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Spatial variations, source apportionment and potential ecological risks of polycyclic aromatic hydrocarbons and synthetic musks in river sediments in Shanghai, China

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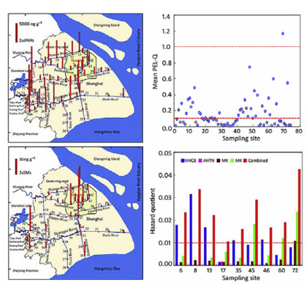
HIGHLIGHTS

- Twenty-six PAHs and four SMs were investigated in river sediments.
- Seven sources of PAHs in sediments were identified by PMF model.
- Domestic and industrial wastewaters were the primary sources of SMs.
- DBPs were the major carcinogenic contributors to total PAHs in sediments.
- PAHs and SMs posed a medium and low risks at most sites, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

The aims of this study were to investigate the levels, possible sources and potential ecological risks of 26 polycyclic aromatic hydrocarbons (PAHs) including highly carcinogenic dibenzopyrene (DBP) isomers and 4 synthetic musks (SMs) in river sediments from Shanghai. 74 sediment samples were collected from the Huangpu River and its main tributaries. The total concentrations ranged from 52.0 to 11400 ng g^{-1} for Σ_{26}PAHs, 25.1–9910 ng g^{-1} for 16 USEPA priority PAHs (Σ_{16}PAHs), 0.769–384 ng g^{-1} for Σ_4DBPs, and 0.080–63.3 ng g^{-1} for Σ_4SMs, respectively. Seven sources of PAHs in river sediments were identified by positive matrix factorization (PMF) model. Coal combustion, vehicle and creosote were the major emission sources for PAHs. SMs came mainly from domestic and industrial wastewaters. The toxic equivalent quantities of the benzo[*a*]pyrene (TEQ_{BaP}) ranged from 7.64 to 3920 ng g^{-1} for Σ_{24}PAHs, 2.07–1150 ng g^{-1} for Σ_{16}PAHs, and 5.53–3150 ng g^{-1} for Σ_4DBPs. The TEQ_{BaP} of Σ_4DBPs made up 73.9% of Σ_{24}PAHs, which indicated that DBPs were the major carcinogenic contributors to total PAHs in sediments. According to sediment quality guidelines (SQGs) and mean PEL-Q values, the risks posed by PAHs in sediments were at medium level at most sampling sites, and SMs posed a low ecological risk to sediment-dwelling organisms in Shanghai.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and synthetic musks (SMs) are identified as toxic chemicals, which are persistent in

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aquatic environment, and have caused increasing worldwide concerns. PAHs are composed of two or more fused aromatic rings, and can be formed by anthropogenic and natural pathways. The anthropogenic pathway has two main sources: pyrolytic and petrogenic sources, pyrolytic PAHs arise from the incomplete burning of fossil fuels; whereas petrogenic PAHs arise from oil and by-products. The natural sources are attributed to fires, biosynthesis by marine or terrestrial organisms and diagenesis of natural precursors (Laflame and Hites, 1978; Hites et al., 1980; Venkatesan, 1988). PAHs are ubiquitous environmental pollutants, and carcinogenic, genotoxic and mutagenic to animals and human health (IARC, 2008). Sixteen PAHs were identified as priority pollutants by USEPA. The four dibenzopyrene isomers including dibenzo[a,l]pyrene (DBalP), dibenzo[a,e]pyrene (DBaeP), dibenzo[a,i]pyrene (DBaiP) and dibenzo[a,h]pyrene (DBahP) were considered as potential human carcinogens (IARC, 2010). They have been identified and determined in environmental matrixes such as soil, working environments and ambient air in recent years (Bergvall and Westerholm, 2007; Wang et al., 2013, 2015; Masala et al., 2016).

Synthetic musks (SMs) are man-made chemicals produced in large quantities, which were used as fragrances and fragrance fixatives in a number of consumer products such as body lotions, perfumers, deodorants, hair care products (Roosens et al., 2007). The most important synthetic musks are nitro musks and polycyclic musks. Musk xylene (MX) and musk ketone (MK) are the only two nitro musks of commercial products today (OSPAR Commission, 2004). MX and MK are of estrogenic activity in an assay using human breast cancer and embryonic kidney 293 cells (Bitsch et al., 2002; Schreurs et al., 2004). MX and MK are also carcinogenic to mice, and they can cause the variation of mouse enzyme cytochrome P450 (Ryoko et al., 2008). The production and use of nitro musks are now greatly reduced in Europe due to their toxic effects (OSPAR Commission, 2004). Because of its very persistent and very bioaccumulative (vPvB) properties, musk xylene was included in the candidate list of a substance of very high concern (SVHC) for authorization under the REACH Regulation (ECHA, 2017). Polycyclic musks were the major substitutes for nitro musks. Two Polycyclic musks, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-*r*-2-benzopyran (HHCB, trade name Galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN, trade name Tonalide) are widely used and have become the most important commercial synthetic musks. HHCB, AHTN, MX, and MK accounted for 95% of the European market for synthetic musks (OSPAR Commission, 2004). Polycyclic musks exhibited higher potentials to induce cytotoxicity compared with nitro musks in aquatic ecosystem (Schnell et al., 2009).

