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Soil environmental quality and risk assessment under combined organic pollution in a typical sewage irrigated area

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Abstract: Due to the shortage of freshwater and the depletion of groundwater, reuse of wastewater for crop irrigation has become essential, although many pollutants, such as antibiotics, are also introduced into the soil-groundwater system. In order to identify the distribution and transport mechanisms of organic pollutants in the "irrigation wastewater-soil-crop" system under long-term soil irrigation conditions and their potential ecological and health risks, soil samples were collected from five sampling sites in Wangyang River basin, a typical sewage irrigation area in North China. The results of the risk assessment showed that the risk quotients (RQ) of sulfamethoxazole (SMZ), naphthalene (Nap), hexachlorocyclohexane (HCH), and dichlorodiphenyltrichloroethane (DDTs) was greater than 1, indicating that their accumulation in root zone soil was at high risk. The non-carcinogenic risk (HQ) of bis (2-ethylhexyl) phthalate (DEHP) was the largest, reaching 0.41 and 0.16 for adults and children, respectively, and the carcinogenic risk (CR) value was 0.00061, which exceeded the limit of 1×10^{-6}, indicating that DEHP poses a potential carcinogenic risk to human health.

1 Introduction

Soil is an important component of natural resources and plays an important role not only in the production of food and fibre, but also in maintaining the quality of the local, regional and global environment [1,2]. The ability of soils to improve water and air quality and to have an impact on human health and habitation, as well as on the productivity of plants and animals, is referred to as soil quality, and the ability to function along ecosystems also falls under the concept of soil quality [3,4]. Due to the importance of soil environmental quality to agricultural products and human safety, it is necessary to obtain information about soil quality and its related ecological risks. The important methods to obtain this information are ecological risk assessment and human health risk assessment [5]. The quality of the soil environment is critical to human survival and development, but freshwater resources are scarce as a result of human activities and climate change around the world, [6], North China, in particular, is located in an arid and semi-arid region, with a dislocation in the spatial distribution of soil and water resources (the Huaihe River Basin and North China account for 63.15% of China's land area, but only 19% of China's water resources), which, together with the impacts of climate change and high-intensity human activities, has resulted in a severe shortage of water resources [7,8], To compensate for the severe scarcity of water for agricultural irrigation, wastewater irrigation has become an irreplaceable way [9]. Studies have found that South-East Asian countries such as India, Pakistan and China use only diluted or even untreated sewage for farm irrigation, contaminating crops with cadmium and lead and causing health problems for consumers [10].

Current research on soil environmental problems caused by sewage irrigation has mainly focused on the irrigation effluent itself and heavy metal contamination in the soil [11–13], and there have been fewer studies on the problem of organic contamination of sewage-irrigated soils and the interactions between the two have been less studied, and the few studies that have been done have only one single organic pollutant affecting the soil, For example, Zhang et al. [14] found that Zhang found that the concentrations of organochlorine pesticides (OCPs) in the soil and groundwater of typical sewage-irrigated areas were significantly higher than those in groundwater-irrigated areas; Song et al. [15] studied residual levels of polycyclic aromatic hydrocarbon (PAHs) and other pollutants and their genotoxicity in soils in Shenyang, Northeast China, which have been irrigated with wastewater for more than 40 years, and found that the results were higher than those of controls; Yan [16] studied the occurrence levels of heavy metals and antibiotics in paddy soils chronically irrigated with municipal secondary treated wastewater and found that the pollution affected the microbial community and promoted resistance to

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heavy metals and antibiotics in paddy crops; Dueñas-Moreno et al. [17] found that 9 of 14 phthalic acid esters (PAEs) were detected and had high concentrations when studying a river in Mexico that received untreated or improperly treated urban and industrial wastewater. The river is often used for farmland irrigation. The authors also evaluated the ecological and human health risks of PAEs, and the results were not optimistic. The impact of organic matter fouling irrigation on the soil environment cannot be ignored [18–20], but in the actual typical fouling irrigation area, pollution is often combined, and the study of the impact of a single pollutant on the soil may be one-sided, and there are relatively few studies on the environmental quality of soils in typical sewage irrigation areas under combined pollution of organic pollutants, therefore, how soil environmental quality problems caused by combined pollution of organic pollutants can further lead to ecological environment changes and health risks should also be the goal of our research.

Therefore, this thesis selected five sampling points along the upstream to downstream of a typical sewage irrigation area in North China to collect samples, study the influence pattern of long-term sewage irrigation on soil quality. A kinetic model (HYDRUS-1D) was used to simulate the environmental behavior of the characteristic pollutants in the soil ecosystem. Based on the model prediction and toxicological indicators of pollutants, and using relevant standards and evaluation methods, the potential ecological and health risks of the characteristic pollutants were evaluated. Exploring the soil pollution due to dirty irrigation in this area is of great significance to guarantee the quality and safety of agricultural products and the health of residents, and provides a basis for clarifying the risk of dirty irrigation and strengthening the management of dirty irrigation, so as to realize the sustainable development of agricultural production.

