Spatiotemporal distributions and ecological risk assessment of pharmaceuticals and personal care products in groundwater in North China

Jin Wu, Jingchao Liu, Zenghui Pan, Boxin Wang and Dasheng Zhang

ABSTRACT

The contamination of surface water by pharmaceuticals and personal care products (PPCPs) has attracted widespread attention, but data regarding their impacts on groundwater (GW) are sparse. In river–GW interaction areas, rivers are likely an important source of PPCPs in aquifers, especially rivers impacted by sewage treatment plant effluent. Understanding the characterization, transport, and risk is valuable for the effective protection of vital aquatic ecosystem services, environmental health, and drinking water supplies. To attain this objective, statistics with spatial analysis and ecological risk were used to assess the effects of artificial recharge (AR) engineering on 16 PPCPs in aquifers in North China. The results indicated that 15 PPCPs were detected in unconfined and confined aquifers, with a few PPCPs being detected up to 1,000 ng/L. The most frequently detected PPCPs were sulfisoxazole, sulfachloropyridazine, sulfamerazine, sulfamethazine, sulfamethoxazole, and ibuprofen. In addition, the spatial and seasonal variations in most PPCPs were significant. Furthermore, the maximum concentrations were compared to the predicted no-effect concentrations to evaluate the ecological risk, and four PPCPs were found to be of medium or high ecological risk. This study highlights that AR engineering has a significant ecological effect on GW.

Key words | ecological risk, groundwater, PPCPs, river–groundwater interaction, spatiotemporal distributions

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INTRODUCTION

China is one of the largest producers and consumers of pharmaceuticals and personal care products (PPCPs) (Liu & Wong 2013; Hanna *et al.* 2018). Due to widespread consumption and inefficient treatment, using PPCPs has put pressure on the environment, resulting in drinking water resources in China being threatened (Thomas *et al.* 2017; Wang *et al.* 2019a). Approximately 92,700 tons of antibiotics were consumed in 2013 in China, and approximately 46% of the antibiotics were ultimately released into rivers through sewage effluent (Zhang *et al.* 2015). PPCPs have been detected in surface water (SW), groundwater (GW), sediment, soil, and vegetables around China, some of which are considered environmentally pseudopersistent with continuous discharge (Kostich *et al.* 2014; Peng *et al.* 2014; Wang *et al.* 2015; Zhang *et al.* 2017). Significant attention is being paid to the presence of PPCP residues in the environment due to their potential adverse effects on ecosystems and human health. Specifically, studies have shown that mixtures of PPCPs exhibit greater effects than those of the individual compounds (Cleuvers 2004; Jiang *et al.* 2014;

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Brandt *et al.* 2015). It is anticipated that environmental legislation will be widened to cover a range of PPCPs. However, the knowledge of their fate within water cycles is still insufficient.

GW maintains flows and levels in rivers and lakes, is essential for the health of GW-dependent ecosystems, and is regarded as the most important source of drinking water in many parts of the world (Barnes *et al.* 2008; Lapworth *et al.* 2012). The riparian zone adjacent to rivers is often an important area for residents in China, where the interactions between rivers and GW are active (Fang *et al.* 2018; Aa *et al.* 2019). The subsurface geochemistry in the riparian zone is changed greatly due to either the leakage of river water to recharge the underlying GW or vice versa (Yang *et al.* 2015; Zhang *et al.* 2019). Increasing evidence shows that rivers are one of the main sources of PPCPs in riverside GW (Kuroda *et al.* 2012; Yang *et al.* 2017a). Artificial recharge (AR) is considered a promising method to alleviate GW depletion by using reclaimed water, particularly in arid areas (Grünheid *et al.* 2005; Li *et al.* 2014; Singh *et al.* 2017; Zheng *et al.* 2018). The PPCPs in rivers can enter GW aquifers through the process of GW–SW exchange (i.e., via bank filtration or AR) (Buerge *et al.* 2009; Dougherty *et al.* 2010; Petrie *et al.* 2015). For example, Einsiedl *et al.* (2010) studied the transport of pharmaceuticals in karst GW systems affected by wastewater treatment. Díaz-Cruz & Barceló (2008) reviewed PPCPs in different source waters used for artificial aquifer recharge purposes. In view of risk management and control, the ecological impact of AR engineering on GW quality needs more attention since previous studies regarding ecological effects are sparse.

The ecological effect of PPCPs in GW, as well as their relationship with environmental factors, is as yet poorly understood compared to those of SW. Previously, the detection frequency and the ecological risk index have been widely employed to describe the spatiotemporal characteristics of PPCPs in rivers and lakes (Sun *et al.* 2016; Yang *et al.* 2017b; Hanna *et al.* 2018; Bexfield *et al.* 2019). Since more PPCPs are likely to have GW threshold values in the coming decades, more data related to occurrence and ecological effects are required. Moreover, studies seldom discuss PPCPs in unconfined and confined aquifers simultaneously recharged by reclaimed water. Among these GW–SW exchange areas with sewage effluent discharge, the infiltration of sewage by artificial aquifer recharge and bank filtration is expected to be the main source of PPCPs in unconfined aquifers (Teijon *et al.* 2010; Yang *et al.* 2016). However, such infiltration processes are not expected to impact unconfined aquifers and deteriorate GW quality. A few works have investigated the occurrence of PPCPs in confined aquifers, examining the selected PPCPs (diethyltoluamide, crotamiton, ethenzamide, propyphenazone, carbamazepine, and caffeine) in confined aquifers (up to 500 m in depth) in Tokyo due to leakage from decrepit sewer networks (Kuroda *et al.* 2012). Generally, the GW in unconfined aquifers is used as a drinking water source in North China and is considered a key factor for the steady development of the national economy (Bo *et al.* 2003; Li *et al.* 2016). Therefore, in developing management strategies to control GW pollution by PPCPs, the contamination and ecological risk of PPCPs in unconfined and confined aquifers both need to be assessed.

