenX	0.00293	0.0068	0.0067

Table S7. Parameters of GenX and PFOA transport under flow-through conditions when GenX was injected prior to PFOA in three scenarios.

	Soil			Soil/BC2			Soil/AC2		
pH	7 ±0.1			7±0.1			7±0.1		
	GenX		PFOA	GenX		PFOA	GenX		PFOA
	Stage 1	Stage 2	Stage 2	Stage 1	Stage 2	Stage 2	Stage 1	Stage 2	Stage 2
^a λ	0.3	0.3	0.3	0.6	0.6	0.6	0.8	0.8	0.8
^b f	0.005	0.495	0.754	0.79	0.875	0.53	0.5	0.82	0.295
^c K _d	0.007	1.02	12.8	98.2	0.875	30	23.5	16.7	54.9
^d β	1	1.46	5.53	6.78	2.772	1.0	1.0	0.717	0.99
^e α	0.01	3.08×10 ⁻⁴	0.176	4.4×10 ⁻²	3×10 ⁻³	2.05×10 ⁻⁴	3×10 ⁻³	7.3×10 ⁻³	6.8×10 ⁻⁴
R ²	0.99	0.98	0.97	0.98	0.98	0.97	0.97	0.97	0.98

Table S8. Parameters of GenX and PFOA transport under flow-through conditions when PFOA was injected prior to GenX in three scenarios.

	Soil			Soil/BC2			Soil/AC2		
pH	7			7			7		
	PFOA		GenX	PFOA		GenX	PFOA		GenX
	Stag 1	Stage 2	Stage 2	Stage 1	Stage 2	Stage 2	Stage 1	Stage 2	Stage 2
^a λ	0.3	0.3	0.3	0.6	0.6	0.6	0.8	0.8	0.8
^b f	0.696	0.763	0.47	0.26	0.2	0.12	0.373	0.639	0.077
^c K _d	9.42	2.3345	0.9694	0.73	1.3	0.60	215	7.55	10.6
^d β	3.48	0.5036	1.578	1.2	1	1	1.15	1.31	0.879
^e α	0.02	0.3×10 ⁻²	0.14×10 ⁻²	0.0054	5.5×10 ⁻⁴	0.0041	2.93×10 ⁻⁷	3.52×10 ⁻³	5.3×10 ⁻⁶
R ²	0.97	0.98	0.97	0.97	0.98	0.99	0.96	0.98	0.98

^a λ (cm) is the dispersivity.

^b f is the fraction of equilibrium sites.

^c K_d is the empirical distribution coefficient in Freundlich isotherm. Units: cm³/g.

^d β is the index of Freundlich isotherm.

^e α is the adsorption rate. Units: T⁻¹.

Stage 1 represents the modeling range of GenX or PFOA in the single solute solution, and Stage 2 shows the transport information of it in the mixed PFOA/GenX solution.

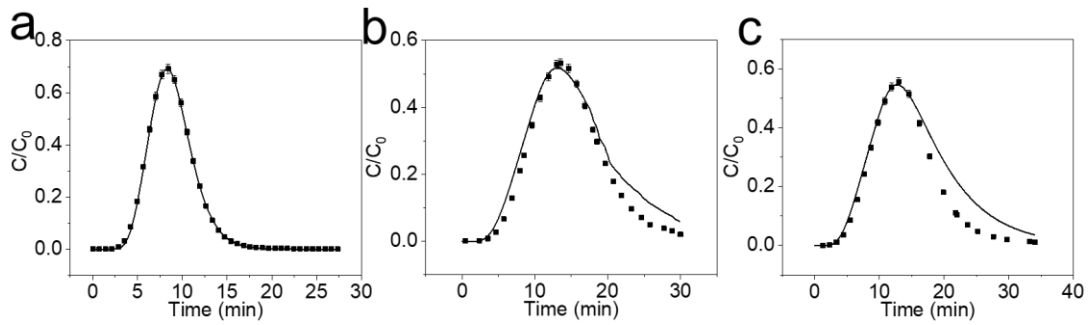


Figure S1. Breakthrough curve of bromide in different scenarios of (a) soil, (b) soil amended with BC2 and (c) soil amended with AC2 packed column, experimental data at 0.5 mL/min and calculations based on the CDE model (Convective-Dispersion equation).

