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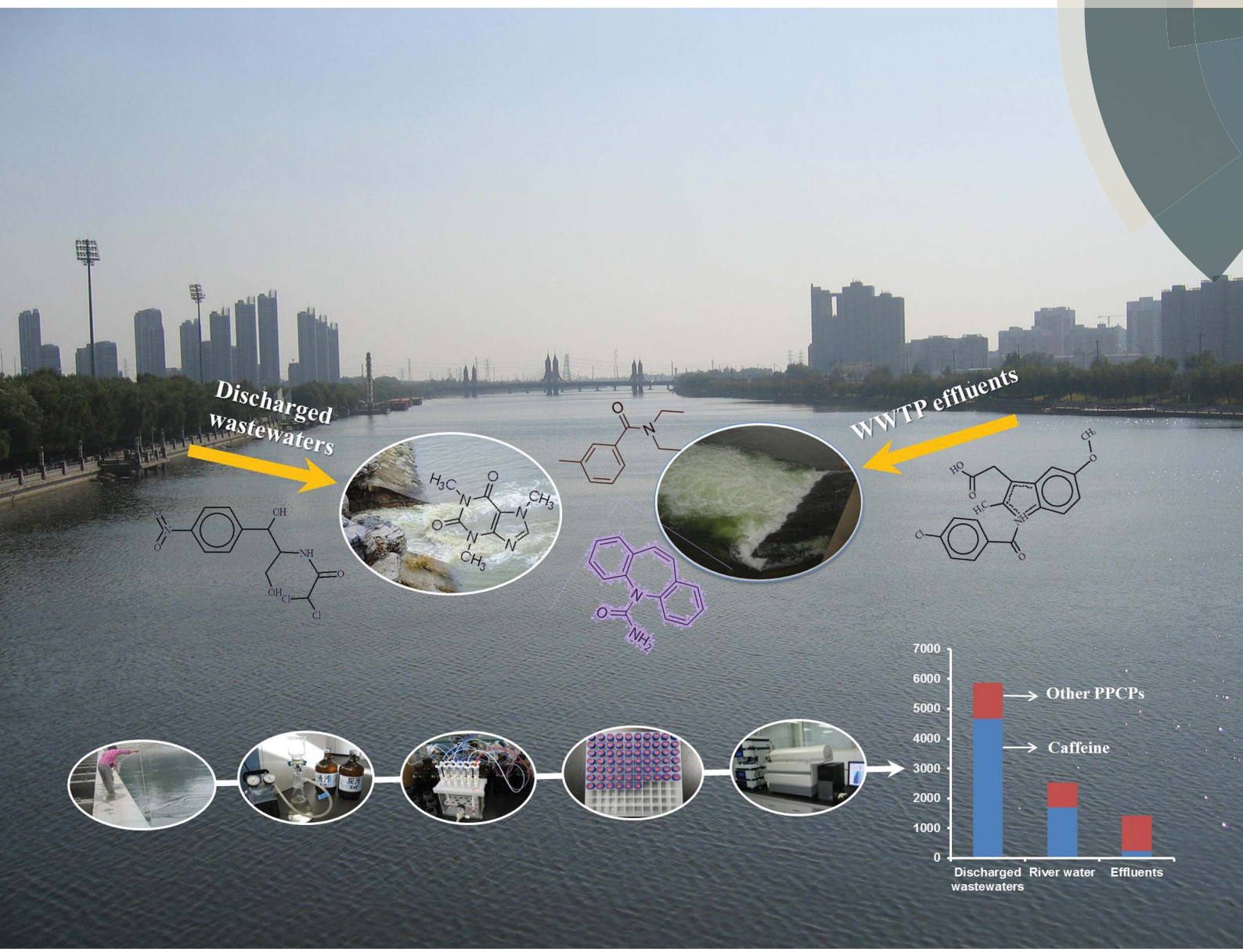

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Pharmaceuticals and personal care products (PPCPs) in urban and suburban rivers of Beijing, China: occurrence, source apportionment and potential ecological risk†

