

Supporting Information Cover Sheet

Facilitated Transport of 2,2',5,5'-Polychlorinated Biphenyl and Phenanthrene by Fullerene
Nanoparticles through Sandy Soil Columns

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Procedures used to pack soil columns

Soil columns were dry-packed using previously developed procedures (*S1*). For each column approximately 3.2 g dry soil was packed into an Omnifit borosilicate glass column (10 cm × 0.66 cm, Bio-Chem Valve Inc., Boonton, NJ). The total length of the packed soil was approximately 6.5 cm. The packed soil was retained by 10 µm stainless steel screens (Valco Instruments Inc., Houston, TX) on both sides of the column. The packed soil columns were first purged with CO₂ gas (purity > 99%) for 30 min. Then, the columns were flushed with DI water at a flow rate of 3 mL/h for 20 h. The trapped CO₂ air bubbles in the columns can dissolve in water quickly and this procedure allows the soil to reach complete water saturation easily (*S2*). Afterwards, approximately 180 mL electrolyte solution containing 0.5 mM NaCl was pumped through each soil column to stabilize soil colloids. The flow velocity was gradually adjusted to the experimental flow velocity as listed in Table 1. The pH of the influent solutions in all column experiments was within the range of 6.5–6.9 (Table 1). No noticeable change of pH was observed in the effluents.

Sorption experiments of PCB to soil

The sorption isotherm of PCB to Lula A was obtained using a previously developed method (S3, S4). First, a series of amber EPA vials each containing 3.0 g soil and approximately 40 mL of the same background solution used in the column experiments (0.5 mM NaCl, pH = 6.7 ± 0.2) were prepared. Then, different amount of PCB stock solution (in methanol) was added to the vials using a micro-syringe, and the volume percentage of the methanol stock solution was kept below 0.1% to minimize co-solvent effects. The vials were filled with the background electrolyte solution immediately to leave minimal headspace and then tumbled end-over-end at 3 rpm for 7 d (the time required to reach sorption equilibrium was predetermined). Afterwards, the vials were centrifuged at 3000 rpm for 30 min, and the supernatant was withdrawn to analyze the concentrations of PCB. The sorbed mass at each equilibrium concentration was calculated from the measured concentration in the solution based on mass balance. Each sorption data point was run in duplicate.

Determination of nC₆₀ concentration using an oxidation-extraction protocol

An oxidation–extraction method developed by Fortner et al. (S5) was used to determine the concentration of nC₆₀ stock suspension and to verify nC₆₀ concentrations of selected samples in this study. The oxidation–extraction method was also combined with the TOC analysis method to check the residual of toluene within the nC₆₀ aggregates of the nC₆₀ stock suspension. The measured nC₆₀ concentrations using the two methods are very close, indicating that the mass of residual toluene within the nC₆₀ aggregates was negligible.

First, 10 mL nC₆₀ stock solution, 4 mL 0.1 M Mg(ClO₄)₂ and 10 mL toluene were added to a 40 mL glass EPA vial. The vial was sealed and mixed vigorously for 1 h. After extraction of nC₆₀ into the toluene phase was complete, the vial was left in a refrigerator until the water phase froze. Then, the toluene phase was withdrawn to measure the UV absorbance at 333 nm. The concentration of nC₆₀ was then determined based on a pre-established calibration curve of C₆₀ in toluene.

Detailed description of desorption experiments

Desorption isotherms

Step 1 (adsorption step). First, a series of amber EPA vials each containing approximately 40 mL of 6.7 mg/L nC₆₀ suspension were prepared. Then, different amount of PCB stock solution (in methanol) was added to the vials using a micro-syringe, and the volume percentage of the methanol stock solution was kept below 0.1% to minimize co-solvent effects. The vials were filled with the background electrolyte solution immediately to leave minimal headspace and then tumbled end-over-end at 3 rpm for 7 d (the time required to reach adsorption equilibrium was predetermined). At the end of the 7-d adsorption the aqueous suspension of PCB–nC₆₀ mixture in each vial was passed through a size-exclusion PD-10 column (GE Healthcare, Buckinghamshire, UK), and the concentration of nC₆₀ and the mass of PCB in the filtrate were measured (see *Analytical methods*). Quality control experiments show that over 98% nC₆₀ can pass through the column, but no dissolved PCB can pass through (Figures S4 and S5, Supporting Information). Thus, the measured PCB mass in the filtrate (denoted as “m₁”) is essentially the mass of PCB adsorbed to nC₆₀ at the end of the adsorption step. The dissolved mass at the end of the adsorption step can be calculated by subtracting m₁ from the total mass of PCB added to the vial in the beginning of the adsorption step (denoted as “m₀”).