Aqueous transport was characterized by tracer experiments. The pulse injection of the non-reactive solute (KBr) induced a bell shaped elution curve characterized by a symmetrical shape at flow rates 0.5 mL/min. Solutes were transported through water-driven convection and dispersion, thereby ensuring contact between solutes and all particles by interstitial waters. The data analysis was conducted by the method of moments and the convective-dispersive model. A certain of mobility and extended tailing observed in the breakthrough curves of soil/BC and soil/AC may result from diffusion-limited process affecting their binding dynamic to reactive sites located inside aggregates.

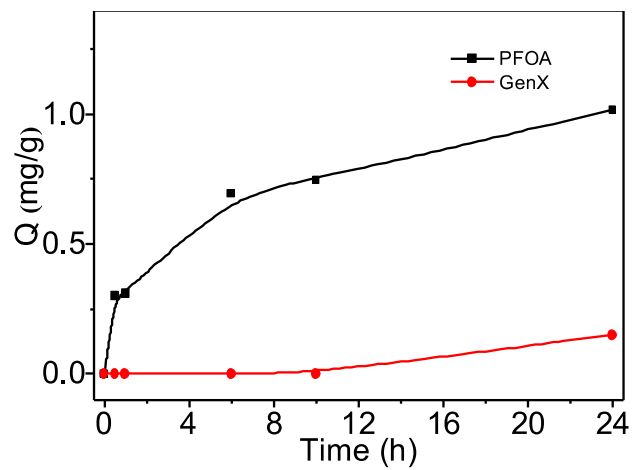


Figure S2. Kinetics adsorption of GenX and PFOA onto soil.

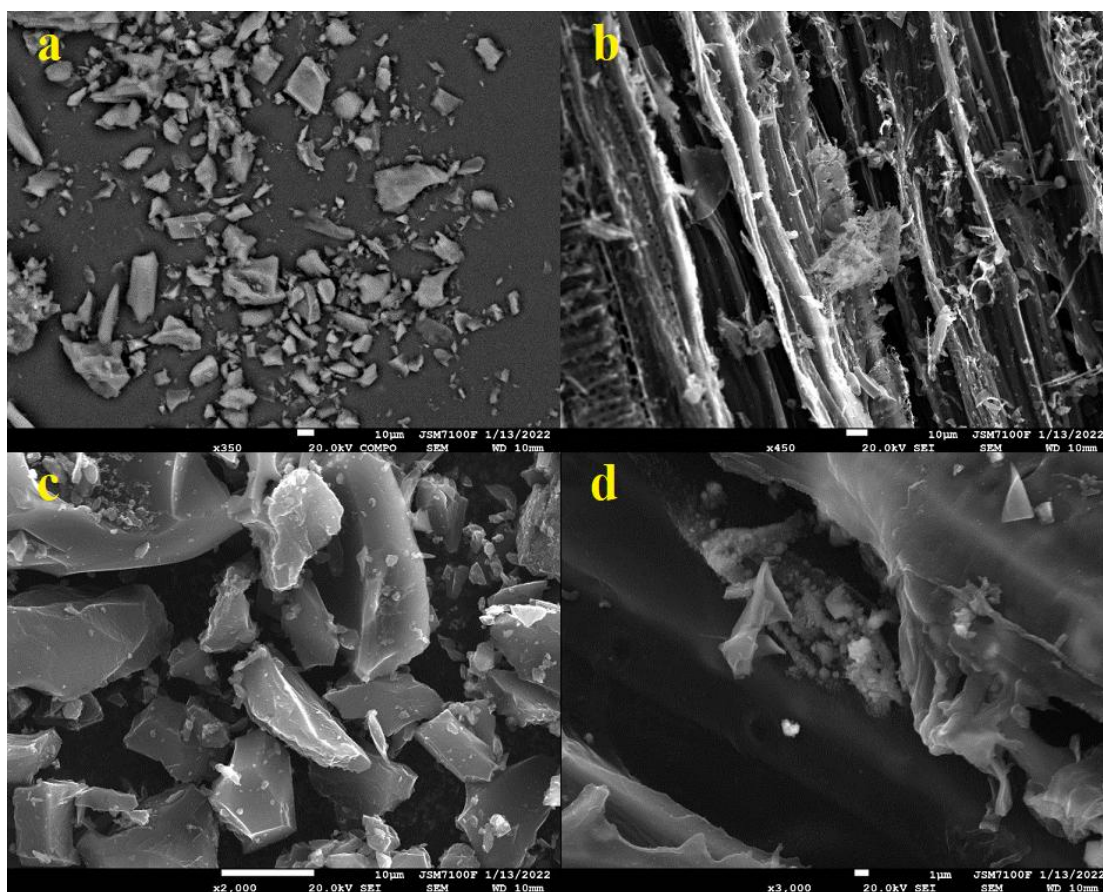


Figure S3. The morphology of AC2 (a) and BC2 (b) and their high-resolution SEM images (c and d).

