

## Article

# Distribution and Risk Assessment of Toxic Pollutants in Surface Water of the Lower Yellow River, China

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**Abstract:** The lower reaches of the Yellow River is known for the rapid development of industry and agriculture, which has also led to some pollution. However, information about the level of toxic contaminants in the surface waters is lacking in this area. Therefore, five sampling points were set in the lower Yellow River to investigate the distribution of various pollutants and analyze the potential risks. The presence of heavy metals (Heavy metals tested for in this study were: Mercury (Hg), Arsenic (As), Copper (Cu), Chromium (Cr), and Zinc (Zn)) and antibiotics (Antibiotics tested for in this study were: Enrofloxacin (ENR), Ciprofloxacin (CIP), and Norfloxacin (NOR)) in water samples taken from the lower Yellow River were measured to reveal the spatial distribution and risk potential of the compounds. Various water quality parameters (Water quality parameters used in this study were: chemical oxygen demand (COD), biological oxygen demand (BOD<sub>5</sub>), total phosphorus (TP), and total nitrogen (TN)) were also tested. Study results showed the main surface water pollution components were COD, BOD<sub>5</sub>, TN, and TP. The average levels were 37.79 mg/L, 16.64 mg/L, 4.14 mg/L, and 0.42 mg/L, respectively. Among the detected metals from the water samples, Hg (LOD-0.1 µg/L) levels were only in line with the surface water class III or worse. Both fish and water samples contained antibiotics. According to an ecological risk assessment conducted along the river, the distribution of pollutants in the waters exhibited a spatial relationship with the land-use pattern in the study region and the Kenli site was the most polluted. Research shows that up-to-date data on the residual levels and distribution characteristics of pollutants in the lower Yellow River could provide valuable baseline data and technical support for relevant government departments and their management going forward.

**Keywords:** lower Yellow River; ecological health; heavy metals; antibiotics; potential risk assessment



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## 1. Introduction

Rapid economic development contributes to deteriorating ecological environments in many countries and regions. With the increasing intensity of human activities, increased discharge of environmental pollutants, such as heavy metals and organic pollutants, exacerbates this problem in natural water bodies [1–3]. Although some pollutants are not widespread, and therefore do not pose the risk of acute toxic effects, many of these water-borne pollutants have characteristics of bioaccumulation, which are harmful to both the biological and human population [4,5]. The presence of pollutants is a cause for serious concern as they can have lasting impacts on the aquatic environment, which has become an important issue that influences ecological quality and the sustainable development of the social economy.

Heavy metal pollution is a well-known problem because of its accumulation through the food chain [3,6]. Once heavy metals enter water bodies they settle in sediment, slowing degradation and prolonging their lifespan [2]. In addition to heavy metals, antibiotics are a major threat to the ecological integrity of natural water bodies. At present, pharmaceuticals—especially antibiotics—are widely used throughout the world. Because

of the generalized nature of antibiotics, adverse effects on ecological health have gradually attracted more attention [7]. The spatiotemporal distribution and potential environmental influences of antibiotics in surface water were not clearly understood until recently. Also, these pollutants—including, but not limited to, heavy metals and antibiotics—may negatively affect the surface water of irrigation and drinking water sources. This process contributes to the bioaccumulation of pollutants that ultimately spread through the entire length of the human food chain. Elevated levels of these surface water contaminants raise serious concerns for aquatic ecosystem health and, potentially, human health via the consumption of contaminated aquatic products, which has been an urgent environmental concern [2,5,8,9].

In China, the pollution in the Pearl River, Liaohe River and Yangtze River in China has attracted widespread concerns since the end of the 1980s [10–18]. The types and concentrations of pollutants in water may also change with the spatial distribution pattern of urban and rural/suburban areas [19]. Therefore, various risk assessment methods have been established to determine the potential risks of pollutants to the ecosystem as well as to support the subsequent management/mitigation of these risks [3], which include the Nemerow pollution index, the geo-accumulation index (Igeo) and potential ecological risk.

