# Importance of the structure and nanoporosity of organic matter on the desorption kinetics of benzo[a]pyrene in sediments☆

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## ARTICLE INFO

## ABSTRACT

The desorption kinetics and mechanism were investigated using a Tenax extraction technique on different sediments spiked with radiocarbon-labeled benzo[a]pyrene (BaP). Five sedimentary fractions were sequentially fractionated, and the only nonhydrolyzable organic carbon fractions (NHC) were characterized using advanced solid-state $^{13}C$ nuclear magnetic resonance spectroscopy (NMR), improved six end-member model, and a $CO_2$ gas adsorption technique. The sediments contained high percentages of algaenan and/or sporopollenin but low percentages of black carbon and lignin. A first-order, two-compartment kinetics model described the desorption process very well ($R^2 > 0.990$). Although some of the organic carbon fractions were significantly related to the desorption kinetics parameters, the NHC fractions showed the highly significant correlation. Moreover, the nanoporosity or specific surface area (SSA) of the NHC fractions was highly related to their OC contents and aliphatic C ($R^2 = 0.960$, $p < 0.01$). The multiple regression equations among the desorption kinetics parameters, structural parameters, and nanoporosity were well established ($R^2 = >0.999$). Nanoporosity and aromatic C were the dominant contributors. Furthermore, the enhanced percentages of desorbed BaP at elevated temperatures significantly showed a linear regression with the structure and nanoporosity. To our knowledge, the above evidence demonstrates for the first time that the transfer (or diffusion) of BaP in the nanopores of condensed aromatic components is the dominant mechanism of the desorption kinetics of BaP at organic matter particle scale.

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## 1. Introduction

Sediment is the most important sink of hydrophobic organic contaminants (HOCs) in the environment. Slow sorption/desorption rates are frequently rate-limiting for biodegradation, bioremediation, and subsurface transport. Recent work has attributed these rates to intra-organic matter diffusion and/or intra-aggregate diffusion (Brusseau et al., 1991; Luthy et al., 1997). Organic matter diffusion models with shallow penetration depths on the order of submicrons to tens of nanometers have also been proposed (Carroll et al., 1994; Ghosh et al., 2000; Pignatello and Xing, 1996). Molecular diffusion in hydrophobic microporous materials occurs by a series of activated jumps and is primarily governed by steric energy barriers (Luthy et al., 1997).

Organic matter diffusion is responsible for the nonequilibrium sorption of HOCs by natural sorbents (Brusseau et al., 1991; Pignatello and Xing, 1996). Dual-mode models have been well accepted and invoke "soft or rubbery" versus "hard or glassy" domains to distinguish two broad categories of expanded and condensed natural organic matter (NOM) (Pignatello and Xing, 1996). Rubbery NOM in sediments consists of fresh biopolymers and hydrolysable NOM and exhibits a low sorption affinity and linear isotherms for HOCs (Xing and Pignatello, 1997). Condensed NOM may consist of kerogen, coal, black carbon, and nonhydrolyzable NOM (Ran et al., 2007a; Song et al., 2002) and exhibits a high sorption affinity and nonlinear isotherms for HOCs. It has been found that the composition and structure of NOM strongly affect the sorption and desorption of HOCs. The binding energy and desorption rates of HOCs among the different types of organic matter fractions greatly differ. To date, some researchers have found that HOCs associated with black carbon are very tightly bound and difficult to desorb from sediments (Accardi-Dey and

Gschwend, 2002; Cornelissen et al., 2005). Other investigators assessed the effects of humin (Liu et al., 2012), lipids and lignin (Kukkonen et al., 2003) on the desorption kinetics of HOCs.

With respect to the effect of the NOM structure, either the aliphaticity (Chin et al., 1997; Xing, 2001) or aromaticity (Mao et al., 2002) of sorbents has been positively related to the sorption affinity of HOCs in previous reports, but the relative importance of these two components is still a matter of debate (Chefetz and Xing, 2009). Moreover, the role of nanoporosity on the sorption of HOCs in sediment, coal, and kerogen samples has recently been demonstrated, suggesting that a nanopore filling significantly contributes to the sorption and sorption kinetics of HOCs in sediments (Han et al., 2014; Ran et al., 2013; Sun et al., 2013). However, the relationships between the nanoporosity and desorption kinetics have not been reported. Furthermore, temperature is another important factor that influences the desorption behavior of HOCs in sediments. Some reports have focused on the effect of temperature on the desorption kinetics (Cornelissen et al., 1997b; Werth and Reinhard, 1997) and found that the activation energy in desorption energy ranged from 9.5 to 70 kJ mol$^{-1}$ for the studied HOCs, similar to the values for the diffusion of organic solutes in polymers. However, the relationship between diffusion of organic solutes and nanopores in NOM domains are not yet clear. In summary, the desorption kinetics mechanism of HOCs by NOM is still under investigation.