Step 2 (Desorption step No. 1). The filtrate from the previous step (approximately 38–39 mL) was equilibrated for 7 d to allow redistribution of PCB mass between nC₆₀ and the aqueous solution. Note that at the beginning of this step (i.e., immediately after the filtrate was collected) the filtrate contained essentially no dissolved PCB (because all

the dissolved PCB was detained by the PD-10 column). This drove the desorption of PCB from nC_{60} to the aqueous solution, until new equilibrium was reached. Upon desorption equilibrium the aqueous suspension of PCB– nC_{60} mixture was passed through a fresh PD-10 column, and the concentration of nC_{60} and the mass of PCB in the filtrate were measured. The measured PCB mass in the filtrate (denoted as “ m_2 ”) was the mass of PCB adsorbed to nC_{60} at the end of desorption step No. 1. The dissolved mass at the end of the desorption step No. 1 was calculated by subtracting m_2 from m_1 . Thus, the equilibrium concentration of PCB adsorbed to nC_{60} and the concentration of PCB in the aqueous phase at the end of desorption step No. 1 can be obtained.

The procedures described in Step 2 were repeated to obtain additional repetitive desorption data. A total of three desorption steps were conducted. PD-10 columns from selected experiments were cut into pieces and Soxhlet-extracted with acetone for 24 h to check mass balance; the recovery of PCB was above 95%.

Desorption kinetics

First, the procedures of Step 1 mentioned above were carried out. Then, the filtrate collected from Step 1 was equilibrated to allow desorption of PCB from nC_{60} to the aqueous solution (which contained no dissolved PCB immediately after the filtrate was collected). At selected time intervals small aliquots of the aqueous suspension were collected. Each sample was passed through a PD-10 column to determine the adsorbed mass of PCB on nC_{60} and the concentration of nC_{60} , and then the concentrations of PCB adsorbed to nC_{60} at different time intervals were obtained.

All the adsorption and desorption experiments were conducted at room temperature (23 ± 1 °C).

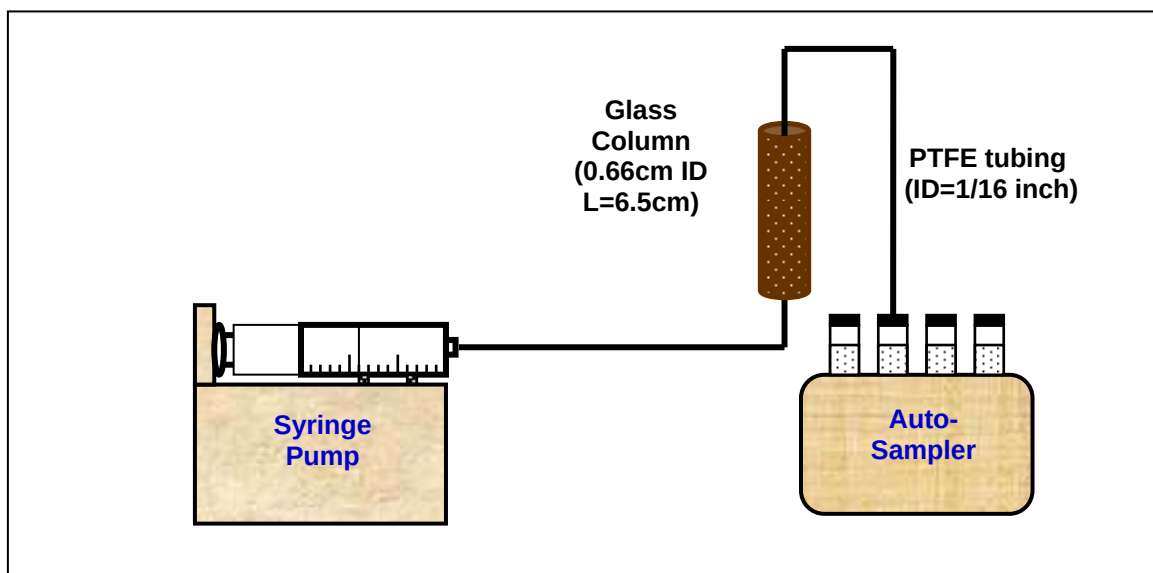


Figure S1. Schematic illustration of the experimental apparatus for column tests.

