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Assessing desorption resistance of PAHs in dissolved humic substances by membrane-based passive samplers

Shan Chen, Yiping Xu, Zijian Wang *

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

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ABSTRACT

Binding of hydrophobic organic compounds (HOCs) to humic substances (HS) has significant influence on their fate and bioavailability in an aquatic environment, yet very little is known on the desorption behavior of HOCs in dissolved HS. In this study, triolein-embedded cellulose acetate membranes (TECAMs) were used as passive samplers in dissolved HS-containing solutions to extract the free polycyclic aromatic hydrocarbons (PAHs). The partitioning coefficients (K_{OC}) of PAHs in dissolved HS from different sources were determined. Then the rapidly desorbable fractions (f_{rd}) of HOCs in dissolved HS were quantified by a quasi-equilibrium model. Results show that the magnitude of K_{OC} of PAHs correlated strongly with the O/C atomic ratio and molecular weight of HS. The PAHs with lower K_{OW} values desorbed almost reversibly from an aquatic fulvic acid, a sediment humic acid (HA), a lignite HA, and Aldrich HA. However, for strongly hydrophobic chrysene binding to the lignite HA, some extent of desorption resistance was found and attributed to sorption hysteresis as well as steric hindrance. The present study illustrated that the quality of HS and the property of solute may play key roles in determining the desorption reversibility.

1. Introduction

The degree and the pattern of contamination in the aquatic system depends mainly on the availability of the contaminants to be transferred in and by water. The availability is in large extent determined by the binding–desorption behavior of contaminants in dissolved organic matter (DOM), 50–80% of which is humic substances (HS) [1,2]. Many researchers have focused on HS interactions with hydrophobic organic compounds (HOCs) in the past few decades, considering their widespread existence and strong binding capacity.

Generally, it was widely believed that the partitioning of HOCs between water and dissolved HS was nonspecific and the binding of contaminants was rapidly reversible with characteristic equilibration times of hours to a few days at most [3–6]. However, numerous findings were reported recently that our fundamental understanding of sorption and desorption might be in need of reexamination [7]. For instance, a few studies showed that the HS–water system exhibits a complex behavior and a small fraction of the sorbed contaminant remained unexpectedly in HS, just as often observed in sediment–water systems [8]. In Schlebaum et al.'s study, the results showed that part of pentachlorobenzene sorbed to a dissolved humic acid (HA) resisted desorption. They speculated that the nonlabile fraction was a consequence of a change of conformation of the HA after the binding of pentachlorobenzene [9]. Several different rate models have been used to describe desorption of HOCs from natural sorbents. Intrinsically, desorption of organic compounds from sediment is generally accepted to be at least biphasic, a rapidly desorbing phase followed by a more slowly desorbing fraction [10]. This biphasic model may correspond to desorption in different humic structures that vary in hydrophobicity or rigidness. Therefore, a biphasic desorption model was proposed in the present study, to give a direct description of irreversible desorption.

As in most cases the division between rapid desorption and resistant desorption is rather arbitrary; batch-mode chemical extraction tests appear not able to mimic resistant desorption. Time-integrated techniques have been used as infinite sink for desorbed compounds in the literature for time frames from a few hours to a few days. Examples of these methods include Tenax-aided desorption and equilibrium dialysis [5,9,11–13]. Tenax extraction has advantages of high sorptive capacity and rapid adsorption from water. However, Tenax could not mimic some aquatic complex processes actually, such as reverse adsorption from water and solute effects on HS, since it keeps aqueous sorbate concentrations very low [14]. In terms of an equilibrium dialysis method, one disadvantage reported was the possible leakage of low molecular weight HS through the dialysis membrane. To overcome the above shortcomings, triolein-embedded cellulose acetate membranes (TECAMs) were used in this study as in situ sink under a quasi-balanced state to concentrate free dissolved solute. The overall objective of this research is to investigate the extent of ra-

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* Corresponding author. Fax: +86 010 62849140.
E-mail address: wangzj@rcees.ac.cn (Z. Wang).

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pid desorption of contaminants in dissolved HS. Several types of HS from either commercial sources or natural sources were tested. PAHs were selected as model compounds because of their ubiquitous existence and wide range of hydrophobicity. Furthermore, it was also expected that a relation between HS properties and binding affinity for PAHs would be found.

2. Materials and methods

2.1. Materials

Three deuterated PAH standards, phenanthrene-d_{10}, pyrene-d_{10}, and chysene-d_{12}, were purchased from Supelco Inc. (Bellefonte, PA). The mixed standard solution was prepared by diluting the original stock solutions with methanol to 20 mg/L. Four kinds of HS obtained from various sources were used in the present study: Aldrich HA (HA sodium salt from Sigma–Aldrich, Steinheim, Germany), Nordic aquatic fulvic acid reference (Nordic FA), and Leonardite HA standard (International Humic Substances Society, Denver, CO, USA), as well as PSHA (a generous gift from professor Pingan Peng, Guangzhou Institute of Geochemistry, isolated from a pond sediment). HS stock solutions were prepared as follows: each HS was dissolved in 0.01 M sodium hydroxide solution (pH 12) separately, and then the solution was stirred for about 24 h and centrifuged at 27,100*g* average relative centrifugal force (20 °C) for 1 h to remove most of the particles and finally filtered with prerinsed cellulose acetate nitrate membrane filters of 0.45-μm pore diameter (Whatman, Clifton, NJ) to remove any remaining particulate material. The organic carbon content of the HS stock solution was measured with a total organic carbon analyzer (Phoenix-8000, Tekmar–Dohrmann, Mason, OH). The ultrapure water (OC < 0.1 mg C/L) used in this study was purified by a Milli-Q Gradient system (Millipore, Bedford, MA). Solvent and other chemicals used in the study were of GC or analytical reagent grade. Small pieces of TECAM (4 × 6 cm) were used and the procedure for preparing was the same as described previously [15]. The TECAM consists of two immiscible phases: an outer hydrophilic membrane and inner hydrophobic triolein drops. The image from a scanning electron microscope (SEM) showed that there were many micropores of nanosize on the surface of the outer layer. The porosity of TECAM is 55.3 ± 3.1%. In TECAM, the triolein drops embed in the matrix of cellulose acetate polymers and closely adhere with the polymers. Our previous study showed that the structure of TECAM was stable and the distribution of triolein drops did not change with the HS concentration, pH, or ionic strength of exposure water samples.

