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Distribution Characteristics and Ecological Risk Assessment of Pharmaceutical and Personal Care Products (PPCPs) in Different Water Sources, Soil Profiles and Rice Crops Under Rural Domestic Reclaimed Water Irrigations

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Abstract: Pharmaceutical and personal care products (PPCPs) have the characteristics of environmental persistence, bioaccumulation, and high toxicity, and their environmental behavior has attracted the attention in the process of sewage resource utilization in recent years. In this study, four kinds of irrigation water sources (the primary treated water of rural domestic sewage (RDS) R1, the secondary treated water of RDS R2, the ecological pond purified water R3 and river water (CK) and three kinds of water level regulations (low-, medium- and high-water level regulation of W1, W2, and W3) were set to study the migration law of 22 kinds of PPCPs in rural domestic reclaimed water (RDRW), paddy soil and rice plants. Five rice plant and soil samples were, respectively, taken from each treatment using the five-point sampling method in this study. The samples were pretreated using the solid-phase extraction (SPE) method. After pretreatment, PPCPs were quantitatively analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The objective of the research was to explore the distribution patterns in soil-crop system, further evaluating the ecological risks of PPCPs in soil and rice plants under the regulation of RDRW irrigation. The results showed that 21 kinds of PPCPs were detected in RDRW and CK, among which the concentration of ofloxacin (OFL) was the highest. Fifteen kinds of PPCPs were detected in paddy soil and rice grain, among which atenolol (ATE) content was relatively higher. Compared with CK, the total content of PPCPs in the soil surface layer (0–20 cm) was the highest under RDRW irrigation. The impacts of different water level regulations on the PPCPs content between soil profile and rice grain were not significant. In addition, the reduction rate of 15 PPCPs in soil under RDRW irrigation was greater than 85%, and the bio-concentration factor (BCF) of PPCPs in rice grain was less than 0.1. The ecological risk assessment showed that ibuprofen (IBU) was a high-risk substance pollutant, triclocarban (TRIC) was a medium-risk pollutant, ofloxacin (OFL) was a low-risk pollutant, while the other PPCPs were all risk-free pollutants under RDRW irrigation. Therefore, R3 water sources can be selected for direct agricultural irrigation, while direct irrigation of R1 and R2 water sources should be avoided.

Keywords: rural domestic reclaimed water irrigation; soil; rice grains; PPCPs; ecological risk

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1. Introduction

With the continually decrease in water resource in China, agricultural water consumption accounts for 60% of the total water resource [1]. Agricultural irrigation water is severely insufficient, and water conservation and high-efficient water utilization in agriculture are becoming more urgent. Meanwhile, with the rapid development of China's economy, rural residents lack awareness of water conservation, and also the sewage treatment technology is outdated, leading to the production of a large amount of domestic sewage in rural areas and serious pollution of the ecological environment [2]. With the background mentioned above, the reuse of rural domestic sewage (RDS) has attracted attention of scholars at home and abroad. Compared with urban sewage, RDS has the characteristics of smaller water quality differences, higher N and P contents [3], and good biodegradability, and therefore it can be used as a fertilizer resource. Therefore, rural domestic reclaimed water (RDRW) can be safely treated for agricultural irrigation, which can effectively reduce the amount of fresh water for agricultural irrigation as well as reduce the discharge of agricultural non-point source pollution. RDRW irrigation is an effective way to alleviate the contradiction between agricultural production and resources and environmental constraints.

As an irrigation water source, recycled water contains abundant nutrients that promote the growth and reproduction of rhizosphere microorganisms, accelerate the cycling and flow of nutrients in the root layer, and make the soil microecological environment more conducive to microbial reproduction and plant growth [4]. Cirelli et al. [5] found that long-term irrigation with recycled water significantly increased soil microbial activity. However, there are also studies indicating that the excessive increase in nutrients in soil caused by reclaimed water irrigation can have a negative impact on microbial communities [6,7]. Wu et al. [8] found that the total abundance of bacteria increased by 16% after irrigation with reclaimed water but had no significant effect on the total abundance of archaea ($p > 0.05$). Huang et al. [9] found through studying the impact of reclaimed water on the ecological community of rhizosphere soil bacteria that with the increase in disturbance intensity of reclaimed water, the richness, evenness, and diversity of rhizosphere bacterial communities showed a decreasing trend.

Pharmaceuticals and personal care products (PPCPs) have become a hot environmental issue due to their frequent detection in various environmental media [10], and effluent from sewage treatment plants is considered to be the main way for PPCPs to enter the water environment. At present, sewage treatment plants mainly remove suspended solids, COD, nitrogen, and phosphorus in sewage, and generally have no ability to remove PPCPs efficiently, resulting in high concentrations of PPCPs in their effluent [11,12]. Previous studies have shown that PPCPs will enter soil, crops, and even groundwater systems through reclaimed water irrigation [13], which not only leads to soil environmental degradation, crop yield, and quality reduction, but also affects the ecological health of the water environment [14,15]. At present, researches on the migration and accumulation behavior of PPCPs in the environment have been limited to laboratory simulations, and mostly for single environments such as water, soil, and crops, and the crop types are mainly vegetable cash crops, while less involved in food crops. Meanwhile, sewage water sources are mainly for urban sewage and lack of the information on the reuse of RDS, which makes it difficult to assess and control the ecological environmental risk. In our preliminary research, it was found that under the irrigation of RDRW, the ability of soil to absorb heavy metals was enhanced, but the enrichment ability of heavy metals in the soil-crop system was not significantly affected, and the ecological environment risk was shown as a slight level [16]. Therefore, if the impact of PPCPs in RDRW on soil-crop systems and ecological risks is also relatively small, it can be considered to replace river water for irrigation.

Therefore, this study took rice as the research object and adopted the field comparative experiment to clarify the migration and cumulative effect of PPCPs in the system of RDRW, paddy soil, and rice crops under RDRW irrigation regulations. The research objectives were (1) to study the distribution of PPCPs in RDRW, soil profile and rice grain under RDRW irrigations, (2) to calculate the reduction rate of PPCPs in soil and the bioconcentration factor (BCF) of PPCPs in rice grains, elucidating the migration mechanism of PPCPs in soil and crops under RDRW irrigations, (3) to evaluate the ecological risk of PPCPs to aquatic organisms and determine the risk level of pollutants. This study could provide a scientific basis for selecting appropriate irrigation methods for the pollution prevention and control of PPCPs under the regulations of RDRW irrigation.

2. Materials and Methods

2.1. Experimental Site

The experiment was conducted in the experimental area of Zhoushan Village, Yongkang City, Zhejiang Province (120°10′E, 28°48′N) from June to November in 2021. The location of the study area is shown in Figure 1 [16]. The experimental study area belongs to a low mountain and hilly area with a sandy loam soil texture. The annual rainfall distribution in the area is uneven, with an average annual precipitation of 1787 mm, a maximum annual precipitation of 2386 mm, and a minimum annual precipitation of 1120 mm. The annual average evaporation is 930 mm, the annual average temperature is 17.5 °C, the annual maximum temperature is 39.9 °C, the annual minimum temperature is −14.5 °C, the annual average sunshine is 1909 h, the annual average wind speed is 2.8 m/s, and the frost-free period is 245 days. There were 36 rice standard experimental plots (20 m × 5 m) with three replications, using pipeline irrigation. As the sewage source for this study, a RDS treatment station with a design scale of 400 m3/d was built in the experimental area of pipeline water transmission irrigation. The treatment process adopted the secondary biological treatment process (primary treatment was conventional process and secondary treatment adopted anaerobic fermentation (A/O) with substrate biological filtration technology), and the effluent quality met the class I A standard in the Discharge Standard of Pollutants for Urban Sewage Treatment Plants [17]. At the same time, an ecological pond with a storage capacity of 3000 m^3 was built to store and purify the secondary effluent of RDS regeneration water.

