

Original Research

Sedimentary Records and Ecological Risks of Organochlorine Pesticides in the Sediments of Qingshui River

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Abstract

In this study, considering the first-level tributary of the Ningxia section of the Yellow River (Qingshui River) as the study area, 210 sediment samples were collected during the seasons in 2018. The distribution characteristics, sources, deposition records, and ecological risks of organochloride pesticides (OCPs) were studied using a 25-cm sedimentation column. Results revealed that 19 types of OCPs were detected in the Qingshui River sediments with detected (average) contents of n.d. ~36.527 (2.061) ng×g⁻¹ and a detection rate of 79.05%. The OCPs in the sediments of the entire basin increased with increasing deposition depth. A distinct pollution peak was observed in the deposition depth range of 15-20 cm (1985-1993); the DDT and endosulfan contents considerably changed with increasing deposition depth. Pollution peaks appeared at 15-20 cm (1985-1993) and 10-15 cm (1993-2001). The component analysis results show that OCPs mainly originated from historical residues; however, in recent years, small amounts of lindane, dicofol, endosulfan, and chlordane compounds were noted in the local environment. Using the low-effect range and median method for potential ecological risk assessment, endosulfan was determined to have potential ecological risks, particularly at depths of 5-10 cm, thereby requiring attention and further research.

Keywords: sedimentary column, organochlorine pesticides, sedimentary records, source analysis, ecological risk

Introduction

Rivers play an important role in the earth's ecosystem, with sediments as their important components. However, with socioeconomic development, persistent and biotoxic trace pollutants produced via human activities and natural processes have exerted considerable ecological pressure on river sediments. Organochlorine pesticides (OCPs) have been previously widely produced and used as broad-spectrum insecticides with remarkable results for preventing and controlling diseases, insects, and pests in agriculture and forestry–animal husbandry. However, because OCPs function as typical persistent organic pollutants, the production and use of OCPs pose serious threats to the environment and human health, thereby becoming a recognized global environmental hazard [1, 2]. Although various countries, including China, have started to prohibit the production and use of some OCPs since the 1880s, high concentrations of OCPs can still be detected in different environmental media owing to their high usage, slow degradation, long retention time, and other characteristics. In particular, OCPs comprise a class of pollutants with the highest detection rate in the global environment [3, 4]. In China, dichlorodiphenyltrichloroethanes (DDT), endosulfan, hexachlorocyclohexane (HCH), chlordane, and hexachlorobenzene (HCB) are extensively produced and used OCPs, among which DDT and HCH are the most synthesized and used OCPs. DDTs and HCH produced in China account for about 33% and 20% of global production, respectively [5]. Sediments are important parts of the water ecology and have received considerable research attention worldwide [6–8]. Research on pesticide residues in China's sediments began in the 1990s. To date, researchers have investigated the current status of OCP residues in typical water areas, such as key watersheds, lakes, estuaries, wetlands, bays, and water sources, and determined the existence of varying degrees of OCP residues in the sediments in Chinese water areas [9–15]; these residues have mainly originated from the early use of pesticides. Moreover, new inflows of similar DDT pesticides have been noted. OCPs were widely used in Ningxia in the 1970s and were still used in the 1980s. Their extensive use polluted the soil and surface water. In 1987, Wang et al. investigated the OCP pollution levels in the surface water of Yinchuan City, Guyuan City, and Shizuishan City of the Ningxia Hui Autonomous Region, thereby detecting 0.076–0.984 $\mu\text{g}\times\text{L}^{-1}$ HCHs, whereas DDTs were not detected [16]. In 2013, Li et al. studied the OCPs in cellar and reservoir waters in the southern mountainous area of Ningxia and the water body in the Ningxia section of the Yellow River. They obtained the HCH content of 0–8.46, 0–15.60, and 0–6.92 $\text{ng}\times\text{L}^{-1}$ and DDT content of 0–73.50, 0–31.24, and 0–7.52 $\text{ng}\times\text{L}^{-1}$, respectively [17]. However, OCPs in the water's sediments in Ningxia have not yet been reported. The Qingshui River basin is characterized by a fragile ecology, backward economic development, and the largest number of low-income

people in Ningxia. This basin was selected to represent a typical arid and economically underdeveloped area. Considering the research significance of this basin, as well as the aforementioned previous studies and lack of studies on the OCPs in the sediments of the waters in Ningxia, this study focused on investigating the sediments of the first branch of the Ningxia Section of the Yellow River (Qingshui River) to clarify the pollution status and vertical distribution of OCPs in the sediments. Based on the sedimentary characteristics, composition characteristics, and source analysis, the OCP residual information in the deposition column was interpreted to obtain the historical pollution information of the Qingshui River, thereby providing a scientific basis for its effective control and risk management of OCPs.

Materials and Methods

Study Area

Qingshui River is the largest tributary of the Yellow River in Ningxia and is located south of the Ningxia Hui Autonomous Region. It originates from the Heici Ditch in Guyuan City, Ningxia, at the northeast foot of Liupan Mountain, flowing north through Guyuan City, Wuzhong City, and Zhongwei City, and finally joining the Yellow River in Zhongning County, Zhongwei City (Fig. 1). Qingshui River is the mother river of Guyuan City. The river has a drainage area of 14,481 km^2 , a river length of 320 km, and an average river channel gradient of 1.49%. The Qingshui River flows from south to north through the southern mountainous region and most of the central arid zone of Ningxia. The Qingshui River basin exhibits low and unstable grain production and is characterized by a fragile ecology, backward economic development, and the largest number of low-income people in Ningxia.

Sample Collection and Preservation

Based on the research objectives combined with the geographical location, hydrological characteristics, and water environment characteristics of the Qingshui River basin, seven sampling sections (Fig. 2) were selected from representative landform locations, namely the Kaicheng (KC), Dongjiao (DJ), Sanying (SY), Liwang (LW), Tongxin (TX), Changshantou (CST), and Quanyanshan (QYS) sections, covering the main nodes of the upper, middle, and lower reaches and the entrance to the Yellow River estuary. A total of 21 high-resolution column samples were collected from seven sections of the Qingshui River using the SA0203 sediment sampler with a diameter of approximately 5 cm during the spring flood (April), summer flood (August), and dry (December) seasons in 2018. The sampler takes a complete core from the river bottom vertically and as gently as possible to ensure that