2 Materials and methods

2.1 Study area and soil sample collection

The study area is located in the Wangyang River basin, a typical sewage irrigation area in Hebei Province, southeast of Shijiazhuang City. The sewage irrigation area along the Wangyang River usually has a semi-arid continental monsoon climate, with an annual rainfall of 556 mm in the area, and a rainy season from July to September; the average annual temperature is 13.1°C. The main cropping pattern is a winter wheat-summer maize rotation (covering about 60% of the arable land). The main soil type in the site was the initiating soil. Farmland in this area has been irrigated with wastewater for more than 30 years due to high demand and shortage of fresh water. The industrial wastewater in Wangyang River is mainly pharmaceutical and chemical wastewater, which is discharged into Wangyang River after secondary treatment by sewage treatment plant for farmland irrigation on both sides of the river. Five soil sample sampling sites were selected along the riverbank from upstream to downstream in June (before wheat harvest) and September (before corn harvest) in 2013 (Figure 1), and the sampling sites were distributed in different river sections along the riverbank, namely, one upstream farmland (site 1#), three midstream farmlands (sites 2#, 3#, and 4#), and one downstream farmland (site 5#), in order to differentiate between the impacts of pollution and irrigation due to different water quality characteristics of different river sections. Soil samples were collected from three adjacent fields at the sampling site as triplicate, and 5 drills were collected from each triplicate with soil drills and mixed. The collected samples were immediately packed into sealed bags. After being transported back to the laboratory, the soil samples were divided into two parts. One part of fresh soil was passed through a 2 mm sieve to remove stones and plant residues, and used to measure soil activity indicators (soil enzymes); Another portion was air-dried at room temperature and ground to remove stones and plant residues for the determination of basic soil physicochemical properties and contaminant content.

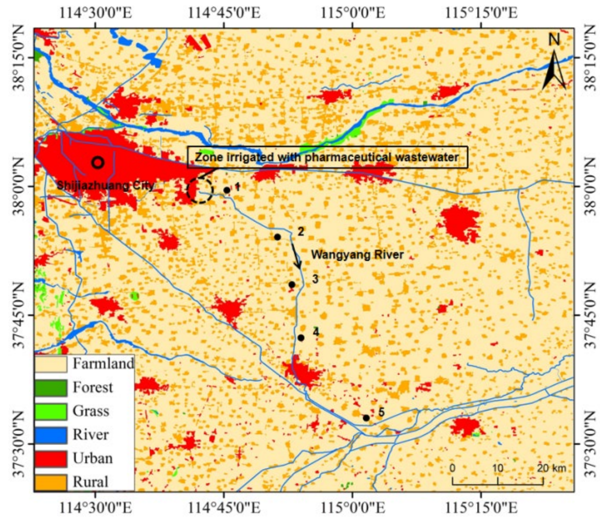

Figure 1. Schematic diagram of sampling point locations

2.2 Analysis of soil pollutants

2.2.1 Chemicals.

The 17 antibiotic standards were purchased from Dr. Enrenstorfer GmbH.All standards were dissolved in methanol: water (V/V=2:1), and all antibiotic reagents were prepared as a standard stock solution of 1.0 mg mL^{-1} except furazolidone, which was prepared to 0.1 mg mL^{-1} and 0.5 mg mL^{-1}, and carbacoxo, which was prepared to 0.5 mg mL^{-1}. Salafloxacin hydrochloride and ofloxacin can be dissolved by adding a certain amount of NaOH solution (0.5 mg mL^{-1}). The stock solution was stored in a refrigerator at 4 °C in the dark. The stock solution was reformulated every 3 months; The 16 EPA-specified standards for preferential control PAHs were purchased from Dr. Enrenstorfer GmbH. The internal standards were phenic-d_{10}, Chrys-d_{12}, and pyrene-d_{12} dissolved with toluene-isooctane (1:1) in the volume of 200 mgL^{-1} (AccuStandard, Inc, USA). The standard samples of 14 PAEs were purchased from AccuStandard, Inc. with the concentration of 1000 µg ml^{-1}, 1 mL volume, the purity was >95.1%, and the solvent was n-hexane. Before use, the standard curve was made with n-hexane diluted to the required concentration gradient according to the need; 17 organochlorine standard samples were purchased from AccuStandard, Inc, USA at a concentration of 2mg/mL with acetone as solvent. Before use, the reagents were diluted with hexane to the required concentration gradient to make a standard curve. The acetone, methanol, acetonitrile and hexane reagents used in this study were purchased from JT Baker Company, USA, and were of chromatographic grade.