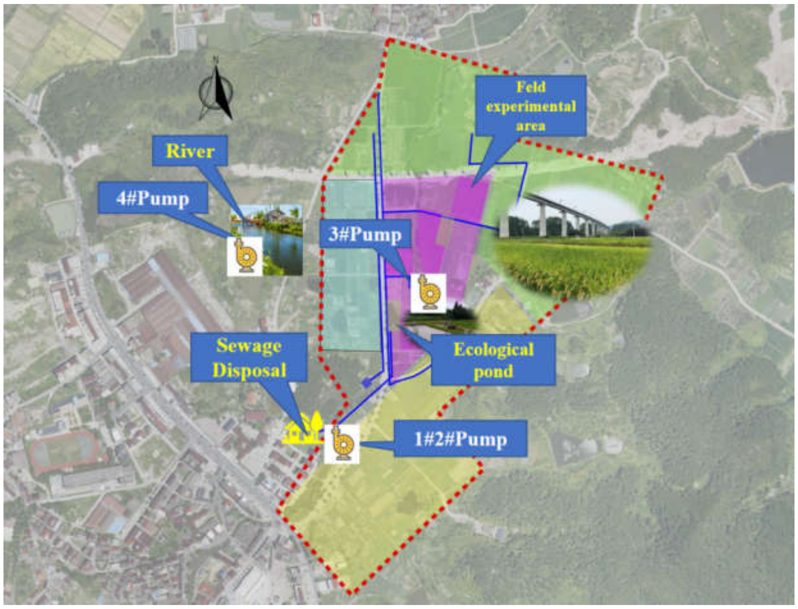


Figure 1. The location of the research area (Zhousan County, Zhoushan Village).

2.2. Experimental Design

In this study, the rice variety tested was Jiayou Zhongke 13-1, and the transplanting density was 10 plants/m2. Four kinds of irrigation water sources were set up, namely the primary treated water of RDS R1, the secondary treated water of RDS R2, the ecological pond purified water R3, and the river water CK, which were lifted and irrigated by four simple submersible pumps, and all indexes met the Standards for Irrigation Water Quality [18]. Three kinds of water level regulation were set up, namely low-water level regulation W1 (0~80 mm), medium-water level regulation W2 (0~100 mm), and high-water level regulation W3 (0~150 mm). Standard of water level regulations of controlled irrigation and drainage in paddy field are shown in Table 1, and the fertilization method was based on local fertilization habits, using base fertilizer and topdressing. Each irrigation water source and water level regulation were designed for three repetitions, with a total of 36 test treatments. The layout of the experimental area is shown in Figure 2.

Table 1. Standard of water level regulations of controlled irrigation and drainage in paddy field. (mm).

Water Control	Upper and Lower Limit	TG	ET	LT	JB	HF	MK
W1	Upper limit of sewage	0	3–5 days exposing field	1–2 days exposing field	1–2 days exposing field	1–2 days exposing field	3–5 days exposing field
	Lower limit of sewage	30	30	exposing field	40	40	30
	Upper limit of storage	50	70		80	80	60
W2	Upper limit of sewage	0	10	10	10	10	10
	Lower limit of sewage	30	50	exposing field	50	50	50
	Upper limit of storage	50	70		100	100	100
W3	Upper limit of sewage	0	40	40	40	40	10
	Lower limit of sewage	30	60	exposing field	60	60	60
	Upper limit of storage	50	100		150	150	100

Notes: [1] The values of the upper and lower limit were water depth maintained by farmland, which means that water depth could be no more than the upper limit and less than the lower limit. The field water level regulation was controlled strictly at each growth period. When the water level dropped to the lower limit, water was supplemented immediately, while it will be drained when heavy rain exceeded the upper limit of rain storage. The core of regulation is to give full play to the flooding resistance of rice, increasing the upper limit of irrigation to increase the consumption of reclaimed water, and increasing the upper limit of rain storage (sewage) to reduce discharge of rainfall and reclaimed water. [2] TG, ET, LT, JB, HF, and MK, respectively, represented turning green, early tillering, later tillering, jointing-booting, heading-flowering and milky of rice growth stages. [3]

In all, 1–2 days and 3–5 days exposing field indicated 1 mm and 2 mm cracks in the paddy field after exposing field.

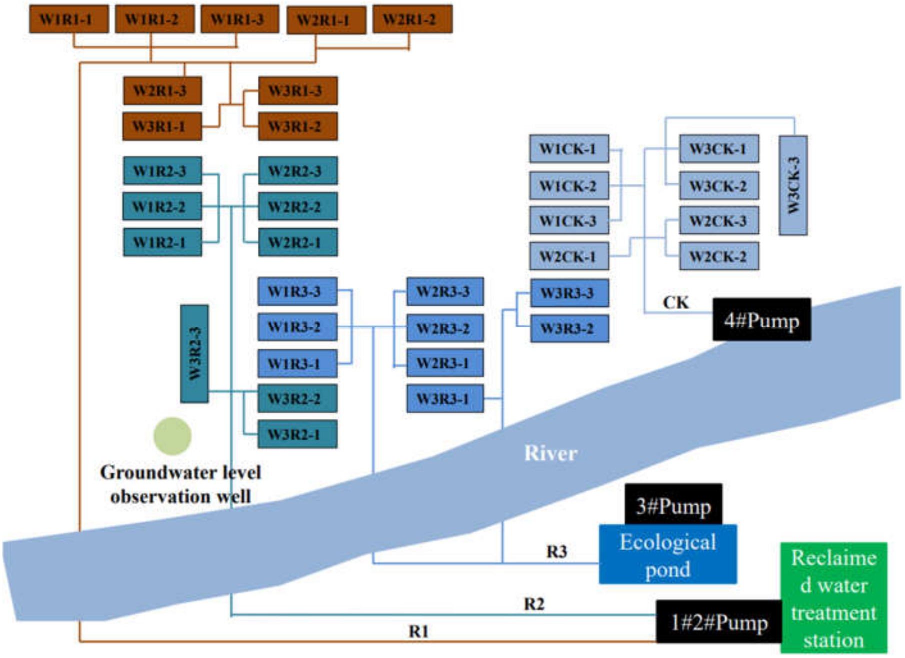


Figure 2. The layout of the experimental area (W represented different water levels, and R and CK represented different water sources).