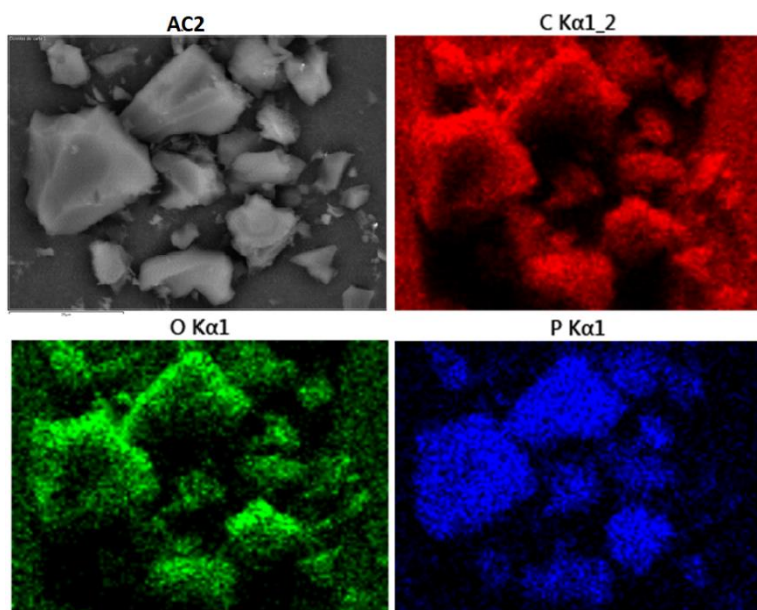


Figure S4. EDS-mapping analysis for the cross section of AC2.

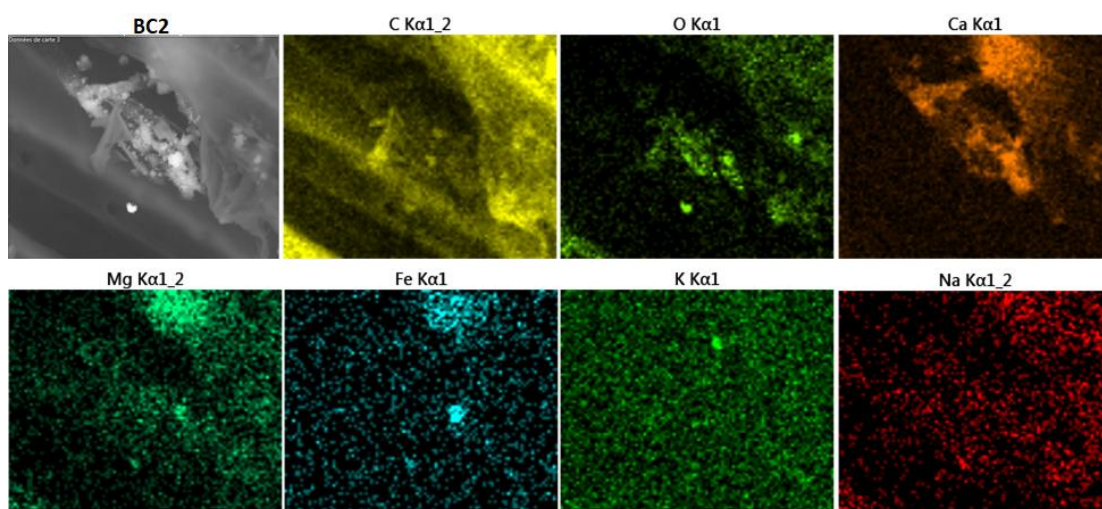


Figure S5. EDS-mapping analysis for the cross section of BC2.

Based on the EDS-mapping analysis, only C, O, and P were contained in the section of AC2.

In contrast, besides the C and O were detected in the section of BC2, Ca, Mg, Fe, K and Na were introduced as well. There was a relatively even distribution of Na and K elements while the enrichment of Mg and Fe was more scattered around the surface rather than concentrated in the main area. The specific content of the metal elements was shown in Table S3.

References

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