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OCCURRENCE PATTERN, SPATIOTEMPORAL DISTRIBUTION AND CHIRAL PROFILES OF PHARMACEUTICAL AND PERSONAL CARE PRODUCTS (PPCPs) IN BEIYUN RIVER BASIN, BEIJING, CHINA

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INTRODUCTION

In recent years, the presence of pharmaceutical and personal care products (PPCPs) in the aquatic environment has been considered as one of the most urgent environmental concerns. The ubiquitous existence of PPCPs has led to a growing concern in their occurrence in aquatic environment, especially the adverse ecological effect caused by their low residual level but “pseudo-persistence” and potential post-therapeutic effects toward the non-target aquatic organism. The enantioselective environmental analysis of PPCPs is an emerging area with important gaps in knowledge. However, only limited research has been undertaken on their enantioselective fate in the environment in China. In view of this, the aim of this study was to determine the occurrence of PPCPs in surface water in Beijing, and to gain an insight into the seasonal variations and spatial distribution, and so far the first time, to conduct a profiling of environmental enantiomeric composition of the selected chiral pharmaceuticals in China.

MATERIALS AND METHODS

Standards and reagents

The analytical standards of 33 PPCPs were obtained from Sigma-Aldrich (Steinheim, Germany). Isotopically labeled compounds, used as internal standards, were sulfamonomethoxine-D4 and penicilline G-D7 acquired from Dr. Ehrenstorfer (Augsburg Germany), 13C-phenacetin from Sigma-Aldrich and gemfibrozil-6d from Toronto Research Chemicals Inc. (Toronto, Canada). HPLC-grade formic acid, ammonium acetate and solvents were purchased from Dikma (USA).

Sample collection and preparation

34 samples covering the upstream and downstream and the four main tributaries were collected in July (wet season) and November (dry season) of 2015, respectively, representing wet season and dry season. The precipitation in July and November was 179 mm and 1.5 mm, respectively (annual average of 197 mm and 0.9 mm). 500 mL of river water spiked with 50 ng IS were extracted using a SPE of Oasis HLB cartridges. Analytes were eluted with 4 mL of MeOH (0.1% HCOOH), then evaporated to dryness, and finally reconstituted in 0.5 mL of mobile phase.

UHPLC-MS/MS analysis

The PPCP residues were analyzed using an UHPLC-ESI-MS/MS (Ultimate3000 HPLC system, Dionex, USA, API3200, AB Sciex, USA). The enantiomers of chiral pharmaceuticals were separated by two chiral columns: (1) Chirobiotic V (Advanced Separation Technologies, USA) and (2) Chiralpak AD-RH column (Daicel Chemical Industry). Target compounds were quantified using multiple reaction monitoring (MRM) mode.

RESULTS AND DISCUSSION

In this study, 33 PPCPs (19 antibiotics included) of different therapeutic classes have been monitored in the Beiyun River basin in Beijing, China. The seasonal occurrence, spatiotemporal distribution as well as the potential source were investigated. All the target micropollutants were detected at least once. The average total levels were at 2163 ng L⁻¹ and 2672 ng L⁻¹ in July and November, respectively. Non-antibiotics were more frequently detected than most antibiotics. Some PPCPs showed significant seasonal occurrence, like acetaminophen (ATP), Erythromycin (EM), Diclofenac (DF), N,N-diethyl-meta-toluamide (DEET) and so on, while Caffeine (CF), Carbamazepine (CBZ), Metoprolol (MTP) and most antibiotics were more stable between seasons. No significant dilution effect was observed by rainfall in wet season. The total burden was most heavy in Qing River in both seasons, probably due to the excessively increasing residents but not sufficient wastewater treatment. Potential sources were inferred by the comparing the composition pattern with influent and effluent from WWTPs, and the antibiotics from veterinary use made minor contribution. The total level of 15 PPCPs dropped significantly in

each river from 2013 to 2015, except for the Qing River. Risk assessment revealed the HQ for most PPCPs reduced significantly, but Carbamazepine (CBZ) may still exert sustained potential effect. From the above, the burden of these ECs in surface water of Beijing was reduced a lot, suggesting the overall situation has been improving. Meanwhile, these results highlight the importance of infrastructure development in predicting PPCP levels in receiving waters in developing countries, such as China.

Eight target chiral drugs were achieved enantioseparation. Seven out of 8 chiral pharmaceuticals were detected in Beijing surface water, except flurbiprofen. The EFs of the pharmaceuticals detected in river water showed obvious enantioselectivity.