The Yellow River, located in the north of China, is one of the longest rivers globally with a total length of 5464 km and a drainage area of 752,443 km<sup>2</sup>. The lower Yellow River is one of the most prosperous areas in China [20,21] and there are many urban areas along its banks. The lower Yellow River basin has experienced rapid industrial and agricultural development in recent decades, supporting 12% of China's population. Therefore, the regular/increasing use of pesticides and fertilizers and the increasing intensity of human activities has seen large volumes of wastewater, containing heavy metals and other contaminants, discharged into aquatic systems. This urbanization has led to an increase in environmental exposure to pollutants [22]. A prime example of this was in 2017; the Yellow River was the source of pollution dumped in the Bohai Sea, which feeds into the North Pacific Ocean. The pollutants included  $1.7 \times 10^5$  tons of chemical oxygen demand (COD) and 300 tons of heavy metals [20]. Although recent environmental protection measures have alleviated some of the aggravation and harm from such events, the baseline challenge of water pollution has not yet been addressed. Pollutants in the Yellow River damage the entire river's ecological service function, directly threatening drinking water sources and the industrial and agricultural water supply [5,22]. Currently, there is a gap in research on the investigation of pollutant toxicity in the lower Yellow River. Consequently, there is limited data and knowledge on the impacts of antibiotics and heavy metals in the basin.

Based on previous data and literature on the lower Yellow River [23–26], pollutants were selected as key investigation targets. These pollutants include the heavy metals Mercury (Hg), Arsenic (As), Copper (Cu), Chromium (Cr), and Zinc (Zn) and the antibiotics Enrofloxacin (ENR), Ciprofloxacin (CIP), and Norfloxacin (NOR). Water quality parameters to test against pollutants were also selected based on previous studies, therefore, “pollution parameters” for this study include chemical oxygen demand (COD), biological oxygen demand (BOD<sub>5</sub>), total phosphorus (TP), and total nitrogen (TN).

The main aims of this study were as follows: (1) investigate and confirm the residual levels and spatial distribution of pollutants, and (2) analyze and evaluate the potential ecological risks of these pollutants. The resulting, up-to-date and relevant pollutant data provided by this study will provide a critical reference for relevant government agencies to make environmental protection policies that protect the ecological integrity of water systems in the lower Yellow River basin.

## 2. Materials and Methods

### 2.1. Sample Sites and Sampling Methods

Five sampling sites were selected between the estuary of the Yellow River and the city of Zhengzhou—a metropolis situated along the river—which is ~780 km from the estuary

(Figure 1). Figure 1 shows the location of Zhengzhou concerning the estuary, including the Kenli District, Changqing District, Liangshan County, and Lankao County.

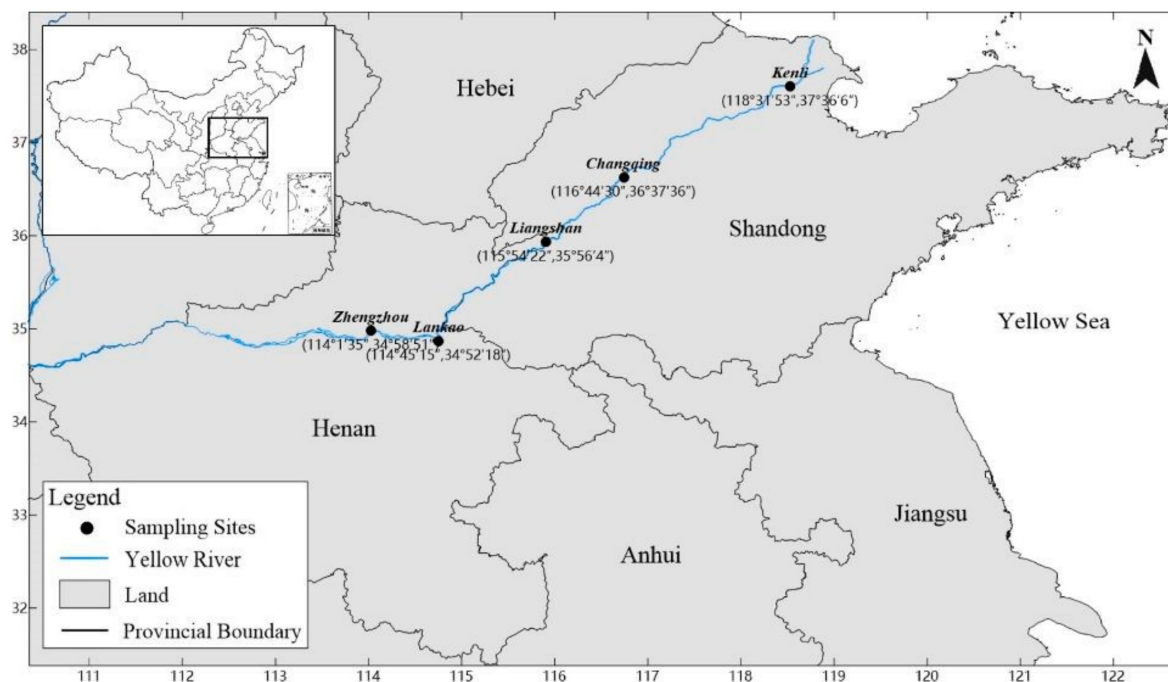


Figure 1. Map of the study region and sampling sites.

