Ecotoxicology and Environmental Safety 160 (2018) 178–183

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Occurrence, distribution and ecological risks of organophosphate esters and synthetic musks in sediments from the Hun River

Xiangying Zeng[a], Qiongpu Hu[a,b], Lixiong He[c], Zhiyang Liu[d], Shutao Gao[a], Zhiqiang Yu[a,*]

[a] State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Guangzhou Hexin Analyt Instrument Co Ltd., Guangzhou 510530, China
[d] Institute of Atmospheric Environment, Guangdong Provincial Academy of Environmental Science, Guangzhou 510000, China

ARTICLE INFO

Keywords:
Organophosphate ester
Flame retardants
Synthetic musks
Source water
Sediment

ABSTRACT

The Hun River is an important main tributary of the Liao River system. It is located in northeast China, and provides water resources for agriculture and industry. A man made reservoir (Dahuofang Reservoir, DHF) has been constructed mid-stream in the Hun River, supplying drinking water to surrounding cities. Pollution from organic contaminants is of great concern. In the present study, 40 sediment samples were collected and analyzed for the occurrence and distribution of two groups of emerging organic pollutants; namely, organophosphate esters (OPs) and synthetic musks (SMs). In all samples taken from upstream of the Hun River (UHR), downstream of the Hun River (DHR), and from DHF, the following concentrations were recorded: 0.141–4.39, 1.21–245, and 0.117–0.726 μg/kg galaxolide (HHCB), and 0.098–3.82, 2.79–213, 0.430–0.956 μg/kg tonalide (AHTN), respectively. For OPs, seven target analytes were detected in most of the sediment samples, with chlorinated OPs Tris-(2-chloroethyl) phosphate and Tris(2-chloro-isopropyl) phosphate being the dominant components, at levels varied in the range of LOD-0.810, ND-49.6, and 0.532–3.18 μg/kg, and LOD-0.786, ND-60.1, and 0.352–1.32 μg/kg from UHR, DHR and DHF, respectively. The elevated levels of these target compounds were detected in DHR, including its two main tributaries, Xi River and Pu River, which drain through cities with industrial development and dense populations. Our results indicate that domestic and industrial wastewater contributed to OPs and SMs sediment pollution, posing low to medium ecological risks to sediment dwelling organisms.

1. Introduction

Liaohe River Basin (LRB), composing of Liao River and Daliaohe River system, is located in northeast of China and represents one of seven river basins in China. Hun River, one of the main tributaries of the Daliaohe River system, runs through several cities, including Fushun and Shenyang, and it receives water from the Pu River and Xi River, which are two of the seven main tributaries flowing into the Hun River. The Dahuofang Reservoir (DHF), the largest man-made lake in Liaoning Province, is situated mid-stream in the Hun River; it acts as the primary source of drinking water for surrounding cities, such as Fushun, Shenyang, Liaoyang and Anshan (Liu et al., 2015a, 2015b). There are major oil, chemical, metallurgical, pharmaceutical and machinery industries in the LRB and wastewater discharge from these industrial sectors causes severe pollution, including heavy metals and traditional persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organic chlorine pesticides (OCPs) (Liu et al., 2015a, 2015b; Gong et al., 2016; He et al., 2016; Zhu et al., 2017). Until recently, limited data was available on emerging organic pollutants, such as organophosphate esters (OPs) and synthetic musks (SMs).

The OPs are widely used flame retardants and/or plasticizers in various consumer products, such as electronic and electrical equipment, textiles, furniture, decorative materials, and building materials due to their excellent flame retardancy and flexibility. Market share has grown because of the ban/restriction on polybrominated diphenyl ethers (PBDEs) in recent years, resulting in their ubiquitous and increasing presence in the environment (Wei et al., 2015; Kim et al., 2017; Wang et al., 2017). Depending on the different substituent group, three subgroups of OPs occur, chlorinated OPs, alkyl OPs, and aryl OPs, which

Abbreviations: LRB, Liaohe River Basin; DHF, Dahuofang Reservoir; UHR, upstream of the Hun River; DHR, downstream of the Hun River; Ops, organophosphate esters; SMs, synthetic musks

* Corresponding author.
E-mail address: zhiqiang@gig.ac.cn (Z. Yu).

https://doi.org/10.1016/j.ecoenv.2018.05.034
Received 1 January 2018; Received in revised form 3 May 2018; Accepted 12 May 2018

