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Characterization of pharmaceutically active compounds in Beijing, China: Occurrence pattern, spatiotemporal distribution and its environmental implication

Ruixue Ma [a], Bin Wang [a,*], Lina Yin [a,b], Yizhe Zhang [a], Shubo Deng [a], Jun Huang [a], Yujue Wang [a], Gang Yu [a]

[a] Beijing Key Laboratory of Emerging Organic Contaminants Control, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Collaborative Innovation Center for Regional Environmental Quality, School of Environment, Tsinghua University, Beijing 100084, China
[b] School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

HIGHLIGHTS

- 33 PPCPs were monitored in Beiyun River and tributaries in summer and winter in 2015.
- Caffeine, acetaminophen and erythromycin were the most abundant compounds.
- Antibiotics had higher concentration in winter, but only accounted 28% of the total.
- The burden of PhACs in 2015 in Beiyun River basin reduced by 37% of that in 2013.
- CBZ level changed little and may exert sustained risks on aquatic environment.

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ABSTRACT

Pharmaceutically active compounds (PhACs) as an important group of "emerging contaminants" (ECs), have been highlighted and received global attentions in last decade. China has tremendous consumption of PhACs and the most pharmaceutical manufacturers worldwide. In this study, 33 PhACs (19 antibiotics included) were monitored in the Beiyun River basin in Beijing, China. The seasonal occurrence, temporal-spatial distribution and potential source were investigated. The total levels were about 2 $\mu g\,L^{-1}$. Non-antibiotics were more frequently detected. The highest median concentrations were observed for caffeine (558 $ng\,L^{-1}$) and erythromycin (319 $ng\,L^{-1}$). Acetaminophen, erythromycin, diclofenac and *N*,*N*-diethyl-*meta*-toluamide showed highly significant seasonal variation, while caffeine, carbamazepine, metoprolol and most sulfonamides were more stable. The burden was most heavy in Qing River in both seasons (up to 4 $\mu g\,L^{-1}$). Antibiotics from veterinary use accounted for minor contribution in this region. The characteristics and trends were overviewed by comparing with our previous survey. The total level of 15 PhACs dropped significantly by 37% on average from 2013 to 2015. The proportion of caffeine, once a major component in 2013, reduced from 77% to 47%. The burden of these ECs in surface water of Beijing is remarkably reduced, suggesting the overall situation has been improving.

1. Introduction

A diverse group of micropollutants, including pharmaceuticals, steroids and hormones, perfluorinated compounds as well as surfactants, which are now referred as "emerging contaminants" (ECs), have been identified in different environmental compartments all over the world. They are not currently covered by existing water-quality regulations, and have not been well understood about their potential threats to environmental ecosystems and human health [1]. Among which, pharmaceutically active compounds (PhACs) have been highlighted and received global attentions in last decade due to their huge quantities of production and usage. The ubiquitous existence of PhACs has led to a growing concern in the adverse ecological effect caused by their "pseudo-persistence" and potential post-therapeutic effects toward the non-target aquatic organisms even at low concentrations [2–5]. One of the main concerns is the possibility of inducing resistant bacteria strains when exposure to low level but multi-class of antibiotics, representing a health threat to humans and ecosystems [6].

* Corresponding author.
E-mail address: thuwb@tsinghua.edu.cn (B. Wang).