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This study analyzed 15 pharmaceuticals and personal care products (PPCPs) in two rivers with different urbanization levels in the surrounding watershed (urban and suburb) in Beijing, China. Along the rivers, effluent samples from wastewater treatment plants (WWTPs) and wastewater samples from direct discharge outlets were also collected to reveal their possible contribution to the occurrence of PPCPs in these two rivers. Among the 15 PPCPs, 14 compounds were detected with caffeine (maximum 11 900 ng L^{-1}) being the dominant compound. The total concentration of the detected PPCPs in direct discharge outlets (median 4706 ng L^{-1}) was much higher than that in river waters (2780 ng L^{-1}) and WWTP effluents (1971 ng L^{-1}). The suburban-influenced Liangshui River had significantly higher PPCP concentrations compared to the urban-influenced Qing River due to more input of untreated wastewater from direct discharge outlets. Source apportionment showed that approximately 55% of the total PPCPs were contributed by untreated wastewater in the suburban-influenced river. Finally, ecological risk assessment has been regarded as a necessary part of general research. According to the environmental risk assessment results, caffeine, trimethoprim and metoprolol were found to be the most critical compounds, due to their high risk quotient values. The results of the present study can provide useful information for future PPCP pollution control and sustainable water management in Beijing, China.

Environmental impact

PPCP pollution has been generally thought to be positively correlated with the regional urbanization level and population density. However, the situation may differ in developing countries, *e.g.* China, due to poor infrastructure development. Our study on the urban-influenced Qing River and suburban-influenced Liangshui River in Beijing shows that, rather than the Qing River influenced by the larger population density, the Liangshui River is more polluted by PPCPs due to a much larger contribution from untreated wastewater. Poor infrastructure development leads to higher PPCP pollution. The study helps readers better understand the relationship between PPCP pollution and urbanization levels and contributes to PPCP source and pollution management.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), which contain diverse organic groups, such as antibiotics, hormones, antimicrobial agents, synthetic musks, *etc.*, have raised significant concerns in recent years for their continuous input and potential threats to the aquatic environment and human health.[1–3] As an important group of organic pollutants with intensive studies in recent years, PPCPs have been found to be ubiquitous in the aquatic environment throughout the world.[2,4–10] China is the largest producer and consumer of PPCPs in the world. The pharmaceutical production can account for more than 20% of the total production volume of the world,[11] and the average usage of antibiotics by Chinese is 10 times more than the usage by Americans.[12] China is also among the top three countries with the largest personal care product consumption, together with America and Japan.[11,13] PPCPs have become pervasive in surface water of China, with levels varying from ng L^{-1} to μg L^{-1}.[14]

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PPCPs can enter the aquatic environment *via* multiple sources including treated and untreated wastewater, industrial discharge, leaching of municipal landfills, leaking of septic systems, *etc.*[1] Previous studies have reported that higher PPCP concentrations are generally associated with higher population densities in urban areas, because of the presence of a PPCP major source, *i.e.* WWTP effluents.[15–17] However, the situation seems to be different in some other regions. For example, Bunch and Bernot[18] found that higher pharmaceutical concentrations were measured in streams with more than 90% agricultural land use in central Indiana due to the higher contribution of nonpoint sources such as septic tanks. Our recent study found that raw sewage significantly contributed to PPCP pollution in the surface water of Beijing, China.[19,20] However, the abundance and sources of PPCPs have not been well compared in between urban- and suburban-influenced rivers in Beijing. The objective of this study was to investigate the occurrence and sources of PPCPs in the urban- and suburban-influenced rivers in Beijing, as well as to evaluate the potential ecological risks of PPCPs in these rivers. The results of the present study can provide useful information for future PPCP pollution control and sustainable water management in Beijing, China.

