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RESEARCH ARTICLE

Pollution levels and ecological risks of PPCPs in water and sediment samples of Danjiangkou Reservoir

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Abstract

The concentrations and distribution patterns of three typical pharmaceuticals and personal care products (PPCPs) in water and sediment samples obtained from Danjiangkou Reservoir during two seasonal sampling periods were studied to determine their impact on water quality. The temporal and spatial variations in concentrations measured were analyzed and related to ecological risks with data obtained during the mean-flow period (in June) and the dry period (in November). We found a high detection rate of ketoprofen (KTP) in water samples from Danjiangkou Reservoir; the concentrations ranged from not detected (ND) to 46.80 ng/L with the highest values measured in the Hanku tributary samples followed by the samples collected in the main body of Danjiangkou Reservoir. The KTP concentrations in the Danku tributary samples were the lowest measured in this study. In addition, the concentrations of KTP in the Shending River, Sihe River, Jianghe River, Guanshan River, and Jianhe River water samples were relatively high in the mean-flow period. The water sample detection rates and concentrations of triclosan (TCS) and triclocarban (TCC) were low in both the mean-flow period and the dry period. All three kinds of PPCPs were detected in the sediment samples with the concentrations of KTP, TCS, and TCC ranging from 0.76 to 7.89 µg/kg, 0.01 to 0.59 µg/kg, and 0.01 to 11.36 µg/kg, respectively. Overall, the concentrations of the three measured PPCPs in the water and sediment samples were all relatively low compared to results reported in the recent literature. The dry period concentrations of PPCPs in the water samples were lower than the concentrations measured in the mean-flow period. However, dry period concentrations were higher in the sediment samples compared to those in the mean-flow period samples. Our interpretation of the spatial and temporal patterns of PPCPs in Danjiangkou Reservoir suggests that these compounds were likely mainly derived from wastewater discharge in the upper reaches of the reservoir. The risk quotient (RQ) method was used for an ecological risk assessment of the detected PPCPs in this study. We found that TCS in water and sediment posed medium ecological risks to algae at different times of the year. In view of the extreme importance of water safety in Danjiangkou Reservoir, the ecological risks of PPCPs require additional attention.

Keywords PPCPs · Danjiangkou Reservoir · Water · Sediment · Risk assessment

Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of pollutants in the environment that include a variety of chemicals, including various drugs (such as steroids, antibiotics, antipsychotics, lipid-lowering drugs, anti-inflammatory drugs, and contraceptives), and disinfectants, cleansers, and cosmetics, among many others (Xiu et al. 2020). PPCPs are considered to be potentially hazardous substances in the environment due to their widespread distribution and persistence in the environment and the endocrine disrupting function of their active substances (Ren 2021). PPCPs have been frequently detected in several countries and regions (Zhang et al. 2023), including Europe, North America, Japan, and

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South Korea, with detected concentrations ranging from nanograms per liter to micrograms per liter. For this reason alone, the distribution, migration, and transformation of PPCPs in the water environment are an emerging focus of water quality research in many parts of the world (Cao et al. 2020; Wu et al. 2021; Li et al. 2021; Jiang et al. 2021).

There are various types of PPCPs in China, and their spatiotemporal distribution has typical regional and temporal differences (Chen et al. 2020; Zhao et al. 2022). Ketoprofen (KTP) is one of the most frequently detected nonsteroidal anti-inflammatory drugs in the global environment (Wang et al. 2018), with concentrations previously detected in surface water in China ranging from several hundreds to thousands of nanograms per liter (Gonzalez and Bebianno 2012). The concentration of KTP detected in some reservoirs in Europe has been reported as high as 1423 ng/L (Marsik et al. 2017). As widely used and effective broad-spectrum antimicrobials, triclosan (TCS) and triclocarban (TCC) are two common kinds of PPCPs with high detection frequency in the environment. For example, Zhao et al. (2013) investigated the distribution of TCS and TCC in samples from the Liaohe River, Haihe River, Yellow River, Pearl River, and Dongjiang River in China, and found that the detection frequency of TCS and TCC in the water and sediment of the five rivers was 100%. The concentrations of TCS in water samples were up to 478 ng/L and 1329 μg/kg in sediment samples in that study. The concentrations of TCC in water samples ranged up to 338 ng/L, and in sediment samples, up to 2723 μg/kg. In a subsequent study, Min et al. (2014) found that TCS and TCC were present in the Jiulong River (China) and its estuarine area, and the highest concentrations of TCS and TCC in the river reached 64 ng/L and 14.1 ng/L, respectively. The measured TCS and TCC concentrations ranged from 2.56 to 27.25 ng/L and 0.38 to 5.76 ng/L respectively in the sediment samples. Gao et al. (2018) studied the pollution levels and ecological risks of PPCPs in the water and sediments of the Hanjiang River and found that the detected concentration of KTP in water samples reached 250.59 ng/L. High concentrations of KTP and TCC were also found in sediment samples. Their interpretation was that KTP, TCS, and TCC presented significant ecological risks to bacteria, algae, invertebrate, and fish at different levels in Hanjiang River Basin. Numerous studies have shown that effluent from sewage treatment plants was one of the important sources of PPCPs in the environment (Gao et al. (2018)). A large number and variety of PPCP compounds enter the water environment with the discharge of industrial wastewater, livestock wastewater, hospital wastewater, and domestic sewage, which creates an important water quality problem threatening human health and the integrity of the ecological environment (Zhao et al. 2022; Wang et al. 2020).

The South-to-North Water Diversion Project is a trans-basin water diversion project with significant international impacts. The diversions include three routes—known as east, middle, and west—in the overall layout of the project. The Danjiangkou Reservoir is the main water source for the middle route project, which supplies the living, production, and ecological water needs of residents in the reservoir area and along the middle and lower reaches of the Hanjiang River and water-receiving area (Zhou et al. 2015; Qin et al. 2019). The water quality of the reservoir is an important component in a safe water supply (Zhang et al. 2018; Xia 2016). Previous studies on the water quality and safety of the Danjiangkou Reservoir focused on conventional pollutants, such as nitrogen, phosphorus, and heavy metals, and did not address new pollutants, such as PPCPs. But the concentration and ecological risk of PPCP in Danjiangkou Reservoir are still unclear nowadays.

