Occurrence of pharmaceuticals and personal care products in Baiyangdian Lake

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Introduction

As the largest shallow freshwater lake in north China, Baiyangdian Lake is located in the center of Hebei province. It consists of more than 140 small and shallow lakes that are linked together by thousands of ditches, covering a total surface area of 366 km^2. There are several rivers flowing into the lake, including Baigouyinhe River, Puhe River, Fuhe River, Tanghe River, and Xiaoyi River. Baiyangdian Lake is also an essential natural wetland for groundwater replenishment, flood control, and biodiversity preservation in this region. In the last 20 years, Baiyangdian Lake has experienced pollution. The aim of this study was to investigate the occurrence and distribution of PPCPs in the surface water and sediments of Baiyangdian Lake, which will provide important data for decision makers in this region.

Materials and methods

HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific International Inc. (Pittsburgh, PA, USA); formic acid (98%) was purchased from Dikma (Lake Forest, CA, USA); and ammonium formate (99%) was purchased from Alfa Aesar (Ward Hill, MA, USA).

Eighteen PPCP compounds (Acetaminophen [ACE, 99.5%], caffeine [CAF, 98.5%], diltiazem [DTZ, 99.0%], carbamazepine [CBZ, 99.5%], fluoxetine [FXT, 99.0%], sulfadiazine [SDZ, 99.0%], sulfamethoxazole [SMX, 99.5%], sulfamethazine [SMZ, 99.6%], trimethoprim [TMP, 99.5%], oxytetracycline [OTC, 96.5%], tetracycline [TC, 98.0%], chlorltetracycline [CTC, 93.0%], doxycycline [DOX, 98.7%], azithromycin [AMZ, 97.0%], erythromycin [ERY, 99%], tylosin [TYL, 98.0%], lincomycin [LIN, 99.0%], and ofloxacin [OFL, 99.0%]) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotope-labeled compounds were used as surrogate standards (100.0μg·L^{-1} in methanol). Sulfadimidine-$^{13}C_6$ (SMZ-$^{13}C_6$), erythromycin-^{13}C, d_3 (ERY-^{13}C, d_3), and atrazine-d_5 (ATZ-d_5) were purchased from WITEGA Laboratorien Berlin-Adiershof GmbH (Berlin, Germany).

Sampling was performed from Baiyangdian Lake as well as its five upstream rivers in March 2017. A total of 31 water samples and 29 sediment samples were collected in the sampling. All samples were placed on ice and transported to the laboratory as soon as possible after collection. Surface water samples were collected from each sampling site with a stainless steel bucket that had been pre-cleaned with methanol and DI water, and then rinsed with water from the sampling site before collection. Water samples were kept at 4°C and target PPCPs were extracted from water samples within four days of sample collection. Sediments were collected with a stainless steel grab from the surface sediment, and were freeze-dried, ground, passed through a 100-mesh sieve, and kept at −20°C prior to analysis.

Chemical analysis was performed following United States Environmental Protection Agency method 1694 with some modifications (EPA, 2007).The eighteen selected PPCPs and three surrogate standards (SMZ-$^{13}C_6$, ERY-^{13}C, d_3, ATZ-d_5) were analyzed by HPLC-MS/MS. The HPLC separation was conducted using an Agilent 1290 series instrument equipped with Zorbax Eclipse Rapid Resolution HD C18 column (2.1 ×100, 1.8 μm: Agilent, Santa Clara, CA, USA)

Results and discussion:

The eighteen surveyed PPCPs were all detected above the limit of quantification (LOQ) in surface water samples from Baiyangdian Lake. CAF and CBZ were detected in all surface water samples, while the detection frequency of the other 16 target PPCPs was above 60%, except TYL (38.7%). With the exception of TYL, all target PPCPs were frequently detected (67.1–100%) in surface water because of their heavy use and high water solubility. CAF was the most abundant PPCP, with the highest mean concentration of 266.24 ng·L^{-1}, followed by LIN,

with a mean concentration of 107.13 ng·L^{-1}. The mean concentrations of DTZ, SDZ, and CTC were only 4.90, 8.79, and 4.87 ng·L^{-1}, respectively, although they were frequently found in the surface water samples.