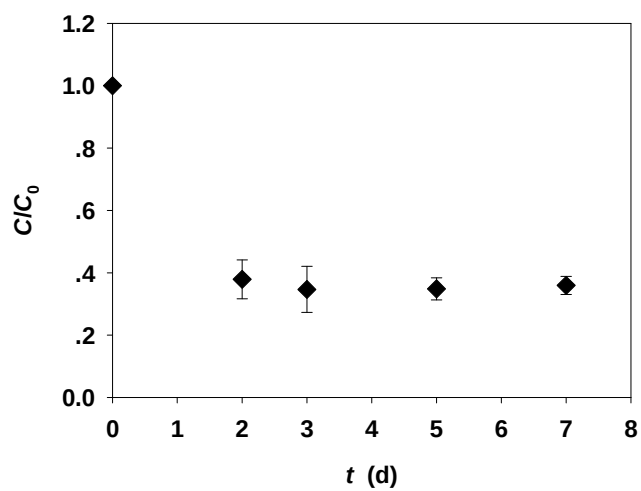


Figure S2. Time required to reach adsorption equilibrium of PCB to nC_{60} (2.5 mg/L). C is freely dissolved PCB concentration at time t ; C_0 (12.4 $\mu\text{g/L}$) is the total PCB concentration in the solution at $t = 0$. Error bars indicate standard deviation of triplicate samples.

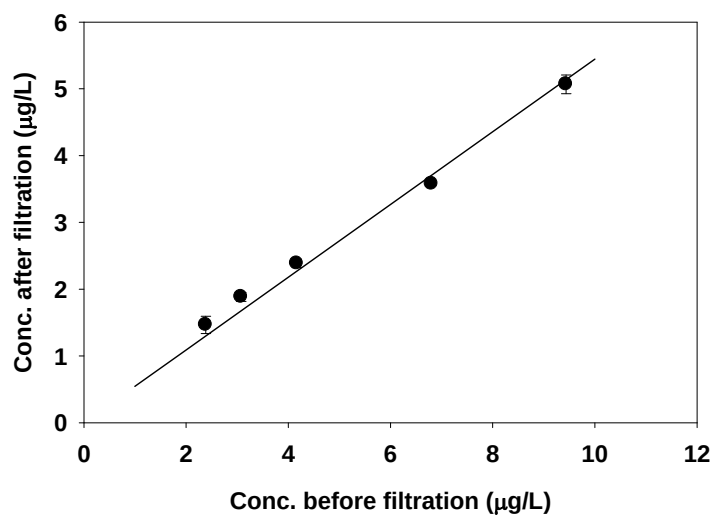


Figure S3. Loss of PCB during the filtration of PCB solution with a 0.02-µm Al₂O₃ membrane. Error bars, in some cases smaller than the symbol, represent variability of duplicate samples.

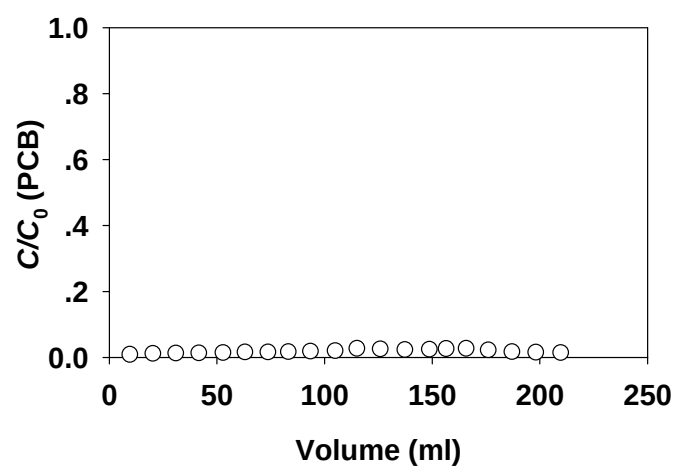


Figure S4. Breakthrough of 200 mL 10 µg/L PCB through a PD-10 Column.

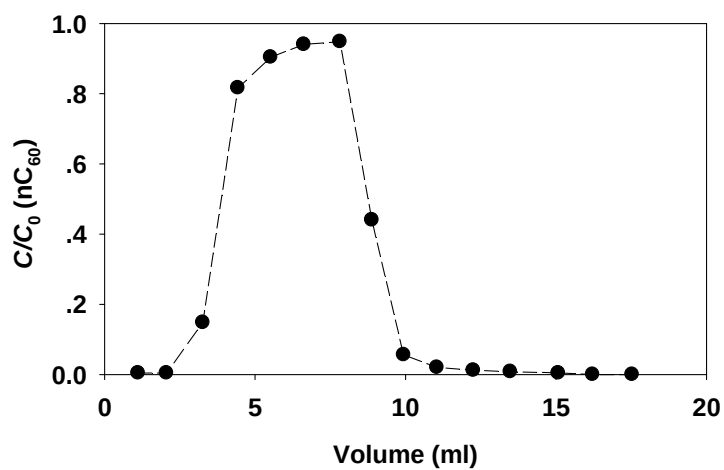


Figure S5. Breakthrough of 5 mL 5.8 mg/L nC₆₀ through a PD-10 column. The total mass recovered from the effluent—calculated by integration of the breakthrough curve—was 98%.

