Supporting Information

Chemicals

The BDE-209 standard was purchased from Sigma-Aldrich (St. Louis, MO, USA), and the BDE-77 and BDE-118 standards were obtained from Accustandard (New Haven, CT, USA). The n-hexane of GC grade was purchased from Concord Technology Co., Ltd. (Tianjin, China). The calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), ammonium sulfate ($(NH_4)_2SO_4$), and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) of analytical grade and sodium hydroxide (NaOH) of reagent grade were obtained from Tianjin Chemical Reagent Co., Ltd. (China). Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) of analytical grade was purchased from Yingda Rare Chemicals Plant (Tianjin, China). Potassium nitrate (KNO_3) was obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. (China). Sodium sulfate (Na_2SO_4) was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. (China). Hydrochloric acid (HCl, 37%) was purchased from Macklin Corporation (Shanghai, China).

Methods for characterization and analysis of soil properties

The basic physicochemical properties of soil were characterized for two soil cores. From each soil core (with a diameter of 7.5 cm and a length of 10 cm) in a pulse sampler, two smaller soil cores were obtained using a soil ring sampler, for computer tomography (CT) scanning and the analysis of bulk density, particle density, porosity, and hydraulic conductivity, respectively. The remaining scattered soil from each sample was used for X-ray diffraction (XRD) characterization and analysis of other physicochemical properties of soil, including soil texture, cation exchange capacity, organic carbon (OC), and black carbon (BC) contents.

The CT scanning was performed for the two ring samples (50.46 mm diameter × 50 mm length) on a high-performance compact industrial microfocus CT scanner (GE phoenix v|tome|x S, USA). The CT analysis parameters are as follows: tube potential at 180 kV, tube current at 180 μA, focus size of 1 μm, resolution of 28 μm, exposure time of 500 ms, source-to-detector distance of 40.81 mm, and voxel dimension of 1980×1980×2000. The other two ring samples with a known volume were dried in an oven at 105℃ until constant weight to measure the bulk density. Particle density of the soil samples was measured by the pycnometer method. The value of porosity was calculated from the bulk and particle densities according to Eq. (S1).

$$\text{porosity} = 1 - \frac{\text{bulk density}}{\text{particle density}} \quad , \quad (S1)$$

The saturated hydraulic conductivity was determined by the falling-head permeability test. The mineralogical composition of soil was determined by powder X-ray diffraction (XRD, SmartLab SE, Rigaku, Japan) with Cu Kα radiation (λ = 1.5418 Å). Soil texture was analyzed by the standard pipette method, with the mass fractions of the sand (0.02–2 mm), silt (0.002–0.02 mm), and clay (< 0.002 mm) fractions determined. Cation exchange capacity (CEC) was measured with the ammonium acetate method. The OC content was determined by potassium dichromate ($K_2Cr_2O_7$)-sulfuric acid oxidation under heating, and ferrous sulfate was used for titration of the excess $K_2Cr_2O_7$. The BC content was measured by a carbon/sulfur determinator (CS230, LECO Corporation, USA), after the organic carbon and carbonates in the soil samples were removed by $K_2Cr_2O_7$-sulfuric acid oxidation.

Preparation of simulated infiltration water stock solution

According to the pH, electrical conductivity, ionic composition and content of rainwater in Tianjin, China (Xiao et al., 2015), simulated infiltration water stock solution was prepared, which contained $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2SO_4$, $CaCl_2 \cdot 2H_2O$, KNO_3, $MgSO_4 \cdot 7H_2O$ and Na_2SO_4 (Table S1). The stock solution was diluted to obtain simulated infiltration water working solutions with different ionic strengths; and the pH was adjusted with 1 mol/L NaOH and HCl solutions to obtain simulated infiltration water solutions with different pH values.