Considering the issues raised above, the objectives of this study were to investigate the occurrence of PPCPs in different types of aquifers, including unconfined and confined aquifers, and to characterize the ecological risk for the development of resistance to PPCPs in the GW as well as to optimize the management of GW recharging.

MATERIALS AND METHODS

Study area

The studied river–GW interaction (RGI) area is located in North China (Figure 1). The area is characterized by hot, humid summers and generally cold, windy, dry winters. Its annual temperature is ~11.5 °C, and the average precipitation is ~600 mm/a. AR engineering is using reclaimed water which is produced by a membrane bioreactor with wastewater treatment plant effluent. Then the reclaimed water, about 38,000,000 m^3/a, is introduced to the river. Besides, some water containing treated and untreated municipal water from nearby factories and villages also flows into the river. The GW near the released reclaimed water area is only recharged by reclaimed water in the wet season. The mean concentrations of NH^{4+}, total nitrogen, and total phosphorus in reclaimed water were 4.30, 10.64,

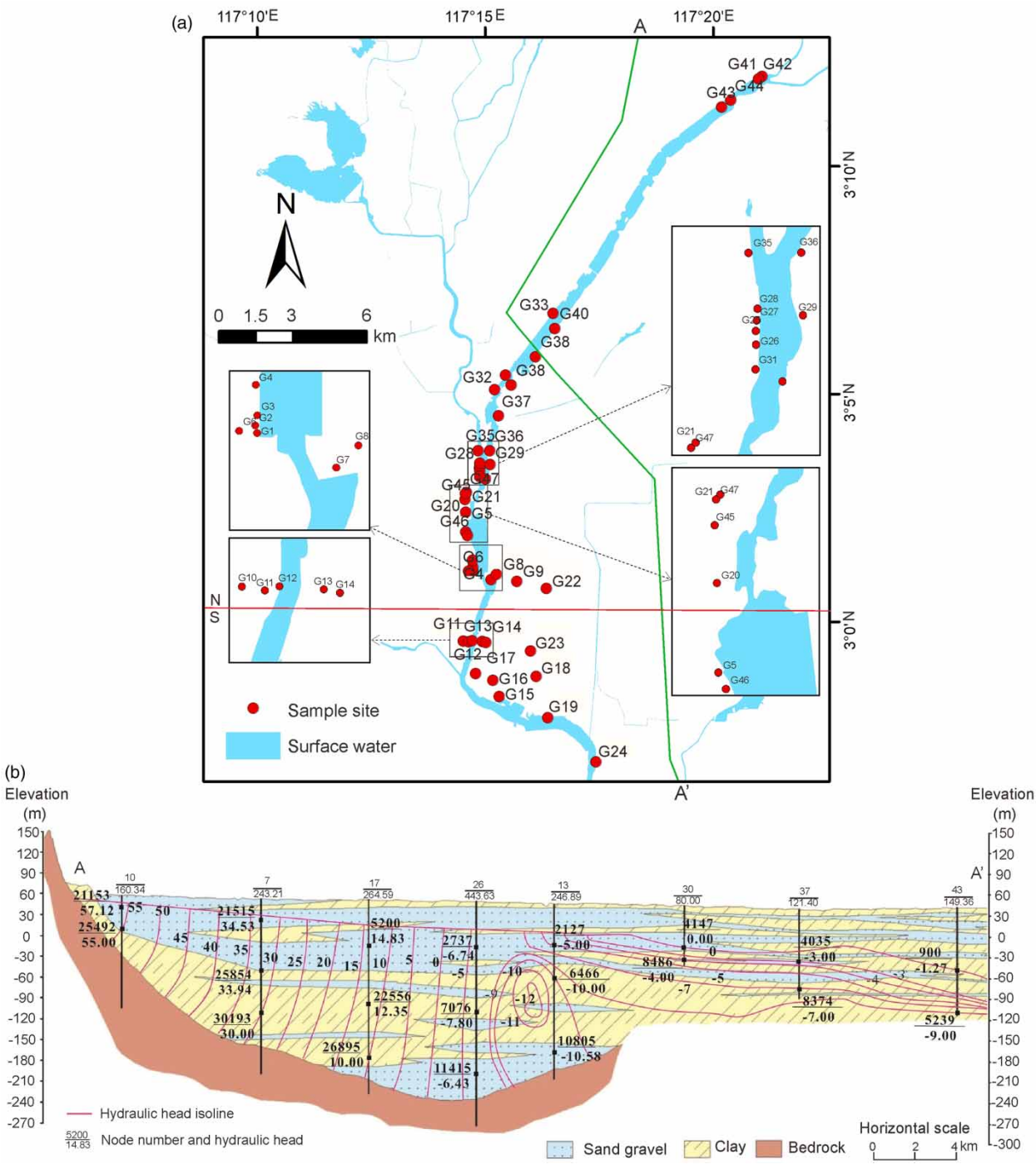

Figure 1 | GW sampling locations (a) and hydrogeological cross-sections of the study area (b).

and 0.78 mg/L, which indicate bad water quality. While other water quality parameters ranged from medial to good quality according to the data analysis of 43 holes collected in 2013 (Figure 1). The quaternary sediments in the study area are widely distributed in plains and mountain valleys. The characteristics of the sedimentary layers are: north thin south thick and east thin west thick. The hydrogeological characteristics in the study area are that the

depth of buried bedrock increases from north to south, the thickness of the quaternary strata is between 50 and 300 m, and gradually increases from northeast to southwest. The lithology changes from coarse particles to fine particles, and the layers change from a single layer to multiple layers. The quaternary strata mainly include a sand pebble layer, a sand gravel layer, and a silty clay layer.