2.3. Sampling Method

Five rice plant and soil samples were taken, respectively, from each treatment using the five-point sampling method in this study. From June to November in 2021–2022, 500 mL of effluent samples from four irrigation water sources was collected during each growth period of rice, amounting to a total of 40 irrigation water samples, and the water samples were packed into brown glass bottles and pretreated on the same day. After the end of the rice growth period, 1 m2 rice samples were collected from each plot, amounting to a total of 72 rice samples, and the rice samples were rinsed with ultrapure water for 5 min, and then drained and separated. At the same time, a total of 288 soil samples were collected and treated from different soil layers (0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm) in the study area, and the soil samples were dried in a naturally ventilated place to remove impurities, and after grinding, they were screened for 100 mesh, and an appropriate amount of soil samples were weighed and sealed for preservation.

2.4. Indicators and Measurements

In this paper, 22 common PPCPs were selected, and the basic information is shown in Table 2. The sample was pretreated by the solid-phase extraction (SPE) method. After pretreatment, PPCPs were quantified by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

For water sample pretreatment, firstly, the water sample was passed through 0.45 μm filter membrane, 0.8 g of ethylene diamine tetraacetic acid (EDTA) disodium salt was added to every 1 L of filtrate, and the pH value was adjusted to 4.8–5.0. Secondly, methanol and ultrapure water were added to the Hydrophile Lipphile Balance (HLB) solid-phase extraction column in order to remove air from the sample mixture. Thirdly, the sample was washed with methanol acetonitrile, the eluent was concentrated with nitrogen blowing, the methanol water mixture was mixed to a constant volume, and then it was stored in a refrigerator at −80 °C. Finally, the quantitative analysis of pollutant concentration in water samples was conducted. During the experimental period, the statistics of irrigation water quality indicators were shown in Table 3.

For soil sample pretreatment, firstly, after freeze-drying, the soil sample was sieved through a 0.15 mm sieve. Secondly, 0.1 g of the sample was taken, 5 mL of methanol and 5 mL of EDTA McDonnell reagent were added, and the sample was centrifuged after ultrasonic shaking. Thirdly, the supernatant was taken and diluted with ultrapure water to ensure that the volume fraction of the organic solvent (nail alcohol) was below 2%, passing through 0.22 μm filter membrane. Lastly, the subsequent extraction, elution, nitrogen blowing concentration, and detection were the same as those of water samples.

For rice sample pretreatment, liquid nitrogen grinding was followed by freeze-drying, and this was followed by the same pre-extraction as the soil sample, extraction, elution, nitrogen blowing concentration, and detection as the water sample.

Table 2. Basic information of pharmaceuticals and personal care products.

Classification	Compound	Abbreviation	CAS	Molecular Structure
β Receptor Blockers	Atenolol	ATE	29122-68-7	$C_{14}H_{22}N_2O_3$
	Metoprolol	MET	37350-58-6	$C_{15}H_{25}NO_3$
Non-steroidal anti-inflammatory drugs	Naproxen	NAP	22204-53-1	$C_{14}H_{14}O_3$
	Ibuprofen	IBU	15687-27-1	$C_{13}H_{18}O_2$
	Acetaminophen	ACE	1219798-53-4	$C_8H_9NO_2$
antipsychotic drug	Carbamazepine	CAR	298-46-4	$C_{15}H_{12}N_2O$
Macrolide antibiotic	Clarithromycin	CLA	81103-11-9	$C_{38}H_{69}NO_{13}$
	Erythromycin	ERY	114-07-8	$C_{37}H_{67}NO_{13}$
	Roxithromycin	ROX	80214-83-1	$C_{41}H_{76}N_2O_{15}$
Sulfamide antibiotics	Sulfadiazine	SDZ	68-35-9	$C_{10}H_{10}N_4O_2S$
	Sulfamethoxazole	SMX	723-46-6	$C_{10}H_{11}N_3O_3S$
	Sulfamethazine	SMA	57-68-1	$C_{12}H_{14}N_4O_2S$
Tetracycline antibiotics	Oxytetracycline	OXY	79-57-2	$C_{22}H_{24}N_2O_9$
	Tetracycline	TET	60-54-8	$C_{22}H_{24}N_2O_8$
New tetracycline antibiotics	Minocycline	MIN	10118-90-8	$C_{23}H_{27}N_3O_7$
	Doxycycline	DOX	100929-47-3	$C_{22}H_{25}ClN_2O_8$
Quinolone antibiotics	Ofloxacin	OFL	82419-36-1	$C_{18}H_{20}FN_3O_4$
Sulfamide synergist	Trimethoprim	TRIM	738-70-5	$C_{14}H_{18}N_4O_3$
Lipid-regulating drugs	Gemfibrozil	GEM	25812-30-0	$C_{15}H_{22}O_3$
Bacteriostatic agent	Triclocarban	TRIC	101-20-2	$C_{13}H_9Cl_3N_2O$
Stimulants	Caffeine	CAF	58-08-2	$C_8H_{10}N_4O_2$
Penicillin antibiotics	Penicillin G	PEG	61-33-6	$C_{16}H_{18}N_2O_4S$

Note: CAS represented the unique numerical identification number of a substance.

Table 3. Water quality description and statistics of irrigation water sources (mg/L).

Water Sources	Indicator	Maximum Value	Minimum Value	Standard Deviation	Mean Value	Kurtosis	Skewness
R1	COD	84	15	26.794	29.5	5.855	2.410
	LAS	0.88	0.06	0.315	0.25	5.199	2.247
	NH_4+-N	11.9	8.25	1.645	9.647	−1.782	0.916
	NO_3+-N	0.061	0.016	0.019	0.034	−1.452	0.642

R2	COD	59	10	16.783	24.1	0.719	1.291
	LAS	0.16	0	0.058	0.048	−0.425	0.827
	NH_4+-N	11.9	3.52	2.837	7.712	−0.946	−0.174
	NO_3+-N	6.25	0.01	2.455	1.364	1.238	1.687
R3	COD	62	11	12.735	24.15	0.710	1.553
	LAS	0.32	0	0.132	0.042	−1.215	0.826
	NH_4+-N	5.45	2.34	0.634	4.415	0.478	0.473
	NO_3+-N	3.16	0.345	0.928	0.823	1.382	1.275
CK	COD	56	7	15.712	23.45	0.710	1.251
	LAS	0.1	0	0.041	0.035	−1.875	0.418
	NH_4+-N	1.49	0.116	0.394	0.711	0.143	0.393
	NO_3+-N	2.56	0.624	0.578	1.048	4.680	2.078

Note: COD and LAS represented chemical oxygen demand and anionic surfactant, respectively.

2.5. Statistical Analysis

1. *Reduction rate calculation of PPCPs*

PPCPs are discharged into the soil environment through reclaimed water, and the content of PPCPs is reduced through soil self-purification. According to the PPCP concentration in soil detected in the irrigation data, the average concentration of PPCPs come from RDRW irrigation and they utilize annual irrigation water consumption and the plant biomass (without roots). The theoretical input concentration of PPCPs from different water sources in the irrigation cycle and the reduction rate in PPCPs from RDRW to soil were calculated. The calculation formula is as follows:

$$\beta = \frac{(A_{ij} - C_{Soil}) \times 100\%}{A_{ij}} \quad (1)$$

$$A_{ij} = \sum^{j} \frac{N_j C_{ij}}{P} \quad (2)$$

In the formula, *i* represented different PPCPs, *j* represented different irrigation water sources, β(%) represented the reduction rate of PPCPs in different water sources, A_{ij} (mg·kg^{-1}) was the input amount of PPCPs in irrigation water, C_{soil} (mg·kg^{-1}) was the content of PPCPs in the soil, N_j (L) was the difference between irrigation water consumption and drainage [19], C_{ij} (mg·L^{-1}) was the concentration of PPCPs in irrigation water, and *P* (kg) was the biomass of rice plants, which were 357.23 kg, 379.79 kg, 399.35 kg, 471.21 kg for R1, R2, R3, and CK, respectively.

