

CONTENTS

The 5th International Symposium on Environmental Economy and Technology (ISEET-2012)

Sensitive voltammetric and amperometric responses of respiratory toxins at hemin-adsorbed carbon-felt Yasushi Hasebe, Yue Wang	1055
Destruction of 4-phenolsulfonic acid in water by anodic contact glow discharge electrolysis Haiming Yang, Baigang An, Shaoyan Wang, Lixiang Li, Wenjie Jin, Lihua Li	1063
Nitrous oxide emissions from black soils with different pH Lianfeng Wang, Huachao Du, Zuoqiang Han, Xilin Zhang	1071
Coulometric determination of dissolved hydrogen with a multielectrolytic modified carbon felt electrode-based sensor Hiroaki Matsuura, Yosuke Yamawaki, Kosuke Sasaki, Shunichi Uchiyama	1077
Palladium-phosphinous acid complexes catalyzed Suzuki cross-coupling reaction of heteroaryl bromides with phenylboronic acid in water/alcoholic solvents Ben Li, Cuiping Wang, Guang Chen, Zhiqiang Zhang	1083

Aquatic environment

Organic matter produced by algae and cyanobacteria: Quantitative and qualitative characterization Maud Leloup, Rudy Nicolau, Virginie Pallier, Claude Yéprémian, Geneviève Feuillade-Cathalifaud	1089
Effects of environmental factors on sulfamethoxazole photodegradation under simulated sunlight irradiation: Kinetics and mechanism Junfeng Niu, Lilan Zhang, Yang Li, Jinbo Zhao, Sidan Lv, Keqing Xiao	1098
Irrigation system and land use effect on surface water quality in river, at lake Dianchi, Yunnan, China Takashi Tanaka, Takahiro Sato, Kazuo Watanabe, Ying Wang, Dan Yang, Hiromo Inoue, Kunzhi Li, Tatsuya Inamura	1107
Temporal and spatial changes in nutrients and chlorophyll- <i>a</i> in a shallow lake, Lake Chaohu, China: An 11-year investigation Libiao Yang, Kun Lei, Wei Meng, Guo Fu, Weijin Yan	1117
Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and ³¹ P NMR Runyu Zhang, Liying Wang, Fengchang Wu, Baoan Song	1124
Effect of ammonium on nitrous oxide emission during denitrification with different electron donors Guangxue Wu, Xiaofeng Zhai, Chengai Jiang, Yuntao Guan	1131
Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite Ping Jing, Meifang Hou, Ping Zhao, Xiaoyan Tang, Hongfu Wan	1139
Differences in rheological and fractal properties of conditioned and raw sewage sludge Hui Jin, Yili Wang, Ting Li, Yujing Dong, Junqing Li	1145
Competitive sorption between 17 α -ethinyl estradiol and bisphenol A/ 4- <i>n</i> -nonylphenol by soils Jianzhong Li, Lu Jiang, Xi Xiang, Shuang Xu, Rou Wen, Xiang Liu	1154
Determination of estrogens and estrogenic activities in water from three rivers in Tianjin, China Kaifeng Rao, Bingli Lei, Na Li, Mei Ma, Zijian Wang	1164

Terrestrial environment

Adsorption and desorption characteristics of diphenylarsenicals in two contrasting soils Anan Wang, Shixin Li, Ying Teng, Wuxin Liu, Longhua Wu, Haibo Zhang, Yujuan Huang, Yongming Luo, Peter Christie	1172
Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from contaminated soils in Hai-Pu, Taiwan Jyoti Prakash Maity, Yuh Ming Huang, Cheng-Wei Fan, Chien-Cheng Chen, Chun-Yi Li, Chun-Mei Hsu, Young-Fo Chang, Ching-I Wu, Chen-Yen Chen, Jiin-Shuh Jean	1180

Environmental biology

Vertical diversity of sediment bacterial communities in two different trophic states of the eutrophic

Lake Taihu, China (**Cover story**)

Keqiang Shao, Guang Gao, Yongping Wang, Xiangming Tang, Boqiang Qin 1186

Abundance and diversity of ammonia-oxidizing archaea in response to various habitats

in Pearl River Delta of China, a subtropical maritime zone

Zhixin Li, Wenbiao Jin, Zhaoyun Liang, Yangyang Yue, Junhong Lv 1195

Environmental catalysis and materials

Effect of pretreatment on Pd/Al₂O₃ catalyst for catalytic oxidation of *o*-xylene at low temperature

Shaoyong Huang, Changbin Zhang, Hong He 1206

Efficient visible light photo-Fenton-like degradation of organic pollutants using *in situ* surface-modified

BiFeO₃ as a catalyst

Junjian An, Lihua Zhu, Yingying Zhang, Heqing Tang 1213

Basic properties of sintering dust from iron and steel plant and potassium recovery

Guang Zhan, Zhancheng Guo 1226

Degradation of direct azo dye by *Cucurbita pepo* free and immobilized peroxidase

Nabila Boucherit, Mahmoud Abouseoud, Lydia Adour 1235

Environmental analytical methods

Determination of paraquat in water samples using a sensitive fluorescent probe titration method

Feihu Yao, Hailong Liu, Guangquan Wang, Liming Du, Xiaofen Yin, Yunlong Fu 1245

Chemically modified silica gel with 1-f4-[(2-hydroxy-benzylidene)amino]phenylgethanone:

Synthesis, characterization and application as an efficient and reusable solid phase extractant
for selective removal of Zn(II) from mycorrhizal treated fly-ash samples

R. K. Sharma, Aditi Puri, Anil Kumar, Alok Adholeya 1252

Serial parameter: CN 11-2629/X*1989*m*207*en*P*25*2013-6



Competitive sorption between 17 α -ethinyl estradiol and bisphenol A/ 4-*n*-nonylphenol by soils

Jianzhong Li*, Lu Jiang, Xi Xiang, Shuang Xu, Rou Wen, Xiang Liu

School of Environment, Tsinghua University, Beijing 100084, China

Received 10 September 2012; revised 30 October 2012; accepted 06 November 2012

Abstract

The sorption of 17 α -ethinyl estradiol (EE2), bisphenol A (BPA), and 4-*n*-nonylphenol (NP) in single systems and the sorption of EE2 with different initial aqueous concentrations of BPA or NP were examined using three soils. Results showed that all sorption isotherms were nonlinear and fit the Freundlich model. The degree of nonlinearity was in the order BPA (0.537–0.686) > EE2 (0.705–0.858) > NP (0.875–0.951) in single systems. The isotherm linearity index of EE2 sorption calculated by the Freundlich model for Loam, Silt Loam and Silt increased from 0.758, 0.705 and 0.858, to 0.889, 0.910 and 0.969, respectively, when BPA concentration increased from 0 to 1000 $\mu\text{g/L}$, but the effect of NP was comparably minimal. Additionally, EE2 significantly suppressed the sorption of BPA, but insignificantly suppressed that of NP. These findings can be attributed to the difference of sorption affinity of EE2, NP and BPA on the hard carbon (e.g., black carbon) of soil organic matter that dominated the sorption in the low equilibrium aqueous concentration range of endocrine-disrupting chemicals (EDCs). Competitive sorption among EDCs presents new challenges for predicting the transport and fate of EDCs under the influence of co-solutes.

Key words: competitive sorption; 17 α -ethinyl estradiol; endocrine-disrupting chemicals; distributed reactivity model; black carbon

DOI: 10.1016/S1001-0742(12)60165-X

Introduction

Endocrine-disrupting chemicals (EDCs) affect the growth and reproduction of many species even at very low concentrations (nanograms per liter) (Hanselman et al., 2003; Xu et al., 2011). The past several decades have witnessed increasing research interest in estrogens and phenolic endocrine disruptors, such as 17 α -ethinyl estradiol (EE2), bisphenol A (BPA), and 4-*n*-nonylphenol (NP) (Paseiro-Losada et al., 1993; Xu et al., 2011). EE2, BPA, and NP are mainly used in oral contraceptives, in food packaging and cosmetic plasticizers, and as the degradation product of alkylphenol ethoxylates (which are widely used surfactants), respectively (Ying et al., 2002). Their concentrations range from a few nanograms per liter to micrograms per liter in wastewater and have even been found to reach 1000 $\mu\text{g/kg}$ in dry, treated biosolids (Citulski and Farahbakhsh, 2010; Pan et al., 2009).

EE2, BPA, and NP enter soils as part of the mechanism for reusing wastewater-treatment plant effluents for ecological compensation of rivers and lakes or farmland irrigation and land application of municipal biosolids

and animal waste. Thus, their sorption behavior in soils is essential to their fate, transport, and environmental risks (Citulski and Farahbakhsh, 2010; Pan et al., 2009). Much research has focused on the sorption behavior and mechanism of EDCs in single-solute systems. The organic matter content and specific surface area (SSA) of soils and sediments have been reported to be correlated with sorption affinity between sorbents and sorbates (Bonin and Simpson, 2007; Mashtare et al., 2011). In addition, the high correlation between the sorption affinity and octanol-water partition coefficients of EDCs suggests that hydrophobic partitioning is the dominant mechanism, but their polarities indicate that hydrophobic interaction is not the sole mechanism of sorption (Lee et al., 2003). Sun et al. (2010) reported that nonhydrolyzable carbon (NHC) and black carbon (BC) have greater adsorption capacity and a lower nonlinearity coefficient for BPA than EE2 due to its smaller molecular diameter and the stronger π - π bond formed with NHC and BC. Similar results have been reported by Hou et al. (2010).

Several types of EDCs have been widely detected in various waters worldwide, and they may also compete with one another for adsorption (Citulski and Farahbakhsh, 2010; Pan et al., 2009). In addition, comparing sorption

* Corresponding author. E-mail: lijianzhong03@163.com

characteristics between single- and multi-solute systems can provide further information about their sorption mechanisms. However, the sorption of EDCs in multi-solute systems remains largely unexplored. Yu et al. (2004) and Bonin and Simpson (2007) reported that estrogen sorption on soils is affected not only by hydrophobic interactions but also by hydrogen and covalent bonds and that the degree of competitive sorption varies with the organic carbon (OC) content in a multi-solute system. Pan et al., (2008a) found that BPA significantly affects EE2 sorption on carbon nanomaterials (CNMs) because of the fit of the BPA butterfly structure on the CNM surface. However, to the best of our knowledge, data on competitive sorption between estrogen and endocrine-disrupting phenolic compounds (BPA or NP) in soil has not been reported.

The objectives of this work are to confirm whether BPA or NP competes with EE2 for sorption on soils and study the extent of the competitive sorption, and to determine possible mechanisms for EDC sorption on soils.