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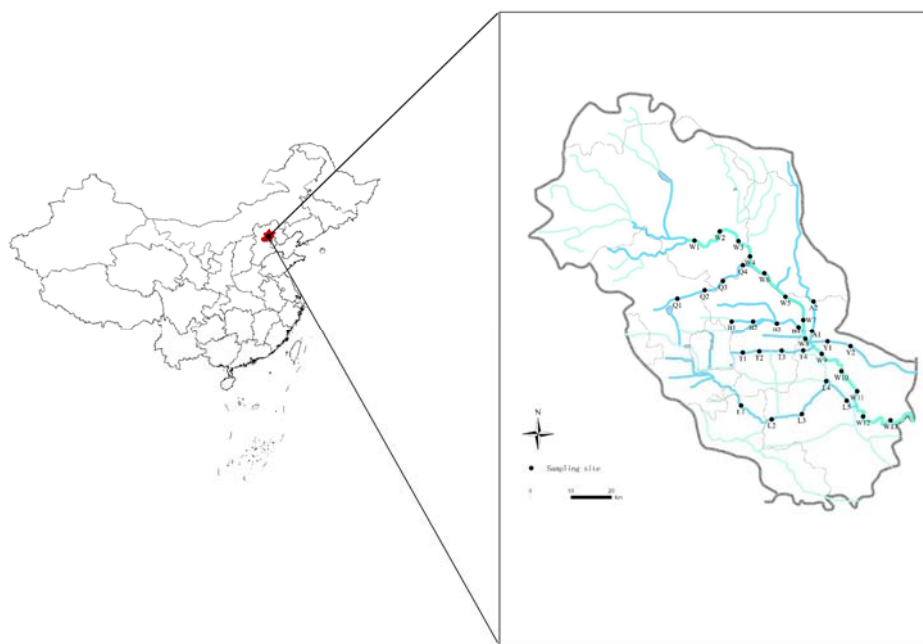


Fig. 1. Sampling locations in the Beiyun River and its tributaries

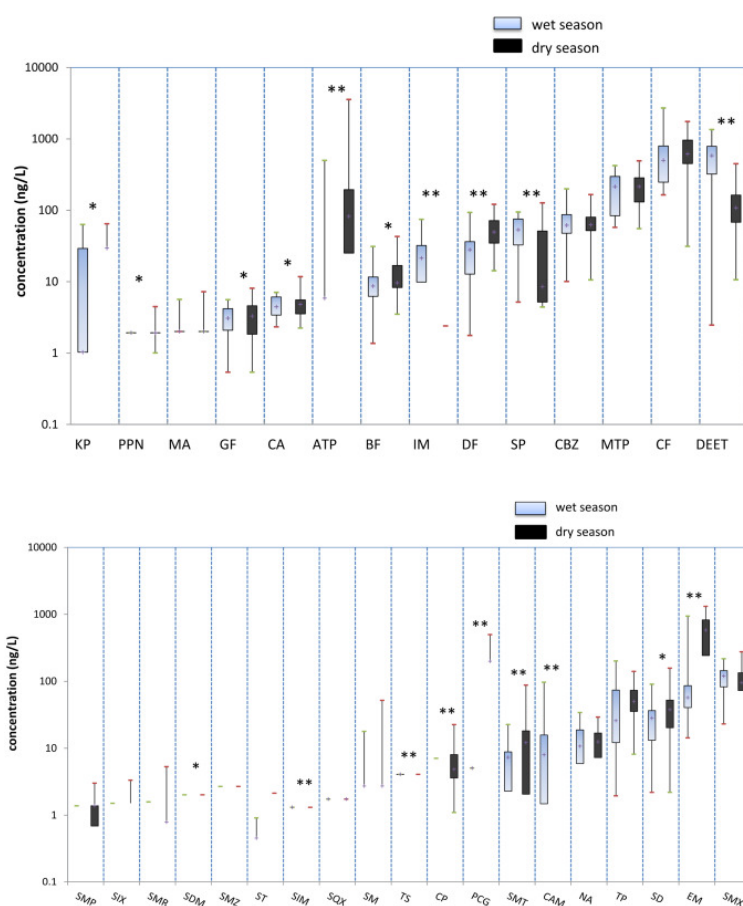


Fig. 2. Concentration ranges of non-antibiotics and antibiotics in both wet and dry season. The cross in box marks the median. The box denotes the 0.25 and 0.75 percentiles. Boxes with single asterisk (*) are considered to be significantly different according to statistical analysis with $p \leq 0.05$ and Boxes with double asterisk (**) indicate highly significant difference with $p \leq 0.01$.