Two subzones of the study area were identified, including the northern part (N zone) and southern part (S zone), based on the hydrogeological conditions. The N zone of the study area was dominated by gravel and sand with good permeability, while the S zone consisted of silty clay with poor permeability. The lithology of the aquifer changed from sandy gravel to fine sand from north to south. The shallow aquifer in the N zone is an unconfined aquifer (UA-N). However, there are multiple layers of aquifers in the S zone with an unconfined aquifer (UA-S), first confined aquifer (FCA-S), and second confined aquifer (SCA-S). The thicknesses of UA-N and UA-S ranged between 0–30 and 0–80 m, respectively. The thicknesses of FCA-S and SCA-S ranged between 30–50 and 50–80 m, respectively.

Sampling and analysis

GW samples were collected from 47 monitoring wells of riverside sections by the QED low-flow sampling equipment (Sample Pro™ sampling pump) in May 2016 (summer, wet season) and December 2016 (winter, dry season) (Figure 1). Twenty-four samples were collected in the N zone to represent the NS aquifer with the sampling depths at 50 m, and 20 samples were collected in the S zone to represent the UA-S, FCA-S, and SCA-S aquifers with the sampling depths at 30, 50, and 80 m, respectively. Detailed information about the analysis procedure was provided elsewhere (Sui *et al.* 2011; Yang *et al.* 2017b; Chen *et al.* 2018). In short, GW samples were pumped into 2 L glass bottles using a stainless-steel submersible pump. All samples were kept in precleaned containers at a cool temperature and then immediately transported to the laboratory for treatment. In the laboratory, the water samples were commonly concentrated by preconditioned solid-phase extraction. The target antibiotics were subsequently analyzed using high/ultra/ultrahigh-performance liquid chromatography–tandem mass spectrometry. Appropriate quality assurance and quality control procedures were followed, usually including solvent blank, procedure blank, and independent check standard. Method detection limits (limits of detection, LODs) and quantification limits (limits of quantification, LOQs) were generally determined as the minimum detectable amount of an analyte with a signal-to-noise ratio. Recoveries obtained by spiking the analytes into GW ranged from 65 to 128%. The LOQs were 0.2–6 ng/L for pharmaceuticals in GW. The concentrations of 16 PPCPs were determined for all GW samples. Sixteen PPCPs were classed and abbreviated as follows: enrofloxacin (EFX), erythromycin (ETM), sulfamonomethoxine (SMM), sulfathiazole (STZ), N4-acetyl-sulfamethoxazol (N4AcSMX), sulfisoxazole (SFS), sulfachloropyridazine (SCP), sulfamerazine (SMR), sulfamethazine (SMZ), sulfamethoxazole (SMX), trimethoprim (TMP), caffeine (CAF), chloramphenicol (CAP), ibuprofen (IBU), triclosan (TCS), and difloxacin (DIF). The main physicochemical properties of the 16 target PPCPs are shown in the Supplementary material, Table S1.

Leaching potential assessment

Leaching potential assessment models were adopted to assess the leaching potential of the selected PPCPs in the vadose zone. The model provides a quantitative value for representing the leaching potential. The model is described by Equation (1) by considering both the mobility and the persistence of chemicals.

$$\mathrm{GUS} = \log t_{1/2}(4 - \log K_{\mathrm{OC}}) \tag{1}$$

where GUS is the groundwater ubiquity score, K_{OC} is the organic carbon partition coefficient, and $t_{1/2}$ is the degradation half-life in the soil (days). The adjusted criteria were as follows: low leaching potential ($\mathrm{GUS} \leq 1.8$), moderate leaching potential ($1.8 < \mathrm{GUS} \leq 2.8$), and high leaching potential ($2.8 \leq \mathrm{GUS}$).

Ecological risk assessment

The ecological risk assessment has been used to quantify the ecological effect exposed by environmental pollutants in previous studies. In this study, risk quotients (RQs) were

applied to assess the ecological risk of PPCPs in GW; a high RQ suggests a high ecological risk and vice versa. The RQs for each PPCP in the GW sample were calculated with the following equation:

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

where MEC is the measured concentration, and PNEC is the predicted no-effect concentration. In this study, the chronic or acute toxicity data of the target antibiotics were collected from previous studies (Supplementary material, Table S2). The PNEC was obtained from the lowest no observed effect concentration (NOEC) with bold marks in Table S2. According to the recommendations of the European technical guidance document (TGD), NOECs were priority toxicity data (EC 2003). Three levels of ecological risks were classified: between 0.01 and 0.1 is low risk; between 0.1 and 1 is medium risk; and larger than 1 is high risk.

Statistical analysis

Statistical tests were performed to identify major factors that likely affect the occurrence and contribution of PPCPs in GW. Most results for individual PPCPs were non-detections in this study, and the datasets do not conform to any distribution. Therefore, nonparametric statistical methods were used to perform hypothesis testing. A paired samples *t*-test was conducted to compare the temporal differences between different seasons. Independent sample tests were conducted to compare the spatial differences between two zones and among different aquifers. Statistical analyses were performed with SPSS Statistics V20.0 (SPSS, Inc. Quarry Bay, HK). The *p*-value used to indicate statistical significance for all tests was 0.05.