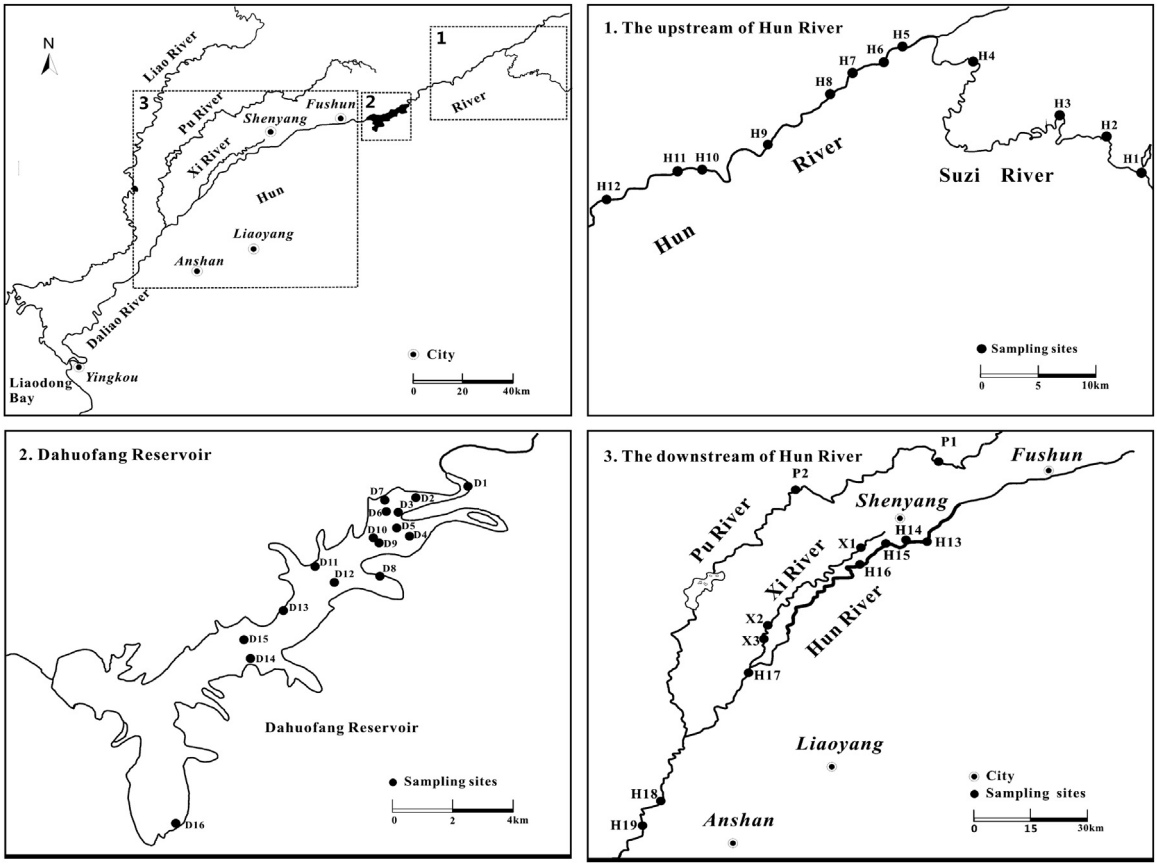

Fig. 1. Illustration of sampling location in the Hun River and Dahuofang Reservoir.

exhibit different physicochemical properties, such as water solubility and Log *K*ow; these properties can affect their distribution and ultimate fate in the environment (Wei et al., 2015). It has been reported that OPs, especially chlorinated OPs, are more toxic and much more persistent than PBDEs (Hou et al., 2016; Greaves and Letcher, 2017).

The SMs, a group of artificial fragrance chemicals, are widely used in daily household products and cosmetics. There are three groups of SMs in use: macrocyclic musks, polycyclic musks and nitro musks. Among polycyclic musks there are two dominant components, galaxolide (HHCB) and tonalide (AHTN) (Wilkinson et al., 2017; Zeng et al., 2018). Many studies have shown that these artificial fragrances materials exhibit a diverse range of effects on freshwater organisms and humans, and they are recognized as 'emerging pollutants'. Recently, Patel (2017) reviewed the published data on their toxicities and described synthetic fragrance chemicals as "wolves in sheep's clothing".

Generally, OPs and SMs are discharged into receiving water via treated/untreated wastewater, and they have been identified as the most prevalent and most hazardous chemicals in effluents from wastewater treatment plants (WWTPs) (Díaz-Garduno et al., 2017; Krzeminski et al., 2017; Wang et al., 2018). In addition, due to their continuous discharge these compounds are frequently detected at elevated levels in aquatic environments affected by domestic and/or industrial wastewater (Lange et al., 2015; Kim et al., 2017; Wang and Kelly, 2017). In recent years, an increasing number of researchers have paid attention to their occurrence, distribution and ultra-fate, as well as their toxicity.

Little is known about the occurrence and levels of these emerging pollutants in the Hun River and Dahuofang Reservoir. The present study aimed to 1) study the occurrence and distribution of OPs and SMs in the Hun River, and try to locate their main emission sources, and 2) make a preliminary assessment of their potential ecological risk based on measured concentrations.

2. Materials and methods

2.1. Chemical standards and reagents

Seven organophosphate ester flame retardants/plasticizers and nine synthetic musks were chosen as target analytes. The OPs standards were purchased from Sigma-Aldrich (St. Louis, MO, USA), including Tributyl phosphate (TNBP, 99%), Tris(2-butoxyethyl) phosphate (TBEOP, 94%), Triphenyl phosphate (TPHP, 99%), Tris(methylphenyl) phosphate (TMPP, 90%), Tris(2-chloroethyl) phosphate (TCEP, 99.5%), Tris(2-chloroisopropyl) phosphate (TCIPP) and Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP, 97%). The synthetic musks were purchased from LGC Promochem GmbH (Mercatorstrasse, Wesel, Germany), including 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl- 4H-inden-4-one (Cashmeran, DPMI, 90%), 4-acetyl-1,1-dimethyl-6-tert-butylindan (Celestolide, ADBI, 98%), 6-acetyl-1,1,2,3,3,5-hexamethylindan (Phantolide, AHMI, 94.5%), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan (Traseolide, ATII, 90%), AHTN (98%), HHCB(75%), 4-tert-butyl-2,6-dimethyl-3,5-dinitroacetophenone (MK, 98.27%), 1-(tert-butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene (MA, 99%) and 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX, 98%). Their detailed information were listed in Table S1. Four deuterated compounds were obtained from C/D/N Isotopes Inc. (Quebec, Canada) and used as surrogate standards, including d27-TNBP (98%), d15-TPHP (98%), d12-TCEP (98%), and d15-MX (97.5%). The internal standard hexamethylbenzene (HMB, 99.5%) was obtained from the laboratories of Ehrenstofer-Schäfer Bgm-Schlosser (Augsburg, Germany).

All solvents used in the present study were of chromatographic grade. Dichloromethane and *n*-hexane were purchased from Merck Co. (Darmstadt, Germany), and ethyl acetate (EtOAc) was purchased from