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Distribution and Ecological Risk Assessment of Pharmaceuticals and Personal Care Products in Sediments of North Canal, China

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Abstract: The pollution of water bodies by pharmaceuticals and personal care products (PPCPs) has attracted widespread concern due to their widespread use and pseudo-persistence, but their effects on sediments are less known. In this study, solid-phase extraction-high performance liquid chromatography–tandem mass spectrometry (SPE-LC/MSMS) was used to investigate the occurrence and ecological risks of five typical pharmaceuticals and personal care products (PPCPs) in thirteen key reservoirs, sluices, dams, and estuaries in the Haihe River Basin. At the same time, the PPCP exchanges of surface water, groundwater, and sediments in three typical sections were studied. Finally, the PPCP's environmental risk is evaluated through the environmental risk quotient. The results showed that the five PPCPs were tri-methoprazine (TMP), sinolamine (SMX), ibuprofen (IBU), triclosan (TCS), and caffeine (CAF). The average concentration of these PPCPs ranged from 0 to 481.19 μg/kg, with relatively high concentrations of TCS and CAF. The relationship between PPCPs in the surface sediments was analyzed to reveal correlations between SMX and TMP, CAF and IBU, CAF and TCS. The risk quotients (RQ) method was used to evaluate the ecological risk of the five detected PPCPs. The major contributors of potential environmental risks were IBU, TCS and CAF, among which all the potential environmental risks at the TCS samples were high risk. This study supplemented the research on the ecological risk of PPCPs in sediments of important reaches of the North Canal to reveal the importance of PPCP control in the North Canal and provided a scientific basis for pollution control and risk prevention of PPCPs.

Keywords: risk assessment; surface sediments; PPCPs; North Canal Basin; spatial distributions

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1. Introduction

In recent years, the existence of pharmaceuticals and personal care products (PPCPs) as emerging pollutants has become a global concern [1]. PPCPs mainly include prescription, over-the-counter, and consumer chemicals, including perfumes and sun-screen. PPCPs have been detected in various water bodies in China and residual PPCPs in the environment can lead to endocrine disorders, reduced reproductive rates, and reduced life expectancy [2,3]. Exposure to even very low concentrations of PPCPs in the environment poses potential risks to the ecosystem and human health [4–7].

Due to the continuous input of PPCPs into the aquatic environment, a large number of PPCPs have been absorbed in river sediments and have been detected in most aquatic sediments in China. Pan et al. [8] showed that the PPCP content in the sediments of the eastern half of Chaohu Lake was higher in the coastal zone than in the open zone,

and showed a decreasing trend from west to east along the main lake flow direction. Chen et al. [9] found that the PPCP pollution was more serious in the Luoma Lake Bay area, with caffeine, ofloxacin, and sulfa-methoxazole in surface sediments of Luoma Lake presenting higher ecological risks.

The binding of PPCPs to sediments affects the bioavailability and bioaccumulation of PPCPs [10,11]. At the same time, when sediments are scoured by river water, PPCPs are re-released into the water environment, causing secondary pollution [12,13]. Therefore, toxicological data and ecological risks of PPCPs in sediments may be overestimated or underestimated [14,15]. At present, studies have shown that the contribution of PPCPs in sediments to water pollution cannot be ignored.

Although PPCPs were reported in some river basins in China [16,17], there are few studies on PPCP concentrations in the North Canal sediments. Meanwhile, as one of the largest PPCP consumption areas in China and even the world, Beijing's daily sewage load is about 3.3 million tons, but the sewage treatment capacity of suburbs and urban areas is only 50% and 83%, respectively [8,18,19]. Therefore, the study of PPCP pollution, sources, and ecological risks in sediments is greatly significant for river pollution control and ecological protection. The purpose of this study is as follows: (i) to determine the content and spatial distribution of PPCPs in surface sediments in the North Canal of China; (ii) to analyze the correlation between PPCP concentration and water quality parameters in river sediments; (iii) to assess the potential risks of PPCPs in the sediment.

2. Material and Method

2.1. Study Area

North Canal is located in the north of China, with a latitude of 40°00′–40°50′ north and longitude of 115°50′–116°25′ east (Figure 1). It originates at the south foot of the Jundu Mountain in Beijing, flows through the Hebei province, before merging into the Haihe River in Tianjin. The region has a temperate monsoon climate, with hot and rainy summers, followed by cold and dry winters. The annual average rainfall is 642.5 mm, with most rainfall concentrated in June to August. The mainstream of the North Canal has a total length of 260 km, a total area of 6166 km^2, and an average annual runoff of 572 million m^3 [19]. As the main drainage channel of Beijing, the North Canal flows through densely populated and highly industrialized areas, resulting in 93% of the water source in the upper reaches of the North Canal belonging to wastewater discharged from sewage treatment plants and 4% to untreated wastewater, while the middle and lower reaches of the North Canal are affected by pesticides, fertilizers, and domestic sewage [20].