2.2.2 Quality Assurance and Quality Control (QA/QC).

The experimental process was subjected to strict quality control, including method blanks, matrix spiking, and sample parallelism. The detection limit of the method was calculated by 3 times the signal-to-noise ratio. The detection limit of antibiotics was 0.01-0.8ug/ml. The recovery rate was 63.4%-106.7%, and the relative standard deviation was less than 14%; The detection limits of 14 PAEs were 0.0835-0.1167ug/ml, the recovery rate was 79.65%-106.21%, and the relative standard deviation was 0.93%-2.54%; The detection limit of OCPs was 0.01ng L^{-1}, the recovery rate was 75.5%-103.2%, the relative standard deviation was 0.78%-2.19%. The detection limits of PAHs contaminants in water and sediment/soil were 0.4-1.3 ngl^{-1} and 0.13-2.2ngg^{-1}, respectively. The recoveries of indicators during water extraction were naphthalen-d_8:63.4±6.8%, acenaphthylene-d_{10}:78.4±9.2%, philippine-d_{10}:94.1±13.2%, Chrys-d_{12}:90.5±10.5%, and pyrene-d_{12}:84.7±8.8%. The recoveries of indicators during sediment extraction were naphthenic-d_8:70.2±7.5%, acenaphthenic-d_{10}:84.5±5.6%, philippine-d_{10}:92.5±5.6%, Chrys-d_{12}:92.4±10.2%, and pyrene-d_{12}:89.0±9.4%. It meets the error requirements of instrumental analysis and has good accuracy and precision.

2.3 Risk Assessment

2.3.1 Ecological risk assessment.

In this study, risk quotients (RQ) were used to characterize the ecological risks of the target pollutants. The method was obtained by comparing the actual monitoring values (EEC) or model estimated values (PEC) with the toxicity data (predicted non-effect concentration (PNEC)) that characterized the harm degree of the pollutants, as shown in Equation (1):

$$\mathrm{RQ} = \mathrm{PEC/PNEC} \tag{1}$$

For the concentration value of pollutants in the profile soil (PEC_{soil}), the dynamic model (HYDRUS-1D) was used to simulate the concentration value when the concentration of pollutants in the root zone soil (0-20 cm) reached equilibrium. Because pollutants accumulate mainly in the soil of the root zone, the highest contamination values of drugs are found in this region. The HYDRUS-1D model was used to simulate the highest concentration of pollutants when the leachate concentration in the profile soil reached equilibrium. PNEC can be obtained from Equations (2) and (3):

$$\mathrm{PNEC_{water}} = \mathrm{LC_{50}\ or\ NOEC/1000} \tag{2}$$

$$\mathrm{PNEC_{soil}} = \mathrm{PNEC_{water}} \times \mathrm{Kd} \tag{3}$$

Among them, NOEC was the non-observed effect concentration of the target pollutant, and LC_{50} was the acute toxicity data of the target pollutant to aquatic organisms, both of which were available through literature review.

2.3.2 Health risk assessment.

The RBCA health risk assessment model was used to evaluate the risk of contaminants in maize and wheat kernels to human health through food intake. The human health risk evaluation was categorized into non-carcinogenic risk (HQ) and carcinogenic risk (CR), which were calculated as shown in equations (4) and (5), respectively:

$$\mathrm{HQ} = \frac{\frac{\mathrm{C_g \times IR \times EF \times ED}}{\mathrm{BW \times AT}} \times 10^{-6}}{\mathrm{RFD_0}} \tag{4}$$

$$\mathrm{CR} = \frac{\mathrm{C_g \times IR \times EF \times ED}}{\mathrm{BW \times AT}} \times 10^{-6} \times \mathrm{SFO} \tag{5}$$

Where Cg is pollutant concentration (mg kg^{-1}), IR is food intake (mg day^{-1}), EF is frequency of exposure (day $year^{-1}$), ED exposure period (years), BW is body weight (kg), AT average effect time (days), and EF is frequency of exposure (day $year^{-1}$). RfDo was the contaminant toxicity reference dose (mg kg^{-1} day^{-1}), and SFO was the carcinogenic slope factor ((mg kg^{-1} day^{-1}) $^{-1}$). Among them, the toxic reference dose and carcinogenic slope factor of organochlorine pollutants were mainly set according to network data, and the setting values of other parameters were mainly set according to Wang et al.[21] The specific values are shown in Table 1.

Table 1. Setting values of non-carcinogenic risk parameters and carcinogenic risk parameters

Parameter			Value
IR	Maize	Adults	31000
		Children	19200
	Wheat	Adults	330000
		Children	204386
EF			365
ED		Adults	30
		Children	6
BW		Adults	65
		Children	16
AT			26280
RfD$_o$	DnBP		0.1
	DEHP		0.02
	HCH		0.0125
	DDT		0.005
SFO	DEHP		0.014
	HCH		0.0833
	DDT		0.885

Theoretically, when the non-carcinogenic risk value HQ < 1, there will be no obvious adverse non-carcinogenic health effects on the exposed population. In terms of carcinogenic risk, the United States Environmental Protection Agency sets that the risk is negligible when the carcinogenic risk caused by a compound is $CR \le 10^{-6}$. When the carcinogenic risk caused by a compound is $CR > 10^{-4}$, the risk is considered unacceptable.

