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# Remobilization and bioavailability of polycyclic aromatic hydrocarbons from estuarine sediments under the effects of *Nereis diversicolor* bioturbation☆

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ABSTRACT

The effects of *Nereis diversicolor* bioturbation on the remobilization and bioavailability of polycyclic aromatic hydrocarbons from estuarine sediment were determined after 60 d in a laboratory experiment. The release fluxes and mass transfer coefficients showed that bioturbation by *N. diversicolor* can lead to a significant remobilization of polycyclic aromatic hydrocarbons (PAHs) from estuarine sediments. Bioturbation enhanced the release of PAHs from sediment to water by accelerating the transport of sediment particles to the sediment-water interface followed by PAHs desorption to the water. The bioavailability of PAHs was described by SPMD-sediment accumulation factors (SSAF). The SSAF of low molecular weight PAHs with bioturbation was significantly higher than that of PAHs without bioturbation, and there were no significant variations in high-molecular-weight PAHs. Our results revealed that *N. diversicolor* bioturbation significantly increased PAHs release from sediment to water but only increased the bioavailability of low-molecular-weight PAHs.



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the environment, especially in the sediments of estuaries throughout the world, and they are of great interest due to their toxic effects on the environment (Ugwu and Ukoha, 2018). Once PAHs enter a water body, they are preferentially associated with suspended particulate matter and then precipitate to the bottom sediment (Sun et al., 2017). Contaminated sediment can release these substances and thereby act as a secondary source of PAHs to the water column (Dong et al., 2016; Mustajärvi et al., 2017). Several processes, such as mechanical water mixing, wave action, tides, and wind, have been demonstrated to significantly affect on the release of PAHs from sediment to water in the field.

Bioturbation is also one of the processes that can lead to direct or indirect PAHs transfer from sediments to water. Bioturbation is a natural process and driven by the activities of invertebrates in the sediment (Hoang et al., 2018), and it generally, refers to all transport processes carried out by animals that directly or indirectly affect sediment matrices (Kristensen et al., 2012). One study by Mustajärvi et al. (2017) showed that the release of PAHs in sediment was enhanced by bioturbation, and in a previous study, we found that the release of dissolved PAHs through bioturbation by crabs was 1.7–3.7 times higher than in treatments without bioturbation (Sun et al., 2017). These results indicate that bioturbation can induce a significant release of PAHs from sediments to the water column.

Once PAHs are released from sediment to water, they may be absorbed by aquatic organisms, posing potential risks to these organisms and even to humans that consume them, so evaluating of bioavailability of PAHs is very important. Traditionally, the bioavailability of PAHs has been evaluated using aquatic organisms, such as fish, bivalves, and oligochaetes (Keshavarzifard et al., 2017; Tian et al., 2018), but some drawbacks to this approach have been found. One of these drawbacks is the complexity of the factors influencing bioavailability, i.e., the sex, age, and health status of the

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organism, and an other is that some species can metabolize PAHs. Additionally, the organisms may not survive during the evaluation process. In recent years, semipermeable membrane devices (SPMDs) have been successfully applied to assess the bioavailability of PAHs in water (Chang et al., 2015; Wang et al., 2016). SPMDs are composed of sealed low-density polyethylene membrane tubes with a thinly spread layer of neutral glycerol triolein inside, which makes the SPMD similar to an aquatic organism: dissolved PAHs can pass through the membrane of the SPMD and accumulate in the internal lipid layer. In contrast to living organisms, SPMDs can provide reproducible results, do not metabolize the PAHs, and are durable in severely polluted environments, so they can overcome the disadvantages of living organisms in tests of bioavailability (Chang et al., 2015).

Historically, Bohai Bay has been subjected to different anthropogenic pressures; it is the only recipient of approximately one billion tons wastewater from Beijing, Tianjin, and Hebei Province in China. High concentrations of PAHs (2.7 μg $g^{-1}$) have been found in the sediment from the estuary of Bohai Bay (Qin et al., 2010). In recent years, several benthic organisms, such as *Nereis diversicolor, Scapharca subcrenata*, *Cyclina sinensis*, *Perinereis aibuhitensis*, and *Venerupis variegata*, were introduced to restore the ecological system of Bohai Bay. Bioturbation by these benthic organisms may enhance the release of PAHs from sediment to water and thus pose a potential ecological risk. However, little relevant information is available for Bohai Bay.