2. Materials and methods

2.1 Study area and sampling

Beijing, the capital of China, is one of the most densely populated cities in the world. Beijing spans an area of over 16 800 km^2 (with an urban area of 1040 km^2), and the population has exceeded 20 million by the end of 2011. Beijing city consists of eight urban districts and ten suburban districts. The Qing River and Liangshui River selected in this study are two major tributaries of the Beiyun River in Beijing (Fig. 1). Detailed information on the Beiyun River basin has been provided in our previous study.[19] The Qing River is mainly situated in Haidian and Chaoyang Districts and predominantly influenced by urban inputs, whereas the Liangshui River is mainly situated in Tongzhou and Daxing Districts and predominantly influenced by suburban inputs. The Qing River is 23.6 km long, with a watershed area of 210 km^2, and has a population of 3.0 million. The land use within the Qing River basin consists of ~6% agricultural cultivation and 70% developed land. The Liangshui River is 56.8 km long, with a watershed area of 624 km^2, and has a population of 4.5 million. The land use within the Liangshui River basin consists of 55% agricultural cultivation and ~10% developed land.

The sampling campaign was conducted between April and May, 2014. River samples were collected from 8 sites (QR1-QR8) in the Qing River and 15 sites (LSR1-LSR15) in the Liangshui River (Fig. 1). Meanwhile, 5 effluent samples were taken as grab samples from five WWTPs (QWTP, XJHWTP, XHMWTP, BSWTP and YJWTP), whose effluents are directly discharged into the two rivers. Detailed information on each WWTP investigated is shown in Table S1 (ESI†). 12 wastewater samples (QD1-QD3 and LD1-LD9) were taken from direct discharge outlets occasionally found along the investigated two rivers, where water was directly discharged into the two rivers; their sources were not very clear but thought to be mainly from residential areas. For all sampling sites, replicate samples were collected. No rain event occurred in the previous week of the campaign or during sampling days. All water samples were stored in pre-cleaned amber glass bottles and maintained at 4 °C. Water samples were extracted within 2 days after collection.

2.2 Chemicals

15 target PPCPs including bezafibrate (BF), carbamazepine (CBZ), caffeine (CF), chloramphenicol (CP), diclofenac (DF), gemfibrozil (GF), indometacin (IM), ketoprofen (KP), mefenamic acid (MA), metoprolol (MTP), nalidixic acid (NA), propranolol (PPN), sulpiride (SP), trimethoprim (TP), and *N*,*N*-diethyl-*meta*-toluamide (DEET) were purchased from Sigma-Aldrich (Steinheim, Germany) (Table S2 in the ESI†). ^{13}C-phenacetin obtained from Sigma-Aldrich, gemfibrozil-d_6 from Toronto Research Chemicals Inc. (Toronto, Canada), and mecoprop-d_3, chloramphenicol-d_5, and DEET-d_7 from Dr. Ehrenstorfer (Augsburg, Germany) were used as internal standards. All standard solutions were stored at −18 °C in the dark

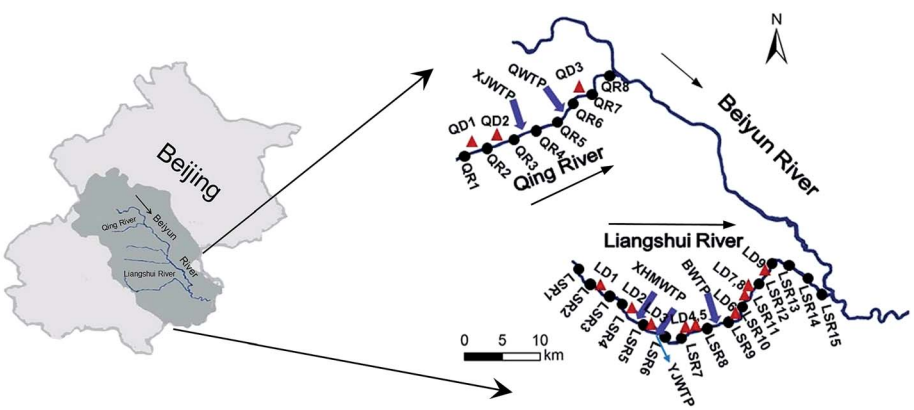

Fig. 1 Map of sampling sites in two rivers of Beijing (arrow indicates the flow direction). The dots, blue arrows and red triangles indicate the river water, WWTP effluent and discharged wastewater sampling sites, respectively.

prior to use. All solvents used were of HPLC grade from Dikma, USA, and ultrapure water was produced by using a Milli-Q unit (Millipore, USA).