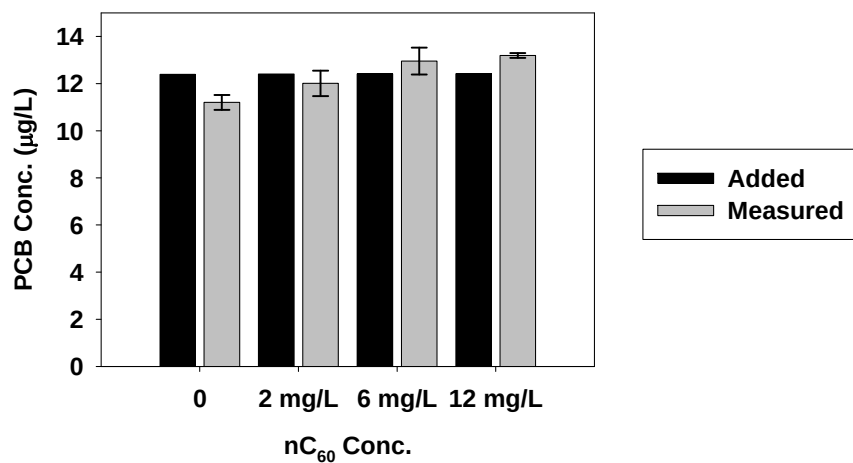


Figure S6. Testing of potential quenching effect of nC₆₀ on radioactivity measurement of ¹⁴C-radiolabeled PCB. No quenching effect of nC₆₀ was observed.

