



Mechanism of and relation between the sorption and desorption of nonylphenol on black carbon-inclusive sediment



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ABSTRACT

Correlation between the sorption and desorption of nonylphenol (NP) and binary linear regression were conducted to reveal the underlying mechanism of and relation between sorption domains and desorption sites in black carbon (BC)-amended sediment. The sorption and desorption data could be fitted well using dual-mode ($R^2 = 0.971\text{--}0.996$) and modified two-domain model ($R^2 = 0.986\text{--}0.995$), respectively, and there were good correlations between these two parts of parameters ($R^2 = 0.884\text{--}0.939$, $P < 0.01$). The NP percentage in desorbable fraction was almost equal to that of the partition fraction, suggesting the desorbed NP came from linear partition domain, whereas the resistant desorption NP was segregated in nonlinear adsorption sites, which were dominated by pores in BC-amended sediment. Our investigation refined theory about the relation between sorption domains and desorption sites in sediment and could be used to predict the release risk of NP using sorption data when BC is used for NP pollution control.

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1. Introduction

Soil/sediment organic matter (SOM) is the principal factor controlling the sorption of hydrophobic organic compounds (HOCs) (Omega, 1968). The mechanism of sorption to SOM had received a great deal of attention because of its fundamental importance to HOC transport, bioavailability, and toxicity (Cornelissen and Gustafsson, 2004; Armitage et al., 2008). Evidence is accumulating from studies on subjects such as nonlinear sorption isotherms (Johnson et al., 2001; Kleineidam et al., 2002), multiphasic desorption kinetics (Pignatello and Xing, 1996; Cornelissen et al., 1999), and strongly elevated TOC-water distribution ratios in the field (Gustafsson et al., 1997; Ehlers and Luthy, 2003; Lohmann et al., 2005; Sun et al., 2012). The sorption of HOCs to SOM can be described as having “dual-mode sorption” (Pignatello and Xing, 1996; Huang et al., 1997), that is, linear absorption in amorphous organic matter (AOM) such as humic/fulvic substances and lignin, and nonlinear adsorption to more condensed materials such as black carbon (BC), coal, and kerogen. SOM has been conceptualized

as an amalgam of rubbery and glassy phases. Each phase has a dissolution domain, but the glassy phase contains additional surface sites and nanopores (Pignatello and Xing, 1996; Huang and Weber, 1997). The sorption of HOCs to the rubbery state occurs by dissolution, and sorption to the glassy state occurs by concurrent dissolution, surface adsorption and hole-filling mechanisms.

The sorption isotherms of HOCs to sediment have been shown to consist of at least two components, namely a Langmuir component and a linear component (Xing et al., 1996; Huang et al., 1997; Xing and Pignatello, 1997), and the desorption of HOCs from soils and sediments occurs in several stages, for example, a rapid desorption phase (hours to days), a slow phase (weeks to months) and a very slow phase (months to years) (Pignatello and Xing, 1996; Cornelissen et al., 1997a; Ten Hulscher et al., 1999). There is a question as to whether there are relations between sorption domains and desorption sites? In the late 1990s and early 2000s, several studies on related research were published (Xing et al., 1996; Huang et al., 1997; LeBoeuf and Weber, 1997; Xia and Ball, 1999; Cornelissen et al., 2000). The authors confirmed that compounds at slow and very slow desorbing sites in sediment exhibited Langmuir-like sorption, whereas compounds at rapidly desorbing sites showed linear sorption. However, these experiments were conducted using natural sediment with little grassy phase content,

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and the HOCs sorbed on natural sediment can desorb almost completely, even if the desorption hysteresis is still apparent and requires long time scales.