1 Materials and methods

1.1 Chemicals and soil samples

EE2 (99%), BPA ($\geq 99\%$), and NP (99.9%) were obtained from Sigma-Aldrich (USA). Some of their physical and chemical properties are shown in **Table S1**, and their structures are provided in **Figs. S1** and **S2**. Ultra-pure water was produced with a Milli-Q system (Millipore, USA). HPLC-grade methanol (MeOH) and acetonitrile were purchased from Fisher (USA). Stock solutions (1 g/L) of individual compounds were prepared in MeOH and stored at -20°C in the dark.

Three soil samples, named Loam, Silt Loam, and Silt, according to their soil texture, were collected using a stainless steel grab sampler in May 2010 from three areas possibly affected by sewage or reclaimed water (**Table S2**). After collection, all samples were freeze-dried for 48 hr, crushed to pass through a 2-mm mesh sieve, and then thoroughly mixed. The total organic carbon (TOC) and BC contents were determined using the method described by Gustafsson et al. (1997).

The SSA and pore volume were analyzed by N_2 adsorption with an Autosorb-1-C system (Quantachrome, USA) and determined using the Brunauer-Emmett-Teller equation with multipoint adsorption isotherms. The major physicochemical properties of the sorbents are shown in

Table 1.

To obtain soil organic matter (SOM) fractions by demineralization, we treated all soil samples with HCl and HCl-HF to remove mineral substances (Gelinas et al., 2001). The Fourier transform infrared spectra of the SOM samples were obtained using an FTIR-5300 spectrometer (Jasco, Japan).

1.2 Single- and binary-solute sorption experiments

The experiments were conducted in glass vials prebaked at 450°C for 4 hr and sealed with screw caps to avoid evaporation loss. All sorption isotherms in single- and binary-solute systems were obtained using batch equilibration at $(20 \pm 1)^{\circ}\text{C}$. Aqueous solutions of EDCs ranging from 10 $\mu\text{g/L}$ to their solubility limits were obtained by diluting the stock solutions using a background solution containing 0.01 mol/L CaCl_2 in ultra-pure water with 200 mg/L NaN_3 as biocide. The MeOH content in the solution was controlled under 0.1% during dilution. According to the results of preliminary experiments, the soil/solution ratios in Loam, Silt Loam, and Silt were set to 1:5, 1:10, and 1:25 (g/mL), respectively, for EE2; 1:5, 1:5, and 1:16 (g/mL), respectively, for BPA; and 1:50, 1:80, and 1:350 (g/mL), respectively, for NP. In the single-solute systems, more than 20 initial concentrations in the range of 10 $\mu\text{g/L}$ to near their solubility limits were set to meet the requirements of Dubinin-Ashtakhov (DA) model fitting. In the binary-solute systems, 14 samples with the initial concentrations of EE2 from 10 $\mu\text{g/L}$ to its solubility limit were set; BPA and NP were added to reach the concentrations of 250, 500, and 1000 $\mu\text{g/L}$, respectively. The preliminary results indicated that equilibrium was achieved within 2 days. Considering the possibility of a slow adsorption process, suspensions were shaken for 7 days to ensure complete equilibrium in the dark at 120 r/min and 20°C (Pignatello and Xing, 1996). Each vial was left to stand for 2 days, and 2 mL of the supernatants was analyzed. This sedimentation method proved to be equivalent to the method of centrifugation at 3000 r/min for 30 min, and the same results were obtained by Yu and Huang (2005).

Each sample was prepared in triplicate. Loss of sorbate was less than 0.5%, as tested by adding standard solution to glass vials without soil. Therefore, volatilization and adsorption by the glass could be considered negligible. Potential biodegradation of EDCs was evaluated following the procedure described by Yu et al. (2004), and no

Table 1 Physicochemical properties of the three soil samples

Sorbent	TOC (g/kg)	BC ^a (%)	SSA (m ² /g)	Pore volume (cm ³ /g)	pH	CEC (mmol/kg)	Soil texture ^b
Loam	19.1	15.6	22.16	0.026	8.24	276	48.1/34.0/17.9
Silt Loam	20.1	18.1	29.07	0.041	7.93	230	13.2/77.6/9.2
Silt	27.9	3.6	23.41	0.035	6.84	224	8.3/83.0/8.7

^a BC content based on TOC; ^b weight percentage of sand/silt/clay.

measurable EDC degradation was observed in the systems within 10 days.

1.3 Detection of EE2, BPA, and NP

In total, 0.4 mL supernatant of each sample was filtered through 0.22- μm nylon filters and then completely mixed with 1.6 mL of MeOH. The composition of the mixture was determined by a Waters Acquity UPLC system (Waters Corporation, USA) equipped with Acquity UPLC BEH C18 column (100 mm \times 2.1 mm, particle size 1.7 μm) and a Quattro Premier XE tandem quadrupole mass spectrometer (Waters, USA) equipped with an electrospray ionization source.

The mobile phase comprised a binary mixture of solvent A (acetonitrile) and solvent B (ultra-pure water) at a constant flow of 0.30 mL/min. The gradient started with 10% solvent A, linearly ramped to 36% solvent A in 0.5 min, remained unchanged for 5.5 min, linearly increased to 90% solvent A in 1 min, and was then maintained for 3 min. At the end of the chromatogram, the column was allowed to equilibrate for 2 min with the initial composition of the mobile phase. The total running time was 12 min. The retention time for EE2, BPA, and NP were 5.75, 3.93, and 8.66 min, respectively. The ionization of the three selected EDCs was realized in the negative mode (ESI⁻). The parent ion (m/z), quantification ion (m/z), cone voltage (V), collision energy (eV) and dwell time (sec) were 295.1, 158.9, 37, 18 and 0.1 for EE2, 227.1, 212.0, 37, 18 and 0.1 for BPA, and 219, 105.9, 40, 20 and 0.1 for NP, respectively. Calibration curves were established following the method of Zhang et al. (2010) to avoid any matrix effects. The detection limit was 0.1 $\mu\text{g/L}$ for each analyte. The linear range was 0.1–1000 $\mu\text{g/L}$ ($R^2 > 0.999$). All samples were diluted within this range before analysis.

1.4 Sorption isotherm model

The Freundlich model was used to fit data measured for single-solute systems and for EE2 sorption of binary-solute systems, according to Eq. (1):

$$\log q_e = \log K_F + n \log C_e \quad (1)$$

where, q_e ($\mu\text{g/g}$) is the equilibrium concentration of solute sorbed on the soil matrix, C_e ($\mu\text{g/L}$) is the equilibrium aqueous concentration, K_F ($(\mu\text{g/g})/(\mu\text{g/L})^n$) is the Freundlich sorption coefficient, and n is the isotherm linearity

index.

The Polanyi theory was extended for use in the sorption of partially miscible solutes from dilute solution onto solid surfaces (Sun et al., 2010). The DA model, a form of the Polanyi theory, was also used to fit the sorption isotherms for single-solute systems, according to Eq. (2):

$$\log q_e = \log Q^0 - (\varepsilon/E)^b \quad (2)$$

where, Q^0 ($\mu\text{g/g}$) is the saturated sorption capacity; E (kJ/mol) is the correlating divisor; b is a fitting parameter; ε (kJ/mol) is the effective sorption potential, as in Eq. (3):

$$\varepsilon = RT \ln(C_S/C_e) \quad (3)$$

where, R (8.314×10^{-3} kJ/(mol·K)) is the universal gas constant; T (K) is the absolute temperature; and C_S ($\mu\text{g/L}$) is the water solubility at 20°C (Table S1).

The single-point distribution coefficients (K_D , Eq. (4)) at four levels of C_e and the OC-normalized sorption distribution coefficient (K_{OC} , Eq. (5)) at $C_e = 0.01C_S$ were calculated from the Freundlich parameters and DA model to compare sorption equilibria among different systems:

$$K_D = q_e/C_e \quad (4)$$

$$K_{OC} = K_D/f_{OC} \quad (5)$$

where, f_{OC} is total organic carbon in soil.

2 Results and discussion

2.1 Sorption equilibria of single-solute systems

The sorption isotherms for NP, EE2, and BPA in the three soils in single-solute systems are shown in Fig. 1. The Freundlich model and DA models fit quite well with the measured data ($R^2 \geq 0.995$) (Tables S3 and S4). The adsorption capacity of soil for EDCs increased with increasing TOC. With EE2 sorption as an example, in the C_e range of 7.6–3800 $\mu\text{g/L}$ (0.001–0.5 C_S), q_e ranged from 0.162 to 18.0 $\mu\text{g/g}$ for Loam (TOC = 1.91%), from 0.327 to 26.1 $\mu\text{g/g}$ for Silt Loam (TOC = 2.01%), and from 0.331 to 68.5 $\mu\text{g/g}$ for Silt (TOC = 2.79%).

The sorption affinity for EDCs was in the order: BPA < EE2 < NP in all sorbents according to the calculation results of the Freundlich model. It followed the same order

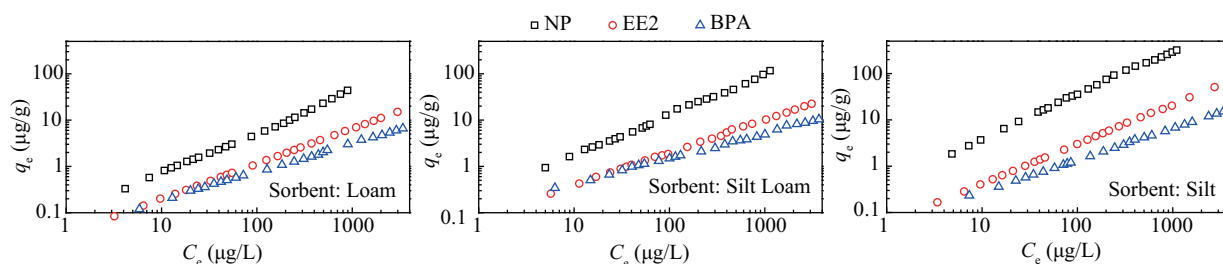


Fig. 1 Single-solute sorption isotherms measured for the three soil samples (20°C).

as their logKOW, which is in accordance with previous research (Lee et al., 2003; Takigami et al., 2011). All the isotherms were nonlinear. The degree of nonlinearity was in the order: BPA (0.537–0.686) > EE2 (0.705–0.858) > NP (0.875–0.951). The sorption isotherms measured for Silt Loam with the highest BC content exhibited the smallest n values (0.705, 0.537, and 0.875 for EE2, BPA, and NP, respectively).