3 Results

3.1 Ecological risk assessment

3.1.1 Simulated cumulative concentrations of pollutants in root zone soils.

The concentration distributions of three pollutants, including sulfamethoxazole (SMZ), ofloxacin (OFL), and oxytetracycline (OTC), in the soil (0-20cm) of the root zone are shown in Figure 2 (a). The concentration of sulfamethoxazole in root zone soil showed an increasing trend at the beginning of irrigation, and reached equilibrium after 20 years of irrigation. At equilibrium, the maximum concentration of sulfamethoxazole in root zone soil was 16.5 $ng \cdot g^{-1}$. At the beginning of irrigation, the concentrations of ofloxacin and oxytetracycline in the root zone soil showed a linear increase, and then gradually stabilized. After 120 years of irrigation, the concentrations of ofloxacin and oxytetracycline in the soil reached a balance, with the concentrations of 65.2 and 162.1$ng \cdot g^{-1}$, respectively.

The concentration distributions of two PAHs, naphthalene (Nap) and phenanthrene (Phe), in the soil of the root zone are shown in Figure 2 (b). At the beginning of irrigation, the concentrations of NAP and PHE in the root zone soil increased linearly, and then gradually became stable. After 120 years of irrigation, the concentrations of NAP and PHE in soil reached a balance, with the concentrations of 279.2 and 241.3$ng \cdot g^{-1}$, respectively.

The concentration distributions of two PAEs, such as DEHP and DnBP, in the profile soil are shown in Figure 2 (c). The concentrations of DEHP and DnBP in root zone soil increased linearly at the beginning of irrigation, and then gradually became stable. After 80 years of irrigation, the concentration of DnBP in soil basically reached the equilibrium, with a concentration of 1.12ng·g-1. DEHP reached equilibrium after 100 years of irrigation, and the concentration in root zone soil was 6.2 ng·g-1 at equilibrium.

The concentration distributions of two OCPs, including HCH and DDT, in the profile soil are shown in Figure 2 (d). The concentrations of HCH and DDT in root zone soil increased linearly at the beginning of irrigation, and then gradually became stable. After 30 years of irrigation, the concentration of HCH in soil basically reached equilibrium, with a concentration of 8.5$ng \cdot g^{-1}$. After 60 years of irrigation, DDT reached equilibrium, and the DDT concentration in root zone soil was 97$ng \cdot g^{-1}$ at equilibrium.

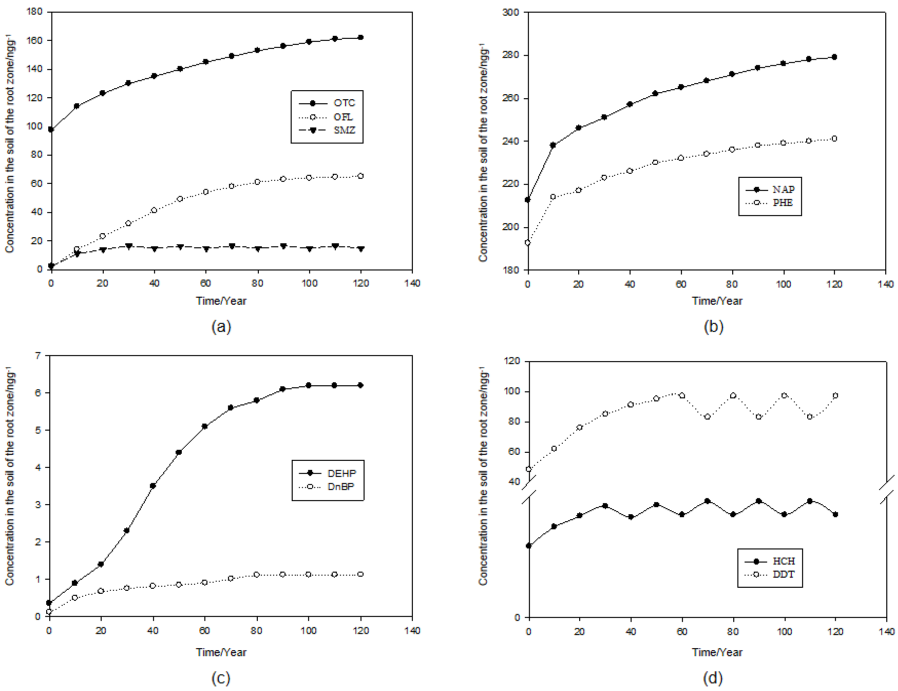

Figure 2. (a) Concentrations of three antibiotics in the soil of the root zone; (b) the concentrations of two PAHs in root soil; (c) the concentrations of two PAEs in root zone soil; (d) concentrations of two OCPs in root zone soil