2. *Calculation of bio-concentration factor*

In this study, the bio-concentration factor (*BCF*) was calculated to represent the migration law of PPCPs from soil to plants, and the BCF characterized the accumulation capacity of plants to a certain element or compound, which was the ratio of PPCPs content in crops to PPCPs content in soil [20]. The calculation formula is as follows:

$$BCF = C_{Plant}/C_{Soil} \quad (3)$$

In the formula, C_{plant} (mg·kg^{-1}) represented the PPCPs content in the grain of the crops, and C_{soil} (mg·kg^{-1}) represented the total amount of PPCPs in soil. The *BCF* was divided into four levels, where $BCF > 1$ indicated strong uptake, $0.1 < BCF \leq 1$ indicated moderate uptake, $0.01 < BCF \leq 0.10$ indicated weak uptake, and $BCF < 0.01$ indicated extremely weak uptake [21].

3. *Calculation of risk quotient*

In this study, the risk quotient (*RQ*) method was used to evaluate the ecological risk of PPCPs in RDRW in the study area. The calculation formula is as follows:

$$RQ_{ij} = MEC_{ij} / PNEC_i \tag{4}$$

In the formula, *RQ* represented the risk quotient value, *MEC* ($mg\cdot L^{-1}$) represented the actual environmental exposure concentration of PPCPs, *PNEC* ($\mu g\cdot L^{-1}$) represented ineffective concentration. These were divided by acute (EC50/LC50) or chronic (NOEC/LOEC/EC10) toxicity concentration by the evaluation factor, acute, or chronic toxicity data obtained by querying the US Ecotoxicity Database. When a single datum has multiple parameters, select the maximum value, chronic toxicity is 100, acute toxicity is 1000 [22]. According to the *RQ* value, it is divided into three risk levels, namely high risk ($RQ > 1$), medium risk ($0.1 < RQ < 1$), and low risk ($0.01 < RQ < 0.1$). When the $RQ < 0.01$, it can be considered risk-free.

3. Results

3.1. PPCPs Distribution in Irrigation Water Sources

The changes of PPCPs concentration in various irrigation water sources are shown in Figure 3. In this paper, 22 kinds common PPCPs were selected, except for PEG. The remaining 21 kinds of PPCPs were detected in RDRW and CK, including two β Receptor blockers (ATE, MET), three non-steroidal anti-inflammatory drugs (NAP, IBU, ACE), one antipsychotic drug (CAR), three Macrolide antibiotic (CLA, ERY, ROX), three Sulfamide antibiotics (SDZ, SMX, SMA), two Tetracycline antibiotics (OXY, TET), two new tetracycline antibiotics (MIN, DOX), one Quinolone antibiotics (OFL), one Sulfamide synergist (TRIM), one lipid-regulating drug (GEM), one Bacteriostatic agent (TRIC), and one Stimulant (CAF). The results showed that the concentration of PPCPs in each irrigation water source was only OFL at the μg/L level, and the rest were at the ng/L level. The concentrations of OFL were the highest in the detected components of PPCPs in R1, R2, R3, and CK, accounting for 87.73%, 74.91%, 65.77%, and 27.78%, respectively, followed by IBU accounting for 3.37%, 5.81%, 7.08%, 8.68%, and CAF, accounting for 3.31%, 6.75%, 9.99%, and 19.06%, respectively. The proportions of the remaining components in the total amount were 0~1.23%, 0~2.08%, 0~3.06%, and 0.02~6.01%. In general, compared with CK, the total concentration of PPCPs in RDRW was higher, and in the R1, R2, and R3 sources it was 5.6 times, 2.4 times, and 1.5 times higher than that in CK.