Preparation of colloid suspension for calibrating measurement of colloidal concentration in effluents

The soil colloidal suspension used for calibration of effluent colloid concentration measurement was a colloidal fraction with hydrodynamic diameters below 1 μm extracted from surface soil collected immediately next to the site where the soil cores were collected, and detailed methods are described as follows:

The surface soil was air-dried at room temperature, passed through a 60-mesh sieve, and stored at 4℃ in the dark before use. First, 30 g of pretreated soil was added to approximately 1.0 L of simulated infiltration water (at pH 5.6 and an ionic strength of 1.2 mmol/L), and the soil suspension was vigorously stirred for 20 min and then settled for 30 min. The liquid was siphoned off with a pipe at a depth 10 cm below the surface to collect the soil colloidal fraction with hydrodynamic diameters < 10 μm (Duan et al., 2022).

Next, this soil colloidal fraction was decanted into 250 mL high-density polyethylene centrifuge bottles and centrifuged under 477 × g for 5 min. Approximately 2/3 of the supernatant was decanted carefully to obtain the stock suspension of soil colloids with hydrodynamic diameters < 1 μm soil (Liu et al., 2019), and the particle size distribution (Fig. S3) was confirmed by dynamic light scattering (DLS) using a particle size analyzer (Litesizer 500, Anton Paar, Austria). The mass concentration of colloids in the stock suspension was measured by drying an aliquot (20 mL) of the suspension in a pre-weighed beaker in an oven at 40℃ and weighing the mass of the dried colloid (Mohanty et al., 2014). Calibration standards for the UV-vis measurement was prepared by diluting the sonicated stock suspension in deionized water to desired concentrations (i.e., 2, 4, 8, 16, 32, and 50 mg/L).

Sample analysis by gas chromatography

The samples were analyzed on a gas chromatograph (Agilent 6890N, Agilent Technologies, USA) equipped with an electron capture detector (GC-ECD). A DB-5ms capillary column (15 m × 0.25 mm × 0.10 μm) was used for the separation of the analytes. Nitrogen was used as the carrier gas, at a flow rate of 3.7 mL/min. A splitless injection mode was used, and the injection volume was 5 μL. The injection port temperature was 280℃, and the detector temperature was 330℃. The temperature program started at 110℃ and held at this temperature for 1 min, then increased to 200℃ at a rate of 20℃/min, followed by an increase to 300℃ at a rate of 15℃/min, and a ramp to 315℃ at a rate of 20℃/min, at which the temperature was maintained for 4 min.

Table S1 Ionic molarity of simulated infiltration water stock solution.

Ionic composition	Molarity (mmol/L)
NO_3^-	9.25
SO_4^{2-}	8.48
Cl^-	12.25
K^+	1.35
Mg^{2+}	2.50
Na^+	2.05
Ca^{2+}	10.08
NH_4^+	9.90

Table S2 Basic physiochemical properties of the soil samples extracted from two soil cores.

Sample No.	Texture [a)] (%)			Bulk density (g/cm^3)	Particle density (g/cm^3)	Porosity (%)	*K* [b)] (m/s)	CEC [c)] (cmol/kg)	OC [d)] (g/kg)	BC [e)] (g/kg)
	Sand	Silt	Clay							
1	35.06	43.39	20.91	1.29	2.57	49.9	5.52×10^{-5}	18.1	6.96	0.22
2	42.54	38.77	17.91	1.48	2.65	44.3	4.67×10^{-5}	18.3	7.40	0.26

Notes: a) The total sum of the sand, silt, and clay fractions was 99.37% and 99.22%, respectively, for samples No. 1 and No. 2, with corresponding losses of 0.63% and 0.78%;

b) *K*: Saturated hydraulic conductivity;

c) CEC: Cation exchange capacity;

d) OC: Organic carbon;

e) BC: Black carbon.

Table S3 The flux, colloid concentration, hydrodynamic diameter, ζ-potential and BDE-209 concentration of effluent samples collected from undisturbed soil core leaching experiments at different ionic strengths.

