Science of the Total Environment 643 (2018) 63–72

Contents lists available at ScienceDirect

Science of the Total Environment

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

The occurrence of home and personal care products in the Haihe River catchment and estimation of human exposure

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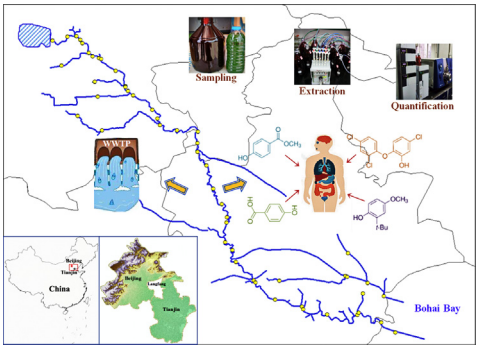
HIGHLIGHTS

- The concentration of individual HPCPs is at a level of ng L^{-1}.
- The predominant HPCPs are OPP, TCS, TCC and MEP in the Haihe River Basin.
- Significant attenuation of HPCPs is found along the catchment.
- WWTP effluents are possibly major contributors to HPCPs in the catchment.
- The backward-calculation method is used to estimate usage and emission of HPCPs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 April 2018
Received in revised form 12 June 2018
Accepted 13 June 2018
Available online xxxx

Editor: Ouyang Wei

Keywords:
Haihe River basin
Parabens
HPCPs
Mass flux
Human exposure

ABSTRACT

A sub-catchment of the Haihe River basin goes through the Beijing-Tianjin region with a population of 26 million, therefore, the use and release of home and personal care product ingredients (HPCPs) to the river catchment could be potentially substantial. Many HPCPs have been shown to be toxic to human and animals. So, it is essential to know the exposure level of HPCPs in the river basin. The average concentrations of five preservatives, three disinfectants and an antioxidant were found to be 398, 352 and 77.7 ng L^{-1}, respectively, in the dry season. The chemical concentrations in the effluents of wastewater treatment plants (WWTPs) and untreated wastewater discharge were respectively ca. 1.3–2.2 and 1.6–7.5 times higher than those in river water. The mass flux of ∑HPCPs has been estimated to be 8.7 g/h at the outfall of the Shahe Reservoir and 181 g/h and 214 g/h at the estuary of the Haihe River and Yongdingxin River to Bohai Bay, respectively. The attenuation of ∑HPCPs was over 79% along the Wenyu River. By using the backward method, the estimated average loadings to WWTPs ranged from 0.51 to 2.0 mg/day/cap for the various individual compounds. They were 1–3 orders of magnitude higher than the estimation from the forward calculation for parabens. This indicates the possible underestimation of chemical usage and human exposure levels by the current published studies or the probably additional

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https://doi.org/10.1016/j.scitotenv.2018.06.153
0048-9697/

industrial release to the target catchment. Such a study provides useful information for the development of chemical management approaches and indicates that further research is needed to improve the estimation of HPCPs usage and emissions to aquatic environment.

1. Introduction

Global concern has been raised over organic micropollutants due to their environmental contamination and risks (Schwarzenbach et al., 2006). During the past decades, China has focused on pollution investigation and control of conventional priority pollutants, such as polychlorinated biphenyls (Chen et al., 2014; Zhang et al., 2004), polycyclic aromatic hydrocarbons (Tao et al., 2007; Sun et al., 2017; Zhu et al., 2015), pesticides (Ouyang et al., 2016a, 2017) and herbicide (Ouyang et al., 2016b, 2016c). However, researches on some emerging contaminants, such as home and personal care products (HPCPs), are still relatively limited.

HPCPs are a class of contaminants of emerging concern which include a diverse collection of compounds, such as disinfectants, preservatives, antioxidants and fragrances (Brausch and Rand, 2011; Bu et al., 2013). These chemicals are widely included in cosmetics, foodstuffs and pharmaceuticals (e.g. parabens) etc. (Guo and Kannan, 2013; Liao et al., 2013a; Ma et al., 2016; Zhu et al., 2016). Human exposure to these chemicals occurs on a daily basis. The detection of HPCPs is ubiquitous across aquatic environments worldwide (Liu and Wong, 2013). Wastewater treatment plants (WWTPs) are important point sources of HPCPs in aquatic systems, as they can only partially remove HPCPs that are released with domestic and industrial wastewater (Boxall et al., 2003; Chen et al., 2017). Diffusive release may additionally exist through untreated wastewater (UW) (Wang et al., 2015).

