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Pharmaceuticals and personal care products in the urban river across the megacity Shanghai: Occurrence, source apportionment and a snapshot of influence of rainfall

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ABSTRACT

Occurrence of eleven pharmaceuticals and personal care products (PPCPs) along Huangpu River, a representative urban river of megacity Shanghai, was investigated in four sampling campaigns. The overall concentrations of PPCPs ranged from < LOQ to 1455 ng/L, and untreated domestic wastewater was proposed as an important source of PPCPs in Huangpu River. Higher contamination levels of target PPCPs were detected in the lower reach (urban area) and dry season, compared to those in the upper reach (rural area) and wet season, respectively. The influence of rainfall on the occurrence of PPCPs was also extensively discussed in different regions along Huangpu River. At sampling sites in the rural area, similar or even lower concentrations of PPCPs were detected after rainfall; while increased concentrations of PPCPs were observed at most sampling sites, especially in the urban area, suggesting that overflow of untreated wastewater exceeding the capacity of wastewater treatment plants and leachates generated at temporary storage and transfer station of solid wastes might be the additional sources of PPCPs in the urban area in rainy days. These findings indicated that management of wastewater or/and solid wastes was more important to solve the problem of PPCPs contamination in the urban river of megacity.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are an important group of emerging contaminants that have aroused worldwide concern over the past decades [1–3]. In the previous studies, the contamination of PPCPs in the urban rivers in China was found to be more severe than that in the rivers in rural areas [3,4], indicated that urban areas, especially those in megacities, were expected to be a “hotspot” of PPCPs in China [5,6].

PPCPs in urban rivers can be released from different sources. The main emission sources of PPCPs in the urban rivers in China were still a highly debatable issue. Several studies indicated that wastewater effluents were the main sources of PPCPs in some urban rivers in China [7,8]. For instance, Zhang et al. [7] investigated the occurrence of selected PPCPs in a wastewater treatment plant (WWTP) and their distribution in the receiving water of Chaobai River in Beijing, suggesting that WWTP discharge was regarded as a dominant point-source input of PPCPs into the river. However, recent findings revealed that other emission sources, such as untreated domestic wastewater, industrial wastewater, hospital wastewater, livestock wastewater, also made large contributions to the total load of PPCPs in some sections of urban rivers [6,9,10]. For example, untreated wastewater significantly contributed to the PPCP pollution in the urban river of Beijing due to the insufficient wastewater treatment capacity or poor management [9]. Therefore, more efforts should be made to clarify the main emission sources of PPCPs in the urban rivers.

Furthermore, the source of PPCPs in rivers might vary under different seasonal or weather conditions. For instance, Mandaric et al. [11] observed an increased PPCPs concentration level in Alpine rivers in the tourist seasons, and linked it with the additional tourist arrival. Rainfall events might also resulted in additional inputs of PPCPs in rivers. Some PPCPs, such as caffeine and DEET, could be detected in the

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precipitation [12], leading to an elevated load during rainfall events. Besides, runoffs from livestock farms [13] and from soil irrigated with reclaimed wastewater [14] could also lead to the increased concentrations of PPCPs and were identified as additional sources during rainy seasons. However, for typical megacities, the researches with the objectives to elucidate the influence of rainfall and identify the additional sources are quite limited.

Shanghai is a highly urbanized megacity in China with a population of 24.2 million and an area of 6341 km^2 [15]. Currently, 53 WWTPs have been installed and in use in Shanghai. The treated wastewater amounts to 2680 million tons per year, accounting for approximately 90% and 56% of the domestic wastewaters in urban and rural area, respectively [15]. Huangpu River is a signature river of Shanghai, of which the total length is 114 km and the basin area reaches 24,000 km^2. It originates from Tai Lake and flows into the Dianshan Lake, then travels across the megacity of Shanghai and finally enters into the Yangtze Estuary. The upper reaches of the Huangpu River flow through the suburbs of Shanghai, providing approximately 30% of the drinking water supply in Shanghai. The lower reaches flow through the urban area with intensive industrial and residential activities, and receive different types of untreated and treated wastewater in Shanghai.

In this paper, we investigated the occurrence of eleven PPCPs along Huangpu River in both mainstream and tributaries from upper reach to lower reach in four sampling campaigns. Sources of target PPCPs were identified according to the concentration levels and corresponding ratios of indicator PPCPs. Particularly, influence of rainfall on their occurrence and potential additional sources were extensively discussed based on sampling campaigns before and after a heavy rain event. The findings in this study will help to gain a better understanding of PPCPs pollution in urban rivers across megacity, and provide useful suggestions for the environmental management of drinking water supply, wastewater collection and treatment, and even solid wastes storage in megacities.