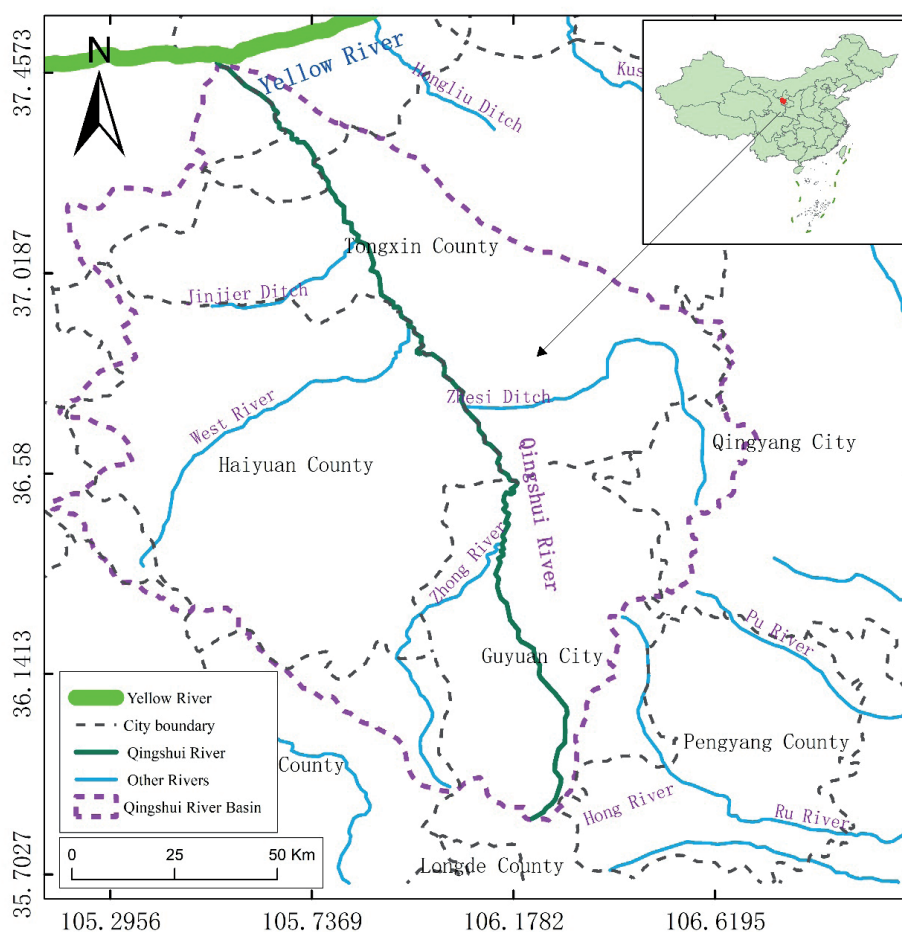


Fig. 1. Map of Qingshui River Basin.

the sedimentary sequence is not disturbed. After the complete mud core was raised to the water surface, the site used the bottom-top core device to push the mud core upward from the bottom. The depth of the collected sediment was 25 cm, and the samples were divided immediately after collection. The samples were divided into slices with a thickness of 5 cm, resulting in a total of 105 sediment samples for the determination and analysis of OCPs. Considering the limited river runoff, low velocity, minimal flow interference, and relatively stable sedimentary environment during the dry season, a single set of samples (140 in total) collected from depths of 0 to 100 cm was chosen for sediment dating. The collected samples were carefully sealed in polyethylene bags, stored with ice cubes in an incubator during transportation back to the laboratory, and subsequently frozen at -20°C prior to analysis.

Analytical Techniques and Quality Assurance for Organochlorine Pesticide Analysis

Standard Materials and Reagents

The organic solvents used in the experiment (acetone and n-hexane) are agricultural residues. First, the quartz

sand was screened through 80 mesh, then baked in a muffle furnace at 400°C for 4 h. After cooling, it was placed in glass bottles with stoppers and sealed for preservation. The packing material of the magnesium silicate purification column was magnesium silicate (1,000 mg), and the column volume was 6-10 mL. The purity of the copper powder (Cu) was 99.5%. Prior to use, the oxide on the surface of the copper powder was removed with a nitric acid solution (high-grade pure nitric acid was mixed with experimental water in a 1:1 volume ratio). The acid was removed by rinsing with laboratory water, then cleaned with acetone, and dried with high-purity nitrogen (purity of 99.999%) for use. The experimental water used was newly prepared ultra-pure water. Standard OCP samples were purchased from the Ministry of Agriculture Environmental Protection Research and Monitoring Institute; Beijing Tanmo Quality Control Technology Co., Ltd.; and Beijing Coast Hongmeng Standard Material Technology Co., Ltd.

Sample Pretreatment

First, 20 g of air-dried, ground, and sifted (80 mesh) sediment sample was accurately weighed, then transferred into the Soxhlet extraction sleeve,

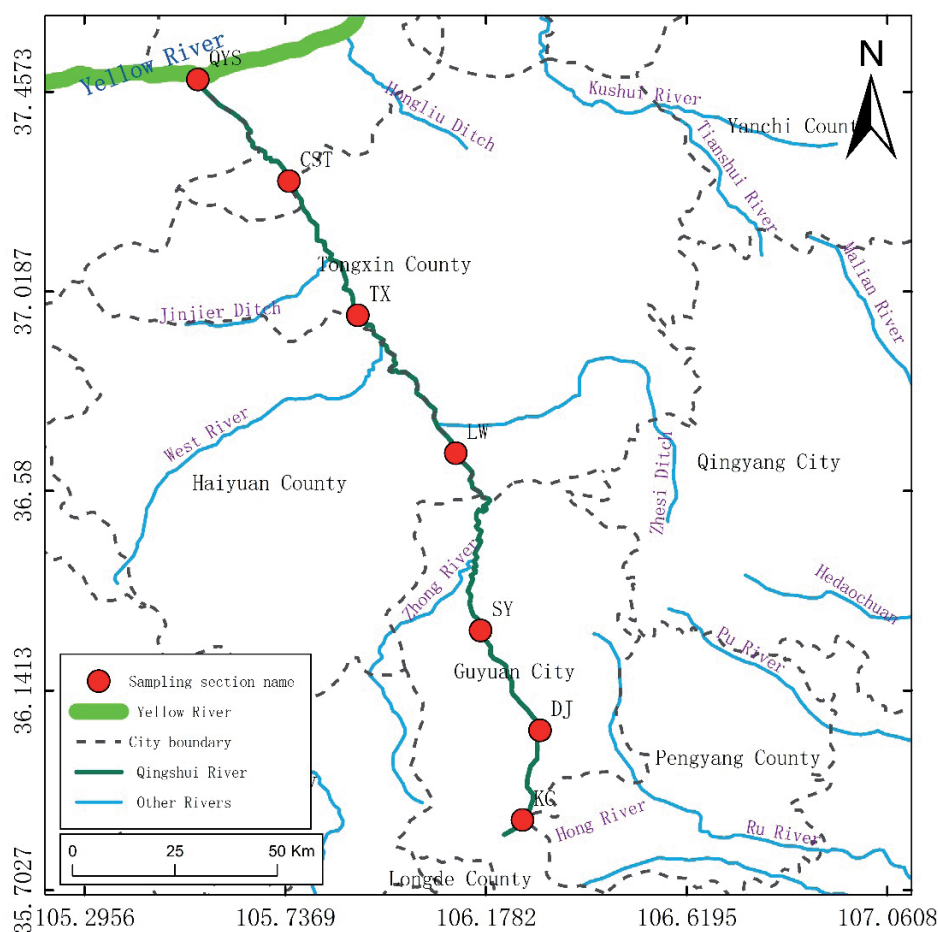


Fig. 2. Distribution map of sampling points in Qingshui River Basin.