In this study, the pollution status of three typical PPCPs (KTP, TCS, and TCC) in Danjiangkou Reservoir and its tributaries was tested and analyzed by collecting water samples and sediment samples at two different water sampling periods. Furthermore, the ecological risks of PPCPs were assessed by considering the concentrations of PPCPs relative to levels considered toxic to algae, invertebrates, and fish. The goals of this study are to provide critical baseline data, analysis, and technical support for PPCP pollution risk control and water quality safety in the Danjiangkou Reservoir area.

Experimental section

Sample collection and pre-treatment methods

The Danjiangkou Reservoir consists of two parts: Hanku Reservoir and Danku Reservoir. Based on the hydrological and water environment characteristics of the Danjiangkou Reservoir and its tributaries, and relying on the water quality monitoring station network in the Danjiangkou Reservoir area, 30 new pollutant sampling points were set up. Among them, 7 sampling points in the reservoir and 12 sampling points in the tributaries were set up in Hanku Reservoir, and 7 sampling points and 4 branch sampling points were set up in Danku Reservoir. The distribution of sampling points is shown in Fig. 1. Samples were collected in June 2022 (mean-flow period) and November 2022 (dry period). It should be noted that there was no obvious flood period in Danjiangkou Reservoir in 2022 due to less than average runoff into the reservoir throughout the year. Hence, only the samples of mean-flow and dry periods were collected in this study.

The specific sampling process used in the study employed a stainless steel water sampler deployed with a graduated rope at each sampling point. A 5-L sample of water was obtained from the surface, middle, and bottom layers

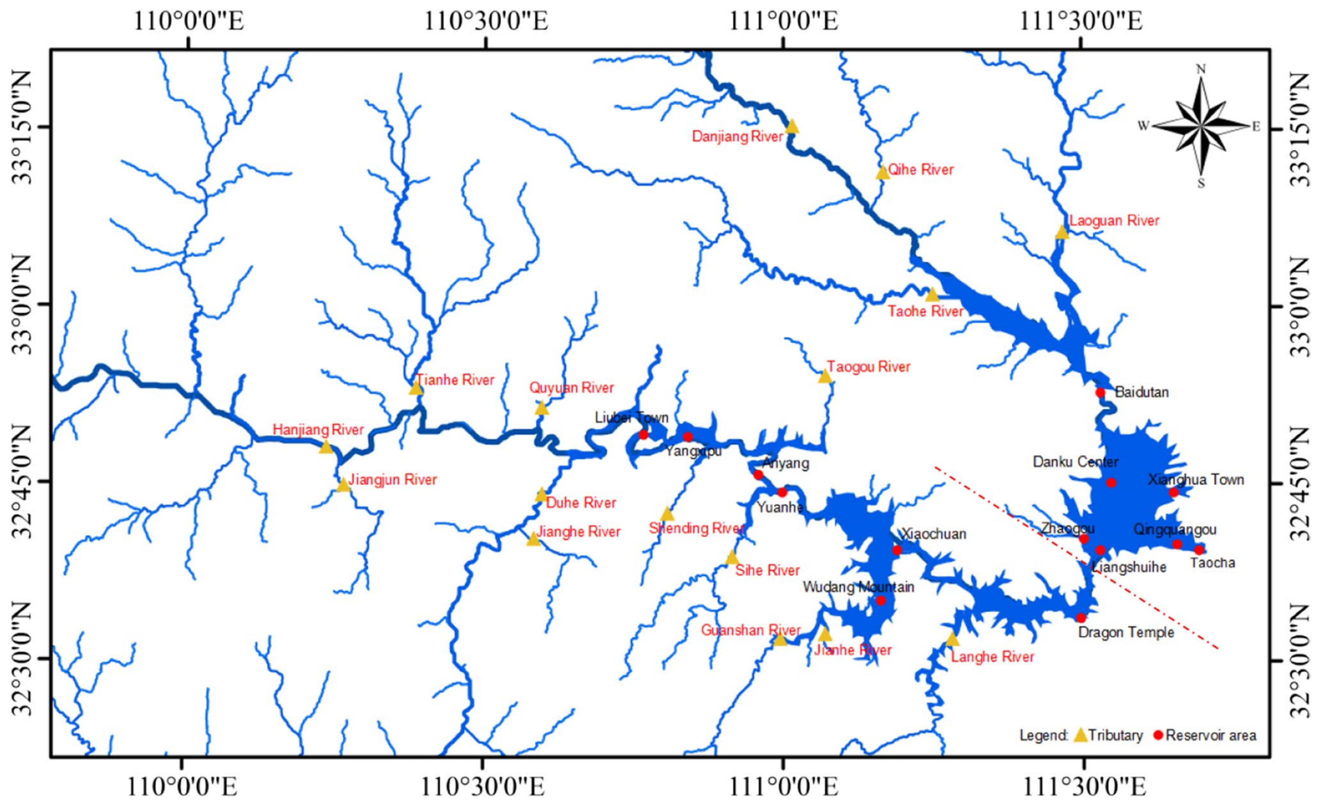

Fig. 1 Distribution of sampling points in Danjiangkou reservoir. (Above the dotted line is the Danku Reservoir, and below the dotted line is the Hanku Reservoir. And the red circle represents the sampling points in the reservoir, and the yellow triangles represent the sampling points in the tributaries)

separately (for tributary sample points, only surface water was collected). All water samples collected were stored in pre-washed brown glass bottles from light and transported to the laboratory for refrigeration at 4℃ after the data collection was completed. A total of 500 g of surface sediment per sample location in the reservoir area was captured using a grab-type mud sampler. The sediment samples were wrapped with aluminum foil and placed in polyethylene dense bags, cooled in a refrigerator at 4℃, and conveyed to the laboratory for treatment. Prior to sampling, all water quality sampling equipment and containers were washed with methanol, ultra-pure water, and the in situ water present at the corresponding sampling site to ensure that no contaminants were introduced.