2.2 Effects of BPA and NP on EE2 sorption

In the binary-solute systems, the effect of co-solutes on EE2 sorption depended on their properties, initial concentration, and $C_e(\text{EE2})$. As shown in **Fig. 2a** and **Table S3**, the presence of BPA suppressed EE2 sorption on Loam when $C_e(\text{EE2})$ was lower than 1000 $\mu\text{g/L}$. When $C_0(\text{BPA})$ increased from 0 to 1000 $\mu\text{g/L}$, the $\log K_F$ value of EE2 isotherms for Loam decreased from -1.458 to -1.884 . The single-point K_D values calculated at a given C_e level could better reflect the competitive effect of BPA on the capacity of the EE2 sorption isotherms. As $C_0(\text{BPA})$ increased from 0 to 250 $\mu\text{g/L}$, the $K_D(\text{EE2})$

values decreased from 21.3 to 18.2, from 12.2 to 11.2, and from 7.02 to 6.88 mL/g at the $C_e(\text{EE2})$ values of 7.6, 76, and 760 $\mu\text{g/L}$, respectively. Meanwhile, the n value increased from 0.758 to 0.788. These results indicate that the competitive effect decreased as EE2 concentration increased. A much stronger competitive effect by BPA was observed in binary-solute systems with $C_0(\text{BPA})$ at 500 and 1000 $\mu\text{g/L}$. As $C_0(\text{BPA})$ increased from 500 to 1000 $\mu\text{g/L}$, the $K_D(\text{EE2})$ values decreased from 14.0 to 10.6 mL/g and from 9.2 to 8.1 mL/g at the $C_e(\text{EE2})$ values of 7.6 and 76 $\mu\text{g/L}$, respectively, whereas the n value increased from 0.832 to 0.889. In summary, the linearity index n of isotherms of EE2 increased with increasing BPA initial concentration. Similar results have been widely reported, especially in research on hydrophobic organic contaminant sorption on soils (Weber et al., 2002; Zhang et al., 2010).

The presence of BPA enhanced the sorption of EE2 on Loam when $C_e(\text{EE2})$ exceeded 1000 $\mu\text{g/L}$, as shown in **Fig. 2a**, as opposed to the observations in the low C_e range. According to the calculation from the Freundlich parameters, $K_D(\text{EE2})$ increased from 4.76 to 5.12 mL/g

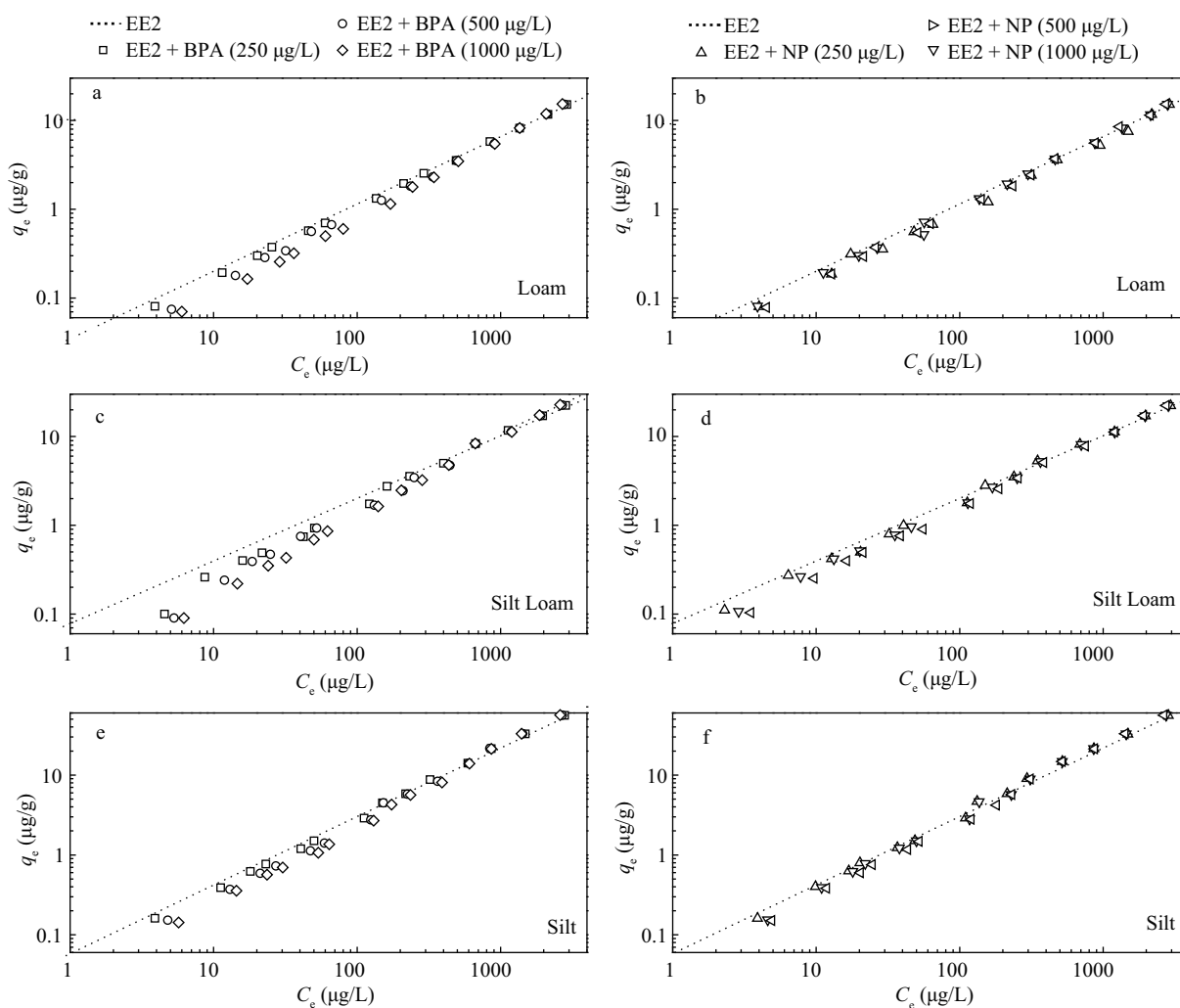


Fig. 2 Bisolute sorption isotherms measured for the three soil samples (20°C).

Supporting materials

Three demineralization samples (DM1, 2, 3) extracted from Loam Silt, Loam, and Silt, respectively, showed very typical infrared spectra of Soil organic matter (SOM), containing aliphatic and aromatic compositions, as indicated by hydroxyl group at around 3430 cm^{-1} , aliphatic C–H stretching at 2960 and 2930 cm^{-1} , alicyclic C–H stretching at 2852 cm^{-1} , aromatic carbonyl/carboxyl C=O groups at around 1720 cm^{-1} , aromatic C=C at around 1640 cm^{-1} , aromatic C=C stretching at around 1640 cm^{-1} , C–H in plane deformation at 1400 cm^{-1} , C–H stretching and OH deformation of COOH at around 1230 cm^{-1} , and C–O stretching at around 1240 and 1040 cm^{-1} (Kang and Xing, 2005; Qing and Lei, 2007; Sun et al., 2010; Wen et al., 2007). A noticeable absorbance of aromatic carbon was observed for DM 1, 2 but not for DM 3. The

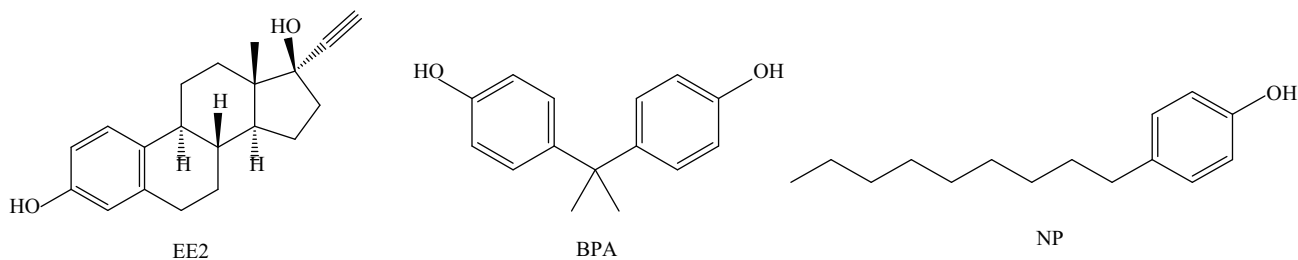


Fig. S1 Structure of EE2, BPA and NP

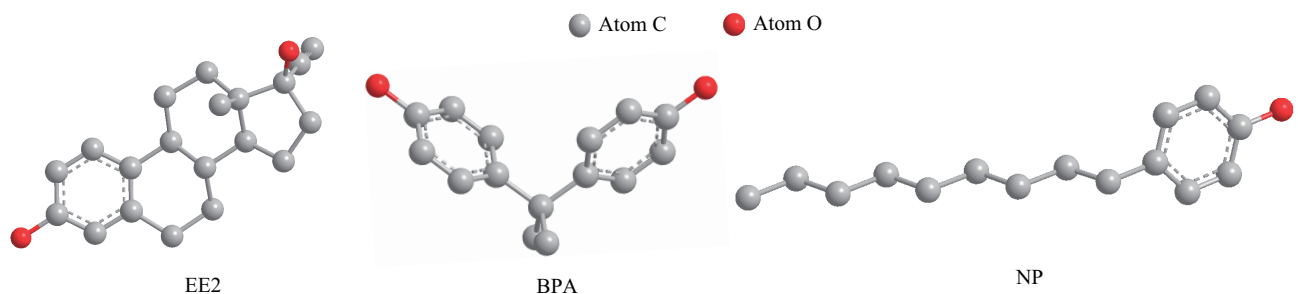


Fig. S2 Optimized 3-dimensional structures EE2, BPA and NP with total energy of 28.4088, 3.3870 and 3.8349 kcal/mol based on minimized steric energy. Steric energy includes stretch, bend, stretch-bend, torsion, non-1,4 van der Waals, 1,4 van der Waals, and dipole/dipole energies, and was calculated using molecular mechanics theory (MM2).

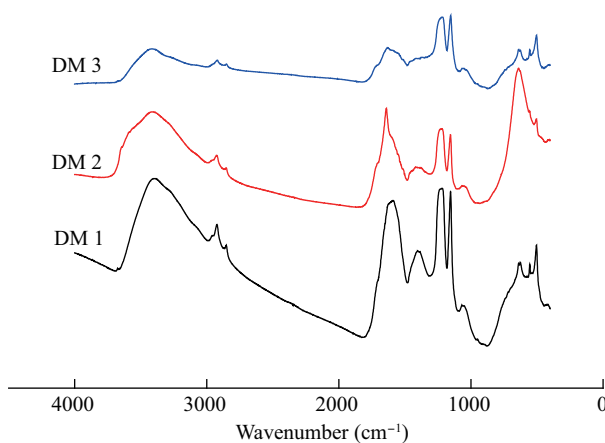


Fig. S3 Fourier transform infrared (FTIR) spectra of soil samples (DM 1–3 represent the SOM extracted from Loam, Silt Loam and Silt, respectively).