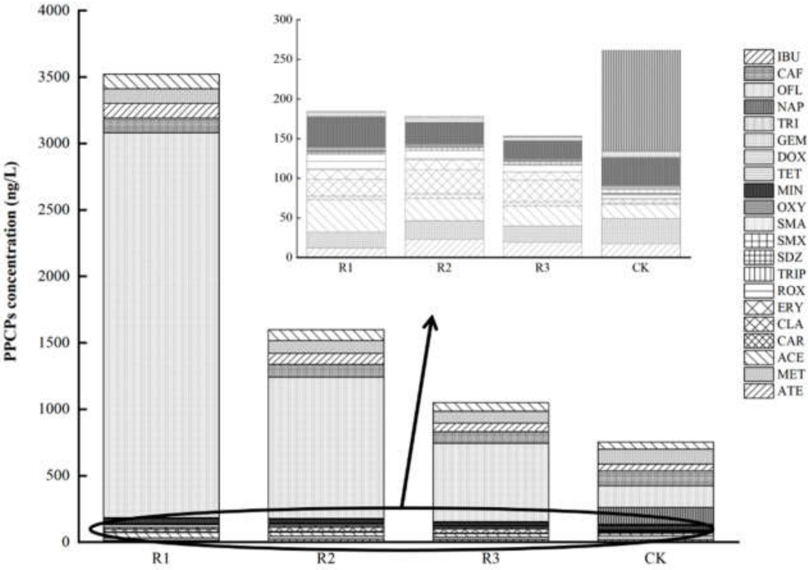
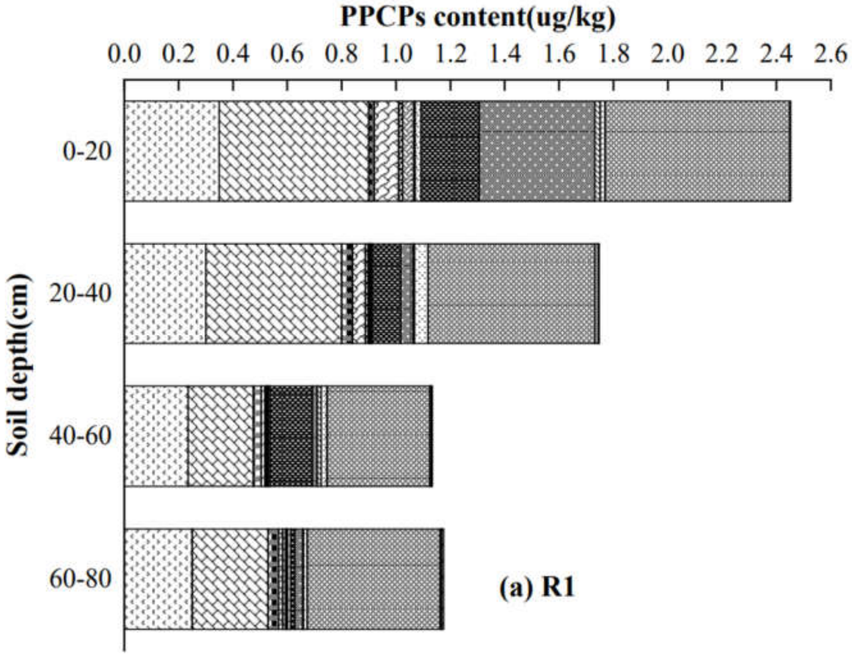
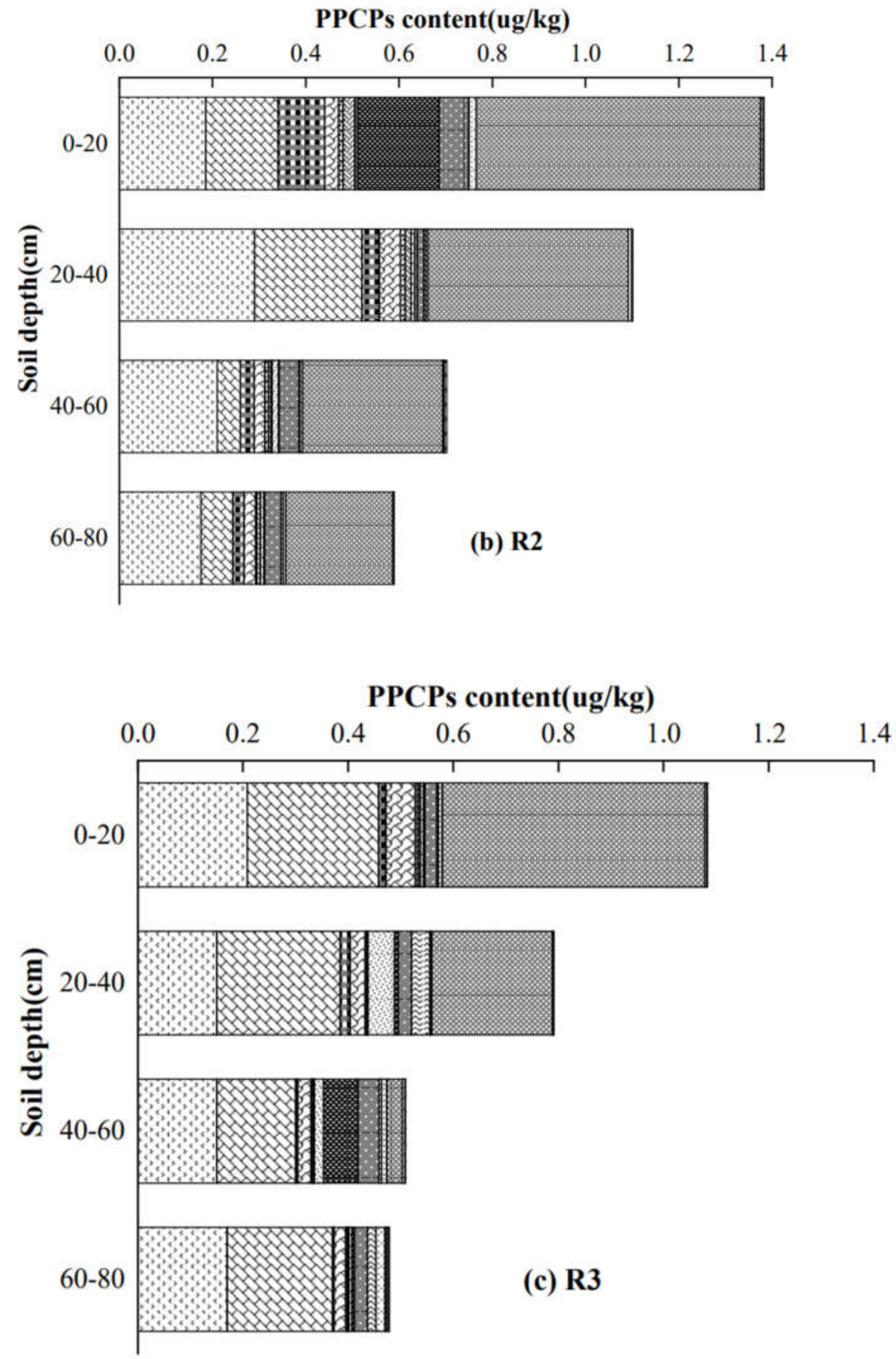


Figure 3. Pharmaceuticals and personal care products concentration in various irrigation water source.

3.2. PPCPs Distribution in Soil Profiles

The changes of PPCPs content in soil profiles under different irrigation water sources and water level regulations are shown in Figures 4 and 5. Fifteen kinds of PPCPs were detected, of which six kinds of PPCPs with high content were found in the soil profile including ATE (0.15~0.39 μg/kg), MET (0.05~0.55 μg/kg), ACE (0.0022~0.23 μg/kg), OXY (0.001~0.32 μg/kg), MIN (0.0025~0.425 μg/kg), and OFL (0.004~0.68 μg/kg). The content of the remaining nine kinds of PPCPs in the soil profile were low (0.001~0.1 μg/kg). The total content of PPCPs was highest in the 0–20 cm soil layer. As the soil depth increased, the PPCPs content showed a decreasing trend. This is mainly because the surface soil has been frequently disturbed by many uncertain factors (both natural and human) for a long time, while the deep soil environment is not sensitive to the impact of natural and human factors on the ground. Under different water source irrigation, the PPCPs content in the soil profile of R3 water source was the smallest, and compared to R3, the PPCPs content in the soil profile of R1, R2, and CK was increased by 127%, 31.9%, and 17.4%, respectively. There was no significant difference in the content of PPCPs in soil profiles under different water level regulations. It indicated that R1 and R2 irrigation have a cumulative effect on the content of PPCPs in soil profiles.




PPCPs content(ug/kg)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Soil depth(cm)
0-20
20-40
40-60
60-80
(b) R2
PPCPs content(ug/kg)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Soil depth(cm)
0-20
20-40
40-60
60-80
(c) R3