RESULTS AND DISCUSSION

Overview of PPCPs in GW

The frequency of detection and the maximum concentrations of the PPCPs in aquifers are summarized in Table 1. All the PPCPs were detected at least once in the whole area, except for EFX. Six PPCPs need priority attention, including IBU, SMX, SMZ, SMR, SFS, and SCP, whose frequencies of detection are higher than 50% in each sampling season. This result was consistent with a previous study in which sulfonamides were the most extensively detected PPCPs in adjacent watersheds (Zou *et al.* 2011). However, sulfonamides in other countries, such as France, Germany, and Korea, had relatively lower concerns regarding GW (Supplementary material, Table S3). This phenomenon can be explained by the different use patterns of PPCPs between countries. In China, sulfonamides are extensively used in poultry and aquaculture because of their low price (Chen *et al.* 2018). The maximum concentrations of each PPCP ranged from below the detectable limit to 1,186 ng/L, spanning several orders of magnitude. Only TCS in FCA-S in the dry season had a peak concentration of >1,000 ng/L. Large variations in PPCP concentrations in this study may be attributed to variations in residence time and attenuation processes, such as dilution, adsorption to aquifer material, and degradation. Therefore, the physicochemical properties of PPCPs also affect the migration and transformation in aquifers. By comparison with other counties, the maximum concentration of PPCPs was at a relatively high level in a global context (Table S3).

Temporal and spatial variations in PPCPs in GW

Temporal variations in PPCPs

The type of PPCP detection frequency can be categorized into three classes. The CAF is different from other PPCPs with a higher detection frequency in the dry season (Table 1). For ETM, SMM, SCP, SMR, SMX, CAP, IBU, and DIF, the detection frequencies in different aquifers were all higher in the wet season. For STZ, N4AcSMX, SFS, SMZ, TMP, and TCS, the highest detection frequencies in different aquifers were different. For instance, STZ had a high detection frequency in the dry season in the N zone and a high detection frequency in the wet season in the S zone. IBU was the most abundant PPCP in the GW in both the dry and wet seasons for the whole study area, indicating that GW pollution by IBU was not a sporadic but continuous event. Figure 2 shows the mean concentrations

Table 1 | Maximum concentration (MC, ng/L) and frequency of detection (FD, %) of PPCPs in the dry and wet season in different aquifers of RGI

	UA-N				UA-S				FCA-S				SCA-S			
	Dry		Wet		Dry		Wet		Dry		Wet		Dry		Wet	
PPCPs	MC	FD	MC	FD	MC	FD	MC	FD	MC	FD	MC	FD	MC	FD	MC	FD
EFX	BLD	0.0	BLD	0.0	BLD	0.0	BLD	0.0	BLD	0.0	BLD	0.0	BLD	0.0	BLD	0.0
ETM	1.55	6.3	1.71	73.3	BLD	0.0	0.37	5.0	BLD	0.0	0.74	13.6	BLD	0.0	BLD	0.0
SMM	3.43	43.8	12.39	73.3	7.83	40.0	3.53	60.0	10.77	9.5	12.92	90.9	4.24	54.5	9.32	71.4
STZ	3.86	68.8	2.24	50.0	2.28	60.0	54.40	85.0	3.64	38.1	23.67	90.9	4.39	36.4	12.57	71.4
N4AcSMX	22.73	25.0	51.69	73.3	77.74	85.0	15.58	35.0	48.81	33.3	35.96	36.4	56.06	63.6	4.37	28.6
SFS	1.51	50.0	16.73	73.3	255.07	80.0	3.16	70.0	155.34	57.1	21.29	95.5	144.04	72.7	2.93	76.2
SCP	3.25	56.3	6.76	73.3	6.77	55.0	2.71	80.0	4.45	52.4	5.13	90.9	12.40	68.2	2.48	76.2
SMR	2.49	62.5	0.69	73.3	2.19	55.0	1.74	65.0	2.89	52.4	1.03	86.4	2.31	59.1	0.66	66.7
SMZ	0.49	56.3	0.83	73.3	56.47	95.0	19.50	95.0	12.57	76.2	9.49	86.4	8.58	95.5	33.44	81.0
SMX	19.29	100.0	11.01	100.0	54.19	75.0	8.12	65.0	15.36	95.2	7.45	81.8	20.56	77.3	15.08	71.4
TMP	1.03	81.3	3.23	100.0	0.54	95.0	0.23	45.0	0.86	90.5	0.64	50.0	4.89	100.0	2.01	52.4
CAF	782.62	56.3	461.87	26.7	249.29	5.0	BLD	0.0	398.51	19.0	BLD	0.0	235.52	4.5	BLD	0.0
CAP	0.55	43.8	0.16	66.7	9.66	60.0	1.07	95.0	9.23	47.6	1.01	95.5	8.37	22.7	0.48	85.7
IBU	24.50	100.0	42.99	100.0	30.92	90.0	34.35	100.0	64.21	95.2	23.19	95.5	190.14	77.3	7.91	90.5
TCS	18.05	25.0	109.90	26.7	5.19	5.0	BLD	0.0	1,186.38	19.0	BLD	0.0	10.81	4.5	BLD	0.0
DIF	BLD	0.0	22.05	73.3	BLD	0.0	BLD	0.0	BLD	0.0	5.59	13.6	BLD	0.0	BLD	0.0
Average FD	55.33	48.4	46.52	66.0	47.38	50.0	9.05	50.0	119.56	42.9	9.26	58.0	43.89	46.0	5.70	48.2