In July 2019, a water sample collector (GLPS, Beijing, China) was used to obtain three water samples at each location. Each sample was taken from 30 cm below the water’s surface. During the sampling process, the sample container was rinsed with distilled/deionized water twice to ensure there was no sample cross-contamination. At each sample site, a water multifunctional parameter analyzer measured the temperature, pH value, and dissolved oxygen level (WDC-PCx, Shanghai, China; Table 1). And some fish tissues were sampled for bioaccumulation analysis (the basic information of fish samples is seen in Table 2). The white muscle was taken from the fish’s back and rinsed with distilled/deionized water; tissues were then freeze-dried. After this, 0.5 g of homogenized freeze-dried tissue were acid-digested with a mixture of nitric acid (HNO<sub>3</sub>)—68% alcohol by volume (*v/v*), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)—30% *v/v*.

Table 1. The basic information about the water samples along the lower Yellow River.

	Temperature (°C)	Dissolved Oxygen (mg/L)	pH
Kenli	27.2	7.07	7.90
Changqing	25	5.81	7.93
Liangshan	25	5.73	7.91
Lankao	25	5.73	7.89
Zhengzhou	25	5.36	7.81

**Table 2.** The basic information about the fish samples along the lower Yellow River.

	Common Carp			Grass Carp		
	Sex	Length (cm)	Weight (g)	Sex	Length (cm)	Weight (g)
Kenli	♀	42.0	707.8	♂	46.3	1028.7
	♂	39.0	573.4	♂	42.0	726.2
	♀	45.5	758.8	♂	46.0	1005.3
Changqing	♂	45.1	1102.8	♂	57.0	2367.1
	♂	43.5	1092.3	♂	53.0	1894.6
	♂	42.0	957.9	♀	45.2	972.4
Liangshan	♂	30.2	419.1	♂	46.3	1198.3
	♀	28.9	268.8	♂	49.5	1339.4
	♂	25.5	243.6	♂	51.0	1938.1
Lankao & Zhengzhou	♂	34.3	441.2	♂	44.6	912.0
	♀	35.1	394.8	♂	51.5	1402.3
	♂	34.5	574.8	♂	46.5	1241.4

Note: The fish samples of Lankao & Zhengzhou were collected from the junction of Lankao and Zhengzhou, so they can represent the fish samples from two sampling points.

## 2.2. Reagents

Potassium dichromate ( $K_2Cr_2O_7$ ) and other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Standard reagents of three antibiotics were obtained from Sigma-Aldrich Co. (New York, NY, USA). All chemicals were chromatographically pure.

## 2.3. Water Quality Parameters and Pollution Indexes Analysis

Water quality parameters (COD, BOD<sub>5</sub>, TP, and TN) and heavy metals in water and tissues (Hg, As, Cu, Cr, and Zn) were determined by the corresponding measurement methods recommended by Environmental Quality Standards for Surface Water (EQSSW; Table 1). COD was determined using the potassium dichromate oxidation method with Hach DRB200 and Hach DR1010 analyzers (Hach, Ames, IA, USA). TN was determined using ultraviolet spectrophotometry with alkaline potassium persulfate digestion. TP was determined using the ammonium molybdate spectrophotometric method (SEPA, 2002). Cu and Zn concentrations were determined using atomic absorption spectrophotometry, with Cr determined using an inductively-coupled plasma mass spectrometer (ICP-MS, Kunshan, China). The As and Hg concentrations were determined by cold atomic fluorescence spectrometry.