and the intermediate liquid of the substitute was added. The intermediate solution of the substitute was diluted 2,4,5,6-tetrachloro-*m*-xylene and dibutyl chlorinate with a mixture of *n*-hexane-acetone (volume ratio 1:1). It was placed in the return tube of the Soxhlet extractor, then 100 mL of *n*-hexane-acetone mixed solvent (volume ratio 1:1) was added to the round-bottom solvent bottle and extracted for 16-18 h. The reflux rate was controlled at 4-6 times·h⁻¹, and after the reflux heating was ceased, the round-bottom solvent bottle was removed. The extracted liquid was concentrated to 2 mL on a rotary evaporator (temperature 40°C). The concentrated liquid was transferred to a graduated concentrator with a disposable dropper, and the bottom of the rotary evaporator was rinsed twice with a small amount of *n*-hexane-acetone mixed solvent (volume ratio 1:1). Then, all the concentrated liquid was combined and concentrated to about 1 mL with nitrogen blowing. The magnesium silicate purification column was fixed on the solid-phase extraction device, and the purification column was first washed with 4 mL of *n*-hexane, then 5 mL of *n*-hexane was added. After the column was full, the flow control valve was closed and soaked for 5 min, and the control valve was slowly opened. At this time, about 2 g of copper powder (purity of 99.5%) was added

to the upper end of the chromatographic column to remove any sulfur from the extraction solution. Another 5 mL of *n*-hexane was added, the control valve was closed, and the effluent was discarded before the copper powder was exposed to air. The concentrated liquid was transferred to the small column, and the concentrated vessel was washed with 2 mL *n*-hexane in batches. All the liquid was transferred to the small column. The control valve was opened, and the contents were eluted with 9 mL of hexane-acetone mixture (volume ratio 9:1). Then, the control valve was slowly opened so the eluent was immersed in the packing layer. The control valve was closed for about 1 min, then opened to collect all the eluent. After purification, the test solution was concentrated once again according to the steps of rotary evaporation concentration, and an appropriate amount of internal standard intermediate solution (pentachloronitrobenzene diluted with a volume ratio of 1:1 of *n*-hexane-acetone mixed solvent) was added. Finally, the volume was fixed to 1.0 mL and transferred to a 2 mL sample bottle for instrument analysis. Preparation of the blank sample: Quartz sand was used instead of the actual sample, and the blank sample was prepared following the same steps as the preparation.

Instrumental Analysis Methods for Organochlorine Pesticides

The samples were analyzed via gas chromatography–mass spectrometry (GCMS-QP2010Plus, Shimadzu Co., Ltd., Japan). The chromatographic column was a quartz capillary column (30 m × 0.25 mm × 0.25 μm) with a stationary phase of 5%-phenyl-methylpolysiloxane. The chromatographic conditions were: splitless injection of the automatic sampler, injection volume = 1.0 μL, and inlet temperature = 250°C. For the column procedure, the temperature was set to 120°C for 2 min, increased to 180°C at a rate of 12°C·min⁻¹ for 5 min, to 240°C at a rate of 7°C·min⁻¹ for 1 min, to 250°C at a rate of 1°C·min⁻¹ for 2 min, and finally, to 280°C for 2 min. The column flow rate was set to a constant value of 1.0 mL·min⁻¹, and the carrier gas was high-purity helium. The mass spectrometry conditions were as follows: electron impact source, ion source temperature = 230°C, ionization energy = 70 eV, interface temperature = 280°C, four-pole temperature of 150°C, mass-scanning range = 45-450 amu, solvent delay time = 5 min, and selected-ion monitoring scanning mode.

Quality Assurance (QA)/Quality Control (QC)

Quality control of the method was carried out to verify the reliability of the measurement method and the accuracy of the analysis data. The QA/QC of the samples was performed according to Soil and Sediment–Determination of OCPs–Gas Chromatography–Mass Spectrometry (HJ835-2017). The entire analysis process was controlled by method blank, label blank, reference material, and parallel sample. The quantitative results of target compounds were corrected by recovery rate. The limit of detection (LOD) of OCPs in the sediment samples was 0.006-0.07 ng·g⁻¹, and the limit of quantitation (LOQ) was 0.024-0.28 ng·g⁻¹. The average recovery rate of OCPs in the 20 g sediments was 69.2-116%.

²¹⁰Pb Isotopic Dating

The dating of the columnar sediment samples was performed by the State Key Laboratory of Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. The analysis instrument was a gamma spectrum analysis system comprising a high-purity germanium well detector (Ortec HPGe GWL) with high resolution and low background value produced by the EG&G company in the United States, an Ortec919 spectrum controller, and a computer composed of a 16k channel multichannel analyzer. The test items and conditions were as follows: ²¹⁰Pb, 46.5 keV; ²²⁶Ra, 352 KeV; and ¹³⁷Cs, 662 keV. ²¹⁰Pb is a naturally radioactive uranium-series element with a half-life of 22.3 years. It is an ideal tracer for studying the deposition rate and flux of sediments in a century-scale environment of modern human

activities. The deposition rate, according to the specific radioactive activity of excess ²¹⁰Pb, can be calculated using two modes: constant initial concentration (CIC) and constant rate of supply (CRS). The CIC model is more suitable when the main source of the sediments is surface erosion. In this case, the source material obviously affects the specific radioactive activity of ²¹⁰Pb in the sediments. In particular, the ²¹⁰Pb content in the sediments increases significantly with the content of the source material. The CRS model is used when atmospheric deposition is the main source of the sediment. The ²¹⁰Pb content provided by provenance did not affect the total ²¹⁰Pb content in the sediment. Since the beginning of this century, the sedimentation rate of each period has been greatly influenced by the environment [18-20]. The Qingshui River is not a closed system, so its sedimentation rate changes with time. Therefore, the CIC model was used in this study to calculate the average sedimentation rate of the Qingshui River basin in the last hundred years. The results of the deposition age showed that the average deposition rate was 0.64 cm·a⁻¹ with the deposition age of 1977-2017.

Results and Discussion

Pollution Characteristics, Pollution Levels, and Historical Tracing of OCPs in Sediments

Pollution Characteristics and Historical Tracing of OCPs

The vertical variations of the OCPs in the sedimentary column reflect the pollution history of the Qingshui River. Nineteen OCPs were detected in the samples of the Qingshui River sedimentary column, namely α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDT, o,p'-DDT, m,p'-DDD, p,p'-DDD, p,p'-DDE, o,p'-DDE, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, cis-chlordane (CC), trans-chlordane (TC), HCB, and heptachlor epoxide, as shown in Table 1. HCH, DDTs, chlordane, and endosulfan had relatively high detection quantities and detection rates. The DDT and endosulfan detection rates were higher in the spring flood season, whereas those of HCHs and chlordane were higher in the dry season. The detection ranges (average) of the OCPs in Qingshui River were n.d. ~36.527 (2.061) ng×g⁻¹ with a detection rate of 79.05%. The detection rates of different seasons followed the order spring flood season > dry season > summer flood season. According to the spatial and temporal distribution of the OCPs in the sedimentary column (Figs. 3, 4, 5, 6, and 7), the detection amount of the OCPs was different in different research sections, sedimentary depths, and seasons. The depth ranges of the highest detection amount of OCPs in the KC, DJ, SY, LW, TX, CST, and QYS sections were 10-15, 20-25, 5-10, 0-5, 15-20, 0-5, and 10-15 cm, respectively. The depth range of the highest detection amount

Table 1. Statistics of OCPs content in the sediment column of Qingshui River ($\text{ng}\cdot\text{g}^{-1}$).