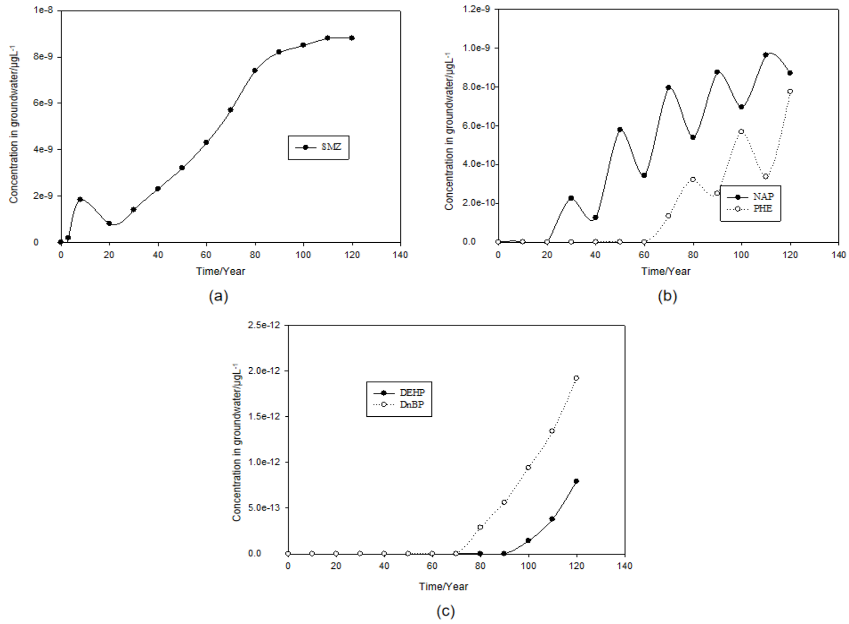

Figure 3. (a) Concentrations of 3 antibiotics in groundwater; (b) Concentrations of 2 PAHs in groundwater; (c) Concentrations of 2 PAEs in groundwater

3.1.2 Simulated cumulative concentrations of pollutants in groundwater.

The concentration distribution of three pollutants, including SMZ, OFL and OTC, in the profile soil leaching solution, namely groundwater, is shown in Figure 3 (a). SMZ gradually leaped from the profile soil after 8 years of irrigation, and the leaching concentration gradually increased with the irrigation time. The concentration of SMZ was 8.81×10^{-9} $\mu g\cdot L^{-1}$ after 120 years of irrigation. After 120 years of irrigation, OTC and OFL did not leach out of the soil.

The concentration distribution of two PAHs, Phe and Nap, in the profile soil leachate, i.e., groundwater, is shown in Figure 3(b) Nap was gradually leached from the profile soil after 20 years of irrigation, and the leachate concentration gradually increased with the irrigation time, and the concentration of Nap was 8.69×10^{-10} $\mu g\cdot L^{-1}$ after 120 years of irrigation, and the concentration of Phe was also gradually leached from the profile soil after 60 years of irrigation, and the concentration of Phe was 7.74×10^{-10} $\mu g\cdot L^{-1}$ after 120 years of irrigation. Phe was also leached from the profile after 60 years of irrigation, and the leaching concentration gradually increased with irrigation time, and the concentration of Phe was $7.74\times10^{-10}\mu g\cdot L^{-1}$ after 120 years of irrigation.

The concentration distribution of two PAEs, such as DEHP and DnBP, in the profile soil leaching solution, namely groundwater, is shown in Figure 3 (c). After 70 years of irrigation, DnBP was gradually leachable from the profile soil, and the leaching concentration gradually increased with the irrigation time. After 120 years of irrigation, the concentration of DNBP in groundwater was 7.92×10^{-13} $\mu g\cdot L^{-1}$. DEHP gradually leaped from the profile soil after 90 years of irrigation, and the leaching concentration gradually increased with the irrigation time. The concentration of DEHP was 1.92×10^{-12} $\mu g\cdot L^{-1}$ after 120 years of irrigation.

In summary, it can be seen that after 120 years of irrigation, SMZ, Nap, Phe, DEHP, and DnBP were leached from the profile soil to varying degrees, except for OFL, OTC, HCH, and DDT, and the leaching concentration was used as the Predicted Environmental Concentration (PEC) value of the target pollutants, as shown in Table 2.