The specific pre-treatment processes for each sample were as follows (Pan et al. 2014). First, the collected water samples were stored in pre-washed brown glass bottles, with sulfuric acid added to adjust pH to about 3.0. Second, the water samples were filtered with a 0.22-μm organic microporous filter membrane and transferred into 1.5-mL glass vials. The sediment samples were air-dried and sifted through a 60-mesh sieve. A sample of 2 g of sifted soil was oscillated for 10 s with a 5-mL citric acid buffer (pH = 3.5) and 5-mL acetonitrile. The mixed solution was subjected to ultrasound at room temperature for 20 min. The final step involved placing the sample in a centrifuge at 3500 r•min^{-1} for 5 min after which the supernatant was transferred to a clean 500-mL beaker. The above operation was repeated twice for each sediment sample. The two samples of supernatant were then combined and fixed to an injection volume of 500 mL by adding ultra-pure water to control the content of organic solvent less than 5%. Subsequently, 0.2 g Na_2EDTA was added to the solution and stirred until dissolved. The treatment was then the same as used for the water samples. A process blank was set for each batch of sample handling.

Reagents and instruments

Three typical PPCP (KTP, TCC, and TCS) substances were purchased from Zhongchang Standard Material Technology Co., Ltd. (Wuhan, China).

Instrument type and analysis parameters were as follows: (i) Q exactive high-resolution liquid mass spectrometry (HR-LC–MS Orbitrap LC/MS) (Q Exactive, Thermo Fisher, Germany), (ii) Accucore aQ 100 column (100 × 2.1 mm, 2.6 μm) (Thermo Fisher, Germany), (iii) ultrasonic cleaner (KQ-300VDE, Kunshan Ultrasonic Instrument Co., Ltd.), and (iv) refrigerated high-speed centrifuge (Mikro220R, Hettich, Germany). The column temperature of the liquid-phase system was 25 ℃, and the sample size was 10 μL. The mobile phase was 0.1% formic acid acetonitrile solution (A) and 0.1% formic acid aqueous solution (B) at a flow rate of 0.20 mL/min. Gradient elution program was set at $t = 0$–10–13–13.1–20 (min) and $A\% = 20$–90–90–20–20. Mass spectrometer conditions were as follows: the ion source was heated electrospray ionization (HESI) with the flow rate of atomizing gas and auxiliary gas set to 40 arb and 8 arb separately. The spray voltage was 3200 V, and the ion transport capillary temperature and auxiliary temperature were 300 ℃ and 280 ℃, again set separately. Scanning mode was full MS with scanning range m/z 220–400. Microsoft Excel and Origin Pro software were used for the data processing.

Risk assessment method

The ecological risk assessment of various PPCP components detected in water and sediments of the Danjiangkou Reservoir was conducted using the risk quotient (RQ) method (Sanderson et al. 2003). RQ was calculated by MEC (measured effect concentration, represented by the detected concentration of the actual sample) and PNEC (predicted no effect concentration) as follows:

$$\mathrm{RQ} = \mathrm{MEC}/\mathrm{PNEC}$$

$$\mathrm{PNEC_w} = (\mathrm{EC_{50}} \mathrm{or} \mathrm{LC_{50}})/\mathrm{AF}$$

where the four levels of ecological risk assessment were (i) very low risk ($\mathrm{RQ} < 0.01$), (ii) low risk ($0.01 < \mathrm{RQ} < 0.1$), (iii) medium risk ($0.1 < \mathrm{RQ} < 1$), and (iv) high risk ($\mathrm{RQ} > 1$). $\mathrm{PNEC_w}$ was the measured concentration of the PPCP of interest in the water phase. $\mathrm{EC_{50}}$ and $\mathrm{LC_{50}}$ were used to represent the half effective and half lethal concentration, respectively. Appropriate values of $\mathrm{EC_{50}}$, $\mathrm{LC_{50}}$, and PNEC for the PPCPs of interest for three different trophic levels of aquatic organisms—algae, zooplankton, and fish—were obtained from the most current literature. AF was the evaluation factor with the recommended value of 1000 (for acute toxicity risk assessment) or 100 (for chronic toxicity risk assessment) of the EU Water Framework Directive (Li et al. 2018).

$\mathrm{PNEC_s}$ (predicted no effect concentration of PPCPs in sediments) was estimated by $\mathrm{PNEC_w}$ and K_d (sediment–water partition coefficient of PPCPs) with the following equation (Yu et al. 2013; Halling et al. 2000; Ong et al. 2018; Karickhoff 1981):

$$\mathrm{PNEC_s} = K_d \times \mathrm{PNEC_w}$$

$$K_d = f_{oc} \times 0.411 \times K_{ow}$$

where f_{oc} was the sediment organic carbon content and K_{ow} was the octanol–water partition coefficient (Gao et al. 2018).

Results and discussion

Analysis of PPCP concentration and potential sources in the Danjiangkou Reservoir

The concentrations of three kinds of PPCPs in the surface water of Danjiangkou Reservoir are shown in Table 1. Generally, the detection rates of all three PPCPs in the water samples differed significantly in the mean-flow period and the dry period. For example, the detection rates of KTP in the water samples in the mean-flow period and the dry period were both high, at 100% and 90%, respectively. The detection rate of TCS was higher in the mean-flow period (up to 71.15%), but TCS was not detected in the dry period samples. The detection rates of TCC in water samples in both the mean-flow period and the dry period were both low, as 5.77% and not detected, respectively.