Table S1 4-*n*-Nonylphenol (NP), 17 α -ethinyl estradiol (EE2) and bisphenol A (BPA) properties

Property	NP	EE2	BPA
Chemical formula	C ₁₅ H ₂₄ O	C ₂₀ H ₂₄ O ₂	C ₁₅ H ₁₆ O ₂
Molecular weight	220.35	296.4	228.28
Solubility (C _s , mg/L)	1.66 ^a	7.6 ^b	380 ^b
log K_{OW}	5.76 ^a	4.15 ^b	2.2 ^b
pK _a	10.25 ^a	10.4 ^b	9.59 ^b
Critical molecular diameter (nm)	4.3 ^c	6.0 ^d	4.3 ^d
H-bonding parameter acceptor ^e	1 ^e	2 ^d	2 ^d
H-bonding parameter donor ^e	1 ^e	2 ^d	2 ^d

^aYamamoto et al., 2003; ^bPan et al., 2008; ^ccritical molecular diameters were calculated using PC Spartan, 2002; ^dSun et al., 2010; ^eH-bonding parameter acceptor and H-bonding parameter donor for NP were calculated as described by Xia et al. 1998.

Table S2 Sources of the three soils and their land use types

Sorbents	Source	Land use type
Loam	Beijing, 39°41'18''N, 116°29'56''E	farmland (maize)
Silt Loam	Tianjin, 39°16'56''N, 117°34'21''E	wetlands
Silt	Jiangsu Province, 31°52'53''N, 119°55'19''E	farmland (rice)

Table S3 Freundlich isotherm parameters and calculated single-point distribution coefficients (K_D) for the samples

Sorbent	Solute	$\log K_F$	n (($\mu\text{g/g}$)/($\mu\text{g/L}$) ^{<i>n</i>})	R^2	N^a	K_D (mL/g)			
						$C_e=0.001C_S$	$C_e=0.01C_S$	$C_e=0.1C_S$	$C_e=0.5C_S$
Loam	BPA	-1.345 \pm 0.012 ^b	0.613 \pm 0.006	0.998	25	4.54	1.87	0.766	0.411
	NP	-1.034 \pm 0.021	0.883 \pm 0.010	0.997	24	87.2	66.6	50.9	42.2
	EE2	-1.458 \pm 0.002	0.758 \pm 0.001	1.000	25	21.3	12.2	7.02	4.76
	EE2+BPA(250 $\mu\text{g/L}$)	-1.552 \pm 0.007	0.788 \pm 0.003	1.000	14	18.2	11.2	6.88	4.90
	EE2+BPA (500 $\mu\text{g/L}$)	-1.700 \pm 0.017	0.832 \pm 0.007	0.999	14	14.0	9.2	6.05	4.51
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.884 \pm 0.017	0.889 \pm 0.007	0.999	14	10.6	8.1	6.17	5.12
	EE2+NP (250 $\mu\text{g/L}$)	-1.532 \pm 0.031	0.782 \pm 0.013	0.996	14	19.5	11.3	6.62	4.54
	EE2+NP (500 $\mu\text{g/L}$)	-1.568 \pm 0.025	0.793 \pm 0.011	0.998	14	17.9	11.0	6.76	4.81
	EE2+NP (1000 $\mu\text{g/L}$)	-1.632 \pm 0.018	0.816 \pm 0.008	0.999	14	16.2	10.5	6.82	5.04
Silt Loam	BPA	-0.901 \pm 0.016	0.537 \pm 0.007	0.997	25	8.91	4.33	2.10	1.27
	NP	-0.516 \pm 0.018	0.875 \pm 0.009	0.998	24	286	215	161	132
	EE2	-1.107 \pm 0.010	0.705 \pm 0.004	1.000	23	43.0	21.8	11.0	6.87
	EE2+BPA (250 $\mu\text{g/L}$)	-1.417 \pm 0.037	0.812 \pm 0.017	0.995	14	26.1	16.9	11.0	8.12
	EE2+BPA (500 $\mu\text{g/L}$)	-1.542 \pm 0.039	0.850 \pm 0.017	0.995	14	21.2	15.0	10.6	8.33
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.723 \pm 0.025	0.910 \pm 0.011	0.998	14	15.8	12.8	10.4	8.98
	EE2+NP (250 $\mu\text{g/L}$)	-1.209 \pm 0.024	0.740 \pm 0.011	0.997	14	36.5	20.0	11.0	7.25
	EE2+NP (500 $\mu\text{g/L}$)	-1.282 \pm 0.018	0.764 \pm 0.008	0.999	14	32.3	18.8	10.9	7.45
	EE2+NP (1000 $\mu\text{g/L}$)	-1.395 \pm 0.016	0.799 \pm 0.007	0.999	14	26.8	16.8	10.6	7.67
Silt	BPA	-1.241 \pm 0.007	0.686 \pm 0.003	1.000	25	8.04	2.77	0.955	0.454
	NP	-0.350 \pm 0.019	0.951 \pm 0.008	0.998	24	436	389	347	321
	EE2	-1.236 \pm 0.005	0.858 \pm 0.002	0.999	23	43.5	31.4	22.6	18.0
	EE2+BPA (250 $\mu\text{g/L}$)	-1.317 \pm 0.020	0.883 \pm 0.009	0.999	14	38.0	29.0	22.2	18.4
	EE2+BPA (500 $\mu\text{g/L}$)	-1.470 \pm 0.029	0.933 \pm 0.013	0.998	14	29.6	25.3	21.7	19.5
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.588 \pm 0.029	0.969 \pm 0.012	0.998	14	24.2	22.6	21.0	20.0
	EE2+NP (250 $\mu\text{g/L}$)	-1.257 \pm 0.028	0.865 \pm 0.013	0.997	14	42.1	30.9	22.6	18.2
	EE2+NP (500 $\mu\text{g/L}$)	-1.328 \pm 0.031	0.887 \pm 0.014	0.997	14	37.4	28.8	22.2	18.5
	EE2+NP (1000 $\mu\text{g/L}$)	-1.397 \pm 0.034	0.912 \pm 0.015	0.996	14	33.5	27.4	22.4	19.4

^a Number of observations; ^b standard error.

Table S4 Dubinin-Ashtakhov (DA) model parameters and organic carbon (OC) normalized concentration-dependent distribution coefficients (K_{OC}) for the samples

Sorbent	Solute	$\log Q^0$	b	E	N^a	R^2	Q_{OC}^0 ^b (mg/g)	$\log K_{OC}$ (mL/g) ($C_e=0.01C_S$) ^c	$\log K_{OC}/\log K_{OW}$ ^d
Loam	NP	2.01 \pm 0.03 ^e	0.82 \pm 0.02	4.94	25	1.000	5.38	3.54	0.62
	EE2	1.48 \pm 0.01	1.00 \pm 0.01	7.44	24	1.000	1.58	2.81	0.68
	BPA	1.92 \pm 0.14	1.09 \pm 0.08	10.46	25	0.998	4.33	1.99	0.90
Silt Loam	NP	2.32 \pm 0.03	0.98 \pm 0.03	6.29	25	0.998	10.34	4.03	0.70
	EE2	1.61 \pm 0.03	1.01 \pm 0.03	8.07	24	0.999	2.05	3.03	0.73
	BPA	2.38 \pm 0.26	0.86 \pm 0.11	8.02	23	0.997	11.81	2.14	0.97
Silt	NP	2.63 \pm 0.01	1.11 \pm 0.02	6.52	25	0.999	15.20	4.14	0.72
	EE2	2.06 \pm 0.01	1.02 \pm 0.01	6.73	24	1.000	4.15	3.05	0.73
	BPA	2.61 \pm 0.12	0.99 \pm 0.05	8.04	23	1.000	14.59	2.19	1.00

^aNumber of observations; ^b Q_{OC}^0 is OC-normalized adsorption capacity (Q^0); ^cOC-normalized sorption distribution coefficient ($\log K_{OC}$ ($C_e = 0.01C_S$)); C_S : the water solubility at 20°C; ^dnormalization of K_{OC} values by octanol-water partition coefficient (K_{OW}) ($\log K_{OC}/\log K_{OW}$); ^e standard error.

absorption band of aromatic C=C (around 1640 cm^{-1}) was obviously stronger than that for aromatic carbonyl/carboxyl C=O groups.

References

- Kang S H, Xing B S, 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science & Technology*, 39(1): 134–140.
- Pan B, Lin D H, Mashayekhi H, Xing B S, 2008. Adsorption and hysteresis of bisphenol A and 17 alpha-ethinyl estradiol on carbon

- nanomaterials. *Environmental Science & Technology*, 42(15): 5480–5485.
- Qing S, Lei Z, 2007. Lignin-based carbon films and controllable pore size and properties. *Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)*, 445-446: 731–735.
- Sun K, Gao B, Zhang Z, Zhang G, Liu X, Zhao Y et al, 2010. Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments. *Chemosphere*, 80(7): 709–715.
- Wen B, Zhang J J, Zhang S Z, Shan X Q, Khan S U, Xing B S, 2007. Phenanthrene sorption to soil humic acid and different humin fractions. *Environmental Science & Technology*, 41(9): 3165–3171.
- Xia C Q, Yang J J, Ren S J, Lien E J, 1998. QSAR analysis of polyamine transport inhibitors in 11210 cells. *Journal of Drug Targeting*, 6(1): 65–77.
- Yamamoto H, Liljestrand H M, Shimizu Y, Morita M, 2003. Effects of physical-chemical characteristics on the sorption of selected endocrine disrntors by dissolved organic matter surrogates. *Environmental Science & Technology*, 37(12): 2646–2657.

at $C_e(\text{EE2}) = 3800 \mu\text{g/L}$ ($0.5C_s$) when the concentration of BPA increased from 0 to $1000 \mu\text{g/L}$ in binary-solute systems using Loam as sorbent. This phenomenon has also been reported for sorption of polycyclic aromatic hydrocarbons (PAHs). The sorption capacities of PAHs at high C_e were enhanced by co-solutes, EE2, trichloroethylene, and dichlorobenzene in binary-solute systems (Weber et al., 2002; Yu and Huang, 2005).

Similar trends were found for the parameters of EE2 isotherms measured for Silt Loam and Silt in binary-solute systems, as shown in Fig. 2c, e and Table S3. However, the extent of the effects varied for EE2 sorption on different sorbents at the same $C_0(\text{BPA})$. When $C_0(\text{BPA})$ increased from 0 to $250 \mu\text{g/L}$, the $K_D(\text{EE2})$ value at $C_e(\text{EE2}) = 7.6 \mu\text{g/L}$ decreased by 14.5% for Loam, by 39.2% for Silt Loam, and by 12.7% for Silt, respectively. These data indicate that BPA exhibited a greater impact on EE2 sorption on soils with higher BC content.