An assessment of the distribution of PPCPs in surface water showed that five non-antibiotic pharmaceuticals (N-Aps [ACE, CAF, DTZ, CBZ, FXT]) were the predominant PPCPs (53.26%) in all samples. They were the most frequently detected PPCPs in surface water because of their heavy use in Baiyangdian Lake. Five N-APs were detected in the surface water from Baiyangdian Lake, each at a mean concentration exceeding 30.00 ng·L^{-1} except DTZ (4.90 ng·L^{-1}). CAF was detected with the highest mean concentration (226.24 ng·L^{-1}), with a maximum concentration of 726.75 ng·L^{-1}, followed by CBZ, FXT, ACE, and DTZ. CAF is present in a wide range of consumer products such as coffee, tea, soft drinks, chocolate, and painkillers and has been reported worldwide with a high occurrence, resulting in it being proposed as a biomarker for anthropogenic inputs into the aquatic environment. The high occurrence of CAF in Baiyangdian Lake and its upstream rivers suggested that there were inputs from both wastewater treatment plants and untreated wastewaters, and indicated a high consumption of caffeine-bearing products. These products are likely to be tea and soft drinks, which are the two most widely consumed beverages in China.

The detection frequency of four sulfonamides (SAs) (SDZ, SMX, SMZ, and TMP) at levels above their LOQs in surface water was greater than 80% in the 31 water samples. The highest detection frequency was 87.1% for TMP, followed by SMX, SDZ, and SMZ. The highest mean concentrations among the five compounds were recorded for SMX and TMP at 21.59 and 20.48 ng·L^{-1}, respectively. Compared with previous studies, which found that SAs, and especially SMX, had a high rate of occurrence, the levels of SA pollution in the surface water of Baiyangdian Lake was not very high. In fact, the concentrations of SA contaminants in this study were at an intermediate level compared with the levels reported in previous studies. In comparison, the SMX concentration in the surface water of Baiyangdian Lake was much lower than that reported in the surface water of Huangpu River, in which the mean concentration was 259.6 ng·L^{-1} as it passed through Shanghai City in China and in the surface water of Taihu Lake, in which the mean concentration was 48.4 ng·L^{-1}. However, the concentration of SMX in the surface water of Baiyangdian Lake was much higher than that reported in the Pearl River Estuary in south China, with mean concentrations of 12.4 and 4.65 ng·L^{-1} in the dry and wet seasons, respectively, and in the surface water of Dongjiang River in south China, in which the mean concentration was 14.9 ng·L^{-1}.

Among the four tetracyclines (TCs) investigated (OTC, TC, CTC, and DOX), three had a detection frequency greater than 87%, while the detection frequency of DOX was greater than 67%. OTC had the highest detection frequency of 96.8%, followed by TC and CTC at 90.3 and 87.1%, respectively. The highest mean concentration was determined for OTC at 22.55 ng·L^{-1}, which also had the highest detection frequency of the four TCs. CTC had the lowest mean concentration (4.87 ng·L^{-1}) of the four TCs in surface water from Baiyangdian Lake. Compared with the results of previous studies in which TCs, and especially OTC and TC, were reported to have a high rate of occurrence, the levels of TC pollution were not very high in Baiyangdian Lake. In comparison, the concentration of OTC in the surface water of Baiyangdian Lake was much lower than that in Huangpu River, Shanghai City and Taihu Lake, China, in which mean concentrations of 78.3 and 44.2 ng·L^{-1}, respectively, have been reported. However, the mean concentration of TC was higher in Baiyangdian Lake than in Huangpu River, Shanghai City and the Pearl River Estuary, with mean concentrations of 4.20 and 7.37 ng·L^{-1}, respectively.

Among the four macrolides (MCs) investigated (AMZ, ERY, TYL, and LIN), three had a detection frequency greater than 90%, while the detection frequency of TYL was lower at 38.7%. ERY had the highest detection frequency of 96.8%, followed by AMZ and LIN, which were both 90.3%. The highest mean concentration was determined for LIN at 107.13 ng·L^{-1}, with a detection frequency of 90.3%. TYL had the lowest mean concentration of the four MCs at 4.71 ng·L^{-1}, and also had the lowest detection rate of 38.7%. In previous studies, MCs and especially LIN, were reported to have high detection frequencies, with concentrations in Baiyangdian Lake being higher than those reported in the central and lower Yangtze River in China, where the reported concentration was 13.3 ng·L^{-1}. The concentration of ERY was much lower than the levels reported previously in the central and lower Yangtze River and Taihu Lake, at 296 and 109.1 ng·L^{-1}, respectively.