In the surface waters of Danjiangkou Reservoir, the average concentration values of KTP in the mean-flow period and the dry period were 11.93 ng/L (ranging from 3.62 to 46.8 ng/L) and 5.14 ng/L (ranging from ND to 16.9 ng/L), respectively. These values were similar to the concentration levels of KTP detected in the Jiulong River basin (ranging from 1.8 to 54.5 ng/L) in earlier water quality research by Lv et al. (2014), but lower than the concentration level of KTP in the water phase of the Hanjiang River basin

Table 1 Concentration of PPCPs in surface water of Danjiangkou Reservoir (ng/L)

Compound	Mean-flow period				Dry period			
	Average	Minimum	Maximum	Detection rate/%	Average	Minimum	Maximum	Detection rate/%
KTP	11.93	3.62	46.8	100	5.14	0.00	16.9	90
TCS	0.15	0.00	0.60	71.15	0.00	0.00	0.00	0
TCC	0.006	0.00	0.10	5.77	0.00	0.00	0.00	0

(13.65–250.59 ng/L) as reported in a previous study by Gao et al. (2018). The concentrations of both TCS and TCC in the waters of Danjiangkou Reservoir were at low levels, ranging from ND to 0.60 ng/L (average 0.15 ng/L) and ND to 0.10 ng/L (average 0.006 ng/L) in the mean-flow period, respectively. TCS and TCC were not detected in the dry period water sampling. Overall, the concentrations of TCS and TCC in Danjiangkou Reservoir in this study were lower than those reported in the recent literature. For example, the concentrations of TCS and TCC detected in the Xiaoqing River basin ranged from 32 to 382 ng/L, and 42 to 294 ng/L, respectively (Wang et al. 2014). The concentrations of TCS and TCC detected in the Jiulong River basin reached up to 64 ng/L and 14.1 ng/L, respectively (Min et al. 2014). TCS and TCC concentrations detected in the water phase of the Hanjiang River basin ranged from ND to 26.35 ng/L (average 8.76 ng/L) and ND to 12.66 ng/L (average 1.81 ng/L), respectively (Gao et al. 2018).

In the mean-flow period, the KTP concentration of the surface water of each sample point ranked from high to low was found in the Hanku tributaries, the main Reservoir area and the Danku tributaries, respectively. The KTP concentrations of the samples from the Shending River, Sihe River, Yaohe River, Guanshan River, and Jianhe River were relatively high, indicating that the pollution likely came from the upper reaches of the Hanjiang River. The concentration level of TCS in surface waters of all sample points was low, with no detection at 11 of the sample points. The concentration of KTP in the Reservoir area exhibited few differences in each layer, which indicated that there were no obvious stratification characteristics in the vertical distribution of KTP. The concentration of TCS in the surface layer samples was lower than the concentrations measured in the middle and bottom water sample layers, indicating that TCS had a downward migration trend in the water column.

In the dry period, the KTP concentrations in the surface water of each sample point ranked as follows: (i) higher concentration values in the Hanku tributaries, (ii) lower concentration values measured in the Reservoir area, and (iii) finally, the lowest concentrations detected in the Danku tributaries. This pattern was consistent with that of the mean-flow period, indicating that the likely sources of pollution mainly originated in the upper reaches of the Hanjiang River. The concentration of KTP in the Reservoir area showed little difference between surface, middle, and bottom water samples, which again indicated there were no obvious stratification characteristics in vertical distribution. Neither TCS nor TCC was detected in the dry period samples.

According to our data review and field investigation, there exist several urban sewage treatment plants in the upper reaches of the Hanjiang River, Shending River, Sihe River, Guanshan River, and other river basins, which correspond to locations with high intense human activities. Compared with the mean-flow period, the concentration of KTP in each layer of water body decreased at most sampling points in the dry period, and the decreasing trend was most obvious in the Hanku tributaries. The concentration of the PPCPs measured in this study decreased in the dry period, which might be due to the decrease of wastewater discharge in the upper reaches of the reservoir.

The comparison of KTP concentration in surface water and the vertical distribution of KTP concentration in each layer at each sampling point in the mean-flow period and the dry period is shown in Fig. 2. The TCS concentration in surface water and the vertical distribution of TCS concentration in each layer at each sampling point in the mean-flow period are shown in Fig. 3.

Analysis of PPCPs concentration and potential sources in sediments of Danjiangkou Reservoir

The concentrations of three PPCPs in the sediments of Danjiangkou Reservoir are shown in Table 2. The three kinds of PPCPs of interest in this study were detected in sediments in both the mean-flow period and the dry period sediment samples. The detection rates of KTP in sediments in the mean-flow period and the dry period were 16.67% and 93.33%, respectively. The detection rate of TCS was higher in the mean-flow period (66.67%) than in the dry period (3.33%). The detection rates of TCC in sediments in both the mean-flow period and the dry period were quite low, as 5.77% and not detected, respectively.

In the sediments of Danjiangkou Reservoir, the average values of KTP in the mean-flow period and the dry period were 2.78 (0–3.74 μg/kg) and 5.14 ng/L (0–7.85 μg/kg), respectively. These values were similar to the concentration levels of KTP detected in surface water sediments in Spain (ranging from 0 to 3.34 μg/kg) by Ferreira et al. (2011), and lower than the concentration levels of KTP detected in the water phase of the Hanjiang River Basin (2.51–66.22 μg/kg) reported by Gao et al. (2018). The concentrations of TCS and TCC in the sediments of the Danjiangkou Reservoir samples in the mean-flow period ranged from ND to 0.03 μg/kg (average 0.008 μg/kg) and ND to 4.39 μg/kg (average 0.31 μg/kg), respectively. The detected concentration of TCS was 2.37 μg/kg in the Sihe River samples, and the TCC concentrations ranged from ND to 11.36 μg/kg (average 0.66 μg/kg) in the dry period. The concentrations of TCS and TCC in the sediments of the Danjiangkou Reservoir in this study were generally lower than those reported in the literature. For example, the concentrations of TCS and TCC detected in the sediments of the Xiaoqing River basin ranged from 85 to 705 μg/kg (average 733 μg/kg) and 42 to 294 μg/kg (average 294 μg/kg), respectively (Wang et al. 2014). The concentrations of TCS and TCC detected in the sediments