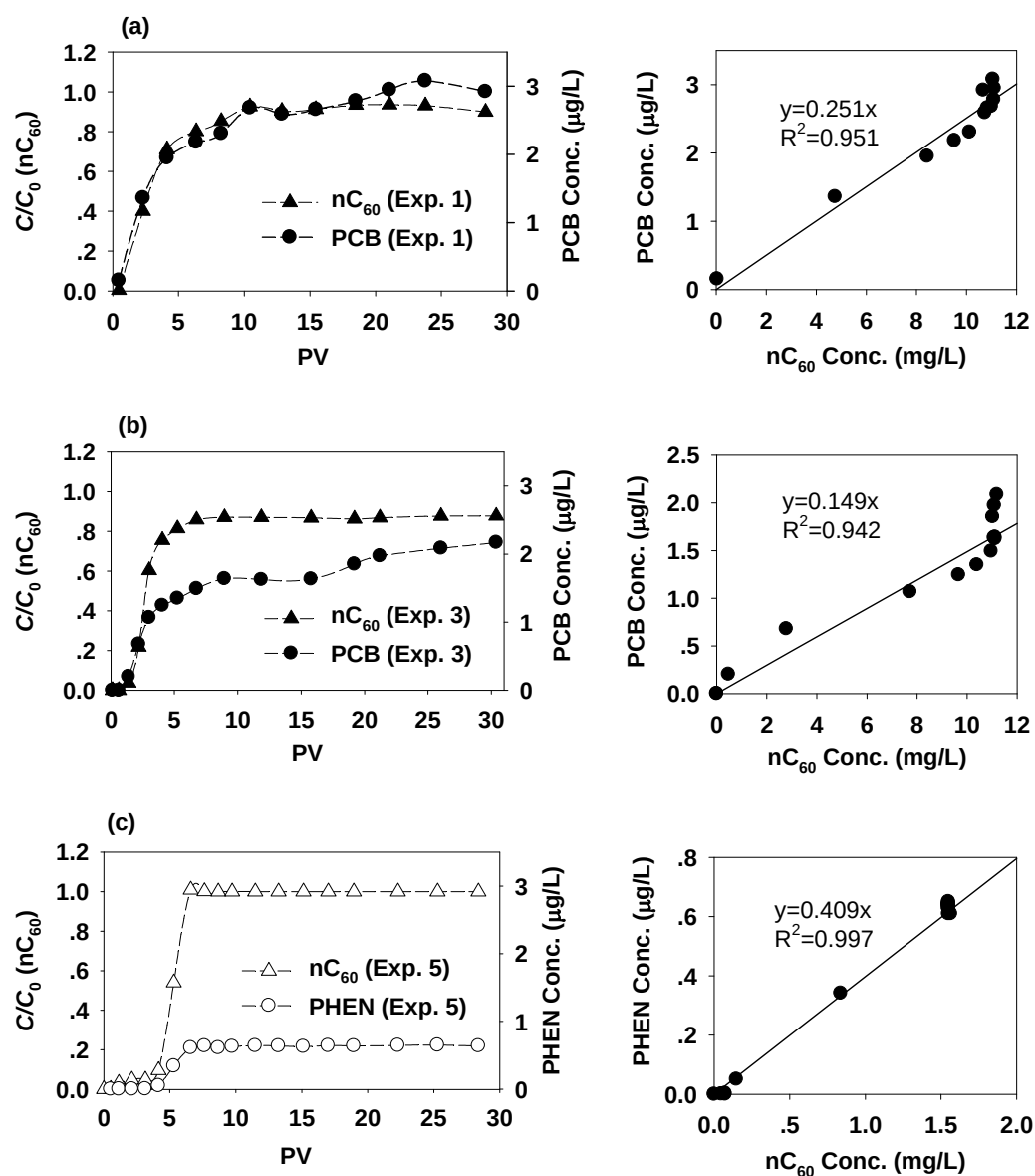


Figure S7. Comparison of nC_{60} concentration and PCB/phenanthrene (PHEN) concentration in the effluent. (a) Exp. 1; (b) Exp. 3; (c) Exp. 5. Note that PCB concentration in the effluent increased after approximately 15 PV in Figs. S7a and S7b, even though nC_{60} concentration remained relatively constant. A possible explanation is that the deposition of nC_{60} within the soil column covered some surface of the soil particles and therefore inhibited the sorption of dissolved PCB to soil.

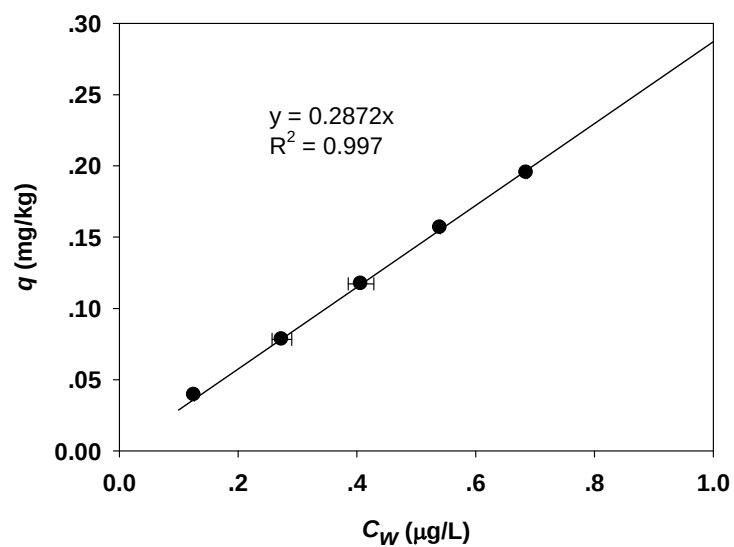


Figure S8. Sorption isotherm of PCB to Lula A.