Table 2. Environmental predicted concentration values of the target pollutants, PEC

Pollutants	PEC_{soil}/ngg^{-1}	$PEC_{water}/\mu gL^{-1}$
OFL	65.2	0
SMZ	16.5	8.81×10^{-9}
OTC	162.1	0
Nap	279.2	8.69×10^{-10}
Phe	241.3	7.74×10^{-10}
DEHP	6.2	1.92×10^{-12}
DnBP	1.12	7.92×10^{-13}
HCH	8.5	0
DDT	97	0

3.1.3 Determination of pollutant toxicity indicator data.

According to relevant studies, algae are generally sensitive to antibiotics, so this study used the toxicity data of algae as the basic toxicity data of antibiotics research (LC_{50}), OFL was 1.44μg L^{-1}, SMZ was 0.03μg L^{-1}, OTC was 0.17 μg L^{-1}; PAHs is chosen from the U.S. Environmental Protection Agency (EPA) ecological toxicity parameter library (http://cfpub.epa.gov/ecotox) to collect more reliable ecological toxicity parameter (LC_{50}) geometric average, Nap is 17032.85 μg L^{-1}, Phe 17046.37 μg L^{-1}; The NOEC values of DnBP and DEHP were collected from the Ecotoxicity Parameter database of EPA. The geometric mean values of NOEC were 110153.39μg L^{-1} for DEHP and 683.18 μg L^{-1} for DnBP. For organochlorine $PNEC_{soil}$, the residue limit of HCH and DDT in the "Environmental Quality Assessment Standard for Edible Agricultural Products" (HJ332-2006) was 0.10 mg/kg. The residue limits of HCH and DDT in the "Sanitary Standard for Drinking Water" (GB5749-2006) were 0.10 mg/kg for $PNEC_{water}$.

3.1.4 Results of ecological risk assessment.

The $PNEC_{water}$ and $PNEC_{soil}$ of the target pollutants were calculated according to Eqs. (2) and (3). The risk of migration to groundwater and its cumulative risk in soil were analyzed using the RQ, and the results of the assessment are shown in Table 3.

Table 3. Risk values for target pollutants in groundwater and soil

Pollutants	$PNEC_{water}$/ μgL^{-1}	$PNEC_{soil}$ /μgkg^{-1}	RQ_{water}	RQ_{soil}
OFL	1.44	410	0	0.16
SMZ	0.03	0.10	2.94×10^{-7}	165
OTC	0.17	85.5	0	1.9
Nap	17.03	34.06	5.12×10^{-10}	8.2
Phe	17.05	630.85	4.53×10^{-10}	0.38
DEHP	110.15	9583	1.74×10^{-14}	0.00065
DnBP	6.83	9.56	1.16×10^{-13}	0.12
HCH	5	100	0	1.7
DDT	1	100	0	97

Table 3 shows that after 120 years of irrigation, most OFL, OTC, HCH and DDT accumulated in the soil and could not migrate to the groundwater. SMZ, Nap, Phe, DEHP and DnBP could move out of 0-100 cm soil profile with low risk values of 2.94×10^{-7}, 5.12×10^{-10}, 4.53×10^{-10}, 1.74×10^{-14} and 1.16×10^{-13}, respectively. The cumulative risks of OFL, OTC, SMZ, Nap, Phe, DEHP, DnBP, HCH and DDT in soil were 0.16, 165, 1.9, 8.2, 0.38, 0.00065, 0.12, 1.7 and 97, respectively.

The RQ was used to evaluate the ecological risk of compounds. The general risk levels were as follows: low risk with RQ between 0.01-0.1, medium risk with RQ between 0.1-1, and high risk with RQ greater than 1. According to the above criteria: OFL, OTC, HCH and DDT have no risk of contaminating groundwater; SMZ, Nap, Phe, DEHP, and DnBP have extremely low risks of groundwater contamination. The accumulation of DEHP in root zone soil had a low risk. The accumulation of OFL, Phe and DnBP in root zone soil had medium risk. The accumulation of SMZ, OTC, Nap, HCH and DDT in root zone soil was at high risk. Therefore, we should give priority to SMZ, Nap, Phe, DEHP and DnBP pollution in groundwater, and SMZ, OTC, Nap, HCH and DDT pollution in soil.

3.2 Health risk assessment

Since antibiotics and PAHs residues in crop plants were not detected, it was not possible to quantitatively assess the health risk from ingestion. Therefore, only PAEs and OCPs pollutants were analyzed for human health risk through ingestion. According to the classification standard [22], the pollutants were classified, DnBP was non-carcinogenic, DEHP, HCH and DDT were carcinogens. According to equations (4) and (5), the risks to human health caused by phthalate esters and organochlorines in corn and wheat kernels through food intake were calculated, and the evaluation results are shown in Table 4.