2.2. Sampling and Analysis

Sediment samples were collected from 13 typical sections of the North Canal by a rigid plexiglas tube gravity sampler in July 2016. The collected columnar sediment samples were divided into three groups by 0–20 cm, 20–40 cm, 40–60 cm and filtered through a 1 mm screen. Water samples were collected 0–50 cm from the surface using a water harvester at the same location as the sediment samples. Groundwater samples were collected from 13 monitoring wells along the north Canal river, and collected at a depth of 50 m by QED low-flow sampling equipment. Sediment river water and groundwater samples were collected and sent to the laboratory for testing. Details of the analytical procedure are provided elsewhere [13,18]. In short, all samples were stored in pre-cleaned cryogenic containers and immediately transported to the laboratory for processing. In the laboratory, the water samples were concentrated by pre-treated solid phase extraction and sediment samples were extracted by ultrasonic extraction, followed by high performance liquid chromatography–tandem mass spectrometry analysis of target antibiotics, following appropriate quality assurance and quality control procedures, usually including solvent blank procedures and independent inspection standards. Concentrations of 5 PPCPS were determined for all samples. The 5 PPCPS were classified and abbreviated as follows: sulfamethoxazole (SMX), trimethoprimethidine (TMP), caffeine (CAF), ibuprofen (IBU);

triclosan (TCS). The main physicochemical properties of the five target PPCPS are shown in Supplementary Materials Table S1. Limits of detection (limit of detection, LOD) and limits of quantification (limit of quantification, LOQ) are generally determined as the minimum detectable amount of analyte with a signal-to-noise ratio. The LOD and LOQ of each PPCPs are shown in Table S2.

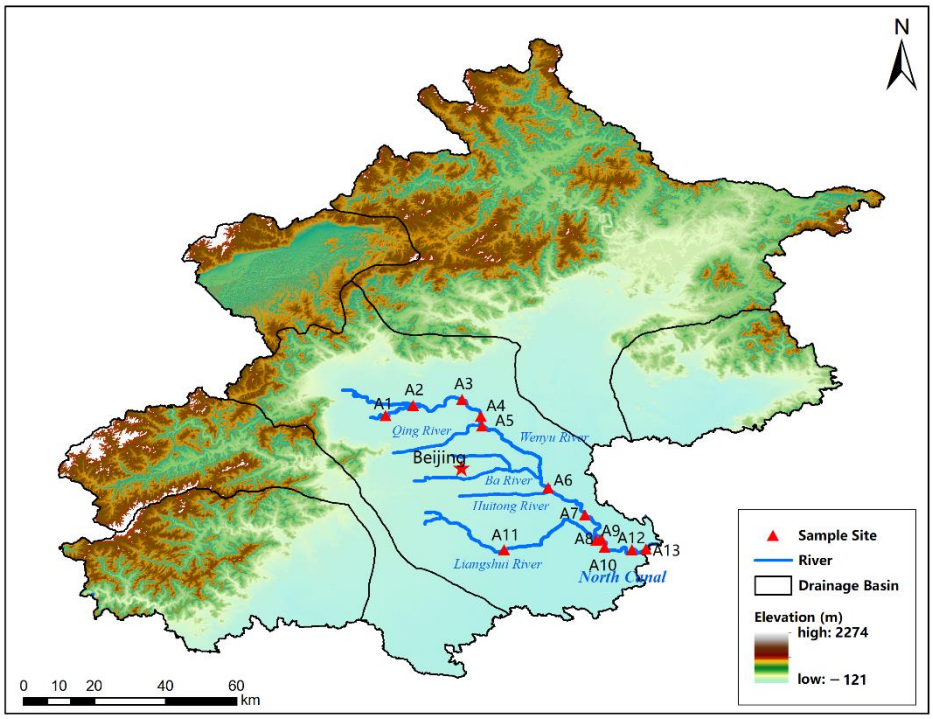

Figure 1. Schematic diagram of the study area and sampling point location.

2.3. Leaching Potential Assessment

In this study, the groundwater ubiquity score (GUS) method was used to evaluate the leaching potential of PPCPs, and the parameters were provided by the leaching potential evaluation mode [21,22]. Its calculation formula is as follows:

$$\mathrm{GUS} = \log \mathrm{t}_{\frac{1}{2}} (4 - \log \mathrm{K_{OC}}) \quad (1)$$

K_{OC} is the organic carbon-water allocation coefficient, and $t_{1/2}$ is the soil degradation half-life (days). GUS value classification criteria were as follows: low leaching potential (GUS < 1.8), medium leaching potential (1.8 ≤ GUS ≤ 2.8), and the high leaching potential (GUS > 2.8).