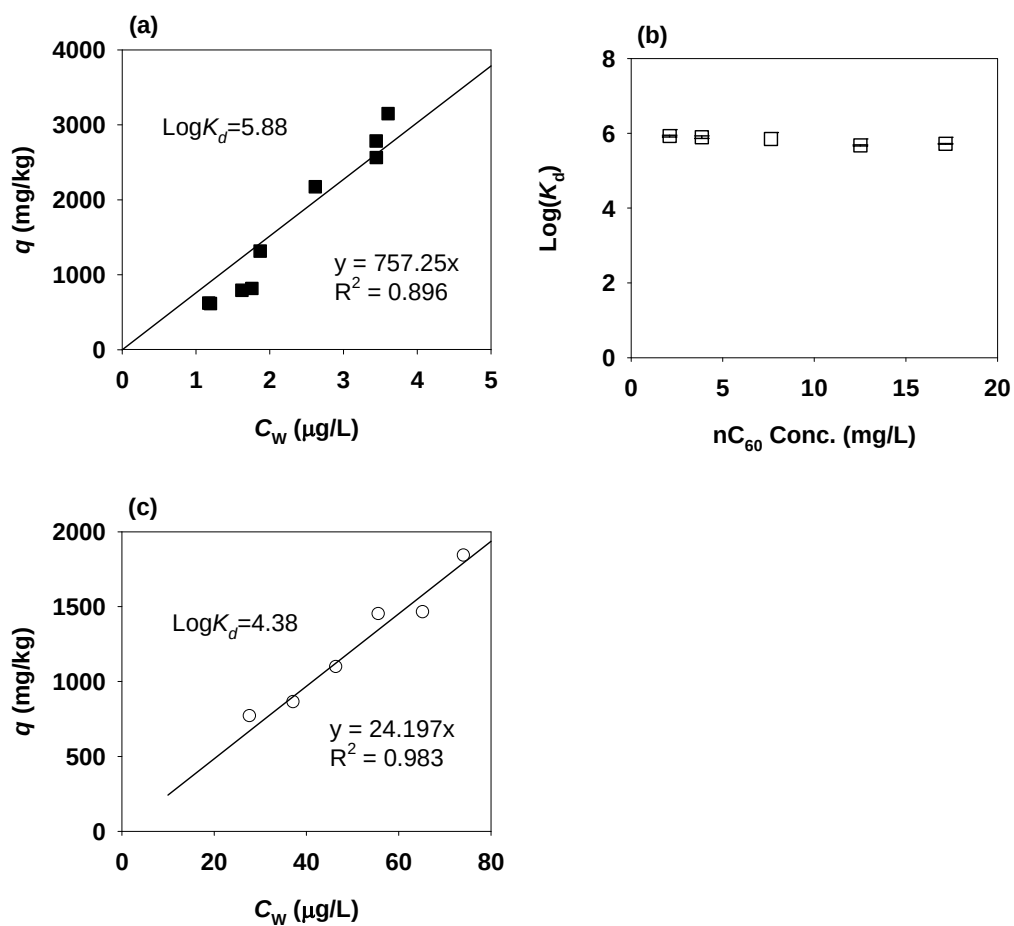


Figure S9. (a) Adsorption isotherm of PCB to nC₆₀; (b) partitioning coefficients of PCB ($C_0 = 12.4 \mu\text{g/L}$) with respect to different nC₆₀ concentrations; (c) adsorption isotherm of phenanthrene to nC₆₀ (2.0 mg/L). The freely dissolved concentrations of PCB/phenanthrene in the influents of the column experiments (Column 9, Table 1) are in general within the ranges of the equilibrium C_w values.

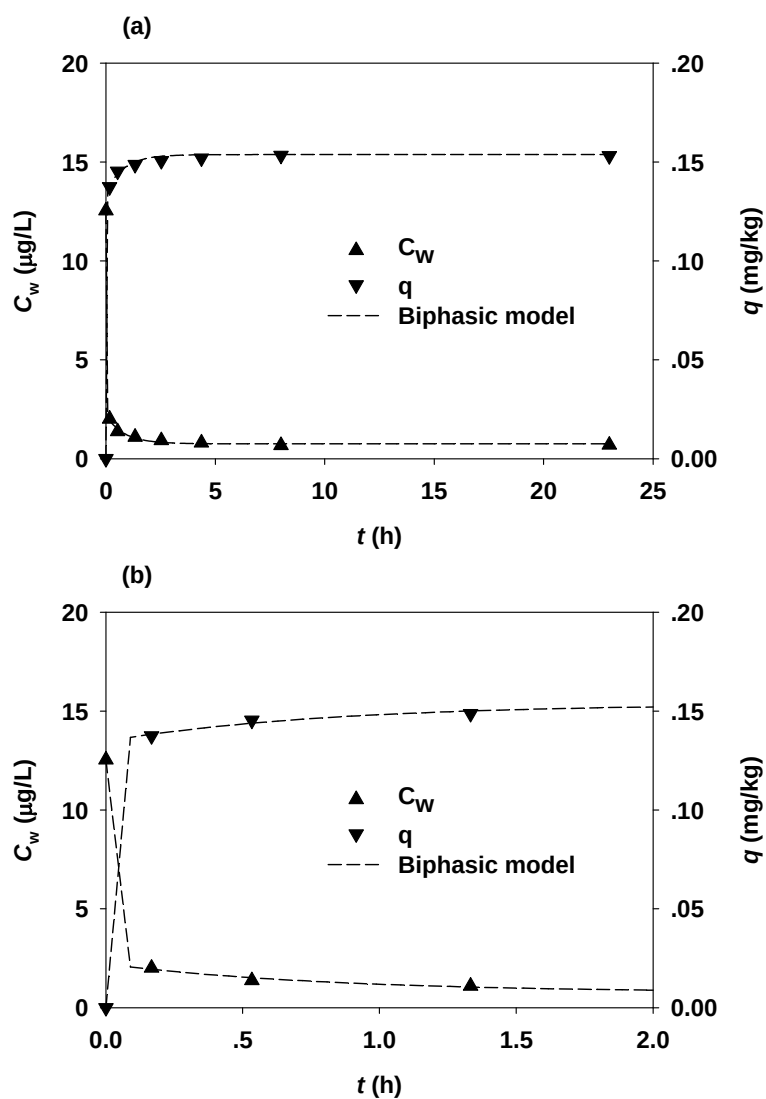


Figure S10. (a) Sorption kinetics of PCB to Lula A (0-24 h); (b) sorption kinetics of PCB to Lula A (0-2 h). Data was obtained by equilibrating 3 g soil in 40 mL PCB solution (initial concentration = 12.5 $\mu\text{g/L}$) and monitoring dissolved PCB concentration with time.