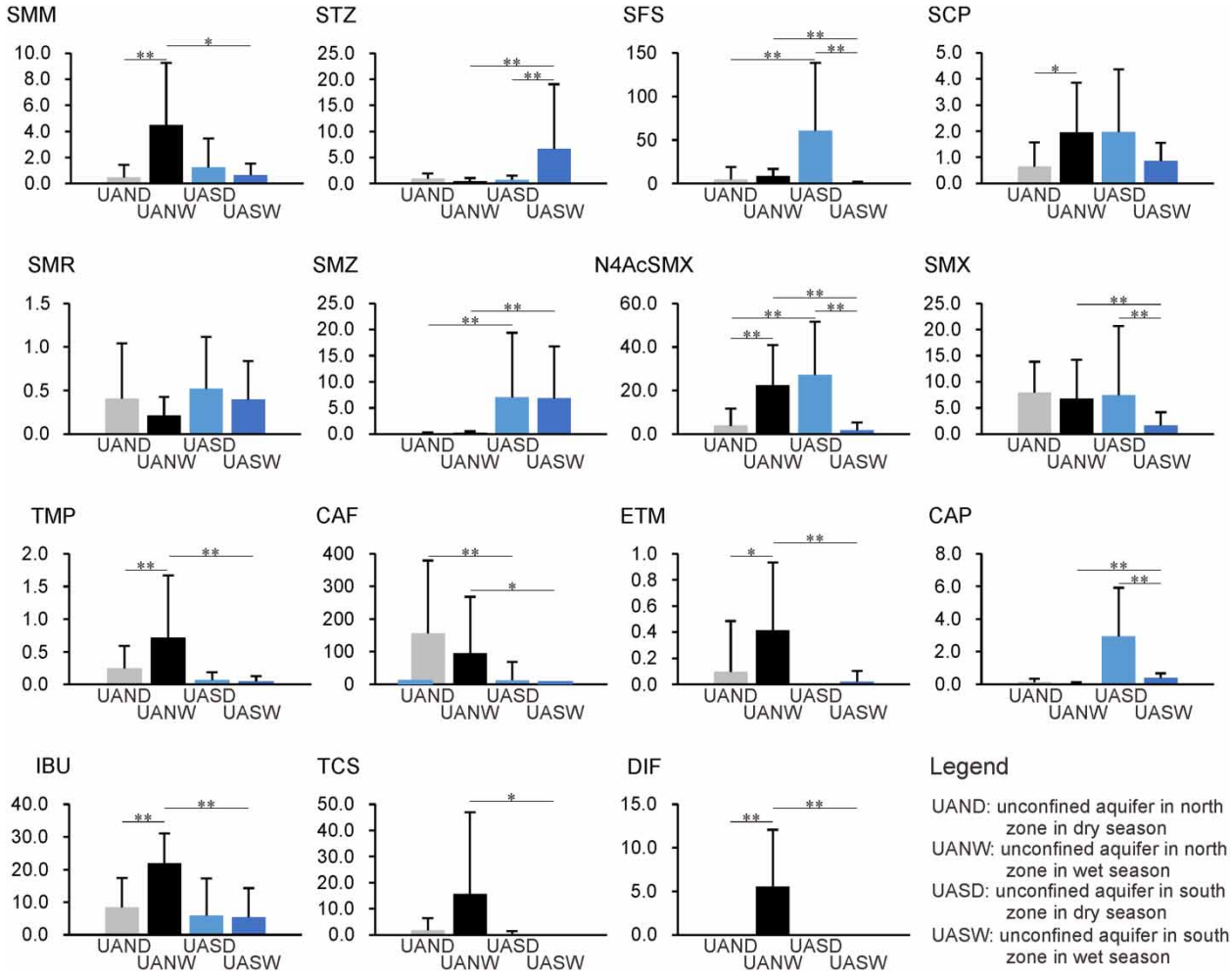

Figure 2 | The mean concentration of the PPCPs in the unconfined aquifer (N and S zones) in different seasons. The concentration of EFX is not listed due to no available data. Bar graphs mean ± standard deviation (paired *t*-test, $*P < 0.05$; $**P < 0.01$).

for the PPCPs in the unconfined aquifer in different seasons. The mean concentrations of SMM, STZ, SCP, N4AcSMX, TMP, ETM, IBU, and DIF in the N zone or the S zone were significantly higher in the wet season than those in the dry season. For SFS, N4AcSMX, SMX, and CAP, the mean concentrations were significantly lower in the wet season. Figure 3 shows the spatial distribution of the cumulative concentration of PPCPs in GW in the RGI area. From the viewpoint of total concentration, PPCPs concentrations in most sites were higher in the dry season than those in the wet season. The higher occurrence of PPCPs in the dry season (winter) was in accordance with previous studies (Sun *et al.* 2016).

Previous studies have shown that many factors influence the seasonal variations in PPCPs in aquatic environments, such as the consumption pattern, physicochemical properties, and the flow conditions of rivers (Sun *et al.* 2016; Wang *et al.* 2019b). Some PPCPs have seasonal uses, indicating that their influent load will vary throughout the year. It is anticipated that high consumption of some PPCPs in the wet season will lead to high occurrence and concentration in rivers containing sewage. However, in the dry season, some factors will reduce the attenuation rate of PPCPs in rivers, such as lower runoff, decreased river flow rate, slower photolysis, thermal degradation, and biodegradation in the cold season. As a result, the PPCPs in GW are directly