HS sample solutions were produced by diluting the HS stock solutions with ultrapure water to reach a content of 5 mg C/L. The solutions were then adjusted to a pH of 7.0 ± 0.3 with 0.1 M HCl and 0.1 M NaOH, transferred to sterilized 1000-mL glass flasks, and spiked with 500 ng/L of each PAH separately. The concentration of carrier did not exceed 0.1 mL/L. The flasks were kept sealed with Teflon-lined caps and shaken gently on a shaker for 48 h in the dark at 20 ± 1 °C.

2.2. Binding experiments

A previous study has shown that the uptake rate of HOCs in TECAM is independent of HA concentrations [16]. The system consists of two round-bottomed flasks connected by a bent tube. One flask was filled up with 1 L of Milli-Q water, the other was filled with 1 L of 15 mg C/L humic acid solution, and both solutions were spiked with 20 OCPs to obtain an aqueous concentration of 200 ng/L for each analyte. Then the two flasks were connected by the vapor-tight air bridge and the flasks were magnetically stirred for 3 weeks to equilibrate the system. After equilibration, one TECAM was put in each flask and sampled for 1 h on a rotatory shaker (90 rpm, 20 °C), and the mean concentration for each OCP in the TECAM samples in the presence and the absence of humic acid was similar ($P > 0.05$). As the free concentrations of OCPs in both flasks of the air-bridge system were equal, the results confirmed our assumption that matrix effects could be neglected in our study. Thereby it can be concluded that the presence of DOM does not influence the uptake kinetics by TECAM, and this method could be used to determine the freely dissolved concentration of analytes in HS-containing samples.

Organic carbon normalized partition coefficients (K_{OC}) of PAHs in HS were determined in batch-mode experiments in three replicates. TECAM exposed for 1 h in solution without HS accumulated less than 5% PAHs of total amount (negligible depletion sampling) [17], suggesting that the aqueous concentration of PAHs remains constant. Therefore, it could be extrapolated that the depletion of TECAM in HS-containing solution also was negligible during this time period. Uptake–time plots of TECAM in 100 ng/L PAHs solutions over 12 h showed that accumulation is in the linear-uptake phase when test solutions were changed per hour. The slopes of fitting lines by linear regression in Fig. 1 were used to calculate K_{OC}. The uptake profiles of PAHs in TECAM were produced in a series of HA-free solutions (50–1000 ng/L) at first for measuring uptake rate constant k_1 according to

$$C_m = k_1 C_w t, \tag{1}$$

where C_m represents the concentration of target compound in the TECAMs; k_1 is the uptake rate constant of compound in TECAMs; C_w is the concentration of compound in aqueous phase; t is the sampling time. Subsequent experiments were carried out in PAH–HS solutions. K_{OC} was determined from the isotherm slopes of solutions with and without HS.

$$K_{OC} = \frac{k_1 - k_1'}{k_1'[OC]}, \tag{2}$$

where k_1' represents the apparent uptake rate constant of TECAM in HS solutions. All regressions were done with relative coefficients above 0.9 and $P < 0.01$ (significant difference value).

Then a dynamic experiment for measurement of K_{TECAM} was performed with a laboratory static aqueous method developed by Banerjee et al. [18]. Distilled water (1000 mL) in conical flasks was spiked with 500 ng/L mixed PAHs and deployed with two pieces of TECAM. To prevent losses of PAHs due to volatilization, the flasks were sealed and shaken on a constant temperature-reciprocating shaker throughout the whole accumulation course. Temperature was kept at 20 ± 1 °C in all experiments. Preliminary

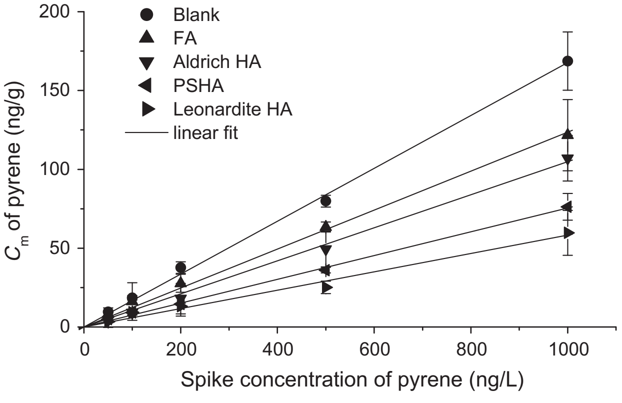

Fig. 1. Determination of the pyrene partition coefficient K_{OC} for HS of different origin from binding experiments. Bars correspond to standard error at $n = 3$.