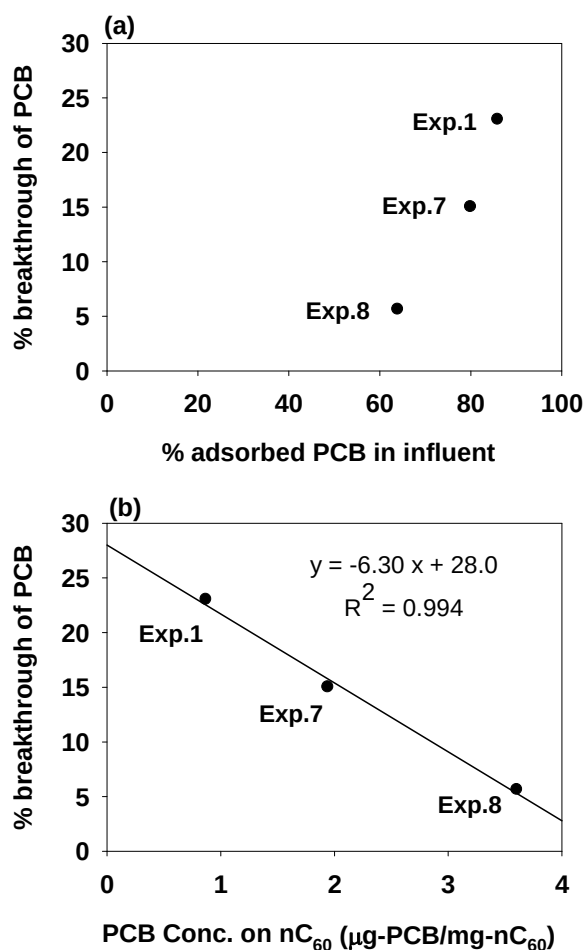


Figure S11. Comparison between percentage breakthrough of PCB with: (a) percentage of PCB mass in the adsorbed state in the influent (column 8 of Table 1); and (b) PCB concentration on nC_{60} ($\mu\text{g-PCB/mg-}nC_{60}$) in the influent. nC_{60} concentrations in the influent are: 12.2 mg/L (Exp. 1), 5.10 mg/L (Exp. 7) and 2.20 mg/L (Exp. 8).

$$\% \text{ breakthrough of PCB} = \frac{\text{PCB concentration in the effluent}}{\text{total PCB concentration in the influent}} \times 100\%$$

PCB concentration on nC_{60} in the influent =

$$\frac{(\text{total PCB concentration in the influent}) \times (\text{fraction of PCB mass in the adsorbed state})}{nC_{60} \text{ concentration in the influent}}$$

Table S1. Summary of Physicochemical Properties of nC₆₀ and DOMs.

Property	nC ₆₀	FA	HA	BSA
Molecular weight (Da)	-	800 ^a	1100 ^a	69000 ^b
Radius of particles/gyration (nm)	86	0.77 ^a	1.1 ^a	3.2 ^c
Zeta potential (mV)	-42	-	-	-
Isoelectric point	<1.0 ^d	-	-	4.8 ^b
Carbon mass percentage (%)	100	52 ^e	53 ^e	47 ^f
Surface charge at pH $\approx$ 7	negative	-	-	negative

^a from Ref. *S6*;^b from Ref. *S7*;^c from Ref. *S8*;^d from Ref. *S9*;^e from Ref. *S10*;^f from Ref. *S11*.

Table S2. Summary of the Parameters Used in the Calculation of R Values.

Exp. No.	Column properties			Influent properties					R^a
	Soil	ρ_b (g/cm ³)	θ (-)	Contaminant	nC ₆₀ /DOM	K_d (L/kg)	K_{DOM} (L/kg)	C_{DOM} (10 ⁻⁶ kg/L)	
1	Lula A	1.44	0.45	PCB	nC ₆₀	287	5.01E+5	12.2	130
2	Lula A	1.49	0.43	PCB	--	287	--	0	996
3	Lula A	1.37	0.48	PCB	nC ₆₀	287	5.01E+5	12.8	112
4	Lula A	1.41	0.46	PCB	--	287	--	0	881
5	Lula B	1.58	0.40	phenanthrene	nC ₆₀	32.7	2.51E+4	1.55	125
6	Lula B	1.41	0.46	phenanthrene	--	32.7	--	0	101
7	Lula A	1.46	0.44	PCB	nC ₆₀	287	7.94E+5	5.10	190
8	Lula A	1.47	0.45	PCB	nC ₆₀	287	7.94E+5	2.20	342
9	Lula A	1.39	0.47	PCB	HA	287	3.16E+4	22.6	496
10	Lula A	1.47	0.44	PCB	FA	287	3.16E+4	18.3	609
11	Lula A	1.40	0.46	PCB	BSA	287	3.16E+4	19.7	539

$$^a R = 1 + \frac{\rho_b}{\theta} \left(\frac{K_d}{1 + K_{DOM} \cdot C_{DOM}} \right).$$

Table S3. Fitted Biphasic Kinetic Parameters for PCB Desorption from nC₆₀ and PCB Sorption to Lula A.