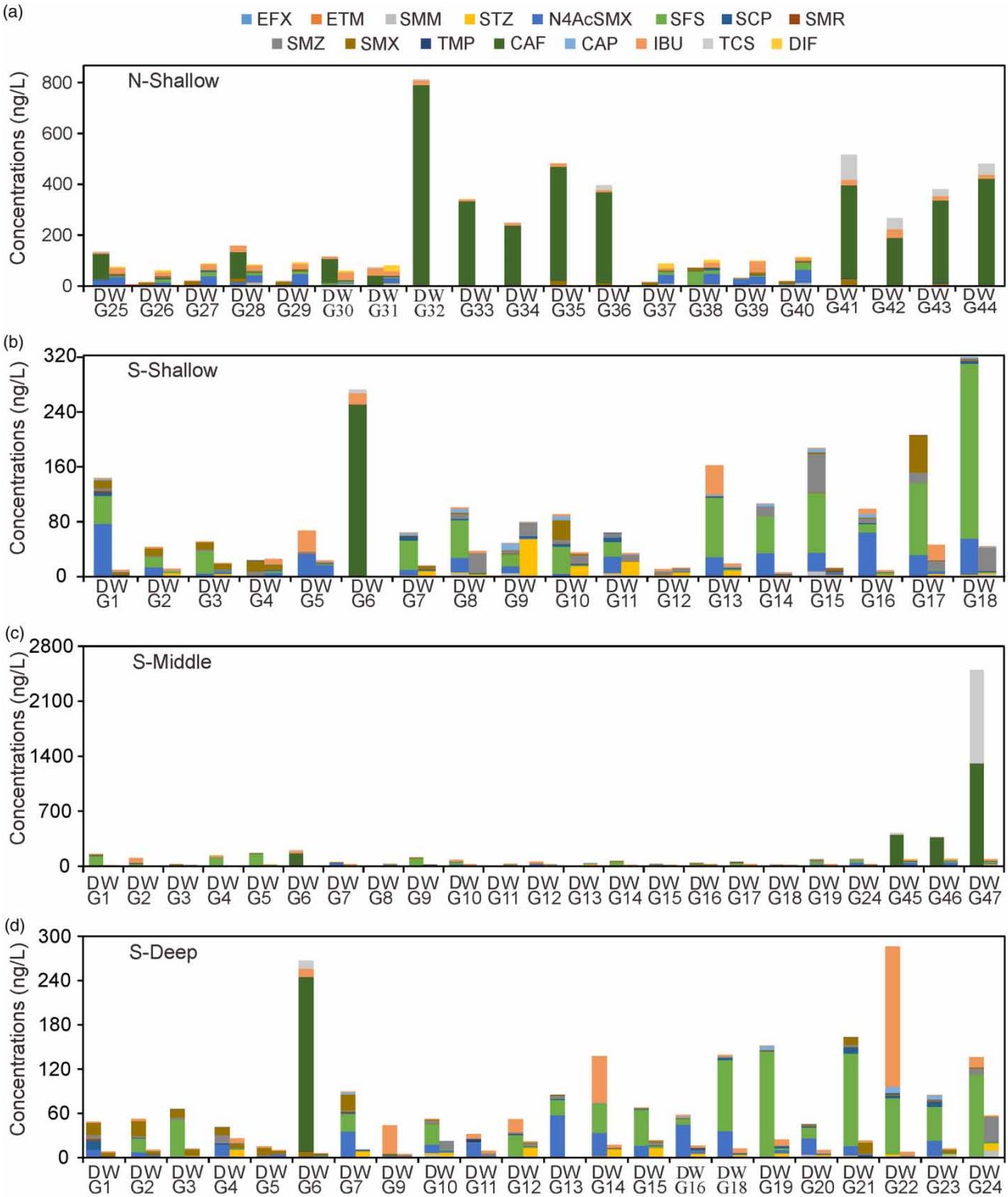

Figure 3 | The distribution of PPCPs in GW in the RGI area.

and/or indirectly affected by the PPCPs in rivers. Therefore, the seasonal variation in PPCPs in aquifers in the RGI area was affected by multiple factors simultaneously. Monitoring PPCPs at least twice a year (dry season/wet season) is essential to obtain representative sample data to reflect the dynamics of the seasonal change.

Spatial variations in PPCPs in different subzones

In general, PPCP concentrations decreased from upstream (N zone) to downstream (S zone) (Figure 3). In the dry season, the mean concentration of CAF in the unconfined aquifer in the N zone was significantly higher than that in the S zone. In the wet season, the mean concentrations of SMM, TMP, IBU, CAF, TCS, N4AcSMX, ETM, DIF, and SMX were significantly higher in the N zone than those in the S zone. It is obvious that the dominant component in the N zone is CAF. In the S zone, SFS, IBU, and CAF were all abundant. CAF is known to be labile and has been suggested as a highly sensitive indicator of immediate contamination by sewage. The high CAF levels in the northern part were probably due to the high burden of sewage in the river water. The high concentrations of SFS and IBU in the southern part may be attributed to effluent from treated/untreated wastewater.

As shown in Table 2, most of the targeted PPCPs appeared to have high leaching potential. Among the high leaching potential group, EFX, SMM, and CAF were most likely to leach because of their high $t_{1/2}$ and low K_{OC}. TMP and IBU had moderate potential for leaching. TCS would be the compound most resistant to leaching. It is noted that due to relatively small chemical inputs, the targeted PPCPs are not expected to remain in the vadose zone for a long time. The different patterns of the 15 PPCPs in the two subzones indicated that other factors would affect the occurrence in addition to the dilution of river flow due to precipitation. Dilution from sewage, degradation within the upstream sewer, rainfall, sampling mode, and pollution source characterization all contribute to this variability.