Composition	Minimum	Maximum	Average	Standard deviation	Detection rate (%)			
					Spring flood season	Summer flood season	Dry season	All samples
α -HCH	n.d.	0.863	0.018	0.105	5.71	0.00	5.71	3.81
β -HCH	n.d.	1.188	0.014	0.119	8.57	0.00	0.00	2.86
γ -HCH	n.d.	2.203	0.090	0.289	2.86	8.57	25.71	12.38
δ -HCH	n.d.	1.484	0.026	0.172	2.86	2.86	2.86	2.86
p,p'-DDT	n.d.	2.747	0.170	0.550	11.43	8.57	11.43	10.48
o,p'-DDT	n.d.	11.431	0.140	1.119	31.43	0.00	11.43	14.29
p,p'-DDE	n.d.	12.482	0.317	1.590	20.00	22.86	25.71	22.86
o,p'-DDE	n.d.	10.960	0.115	1.072	5.71	2.86	0.00	2.86
p,p'-DDD	n.d.	13.665	0.234	1.383	25.71	2.86	0.00	9.52
m,p'-DDD	n.d.	0.547	0.010	0.067	11.43	0.00	0.00	3.81
CC	n.d.	0.380	0.025	0.079	2.86	5.71	22.86	10.48
TC	n.d.	0.689	0.025	0.090	2.86	17.14	17.14	12.38
Endosulfan I	n.d.	13.335	0.523	1.831	74.29	0.00	0.00	24.76
Endosulfan II	n.d.	1.358	0.025	0.157	2.86	5.71	0.00	2.86
Aldrin	n.d.	1.681	0.032	0.176	11.43	2.86	8.57	7.62
Dieldrin	n.d.	0.929	0.039	0.154	40.00	0.00	0.00	13.33
Endrin	n.d.	7.777	0.096	0.791	0.00	0.00	5.71	1.90
Heptachlor epoxide	n.d.	2.438	0.045	0.267	2.86	0.00	11.43	4.76
HCB	n.d.	11.902	0.116	1.161	8.57	2.86	0.00	3.81
HCHs	n.d.	2.203	0.149	0.372	17.14	11.43	31.43	20.00
DDTs	n.d.	24.625	0.986	3.117	65.71	31.43	42.86	46.67
Chlordane	n.d.	0.755	0.049	0.130	5.71	22.86	34.29	20.95
Endosulfan	n.d.	13.335	0.547	1.839	74.29	5.71	0.00	26.67
OCPs	n.d.	36.527	2.061	4.473	94.29	60.00	82.86	79.05

Note: n.d. means not detected.

and average annual maximum value of the entire basin in the spring flood, summer flood, and dry seasons were 5-10, 15-20, 20-25, and 15-20 cm, respectively.

Figs. 5, 6, and 7 show that the average annual detections of different OCPs in the sedimentary columns of the entire basin present different distribution characteristics. In particular, the DDT and endosulfan concentrations of 0.219-1.592 and 0.157-1.206 $\text{ng}\cdot\text{g}^{-1}$ were more noticeable with the changes in the sediment depth. For example, the DDT content at a depth of 15-25 cm was higher than at a depth of 0-15 cm. The highest peak occurred in the depth range of 15-20 cm, indicating the higher DDT inflow during 1985-1993. The peak value of endosulfan was observed at a deposition depth of 10-15 cm. The HCH and chlordane detection quantities of 0.066-0.307

and 0.012-0.085 $\text{ng}\cdot\text{g}^{-1}$, respectively, did not change considerably with increasing depth, and no distinct pollution peak was noted. Low peaks appeared in the depth range of 20-25 and 5-10 cm, respectively. The OCP content in the entire basin largely increased with increasing deposition depth. The content of 1.474-2.699 $\text{ng}\cdot\text{g}^{-1}$, which was within the sedimentation range at a depth of 10-20 cm, exhibited an obviously increasing trend from 1985 to 2001 with increased OCP inflow. In particular, in the depth range of 15-20 cm (1985-1993), the increase is obvious, indicating an obvious pollution peak and slight fluctuation of the content of the other layers. In the entire basin, the OCP detection quantities of the CST and LW research sections were relatively high, particularly the DDT detection quantity of these two research sections.

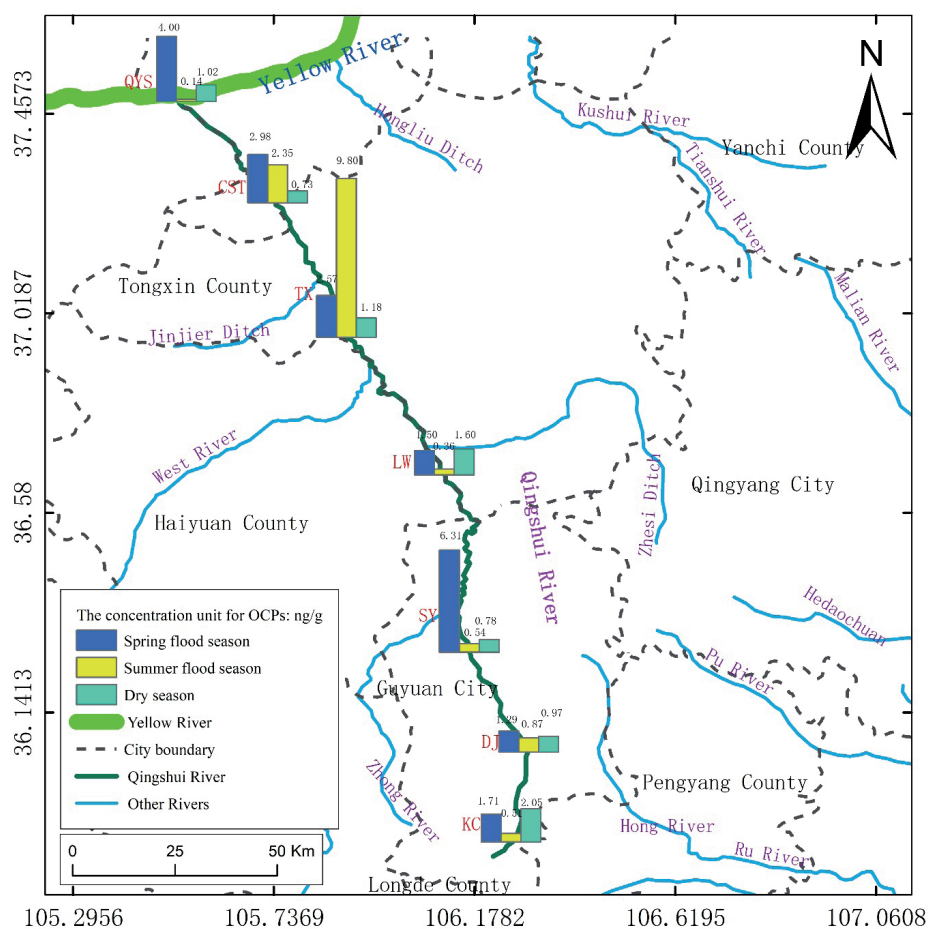


Fig. 3. Seasonal Variation of Average OCP Concentrations in the 0-25 cm Sedimentary Column of the Qingshui River.

