Pyrene partition behavior to the NOM: Effect of NOM characteristics and its modification by ozone preoxidation

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Abstract Hydrophobic organic contaminants (HOCs)—pyrene, and natural organic matters (NOM) from different sources were taken as the test compounds to investigate the impact of physicochemical characteristics of NOM on HOCs’ partition to the NOM in this study. The effects of solution property, NOM characteristics, and modification by ozone preoxidation on pyrene partition to NOM were systematically evaluated. According to the fluorescence quenching method, the partition coefficient $K_{oc}$ of pyrene to NOM was calculated, which was found to have a great relationship with the aromatic structures and hydrophobic functional groups of the NOM. The NOM characteristic modification corresponding to solution property could influence the interactions between the NOM and pyrene. Preozonation could destroy the aromatic or hydrophobic structures of the NOM and decrease $K_{oc}$ of pyrene.

Keywords natural organic matters (NOM), pyrene, partition coefficient, ozone

1 Introduction

Natural organic matters (NOM) are present in all aqueous environments which control the fate of hydrophobic organic contaminants (HOCs). To understand the transformation of HOCs and evaluate their toxicity, it is necessary to investigate the interactions between the NOM and the HOCs. However, various biogeochemical phenomena occurring in terrestrial and aquatic systems (including soil erosion, microbe degradation, season alternation, water quality change, solid-water interface partitioning, and photodegradation) lead to the intricate structure of NOM; as a result, the partition of HOCs in NOM is quite complicated.

Usually, organic carbon-normalized partition coefficient $K_{oc}$ is used to evaluate the binding or partitioning affinity of HOCs to NOM, which was defined as [1]:

$$K_{oc} = \frac{[\text{HOC} - \text{NOM}]}{[\text{HOC}]_{\text{free}}[\text{OC}]}$$

(1)

where $[\text{HOC} - \text{NOM}]$ refers to the content of HOCs binding with the NOM; $[\text{HOC}]_{\text{free}}$ refers to the concentration of free HOCs; $[\text{OC}]$ refers to the organic carbon concentration. The total concentration of HOCs is the sum of $[\text{HOC} - \text{NOM}]$ and $[\text{HOC}]_{\text{free}}$.

The previous investigation had reported that the partition or binding affinity of HOCs to NOM was related to the composition or structures of the NOM. The modification of NOM characteristics could affect the level of HOCs partition to the NOM [2–6]. As reported, the $K_{oc}$ values were strongly correlated with the content of aromatic carbon in humic substances [7–10], and a positive trend was also observed between $K_{oc}$ level and the aliphaticity of NOM [11]. At the same time, positive [9] or inverse [10] correlation between $K_{oc}$ and the molecular weight were reported depending on the origin and/or fractional composition of the aggregated humic materials. Besides the investigation on NOM structures, solution properties including pH value, ionic strength, and cationic electrolyte characteristics had been demonstrated to greatly alter the structure of NOM [4,12]. However, only few researches were focused on the impact of solution property on HOCs’ partition to NOM. Ozone, as a commonly used pre-oxidant in water treatment, had been proven to greatly change the characteristics of NOM. It was reported that preozonation could decrease the molecular weight [13] and aromaticity of NOM [14,15], and change the hydrophobic fractions to more hydrophilic products [16,17]. No investigation, yet, was performed with respect to the impact of modification by ozone on HOCs’ partition behavior.

To make a systematic analysis concerning the impact of physicochemical characteristics of NOM and the solution
property on HOC partition to the NOM, the NOM from different sources including a commercial humic acid (CHA) and the fractions of NOM (Hydrophobic fraction—HyO, and Hydrophilic fraction—HyI) isolated from a surface water were taken to investigate the partition behavior of a typical HOC—pyrene to NOM. Furthermore, the impact of NOM characteristic modification with respect to preozonation was also studied in this paper.