2.4. Ecological Risk Assessment

In this study, the environmental risk quotients (RQ) method was selected to assess the potential risk of PPCPs in sediments to aquatic organisms. This entropy is based on the risk assessment method in the European Technical Guidance document [23]. The RQ value is calculated from the measured concentration (MEC) and the predicted no-effect concentration (PNEC) by the following formula:

$$\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \quad (2)$$

$$\mathrm{PNEC} = \frac{\mathrm{EC_{50}}}{\mathrm{AF}} \text{ or } \mathrm{PNEC} = \frac{\mathrm{NOEC}}{\mathrm{AF}} \quad (3)$$

RQ represents the risk quotient calculated by EC_{50} or NOEC, and MEC represents the measured environmental concentration. PNEC is the predicted no-effect concentration,

which is the maximum concentration of a drug known to have no adverse effects on microorganisms or ecosystems in the environment. PNEC is obtained by dividing EC_{50} or NOEC by the assessment factor (AF, 1000 for acute toxicity, 100 for NOEC). The sources of EC50 and NOEC are shown in Table S3. The RQ were divided into the following four categories: RQ < 0.01 (no significant risk), 0.01 < RQ < 0.1 (low risk), 0.1 < RQ < 1 (medium risk), RQ > 1 (high risk) [23].

2.5. Pseudo-Partitioning (P-PC)

To obtain a quantitative understanding of the relationship of the antibiotics between the sediment and water phases, the pseudo-partitioning coefficient ($k_{d,s}$) was used to describe the system and was calculated according to the following equation:

$$k_{d,s} = C_s/C_w \left(L\ kg^{-1}\right) \quad (4)$$

where C_s is the concentration in the sediment, and C_w is the corresponding concentration in the water phase [24].

3. Results and Discussion

3.1. Occurrence of PPCPs in Surface Sediments

The detection results showed that the five PPCPs were detected in the North Canal. The detection rates of TMP, SMX, IBU, TCS, and CAF were 100.00%, 61.53%, 76.92%, 100.00% and 69.00%, respectively. The average concentrations were ND–1.55 μg/kg, ND–0.46 μg/kg, ND–7.47 μg/kg, 1.45–697.63 μg/kg and ND–246.59 μg/kg, respectively. The total concentration of the five PPCPs in the North Canal was 5.53–641.93 μg/kg, and the main pollutants were TCS and CAF. The proportion of the average concentration of the five PPCPs to the total concentration was TCS (65.26%), CAF (32.32%), IBU (2.25%), TMP (0.11%), SMX (0.05%), respectively. The average concentrations of TCS and CAF were the highest among the five PPCPs, which were 57.77 μg/kg and 28.618 μg/kg, 14 to 585 times higher than the other PPCPs. TCS is widely used as an antibacterial agent in a variety of soaps, different kinds of toothpaste, and health care products [25]. CAF, as a stimulant, is ubiquitous in our daily life and has been detected in waters around the world [26].

Compared to previous reports, TCS concentrations in Liuxi River and Zhujiang River sediments were lower than those in the North Canal, while TCS concentrations in Shijing River sediments were higher than those in the North Canal, and CAF concentrations in the North Canal sediments were higher than those in Baiyang Lake. Additionally, CAF concentrations in the North Canal sediments exceeded concentrations in the Songhua River. The contents of the TMP, SMX, and IBU in the sediments of the North Canal were lower than those in other regions of China (Table 1).

3.2. Spatial Variation in PPCPs in Surface Sediments

As shown in Figure 2, the five PPCPs in the North Canal showed no obvious increase or decrease in the upstream and downstream regions but fluctuated constantly from upstream to the downstream. In particular, PPCPs suddenly increased in some stations. The levels of SMX, IBU, and TCS all fluctuate at the A5 site. The A5 site is located at the confluence of the Qinghe River and Wenyu River, where there are three sewage treatment plants. The discharge of reclaimed water may affect the concentration level of PPCPs in the sediment. At the confluence points A8 and A9 of the Liangshui River and North Canal, the PPCP concentration also showed the same level of fluctuations. At the sampling points A3, A8, and A9, the distribution of CAF fluctuates more obviously than the other PPCPs. In summary, the concentration fluctuation range was large in the upstream population aggregation area, while the concentration was low in the downstream villages, towns, and the fluctuation range was small.

Table 1. Occurrence and concentration of PPCPs in sediments in different study areas (μg/kg).