Condition			Port ID	Flux (cm/h)	Colloid concentration (mg/L)	Hydrodynamic diameter (nm)	ζ-potential (mV)	BDE-209 concentration (ng/L)
Ionic strength (mmol/L)	pH	Darcy velocity (cm/h)						
10	5.6	1.5	1	18.39 ± 0.30	2.18 ± 0.21	399 ± 28	−5.25 ± 1.64	1.11
			5	7.32 ± 0.32	2.09 ± 0.44	394 ± 22	−6.70 ± 1.16	ND [a)]
			6	5.89 ± 0.19	1.81 ± 0.37	405 ± 24	−4.12 ± 1.14	ND
5	5.6	1.5	1	18.48 ± 0.24	1.73 ± 0.57	423 ± 30	−6.40 ± 1.64	ND
			5	8.19 ± 0.24	1.55 ± 0.28	402 ± 43	−5.33 ± 1.94	ND
			6	5.06 ± 0.38	3.75 ± 0.50	407 ± 43	−9.54 ± 1.82	ND
1	5.6	1.5	1	17.58 ± 0.38	5.68 ± 1.22	396 ± 44	−14.85 ± 1.92	1.21
			5	9.34 ± 0.64	5.20 ± 1.36	400 ± 28	−14.28 ± 1.72	1.69
			6	4.89 ± 0.41	6.82 ± 1.08	400 ± 25	−16.19 ± 2.69	ND
0.1	5.6	1.5	1	13.73 ±0.20	12.98 ± 1.20	408 ± 38	−17.44 ± 1.73	2.22
			5	10.43 ± 0.23	13.67 ± 0.44	406 ± 26	−17.15 ± 2.45	2.33
			6	6.20 ± 0.21	13.56 ± 0.31	374 ± 28	−17.05 ± 1.00	3.43
0.01	5.6	1.5	1	3.84 ± 0.12	10.84 ± 1.55	385 ± 31	−17.77 ± 1.40	ND
			2	18.07 ± 0.22	11.18 ± 1.70	356 ± 20	−16.41 ± 2.02	2.06
			5	6.15 ± 0.11	12.99 ± 1.92	361 ± 18	−18.26 ± 2.24	3.22
			6	3.81 ± 0.19	12.59 ± 1.37	347 ± 11	−20.16 ± 2.26	ND

Notes: a) ND (Not Detected) means concentration below the method detection limit.

Table S4 The flux, colloid concentration, hydrodynamic diameter, ζ-potential and BDE-209 concentration of effluent samples collected from undisturbed soil core leaching experiments at different pH values.

Condition			Port ID	Flux (cm/h)	Colloid concentration (mg/L)	Hydrodynamic diameter (nm)	ζ-potential (mV)	BDE-209 concentration (ng/L)
Ionic strength (mmol/L)	pH	Darcy velocity (cm/h)						
1	4.0	1.5	1	7.17 ± 0.48	4.66 ± 1.26	414 ± 35	−13.18 ± 3.89	ND [a)]
			2	15.30 ± 0.20	3.22 ± 0.49	399 ± 23	−10.66 ± 2.82	1.10
			5	5.20 ± 0.46	4.65 ± 0.82	420 ± 29	−16.07 ± 1.92	ND
			6	3.78 ± 0.37	5.84 ± 0.97	376 ± 27	−15.72 ± 2.40	ND
1	6.0	1.5	1	6.36 ± 0.60	3.41 ± 0.62	435 ± 42	−12.77 ± 1.81	ND
			2	15.39 ± 0.21	3.76 ± 0.49	436 ± 41	−12.52 ± 2.23	1.26
			5	6.09 ± 0.24	4.28 ± 0.60	451 ± 56	−15.90 ± 1.84	ND
			6	4.07 ± 0.28	5.79 ± 0.97	421 ± 30	−17.67 ± 1.03	ND
1	8.0	1.5	1	10.05 ± 0.14	3.60 ± 0.39	400 ± 34	−16.22 ± 1.02	ND
			2	16.02 ± 0.21	3.08 ± 0.34	405 ± 22	−14.11 ± 1.83	1.11
			5	5.74 ± 0.26	5.21 ± 0.76	410 ± 39	−14.67 ± 2.21	ND
1	10.0	1.5	1	9.41 ± 0.16	4.74 ± 0.24	411 ± 40	−13.18 ± 2.55	1.49
			2	15.87 ± 0.29	4.31 ± 0.62	403 ± 45	−10.24 ± 2.73	1.16
			5	6.45 ± 0.16	5.18 ± 0.65	424 ± 45	−11.40 ± 1.49	ND

Notes: a) ND (Not Detected) means concentration below the method detection limit.