After completing the concentration, liquid chromatography-mass spectrometry (LC-MS) was used to detect the levels of antibiotics in water and tissues [27]. After filtering through 0.45  $\mu$ m glass fiber filters (Millipore, MA, USA), solid-phase extraction was sequentially preconditioned with 6.0 mL methanol, 6.0 mL distilled/deionized water, and 6.0 mL of a 10 mmol/L Na<sub>2</sub>EDTA buffer (pH 3.0). It was then dried under nitrogen gas for 1 h. Analytes were collected in a 10 mL brown glass vial for further analysis. The LC system used was an HP 1100 (Agilent Technologies, Palo Alto, CA, USA) controlled gradient system. MS measurements were performed on a Sciex API 4000<sup>TM</sup> (Applied Biosystems, Foster City, CA, USA) equipped with an electrospray ionization source.

Recovery ratios using this analytical approach ranged from 61%  $\pm$  10% to 86%  $\pm$  4% for antibiotics; detection limits were 5.0–10.0 ng/L. Also, sampling errors were assessed by obtaining water samples in triplicate at each site to analyze sample extracts.

## 2.4. Quality Assurance

All samples were analyzed in strict accordance with corresponding national standards. Besides reagent blanks and standard references, each sample was measured at least three times to reduce the risk of analysis error and to ensure data accuracy. Quality standards

referred to included GB 11914-89 (COD), GB 7488-87 (BOD<sub>5</sub>), GB 11893-89 (TP), GB 11894-89 (TN), GB7475-87 (Cu, Zn, and Cr), GB 7485-87 (As), and GB 7468-87 (Hg).

### 2.5. Potential Ecological Risk Assessment and Data Statistics

Based on the measured values of water samples in the lower Yellow River, the surface water quality of each sampling site was classified, with reference to the EQSSW (Table 1). By using the methods of a single factor pollution index and pollution sharing ratio, the potential risk assessment of COD, BOD<sub>5</sub>, TN, TP and of heavy metal pollution of the surface water samples was calculated. The calculation formula is as follows:

$$CPI = \frac{1}{n} \sum_{i=1}^n CPI_i = \frac{1}{n} \sum_{i=1}^n \frac{C_i}{S_i} \quad (1)$$

$$K_i = \frac{CPI_i}{\sum_{i=1}^n CPI_i} \times 100\% \quad (2)$$

where:

- $CPI$  is the comprehensive pollution index;
- $CPI_i$  is the single factor pollution index;
- $C_i$  is the single pollutant tested in surface water;
- $S_i$  is the evaluation standard of corresponding pollutants (i.e., EQSSW);
- $n$  is the number of test samples;
- $K_i$  is the pollution sharing rate;
- $i$  represents the parameters of COD, BOD<sub>5</sub>, TP, TP, and heavy metal pollutants.

Based on common standards widely used in water pollution risk assessments, the potential risk levels of sampling sites in this study were classified [4,28,29]. SPSS 22.0 software was used for all data processing.