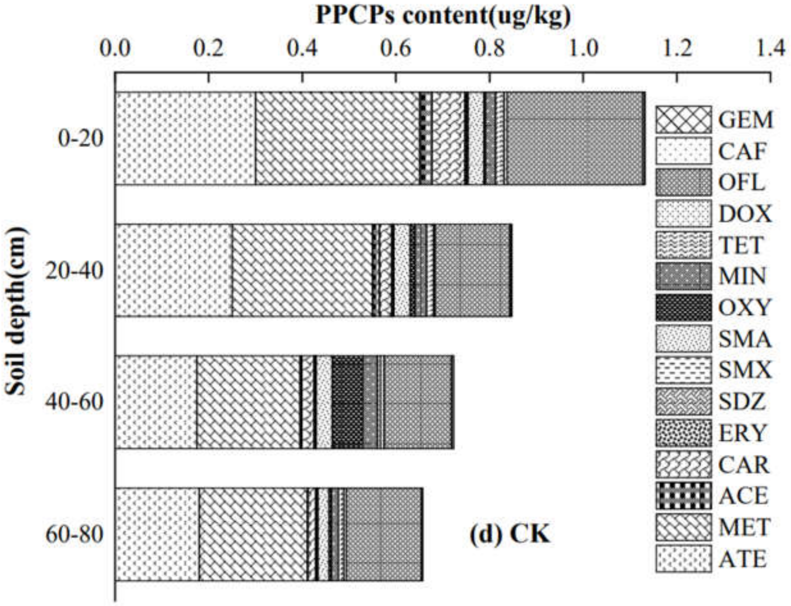
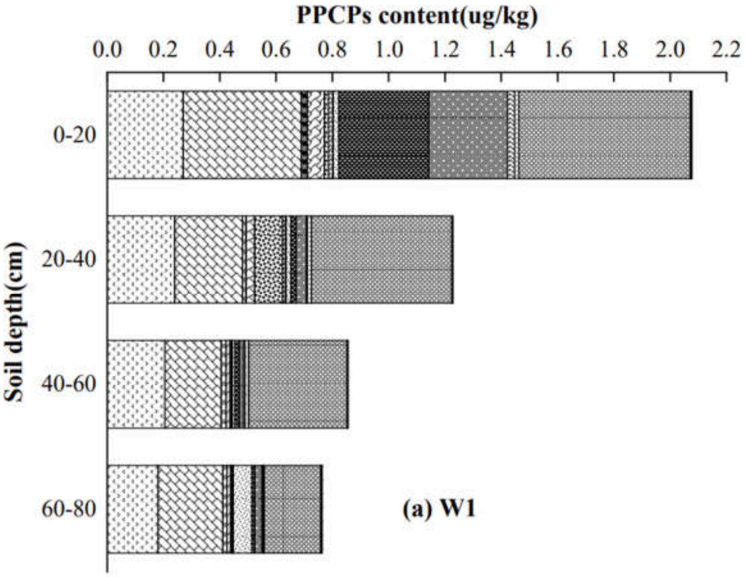


Figure 4. Pharmaceuticals and personal care products content in soil profiles under different irrigation water sources (R1, R2, R3 and CK represented the primary treated water of RDS, the secondary treated water of RDS, the ecological pond purified water and river water , respectively).



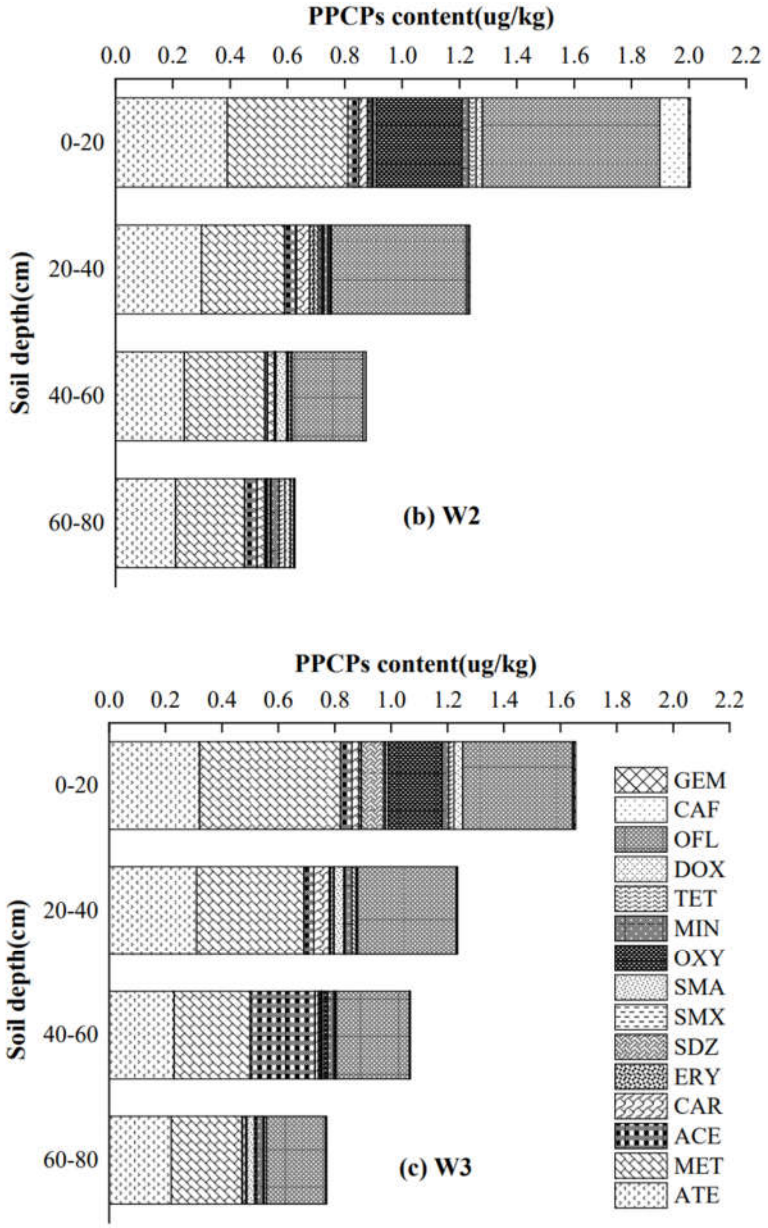


Figure 5. Pharmaceuticals and personal care products content in soil profiles under different water level regulations (W1, W2, and W3 represented low-, medium- and high-water level regulation, respectively).

3.3. PPCPs Distribution in Rice Grains

The above analysis demonstrated that different water level regulations had little effect on PPCPs contents in paddy fields, so the changes of PPCPs content in rice grains were only analyzed under different irrigation water sources (Figure 6). Fifteen kinds of PPCPs in rice grains were detected, of which four kinds of PPCPs with higher content were found in rice grains including ATE (0.235~0.35 ng/kg), MET (0.24~0.55 ng/kg), OXY (0.015~0.215 ng/kg), and OFL (0.38~0.68 ng/kg). The remaining 11 kinds of PPCPs had lower content in rice grains (0.001~0.09 ng/kg). For different irrigation sources, the total content of PPCPs in rice grains showed a variation of R1 (2.45 ng/kg) > R2 (1.75 ng/kg) > R3 (1.13 ng/kg) ≈ CK (1.18 ng/kg). Compared with CK, the total content of PPCPs in R1 and R2 water sources was increased by 109% and 48.7%, respectively. In general, the content of PPCPs in rice grain was at an extremely low level, and it was worth noting that there was a cumulative effect on the PPCPs content in rice grains under R1 and R2 irrigation.

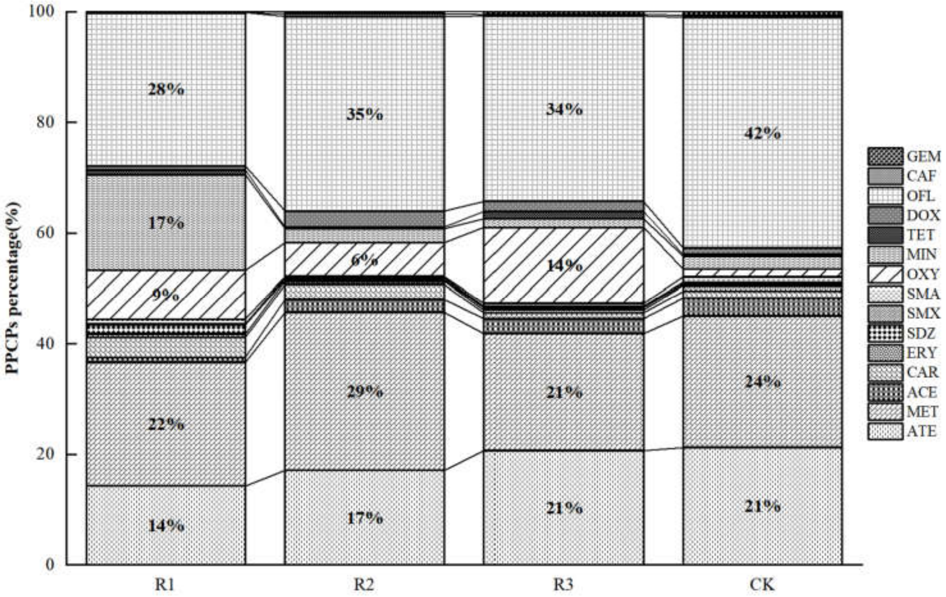


Figure 6. Pharmaceuticals and personal care products percentage in rice grain under different irrigation sources.