Table S5 The flux, colloid concentration, hydrodynamic diameter, ζ-potential and BDE-209 concentration of effluent samples collected from undisturbed soil core leaching experiments at different flow rates.

Condition			Port ID	Flux (cm/h)	Colloid concentration (mg/L)	Hydrodynamic diameter (nm)	ζ-potential (mV)	BDE-209 concentration (ng/L)
Ionic strength (mmol/L)	pH	Darcy velocity (cm/h)						
1	5.6	1.5	1	9.35 ± 0.13	6.70 ± 0.88	416 ± 33	−13.55 ± 2.24	1.73
			2	15.58 ± 0.21	4.65 ± 0.52	418 ± 27	−12.72 ± 1.61	1.09
			5	6.83 ± 0.20	7.20 ± 0.77	410 ± 18	−13.63 ± 2.28	ND [a)]
1	5.6	3.0	1	11.98 ± 0.27	5.29 ± 0.59	443 ± 36	−14.70 ± 1.50	ND
			2	14.30 ± 0.52	4.95 ± 0.66	417 ± 34	−18.32 ± 2.35	ND
			4	25.62 ± 0.64	4.73 ± 0.57	418 ± 40	−14.70 ± 2.01	1.36
			5	12.21 ± 0.25	5.54 ± 1.01	412 ± 52	−15.65 ± 2.24	ND
1	5.6	4.5	1	9.99 ± 0.15	3.64 ± 1.69	436 ± 50	−14.62 ± 2.34	ND
			2	20.23 ± 1.06	3.16 ± 1.11	428 ± 40	−17.29 ± 2.03	ND
			4	57.14 ± 1.30	4.20 ± 1.12	419 ± 33	−15.26 ± 2.45	1.09
			5	8.50 ± 0.30	4.38 ± 0.93	420 ± 25	−13.09 ± 2.59	ND
1	5.6	6.0	1	13.77 ± 0.35	3.45 ± 0.45	446 ± 53	−9.37 ± 2.55	ND
			2	31.23 ± 2.01	3.58 ± 0.43	439 ± 46	−10.54 ± 1.81	ND
			4	72.29 ± 2.69	3.41 ± 0.54	441 ± 41	−8.69 ± 2.78	1.16
			5	10.59 ± 0.37	3.58 ± 0.60	423 ± 23	−9.24 ± 1.55	ND

Notes: a) ND (Not Detected) means concentration below the method detection limit.