Table 4. Human health risk assessment of contaminants in maize and wheat kernels for adults and children

Congener	HQ_{maize}		HQ_{wheat}	
	Adults	Children	Adults	Children
DnBP	$(6.16\pm2.02)\times10^{-3}$	$(3.10\pm1.02)\times10^{-3}$	$(4.59\pm1.87)\times10^{-2}$	$(2.31\pm0.94)\times10^{-2}$
DEHP	$(2.42\pm1.46)\times10^{-2}$	$(1.22\pm0.73)\times10^{-3}$	$(2.27\pm1.78)\times10^{-1}$	$(1.14\pm0.49)\times10^{-1}$
HCH	-	-	$(4.23\pm0.61)\times10^{-3}$	$(2.12\pm0.34)\times10^{-3}$
DDT	-	-	$(5.24\pm0.31)\times10^{-2}$	$(2.62\pm0.57)\times10^{-2}$
	CR_{maize}		CR_{wheat}	
	Adults	Children	Adults	Children
DEHP	$(5.76\pm7.94)\times10^{-6}$	$(2.90\pm3.99)\times10^{-6}$	$(6.37\pm0.24)\times10^{-5}$	$(3.20\pm0.64)\times10^{-5}$
HCH	-	-	$(1.23\pm0.16)\times10^{-7}$	$(6.24\pm0.76)\times10^{-7}$
DDT	-	-	$(1.06\pm0.31)\times10^{-6}$	$(5.32\pm0.42)\times10^{-6}$

As shown in Table 4, the non-carcinogenic risk coefficients HQ of the target pollutants for both adults and children did not exceed the recommended permissible levels (HQ<1), indicating that there is no non-carcinogenic risk posed by PAEs and OCPs to the residents of this region through the intake of wheat and maize from the tainted irrigation areas. Among the four contaminants, DEHP had the highest non-carcinogenic risk factor HQ of 0.41 and 0.16 for adults and children, respectively, followed by DnBP, and HCH had the lowest non-carcinogenic risk factor HQ. Among the possible carcinogens DEHP, HCH and DDT, only the carcinogenic risk value CR (0.00061) of DEHP exceeded the standard set by our country by 1×10^{-6}, indicating that DEHP poses a potential carcinogenic risk to human health, and therefore requires attention for food security in the region. The non-carcinogenic risk factor HQ and the carcinogenic risk value CR of PAEs in wheat were both greater than those of maize, indicating that food security concerns caused by PAEs in wheat should be prioritized in this region.

4 Discussion

4.1 Ecological risk assessment of soil contamination

The ecological risk analysis based on Hydrus-1D model showed that 92.02%, 88.68%, 95.89%, 97.74%, 86.47%, 69.53%, 98.21%, 96.56% of OFL, OTC, Nap, Phe, DEHP, DnBP, HCH and DDT were accumulated in soil. However, only 5.11% of SMA remained in soil. OTC, OFL and Phe, SMZ, Nap, DEHP, DnBP, HCH and DDT mainly accumulated in 0-5cm soil layer, 0-10 cm soil layer and 0-20cm soil layer, respectively. Only SMZ gradually leached from the profile soil after 10 years of irrigation, and the leaching concentration gradually increased with irrigation time.

The ecological risk evaluation of the compounds was carried out using the quotient method, and after 120 years of irrigation, OFL, OTC, HCH, and DDT had no risk of contaminating the groundwater; SMZ, Nap, Phe, DEHP, and DnBP had very low risk of contaminating the groundwater; DEHP had low risk of accumulating in the soil of the rhizosphere zone; OFL, Phe, and DnBP had medium The accumulation of OFL, Phe and DnBP in the soil of the rhizosphere zone is of medium risk; the accumulation of SMZ, OTC, Nap, HCH and DDT in the soil of the rhizosphere zone is of high risk. Haddaoui et al. [23]reported that phenanthrene (Phe) was one of the most abundant polycyclic aromatic hydrocarbons (PAHs) in the topsoil (0-10 cm) of wastewater-irrigated soils in Tunisia, while dichlorodiphenyltrichloroethane (DDT) was the predominant organochlorine pesticide (OCP) detected in these soils, findings consistent with the results of this study. Murrell et al. [24]observed that the concentration of di(2-ethylhexyl) phthalate (DEHP) in the Living Filter area irrigated with wastewater was tenfold higher than in the control area, and di-n-butyl phthalate (DnBP) was also detected in corn crops from this region, which aligns closely with the findings of this study. Liu et al. [25], when evaluating soil and various crops in wastewater-irrigated farmlands with irrigation histories of 20, 30, and 40 years in southeastern Beijing, found sulfamethoxazole (SMZ) present in all samples. Lyu et al. [26], analyzing the impact of reclaimed water irrigation on soil and crops in China, identified SMZ and ofloxacin (OFL) as posing the greatest pollution risks among antibiotics, results that are congruent with those of this study.