3.4. PPCPs Migration in Soil-Crops

The reduction rate of PPCPs in soil under different irrigation water sources is shown in Table 4. The reduction rates of 15 kinds of PPCPs in soil were all greater than 85%, and the average reduction rates of OFL and CAF reached 100%. IBU was not detected in the soil. The reduction effect of soil on PPCPs under R1, R2, R3, and CK was roughly the same, with the total reduction rates of 96%, 98%, 97%, and 98%, respectively. It indicated that the reduction ability of soil to PPCPs was similar under different irrigation water sources— in other words, that RDRW did not significantly affect the reduction ability of PPCPs in soil.

The BCF of PPCPs in rice grains under different irrigation water sources is shown in Table 5. In general, the BCF of PPCPs in rice grain was less than 0.1. The enrichment capacity of rice grain to different components of PPCPs was different under different irrigation water sources. The four kinds of DOX, ACE, CAF, and GEM showed extremely weak uptake, and the remaining 11 kinds of PPCPs showed weakly uptake under R1 irrigation. The three kinds of ACE, SMA, and SDZ showed extremely weak uptake, and the remaining 12 kinds of PPCPs showed weakly uptake under R2 irrigation. The four kinds of TET, MIN, CAR, and SMA showed extremely weak uptake, and the remaining 11 kinds of PPCPs showed a weak uptake under R3 irrigation. The four kinds of OXY, CAR, SMA, and TET showed an extremely weak uptake, and the remaining eleven kinds of PPCPs showed a weakly uptake under CK irrigation. The results showed that the enrichment ability of PPCPs in rice grains was similar under different irrigation water sources, indicating that the enrichment ability of PPCPs in rice grains was not affected under RDRW irrigation.

Table 4. The reduction rate of pharmaceuticals and personal care products in soil under different irrigation water sources.

Treatment	ATE	MET	ACE	CAR	ERY	SDZ	SMX	SMA	OXY	MIN	TET	DOX	OFL	CAF	GEM
R1	93%	95%	100%	97%	100%	97%	96%	90%	92%	99%	98%	98%	100%	100%	87%
R2	98%	99%	100%	99%	100%	99%	99%	97%	94%	100%	98%	100%	100%	100%	95%
R3	98%	97%	100%	98%	100%	100%	100%	92%	97%	100%	85%	99%	100%	100%	97%
CK	97%	98%	100%	96%	99%	99%	100%	96%	99%	100%	98%	100%	100%	100%	98%

Table 5. The bio-concentration factor of pharmaceuticals and personal care products in rice grains under different irrigation water sources.

Treatment	ATE	MET	ACE	CAR	ERY	SDZ	SMX	SMA	OXY	MIN	TET	DOX	OFL	CAF	GEM
R1	0.0123 ± 0.0009	0.0140 ± 0.0009	0.0063 ± 0.0004	0.0217 ± 0.0010	0.0146 ± 0.0003	0.0296 ± 0.0017	0.0125 ± 0.0007	0.0191 ± 0.0010	0.0176 ± 0.0010	0.0329 ± 0.0003	0.0182 ± 0.0009	0.0071 ± 0.0003	0.0126 ± 0.0004	0.0038 ± 0.0001	0.0022 ± 0.0001
R2	0.0140 ± 0.0007	0.0397 ± 0.0016	0.0084 ± 0.0006	0.0156 ± 0.0008	0.0131 ± 0.0007	0.0040 ± 0.0002	0.0167 ± 0.0008	0.0067 ± 0.0002	0.0234 ± 0.0014	0.0118 ± 0.0002	0.0138 ± 0.0008	0.0667 ± 0.0017	0.0157 ± 0.0008	0.0223 ± 0.0007	0.0167 ± 0.0007
R3	0.0139 ± 0.0007	0.0115 ± 0.0008	0.0306 ± 0.0004	0.0039 ± 0.0003	0.0143 ± 0.0007	0.0200 ± 0.0009	0.0300 ± 0.0020	0.0030 ± 0.0002	0.0768 ± 0.0026	0.0065 ± 0.0004	0.0100 ± 0.0004	0.0216 ± 0.0004	0.0199 ± 0.0010	0.0118 ± 0.0007	0.0500 ± 0.0009
CK	0.0110 ± 0.0005	0.0102 ± 0.0004	0.0319 ± 0.0002	0.0043 ± 0.0002	0.0423 ± 0.0022	0.0225 ± 0.0015	0.0300 ± 0.0007	0.0038 ± 0.0002	0.0072 ± 0.0003	0.0121 ± 0.0007	0.0031 ± 0.0002	0.0217 ± 0.0006	0.0260 ± 0.0011	0.0150 ± 0.0004	0.0700 ± 0.0043

3.5. Ecological Risk Assessment

In this paper, the risk quotient (RQ) value method was used to evaluate the ecological risk of 18 kinds of PPCPs detected in irrigation water sources (no toxicity data was found for ACE, MIN, and DOX). The toxicity data of the corresponding sensitive species are shown in Table 6, and the ecological risk assessment results of PPCPs are shown in Figure 7. This study identified that IBU has the highest environmental ecological risk in irrigation water, followed by TRIC and OFL. Therefore, the potential harm of IBU to aquatic organisms should merit more attention. The RQ values of the other 15 kinds of PPCPs were all less than 0.01, indicating that there was no environmental or ecological risk to the study area. The ecological risk quotient method used in this paper only evaluated the ecological risk of a single compound. However, environmental risks caused by the combined action of multiple substances in the water environment, and the cumulative effect of PPCPs on the ecological risks, deserves attention [23].

Table 6. Toxicity data for 18 kinds of pharmaceuticals and personal care products sensitive species.