As shown in Fig. 2b, d, and f and Table S3, NP exhibited a similar impact on EE2 sorption on soils as BPA. The presence of NP inhibited EE2 sorption in the low $C_e(\text{EE2})$ range and enhanced it in the high $C_e(\text{EE2})$

range. The effect of NP on EE2 sorption increased, and the isotherms for EE2 in binary systems with NP exhibited more linearity with increasing NP initial concentration.

BPA affected EE2 sorption notably more compared with NP. This observation was most prominent for EE2 sorption on Silt Loam. As shown in Fig. 2c and d and Table S3, when the initial concentration increased from 0 to $250 \mu\text{g/L}$ for BPA and NP, respectively, $\log K_F$ decreased from -1.107 to -1.417 and -1.209 ; the linearity index n value increased from 0.705 to 0.812 and 0.740; and $K_D(\text{EE2})$ decreased by 39.2% and 15.2%, respectively, at $C_e(\text{EE2}) = 7.6 \mu\text{g/L}$ but increased by 18.2% and 5.5%, respectively, at $C_e(\text{EE2}) = 3800 \mu\text{g/L}$. These results indicate that, compared with NP, BPA showed stronger competitive sorption in the low $C_e(\text{EE2})$ range and synergetic sorption in the high $C_e(\text{EE2})$ range.

2.3 Effects of EE2 on BPA and NP sorption

The equivalent concentrations of BPA and NP in binary systems were also determined to calculate the K_D value that can be used to estimate the effect of EE2 on BPA/NP sorption equilibrium (Fig. 3).

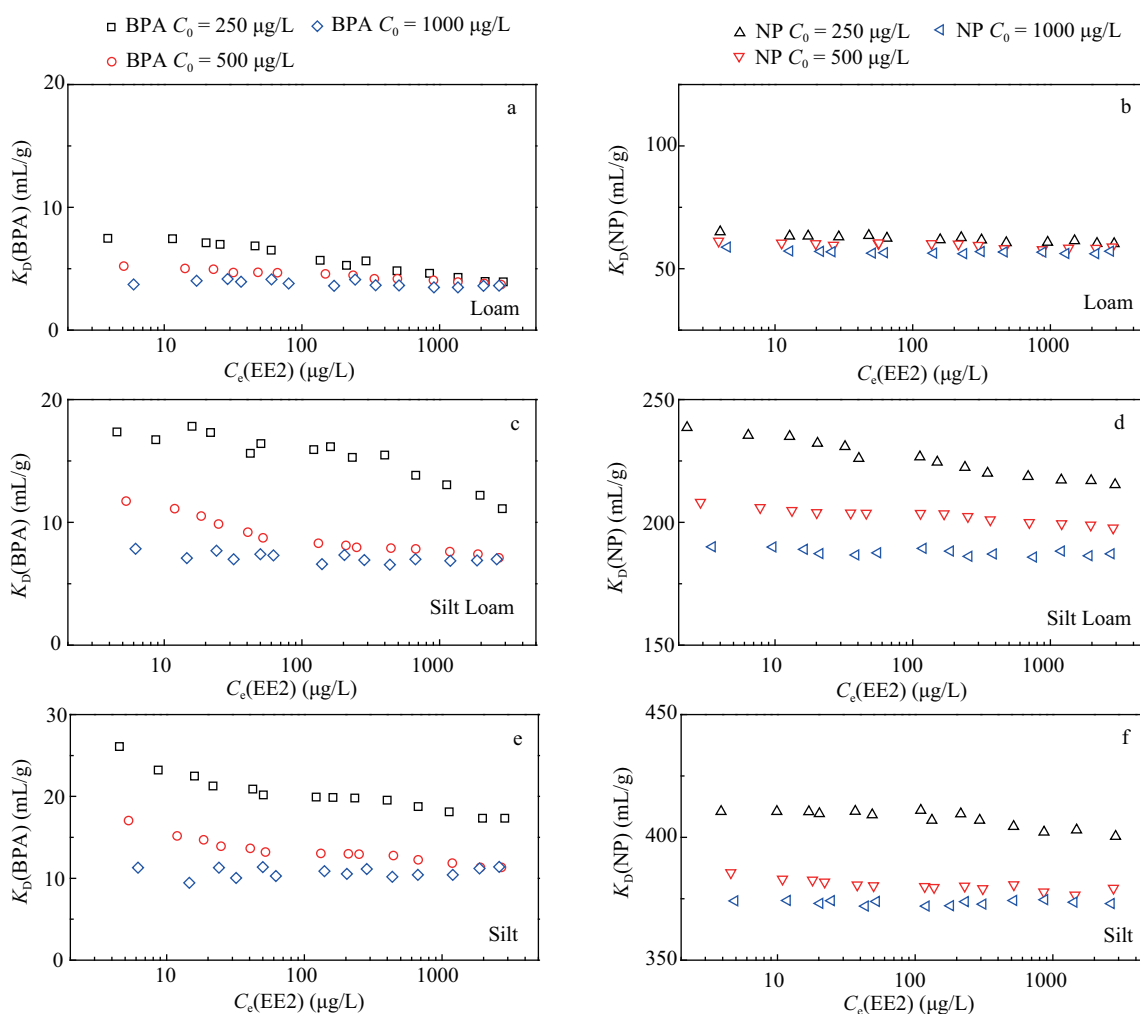


Fig. 3 Changes in single-point distribution coefficients (K_D) of BPA (a, c, and e) and NP (b, d, and f) (20°C) as a function of $C_e(\text{EE2})$.

The influence of EE2 on BPA sorption increased with increasing C_e (EE2) and decreasing C_0 (BPA). As shown in **Fig. 3a**, when C_e (EE2) increased from 3 to 3000 $\mu\text{g/L}$, the K_D (BPA) value decreased from 7.47 to 3.92 mL/g for C_0 (BPA) = 250 $\mu\text{g/L}$ and from 5.21 to 3.7 mL/g for C_0 (BPA) = 500 $\mu\text{g/L}$ in binary systems using Loam as sorbent. However, for C_0 (BPA) = 1000 $\mu\text{g/L}$, no significant difference in K_D (BPA) value was observed. The K_D (BPA) value decreased and got closer with increasing C_0 (BPA) due to the nonlinear sorption of BPA, which indicated that the isotherm for BPA sorption might trend toward linearity under the influence of EE2.

EE2 had a similar influence on BPA sorption on the other two sorbents. As shown in **Fig. 3c** and **e**, when C_e (EE2) increased from 3 to 3000 $\mu\text{g/L}$, the K_D (BPA) values for C_0 (BPA) = 250 and 500 $\mu\text{g/L}$ decreased by 57.4% and 39.4%, respectively in Silt Loam sorption and

by 11.8% and 7.7% in Silt sorption, respectively.

Compared with sorption of BPA, that of NP was insignificantly affected by the presence of EE2. As shown in **Fig. 3b, d, and f**, the K_D (NP) values for C_0 (NP) = 250 $\mu\text{g/L}$ decreased by 7.5%, 9.7%, and 2.5% in Loam, Silt Loam, and Silt sorption, respectively. In addition, the presence of EE2 had almost no effect on K_D (NP) values for C_0 (NP) = 500 and 1000 $\mu\text{g/L}$.

2.4 Possible mechanisms of single and binary sorption

Q^0 from the DA model can express the saturated sorption capacity of sorbents. As shown in **Fig. 4a**, the Q^0 for each sorbate was in the order: Loam < Silt Loam < Silt, which is consistent with the order of their TOC content (especially for EE2; $r^2 = 1.000$; $p < 0.01$). In addition, as shown in **Fig. 4a**, the Q^0 values for NP and BPA for all sorbents were very close and 1.7–4.7 times larger than the value for EE2.

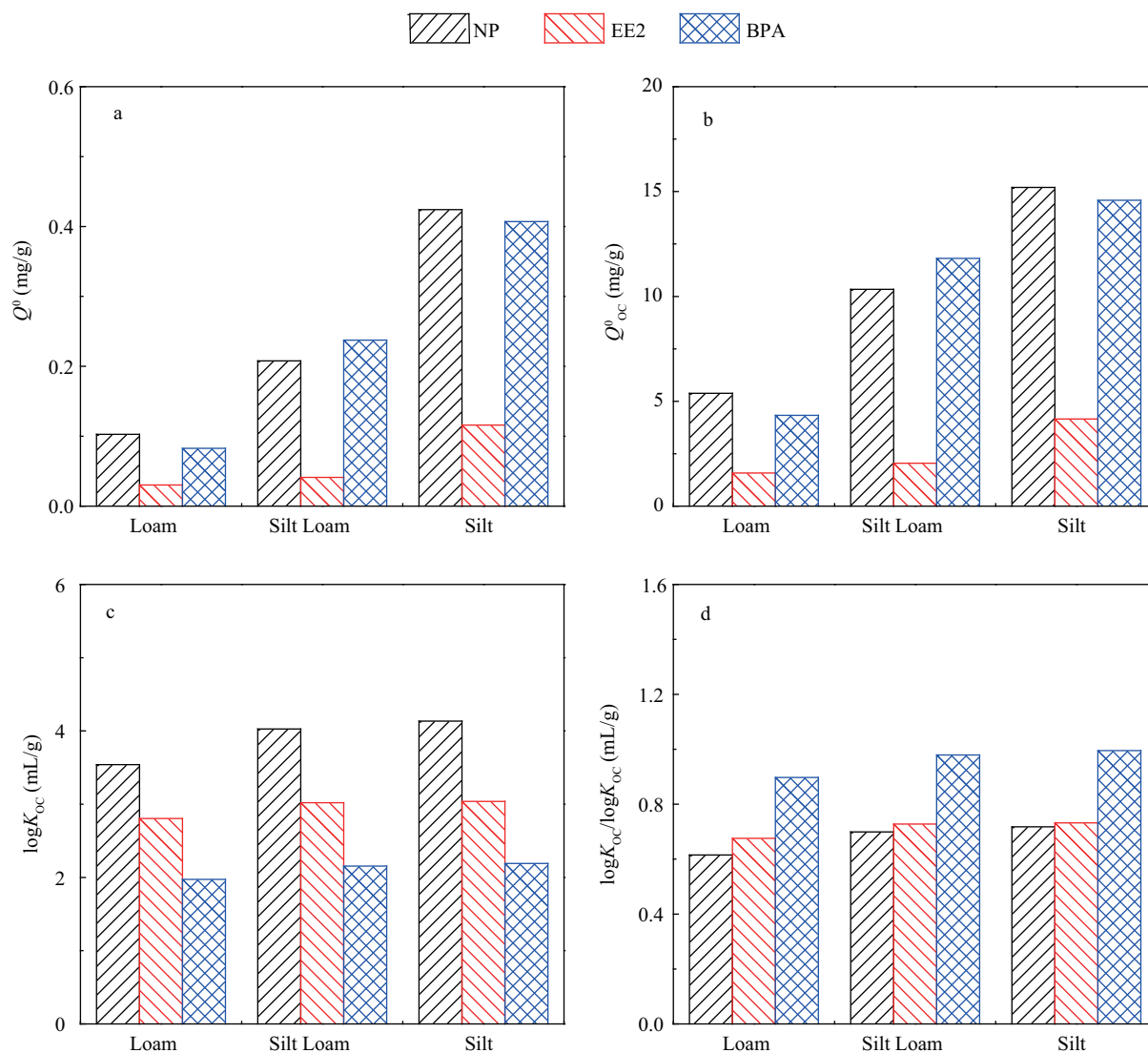


Fig. 4 Comparison of sorption parameters based on the DA model for NP, EE2, and BPA on three sorbents. (a) sorption capacity (Q^0); (b) OC-normalized adsorption capacity (Q_{OC}^0); (c) OC-normalized sorption distribution coefficient ($\log K_{OC}$ ($C_e = 0.01C_s$)); and (d) normalization of K_{OC} values by octanol-water partition coefficient (K_{OW}) ($\log K_{OC}/\log K_{OW}$).