The discharge of SMZ and other antibiotics may pose risks to organisms with different nutritional levels. Among them, bacteria are the most critical concern. When bacteria come into contact with an antibiotic concentration insufficient to eradicate themselves, it will trigger bacterial resistance, thereby generating and enhancing the ecological risk of antibiotic resistance[27,28]. Zhao et al. [29]significantly reduced the risk of antibiotic resistance gene leaching by using organic fertilizer for black fruit flies, and inhibited its vertical migration risk. This might be an efficient solution to deal with such contaminated farmland. PAHs in the environment are mainly transferred from lower trophic level organisms to higher trophic level organisms through the food chain, thereby increasing the pollution load of the latter. Many types of PAHs have been confirmed to have carcinogenicity, mutagenicity and teratogenicity[30]. Wang et al. [31]found that Nap, Fla and Phe play a more important role than other polycyclic aromatic hydrocarbons in the concentration relationship of nutrients along the food chain; Tang et al. [32]discovered that Pyrochars have strong adsorption capacity for polycyclic aromatic hydrocarbons, and its sources may include pyrolysis treatment of corn straw, cotton straw, etc., which are widely available and cost-effective. At the same time, it can improve soil fertility and increase crop yield. This may be the most suitable treatment method for cultivated land in polluted irrigation areas. PAEs can affect the soil microenvironment by altering the structure of soil microbial communities, impairing the normal functions and metabolism of animal cells, and thereby causing extensive pollution to agricultural soil[33,34]. Besides, PAEs can accumulate further in the human body through the food chain by being accumulated by plants, attacking the endocrine system of humans and causing reproductive damage[35]. Zou et al. [36]prepared an immobilized bacterial agent (IBA) using cedar biochar carriers. This agent increases the relative abundance of PAEs-degrading bacteria (Streptomyces) by altering the soil bacterial community, thereby achieving the purpose of remediation of PAEs-contaminated soil. It can effectively prevent the accumulation of PAEs in plants and vegetables in polluted irrigation areas, thereby affecting human health. OCPs have been banned for a long time ago due to their difficulty in degradation and their tendency to accumulate in organisms. However, a large amount of OCPs and their degradation products still remain in the environment[37,38]. They may be transported through land reclamation, soil erosion, rainwater runoff, river input and environmental deposition, and distributed from terrestrial sources to coastal environments. For humans, OCPs can induce various health problems, including immune deficiency, developmental delay, cardiovascular and endocrine diseases, neurological and behavioral changes, as well as tumors and carcinogenic diseases. In the long run, they can alter the vertebrate and invertebrate communities, leading to the reduction of sensitive species and the increase of drug-resistant species, as well as inhibiting the growth of algae, ultimately resulting in the loss of biodiversity. Currently, the treatment of OCPs mainly involves methods such as adsorption by porous materials or electrochemical remediation, and there are no particularly applicable treatment methods for agricultural farmland use. Only by controlling the related human activities of OCPs can pollution be reduced[39].

4.2 Evaluation of human health risks of soil contamination

The results of the health risk evaluation indicated that there is no non-carcinogenic risk from PAEs and OCPs from the intake of wheat and maize by the residents of the region through the dirty irrigation area. Among the four pollutants, DEHP had the highest non-carcinogenic risk factor HQ, followed by DnBP and HCH had the lowest non-carcinogenic risk factor HQ. Among the possible carcinogens DEHP, HCH and DDT, only DEHP posed the highest non-carcinogenic risk to adults and children, which is consistent with previous studies on vegetables and other plants [40–42]; In addition, the non-carcinogenic risk coefficient HQ and carcinogenic risk value CR of PAEs in wheat were higher than those in maize, indicating that priority should be given to the food security problems caused by PAEs in wheat in this region. Almost all of the noncarcinogenic and carcinogenic risks of PAE to humans are due to direct ingestion of the edible part [40]. PAEs ingestion may pose a particular health hazard to vulnerable populations such as pregnant women and children [43–45]. Even if the overall health risk of PAEs is low in maize and wheat crop systems, the potential harm of PAEs to human health through long-term low-dose exposure may still warrant further attention.

5 Conclusions

This study revealed the interaction mechanism the characteristics of ecological health risk in Wangyanggou sewage irrigation area. Hydrus-1D model prediction showed that only PAEs had no high risk in root zone soil, but all the four pollutants posed potential threats to groundwater. The health risk assessment showed that DEHP had carcinogenic risk, and the risk of PAEs in wheat was significantly higher than that in maize, suggesting that priority should be given to the migration and accumulation mechanism of PAEs in wheat.

In this paper, the impact of typical organic pollutants on soil environmental quality and risk evaluation in Wangyang River basin was studied, but due to time and condition limitations, there are still many deficiencies, and the research can be strengthened in the following aspects:

(1) Most of the ecotoxicity parameters used in the risk evaluation of organic pollutants in Wangyang River basin come from the recommended values of the U.S. EPA, which are based on the relevant experimental data from abroad, and there is a certain difference with the local biotoxicity parameters; Moreover, the method of commercial value relies on a single toxicity data set, and the toxicity data are input as point estimates. Probability-based methods are not employed to quantify the variability of parameters, which may affect the accuracy of the evaluation.

(2) The HYDRUS-1D model lacks the ability to adjust dynamic parameters. In long-term (such as several decades) dynamic simulations, errors may accumulate due to the fixed nature of parameters (such as ignoring the effects of climate change or land use change on soil properties).

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