It has been demonstrated that BC, one type of glassy organic matter in sediment, engaged in extraordinarily strong and nonlinear adsorption to HOCs, leading to distribution coefficients that were several orders of magnitude higher than in natural sediments (Bucheli and Gustaffson, 2000; Accardi-dey and Gschwend, 2002; Chun et al., 2004; Cornelissen et al., 2004a). The decline in desorption rates and fractions, and the occurrence of desorption resistance have also been attributed to the presence of BC (Chai et al., 2006, 2007; Zhang et al., 2010; Yang et al., 2012; Marchal et al., 2013). Therefore, applying BC to treat contaminated sediment is a practical approach to reducing the ecological risk of HOCs (Jones et al., 2011; Martin et al., 2012; Teixidó et al., 2013). However, we wondered whether the addition of glassy phase organic matter, namely BC, would change the relation between sorption domains and desorption sites in sediment. In addition, desorption experiments are tedious, so we wanted to determine whether we could predict the NP percentage in the desorption fraction by using adsorption data.

In the present study, one typical endocrine disruptor and persistent pollutant called nonylphenol (NP) was used as a representative HOC. Substantial ecotoxicological data have demonstrated that NP has significant estrogenic effects, toxicity and biological accumulation (Granmo et al., 1989). And more than 60% of NP is distributed in sediments. Sorption/desorption to/from sediment is a fundamental process controlling the fate, toxicity and bioavailability of NP. So we investigated the sorption and desorption properties of NP on/from sediment amended with rice straw biochar and fly ash, respectively. The correlation between sorption isotherm and desorption kinetic parameters was analyzed to determine the quantitative relation and mechanism between the sorption and desorption of NP on sediment containing BC. The objective of this study was to reveal the relation between sorption domains and desorption sites in BC-amended sediment and predict NP percentage in the desorption fraction from sorption data when fresh BC is used for NP pollution control.

2. Materials and methods

2.1. Chemicals and materials

NP with a purity of >99% was purchased from Aladdin (Shanghai, China) and prepared as a concentrated stock solution with acetonitrile. Tenax TA (60–80 mesh) was obtained from Supelco (Bellefonte, Pennsylvania, USA). Tenax TA was activated or regenerated by ultrasonic washing with methanol, acetone and hexane in order (Cornelissen et al., 1997b).

The sediment was obtained by a clam sampler to collect surface sediment of the Qian-tang River, Hangzhou, Zhejiang province, China. The TOC and BC content of the sediment was 0.964% and 0.37%, respectively. For more details, see Luo et al. (2011).

Rice straw black carbon (RC) was prepared from air-dried rice straw collected from the Hua-jia-chi farm of Zhejiang University in China. The rice straw was burned on a stainless steel plate in an open field under uncontrolled conditions. Fly ash black carbon (FC) was collected from the electrostatic precipitation division of a thermoelectric plant in Hangzhou, Zhejiang province, China. To obtain purified RC and FC, the BC samples were treated with 2 M HCl and 1 M: 1 M HCl–HF solutions, washed with distilled water, and oven-dried overnight at 105 °C. The RC and FC properties were detailed in our previous works (Luo et al., 2011).

The BC-amended sediments used in this experiment were prepared by mixing the sediment and specific quantities of RC and FC to achieve amendment rates of 0%, 0.5%, 2.0% and 5.0% (w/w) (Chi, 2014). The BC-amended sediments were thoroughly mixed before use in the NP sorption and desorption experiments.

2.2. Sorption of NP on BC and BC-amended sediment

The sorption of NP by BC and BC-amended sediment were measured by using the batch equilibration technique (Düring et al., 2002). The sorbents were added to 50-mL glass centrifuge vials, and each vial received 30 mL of NP solution ranging from 0.2 to 4.0 mg/L with an electrolyte matrix containing 200 mg/L NaCl and 200 µg/mL NaNO₃, which was added to inhibit biodegradation (Chen et al., 2004). All sorption experiments were conducted in triplicate. The vials were shaken at

150 rpm on a horizontal shaker at 25 ± 1 °C for 16 h in the dark. Preliminary tests indicated that 16 h was sufficient to reach apparent equilibrium.