Chemical	Location	Range	Reference
TMP	Nanjing	ND–1.07	Xue et al. 2013 [27]
	Taihu Lake	ND–39.3	Xu et al., 2014 [28]
	Beijing	ND–5.02	Zhang et al. 2017 [29]
	Hanjiang River	ND–10	Hu et al., 2018 [30]
	Baiyang Lake	ND–7.26	Zhang et al., 2018 [31]
	Pearl River	0.1–0.2	Xie et al., 2019 [32]
	This study	ND–1.55	
SMX	Jiulong River	1.2–3.4	Zhang et al., 2011 [33]
	Baiyang Lake	ND–7.9	Li et al., 2012 [34]
	Taihu Lake	ND–49.3	Xu et al., 2014 [28]
	Beijing	ND–0.35	Zhang et al., 2017 [29]
	Hanjiang River	ND–1.2	Hu et al., 2018 [30]
	Haihe River	1.2–2.54	Chen et al., 2018 [35]
	Pearl River	ND	Xie et al., 2019 [32]
	This study	ND–0.46	
IBU	Taihu Lake	ND–21	Xie et al., 2015 [36]
	Guangzhou	ND–3.19	Peng et al., 2017 [37]
	Songhua River	25.2–95.0	He et al., 2018 [38]
	Pearl River	ND–0.02	Xie et al., 2019 [32]
	This study	ND–7.47	
TCS	Liuxi River	ND–116	Zhao et al., 2010 [39]
	Zhujiang River	12.2–196	Zhao et al., 2010 [39]
	Shijing River	345–1329	Zhao et al., 2010 [39]
	Yangtze River	0.18–0.63	Liu et al., 2015 [40]
	Guangzhou	0.84–689	Peng et al., 2017 [37]
	Hanjiang River	0–7.73	Gao et al., 2018 [41]
	Pearl River	ND–0.1	Xie et al., 2019 [32]
	This study	1.45–697.63	
CAF	Taihu Lake	25.4–482	Zhang et al., 2016 [42]
	Chaohu Lake	1.87–3.27	Pan et al., 2016 [14]
	Beijing	ND–1.74	Zhang et al., 2017 [29]
	Songhua River	ND–63.7	He et al., 2018 [38]
	Baiyang Lake	1.37–30.51	Zhang et al., 2018 [31]
	This study	ND–246.59	

ND: not detected.

In the vertical direction, PPCPs were detected in different layers of each point. Although it is currently difficult to prove the exact rate and timing of PPCP infiltration, PPCPs in surface water may migrate vertically and laterally through hydraulic exchange between surface water and groundwater [43,44]. The downward migration of surface PPCPs contaminates sediments as a whole and increases the ecological risk level of sediments. The detection results of PPCPs in sediments show certain spatial and species differences, which are caused by the comprehensive influence of factors, such as input source differences, dilution effects, location differences, sediment properties, and drug properties. It has been reported that photodegradation greatly reduces CAF in rivers [45,46]. It can be observed that the content of PPCPs in sediments is higher than that in water bodies. Meanwhile, it is worth noting that SMX, IBU and TCS are only detected in water bodies at some sites, but not in sediments.

3.3. Pearson Correlation Analysis of PPCP Concentration and Hydrochemical Parameters in Surface Sediments

The hydrochemical parameters of river sediments from 13 stations in the Yunhe River Basin were tested (Figure 3); TP concentrations of A6, A8 and A9 were higher than those of other samples, NH_4-N concentrations of A2, A4 and A9 were higher than those of other samples, and NH_2-N concentrations of A6, A8 and A12 were slightly higher than those of other samples. The concentrations of TN, NH_3-N and OM were stable, and there was

no difference among the different stations. From the analysis of the spatial location of the stations, it can be found that the sudden change in concentration at stations A6 and A9 may be related to the intersection of the two rivers [47,48].