This may be attributed to the relatively wide river surface of these two research sections and slow water flow, which are conducive to the deposition of OCPs. In particular, these sections are farmlands because they are relatively far from the towns and surrounding areas. The continuous inflow of farmland drainage ditch increased the OCP content and deposition. Furthermore, some of the other studied sections are near cities with low pesticide use and in river reaches with strong currents, which are not conducive to OCP deposition. In general, the OCP content was relatively low in the study sections near towns or with large water flow and relatively high in the study sections with more farmland and slow water flow.

Table 1 shows that the detection rates of the four typical OCPs followed the order DDTs (46.67%) > endosulfan (26.67%) > chlordane (20.95%) > HCHs (20.00%). The average detected concentrations followed the order: DDTs ($0.986 \text{ ng} \times \text{g}^{-1}$) > endosulfan ($0.547 \text{ ng} \times \text{g}^{-1}$) > HCHs ($0.149 \text{ ng} \times \text{g}^{-1}$) > chlordane ($0.049 \text{ ng} \times \text{g}^{-1}$). DDT and endosulfan showed relatively high detection rates and quantities in the sedimentary columns, reflecting their historically wide use in the area. These compounds can enter the sediments through sewage discharge, atmospheric deposition, runoff, and other routes. A total of 270 kt of industrial DDT was used in

China before it was banned in 1983 [21]. Subsequently, industrial DDTs were mainly used for malaria control, rust prevention paint, and synthetic dicofol. From 1988 to 2002, approximately 80% of DDTs produced in China were used to produce dicofol, and approximately 80 million tons of DDTs derived from dicofol were invested in agricultural land [22]. Several studies have shown that dicofol DDTs have become a new major source of DDT pesticide residues in Chinese environmental media and that controlling the use of dicofol will effectively prevent the pollution of DDTs in China [23]. Moreover, studies have discussed a positive correlation between the DDT residue in the sediment column and the amount used in China from 1974 to 1984 [20] and the downward trend of DDTs in the sediment of the Qingshui River from 1993 to 2001. This phenomenon can be ascribed to the tendency of some historical pesticides to degrade in the environment, thereby reducing the concentrations in the sedimentary columns. The rapid increase in the DDT concentration from 1977 to 1993 was associated with the large-scale use of DDTs during this period, the continuous inflow of DDTs from the basin, and the continuous loss of historical DDTs in the soil due to land reclamation. Therefore, the DDT inflow in this area may mainly depend on historical residues, soil erosion, and runoff. Approximately 30 years are required

to degrade 95% of the DDTs in the environment [24]. Therefore, the amount of DDT used in the Qingshui River basin is also expected to affect the DDT residue in the sedimentary column. Compared with the first 20 of the 40 years studied, the Qingshui River sediments' DDT content has decreased in the last 20 years.

The HCH content is relatively high in sediments in the depth range of 20-25 cm (1977-1985). The HCH content decreased considerably with the decreasing deposition depth. In China, 4,460 tons of industrial HCHs were produced and used from the 1950s until OCPs were banned in 1983 [25]. In particular, γ -HCH (99.9%)

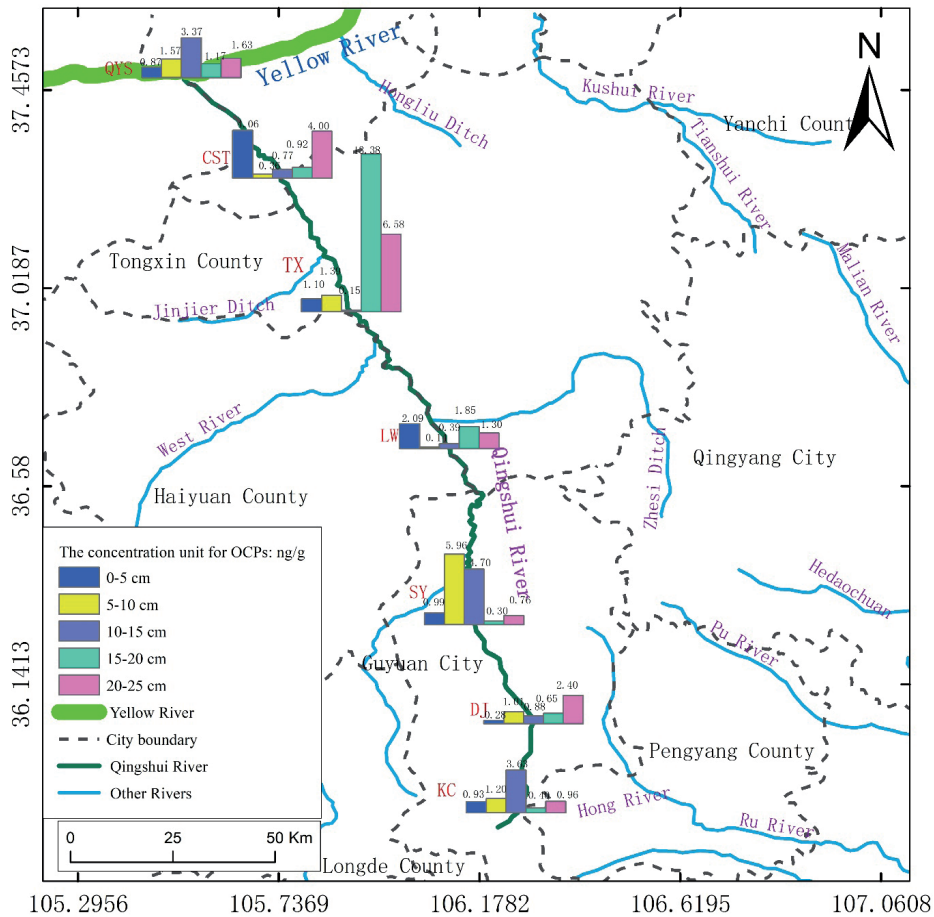


Fig. 4. Mean Annual Concentrations of OCPs in Sediments at Various Depths in the Qingshui River.