2 Methods

2.1 NOM samples

The NOM was concentrated with a reverse osmosis system from water in the Songhua River, Northeast China. Amberlite resin (XAD-7HP, Rohm & Haas, China) was used to fractionate NOM into hydrophobic fraction (HyO) and hydrophilic fraction (HyI). The concentrated and purified NOM was acidified to pH 2 with concentrated HCl and pumped through the resin column. The permeating fraction was the HyI, while the fraction retained on the resin was the HyO of NOM. After being diluted with 0.1 mol/L of NaOH, the HyO was obtained. According to the mass balance calculation, the HyO was the main component in water from the Songhua River. The HyO accounted for 64%, while the HyI accounted for 18% of the total dissolved organic carbon. The loss of the dissolved organic carbon was 18%. CHA was purchased from Shanghai Hengxin Chemical Regent Co., Ltd., China. Following the dissolution and precipitation, the stock solution of CHA (1000 mg/L) was further filtered with 0.2 μm membrane.

2.2 Molecular weight determination [18]

High pressure liquid chromatograph (LC-10A, SHIMADZU, Japan) equipped with a Waters BondageTM E-125 column was used to determine the weight average molecular weight (\(M_w\)), number average molecular weight (\(M_n\)), and polydispersity (\(M_w/M_n, \rho\)) of CHA, HyO, and HyI. Sodium polystyrene sulphonates (PSS, Fluka, Switzerland) with molecular weight of 17000, 4300, 2400, salicylic acid (138) and acetone (58) were used as the standards. The mobile phase was Milli-Q water which was buffered with phosphate (1.39 g/L of Na2HPO4 + 0.73 g/L of KH2PO4) and 0.1 mol/L of NaCl to pH 7.0. After ultrasonic degassing, the mobile phase was then vacuum-filtered through a 0.2 μm membrane filter in an all-glass filtration apparatus. The sample volume was 200 μL and the flow rate was controlled at 0.4 mL/min. The sample effluent was detected at a wavelength of 254 nm with a UV detector (SPD-10A VP, SHIMADZU, Japan).

2.3 Polarity measurement [19,20]

The polarity distribution was determined by the Reverse Phase-HPLC system (LC-10A, SHIMADZU, Japan) equipped with a C-18 column (shim-pack Vp-ODS 150 L×4.6). The mobile phase was 70% of methanol and 30% of acetic acid/acetate buffer (0.1 mol/L) at pH 4. The sample volume was 20 μL and the flow rate was controlled at 1 mL/min. The sample effluent was detected with SPD-10A VP UV detector at a wavelength of 254 nm.

2.4 UV-spectrophotometer

The \(E_{465}/E_{665}\) (the ratio of absorbance at 465 nm to 665 nm) and the SUVA (UV254/TOC×100) was performed on a scanning UV/VIS spectrophotometer (UV-2550, SHIMADZU, Japan). Total organic carbon was analyzed with TOC analyzer (TOC-VCPN, SHIMADZU, Japan).

2.5 Preozonation experiment

Preozonation experiment was operated in a semi-batch mode. The reaction temperature was controlled at 20°C by circulated cooling water. Ozone dosage was 0.8 and 2.2 mg/L respectively, which was the transferred dosage determined by Indigo blue methods. After being oxidized with ozone, the CHA, HyO, and HyI solutions were given enough time to settle.

2.6 Fluorescence quenching method

Pyrene (C_{16}H_{10}) was purchased from Aldrich (99% pure, molecular weight of 202.26, USA). \(K_{oc}\) of pyrene from aqueous phase into humic phase could be obtained by the linear Stern–Volmer equation as follows:

\[
\frac{F}{F_0} = 1 + K_{oc}[DOC]
\]

where \(F_0\) denotes the fluorescence intensity of the pyrene in the absence of humic acids; \(F\) represents the intensity of the pyrene in the presence of humic acids; [DOC] is the concentration of organic carbon of humic acid (kg/L), which served as the fluorescence quencher of this system. The pyrene stock solution of 5 mmol/L was prepared by dissolving 0.0506 g pyrene in 50 mL of methanol. A small amount of this stock solution was pipetted into 10 mL centrifuge tubes. Buffered aqueous solutions (sodium acetate and acetic acid, pH 4.5; phosphate buffer, pH 7; phosphate buffer, pH 10) containing various concentrations of humic material were added to each tube. The initial concentration of pyrene was 110 μg/L, and the volumetric content of methanol did not exceed 0.1%. Fluorescence spectra of pyrene and humic acids were recorded with a fluorescence spectrophotometer (RF-5000, SHIMADZU, Japan). The wavelengths of excitation and emission for