Continuous exposure to HPCPs has been linked with detrimental effects on aquatic ecosystems and human health (Brausch and Rand, 2011; Guo et al., 2014). Studies have suggested that parabens (the esters of *p*-hydroxybenzoic acid) may act as endocrine disruptors in aquatic systems (Yamamoto et al., 2011). And the occurrence of parabens in human serum, placenta, urine and breast tumors has been reported by the previous studies (Darbre et al., 2004; Sandanger et al., 2011; Wang et al., 2013). Disinfectants, such as triclosan (TCS) and triclocarban (TCC), have been shown to inhibit the growth of algae (Yang et al., 2008). TCS is linked to the change in sex ratios and fin length of medaka (Brausch and Rand, 2011; Foran et al., 2000). US FDA (Food and Drug Administration) has banned the use of TCS and TCC in soaps due to their potential health risks (FDA, 2016). Butylated hydroxyanisole (BHA), an antioxidant, has been suggested to be carcinogenic to rodents and humans as well as an environmental endocrine disruptor (IARC, 1987; Jimenez, 1997; Williams et al., 1999).

Therefore, it is essential to investigate the environmental concentration and potential human exposure level of HPCPs. A backward-calculation method for estimating chemical release to rivers based on the measurement of chemicals in surface water was firstly applied on the illicit drug (Zuccato et al., 2005). It was then extended on alcohol, nicotine, caffeine, plasticizers and pharmaceuticals (Gonzalez-Marino et al., 2017; Rodriguez-Alvarez et al., 2015; Senta et al., 2015; Verlicchi et al., 2014) for a rough estimation of the usage. The methodology was also called wastewater-based epidemiology. Another more commonly used method for estimating the chemical usage and emission is based on market data of products or materials being sold or consumed. This method is more straightforward and has been applied on different types of chemicals including HPCPs, which can be called as forward calculation (Zhu et al., 2016; Shen et al., 2013; Zhang et al., 2015). The backward calculation can be applied to validate the forward calculation. However, such validation has never been conducted by previous studies, to the best of the authors' knowledge.

Approximately 156 million people live in the Haihe River basin in China (Rong et al., 2016), in which the Beijing-Tianjin-Hebei region is one of the regions with the densest population and the largest economy in China and represents an important industrial base in Northern China. The consumption and release of HPCPs could potentially be substantial in this region, but relevant studies are limited (Zhu et al., 2016). Monitoring data for TCS and TCC across China are relatively abundant compared to other HPCPs (Zhao et al., 2013). On the contrary, measurements of parabens in freshwaters across China are limited with few data on BHA. Most existing monitoring campaigns on HPCPs have focused on catchments in the Pearl River Delta (PRD) (Gong et al., 2011; Peng et al., 2008; Zhao et al., 2013). Relevant studies on the Haihe River basin are limited, although the emission of HPCPs is potentially high whilst river discharge flow rates could be lower compared to rivers in the PRD. The usage of TCS, TCC across China and levels of daily human exposure to some parabens through different routes have been investigated by surveys of the content of parabens in products (Guo and Kannan, 2013; Liao et al., 2013a; Ma et al., 2016; Zhu et al., 2016). However, these estimates have not been validated regionally.

This study aims to investigate the occurrence, spatial distribution and mass flux of nine typical HPCPs in a sub-catchment in the Haihe River basin in the dry season, as well as the potential human exposure level of HPCPs. The backward-calculation method has been introduced to trace back the loading of HPCPs into WWTPs by using the concentrations of compounds determined in this study. The results were then compared with those from the forward calculation. Such method can potentially be used to validate the estimation of usage and emissions of chemicals that mainly derive from anthropogenic sources and are released with domestic wastewater. This information would be useful to support the regional management of water contaminants.

2. Materials and methods

2.1. Study area and sample collection

The Haihe River basin covers Beijing, Tianjin, most areas of Hebei province and a part of Shanxi province in North Plain China (NPC). A sub-catchment of it running through Beijing, Langfang (Hebei province) and Tianjin was studied in this study (Fig. 1), where around 70% of population (>26 million capita) in Beijing and Tianjin reside. The study area includes Wenyu River (length, 48 km), Beiyun River (42 km), Haihe River (73 km) and Yongdingxin River (66 km). It receives the untreated wastewater around this area and the effluent from wastewater treatment plants (WWTPs) connected to a predominant proportion of population in Beijing and Tianjin.

The sampling campaign was conducted during the dry season in late October 2016. There was no rainfall during the sampling period and the average temperature was about 10 °C. Water samples from 51 sites (Fig. 1) were collected. Station S1 was located at the Shahe reservoir outfall. Stations S2, S5 and S10 were located at the outfalls of UW sewers. Stations S7, S13, S16, S20, S42 and S47 were located at the WWTP discharge points. The first four WWTPs were the top four largest WWTPs in Beijing and afford the treatment of ca. 60% of wastewater treated by all WWTPs in Beijing. WWTP6 (S47) is among the largest WWTPs in Tianjin. More details on WWTPs are given in Table S1 in the Supporting Information (SI). The grab surface water (0–20 cm) samples were collected into pre-cleaned amber glass bottles, acidified to pH = 2.5 by using 2 M HCl and stored in iceboxes during transport to the