A similar difference between EE2 and BPA adsorption was reported for CNMs, NHC, and BC, and it was accounted for by the differences between their molecular diameters and structures (Pan et al., 2008a; Sun et al., 2010, 2011). The molecular diameters of BPA and NP were 0.43 nm, but that of EE2 was 0.6 nm. As previously reported, SOM plays a very important role in EDC sorption, and its surface area is mainly formed by micropores with maximum pores of approximately 0.3–0.5 nm (Braidia et al., 2002; Sun et al., 2010). Thus, NP and BPA can access more sorption sites compared with EE2.

The OC-normalized sorption capacity (Q_{OC}^0) and sorption distribution coefficient ($\log K_{OC}$ ($C_e = 0.01C_s$)) were in the order Silt > Silt Loam > Loam for all sorbates (Fig. 4b and c), which can be attributed to various reasons. The SOM and BC contents of Loam approximated those of Silt Loam; however, Q_{OC}^0 was much higher for Silt Loam than for Loam, which might be a result of the finer particles and larger SSA of Silt Loam, which may generate more sorption sites. The Q_{OC}^0 for Silt was higher than that for Silt Loam even though Silt Loam had a larger SSA. Possible reasons for this are (1) the fact that the calculated Q_{OC}^0 did not consider the contribution of the mineral matrix and (2) the combinative state of the SOM and mineral matrix.

As shown in Fig. 4c, the $\log K_{OC}$ values for NP, EE2, and BPA decreased by the order of their magnitude, which followed the same order as their $\log K_{OW}$. This indicates that sorption was mainly controlled by hydrophobic interactions, which is in agreement with other studies (Sun et al., 2010; Ying and Kookana, 2005). Normalization of K_{OC} values using the hexadecane-water partition coefficient (K_{HW}) or octanol-water partition coefficient (K_{OW}) can factor out the hydrophobic effect, thereby enabling assessment of other potential adsorption mechanisms (Pan et al., 2008a; Sun et al., 2010). Due to the lack of data on K_{HW} for NP, the following analysis is based on K_{OC}/K_{OW} . As shown in Fig. 4d, $\log K_{OC}/\log K_{OW}$ was in the order BPA > EE2 > NP.

Previous research has suggested that the specific sorption between the functional groups of sorbates and the specific sorption sites of NHC and BC is responsible for their sorption (Sun et al., 2010; Zhu et al., 2004). The distributed reactivity model is widely accepted, and SOM was conceptualized as an adsorbent with sorption sites of distributed energy. SOM is composed of two domains, namely, a hard carbon SOM domain and a soft carbon SOM domain, according to their different sorption characteristics for organic pollutants. Sorption on soft carbon domains follows a partition mechanism and exhibits linear sorption. Conversely, sorption on hard carbon domains, such as NHC and BC, is dominated by nonlinear sorption with limited capacity (Pan et al., 2008b; Weber et al., 1992; Yu and Huang, 2005). A benzene ring connected to a hydroxyl group could form a π - π bond with the hard carbon domains of SOM (Sun et al., 2010; Zhu et al.,

2004). However, BPA has one more ring than NP and EE2. Therefore, the π - π bond formed between BPA and hard carbon domains is stronger than that between NP or EE2 and hard carbon domains. Another important mechanism for specific sorption is hydrogen bonding. BPA and EE2 have one more hydroxyl group than NP. As a result, the bond strength between EDCs and specific sorption sites in SOM is in the order BPA > EE2 > NP, which follows the order for $\log K_{OC}/\log K_{OW}$.

These findings are also supported by the order of linearity coefficient n values in single-solute systems and the competitive sorption between EE2 and BPA/NP in binary-solute systems. Hydrophobic interactions dominated NP sorption in the whole test concentration range as NP was the most hydrophobic chemical among the three sorbates. The π - π and hydrogen bonds formed between NP and the hard carbon domain with specific sorption sites had limited contribution to the entire sorption of NP even at very low C_e (NP) and resulted in the most linear NP sorption isotherm. However, the hydrophobicity of BPA was the weakest, and the contribution of the partition effect to the entire sorption was concentration dependent. The specific sorption sites of the hard carbon domain could form π - π and hydrogen bonds with BPA at a low C_e (BPA) range. As C_e (BPA) increased, they were gradually saturated, their contribution to the entire sorption decreased, and the partition effect gradually dominated the sorption. As for the specific sorption site with high energy, the K_D (BPA) at low C_e (BPA) range was much higher than that at high C_e (BPA) and resulted in a very nonlinear isotherm for sorption of BPA. The hydrophobicity of EE2 and its ability to bind with specific sites were observed between NP and BPA. Therefore, the nonlinearity index was observed between NP and BPA.

Our observation of competitive sorption between EE2 and NP/BPA is in congruence with previously reported data on competitive sorption between, EE2 and BPA, between EE2 and naphthalene/phenanthrene, between PAHs, and between pesticides on nanocarbon materials, soils, and sediments (McGinley et al., 1993; Pan and Xing, 2010; Pateiro-Moure et al., 2010; Weber et al., 2002; Xia and Ball, 2000; Xiao et al., 2004; Xing et al., 1996; Yang et al., 2006; Yu and Huang, 2005). Research has also shown that kerogen, glassy humic acid, NHC, and BC for PAHs and EDCs sorption exhibit nonlinear and competitive sorption (Johnson et al., 2001; Sun et al., 2010; Weber et al., 2002; Yu and Huang, 2005). As shown in Table S3, three sorbents containing BC exhibited nonlinear and competitive sorption. Clearly, the linearity index n of the isotherm sorption of EE2 increased with the concentration of the co-solute. The competitive effect was at its greatest when the primary sorbate (EE2) concentration was low and the competing sorbate (BPA/NP) concentration was high. Due to the limitation of sorption sites of hard carbon domains, these exhibited strong competitive sorption for EDCs in

the low C_e range. Moreover, the soft carbon SOM, having no competition among different sorbates, dominated the sorption in the relatively high C_e range (Huang and Weber, 1997; Xiao et al., 2004; Yu and Huang, 2005).

The $K_D(\text{EE2})$ value at $C_e(\text{EE2}) = 7.6 \mu\text{g/L}$ decreased in the order of Silt Loam > Loam > Silt in binary-solute systems with the same order as their BC content in TOC. Compared with Loam, Silt Loam had similar TOC and BC contents, but much stronger competitive sorption was observed in Silt Loam sorption, which can be explained by the fact that Silt Loam had much finer particles and higher SSA, indicating that the sorption sites of BC were easier to access (Bermudez-Couso et al., 2011).

The presence of co-solutes enhanced the sorption of EE2 by soils at high C_e (> 1000 $\mu\text{g/L}$). Yu and Huang (2005) and Weber et al. (2002) reported a similar phenomenon in binary-solute systems and suggested that increasing concentrations of co-solutes could swell the SOM matrix because the increased energy input leads to increased disordering of the SOM structure and enhanced capacity of the SOM matrix for accommodating more sorbate molecules.

The π - π bond formed between BPA and hard carbon domains was stronger than that between EE2 and hard carbon domains. Thus, BPA could compete with EE2 for the specific sites even at very low $C_0(\text{BPA})$. However, the π - π bond and hydrogen bonds between EE2 and hard carbon domains were stronger than those between NP and hard carbon domains. Therefore, competitive sorption could only be observed at very high concentrations of NP. Despite this, given the strong hydrophobic effect for NP sorption, EE2 had almost no influence on NP sorption even though the EE2 concentration was high and the NP concentration was low.

Notably, the competitive sorption between EE2 and BPA/NP significantly differed from that between such chemicals as PAHs with a similar molecular structure but different hydrophobicity. Yu and Huang (2005) suggested that the difference in hydrophobicity caused the different effects of phenanthrene and naphthalene on EE2 sorption, because a sorbate with higher hydrophobicity could compete for the sorption site with a sorbate of lower hydrophobicity. However, in the present study, BPA with low hydrophobicity competed more with EE2 sorption than NP with high hydrophobicity, which could have been due to the differences in the functional groups of the EDCs.

3 Conclusions

This study investigated the sorption of three EDCs in single- and binary-solute systems for three sorbents. The distributed reactivity model was used to determine their mechanisms of sorption. The hydrophobic effect dominated the sorption of the entire test concentration range of NP. The specific sorption of the hard carbon domains

of SOM dominated sorption for low C_e values of EE2 and BPA, and the hydrophobic effect of the soft carbon domains dominated sorption for high C_e values of EE2 and BPA. The SOM content, SSA of sorbents, and critical diameters of sorbates affect the saturated sorption capacity of sorbents. In binary systems, BPA and NP competed with EE2 sorption at low $C_e(\text{EE2})$ and enhanced the sorption of EE2 at high $C_e(\text{EE2})$. BPA and EE2 affected each other's sorption much more than did NP and EE2 due to the stronger specific sorption between BPA or EE2 and the hard carbon domains of SOM.