## 3. Results and Discussion

### 3.1. Surface Water Contaminants in Lower Yellow River

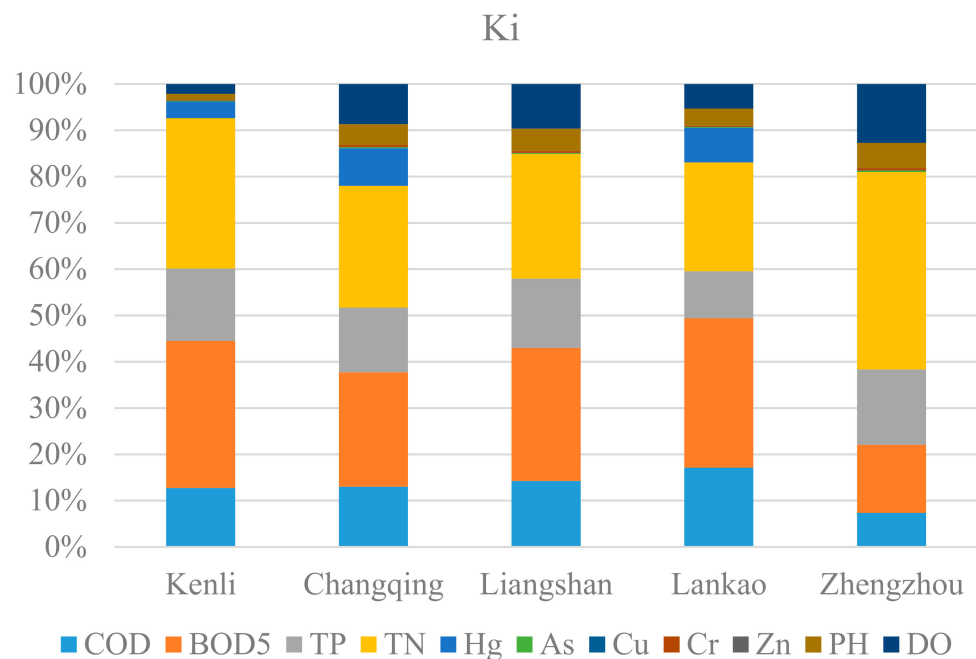
Table 3 lists the measured selected water quality parameters and heavy metals tested in the surface water sampled from the lower Yellow River. Ranges of COD, BOD<sub>5</sub>, TN, and TP levels were 11.00–86.00 mg/L, 4.40–42.40 mg/L, 2.50–10.90 mg/L, and 0.24–1.05 mg/L, respectively; with average concentrations at 37.79 mg/L, 16.64 mg/L, 4.14 mg/L, and 0.42 mg/L. All heavy metals tested for in this study were found at sample sites. However, Zn was only detected at the Kenli site. The maximum levels of Hg, As, Cu, Cr, and Zn tested across the sites were 0.13 µg/L, 2.70 µg/L, 2.52 µg/L, 7.60 µg/L, and 2.34 µg/L, respectively. Except for Hg, residual levels of heavy metals in all water samples were lower than the specified value at class I or II. At all sites, Hg concentrations were only close to surface water class III (i.e., Changqing and Lankao sites) or worse (i.e., Kenli site). Results showed heavy metal levels from each sample site met the common surface water standard (Class III, see Table 1), Hg levels should be continually observed in the future. Compared to other rivers in north China (Cui et al., 2019; Huang et al., 2019), the low content of heavy metals in the lower basin responded to the local industrial production layout and environmental protection measures in place by the local government.

**Table 3.** Levels of COD, BOD<sub>5</sub> TN, TP and heavy metals in surface waters.

	Comp	COD	BOD <sub>5</sub>	TN	TP	Hg	Cu	Zn	Cr	As
		mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Kenli	Max	86	42.40	10.90	1.05	0.13	2.52	7.60	2.34	2.70
	Min	83	42.40	10.80	1.04	0.10	2.51	7.50	2.26	2.20
	Mean	84.67	42.40	10.83	1.04	0.12	2.52	7.57	2.30	2.43
	SD	1.53	0	0.06	0.01	0.02	0.01	0.06	0.04	0.25
Changqing	Max	27	10.30	2.80	0.29	0.10	2.42	ND	2.30	1.20
	Min	26	10	2.62	0.28	0.07	2.25	ND	2.14	1.20
	Mean	26.67	10.17	2.71	0.29	0.08	2.36	ND	2.21	1.20
	SD	0.58	0.15	0.09	0.01	0.02	0.10	ND	0.08	0
Liangshan	Max	27	10.80	2.55	0.29	ND	2.05	ND	1.98	0.90
	Min	26	10.70	2.50	0.27	ND	1.90	ND	1.87	0.80
	Mean	26.67	10.77	2.52	0.28	ND	1.99	ND	1.92	0.83
	SD	0.47	0.05	0.02	0.01	ND	0.06	ND	0.05	0.05
Lankao	Max	44	15.60	2.86	0.25	0.09	1.65	ND	1.41	1
	Min	39	15.40	2.77	0.24	0.09	1.61	ND	1.31	0.90
	Mean	41	15.47	2.82	0.24	0.09	1.63	ND	1.38	0.97
	SD	2.16	0.09	0.04	0	0	0.02	ND	0.05	0.05
Zhengzhou	Max	11	4.40	3.24	0.25	ND	2.31	ND	2.06	1.1
	Min	11	4.40	3.12	0.24	ND	2.18	ND	1.95	1.1
	Mean	11	4.40	3.19	0.24	ND	2.25	ND	2.02	1.1
	SD	0	0	0.05	0	ND	0.05	ND	0.05	0
EQSSW I	≤	6~9	15	0.15	0.02	0.05	0.01	0.05	10	0.05
EQSSW II	≤	6~9	15	0.5	0.1	0.05	1	1	50	0.05
EQSSW III	≤	6~9	20	1.0	0.2	0.1	1	1	50	0.05
EQSSW IV	≤	6~9	30	1.5	0.3	1.0	1	2	50	0.1
EQSSW V	≤	6~9	40	2.0	0.4	1.0	1	2	100	0.1