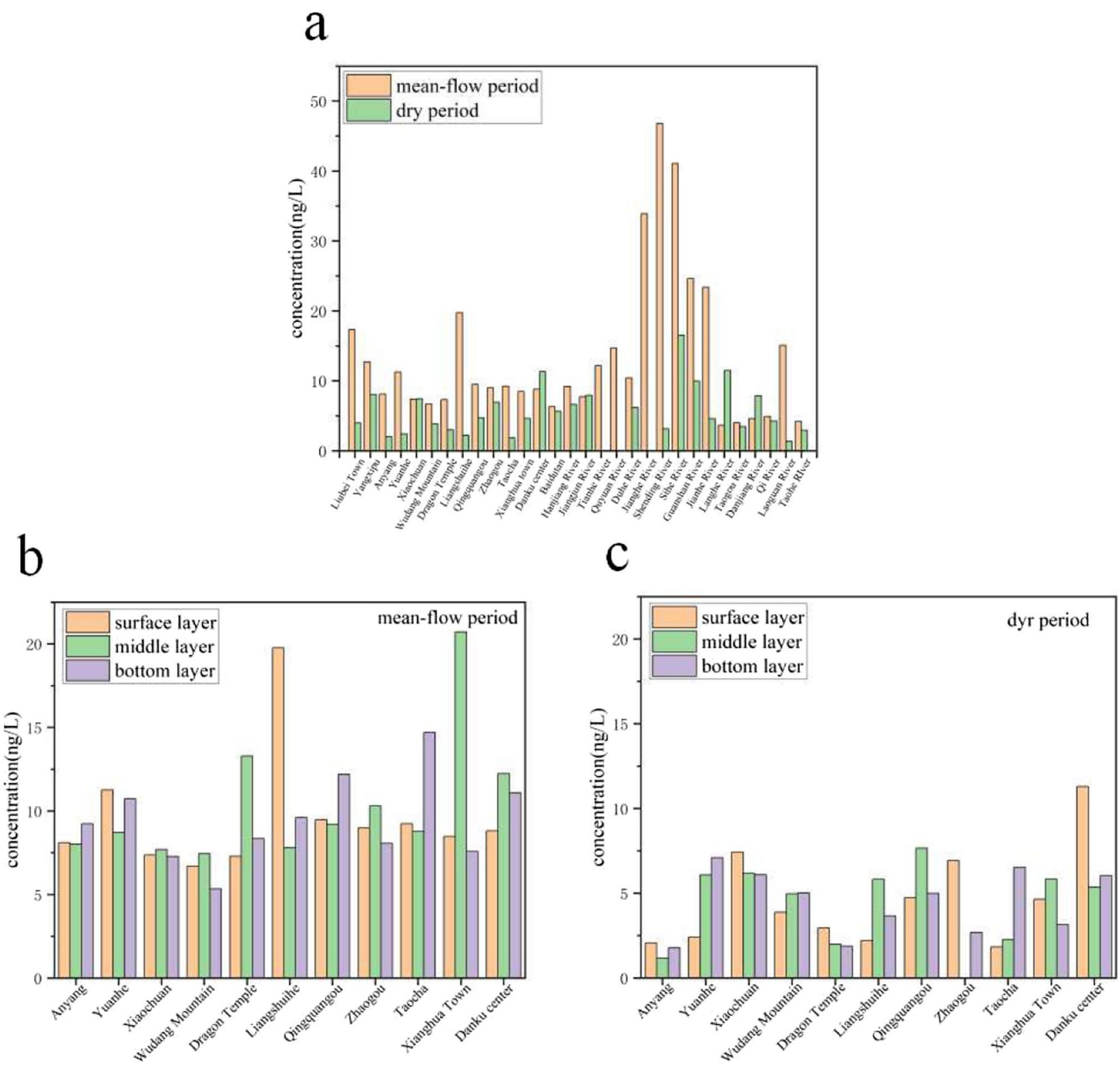

Fig. 2 The comparison of KTP concentration in surface water (**a**) and the vertical distribution of KTP concentration in each layer at each sampling point in mean-flow period (**b**) and dry period (**c**)

of the Hanjiang River basin ranged from ND to 7.73 μg/kg (average 3.82 μg/kg) and from 1.85 to 52.32 μg/kg (average 17.2 μg/kg), respectively (Gao et al. 2018). The highest concentrations of TCS and TCC detected in the Liaohe River basin, Haihe River basin, Yellow River basin, Pearl River basin, and Dongjiang River basin were 1329 μg/kg and 2723 μg/kg, respectively (Zhao et al. 2013). In comparison, the concentration levels of the three PPCPs studied here and found in the sediments of Danjiangkou Reservoir were relatively low. The concentrations of the three PPCPs of interest in this study in the sediments increased in the dry period compared with the mean-flow period. This was likely because the water flow was lower during the dry period than during the mean-flow period, and therefore the water velocity was slower in the dry period. Such conditions are more conducive to the accumulation and adsorption of pollutants in sediments.

The concentrations of KTP, TCS, and TCC in sediments at each sampling point in the mean-flow period and the dry period are displayed in Fig. 4.