Compound	Sensitive Species	EC_{50}/LC_{50}/NOEC/LOEC/EC10	Toxicity Concentration (mg/L)	AF	PNEC (μg/L)
ATE	flatworm	LC50	500	1000	500
MET	water flea	EC50	9.32	1000	9.32
NAP	water flea	LC50	82	1000	82
IBU	water flea	NOEC	0.01	100	0.1
CAR	fathead minnow	NOEC	0.86	100	8.6
CLA	fairy shrimp	LC50	33.6	1000	33.6
ERY	water flea	NOEC	150	100	1500
ROX	Crescent algae	NOEC	40	100	400
SDZ	daphnia magna	EC10	8.8	100	88
SMX	Rotifera	LC50	26.27	1000	26.27
SMA	daphnia magna	NOEC	50	100	500
OXY	fairy shrimp	LC50	25	1000	25
TET	Rotifera	NOEC	5	100	50

OFL	flatworm	LC50	32.5	1000	32.5
TRIM	hydra	LC50	100	1000	100
GEM	green algae	LC50	56	1000	56
TRIC	daphnia magna	NOEC	0.0016	100	0.016
CAF	fathead minnow	EC50	70	1000	70

Notes: ECx is the concentration at which x% effects (mortality, growth inhibition, reproduction, etc.) are observed compared to the control group. NOEC is unobserved effect concentration. LOEC is the minimum observed effect concentration.

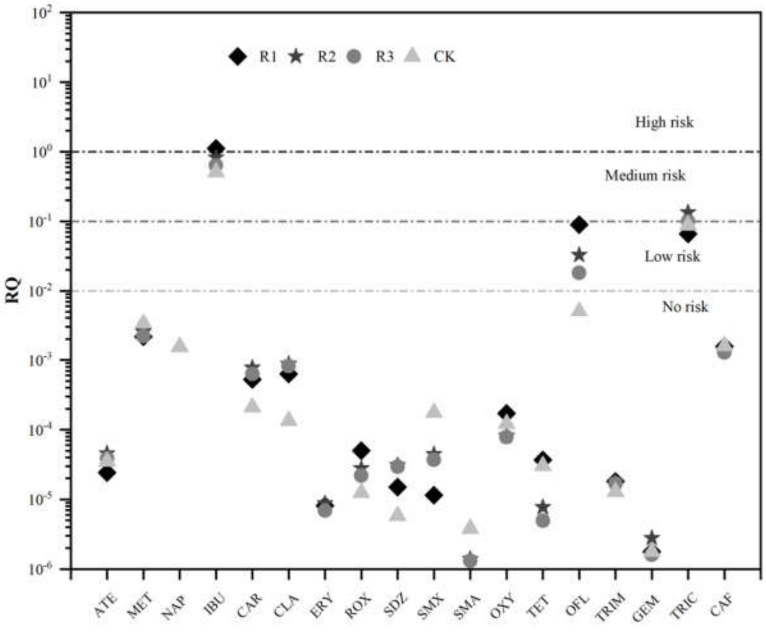


Figure 7. The ecological risk assessment results of pharmaceuticals and personal care products in the study area.

4. Discussion

4.1. Accumulation of PPCPs in Rice Field Systems Under RDRW Irrigation

The PPCPs enter the water and soil environment through reclaimed water reuse. Part of the residual PPCPs in the soil enter surface water and groundwater through leaching, seepage, and some accumulate in plants through plant absorption [24]. The studies at home and abroad were focused on the migration and transformation of PPCPs in the natural environment of water and soil, less involved in the systems of water, soil, and crops. Research has found that the higher the concentration of recycled water, the greater the impact on soil pollution. Therefore, it is necessary for sewage treatment plants to carry out secondary treatment after primary treatment. In this study, results showed that the content of PPCPs in soil profile increased with the increase in reclaimed water concentration after RDRW irrigation, which was similar to the results of Huang et al. [25], who found that the content level of PPCPs in soil was correlated with the initial concentration of reclaimed water irrigation water. At the same time, this study showed that there was a cumulative effect on the PPCPs content in rice grains under R1 and R2 water source irrigation. Bax et al. [26] showed that PPCPs have a significant cumulative effect on crop roots and can migrate to other parts such as stems and leaves. Research has shown that the factors affecting the absorption, transport, and accumulation of PPCPs by crops mainly include crop growth rate, transpiration rate, lipid content, metabolic system, detoxification effect, as well as exposure time, soil properties, humidity, temperature, and concentration of PPCPs [27]. In addition, studies by Wu et al. [8]and by Chen et al. [28] found that PPCPs such as TRIM, SMX, IBU, and NAP mainly accumulate in the 0–30 cm surface soil under reclaimed water irrigation conditions, which was consistent with the results of this study. When the traces of pollutants migrate and accumulate in plants under irrigation water, it will threaten human health [29], and we need to pay special attention.

4.2. Ecological Risk of PPCPs Under RDRW Irrigation

Chen et al.'s research shows that although recycled water is treated by sewage treatment plants, it still contains some pollutants such as COD, heavy metals, pathogenic microorganisms, PPCPs, etc., which may cause pollution to the soil ecological environment or groundwater environment [30]. In this study, the results indicated that RDS treated by sewage treatment plants can reduce a portion of PPCPs [31,32]. The total RQ value of RDRW increased with the increase in the concentration of RDRW. Compared with R1 and R2, the RQ value of R3 purified by ecological ponds showed a decreasing trend, indicating that ecological pond was a technical measure to effectively reduce PPCPs in reclaimed water. A large number of studies have shown that large-scale plant pond-constructed wetland systems can effectively reduce the ecological risk of some PPCPs in wastewater [33–35], which was consistent with the results of this study.

The results of this study indicate that IBU exhibits a higher concentration trend in irrigation water, which may be related to COVID-19. IBU has a low human metabolism after ingestion and is ultimately discharged as wastewater and enters rural sewage [36]. Through ecological risk assessment, it was found that IBU is a high pollutant, indicating that its widespread use may have potential ecological impacts on the water environment. Therefore, further analysis is needed to determine the long-term impact of IBU on the ecological environment. In addition, by analyzing the content of IBU in irrigation water of different treatment levels, we found that the content of IBU in rural sewage gradually decreased with the increase in treatment level, indicating that the removal rate of IBU by sewage treatment plants was relatively high [37]. Therefore, to protect the water environment, it is necessary to deeply treated the residual IBU in effluent of wastewater treatment.

5. Conclusions

In this paper, the distribution characteristics and migration of PPCPs in the system of RDRW, soil, and rice grains system under different irrigation regulations by using RDRW with different treatment grades were studied, and the potential ecological risks were evaluated under RDRW irrigation. The main conclusions are as follows.

1. A total of 21 PPCPs were detected in RDRW and CK. Compared with CK, the total concentration of PPCPs in RDRW was higher, and in R1, R2 and R3 sources it was 5.6 times, 2.4 times, and 1.5 times higher than that in CK, respectively. The effect of irrigation water sources on the PPCPs content in soil profile and rice grain was significant, while the water level regulation was not significant.
2. The reduction rate of 15 kinds of PPCPs in soil was greater than 85%, and the BCF of PPCPs in rice grain was less than 0.1. The migration ability of PPCPs in soil-rice plants system was not significantly affected by RDRW irrigation. Through the ecological risk assessment of 18 kinds of PPCPs, it was found that ibuprofen (IBU) was a high-risk substance pollutant, triclocarban (TRIC) was a medium-risk pollutant, ofloxacin (OFL) was a low-risk pollutant, and other PPCPs were all risk-free pollutants.

3. The primary and secondary treatment water (R1, R2) of RDRW had a cumulative effect on soil profiles and rice grains, which deserves special attention. It was suggested that R3 water sources can be selected for agricultural irrigation, while direct irrigation of R1 and R2 water sources should be avoided.

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