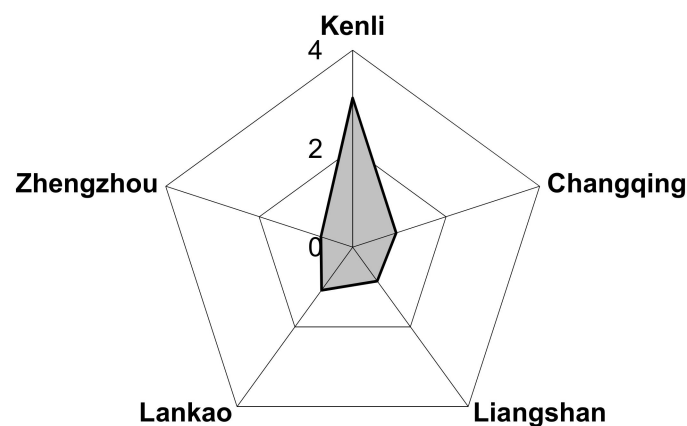
Min: minimum; Max: maximum; SD: standard deviation; ND: less than the limit of detection; EQSSW: Environmental Quality Standards for Surface Water; I: mainly suitable as a general source of water, state reserve; II: mainly suitable for centralized drinking water, surface water source, primary reserve, rare aquatic habitats, etc.; III: mainly suitable for centralized drinking water, surface water source, secondary reserve, fishing and swimming areas, etc.; IV: mainly suitable for general industrial water use and recreational water areas with indirect contact with the human body; V: mainly suitable for agricultural water and general landscape water.

Figure 2 presents pollutant share rates. The main components of water pollution in the lower Yellow River was TN (23.51–42.65%), followed by BOD<sub>5</sub> (14.71–31.79%), TP (10.15–16.27%) and COD (7.35–17.12%). The lower Yellow River is one of the most prosperous areas in China (Fu et al., 2004, Han et al., 2020), which has experienced rapid industrial and agricultural development in recent decades, supporting 12% of China's population. In recent years, large-scale livestock, poultry, and aquaculture farms developed very quickly in the area. The effects of these industries, combined with the direct discharge of domestic sewage from urban and rural residents, have led to rapidly increasing eutrophication of the lower Yellow River. The present results confirmed the excess chemical nutrients occurred in this river, and TN and TP were found to be the important factors affecting the water quality as they were always the worst-rated factor in water quality ratings [30]. These pollutant characteristics showed that the main contributing sources for this were the discharge of industrial and domestic wastewater and farmland irrigation, which was closely related to the relatively developed industry and agriculture sector in this area [4]. Other main rivers in China, such as the Yangtze River, Haihe River, Pearl River and the Minjiang River, share a similar eutrophication pattern [30–33].



**Figure 2.** Pollution share ratios of different contaminants in surface water in the lower Yellow River.

Based on the calculated CPI value (Figure 3), sample sites were classified as follows: three sites (i.e., Changqing, Liangshan, and Zhengzhou) as class III, one site (i.e., Lankao) as class IV, and one site (i.e., Kenli) as class V, which showed the extreme pollution site occurred in Kenli. The pollution is mainly caused by livestock and poultry breeding, sewage discharge from small chemical plants, especially the production and domestic wastewater discharge from Shengli Oilfield Development Zone. Additional pollution may be due to these areas being located in the Yellow River Delta, whether the water pollution in the Kenli area is affected by the sea also needs to be further studied.



**Figure 3.** Comprehensive pollution index (CPI) value in the lower Yellow River.

All tested antibiotics were below LOD in the surface water of sampled sites, which was lower than that in the other rivers of China [34–39] and also lower than the previous survey results of the middle and lower reaches of the Yellow River [5]. The possible reason is that the sampling season took place during the wet season, in addition to the strict control of antibiotic emissions.