2.3 Sample extraction and analysis

PPCPs were extracted and analyzed following the methods described in our previous studies with minor modifications.[19,21] Briefly, the collected samples (500 mL) were first filtered through pre-baked glass-fiber filters (GF/F, 0.7 μm; Whatman) and were subsequently spiked with 50 ng internal standards before solid phase extraction (SPE) using Oasis HLB cartridges (200 mg, 6 mL, Waters). The SPE cartridges were first conditioned with 10 mL of methanol and 10 mL of ultrapure water, before the water samples were percolated at a flow rate of 6 mL min^{-1}. After loading the samples, the cartridges were washed with 10 mL of ultrapure water and vacuum dried for 15–20 min to remove excess water. The target compounds were eluted from the SPE cartridges using 8 mL of methanol, which were evaporated to near dryness under a gentle stream of N_2. Finally, the extracts were reconstituted with 500 μL methanol–water (25 : 75, v/v) before being analyzed.

PPCPs were analyzed using high-performance liquid chromatography (Ultimate3000 HPLC system, Dionex, USA) followed by electrospray ionization and tandem mass spectrometry (ESI-MS/MS, API3200, AB Sciex, USA). PPCPs were separated by using two chromatographic columns. An Agilent XDB C18 column (150 mm × 3.0 mm, particle size of 3.5 μm) was used to separate CBZ, CF, DEET, MTP, NA, PPN, TP, SP, DEET-d_7 and ^{13}C-phenacetin in positive ion mode (ESI^+), while a Capcell PAK C18 column (100 mm × 3.0 mm, particle size of 3.0 μm) was used for BF, CP, DF, GF, KP, IM, MA, mecoprop-d_3, chloramphenicol-d_5 and gemfibrozil-d_6 in negative ion mode (ESI^-). The injection volume was 10 μL, and the column temperature was 30 °C. A mobile phase of 0.1% (v/v) formic acid in ultrapure water (mobile phase A) and methanol (mobile phase B) was used for ESI^+ at a flow rate of 0.30 mL min^{-1}, and the mobile phase gradient was ramped from 15% to 40% B in 4 min and 40–100% B in 14 min, maintained at 100% B for 7 min, and then ramped down again to 15% B and kept for 10 min. A mobile phase of 2 mM ammonium acetate in ultrapure water (mobile phase A) and methanol (mobile phase B) was used for ESI^- at a flow rate of 0.35 mL min^{-1}, and the gradient was ramped from 20% to 40% B in 8 min and 40% to 100% B in 7 min, maintained at 100% B for 7 min, and then ramped down again to 20% B and kept for 10 min. Multiple reaction monitoring (MRM) mode was applied for detection and quantification. The MRM parameters of the target analytes and the internal standards were optimized by direct infusion of the pure analytes into the MS/MS compartment. Detailed information concerning optimized MRM conditions is presented in Table S2 (ESI†).

2.4 Quality assurance and quality control

Calibration of the compounds was done from 0.5 to 1500 ng mL^{-1}. Recoveries of target PPCPs and matrix effects (MEs) were assessed according to our previous study.[21] Among the 15 target compounds, the recoveries ranged from 45–117% and MEs were less than 30% for most target compounds. Recoveries and MEs were reproducible with the relative standard deviation below 20% for each compound. Calculations of the limit of quantification (LOQ) were based on the variability of seven times analyses of Milli-Q water fortified at 10 ng L^{-1} of the analytes. The LOQ was determined by multiplying the sample standard deviation calculated from each group of fortified solutions by the Student's t-variate for a one-sided t-test at the 99% confidence level with $n - 1$ degrees of freedom.[22] The LOQs for the target analytes were in the range of 1.78–11.0 ng L^{-1}. Detailed method performance parameters are described in Table S3 (ESI†). Field control, procedural blanks and solvent blanks were run for each batch of samples to check background pollution. PPCPs were not detected in any of these extraction blanks.