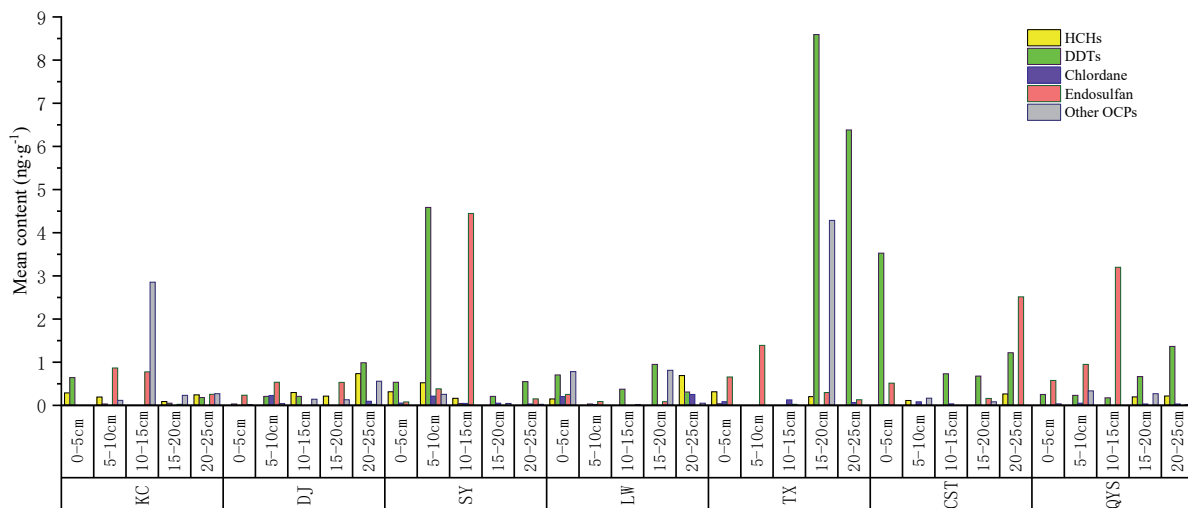


Fig. 5. Content of OCPs in the sediment column of Qingshui River.

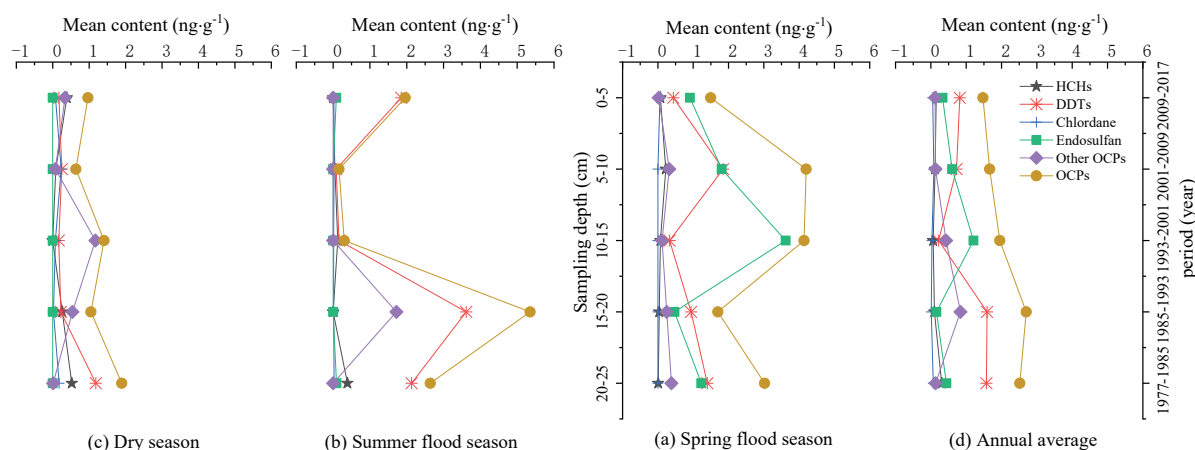


Fig. 6. Content of OCPs in the sediment column of Qingshui River over different periods.

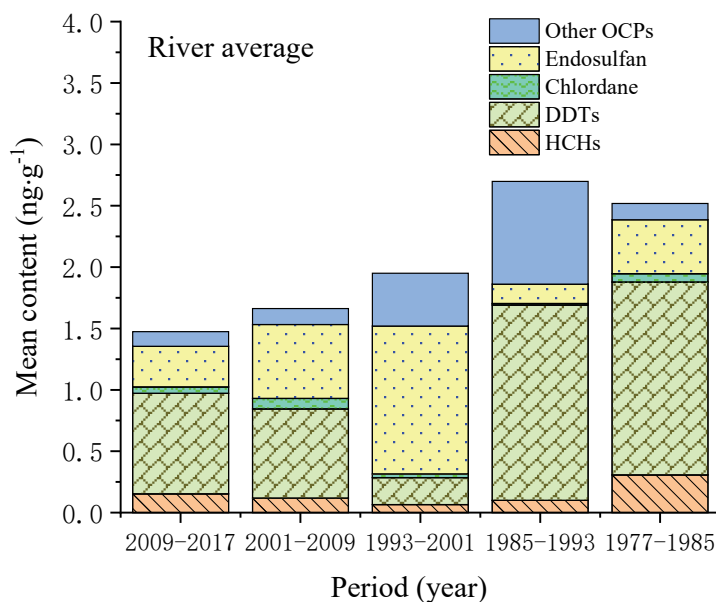


Fig. 7. Content of OCPs in the sediment column of Qingshui River over different periods.

has been used for agricultural pest control since the 1990s [26]. Although historical HCH use affects the pesticide residues in the sediment column, it can also be related to the runoff in the soil surface and pesticide residues in the soil. Reportedly, approximately 20 years are required to degrade 95% of HCHs in the environment [24]. Therefore, the amount of HCHs used will affect the residual amount of HCHs in the sedimentary column. The HCH content in the sediments of the Qingshui River has decreased substantially in the past 30 years.

Endosulfan is mainly used as an agricultural insecticide to control different insects, including corn earworms, cotton bollworms, and potato beetles [27]. The cumulative consumption amount of endosulfan was approximately 25,700 tons from 1994 to 2004 [24]. The production and use of endosulfan was banned in 2013 [28]. The detected amount in the sediments of Qingshui

River at a depth of 10-15 cm was significantly higher than that in the other layers. The corresponding pollution peak period was from 1993 to 2001, which was related to its extensive use in this period and the planting of corn, potatoes, and other crops in the surrounding farmland.

Pollution Levels of OCPs

From the comparison of the OCP content in the sediment of the Qingshui River and other bodies of water (Table 2) [23, 29-37], the mean values of HCH, DDT, chlordane, endosulfan, and total OCP content in the Qingshui River sediment were 0.15, 0.99, 0.05, 0.55, and 2.06 $\text{ng}\times\text{g}^{-1}$, respectively. The average values of the HCH, DDT, chlordane, endosulfan, and total OCP contents in the Qingshui River sediment were considerably lower than those observed in the referenced

Table 2. Comparison of OCPs content in the sediment of Qingshui River with other waters (ng·g⁻¹).