OFL was the only quinolone (QN) antibiotic detected in this study, with a high detection frequency of 96.8% and a mean concentration of 27.94 ng·L^{-1}. Compared with previous studies of OFL, in which a high rate of occurrence has been reported, the level of QN pollution in the surface water of Baiyangdian Lake was not very high. The concentrations were at an intermediate level compared with those reported in previous studies. In comparison, the concentration of OFL in the surface water of Baiyangdian Lake was much lower than the levels

reported in the surface water of Qiantang River, in which the range of concentration was 60–85 ng·L^{-1} in Zhejiang province and Duliujian River in Tianjin here the range of concentration was 49.2–89.4 ng·L^{-1}. However, the concentration of OFL was much higher than that reported in the surface water of the Pearl River Estuary in China, where concentrations of 7.10 and 6.16 ng·L^{-1} were reported in the wet and dry seasons, respectively. The concentration of OFL in the surface water of Baiyangdian Lake was similar to the concentration of 32.2 ng·L^{-1} reported previously in Taihu Lake. This suggests that different antibiotics are used in different geographic regions of China.

Among the 31 surface water samples, the total PPCP concentrations from Baigouyinhe River (871.78–923.16 ng·L^{-1}), Puhe River (1059.53–1782.94 ng·L^{-1}), Fuhe River (1814.88–2011.59 ng·L^{-1}), and Tanghe River (1513.14 ng·L^{-1}) were greater than those in Baiyangdian Lake (175.09–819.22 ng·L^{-1}) and Xiaoyi River (357.12–541.77 ng·L^{-1}). The highest levels (2011.59 ng·L^{-1}) of the 18 PPCPs was found in Fuhe River. Along the flow direction, the total concentrations of the 18 PPCPs almost tended to decrease in the river. As the only perennial inflowing river to Baiyangdian Lake, Fuhe River may make a significant contribution to the PPCP input to the Lake. It has been reported that Fuhe River receives a huge amount of domestic sewage and industrial wastewater (250,000 m^3·d^{-1}) from Baoding City. Therefore, the sewage discharge from Baoding City, with over eight million residents was likely to be the main source of PPCPs in Baiyangdian Lake. Human activities play a key role in the distribution of PPCPs in Baiyangdian Lake. Low levels of total PPCPs in surface water samples were found in the central part of Baiyangdian Lake (116.80–396.55 ng·L^{-1}), where there was little disturbance by human activities. In contrast, relatively high levels of PPCPs were found in densely populated lakeshores (774.78–819.22 ng·L^{-1}). These results indicate that Baiyangdian Lake might be influenced to some extent by the wastewater continuously discharged by the residents of local coastal areas.

In sediments, the total concentrations of PPCPs ranged from 43.00 to 222.21 μg·kg^{-1} (dw), in which the dominant classes of contaminants were the N-APs and MCs. The mean concentrations of the different classes of PPCPs followed the order: N-APs (42.70%) > MCs (25.43%) > TCs (14.69%) > SAs (13.90%) > QNs (3.24%).

All five N-APs were detected in the sediments from Baiyangdian Lake. The detection frequencies of CAF and CBZ were 100%, followed by FXT, ACE, and DTZ, with detection frequencies of 89.7, 86.2, and 79.3%, respectively. The five N-APs were the predominant PPCPs (42.7%) in all samples. The mean concentrations of CBZ and CAF at 14.73 and 11.11 μg·kg^{-1} (dw), respectively, were much higher than those of DTZ and FXT at 5.07 and 5.35 μg·kg^{-1}, respectively. The concentration of CBZ was much higher and the concentration of CAF was much lower than in marine sediments in the Todos os Santos Bay and the north coast of Salvador, Bahia, Brazil, with mean concentrations of 4.81 and 23.40 μg·kg^{-1}, respectively.

The detection frequency of the four SAs at levels above their LOQs in sediments was above 82% among the 29 samples. The highest mean concentration was determined for SMX at 7.30 μg·kg^{-1}, followed by TMP with a mean concentration of 3.78 μg·kg^{-1}. SDZ and SMZ had the lowest mean concentrations at 2.03 and 2.26 μg·kg^{-1}, with detection frequencies of 82.8 and 93.1%, respectively, in sediments from Baiyangdian Lake. Compared with previously reported concentrations, SMX in sediments from Baiyangdian Lake was present at intermediate concentrations. The concentration of SMX was higher than in the Huangpu River with a mean concentration of 0.2 μg·kg^{-1}, and lower than in Taihu Lake and the Pearl River, with mean concentrations of 16.10 and 12.4 μg·kg^{-1}, respectively.

The detection frequency of the four TCs at levels above their LOQs in sediments was above 72% among the 29 samples. The concentrations of TCs were similar among the different sampling sites, ranging from 3.00 to 5.17 μg·kg^{-1}. Compared with the mean concentrations of OTC, TC, and CTC in Taihu Lake, China, at 52.80, 47.90, and 19.00 μg·kg^{-1}, respectively, the concentrations of SAs in the sediments of Baiyangdian Lake were lower.