Sediment was considered to be an important reservoir for hydrophobic organic pollutants in the environment. Due to their hydrophobic properties, PAHs and SMs are easily absorbed by suspended particular matters and accumulated in the sediment. PAHs and SMs can also be bioaccumulated in organisms and then threaten the aquatic ecosystems and food safety (Kannan et al., 2005; IARC, 2010). The occurrence and potential toxicity of PAHs and SMs in environmental media have aroused widespread concerns about their adverse effects on ecosystems and human health.

Along with the rapid development of the industrialization and urbanization, Shanghai and its adjacent area are faced with serious environment pollution during the last few decades. Investigation on pollution of PAHs in river sediment of Shanghai was mainly focused on 16 USEPA priority PAHs in previous studies (Liu et al., 2008, 2016, 2009). SMs in sediment from Suzhou River and Dianshan Lake in Shanghai were investigated in previous studies (Zhang et al., 2008; Song et al., 2015; Gu et al., 2017). The highly carcinogenic DBP isomers are rarely measured in environmental samples during routine monitoring all over the world. No comprehensive investigation on the occurrence of 4 DBPs and SMs in river sediments from whole Shanghai region is conducted to date. The aims of the present study were to investigate the levels and spatial distributions of PAHs including DBP isomers and SMs in sediments, to identify and quantitatively assess source contributions to the sediment PAH burden, ultimately to evaluate the potential ecological risks of PAHs and SMs.

2. Materials and methods

2.1. Study area and sample collection

Shanghai is an international metropolis and also a significant national central city with economy, trade, transport, technology, industry and shipping in China. There are a population of 24.15 million with the population density of 3809 inhabitants/km^2, and the number of automobiles exceeds 3.32 million in 2015 in Shanghai (SMSB and SONBS, 2016), which may cause more and more serious traffic jam. There are six pillar industries including electronic information products manufacturing, automotive manufacturing, petrochemical and fine chemical manufacturing, fine steel manufacturing, equipment manufacturing and biomedical manufacturing industries in Shanghai (SMSB and SONBS, 2016). Crop farming, animal husbandry, fisheries and aquaculture are the major agricultural activities in Shanghai (SMSB and SONBS, 2016). The studied area and sampling locations are illustrated in Fig. S1. A total of 74 sediment samples were collected from Huangpu River and its main tributaries in Shanghai in May 2016. Sediments were collected using a stainless steel grab sampler. The top 10-cm layer of sediment was scooped using a precleaned stainless steel scoop, wrapped in a tinfoil and enclosed in ziplock bags. After transported to the laboratory, all samples were dried in a vacuum freeze dryer for 50 h. Then, samples were crushed and sieved through an 80-mesh screen, and stored at −20 °C until analysis. The organic carbon content of the sediment sample was determined using the potassium bichromate volumetry-external heating method (Lou et al., 2016).

2.2. Chemicasl and materials

The target analytes measured in this study include 26 PAHs, two polycyclic musks and two nitro musks. Standard solutions of PAHs including naphthalene (Nap), 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), pyrene (Pyr), phenanthene (Phe), anthracene (Ant), fluoranthene (Flu), retene (Ret), chrysene (Chr), benzo(*a*)anthracene (BaA), benzo(k)fluoranthene (BkF), benzo(*b*)fluoranthene (BbF), perylene (Per), benzo(*a*)pyrene (BaP), dibenzo(ah)anthracene (DBA), indeno(1,2,3-*cd*)pyrene (InP), benzo(ghi)perylene (BP), coronene (Cor), benzo(e)pyrene (BeP), dibenzo[a,l]pyrene (DBalP), dibenzo[a,e]pyrene (DBaeP), dibenzo[a,i]pyrene (DBaiP) and dibenzo[a,h]pyrene (DBahP) were purchased from Supelco (Bellefonte, PA, USA). Surrogate standards (d_8-Nap, d_{10}-Ace, d_{10}-Phe, d_{12}-Pyr, d_{12}-Chr, d_{12}-Per, d_{12}-DBA, d_{14}-DBahP) and injection internal standard (2-fluorobiphenyl) were obtained from Supelco (Bellefonte, PA, USA). Standard solutions of synthetic musks including MX, MK, HHCB and AHTN and a surrogate standard d_3-AHTN were purchased from Dr. Ehrenstorfer (Augsberg, Germany). Silica gel (100–200 mesh) (Qingdao Haiyang Chemical Co., Shandong, China) was activated for 16 h at 130 °C, then kept in sealed desiccator. Anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Shanghai, China) was baked at 450 °C for 5 h. All solvents (Sinopharm Chemical Reagent Co., Shanghai, China) were of analytical grade and redistilled in an all-glass system before use.