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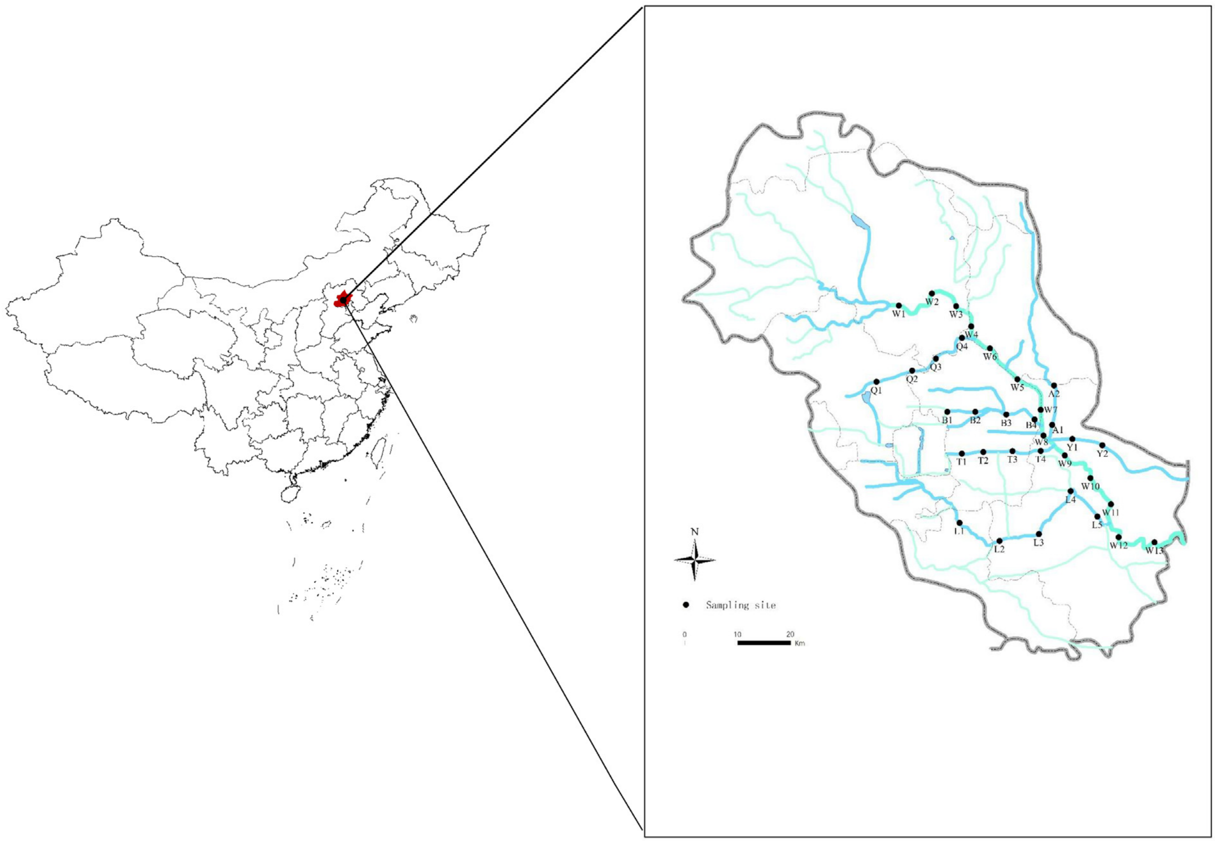

Fig. 1. Sampling sites in Beiyun River basin.

Although some of these substances have been demonstrated about their effects on human health [7–10], the knowledge on thresholds of residues in environment is still not well documented. The occurrence of pharmaceuticals in environment vary among areas and countries, depending on their consumption and use patterns. Concentrations of pharmaceuticals may also fluctuate during different sampling campaigns in the same WWTP. Rainfall might be one of the causes associated with this phenomenon. Moreover, it is also affected by their chemical stability and properties. For example, sulfonamides exhibit high solubility and chemical stability in water, whereas macrolides tend to be hydrolyzed or adsorbed to soil and sediment [11].

China has the largest population and the most pharmaceutical manufacturers in the world. In 2011, more than 1500 types of pharmaceutically active ingredients were produced in China, and the estimated domestic production was approximately 2,000,000 t [12]. Annual consumption of antibiotic worldwide is estimated at 100,000–200,000 t, of which more than 25,000 t for China [13]. The tremendous consumption of pharmaceuticals in China would likely lead to serious PhACs pollution. A great deal of work has been done to monitor the concentration in both influent and effluent of WWTPs in China and worldwide [14–16]. Numerous antibiotics have been detected in groundwater, river basins and seawater [17–19]. Besides, in recent years, a number of researches have reported the occurrence of PhACs in China, mainly focused on Pearl River Delta [20,21], Yangtze River estuary [22–24], Bohai bay [25], Yellow River [26,27] and freshwater lakes [28–30]. These studies have provided necessary fundamental data helpful to the pollution assessment and the improvement for higher removal efficiency.

Beijing, the capital of China, is one of the world's most densely populated cities, with a population over 20 million and about 3.3 million tons of domestic sewage produced per day [31]. A significant percentage of antibiotics (25–75%) is estimated to be excreted unaltered after application [32]. However, the wastewater treatment efficiency is only 83% for urban areas and may be far less in suburb [33]. Moreover, in view of the insufficient infrastructures, a considerable amount of PhACs residues would be directly discharged into receiving waters as a major non-point source pollution. However, few comprehensive regional studies have been conducted to characterize the occurrence, temporal-spatial variation, and environment risks of multi-class of frequently prescribed PhACs in surface water across Beijing. Moreover, many surveys were conducted by collecting samples only once or twice during the study period due to the costly and time-consuming monitoring campaign. Thus, follow-up investigation was scarce.

Given this, 33 pharmaceuticals were selected including β-blockers, non-steroidal anti-inflammatory drugs, lipid regulators, psychiatric drugs and 19 antibiotics based on the reported priority lists of pharmaceuticals that should be monitored [34–36] as well as their consumption, removal performance in WWTPs and potential ecological effects. Our work aims to conduct a systematic survey years to assess multiresidue PhACs in surface water of Beijing and gain an insight into the spatial-temporal variation and use patterns. This work will help to elucidate whether sensitive ecosystems are at risk or not in this region, and subsequently provide scientific support for pollution management.

2. Method and material

2.1. Standards and reagents

The analytical standards of 33 PhACs were obtained from Sigma-Aldrich (Steinheim, Germany). The physicochemical characteristics are shown in Table S1 (Supporting Information).