Among the 29 samples, the detection frequency of the four MCs at levels above their LOQs in sediments was above 86%, with the exception of TYL (34.5%). The mean concentrations ranged from 5.09 to 12.07 μg·kg^{-1}. The mean concentration of ERY in Baiyangdian Lake was similar to that reported (10.2 μg·kg^{-1}) in the Pearl River in southern China.

OFL was the only QN antibiotic investigated in this study, and had a high detection frequency of 93.1%, with a mean concentration at 3.53 μg·kg^{-1}. The mean concentration was similar to that reported in Huangpu River, the Pearl River, and the Yellow River, Haihe River, and Liaohe River, with mean concentrations of 6.50, 3.50, 3.07, 10.30, and 3.56 μg·kg^{-1}, respectively. However, it was lower than the concentration of 16.5 μg·kg^{-1} reported in Taihu Lake.

In pore water samples, the total concentrations of PPCPs ranged from 22.17 to 369.80 ng·L^{-1}, with the dominant classes of contaminants being MCs and N-APs. The mean concentrations of the different classes of PPCPs followed the order: MCs (42.12%) > N-APs (34.80%) > SAs (11.71%) > TCs (7.48%) > QNs (3.88%). All five N-APs were detected in pore water from Baiyangdian Lake, each at a mean concentration below 7.25 ng·L^{-1} except CAF (31.67 ng·L^{-1}). The detection frequency of these pharmaceuticals among the 29 samples was above 75%, with the exception of DTZ (37.9%). The detection frequency of the four SAs at levels over their LOQs in pore water was above 55% among the 29 samples. The mean concentration of the four SAs was 6.30 ng·L^{-1}, with a detection frequency that ranged from 55.2 to 89.7%. The detection frequency of the four TCs at levels over their LOQs in pore water was above 44% among the 29 samples. The mean concentration of the four TCs was 4.20 ng·L^{-1}, followed by the detection frequency ranged from 44.8% to 89.7%. The detection frequency of four MCs at levels over their LOQs in pore water was above 75%, with the exception of TYL (17.2%). Of the four MCs in pore water samples, ERY had the highest mean concentration at 29.92 ng·L^{-1}, followed by LIN at 20.15 ng·L^{-1}. TYL had the lowest mean concentration at 0.97 ng·L^{-1}, with the lowest detection frequency of 17.2% in pore water samples from Baiyangdian Lake. OFL, as the only QN antibiotic investigated in this study, had a high detection frequency of 93.1%, with a mean concentration of 5.43 ng·L^{-1}.

The mean concentrations of selected PPCPs in surface water samples were low and at similar levels in pore water samples. CAF, SMX, TMP, OTC, ERY, and OFL were the most frequently detected PPCPs (>80%), with mean concentrations of 31.67, 4.44, 4.13, 4.19, 29.92, and 5.43 ng·L^{-1}, respectively. The PPCP present at the highest mean concentration was CAF, with a mean concentration of 31.67 ng·L^{-1}, followed by ERY with a mean concentration of 29.92 ng·L^{-1}. To the best of our knowledge, only two studies have reported the occurrence of PPCPs in pore water from Taihu Lake and Baiyangdian Lake. The levels of SMX and TMP found in this study were similar to those reported previously in Taihu Lake. The levels of other PPCPs, e.g., SDZ, OTC, TC, CTC, and OFL, were higher in Taihu Lake, with mean concentrations of 5.30, 47.8, 11.7, 18.5, and 33.6 ng·L^{-1}. The levels of OFL found in this study were similar to those reported previously in Baiyangdian Lake. The levels of OTC and TC reported previously in Baiyangdian Lake were higher than those found in this study, with concentrations of 18.86 and 24.54 ng·L^{-1}.

Eighteen selected PPCPs were detected in surface water, pore water, and sediments from Baiyangdian Lake. Most of these compounds had a high detection frequency. The total concentrations in surface water, pore water, and sediment samples of five N-Aps were much higher than the corresponding concentrations of SAs, TCs, MCs, and QNs. Compared with the major rivers and lakes in China and worldwide, the concentrations of the 18 selected PPCPs showed were considered to be at an intermediate level. The total concentrations of PPCPs in five upstream rivers were higher than in Baiyangdian Lake. The worst case scenario from an environmental risk assessment indicated potential risks from ERY toward sensitive species in Baiyangdian Lake and its upstream rivers. Further information regarding the relationship between concentrations of PPCPs and water quality parameters should be collected in future studies.

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