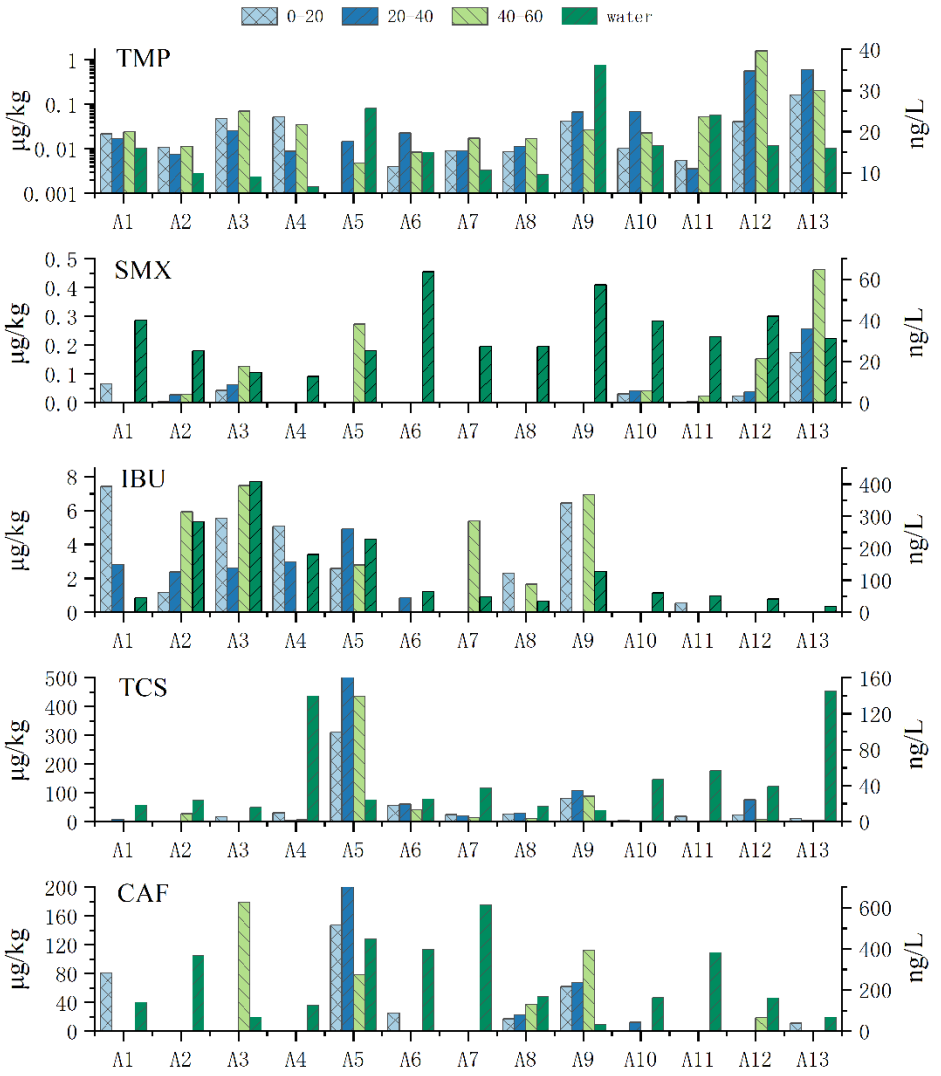

Figure 2. Spatial distribution of PPCP concentration in sediments of the North Canal.

The correlation between the PPCP concentration and hydrochemical parameters in the sediments of the North Canal Basin is shown in Figure 4. The river water quality parameters analyzed include TP (4.11–33.8 mg/kg) and TN (0.16–0.26 g/100 g), NH_4-N (0.03–0.07 mg/g), NH_2-N (0.01–0.02 mg/g), NH_3-N (0.02–0.57 mg/g), OM (113.04–131.59 g/kg). According to Pearson's correlation analysis, TCS and NH_4-N ($p < 0.05$), CAF and NH_4-N ($p < 0.01$), SMX and TMP ($p < 0.05$), CAF and IBU ($p < 0.01$), CAF and TCS ($p < 0.01$), indicating that SMX, TMP, CAF, IBU, and TCS may come from similar sources. However, the correlation coefficient between PPCPs is not high, and the similarity of its sources still needs to be further explored. Meanwhile, NH_4-N is negatively correlated with PPCPs, which may be related to the influence of inorganic conditions in sediments (NH_4-N) on the distribution of PPCPs in sediments [49].