Table 2 | The log$t_{1/2}$, logK_{oc}, and GUS of PPCPs in soils

Name	log$t_{1/2}$	logK_{OC}	GUS	Leaching potential
EFX	2.56	1.174	7.22	High
ETM	2.56	2.754	3.19	High
SMM	1.88	1.678	4.35	High
STZ	1.88	2.207	3.36	High
SMR	1.88	2.076	3.61	High
SMZ	1.88	2.282	3.22	High
SMX	1.88	2.412	2.98	High
TMP	1.89	2.857	2.16	Middle
CAF	1.48	1	4.43	High
IBU	1.48	2.626	2.03	Middle
TCS	2,880	4.369	−0.77	Low
DIF	2.56	2.743	3.21	High

Spatial variations in PPCPs in different aquifers

Because information on confined aquifers in the northern part was not available, spatial variations in the PPCPs in different aquifers were analyzed in the southern part. As shown in Table 1, PPCPs in the dry season were more frequently detected in unconfined aquifers (50% for average frequency) than in the first confined aquifers (42% for average frequency in confined aquifers) and in the second confined aquifers (46% for average frequency). With regard to PPCPs in the wet season, the average frequency of detection in the second confined aquifers (48%) was lower than that in the unconfined aquifers (50%). For PPCPs in the first confined aquifers, the average frequency of detection (58%) was higher than that in the unconfined aquifers (50%). Figure 4 shows the mean concentrations of PPCPs in the confined aquifer in different seasons. Generally, PPCPs in confined aquifers have seldom been investigated, possibly because they were supposed to be protected from pollution by the vadose zone and the upper confining bed. However, it can be seen that the mean concentrations of some PPCPs in the two confined aquifers were relatively higher than those in the unconfined aquifer, suggesting insignificant attenuation effects by the upper confining bed.

For many PPCPs, there may be multiple pathways into the GW, and difficulties in understanding these processes are compounded by the paucity of information compared to that for SW. The environmental behavior of PPCPs in aquifers depends not only on the specific hydrogeochemical conditions (Wang *et al.* 2019b) but also on the physicochemical properties of the PPCPs in the GW system (Koh *et al.*

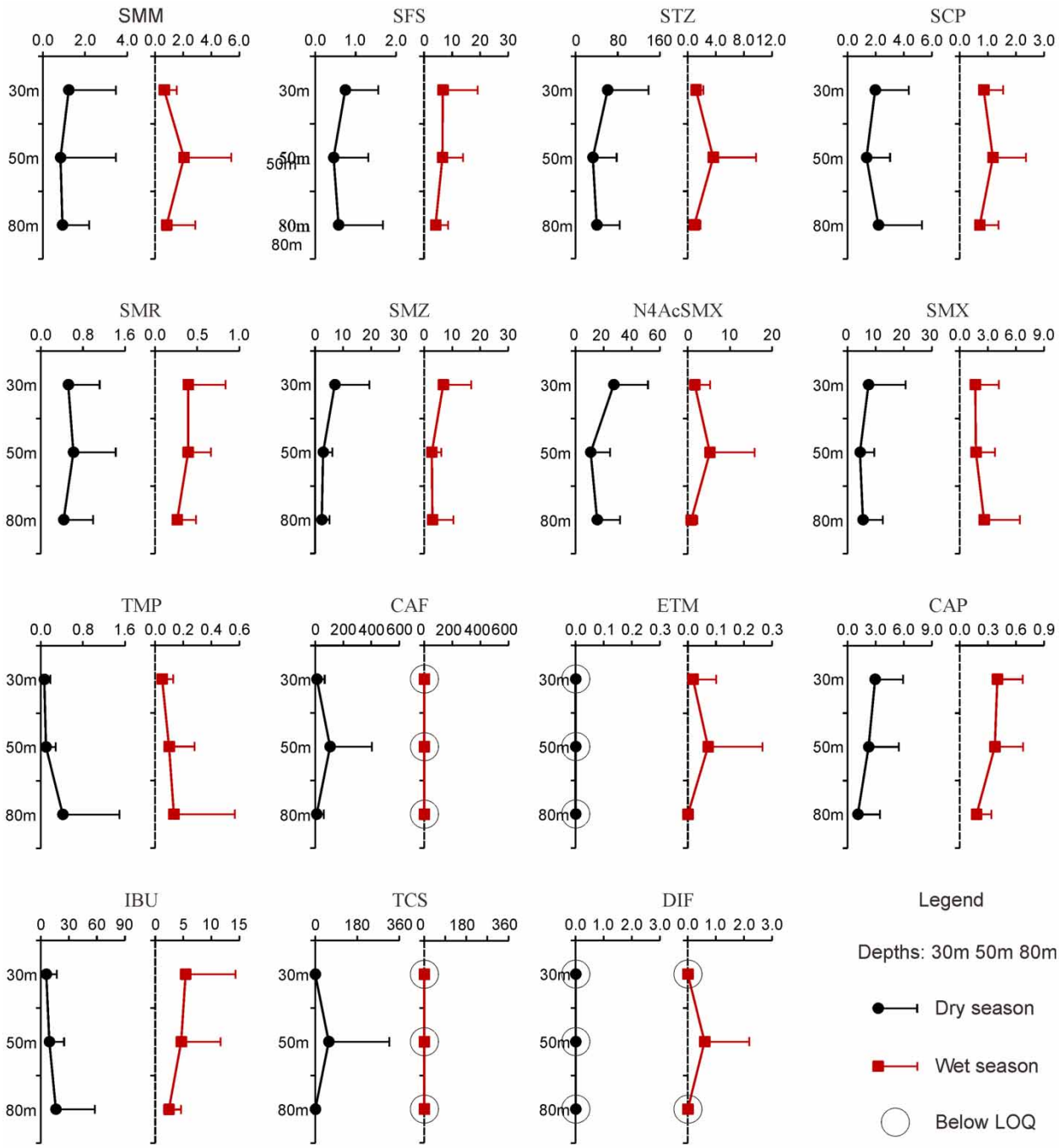

Figure 4 | The mean concentration of the PPCPs in aquifers (S zone) in different seasons. The concentration of EFX is not listed due to no available data. Mean contribution to each heavy metal concentration from each source.

2009). One explanation for the phenomenon of PPCPs in two confined GW samples is that those aquifers are considered to be recharged from the upper aquifers. Another reason involves contamination by unconfined GW via defects in the well casing or via the backfilling sand around the well casing, driven by the difference in the potential of aquifers. The GW was recharged by the river flows deeper than 80 m in the area of the studied well.