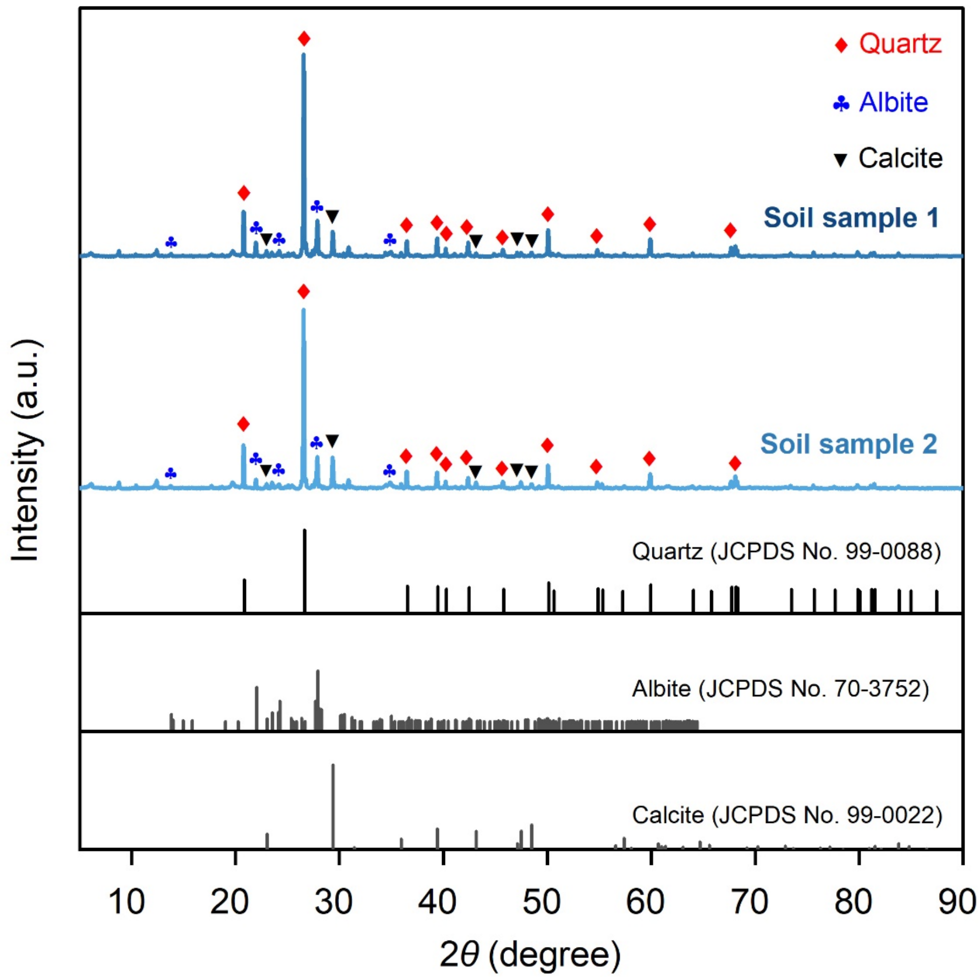

Fig. S1 X-ray diffraction patterns of two soil samples. The predominant mineral components of both samples were quartz, albite, and calcite.

