Journal of Hazardous Materials 272 (2014) 66–74

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Accelerated removal of pyrene and benzo[*a*]pyrene in freshwater sediments with amendment of cyanobacteria-derived organic matter

Zaisheng Yan [a], Helong Jiang [a,*], Xiaohong Li [a,b], Yuan Shi [a]

[a] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
[b] University of the Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Amendment of cyanobacterial biomass enhanced pyrene and B*a*P degradation in sediments.
- Amended cyanobacterial biomass improved PAHs bioavailability and microbial activity.
- Cyanobacterial biomass was superior to humic substances for PAHs removal in sediments.
- Settled cyanobacterial biomass strongly affected the fate of PAHs in lake sediments.
- Cyanobacterial biomass could be used for remediation of PAHs-contaminated sediments.

ARTICLE INFO

Article history:
Received 27 October 2013
Received in revised form 2 February 2014
Accepted 26 February 2014
Available online 13 March 2014

Keywords:
Cyanobacterial blooms
Freshwater sediments
Natural attenuation
Polycyclic aromatic hydrocarbon (PAH)
Priming effect

ABSTRACT

The removal of pyrene and benzo[*a*]pyrene (B*a*P) were investigated in freshwater sediments with amendment of seven different organic matters including cyanobacteria-derived organic matter (COM), plant-derived organic matter (POM), and humic substances (HS). During the 210 days of experiments, the amendment of COM or HS enhanced significantly the removal of pyrene and B*a*P in sediments, especially with fresh COM (FCOM) treatment much superior to HS. On the contrary, degradation of these polycyclic aromatic hydrocarbons (PAHs) was not significantly improved and even inhibited in POM-amended sediments. The first-order rate constants of pyrene and B*a*P degradation in the FCOM-amended sediments reached $0.00540 \pm 0.00017\ d^{-1}$ and $0.00517 \pm 0.00057\ d^{-1}$, respectively, and were about three and five folds of those in the control treatment. The enhanced PAHs degradation in FCOM-amended sediments was related to higher PAH-degrading bacteria number and bioavailability with a result of biostimulation and priming effect by labile carbon and high-value nutrition in FCOM. Thus, this study improved our understanding about effects of settled biomass from cyanobacterial blooms, which occurred frequently in eutrophic aquatic ecosystems, on the natural attenuation of PAHs in sediments. Furthermore, this study would also help develop a new promising approach to remediate PAH-contaminated sediments through utilization of cyanobacterial bloom biomass.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants that are of environmental concern due to their potential toxicity, mutagenicity, and carcinogenicity [1,2]. In aquatic environments, PAHs generally accumulate as a mixture of several aromatic compounds in sediments because of their hydrophobicity [3]. Recently, concentrations of high molecular weight (HMW) PAHs, such as pyrene and benzo[*a*]pyrene, in sediments of shallow lakes show an increasing trend [1,2]. Compared to low molecular weight PAHs, HMW-PAHs pose high risk to the human health and ecological systems because of the persistence and genotoxicity of PAHs increase with increasing molecule size [3,4].

PAHs, once entering into sediments, are subject to natural attenuation which involved biotic/abiotic degradation and transformation [5]. Microbial degradation by bacteria and fungi represented the major mechanism responsible for the ecological recovery of PAHs-contaminated sites [6–8], but restricted by various factors that often resulted in a lower than expected removal efficiency [6,9]. As one of the key factors controlling the

* Corresponding author. Tel.: +86 25 8688 2208; fax: +86 25 8688 2208.
E-mail address: hljiang@niglas.ac.cn (H. Jiang).

http://dx.doi.org/10.1016/j.jhazmat.2014.02.042
0304-3894/

biodegradation of PAHs, bioavailability of PAHs in sediments was directly related to their desorption behaviors [9,10]. A positive correlation between the rapidly desorbed fraction of PAHs and the achievable extent of biodegradation in sediments had been demonstrated [10]. In sediments, the desorption behavior was strongly affected by the interaction between PAHs and sediment organic matter (SOM) [9,11,12].

SOM is a heterogeneous material including both labile organic matter and refractory organic matter [13]. Complex components of SOM showed various characteristics for PAH desorption behavior in sediments [9,14]. For example, geologically mature SOM as geosorbents exhibited slower desorption behavior for PAHs than diagenetically young SOM [9,11]. In addition, SOM could regulate potential of PAHs biodegradation, and even be used as substrate for co-metabolism [15]. However, plant-derived SOM such as cellulose and lignin had no effect on PAHs dissipation and metabolism [15,16]. Humic substance (HS), which constitutes the major part of the complex mixture of organic material, was found to enhance PAHs degradation, but effects of HS were contradictory [17–19]. It was also indicated that HS had no or even a negative effect on PAH degradation in sediments [19]. Thus, the roles of SOM in biodegradation of HMW-PAHs in sediments remained unclear, and deserved more detailed study.