Tenax resin is a porous polymer resin that is considered to infinitely absorb HOCs desorbed from sediments. Due to its strong sorption affinity for a variety of HOCs, Tenax has been widely used as an "infinite" sink to measure the desorption of HOCs from sediments (Cornelissen et al., 1997a; Kukkonen et al., 2003). Benzo[a]pyrene (BaP), as a typical hydrophobic organic contaminant, has been of great concern because it is genotoxic and carcinogenic to various organisms. In this study, Tenax resin was selected as a sink to investigate the desorption kinetics of BaP in five sediments of the Pearl River Delta. In addition, organic fractions, such as demineralized carbon (DM), lipid-free carbon (LF), lipid (LP), and non-hydrolyzable carbon (NHC), were isolated, and their NHC structures and surface properties were investigated using advanced solid-state $^{13}$C CP/MAS NMR spectroscopy and an updated $CO_2$ gas adsorption technique, in order to understand the roles of the different organic fractions, NHC structure and nanoporosity on the desorption kinetics of BaP. Finally, the effect of temperature on the relationship between the NHC structure and desorption of BaP was also explored.

## 2. Materials and methods

### 2.1. Chemicals and materials

7-$^{14}$C-Benzo[a]pyrene (BaP, >95% radiochemical activity, 26.6 mCi/mmol) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Non-labeled BaP (analytical grade, purity >98%) was obtained from Sigma-Aldrich (St. Louis, MO, USA). The physicochemical properties of BaP are as follows: molecular weight (MW) of 252.32 g/mol, bulk density of 1.24 g/cm$^3$ at 25 °C, water solubility ($S_w$) of $1.62 \times 10^{-3}$ mg/L, octanol-water partition coefficient (log $K_{ow}$) of 6.13, fusion temperature of 178.1 °C, and boiling point of 496 °C. Tenax® resin (60–80 mesh, i.e., 177–250 μm) was obtained from Supelco (Bellefonte, PA, USA). All solvents and other chemicals used in this study were of gas chromatography or analytical grade.

### 2.2. Sediment collection

The sediments were collected from rivers and reservoirs in the Pearl River Delta of China to represent a range of TOC contents and OM compositions. Three sediment samples (Z, E and A) were collected from the Dongjiang River using a box sampler in 2009. Two sediment samples (X and L) were collected from the Xinfengjiang Reservoir and Lian'an Reservoir in 2012 (Duan et al., 2015). The sample details are listed in the Supplemental Data. The sampling sites are presented in Fig. S1 in the Supplemental Data. The samples were transported to the laboratory after collection, freeze-dried, ground, and passed through an 80 mesh sieve for later use.

### 2.3. Sediment spiking with BaP and aging

Sediments were spiked with 500 ng/g BaP on a dry weight basis, including 50 ng/g $^{14}$C-BaP and 450 ng/g non-labeled BaP. The spiking procedure was as follows: 20 g (dry weight) of each sediment sample was placed in a 250 mL conical flask, and a quantitative BaP stock solution (in acetone) was added into the conical flask. The aging treatments are detailed in Supplemental Data. The final concentrations of BaP normalized by the OC contents of the five samples (X, Z, E, A and L) are 71.4, 44.6, 30.3, 24.0 and 15.6 μg/g OC (Fig. S2).

### 2.4. Desorption experiment

Before use, the Tenax resin was rinsed by sonicating three times in acetone and three times in hexane and dried overnight at 60 °C. Aliquots of 0.5 g (dry weight) of the sediment samples were transferred to 25 mL glass vials. Tenax resin (0.1 g) and 20 mL deionized water were then added to each vial. A mercury chloride solution (50 mg/L) was added to inhibit microbial activity. The samples were shaken in an incubator at approximately 120 rpm at room temperature for 1, 2, 6, 12, 24, 48, 96, 192, 288 or 384 h, with three replicates of each desorption interval. At each predetermined time, Tenax was separated from the sediment by centrifugation at 3000 rpm for 15min, and this process was simplified as Tenax resin floats on the water. For consecutive Tenax extractions, fresh Tenax resin was added to resume the desorption process. The trapped Tenax resin was rinsed thoroughly with deionized water and then extracted by sonicating in 5 mL of acetone/hexane mixture (1:1, v/v) in 8 mL glass vials. The extraction treatment was repeated three times. The extracts from the same sample were combined and concentrated to 2–3 mL by evaporation, and mixed with 10 mL Ultima Gold LSC cocktail. The $^{14}$C radioactivity was analyzed by LSC to calculate the desorbed amount of BaP.

To examine the effect of temperature on the desorption of BaP, the desorption of BaP at various temperatures was performed. The temperature was set at 25 °C, 40 °C, 60 °C by an incubator for the five spiked samples (X, Z, E, A, L). Desorption experiments were conducted for 24 h for each sample at different temperature. The desorbed amount of BaP was measured by LSC.

### 2.5. Data analysis

The desorption of HOCs from soils or sediments is usually characterized by a rapid process followed by a slow process. A first-order, two-compartment kinetics model is often chosen, in which each compartment is defined by its respective rate constant (Barnier et al., 2014; Cornelissen et al., 1997a).

$$\frac{S_t}{S_0} = F_{rap}.e^{-k_{rap}.t} + F_{slow}.e^{-k_{slow}.t} \qquad (1)$$

$$F_{rap} + F_{slow} = 1 \qquad (2)$$

where $S_t$ and $S_0$ (ng/g) are the concentrations of BaP in the sediment