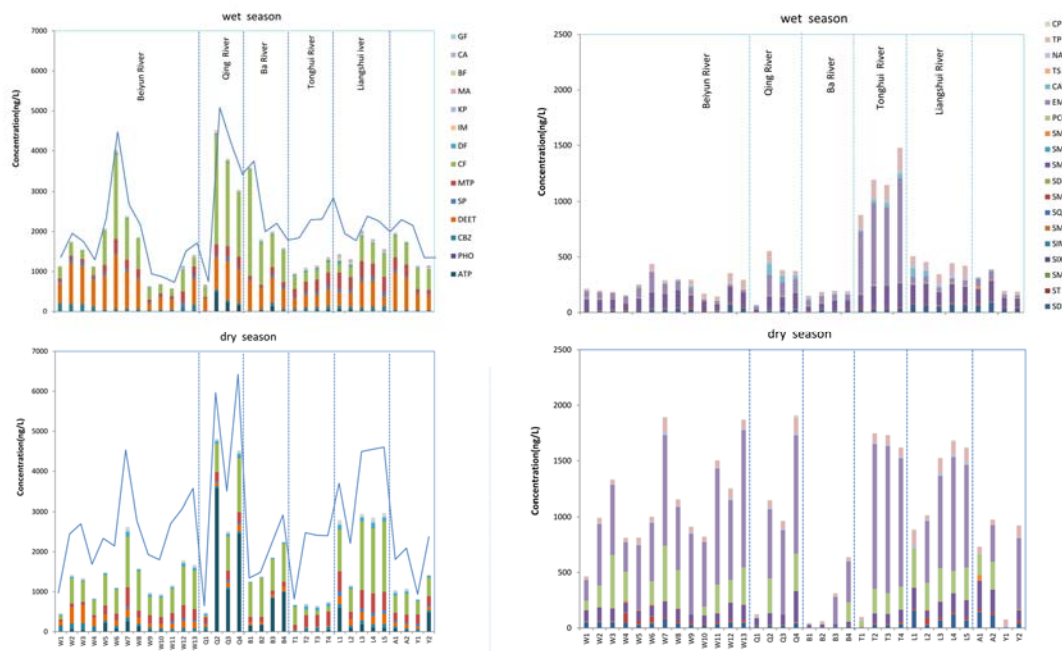


Fig. 3. Accumulative concentration of detected non-antibiotics and antibiotics at each sampling site in wet and dry season, respectively. The line represents the total concentration of 33 target PPCPs detected in this study.

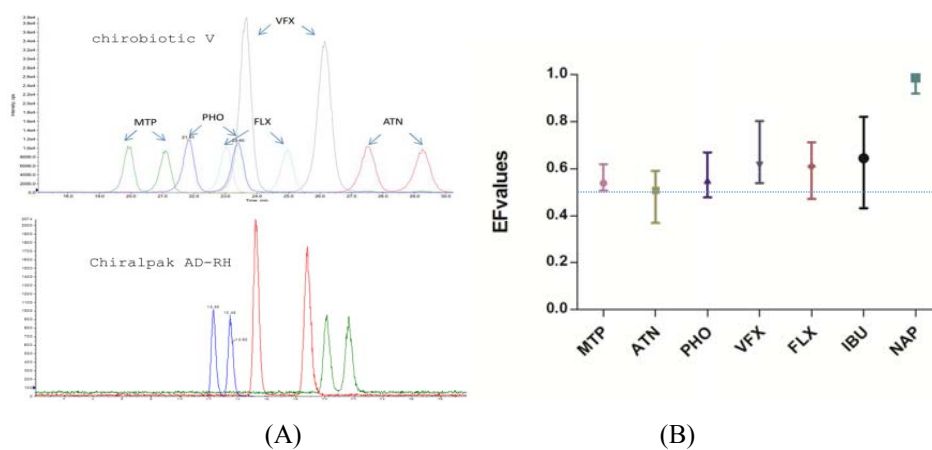


Fig.4. HPLC-MS chromatograms of chiral pharmaceuticals enantiomers separated on two chiral columns (A) and EF values in Beiyun River (B)