Data set	Fitted parameters of two-compartment kinetic model ^a						
	F_1	k_1 (h ⁻¹)	F_2	k_2 (h ⁻¹)	q_e (mg/kg)	C_e (μg/L)	R^2
Desorption without Tenax ^b	0.683 (0.050)	3.07 (0.40)	0.315 (0.047)	0.170 (0.101)	229 (5.76)	--	0.999
Desorption with Tenax ^b	0.489 (0.018)	3.49 (0.26)	0.512 (0.016)	0.153 (0.011)	164 (1.92)	--	0.999
Sorption to Lula A ^c	0.876 (0.011)	99600 (0)	0.124 (0.022)	1.22 (0.05)	--	0.754 (0.103)	0.999

^a Desorption kinetic data was fitted with: $\frac{q - q_e}{q_0 - q_e} = F_1 \cdot e^{-k_1 \cdot t} + F_2 \cdot e^{-k_2 \cdot t}$, and sorption

kinetic data was fitted with $\frac{C - C_e}{C_0 - C_e} = F_1 \cdot e^{-k_1 \cdot t} + F_2 \cdot e^{-k_2 \cdot t}$. q , q_0 and q_e represent

adsorbed PCB concentrations at time t (h), time zero and desorption equilibrium; C ,

C_0 and C_t represent dissolved PCB concentrations at time t (h), time zero and

adsorption equilibrium; k_1 (h⁻¹) and k_2 (h⁻¹) represent apparent first-order rate

constants for the rapid and slow adsorption/desorption fractions, respectively; F_1 and

F_2 represent mass fractions associated with the fast and slow adsorption/desorption

fractions, respectively. Values in the parentheses indicate standard error associated

with the fitted parameters.

^b Data in Figure 4a was used.

^c Data in Figure S10 was used.

Literature cited

- (S1) Cheng, X. K.; Kan, A. T.; Tomson, M. B. Study of C₆₀ transport in porous media and the effect of sorbed C₆₀ on naphthalene transport. *J. Mater. Res.* **2005**, *20*, 3244–3254.
- (S2) Kretzschmar, R.; Sticher, H. Transport of humic-coated iron oxide colloids in a sandy soil: Influence of Ca²⁺ and trace metals. *Environ. Sci. Technol.* **1997**, *31*, 3497–3504.
- (S3) Yang, W. C.; Mang, J.; Zhang, C. D.; Zhu, L. Y.; Chen, W. Sorption and resistant desorption of atrazine in typical Chinese soils. *J. Environ. Qual.* **2009**, *38*, 171–179.
- (S4) Yang, W. C.; Duan, L.; Zhang, N.; Zhang, C. D.; Shipley, H. J.; Kan, A. T.; Tomson, M. B.; Chen, W. Resistant desorption of hydrophobic organic contaminants in typical Chinese soils: Implications for long-term fate and soil quality standards. *Environ. Toxicol. Chem.* **2008**, *27*, 235–242.
- (S5) Fortner, J. D.; Lyon, D. Y.; Sayes, C. M.; Boyd, A. M.; Falkner, J. C.; Hotze, E. M.; Alemany, L. B.; Tao, Y. J.; Guo, W.; Ausman, K. D.; Colvin, V. L.; Hughes, J. B. C₆₀ in water: Nanocrystal formation and microbial response. *Environ. Sci. Technol.* **2005**, *39*, 4307–4316.
- (S6) Averett, R. C.; Leenheer, J. A.; McKnight, D. M.; Thorn, K. A., *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*. U.S. Geological Survey Water-Supply Paper 2373. 1994; p 224.
- (S7) Sethuraman, A.; Han, M.; Kane, R. S.; Belfort, G. Effect of surface wettability on the adhesion of proteins. *Langmuir* **2004**, *20*, 7779–7788.
- (S8) Santos, S. F.; Zanette, D.; Fischer, H.; Itri, R. A systematic study of bovine serum albumin (BSA) and sodium dodecyl sulfate (SDS) interactions by surface tension and small angle X-ray scattering. *J. Colloid Interface Sci.* **2003**, *262*, 400–408.
- (S9) Bouchard, D.; Ma, X.; Isaacson, C. Colloidal properties of aqueous fullerenes: isoelectric points and aggregation kinetics of C₆₀ and C₆₀ derivatives. *Environ. Sci. Technol.* **2009**, *43*, 6597–6603.
- (S10) International Humic Substances Society website; (<http://www.ihss.gatech.edu/elements.html>).
- (S11) Saleh, N. B.; Pfefferle, L. D.; Elimelech, M. Influence of biomacromolecules and humic acid on the aggregation kinetics of single-walled carbon nanotubes. *Environ. Sci. Technol.* **2010**, *44*, 2412–2418.