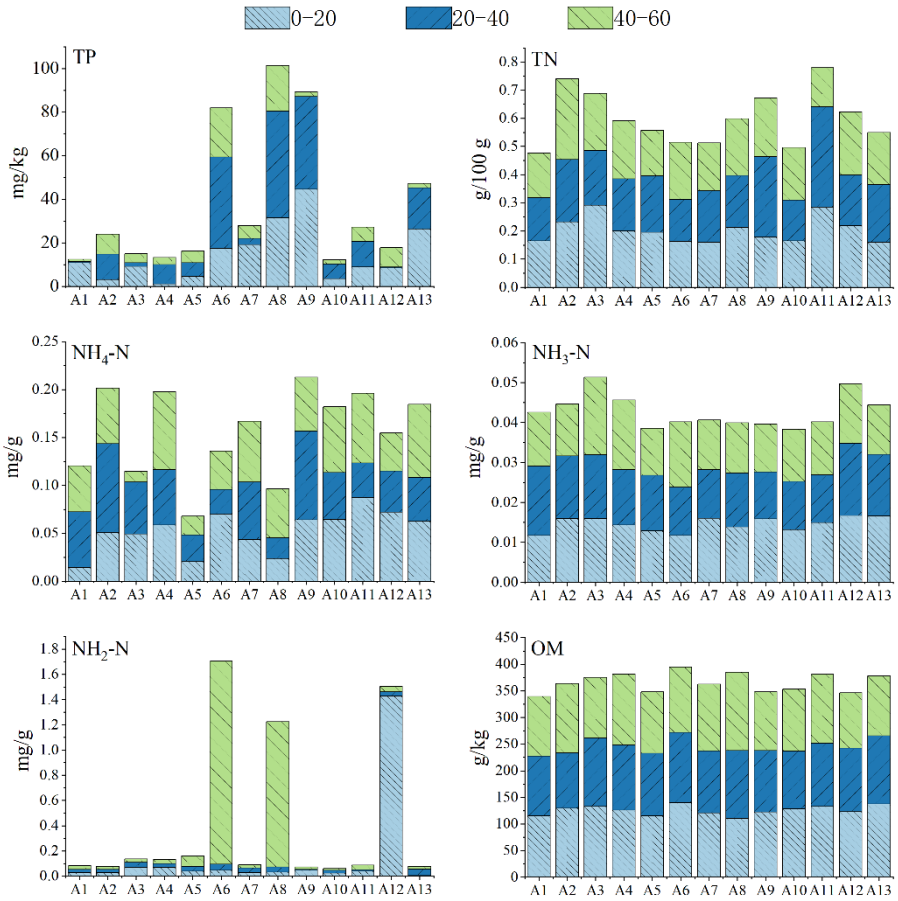

Figure 3. Basic environmental parameters in sediments of the North Canal.

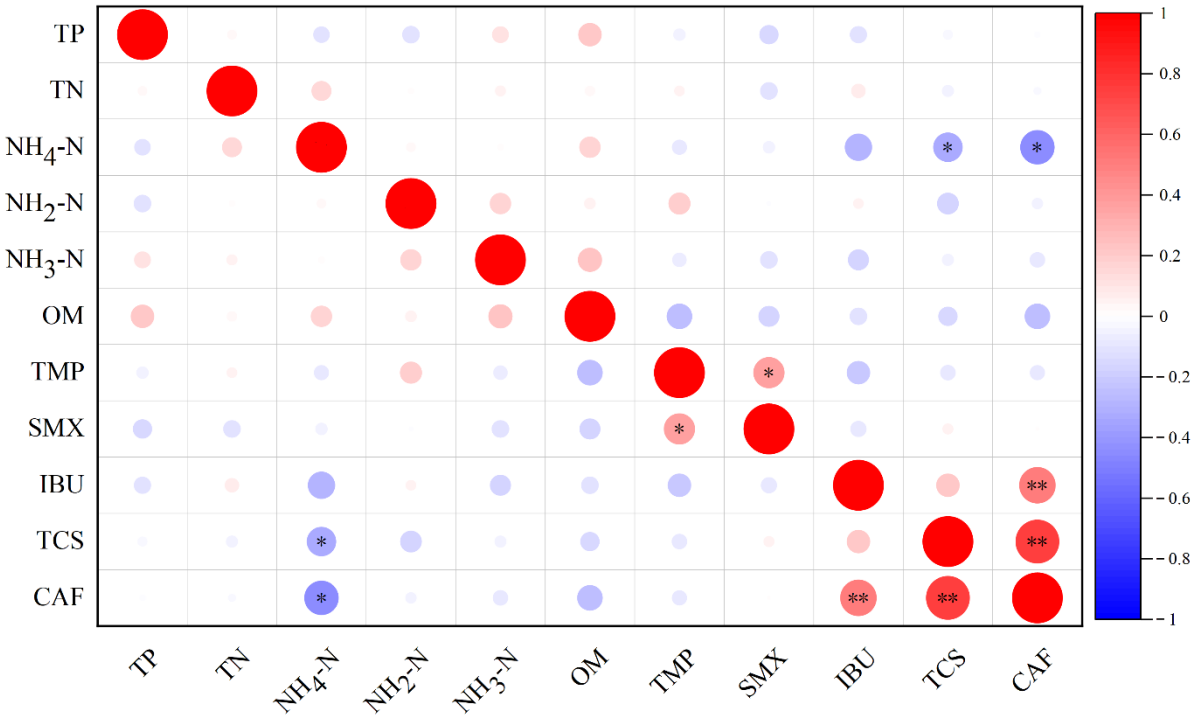

Figure 4. Pearson correlation analysis of PPCPs and environmental parameters. * Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.

3.4. The Relationship between PPCP Concentration in Surface Sediments and Water

Pseudo-partitioning is used to better understand the relationship between the solid phase and the water phase of PPCPs [50]. The P-PC value is calculated by dividing the concentration in the sampled sediment by its concentration in the water phase. It can be observed from Table 2 that the P-PC value of the TMP, SMX, IBU are at a low level, while the relative P-PC value of TCS and CAF are at a high level, indicating that it is easier for TCS and CAF to accumulate in the North Canal sediments.