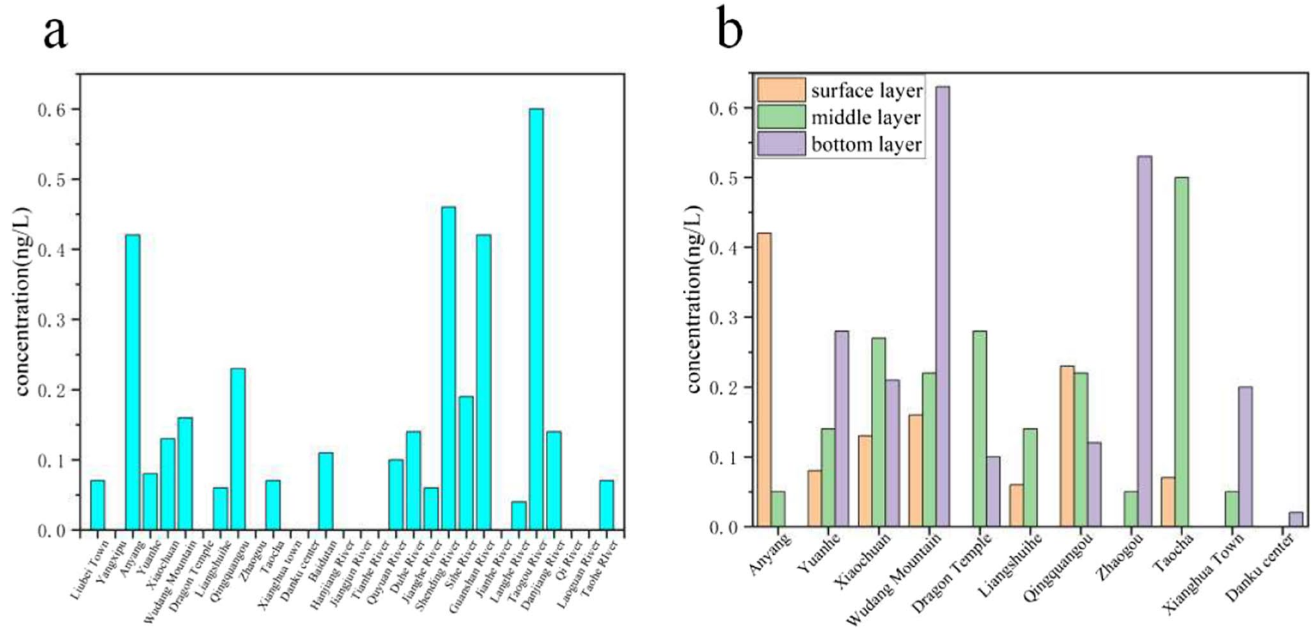

Fig. 3 The TCS concentration in surface water (**a**) and the vertical distribution of TCS concentration in each layer of water (**b**) at each sampling point in mean-flow period

Table 2 Concentration of PPCPs in sediments of Danjiangkou Reservoir (μg/kg)

Compound	Mean-flow period				Dry period			
	Average	Minimum	Maximum	Detection rate/%	Average	Minimum	Maximum	Detection rate/%
KTP	0.33	0.00	3.74	16.67	2.78	0.00	7.89	93.33
TCS	0.008	0.00	0.03	66.67	0.079	0.00	2.37	3.33
TCC	0.31	0.00	0.49	43.33	0.66	0.00	11.36	30

Ecological risk assessment

Acute (slow) toxicity data of EC_{50}, LC_{50}, and PNEC of the three PPCPs measured in this analysis (KTP, TCS, and TCC) for three trophic levels (algae, invertebrates, and fish) were obtained from relevant literature as shown in Table 3.

Due to the lack of consistent experimental toxicity data obtained under different test conditions, the lowest EC_{50} or LC_{50} estimate for each trophic class (algae, invertebrates, fish) in Table 3 was used to assess the acute ecological risk of the three PPCPs sampled in the Danjiangkou Reservoir in the present study. At the same time, the maximum measured concentration of each kind of PPCP in the water and sediments was taken as MEC to simulate a worst-case scenario (Kim et al. 2007). The ecological risk levels of three PPCPs to algae, invertebrates, and fish in water and sediment of Danjiangkou Reservoir in the mean-flow and the dry period are listed in Table 4 and Table 5, respectively. We used MEC_w as the maximum measured concentration in the water phase, expressed in ng/L, and MEC_s as the maximum measured concentration in the sediment, noted as micrograms per kilogram. We also applied f_{oc} as the organic carbon content of sediment for each sample corresponding to the sites with the maximum detection concentration, expressed as %. In addition, lgK_{ow} was used as the octanol–water partition coefficient, EC_{50} was the half effective concentration (mg/L), and LC_{50} was the half lethal concentration (mg/L). The results of the ecological risk assessment are expressed as RQ_w, which is the risk quotient of PPCPs in water, and RQ_s, which is the risk quotient of PPCPs in sediments. ND is used in Table 4 and 5 to indicate that the substance of interest was not detected.

Risk quotient (RQ) was interpreted to assess the degree of harm related to the three PPCPs detected in the water and sediment of the Danjiangkou Reservoir in this study. According to the calculated RQ values of PPCPs in the water environment and using the above ecological risk evaluation principles, we found that the risks were generally low, but that some ecological risks for algae from