Ecological risk of PPCPs

The highest concentration and lowest PNEC were simultaneously used as a worst-case scenario assuming ecological risk. Due to the lack of predictive toxicity data on the chronic effects of SMM N4AcSMX and DIF, their RQs were ignored. As shown in Table 3, eight PPCPs were detected in aquifers at low-risk levels. The ecosystem risks of SFS, CAF, IBU, and TCS were found to be at least middle risk by using a RQ. Similar to the concentration of PPCPs, the potential ecological risks also exhibited spatial and seasonal variations to some extent. Overall, the potential ecological risks posed by PPCPs to GW could be a serious issue. The results of this study indicated that PPCPs in GW in the RGI area also need to be monitored for regulation and control by legislation due to their wide distribution and significant adverse ecological effects.

From the perspective of ecological risk, SFS, CAF, IBU, and TCS can be viewed as priority PPCPs because of middle or high ecological risk. These results indicated that AR was a source of PPCPs in GW, particularly in GW with short residence times, and poses a threat to ecological systems. In addition, another GW–SW exchange engineering method, river bank filtration, has been proved to be an important, effective, and inexpensive technique for SW purification due to filtration, adsorption, and biodegradation (Munz *et al.* 2019; Wang *et al.* 2019c). However, these processes are insufficient to reduce the ecological risk of all PPCPs to below the high or medium level in these areas. These priority PPCPs should be given special attention to be strictly regulated during GW recharging.

CONCLUSIONS

With increasing artificial sewage recharge activities in the past several years, the detection frequencies and concentration levels of PPCPs in aquifers in North China were generally higher than those reported in global GW. As a whole, IBU, SMX, SMZ, SMR, SFS, and SCP were widely detected in aquifers. The seasonal dynamics of some PPCPs showed statistically significant changes. Significant spatial variations in PPCPs in different subzones and in different aquifers were also found. However, the reasons for the spatiotemporal variation were supposed to be complex and most likely caused by the combination of specific hydrogeochemical conditions and the physicochemical properties of the PPCPs in the GW system. Risk assessment revealed that four antibiotics (DIF, IBU, CAF, and SFS) posed at least a medium risk in GW under the worst scenarios. Finally, eight PPCPs (IBU, SMX, SMZ, SMR, SFS, SCP, CAF, and TCS) were identified as priority control antibiotics in the RGI area in North China.

Table 3 | The ecological risk value of PPCPs in the dry and wet season in different aquifers of RGI

	UA-N		UA-S		FCA-S		SCA-S	
PPCPs	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
ETM	7.75×10^{-4}	8.55×10^{-4}	NA	1.85×10^{-4}	NA	3.7×10^{-4}	NA	NA
STZ	3.86×10^{-4}	2.24×10^{-4}	2.28×10^{-4}	5.44×10^{-3}	3.64×10^{-4}	2.37×10^{-3}	4.39×10^{-4}	1.25×10^{-3}
SFS	2.44×10^{-3}	2.7×10^{-4}	4.1×10^{-1}	5.1×10^{-3}	2.5×10^{-1}	3.4×10^{-2}	2.3×10^{-1}	4.73×10^{-3}
SCP	1.31×10^{-3}	2.72×10^{-3}	2.73×10^{-3}	1.09×10^{-3}	1.8×10^{-3}	2.07×10^{-3}	5×10^{-3}	1×10^{-3}
SMR	3.66×10^{-3}	1.02×10^{-3}	3.22×10^{-3}	2.56×10^{-3}	4.25×10^{-3}	1.52×10^{-3}	3.4×10^{-3}	9.7×10^{-4}
SMZ	1.64×10^{-6}	2.77×10^{-6}	1.88×10^{-4}	6.5×10^{-5}	4.19×10^{-5}	3.16×10^{-5}	2.86×10^{-5}	1.11×10^{-4}
SMX	2.05×10^{-3}	1.17×10^{-3}	5.77×10^{-3}	8.63×10^{-4}	1.63×10^{-3}	7.93×10^{-4}	2.19×10^{-3}	1.61×10^{-3}
TMP	3.55×10^{-3}	1.12×10^{-2}	1.85×10^{-3}	8.09×10^{-4}	2.96×10^{-3}	2.19×10^{-3}	1.69×10^{-2}	6.92×10^{-3}
CAF	78.26×10	46.18×10	24.93×10	NA	39.85×10	NA	23.55×10	NA
CAP	7.4×10^{-9}	2.17×10^{-9}	1.3×10^{-7}	1.45×10^{-8}	1.25×10^{-7}	1.37×10^{-8}	1.13×10^{-7}	6.44×10^{-9}
IBU	2.45×10	4.3×10	3.09×10	3.43×10	6.42×10	2.32×10	19.01×10	7.9×10^{-1}
TCS	9.02×10^{-2}	5.5×10^{-1}	2.59×10^{-2}	NA	5.93×10	NA	5.4×10^{-2}	NA

Despite the uncertainties associated with sampling, geology, hydrology, and environment and parameters, the results obtained from this study are valuable. The environmental risk of PPCPs in GW recharged by river water has been questioned due to dilution, filtration, and degradation. However, the concentration and associated ecological risk indicate a significant threat by PPCPs to the RGI area, particularly to riverbank organisms. This work will help us gain insights into the contamination and monitoring of PPCPs in a GW–river interactive system and provide a basis to propose an appropriate mitigation strategy for PPCP management in similar watersheds around the world. Further studies should focus on the influencing factors of PPCPs during SW and GW exchange processes.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/nh.2020.001.

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