Table 2. Pseudo-partitioning of 5 PPCPs in the North Canal.

Site	TMP	SMX	IBU	TCS	CAF
A1	1.21	1.12	14.58	ND	22.69
A2	1.13	1.17	20.99	11.46×10^2	ND
A3	7.64	8.52	18.30	74.50	26.02×10^2
A4	5.34	ND	ND	45.38	ND
A5	0.18	10.76	12.20	18.01×10^3	17.40×10
A6	0.56	ND	ND	16.67×10^2	ND
A7	1.60	ND	11.44×10	34.93×10	ND
A8	0.47	ND	12.91	80.59×10	11.59×10^2
A9	2.71	ND	20.18×10	51.08×10^2	66.5×10
A10	1.36	1.06	ND	7.31	ND
A11	2.22	1.78	ND	7.39	ND
A12	93.74	3.66	ND	18.96×10	11.58×10
A13	12.49	14.80	ND	29.10	ND

ND: not detected.

The leaching capacity of the five PPCPs was shown in Table 3, among which CAF was the most easily leaching due to its high $T_{1/2}$ and low Koc, followed by SMX. TMP and IBU have medium leaching capacity, and TCS has low leaching potential. Infiltration is mainly affected by adsorption and decreases with the increase in PPCP adsorption. The GUS value of PPCPs can better predict the risk of PPCP pollution to groundwater. Although TCS has a low GUS value, it has a relatively high concentration in the surface sediments, which may be related to its extensive and massive use and discharge. Therefore, more attention should be paid to the risk of groundwater pollution. Although the concentration of CAF in surface sediments is lower than that of TCS, its risk of groundwater pollution cannot be ignored because of its strong permeability [22].

Table 3. The $\log T_{1/2}$, $\log K_{oc}$ and GUS of PPCPs in sediment.

Name	log $T_{1/2}$	logK_{OC}	GUS	Leaching Potential
TMP	1.89	2.857	2.16	Middle
SMX	1.88	2.412	2.98	High
IBU	1.48	2.626	2.03	Middle
TCS	2.08	4.369	−0.77	Low
CAF	1.48	1	4.43	High

Although the PPCP migration rule between surface water sediment and groundwater cannot be analyzed as a typical seasonal river, the hydraulic connection between river water and groundwater is mainly that surface water supplies groundwater [51]. According to the P-PC and GUS values, river sediments are the key channel for PPCPs in river water to enter groundwater. PPCPs in the river water will accumulate in sediments first and then spread further into groundwater through the three typical sections in Table 4.

Table 4. Concentrations of PPCPs in three media in typical sections.

Site	Type	TMP	SMX	IBU	TCS	CAF
A12	surface water (ng/L)	0.45	10.02	176.79	133.67	304.02
	sediment (0–20) (μg/kg)	0.04	0.02	0.00	22.64	0.00
	sediment (20–40) (μg/kg)	0.55	0.04	0.00	75.75	0.00
	sediment (40–60) (μg/kg)	1.56	0.15	0.00	7.41	18.73
	groundwater (ng/L)	0.17	7.32	189.07	6.49	612.30
A10	surface water (ng/L)	0.64	14.10	172.18	171.16	280.75
	sediment (0–20) (μg/kg)	0.01	0.03	0.00	2.83	0.00
	sediment (20–40) (μg/kg)	0.07	0.04	0.00	1.16	12.04
	sediment (40–60) (μg/kg)	0.02	0.04	0.00	0.34	0.00
	groundwater (ng/L)	0.01	0.74	144.70	13.05	170.67
A3	surface water (ng/L)	0.12	4.49	369.06	79.13	444.68
	sediment (0–20) (μg/kg)	0.05	0.04	5.54	16.63	0.00
	sediment (20–40) (μg/kg)	0.03	0.06	2.62	0.74	0.00
	sediment (40–60) (μg/kg)	0.07	0.13	7.48	1.18	178.51
	groundwater (ng/L)	ND	ND	10.93	2.67	153.37

Compared with the concentration of sediment, it can be observed that part of the PPCPs are enriched in the sediment during the infiltration of surface water, except IBU, into groundwater. Therefore, PPCPs in sediment have the risk of water diffusion to groundwater, and is a key indicator affecting the ecological risk to water environments [52–54].

3.5. Environmental Risks of PPCPs in Surface Sediments

To evaluate the possible environmental risks caused by five PPCPs in the water sediments of the North Canal, the potential environmental risks of PPCPs in the sediments of thirteen sampling points in the North Canal basin were evaluated by the RQ values. RQ values corresponding to TMP, SMX, IBU, TCS, and CAF are in the range of 0.02 to 2.47, 0 to 1.03, 0 to 2.52 × 10, 4.63 to 1.24 × 10^3, and 0 to 5.07 × 10^2, respectively (Figure 5).