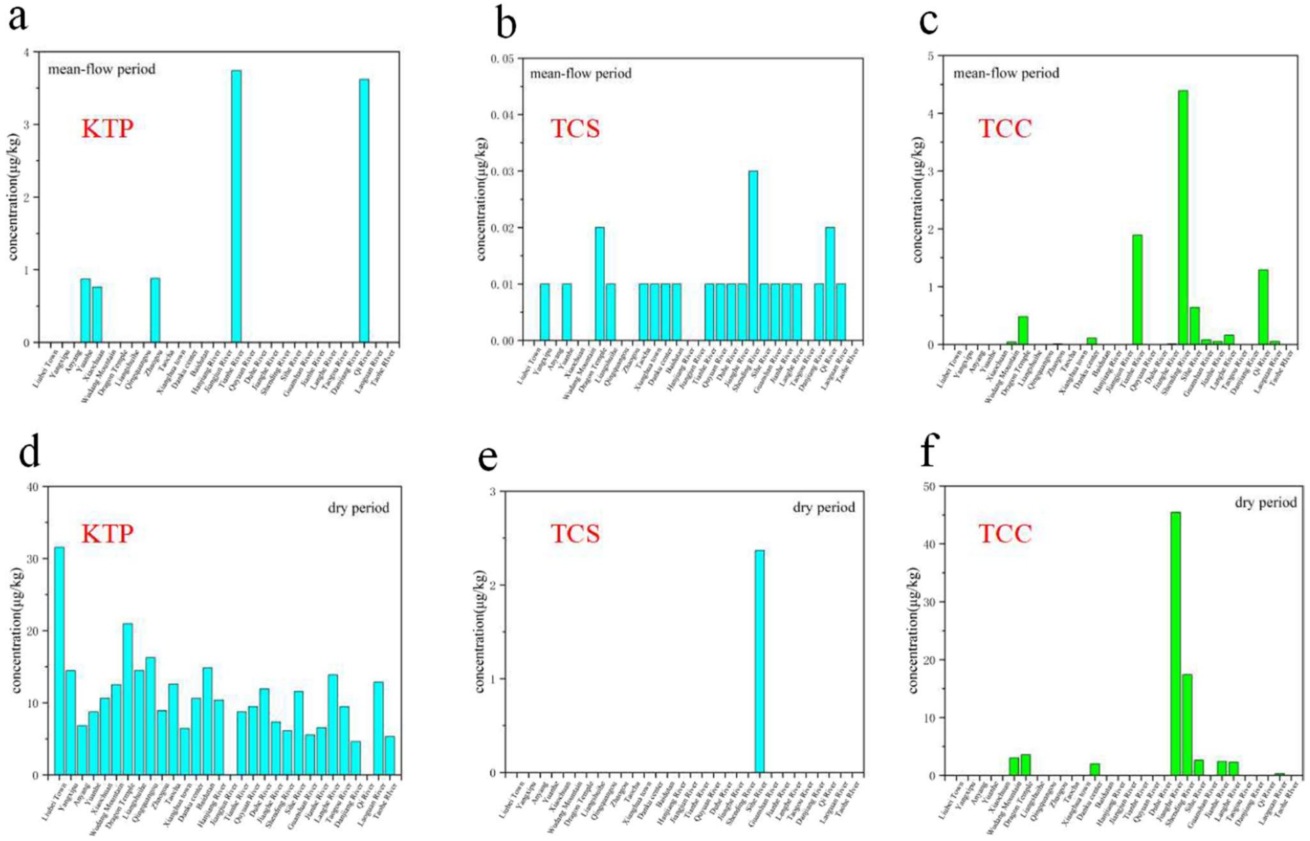

Fig. 4 The concentrations of KTP, TCS, and TCC in sediments at each sampling point in mean-flow period (**a**, **b**, **c**) and dry period (**d**, **e**, **f**)

certain PPCPs in the water environment should not be ignored. We note that different biological receptors face different ecological risks.

As seen from Table 4, in water samples of the Danjiangkou Reservoir and its tributaries in the mean-flow period, algae showed medium risk for TCS (RQ = 0.18). In these water samples, TCC was at the very low risk level, and KTP was at the low risk level. For invertebrates, TCS was at the very low risk level, and TCC and KTP were both at low risk levels. For fish, TCS, TCC, and KTP were all at the very low risk level. In the sediment samples of the Danjiangkou Reservoir and its tributaries, we found that algae were at low risk levels for TCS, and both TCC and KTP were at very low risk levels. For invertebrates, TCS was at the low risk level, and both TCC and KTP were at very low risk levels. For fish, TCS and TCC were at low risk levels and KTP was at the very low risk level.

As seen from Table 5, in water samples of the Danjiangkou Reservoir and its tributaries in the dry period, the risks of all three PPCPs measured in this study were at the very low level for algae, invertebrates, and fish. In the sediment samples of the Danjiangkou Reservoir and its tributaries, algae showed medium risk for TCS (RQ = 0.19), but TCC and KTP were at very low risk levels. The risks of three PPCPs were all at the very low levels for invertebrates and fish.

In conclusion, except for the medium risk of TCS to algae in water in the mean-flow period, and the medium risk of TCS to algae in sediment in the dry period, the other two PPCPs measured in water and sediment samples in this study showed low risk or very low risk levels. The results show that the sensitivity of algae to TCS was the highest among the three organisms considered here (algae, invertebrates, and fish), which is consistent with the research results of Li et al. (2015). TCS is relatively toxic to algae according to research by Ramaswamy et al. (2011) and Orvos et al. (2002).

The results of PPCP ecological risk assessment in water and sediment of the same water sampling periods for our study (i.e., mean-flow period (June) and dry period (November)) did not generate a consistent pattern. Our results show that the detection levels of PPCPs in the two phases (water and sediment) were different, as were the PNEC values. PPCPs with high detected concentrations did not necessarily have a high risk quotient (such as KTP), and vice versa. At present, common assessment methods used to calculate the ecological risk of PPCPs in the water environment do not adequately consider chronic impacts and do not accurately

Table 3 Acute (slow) toxicity data of EC_{50}, LC_{50}, and PNEC of three PPCPs in freshwater