After the establishment of sorption equilibrium, the NP concentrations in the initial and equilibrated supernatants were analyzed by high performance liquid chromatography (HPLC, Agilent 1100 series) with a diode array fluorescence detector (FLD) detector and a C18 reversed-phase column (ODS, 5 µm, 2.1 mm × 250 mm). Acetonitrile and water (70:30, v/v) were used as the mobile phase at a flow rate of 1.0 mL/min, and the injection volume was 20 µL. The FLD wavelength for detecting NP was set at detection and excitation wavelengths of 233 nm and 302 nm, respectively. The NP concentrations were quantified with an external standard method. Blanks loaded with NP solution without adsorbents were also run to assess the solute losses to reactor components during the sorption process.

2.3. Desorption of NP from BC and BC-amended sediment

BC and BC-amended sediment were spiked with NP at 5000 mg/kg and 100 mg/kg (dry weight), respectively. After the carrier solvent was allowed to evaporate for approximately 12 h in a fume hood until dry, the treated BC and BC-amended sediment samples were capped and shaken at 25 °C and 80 g in the dark at room temperature for 24 h.

The spiked samples were desorbed for different time increments by using a method similar to that described in Xu et al. (2008). In brief, spiked samples were transferred to 50 mL glass centrifuge tubes. Tenax beads (0.1 g) and 30 mL of electrolyte matrix were then added to each container. The samples were shaken on a horizontal shaker at 100 rpm at room temperature for 0.5, 2, 4, 6, 12, 24, 48, 96, 192 and 384 h, three replicates. For each desorption time interval, the Tenax beads were separated from the sediment suspension. The Tenax beads were collected and then transferred to a 30-mL clear glass vial. Another 0.1 g of clean Tenax beads was added to the vial to continue the desorption experiment. The collected Tenax beads were extracted by sonication using 5 mL of dichloromethane-methanol mixture (1:1, v/v) for three consecutive times. The extracts from the same sample were combined, after which the collected solvent was concentrated to 1 mL through nitrogen blowing and then analyzed by HPLC.

Quality control measures were carried out in the Tenax-aided desorption kinetics experiment. First, the efficiency of Tenax has been checked and recovery of NP using Tenax adsorption was >98%. Furthermore, after Tenax-aided desorption kinetics experiment, methanol was used to extract the residual NP in sorbent and to calculate the loss of NP during desorption process. Losses of NP during desorption process were all <10%.

2.4. Data analysis

2.4.1. Adsorption models

Two different models were used to fit the adsorption data. The Freundlich model (FM), which is commonly used for quantifying HOC sorption equilibria for soils and sediments, takes the following form

$$Q_e = K_F(C_e)^n \quad (1)$$

where Q_e represents the equilibrium sorption capacity (mg/kg); C_e represents the equilibrium aqueous concentration (mg/L); K_F is the Freundlich model capacity factor ((mg/kg)/(mg/L)ⁿ), and n is the isotherm linearity parameter, an indicator of energy heterogeneity at the site (He et al., 2006).

There are two sorption mechanisms, i.e., partition and adsorption, associated with the interfacial behavior of HOCs in the sediment-BC/water system, which can be described well by the dual-mode model (DMM) proposed by Xing and Pignatello (1997).

$$Q_T = Q_P + Q_A \quad (2)$$

where Q_T is the total amount of NP sorbed to the sediment-BC system (mg/kg), and Q_P (mg/kg) and Q_A (mg/kg) are the amounts contributed by partitioning and adsorption, respectively.

In a mixed adsorption-partition system, the partition effect is progressively favored by increasing solute concentrations, and the adsorption contribution reaches saturation more rapidly with increasing solute concentration. The isotherm at high concentrations should approach linearity. The model for a linear equation is

$$Q_T = K_{om}C_e + Q_{max} \quad (3)$$

where K_{om} and Q_{max} are constants. $K_{om}C_e$ is the sorption contribution by partition at a high concentration, with K_{om} representing the partition coefficient (L/kg). Q_{max} is the saturated adsorption capacity estimated from the high concentration data (mg/kg).

According to Eqs. (2) and (3), $K_{om}C_e$ is the partition capacity, so the adsorption capacity is

$$Q_A = Q_T - Q_P = Q_T - K_{om}C_e \quad (4)$$

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