2. Material and methods

2.1. Chemicals

Standards including bezafibrate (BF), carbamazepine (CBZ), gemfibrozil (GF), sulpiride (SP), trimethoprim (TP), indomethacin (IM) and diclofenac (DF) were obtained from Sigma-Aldrich (Germany). Caffeine (CF), *N*,*N*-diethyl-meta-toluamide (DEET) and metoprolol (MTP) were purchased from Dr. Ehrenstorfer (Germany) and chloramphenicol (CP) was from TCI (China). These eleven PPCPs were chosen in accordance with the reported priority lists of pharmaceuticals that should be monitored [16,17] as well as their consumption, removal performance in WWTPs and potential ecological effects. Isotopically labeled internal standards included phenacetin-^{13}C (PNT-^{13}C), DEET-^{7}D and GF-^{6}D from CIL (USA), atrazine-^{5}D (ATZ-^{5}D) and mecoprop-^{3}D (MCPP-^{3}D) from CDN (Canada), CP^{-5}D from Witega (Germany), and SMT-^{13}C from Sigma-Aldrich (Germany).

Ultra-pure water used in this study was produced by a water purification system Classic DI from ELGA (UK). Stock solutions of individual compounds were prepared in methanol (HPLC-grade, J&K USA). Working solutions were prepared by mixing and diluting the stock solutions. All the solutions were stored at 4 °C in the dark.

2.2. Sampling

Surface water samples were collected in duplication from 18 sampling sites (9 in the mainstream and 9 in the tributaries) from upper reach to lower reach of Huangpu River, as shown in Fig. 1. Some sampling sites (S1, S2, T1 and T2) are located in the suburb area of Shanghai, and the others are in the urban area. Besides, surface water at sampling sites S1-S4 and T1-T3 are used as drinking water supply in Shanghai.

Totally, we conducted four sampling campaigns, two of which were in the wet season (August), while the other two were in the dry season (December and March). The two sampling campaigns in the wet season were carried out before and just after a heavy rainfall event, of which the precipitation was higher than 100 mm according to the local weather station. Although the first-flush-effect could not be equally considered in all the sampling sites due to the duration of sampling along Huangpu River, the results could provide a representative snapshot of the rainfall effects on PPCPs in the urban river of Shanghai.

2.3. Analytical method

Target compounds were extracted using solid phase extraction (SPE) and analyzed by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). The detailed description of the analytical method was reported in Sui et al. [18]. Briefly, filtered water sample spiked with internal standards were loaded in Oasis HLB SPE cartridges (200 mg, 6 mL, Waters). Then, PPCPs were eluted from the SPE cartridges by methanol or acetonitrile, which was either evaporated to near dryness under a gentle stream of N_2. Finally the extracts were reconstituted with methanol–water prior to instrument analysis. The PPCP residues were analyzed using HPLC (Ultimate3000 HPLC system, Dionex, USA) followed by electrospray ionization and tandem mass spectrometry (ESI-MS/MS, API3200, AB Sciex, USA). Multiple reaction monitoring was applied for detection. The precursor ion and product ion of target PPCPs are listed in Table S2, and working conditions of HPLC and MS for the quantification of investigated PPCPs are given in Table S3.

2.4. QA/QC

Strict QA/QC was implemented to ensure accurate quantification of target compounds. To determine the recoveries of PPCPs, six replications of surface water samples spiked with 0.2 mL of PPCPs mixture (0.4 mg/L) were extracted and analyzed. The recoveries were determined as the ratio of concentrations detected in the spiked samples (the concentrations in the non-spiked sample was subtracted) to the known concentrations of target PPCPs spiked. The recoveries of investigated PPCPs except MA were 73–108% (Table 1), and the standard deviations were less than 20%, which was considered to be acceptable [19]. The recovery of MA was not satisfactory (50 ± 5%). Therefore, the concentrations of MA were not reported in the present study. The instrumental quantification limit (IQL) was defined as the concentration that yielded a signal-to-noise ratio of 10:1, and the limit of quantification of (LOQ) was calculated considering IQL, recoveries and concentration factor. The IQL and LOQ of PPCPs in surface water samples were also summarized in Table 1. For each sampling, ultrapure water in amber glass bottles as field blanks were brought, exposed to the environment of sampling sites, and delivered back to the laboratory with samples. For each set of samples (normally 10 samples), at least one procedural blank was prepared from ultra-pure water in the laboratory. Both the procedural blanks and field blanks were processed identically to surface water samples and the results indicated that concentrations of PPCPs were below LOQ in all the blanks.

3. Results and discussion

3.1. Occurrence

As shown in Fig. 2, all the target compounds were detected in at least one sample collected at 18 sampling sites during all the sampling campaigns. CF (100%), DEET (100%), SP (100%), TP (100%), CBZ (99%) and MTP (96%) exhibited the highest frequencies of detection, whereas GF (22%), CP (25%), IM (33%) and BF (50%) were detected in less than half of the samples.

The overall concentration levels of target PPCPs in Huangpu River