2.5 Source apportionment of PPCPs

Source apportionment analysis was conducted using principal component analysis followed by multiple linear regression (PCA-MLR) based on the profiles of all detected compounds to interpret the contribution from different sources to total PPCPs. In PCA with Kaiser Normalization and varimax rotation, only factors with eigen values >1 were used for identification of the possible sources. MLR analysis of the PCA factor scores is used to quantify the source contribution.[23] Using the PCA factor scores as independent variables, MLR was run with the standard normal deviate of the SumPPCP values as the dependent variables as shown in eqn (1). Stepwise MLR modeling was used to remove any insignificant parameters, and only parameters that were significant at the 0.10 significance level were retained as eqn (1). After normalization, the multiple regression model is represented by the simple formula:

$$\hat{Z}_{\mathrm{SumPPCP}} = \sum B_k t_k \quad (1)$$

where SumPPCP is the total concentrations of the detected PPCPs in the present study, $\hat{Z}$ is the standard normalized deviate of the SumPPCP values, B_k is the modeled regression coefficient, and t_k is the factor score calculated by PCA.

The mean percentage contributions of each factor are calculated by eqn (2):

$$\text{Mean contribution of source } k\ (\%) = 100 \times (B_k/\textstyle\sum B_k) \quad (2)$$

The contribution of each source k to the SumPPCP is calculated by eqn (3).

$$\text{Contribution of source } k\ (\text{ng L}^{-1}) = \text{mean}_{\mathrm{SumPPCP}} \times (B_k/\textstyle\sum B_k) + B_k \sigma_{\mathrm{SumPPCP}} t_k \quad (3)$$

where $\text{mean}_{\mathrm{SumPPCP}}$ is the mean concentration of SumPPCP, and $\sigma_{\mathrm{SumPPCP}}$ is the standard deviation of SumPPCP for all samples.

2.6 Potential ecological risks

The potential risk posed by each PPCP was assessed based on the risk quotient (RQ) value, which is expressed as the ratio between the maximum measured environmental concentration

(MEC) and the predicted no-effect concentration (PNEC) of an individual compound, as suggested by the EMEA.[24] PNEC values used in the risk analysis are 1000 times lower than the lowest ecotoxicity concentration values found for three representative trophic levels of the ecosystem, fish, daphnia and algae. Data from the literature about the toxicity of the detected PPCPs to tested organisms are given in Tables S4 and S5 (ESI†). The potential environmental adverse effect on aquatic organisms fell into three levels: RQ < 0.1, low risk; 0.1 ≤ RQ ≤ 1, medium risk; RQ ≥ 1, high risk.[25]

3. Results and discussion

3.1 PPCPs in river water and wastewater

The concentration ranges of the selected PPCPs in river water and wastewater are shown in Fig. 2 and Table S3 (ESI†). Among the 15 PPCPs, 12 PPCPs (including CF, DEET, CBZ, MA, SP, IM, CP, GF, BF, MTP, KP and DF) were detected in 100% of the river water samples. NA (91%) and TP (69%) also exhibited high frequencies of detection, whereas PPN, a β-blocker, was not detected in any river sample (Table S3†). The total concentrations of the 14 detected PPCPs ranged from 276 to 6109 ng L^{-1} (median, 2780 ng L^{-1}) in river samples. The highest concentration was observed for CF, with a median concentration of 1870 ng L^{-1}. MTP (median, 115 ng L^{-1}), SP (90.0 ng L^{-1}), NA (89.7 ng L^{-1}), DEET (83.4 ng L^{-1}), KP (77.6 ng L^{-1}), DF (71.5 ng L^{-1}) and TP (51.5 ng L^{-1}) were also found in higher concentrations (Fig. 2). Other frequently detected PPCP compounds, including CBZ, IM, BF, GF, CP, and MA, showed relatively lower concentrations, with median concentrations below 50 ng L^{-1} in river samples (Fig. 2). Compared with our previous study on the surface water of Beijing, the concentration levels of all detected PPCPs in the present study were similar to those found in 2013 (Table 1).[19] CF showed the highest concentration in most river samples likely due to the universal use of caffeine, such as coffee, tea, cakes, chocolates and soft drinks.[15] The maximum concentration of CF (4720 ng L^{-1}) in the present study is higher than that observed in the Tennessee River, USA (175.7 ng L^{-1}),[26] Tone River, Japan (2100 ng L^{-1})[4] and Han River, Korea (250 ng L^{-1}),[7] but lower than that in the rivers in the USA (10 000 ng L^{-1})[27] and Costa Rica (1121446 ng L^{-1}).[9] In comparison, the median concentrations of CF, CP, NA, BF, DF, IM, MTP and SP in the present study were relatively higher than those observed in other water bodies, such as those in the USA, UK, Spain and Costa Rica and some rivers in Asia, while the median concentrations of DEET, TP, KP, GF, PPN, MA and CBZ were at middle levels compared to those of other water bodies, as shown in Table 1.