The present study was conducted to investigate the remobilization and bioavailability of PAHs from estuarine sediment by bioturbation by a laboratory experiment. The sediments were collected from Bohai Bay, and *N. diversicolor*, which is one of the dominant benthic organisms in the estuary of Bohai Bay, was used as the bioturbator in the experiment. The main objectives of this study were (1) to investigate the release of PAHs from contaminated estuary sediment by bioturbation and (2) to evaluate the bioavailability of the released PAHs from sediment to water by *N. diversicolor* bioturbation using SPMDs. The results of this study are very useful in understanding the ecological risks caused by the benthic organisms introduced to restore the ecological system of Bohai Bay.

## 2. Materials and methods

### 2.1. Chemicals and materials

Details about the chemicals, materials, pretreatment of materials, and analyses are provided as Supporting Information.

### 2.2. Collection of sediment and organisms

We collected sediment in the Dagu Estuary of Bohai Bay, China (40°7′ N and 117°7′ E). The sediment was sieved through a one mm mesh to remove macrofauna and was frozen at −20 °C to kill residual organisms (Sun et al., 2017). *N. diversicolor* was purchased from a company in Tianjin, China, and then was acclimatized in the laboratory for 30 d at 20 ± 0.50 °C in breeding tanks with sediment before the experiment.

### 2.3. Microcosm design and experimental setup

Each microcosm was a glass cylinder with a diameter and height of 9 cm and 40 cm, respectively. The microcosm contained sediment (height of 20 cm) and overlying artificial seawater (height 15 cm and salinity of 15‰) composed of distilled water and sea salt crystals (China Salt Group Tianjin Division, Tianjin, China). An air pump was used to gently bubble the air to maintain fully oxygenated water in each microcosm.

Four treatments were established: (1) NN, in which there was no *N. diversicolor* in the microcosms. This treatment was used to evaluate the PAHs transfer from sediment to water without bioturbation; (2) YN, in which there were 4 *N. diversicolor* in the microcosm. This treatment was used to determine the release of PAHs from sediment to water by bioturbation; (3) NNS, in which an SPMD was added to NN to measure the bioavailability of the PAHs released to water without bioturbation; and (4) YNS, in which SPMDs were added to YN to investigate PAHs bioavailability with bioturbation. Additionally, blank microcosms containing only 3 L of artificial seawater were used as negative controls. Five microcosms were designed for each treatment (blank microcosms were run in triplicate). The exposures were run at 20 ± 0.50 °C under natural light. The glass cylinders were wrapped with black plastic bags to prevent illumination. The experiment lasted 60 d, and *N. diversicolor* was not fed during the experiments. The artificial seawater in the microcosm was not replaced during the experiment. Due to evaporation, distilled water was added every day to maintain the water level in the microcosms.

### 2.4. SPMD sediment accumulation factors (SSAF)

The biota-sediment accumulation factor (BSAF) is used to describe the bioaccumulation potential of pollutants sorbed in sediments, and it is the ratio between contaminant concentrations in the biota (based upon lipid weight) and sediments (based on organic carbon). In the present study, the SPMD was a mimetic biota, so the SPMD-sediment accumulation factors (SSAF), are defined as follows:

$$SSAF = \frac{C_{SPMD}}{C_{sed}/f_{oc}} \tag{1}$$

where $C_{SPMD}$ is the PAHs concentration in SPMD (ng $L^{-1}$), $C_{sed}$ is the PAHs concentration in the sediment (ng $g^{-1}$), and $f_{oc}$ is the total organic carbon content of sediment.

### 2.5. Release fluxes and mass transfer coefficients

The release flux ($N$, ng $m^{-2}$ $d^{-1}$) of PAHs from the sediment to the water was calculated according to the following equation:

$$N = \frac{M}{A \times t} \tag{2}$$

where $M$ is the total mass of PAHs measured in the water column (in ng), $A$ is the sediment surface area, and $t$ is the exposure time.

Sediment-to-water mass transfer coefficients (MTC, cm $d^{-1}$) for the transport of dissolved PAHs were calculated based on the following model by Thibodeaux et al. (2001):

$$MTC_{diss} = \frac{N_{diss}}{C_{PW} - C_{WC}} \times 10 \tag{3}$$

$$C_{PW} = \frac{C_{sed}}{f_{OC} \times K_{OC}} \tag{4}$$

where $N_{diss}$ is the flux of dissolved PAHs (ng $m^{-2}$ $d^{-1}$), $C_{PW}$ is the PAHs concentration in sediment porewater (ng $L^{-1}$), $C_{WC}$ is the PAHs concentration in the dissolved phase in the overlying water column (ng $L^{-1}$), $C_{sed}$ is the initial sediment contaminant concentration (ng $g^{-1}$), $f_{oc}$ is the fraction of sedimentary organic carbon, and $K_{oc}$ is the organic carbon-water partition coefficient. $K_{oc}$ was calculated based on the experimental relationship between $K_{oc}$ and