Sources	HCHs	DDTs	Chlordane	Endosulfan	OCPs
Zhanjiang Bay [23]	n.d.-16.33 (5.81)	n.d.-173.19 (26.90)	-	-	n.d.-198.03 (38.94)
Taihu Lake [29]	3.2-64.5 (12.1)	0.2-55.9 (7.6)	1.5-32.4 (6.0)	0.4-5.6 (0.8)	16.3-96.9 (35.0)
Tuojiang River [30]	2.83-86.0 (20.12)	0.34-40.85 (3.26)	-	-	3.17-126.89 (23.38)
Baiyangdian Lake [31]	0.41-30.46 (7.01)	n.d.-2.66 (0.45)	-	-	1.22-52.45 (16.12)
Chaohu Lake [32]	-	-	-	-	2.55-19.03 (6.08)
Dongping Lake [33]	2.30-5.74 (4.86)	69.10-134.52 (87.99)	-	-	73.23-140.26 (-)
Jianhu Lake [34]	n.d.-15.8 (1.32)	-	-	-	n.d.-1920.00 (340.00)
Huaihe River [35]	2.54-13.91 (7.52)	0.016-2.54 (0.45)	n.d.-0.47 (0.10)	n.d.-0.12 (0.04)	4.14-14.38 (8.15)
Beiluo River [36]	0.02-0.84 (0.17)	0.20-59.74 (4.35)	0.003-0.27 (0.07)	0.02-5.48 (1.29)	0.53-61.68 (8.68)
Qiantang River [37]	6.13-51.65 (20.82)	1.58-45.34 (14.67)	-	-	2.12-65.96 (20.98)
Qingshui River	n.d.-2.20 (0.15)	n.d.-24.63 (0.99)	n.d.-0.76 (0.05)	n.d.-13.34 (0.55)	n.d.-36.53 (2.06)

Note: 1) The average value in brackets; 2) „-“ means no data; 3) n.d. means not detected.

water bodies, with values of 8.86, 18.21, 2.06, 0.71, and 55.26 ng·g⁻¹ respectively. Moreover, the HCHs and chlordane levels in the sediment column and surface sediments of the Qingshui River were lower than those in other waters. In addition, the DDT content in the Qingshui River sediment was considerably lower than that in the Taihu Lake [29], Tuojiang River [30], Dongping Lake [33], Beiluo River [36], Zhanjiang Bay [23], and Qiantang River [37] but higher than that in the Baiyangdian Lake [31] and the Huaihe River [35]. The amount of endosulfan detected in the Qingshui River sediment was considerably lower than that in the Taihu Lake [29] and the Beiluo River [36] yet higher than that in the Huaihe River [35]. The OCP content detected in the Qingshui River sediment was maintained at a low level, falling below the average concentrations found in the sediment samples from the waters listed in the table. The low OCP content in the sediments of the Qingshui River may be ascribed to the large water exchange ratio of the Qingshui River basin, high flow rate in spring and summer, persistent pollutants, and small deposition amount of the OCPs. Moreover, the Qingshui River basin belongs to the arid region of the Loess Plateau, which has relatively poor soil and crops that can only be harvested once a year. In addition, some areas around the basin are barren valleys that cannot cultivate crops, resulting in the low use of OCPs. Therefore, the OCP pollution in the Qingshui River basin is relatively low, with main contributions from DDTs and endosulfan.

Main Composition and Source of OCPs in the Sediments

OCPs in sediments are mainly terrestrial inflows, which are noted after the weathering erosion of farmland soil applied with OCPs. OCPs flow into rivers and lakes along with surface runoff. Studying the ratio of the parent compounds and their metabolites will help determine old and new sources of pollution [38]. DDTs, HCHs, chlordane, and endosulfan all comprise different isomers or metabolites. The proportion of these isomers and metabolites can further determine the source of OCP.

As a major environmental residual OCP, HCHs are mainly derived from the pesticides from industrial pure HCH and γ -HCH (99.9%) [36]. In the Qingshui River sediments, α -HCH, β -HCH, γ -HCH, and δ -HCH account for 11.88%, 9.90%, 60.40%, and 17.82%, respectively. γ -HCH had a relatively high detection amount, which can be related to the γ -HCH inflow. Among the isomers of HCHs, β -HCH showed the strongest stability and resistance to degradation. The high content of β -HCH indicated that the contamination was mostly from historical inflows. By calculating the ratio of α -/ γ -HCH, it can be concluded that HCHs in the environment are attributed to early HCHs from industrial products, pesticide γ -HCH, or recent sources [39]. If α -/ γ -HCH in the sample was 4-7, the HCH source is considered an industrial product.

If α/γ -HCH is less than 4, the HCH source is γ -HCH [40]. The α/γ -HCH ratios were all between 0 and 0.99 from the analysis of the samples with detected HCHs in the seven sections of the Qingshui River in spring flood, summer flood, and dry seasons. The results showed that the pesticide γ -HCH flowed in the Qingshui River basin in recent years and was enriched in the sediment; however, low amounts were noted. This can be ascribed to the wide use of industrial HCHs in agricultural activities in the 1950s-1980s, whereas γ -HCH was used in agriculture for pest control from the 1990s [20].

The DDTs are the sum of DDT, DDE, and DDD. Among them, DDE and DDD are the degradation products of DDT under aerobic and anaerobic conditions, respectively [41]. If $DDD/DDE > 1$, the metabolic environment is mainly anaerobic; otherwise, the metabolic environment is mainly aerobic [42]. If $DDT/(DDE + DDD)$ is greater than 1, there are new DDT sources; otherwise, DDT comes from historical residues [43]. The o,p' -DDT/ p,p' -DDT ratio can be used to determine whether the DDTs are derived from dicofol use. In industrial DDTs, the o,p' -DDT/ p,p' -DDT ratio was 0.2-0.3. Meanwhile, in dicofol, the ratio of o,p' -DDT/ p,p' -DDT was 7.0 ± 2.2 [21]. DDTs are the OCPs with the highest detection rate in Qingshuihe sediments. Their isomer content is as follows: p,p' -DDE (32.12%) > p,p' -DDD (23.74%) > p,p' -DDT (17.20%) > o,p' -DDT (14.23%) > o,p' -DDE (11.65%) > m,p' -DDD (1.06%); among these, the DDE proportion was relatively high because DDE is more difficult to degrade in the environment than DDD is. By calculating the proportions of DDT and its metabolites in the sediment samples of the Qingshui River in the spring flood, summer flood, and dry seasons, the o,p' -/ p,p' -DDT ratios ranged from 0 to 1.32, which were all less than 0.3 except for 1.32 in the SY study section during the spring flood season. This indicates that DDT pollution in the Qingshui River basin was mainly caused by industrial DDT residues, and local areas (SY study section) were contaminated by dicofol. The calculated $DDT/(DDE + DDD)$ value was between 0 and 31.27, and 83% of the $DDT/(DDE + DDD)$ value is lower than 1, indicating that the DDT pesticides in the study area were mainly derived from historical use residues, sediment release, or atmospheric deposition. The $DDT/(DDE + DDD)$ ratios in some areas (KC section at a depth of 0-5 cm, SY section at a depth of 0-10 cm, TX section at a depth of 20-25 cm, and CST section with depths of 10-15 and 20-25 cm) were higher than 1, especially in the CST section, which was as high as 31.27. This indicates that the DDT pesticides may have flowed into the sediments of these sections in recent years, resulting in the DDT enrichment in the sediments of the Qingshui River. As DDTs have been banned in agriculture for more than 30 years owing to their stable chemical properties, DDTs are mainly ascribed to their residual source in the atmosphere, soil, and other environmental media near this area, which entered

the water with atmospheric deposition, surface runoff, and scouring. For all sediment samples with detected DDTs, the DDD/DDE of the TX section (deposition depth of 15-20 cm) and CST section (deposition depth of 20-25 cm) were 1.25 and 10.94, respectively, which are both greater than 1, indicating a mainly anaerobic metabolic environment. In other sediment samples, DDD/DDE was 0-0.57, less than 1, indicating that the DDTs were mainly ascribed to aerobic biodegradation. Based on the above-mentioned analysis, the DDTs in the Qingshui River sediment were mainly attributed to the joint contribution of the historical industrial DDTs and dicofol.