In addition to the river samples, we also analyzed 5 WWTP effluents and 12 wastewater samples collected from direct discharge outlets along the investigated rivers, which might contribute to the PPCP pollution in rivers (Fig. 2). Overall, the total PPCP concentrations in 12 wastewater samples from discharge outlets ranged from 219 ng L^{-1} (site QD2) to 13 805 ng L^{-1} (site QD3), with a median concentration of 4706 ng L^{-1}, 2 times higher than that in river samples (Fig. 3). CF (median 3570 ng L^{-1}) was found to be the compound with the highest concentration, followed by SP (median 173 ng L^{-1}), MTP (165 ng L^{-1}), DEET (127 ng L^{-1}) and KP (124 ng L^{-1}) (Table S3†). Analysis of the WWTP effluents showed that the

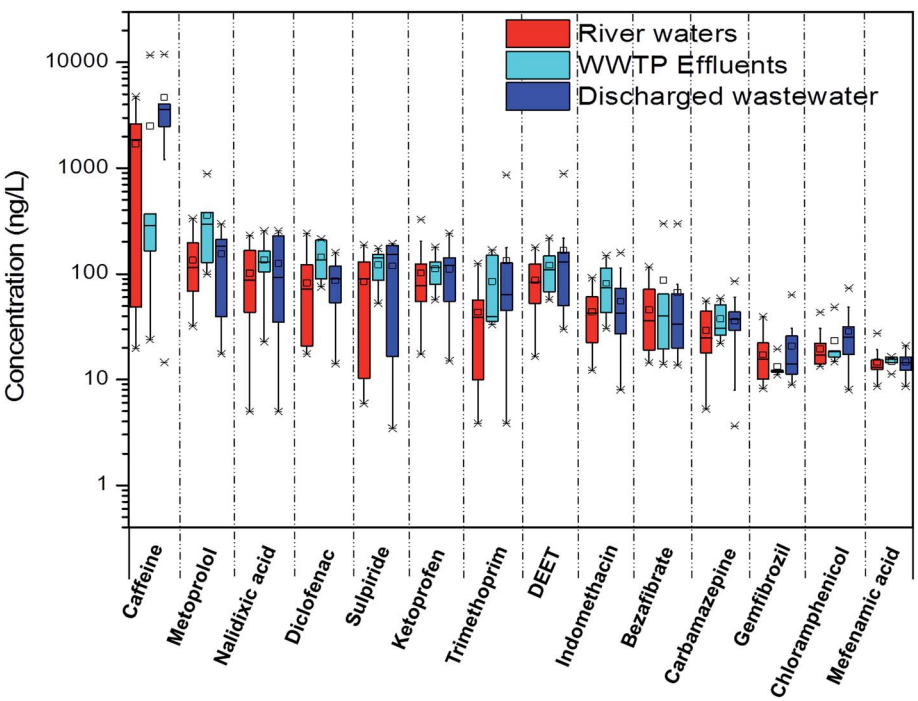

Fig. 2 Concentration ranges of PPCPs in river waters and wastewaters from WWTP effluents and direct discharge outlets. The solid bar in box marks the median, and the square in box marks the mean. The box denotes the 0.25 and 0.75 percentiles.