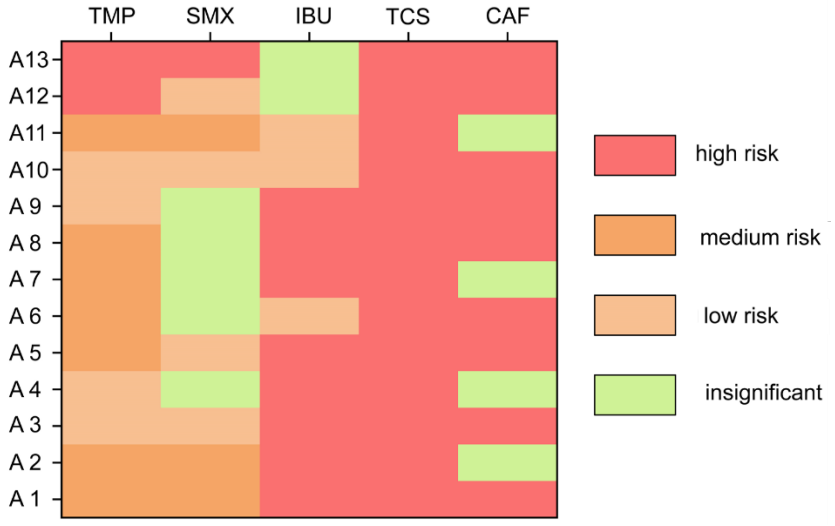

Figure 5. Ecological risks of PPCPs in the sediment samples of the North Canal Basin.

TMP and SMX are at medium and low risk upstream, TMP is at a high risk at A12 and A13, and SMX is at high risk at A13. IBU, CAF, and TCS are highly toxic to the surface sediments in the study area and are the main potential ecological risk factors for the surface sediments in the study area. IBU, TCS, and CAF are the main contributors to the potential environmental risks of the five PPCPs in the North Canal, and the potential environmental risks of the TCS samples are all high risks. The potential ecological risks of TCS and CAF

of A5 and A9 are extremely high. At the same time, the combined effect of multiple PPCPs may further increase the level of ecological risk, and the impact and persecution of the aquatic environment cannot be ignored.

PPCPs in most areas pose a threat to the ecosystem and may have adverse effects on aquatic organisms [52]; therefore, it is worth paying attention to the control and elimination of PPCPs in sediments. It is difficult to completely remove PPCPs in sediments of urban rivers, and their accumulation in sediments will affect the survival and reproduction of benthic animals as recently reported; CAF is a psychoactive compound with high ecotoxicological relevance in many other natural water domains. TCS has been shown to produce cytotoxic genotoxicity and endocrine disruptor effects, while TCS in the environment can increase bacterial resistance at the same time. PPCPs in sediments will further spread into groundwater, thus threatening the safety of drinking water. For example, IBU entering the body for a long time will lead to renal failure [22,34].

4. Conclusions

As an important tributary of the Haihe River system, the North Canal flows through the most densely populated area with the highest urbanization intensity in China and plays a major role in urban drainage and landscape greening. With the development of the regional economy and society and the need for water environment protection, the ecological risk caused by PPCP pollution is widely concerning.

In this study, the distribution and migration of five PPCPs in sediments of the North Canal were investigated, and the ecological risk of PPCPs was evaluated by using environmental risk quotients. The relationship between sediment PPCPs and the river ecological environment was analyzed from the perspective of aquatic organisms. According to the analysis results, the concentrations of trimethopretin (TMP), sinolamine (SMX), and ibuprofen (IBU) in the sediments of the North Canal were low, while the concentrations of triclosan (TCS) and caffeine (CAF) were relatively high, and TCS and CAF have been enriched in some reaches. IBU, TCS, and CAF in the sediments have high ecological risk levels, which may affect the survival of regional organisms. Therefore, the existence of new pollutants, such as PPCPs, should not be ignored in order to maintain the stability of the river ecosystem. This paper has practical guiding significance for river water quality management and integrated river management.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14131999/s1, Table S1: Physiochemical properties of the antibiotics considered in the study; Table S2: Limit of detection (LOD) and limit of quantification (LOQ) for the the target compounds; Table S3: Toxicity data used to derivate the predicted no effect concentrations (PNECs) in this study. Bold is the lowest NOEC. References [55–67] are cited in the supplementary material.

Author Contributions: S.P., methodology, data curation and software; B.L., conceptualization, formal analysis and supervision; B.W., methodology and supervision; J.L., data curation and software; X.S., data curation. All authors have read and agreed to the published version of the manuscript.

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