The behavior of EDC sorption in binary-solute systems, especially the strong competitive adsorption at low equilibrium concentration, presents new challenges for wastewater reuse and reutilization of sludge with estrogen, especially because EE2 with very high estrogenic activity but strong hydrophobicity was once considered to be slowly mobile in water-soil systems. The concentrations of phenolic endocrine disruptors are usually 2–3 orders of magnitude higher than those of estrogens. Moreover, phenolic endocrine disruptors are more persistent toward biodegradation than estrogen. These findings suggest that phenolic endocrine disruptors cause strong and long-term competitive sorption with estrogen, enhance the mobility of estrogen, and enhance its bioavailability. Thus, the influence of co-solutes on the transport and fate of EDCs needs to be emphasized.

Acknowledgments

This work was supported by the Special Environmental Research Funds for Public Welfare (No. 201209053) and the National High Technology Research and Development Program (863) of China (No. 2008AA062502).

Supporting materials

Supplementary data associated with this article can be found in the online version.

References

- Bermúdez-Couso A, Fernández-Calviño D, Pateiro-Moure M, Nóvoa-Muñoz J C, Simal-Gándara J, Arias-Estévez M, 2011. Adsorption and desorption kinetics of carbofuran in acid soils. *Journal of Hazardous Materials*, 190(1-3): 159–167.
- Bonin J L, Simpson M J, 2007. Sorption of steroid estrogens to soil and soil constituents in single- and multi-sorbate systems. *Environmental Toxicology and Chemistry*, 26(12): 2604–2610.
- Braida W J, Pignatello J J, Lu Y, Ravikovitch P I, Neimark A V, Xing B, 2002. Sorption hysteresis of benzene in charcoal particles. *Environmental Science & Technology*,

- 37(2): 409–417.
- Cituluski J A, Farahbakhsh K, 2010. Fate of endocrine-active compounds during municipal biosolids treatment: a review. *Environmental Science & Technology*, 44(22): 8367–8376.
- Gelinas Y, Prentice K M, Baldock J A, Hedges J I, 2001. An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. *Environmental Science & Technology*, 35(17): 3519–3525.
- Gustafsson O, Haghseta F, Chan C, MacFarlane J, Gschwend P M, 1997. Quantification of the dilute sedimentary soot phase: implications for pah speciation and bioavailability. *Environmental Science & Technology*, 31(1): 203–209.
- Hanselman T A, Graetz D A, Wilkie A C, 2003. Manure-borne estrogens as potential environmental contaminants: a review. *Environmental Science & Technology*, 37(24): 5471–5478.
- Hou J A, Pan B, Niu X K, Chen J Z, Xing B S, 2010. Sulfamethoxazole sorption by sediment fractions in comparison to pyrene and bisphenol A. *Environmental Pollution*, 158(9): 2826–2832.
- Huang W L, Weber W J, 1997. A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environmental Science & Technology*, 31(9): 2562–2569.
- Johnson M D, Huang W L, Weber W J, 2001. A distributed reactivity model for sorption by soils and sediments. 13. Simulated diagenesis of natural sediment organic matter and its impact on sorption/desorption equilibria. *Environmental Science & Technology*, 35(8): 1680–1687.
- Lee L S, Strock T J, Sarmah A K, Rao P S C, 2003. Sorption and dissipation of testosterone, estrogens, and their primary transformation products in soils and sediment. *Environmental Science & Technology*, 37(18): 4098–4105.
- Mashtare M L, Khan B, Lee L S, 2011. Evaluating stereoselective sorption by soils of 17 α -estradiol and 17 β -estradiol. *Chemosphere*, 82(6): 847–852.
- McGinley P M, Katz L E, Weber W J, 1993. A distributed reactivity model for sorption by soils and sediments. 2. Multicomponent systems and competitive effects. *Environmental Science & Technology*, 27(8): 1524–1531.
- Pan B, Ning P, Xing B S, 2009. Part V-sorption of pharmaceuticals and personal care products. *Environmental Science and Pollution Research*, 16(1): 106–116.
- Pan B, Lin D H, Mashayekhi H, Xing B S, 2008a. Adsorption and hysteresis of bisphenol A and 17 alpha-ethinyl estradiol on carbon nanomaterials. *Environmental Science & Technology*, 42(15): 5480–5485.
- Pan B, Ning P, Xing B S, 2008b. Part IV-sorption of hydrophobic organic contaminants. *Environmental Science and Pollution Research*, 15(7): 554–564.
- Pan B, Xing B S, 2010. Competitive and complementary adsorption of bisphenol A and 17 α -ethinyl estradiol on carbon nanomaterials. *Journal of Agricultural and Food Chemistry*, 58(14): 8338–8343.
- Paseiro-Losada P, Simal-Lozano J, Paz-abuín S, López-Mahía P, Simal-Gándara J, 1993. Kinetics of the hydrolysis of bisphenol A diglycidyl ether (badge) in water-based food simulants-implications for legislation on the migration of badge-type epoxy-resins into foodstuffs. *Fresenius Journal of Analytical Chemistry*, 345(7): 527–532.
- Pateiro-Moure M, Arias-Estévez M, Simal-Gándara J, 2010. Competitive and non-competitive adsorption/desorption of paraquat, diquat and difenzoquat in vineyard-devoted soils. *Journal of Hazardous Materials*, 178(1-3): 194–201.
- Pignatello J J, Xing B S, 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology*, 30(1): 1–11.
- Sun K, Gao B, Zhang Z Y, Zhang G X, Liu X T, Zhao Y et al., 2010. Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments. *Chemosphere*, 80(7): 709–715.
- Sun K, Ro K, Guo M X, Novak J, Mashayekhi H, Xing B S, 2011. Sorption of bisphenol A, 17 alpha-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars. *Bioresource Technology*, 102(10): 5757–5763.
- Weber W J Jr, Kim S H, Johnson M D, 2002. Distributed reactivity model for sorption by soils and sediments. 15. High-concentration co-contaminant effects on phenanthrene sorption and desorption. *Environmental Science & Technology*, 36(16): 3625–3634.
- Weber W J Jr, McGinley P M, Katz L E, 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environmental Science & Technology*, 26(10): 1955–1962.
- Xia G S, Ball W P, 2000. Polanyi-based models for the competitive sorption of low-polarity organic contaminants on a natural sorbent. *Environmental Science & Technology*, 34(7): 1246–1253.
- Xiao B H, Yu Z Q, Huang W L, Song J, Peng P A, 2004. Black carbon and kerogen in soils and sediments. 2. Their roles in equilibrium sorption of less-polar organic pollutants. *Environmental Science & Technology*, 38(22): 5842–5852.
- Xing B S, Pignatello J J, Gigliotti B, 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental Science & Technology*, 30(8): 2432–2440.
- Xu Y L, Luo F, Pal A, Gin K, Reinhard M, 2011. Occurrence of emerging organic contaminants in a tropical urban catchment in singapore. *Chemosphere*, 83(7): 963–969.
- Yang K, Wang X, Zhu L Z, Xing B S, 2006. Competitive sorption of pyrene, phenanthrene, and naphthalene on

Supporting materials

Three demineralization samples (DM1, 2, 3) extracted from Loam Silt, Loam, and Silt, respectively, showed very typical infrared spectra of Soil organic matter (SOM), containing aliphatic and aromatic compositions, as indicated by hydroxyl group at around 3430 cm^{-1} , aliphatic C–H stretching at 2960 and 2930 cm^{-1} , alicyclic C–H stretching at 2852 cm^{-1} , aromatic carbonyl/carboxyl C=O groups at around 1720 cm^{-1} , aromatic C=C at around 1640 cm^{-1} , aromatic C=C stretching at around 1640 cm^{-1} , C–H in plane deformation at 1400 cm^{-1} , C–H stretching and OH deformation of COOH at around 1230 cm^{-1} , and C–O stretching at around 1240 and 1040 cm^{-1} (Kang and Xing, 2005; Qing and Lei, 2007; Sun et al., 2010; Wen et al., 2007). A noticeable absorbance of aromatic carbon was observed for DM 1, 2 but not for DM 3. The

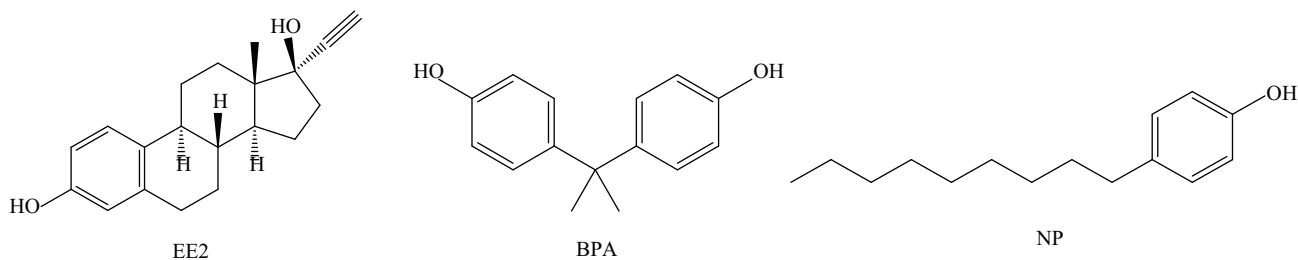


Fig. S1 Structure of EE2, BPA and NP

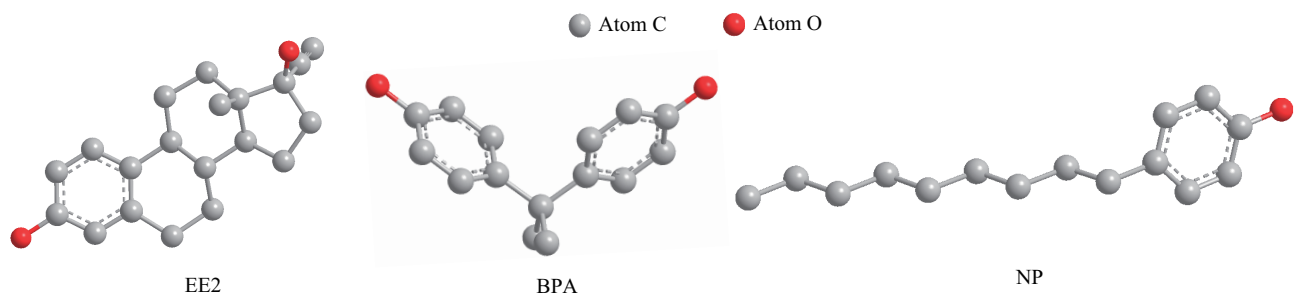


Fig. S2 Optimized 3-dimensional structures EE2, BPA and NP with total energy of 28.4088, 3.3870 and 3.8349 kcal/mol based on minimized steric energy. Steric energy includes stretch, bend, stretch-bend, torsion, non-1,4 van der Waals, 1,4 van der Waals, and dipole/dipole energies, and was calculated using molecular mechanics theory (MM2).