Organic matter (OM) in natural sediments has very variable compositions depending on their origins and the primary production in lake ecosystems. In recent decades, anthropogenically induced eutrophication has caused excessive growth of emergent and submerged macrophytes in lakes, especially in eutrophic shallow lakes. Furthermore, due to climatic changes and nutrient enrichment, cyanobacterial blooms are spreading frequently and globally in freshwater lakes and estuaries [20]. After decaying, those detritus from macrophyte and algal biomass settled into sediments and underwent mineralization, resulting in much vascular plant-derived organic matter (POM) and cyanobacteria-derived organic matter (COM) into sediments [13,21]. The autochonous OM input to sediments should be considered in evaluating the fate of PAHs in sediments in aquatic systems. Currently, however, it was unknown how settled cyanobacterial bloom-derived biomass affected PAHs degradation in sediments, although effects of POM on PAHs transformation were previously investigated. In addition, information was scarce about systematically comparing the effect of SOMs with different origin on the degradation of HMW-PAHs in freshwater sediments.

In this study, a series of OM-amended treatments in microcosm experiments were constructed to assess the effects of different OMs on the pyrene and B*a*P biodegradation in sediments. Seven different OMs from COM, POM, and HS were used as organic amendments. This study would be useful in evaluating the effect of eutrophication on degradation of PAHs in lake sediments as well as developing a new strategy for remediation of PAH-contaminated sediments.

2. Material and methods

2.1. Sediment sampling

Bulk samples of surface sediments were collected from the cyanobacterial bloom-occurring zone in Meiliang Bay (31°30′N, 120°11′E) and the macrophyte-growing zone in the east area (30°58′N, 120°22′E) of Taihu Lake (a large shallow lake in China), and transported to laboratory within several hours. After sieved at 2 mm, sediment samples from the two sites were mixed with equal wet weight, and homogenized to reduce heterogeneity within sediments. To spike PAHs into sediments, the stock solutions of pyrene or B*a*P (98% purity, Alfa Acsar Co., UK), were firstly prepared in acetonitrile (HPLC grade), and then added drop-wise to wet sediments followed by mixing mechanically at low speed for 2 h [22]. The amounts of pyrene and B*a*P to sediments were 2 and 0.5 mg kg^{-1} dry sediment, respectively. Prior to experiments, the spiked sediment samples were stored at 4 °C in dark and aged for up to 1 year.

2.2. Source of organic matter (OM)

Fresh cyanobacterial bloom biomass (fresh cyanobacteria OM, FCOM) was collected from Meiliang Bay of Taihu Lake (31°30′N, 120°11′E). Air-dried cyanobacterial biomass (dry cyanobacteria OM, DCOM) was ground to powder using pestle and mortar. The emergent plant (*Phragmites australis*) and submerged plant (*Potamogeton malaianus*) were collected from East Taihu Lake (30°58′N, 120°22′E), and named as emergent plant OM (EPOM) and submerged plant OM (SPOM), respectively. All parts of plant were mixed together and then crushed after air-dried and sifted through a 0.45 mm sieve as carbon amendment to sediments. Water contents of wet sediments, cyanobacterial bloom biomass, and air-dried plant material were approximately 57%, 97% and 10% by weight, respectively. Humic acid (HA, ≥90% purity) and microcrystalline cellulose (MC, ≥98% purity) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Stable compost humic substances (CHS) were obtained after composting aerobically sewage sludge in a pilot-scale plant in Nanjing (China) for three months, during which composting temperatures higher than 60 °C lasted two weeks. Humic acid content in CHS was 49%. In total, there were seven OMs including FCOM, DCOM, EPOM, SPOM, MC, HA, and CHS, which were amended to sediments. The contents of pyrene in COM, EPOM, SPOM and CHS were 0.027, 0.037, 0.002 and 0.056 mg kg^{-1} dry biomass, respectively. The concentrations of B*a*P in COM and CHS were 0.003 and 0.011 mg kg^{-1} dry biomass, respectively. The levels of pyrene and B*a*P in the other OM samples were below detection limit.

2.3. Experimental design

Plexiglass columns with approximately 1-L volume were used as sediment column bioreactors to perform the biodegradation experiment in a dark environment at 25 °C. Each bioreactor contained 600 g wet sediments and 0.3 L overlying water. The compositions of the mineral salts medium in the overlying water was (g L^{-1}): $K_2HPO_4{\cdot}3H_2O$, 0.0001; KH_2PO_4, 0.0002; NH_4Cl, 0.0115; $MgCl_2{\cdot}6H_2O$, 0.1; $CaCl_2{\cdot}2H_2O$, 0.1; and $FeCl_2{\cdot}4H_2O$, 0.02. Sediments were amended with FCOM, DCOM, EPOM, SPOM, MC, HA, and CHS, respectively. The amended amount into sediments for each OM was 1.5% (w/w) of dry weight sediments. After amendment, sediments were agitated for 24 h in darkness. The nutrient contents in different OMs and amended sediment samples were shown in Table 1. It is generally accepted that optimum C:N:P ratio for PAHs biodegradation is approximately 100:10:1 [23]. In this study, the nutrient contents in sediments in all treatments were sufficient to meet the need of microbes for PAHs biodegradation (Table 1). One treatment without OM addition was used as the control. All treatments had two replicates. At days 30, 90, 120, 150 and 210, sedimentary sample in each bioreactor was taken and analyzed.

2.4. Biodegradation kinetics

The biodegradation of PAHs was described by the first order kinetics Eq. (1) [24],

$$C = C_0 e^{-kt} \quad (1)$$

where C_0 is the concentration of PAH at time zero, C is the concentration of PAH after subtracting the abiotic loss at time t, and k is the first-order rate constant (biodegradation rate) of the reaction.