TC degrades more easily than CC in environmental media. As such, the ratio between them is often used to distinguish historical residues and inflows from new sources [44]. Chlordane is considered to be of older origin when the CC/TC ratio is greater than 1; that is, chlordane residues are considered to be derived from earlier pollution [30]. The content of the chlordane isomer in the Qingshui River sediments showed that the CC content (50.27%) was slightly higher than the TC content (49.73%). The chlordane samples detected in the seven sections of the Qingshui River in the spring flood, summer flood, and dry seasons were analyzed. The CC/TC values were 0-2.15, of which $CC > TC$ has been noted for 45% of the samples, whereas $TC > CC$ was noted for 55% of the samples at the specific sampling depths of 0-25 cm for the SY section, 0-5 and 20-25 cm for the LW section, 5-10 and 20-25 cm for the QYS section, 5-10 cm for the DJ section, and 10-20 cm for the CST section. This suggests that the chlordane content in the sediments of the Qingshui River is partly ascribed to early pollution; however, a small amount of chlordane inflow has been noted in recent years.

Industrial endosulfan is mainly composed of endosulfan I (approximately 70%) and endosulfan II (approximately 30%) [29]. Studies have shown that the degradation rate of endosulfan differed in different types of soil, with a higher degradation rate for endosulfan I and the metabolite of endosulfan salt [45]. The endosulfan I/endosulfan II ratio of industrial endosulfan was approximately 2.33, which can be used to determine the duration of endosulfan contamination in the soil and sediment [29]. The endosulfan isomer contents in the Qingshui River sediments were as follows: endosulfan I (95.47%) > endosulfan II (4.53%). The proportion of endosulfan I was significantly higher, indicating a new source of endosulfan. In addition, endosulfan was detected in 28 of 105 sedimentary column samples (25 of which were endosulfan I) from the seven study sections of the Qingshui River in the spring flood, summer flood, and dry seasons. Whether from the entire basin or the analysis of the composition and content of the endosulfan isomers in each sample, new endosulfan sources were noted in the sediments of the Qingshui River basin.

Table 3. Results of ecological risk assessment of OCPs in the sedimentary column from Qingshui River.

OCPs	TECs/ ng·g ⁻¹	PECs/ ng·g ⁻¹	Qingshui River / ng·g ⁻¹	≤TEC/ %	TEC-PEC/ %	≥PEC / %
Chlordane	3.24	17.60	n.d.~0.755	100.00	0.00	0.00
Dieldrin	1.90	61.80	n.d.~0.929	100.00	0.00	0.00
DDD	4.88	28.00	n.d.~13.665	99.05	0.95	0.00
DDE	3.16	31.30	n.d.~12.482	97.14	2.86	0.00
DDT	4.16	62.90	n.d.~11.431	99.05	0.95	0.00
DDTs	5.28	572.00	n.d.~24.625	96.19	3.81	0.00
Endrin	2.22	207.00	n.d.~7.777	98.10	1.90	0.00
Heptachlor epoxide	2.47	16.00	n.d.~2.438	100.00	0.00	0.00
γ-HCH	2.37	4.99	n.d.~2.203	100.00	0.00	0.00

Note: n.d. is not detected.

Ecological Risk Assessment of OCPs in Sediments

Currently, there is no internationally recognized standard for the systematic ecological risk assessment of sediments. MacDonald et al. [46] comprehensively classified and compared existing freshwater sediment quality benchmarks. Based on an extensive review of relevant research data, they proposed the Consensus-Based Sediment Quality Guidelines (CB-SQGs) for freshwater environments. These guidelines utilize two key benchmarks: the Consensus-Based Threshold Effect Concentration (TEC), indicating a low hazard (<25%), and the Consensus-Based Probable Effect Concentration (PEC), representing a high hazard (>75%). According to these benchmarks, benthic organisms are generally not expected to exhibit adverse effects at concentrations ≤TEC, are likely to experience adverse effects at concentrations ≥PEC, and may potentially be affected at concentrations within the intermediate range [46, 47].

This study assessed eight OCPs with established TEC and PEC values—Chlordane, Dieldrin, DDD, DDE, DDT, Endrin, Heptachlor epoxide, and γ-HCH. Other OCPs were not evaluated due to the lack of standardized reference values. The results of the ecological risk assessment for OCPs in the sediment column of the Qingshui River are presented in Table 3.

Among the analyzed sediments, none of the eight OCPs exceeded their respective PEC values. The residual concentrations of Chlordane, Dieldrin, Heptachlor epoxide, and γ-HCH were all below their TEC values, indicating minimal ecological risk and negligible adverse effects on aquatic organisms. However, the concentrations of DDD, DDE, DDT, DDTs, and Endrin at various sampling points were within the TEC-PEC range, suggesting a potential risk to benthic organisms. Specifically, DDD was detected in the 15-20 cm depth layer during the summer flood season; DDE was found in the 15-20 cm depth layer

during the summer flood season and in the 0-5 cm depth layer at the CST section; DDT was present in the 5-10 cm depth layer in the SY section during the spring flood season; DDTs were observed in the 5-10 cm depth layer in the SY section during the spring flood season, the 15-25 cm depth layer during the summer flood season, and the 0-5 cm depth layer at the CST section; and Endrin was identified in the 10-15 cm depth layer during the low-water period at the KC section and in the 0-5 cm depth layer at the LW section. DDD, DDE, DDT, DDTs, and Endrin proportions in sediments within the TEC-PEC range were 0.95%, 2.86%, 0.95%, 3.81%, and 1.90% of all samples, respectively. These concentrations indicate a potential ecological risk to benthic organisms in the affected river sections.

Overall, while certain OCPs in Qingshui River sediments may pose ecological risks in specific locations, their overall environmental impact appears to be limited. It is important to note that sediment quality assessments primarily predict potential toxicity but do not account for the bioaccumulation and biomagnification of OCP pollutants. Therefore, additional management and control measures for OCP pollution are necessary, even in areas classified as low-risk.

Conclusions

Considering the OCPs in the sediments of the Qingshui River as the research object, this study investigated the pollution characteristics, occurrence regularity, historical sedimentation records, main sources, and ecological risks of OCPs in the sediments. The main conclusions are as follows:

(1) Based on the study of the pollution characteristics and occurrence regularity of the OCPs, 19 types of OCPs were detected in the sediment column samples of the Qingshui River. The detection amount and mean

value of the OCPs were n.d. ~ 36.527 (2.061) $\text{ng}\times\text{g}^{-1}$, and the detection rate was 79.05%.

(2) The settlement records of the OCPs were studied using the ^{210}Pb isotope dating method, revealing that the settlement records of the OCPs from 1977 to 2017 were related to their historical usage.

(3) The isomer ratio method determined the HCHs, DDTs, endosulfan, and chlordane sources in the Qingshui River sediments. The four typical OCPs mainly originated from historical residues.

(4) The ecological risk assessment of OCPs in Qingshui River sediments, based on CB-SQGs, indicates that certain OCPs may pose ecological risks in specific locations; their overall environmental impact appears to be limited.

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Conflict of Interest

The authors declare no conflict of interest.

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