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

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Abstract

The sorption of 17α-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 (0.875–0.0.951) 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 µg/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; 17α-ethinyl estradiol; endocrine-disrupting chemicals; distributed reactivity model; black carbon

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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 disrupters, such as 17α-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 µg/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 saturated 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

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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 (≥ 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 (Jacsco, 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 ± 1)°C. Aqueous solutions of EDCs ranging from 10 μg/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 μg/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 μg/L to its solubility limit were set; BPA and NP were added to reach the concentrations of 250, 500, and 1000 μg/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.