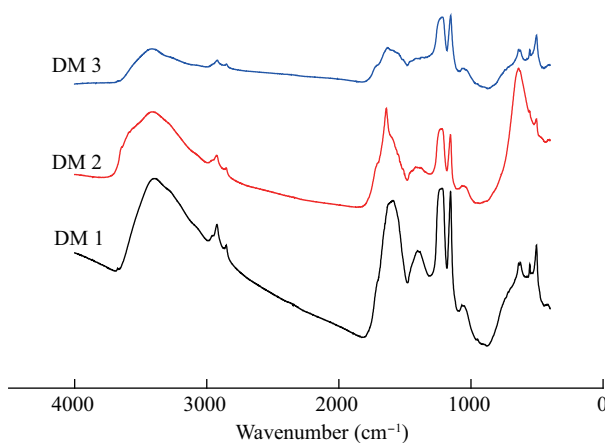


Fig. S3 Fourier transform infrared (FTIR) spectra of soil samples (DM 1–3 represent the SOM extracted from Loam, Silt Loam and Silt, respectively).

Table S1 4-*n*-Nonylphenol (NP), 17 α -ethinyl estradiol (EE2) and bisphenol A (BPA) properties

Property	NP	EE2	BPA
Chemical formula	C ₁₅ H ₂₄ O	C ₂₀ H ₂₄ O ₂	C ₁₅ H ₁₆ O ₂
Molecular weight	220.35	296.4	228.28
Solubility (C _s , mg/L)	1.66 ^a	7.6 ^b	380 ^b
log K_{OW}	5.76 ^a	4.15 ^b	2.2 ^b
pK _a	10.25 ^a	10.4 ^b	9.59 ^b
Critical molecular diameter (nm)	4.3 ^c	6.0 ^d	4.3 ^d
H-bonding parameter acceptor ^e	1 ^e	2 ^d	2 ^d
H-bonding parameter donor ^e	1 ^e	2 ^d	2 ^d

^aYamamoto et al., 2003; ^bPan et al., 2008; ^ccritical molecular diameters were calculated using PC Spartan, 2002; ^dSun et al., 2010; ^eH-bonding parameter acceptor and H-bonding parameter donor for NP were calculated as described by Xia et al. 1998.

Table S2 Sources of the three soils and their land use types

Sorbents	Source	Land use type
Loam	Beijing, 39°41'18''N, 116°29'56''E	farmland (maize)
Silt Loam	Tianjin, 39°16'56''N, 117°34'21''E	wetlands
Silt	Jiangsu Province, 31°52'53''N, 119°55'19''E	farmland (rice)

Table S3 Freundlich isotherm parameters and calculated single-point distribution coefficients (K_D) for the samples

Sorbent	Solute	$\log K_F$	n (($\mu\text{g/g}$)/($\mu\text{g/L}$) ^{n})	R^2	N^a	K_D (mL/g)			
						$C_e=0.001C_S$	$C_e=0.01C_S$	$C_e=0.1C_S$	$C_e=0.5C_S$
Loam	BPA	-1.345 \pm 0.012 ^b	0.613 \pm 0.006	0.998	25	4.54	1.87	0.766	0.411
	NP	-1.034 \pm 0.021	0.883 \pm 0.010	0.997	24	87.2	66.6	50.9	42.2
	EE2	-1.458 \pm 0.002	0.758 \pm 0.001	1.000	25	21.3	12.2	7.02	4.76
	EE2+BPA(250 $\mu\text{g/L}$)	-1.552 \pm 0.007	0.788 \pm 0.003	1.000	14	18.2	11.2	6.88	4.90
	EE2+BPA (500 $\mu\text{g/L}$)	-1.700 \pm 0.017	0.832 \pm 0.007	0.999	14	14.0	9.2	6.05	4.51
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.884 \pm 0.017	0.889 \pm 0.007	0.999	14	10.6	8.1	6.17	5.12
	EE2+NP (250 $\mu\text{g/L}$)	-1.532 \pm 0.031	0.782 \pm 0.013	0.996	14	19.5	11.3	6.62	4.54
	EE2+NP (500 $\mu\text{g/L}$)	-1.568 \pm 0.025	0.793 \pm 0.011	0.998	14	17.9	11.0	6.76	4.81
	EE2+NP (1000 $\mu\text{g/L}$)	-1.632 \pm 0.018	0.816 \pm 0.008	0.999	14	16.2	10.5	6.82	5.04
Silt Loam	BPA	-0.901 \pm 0.016	0.537 \pm 0.007	0.997	25	8.91	4.33	2.10	1.27
	NP	-0.516 \pm 0.018	0.875 \pm 0.009	0.998	24	286	215	161	132
	EE2	-1.107 \pm 0.010	0.705 \pm 0.004	1.000	23	43.0	21.8	11.0	6.87
	EE2+BPA (250 $\mu\text{g/L}$)	-1.417 \pm 0.037	0.812 \pm 0.017	0.995	14	26.1	16.9	11.0	8.12
	EE2+BPA (500 $\mu\text{g/L}$)	-1.542 \pm 0.039	0.850 \pm 0.017	0.995	14	21.2	15.0	10.6	8.33
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.723 \pm 0.025	0.910 \pm 0.011	0.998	14	15.8	12.8	10.4	8.98
	EE2+NP (250 $\mu\text{g/L}$)	-1.209 \pm 0.024	0.740 \pm 0.011	0.997	14	36.5	20.0	11.0	7.25
	EE2+NP (500 $\mu\text{g/L}$)	-1.282 \pm 0.018	0.764 \pm 0.008	0.999	14	32.3	18.8	10.9	7.45
	EE2+NP (1000 $\mu\text{g/L}$)	-1.395 \pm 0.016	0.799 \pm 0.007	0.999	14	26.8	16.8	10.6	7.67
Silt	BPA	-1.241 \pm 0.007	0.686 \pm 0.003	1.000	25	8.04	2.77	0.955	0.454
	NP	-0.350 \pm 0.019	0.951 \pm 0.008	0.998	24	436	389	347	321
	EE2	-1.236 \pm 0.005	0.858 \pm 0.002	0.999	23	43.5	31.4	22.6	18.0
	EE2+BPA (250 $\mu\text{g/L}$)	-1.317 \pm 0.020	0.883 \pm 0.009	0.999	14	38.0	29.0	22.2	18.4
	EE2+BPA (500 $\mu\text{g/L}$)	-1.470 \pm 0.029	0.933 \pm 0.013	0.998	14	29.6	25.3	21.7	19.5
	EE2+BPA (1000 $\mu\text{g/L}$)	-1.588 \pm 0.029	0.969 \pm 0.012	0.998	14	24.2	22.6	21.0	20.0
	EE2+NP (250 $\mu\text{g/L}$)	-1.257 \pm 0.028	0.865 \pm 0.013	0.997	14	42.1	30.9	22.6	18.2
	EE2+NP (500 $\mu\text{g/L}$)	-1.328 \pm 0.031	0.887 \pm 0.014	0.997	14	37.4	28.8	22.2	18.5
	EE2+NP (1000 $\mu\text{g/L}$)	-1.397 \pm 0.034	0.912 \pm 0.015	0.996	14	33.5	27.4	22.4	19.4

^a Number of observations; ^b standard error.

Table S4 Dubinin-Ashtakhov (DA) model parameters and organic carbon (OC) normalized concentration-dependent distribution coefficients (K_{OC}) for the samples

Sorbent	Solute	$\log Q^0$	b	E	N^a	R^2	Q_{OC}^0 ^b (mg/g)	$\log K_{OC}$ (mL/g) ($C_e=0.01C_S$) ^c	$\log K_{OC}/\log K_{OW}$ ^d
Loam	NP	2.01 \pm 0.03 ^e	0.82 \pm 0.02	4.94	25	1.000	5.38	3.54	0.62
	EE2	1.48 \pm 0.01	1.00 \pm 0.01	7.44	24	1.000	1.58	2.81	0.68
	BPA	1.92 \pm 0.14	1.09 \pm 0.08	10.46	25	0.998	4.33	1.99	0.90
Silt Loam	NP	2.32 \pm 0.03	0.98 \pm 0.03	6.29	25	0.998	10.34	4.03	0.70
	EE2	1.61 \pm 0.03	1.01 \pm 0.03	8.07	24	0.999	2.05	3.03	0.73
	BPA	2.38 \pm 0.26	0.86 \pm 0.11	8.02	23	0.997	11.81	2.14	0.97
Silt	NP	2.63 \pm 0.01	1.11 \pm 0.02	6.52	25	0.999	15.20	4.14	0.72
	EE2	2.06 \pm 0.01	1.02 \pm 0.01	6.73	24	1.000	4.15	3.05	0.73
	BPA	2.61 \pm 0.12	0.99 \pm 0.05	8.04	23	1.000	14.59	2.19	1.00

^aNumber of observations; ^b Q_{OC}^0 is OC-normalized adsorption capacity (Q^0); ^cOC-normalized sorption distribution coefficient ($\log K_{OC}$ ($C_e = 0.01C_S$)); C_S : the water solubility at 20°C; ^dnormalization of K_{OC} values by octanol-water partition coefficient (K_{OW}) ($\log K_{OC}/\log K_{OW}$); ^e standard error.

absorption band of aromatic C=C (around 1640 cm^{-1}) was obviously stronger than that for aromatic carbonyl/carboxyl C=O groups.

References

- Kang S H, Xing B S, 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science & Technology*, 39(1): 134–140.
- Pan B, Lin D H, Mashayekhi H, Xing B S, 2008. Adsorption and hysteresis of bisphenol A and 17 alpha-ethinyl estradiol on carbon

- nanomaterials. *Environmental Science & Technology*, 42(15): 5480–5485.
- Qing S, Lei Z, 2007. Lignin-based carbon films and controllable pore size and properties. *Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)*, 445-446: 731–735.
- Sun K, Gao B, Zhang Z, Zhang G, Liu X, Zhao Y et al, 2010. Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments. *Chemosphere*, 80(7): 709–715.
- Wen B, Zhang J J, Zhang S Z, Shan X Q, Khan S U, Xing B S, 2007. Phenanthrene sorption to soil humic acid and different humin fractions. *Environmental Science & Technology*, 41(9): 3165–3171.
- Xia C Q, Yang J J, Ren S J, Lien E J, 1998. QSAR analysis of polyamine transport inhibitors in 11210 cells. *Journal of Drug Targeting*, 6(1): 65–77.
- Yamamoto H, Liljestrand H M, Shimizu Y, Morita M, 2003. Effects of physical-chemical characteristics on the sorption of selected endocrine disrntors by dissolved organic matter surrogates. *Environmental Science & Technology*, 37(12): 2646–2657.

JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)
(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 6 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	Distributed by	Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742