Compounds	Taxon	Species	Toxicological endpoint	Ecotoxicity data (mg/L)	Reference
KTP	Algae (green)	*S. capricornutum*	EC_{50} (48 h)	164.00	Li et al. (2018)
	Algae (green)	*P. subcapitata*	EC_{50} (72 h)	49.3	Minguez et al. (2016)
	Algae (green)	*P. subcapitata*	EC_{50} (96 h)	2.0	Ramaswamy et al. (2011)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	248.00	Li et al. (2018)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	2.3	Harada et al. (2008)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	32.93	Minguez et al. (2016)
	Fish	*P. promelas*	EC_{50} (96 h)	32.00	Li et al. (2018)
TCS	Algae (green)	*P. ubcapitata*	EC_{50} (72 h)	0.0051	Tamura et al. (2013)
	Algae (green)	*P. subcapitata*	EC_{50} (96 h)	0.012	Harada et al. (2008)
	Algae (green)	*D. tertiolecta*	EC_{50} (96 h)	0.00355	Delorenzo et al. (2008)
	Invertebrate (crustacean)	*T. platyurus*	LC_{50} (24 h)	0.47	Kim et al. (2009)
	Invertebrate (crustacean)	*P. pugio*	LC_{50} (24 h)	0.482	Delorenzo et al. (2008)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	0.26	Harada et al. (2008)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	0.39	Orvos et al. (2002)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	0.18	Tamura et al. (2013)
	Invertebrate (crustacean)	*P. pugio*	LC_{50} (96 h)	0.305	Delorenzo et al. (2008)
	Invertebrate (crustacean)	*H. azteca*	EC_{50} (10 d)	0.25	Dussault et al. (2008)
	Invertebrate (crustacean)	*H. azteca*	LC_{50} (10 d)	0.2	Dussault et al. (2008)
	Invertebrate (Oligohymenophorea)	*T. pyriformis*	EC_{50} (96 h)	0.21	Harada et al. (2008)
	Fish	*O. latipes*	EC_{50} (96 h)	0.21	Tamura et al. (2013)
	Fish	*L. macrochirus*	LC_{50} (96 h)	0.37	Orvos et al. (2002)
	Fish	*O. latipes*	LC_{50} (96 h)	0.6	Kim et al. (2009)
	Fish	*P. promelas*	EC_{50} (96 h)	0.26	Orvos et al. (2002)
TCC	Algae (green)	*P. ubcapitata*	EC_{50} (72 h)	0.029	Tamura et al. (2013)
	Invertebrate (crustacean)	*D. magna*	EC_{50} (48 h)	0.010	Tamura et al. (2013)
	Fish	*O. latipes*	LC_{50} (96 h)	0.085	Tamura et al. (2013)

Table 4 The ecological risk levels of three PPCPs to algae, invertebrates, and fish in water and sediment of Danjiangkou Reservoir in mean-flow period

Compounds	TCS	TCC	KTP
MEC_w (ng/L)	0.63	0.16	46.80
MEC_s (μg/kg	0.03	4.39	0.88
f_{oc}/%	0.03	0.03	0.06
lgK_{ow}	3.12	4.76	4.90
Lowest E (L) C_{50} for algae (mg/L)	0.03	1.51	2.08
RQ_w	0.18	<0.01	0.02
RQ_s	0.06	ND	ND
Lowest E (L) C_{50} for invertebrate (mg/L)	0.03	1.45	2.00
RQ_w	ND	0.02	0.02
RQs	0.06	ND	ND
Lowest E (L) C_{50} for fish (mg/L)	0.03	1.36	1.87
RQ_w	ND	ND	ND
RQs	0.07	<0.01	ND

Table 5 The ecological risk levels of three PPCPs to algae, invertebrates, and fish in water and sediment of Danjiangkou Reservoir in dry period

Compounds	TCS	TCC	KTP
MEC_w (ng/L)	ND	ND	16.50
MEC_s (μg/kg)	0.59	11.36	7.89
f_{oc}/%	0.6	2.2	4.0
lgK_{ow}	3.12	4.76	4.90
Lowest E (L) C_{50} for algae (mg/L)	0.03	1.51	2.08
RQ_w	ND	ND	<0.01
RQ_s	0.19	ND	ND
Lowest E (L) C_{50} for invertebrate (mg/L)	0.03	1.45	2.00
RQ_w	ND	ND	ND
RQ_s	ND	<0.01	ND
Lowest E (L) C_{50} for fish (mg/L)	0.03	1.36	1.87
RQ_w	ND	ND	ND
RQ_s	ND	ND	ND

reflect the actual ecological effect of PPCPs. In addition, the biological toxicological impacts of other PPCPs in water and sediments are still relatively unknown due to the lack of experimental data and the diversity of potential pollutants, products, and environmental conditions. Hence, it is recommended that further study of the concentrations and potential environmental ecological risks of PPCPs be considered a water quality research priority.

Conclusions

In this study of water samples from the Danjiangkou Reservoir, the detection rate of ketoprofen (KTP) was high and the detection rates of triclosan (TCS) and triclocarban (TCC) were low in both the mean-flow period and the dry period. The KTP concentrations ranged from ND to 46.8 ng/L. All three kinds of PPCPs were detected in the sediments of the Danjiangkou Reservoir; however, the concentrations of all three PPCPs were relatively low. In our interpretation of the spatial distribution of the measured PPCPs found in Danjiangkou Reservoir, the pollutants were likely mainly derived from wastewater discharge in the upper reaches of the reservoir. Compared with the mean-flow period, the dry period concentrations of the PPCPs of interest in this research in water samples decreased, which was interpreted to be a consequence of the decreased wastewater discharge in the upper reaches of the reservoir. The concentration of the three PPCPs measured in the sediments increased in the dry period compared with the mean-flow period. Except for the medium risk of TCS to algae in water in the mean-flow period and the medium risk of TCS to algae in sediment in the dry period, KTP and TCC in water and sediments showed low risk or very low risk levels. In general, this research has confirmed that there exist certain ecological risks of PPCPs in the Danjiangkou Reservoir. The biological toxicological data of other PPCPs in water and sediments are less well known. In view of the extreme importance of water quality and safety in the Danjiangkou Reservoir, this study has shown that the ecological risks of PPCPs in water and sediments, particularly to algae, should receive additional attention. Based on our research, we recommend that the environmental and ecological effects of the three PPCPs studied here, and additional PPCPs in water and sediments, should be studied more deeply and systematically.

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Author contribution Haiyang Jin: methodology, validation, formal analysis, investigation, writing—original draft.

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Data availability Due to the nature of this research, participants of this study did not agree for their data to be shared publicly, so supporting data is not available.

Declarations

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