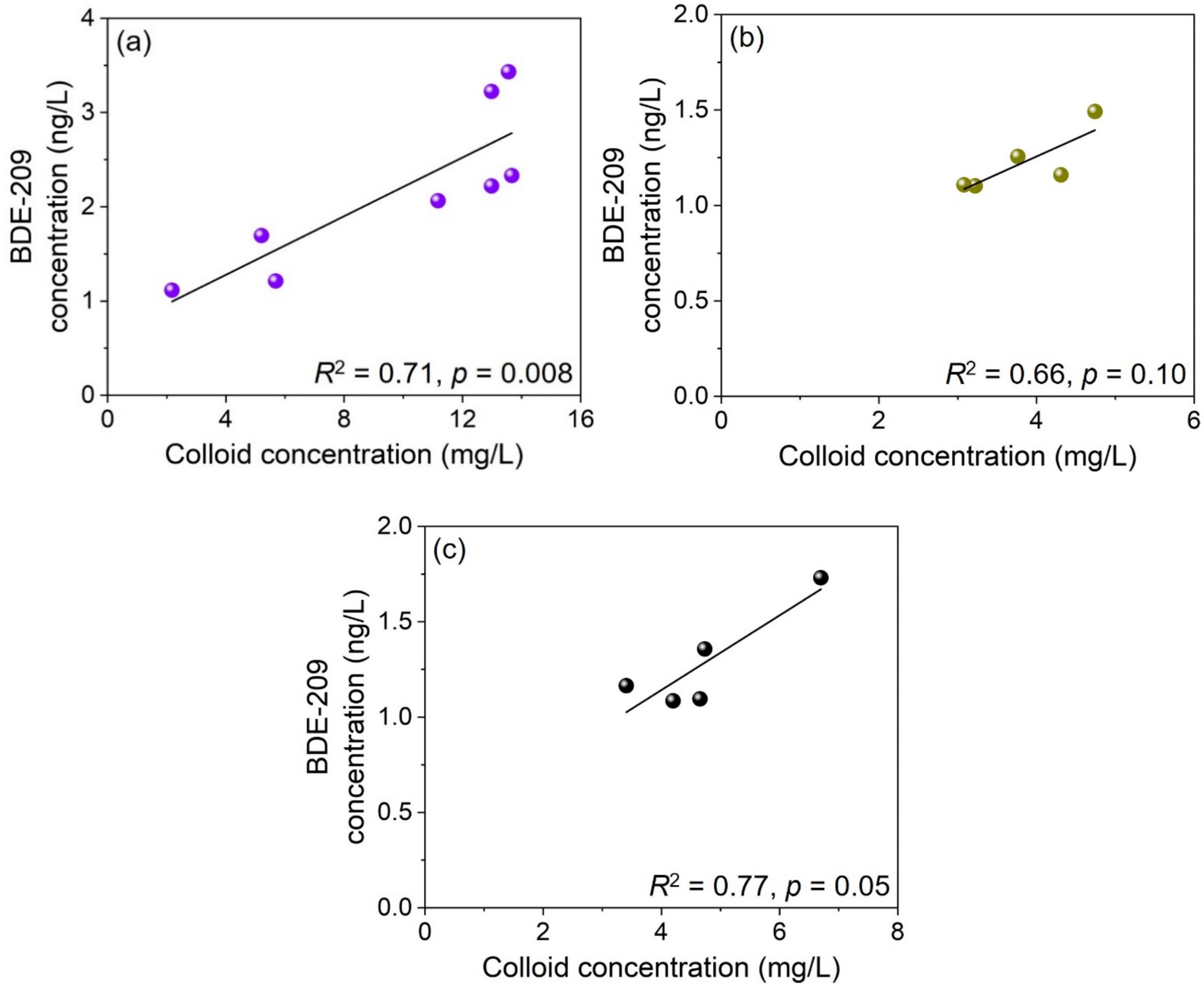

Fig. S2 Relationship between colloid and BDE-209 concentrations in leaching experiments with ionic strength perturbation (a), pH perturbation (b), and flow rate perturbation (c).

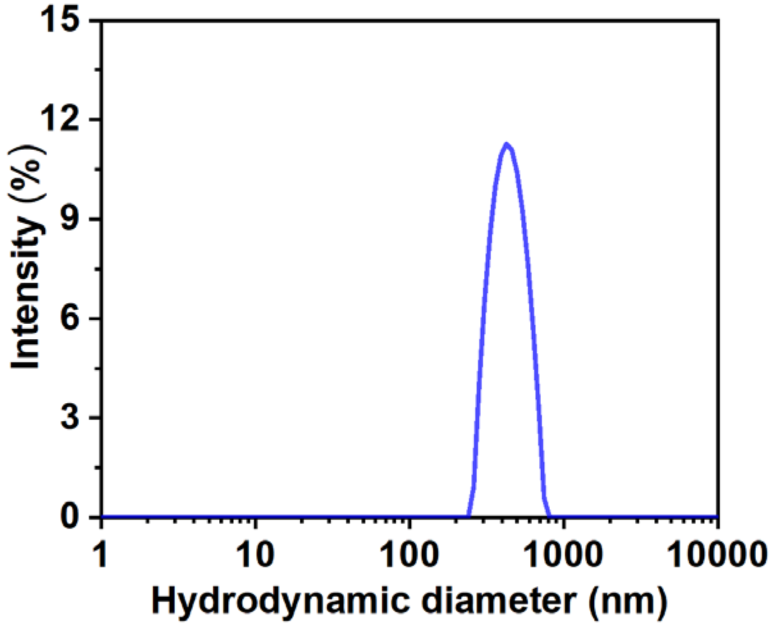

Fig. S3 Typical hydrodynamic diameter distribution of the extracted colloidal suspension measured by dynamic light scattering (DLS).

References

Duan L, Ying Y Q, Zhong J Y, Jiang C J, Chen W (2022). Key factors controlling colloids-bulk soil distribution of polybrominated diphenyl ethers (PBDEs) at an e-waste recycling site: Implications for PBDE mobility in subsurface environment. Science of the Total Environment, 819: 153080

Liu G N, Xue W, Wang J, Liu X H (2019). Transport behavior of variable charge soil particle size fractions and their influence on cadmium transport in saturated porous media. Geoderma, 337: 945–955

Mohanty S K, Saiers J E, Ryan J N (2014). Colloid-facilitated mobilization of metals by freeze-thaw cycles. Environmental Science & Technology, 48(2): 977–984

Xiao Z M, Li P, Sun R, Feng Y C, Liu B S, Qiao C M (2015). Characteristics and sources of chemical composition of atmospheric precipitation in Tianjin. Huanjing Kexue Yanjiu, 28(07): 1025–1030 (in Chinese)