### 3.2. Contaminants in Fish Samples

Besides analyzing the contaminants in surface water, tested pollutants were discovered in fish samples (Table 4). Baseline information about the fish samples is outlined in Table 2. Two antibiotics, ENR and CIP, were detected in fish samples; however, NOR concentration was lower than LOD concentration in all samples. The two antibiotic (NOR and LOD) concentrations in the fish samples tested lower than the water sample LOD levels, at  $3411.00 \pm 10.15$  ng/kg. ENR was found in 75% of the water samples with levels from  $54.67 \pm 0.58$  ng/kg to  $3411.00 \pm 10.15$  ng/kg; CIP was found in 62.5% of the water samples with levels from  $22.67 \pm 1.53$  ng/kg to  $52.67 \pm 9.50$  ng/kg.

**Table 4.** The residual contents of the selected pollutants in fish along the lower Yellow River (Mean  $\pm$  SD).

	Kenli	Changqing	Liangshan	Zhengzhou	
Common carp	Hg ( $\mu\text{g}/\text{kg}$ )	$8.24 \pm 0.21$	$1.16 \pm 0.02$	$21.00 \pm 1.00$	$14.80 \pm 0.10$
	As ( $\mu\text{g}/\text{kg}$ )	$5.67 \pm 0.20$	$17.07 \pm 0.55$	$14.10 \pm 0.62$	$7.86 \pm 0.06$
	Cu ( $\mu\text{g}/\text{kg}$ )	$411.33 \pm 4.51$	$2156.67 \pm 75.06$	$1883.33 \pm 11.55$	$363.00 \pm 1.00$
	Cr ( $\mu\text{g}/\text{kg}$ )	$313.67 \pm 4.04$	$375.00 \pm 7.81$	$1156.67 \pm 5.77$	$313.33 \pm 5.77$
	Zn ( $\mu\text{g}/\text{kg}$ )	$4310.00 \pm 10.00$	$4783.33 \pm 5.77$	$4810.00 \pm 20.00$	$3806.67 \pm 5.77$
	ENR (ng/kg)	ND	$1190.00 \pm 45.83$	ND	$94.00 \pm 2.00$
	CIP (ng/kg)	$51.67 \pm 4.51$	$52.67 \pm 9.50$	ND	$38.67 \pm 3.51$
	NOR (ng/kg)	ND	ND	ND	ND
Grass carp	Hg ( $\mu\text{g}/\text{kg}$ )	ND	$33.90 \pm 1.37$	$9.55 \pm 0.15$	$7.32 \pm 0.11$
	As ( $\mu\text{g}/\text{kg}$ )	$3.63 \pm 0.08$	$3.29 \pm 0.18$	$3.86 \pm 0.06$	$2.17 \pm 0.11$
	Cu ( $\mu\text{g}/\text{kg}$ )	$415.00 \pm 5.57$	$356.67 \pm 5.77$	$2883.33 \pm 11.55$	$1753.33 \pm 5.77$
	Cr ( $\mu\text{g}/\text{kg}$ )	$327.00 \pm 4.36$	$356.67 \pm 11.55$	$343.33 \pm 2.52$	$435.33 \pm 1.53$
	Zn ( $\mu\text{g}/\text{kg}$ )	$4940.00 \pm 0$	$2536.67 \pm 5.77$	$3446.67 \pm 5.77$	$3280.00 \pm 0$
	ENR (ng/kg)	$54.67 \pm 0.58$	$164.67 \pm 4.16$	$93.33 \pm 1.53$	$3411.00 \pm 10.15$
	CIP (ng/kg)	$22.67 \pm 1.53$	ND	$26.00 \pm 1.00$	ND
	NOR (ng/kg)	ND	ND	ND	ND

Note: the fish samples were not collected at the Lankao site. SD: standard deviation; ND: less than the limit of detection.

According to study results, higher antibiotic concentrations were in Changqing (a district of Jinan, the capital of Shandong Province, China) and Zhengzhou (the capital of Henan Province, China). These locations are the provincial capital cities and consequently have a highly concentrated population and greater industrialization [5,8]. These observations are consistent with other studies [40]. This study's results indicated that the main source of antibiotics in the surface water is municipal wastewater; e.g., high residue levels of the antibiotic fluoroquinolone in the Luohe River came from wastewater discharge from Luoyang City, a large urban center with a population of more than 6.4 million people [5,40]. In addition, human and animal wastes containing high concentrations of antibiotics may be used as soil amendments in this area. Therefore, antibiotics may also enter surface water or groundwater through non-point source pollution, and farmland in the lower Yellow River may be an important source of antibiotics [5].

As a new class of synthetic antibiotics, the use of quinolones has increased rapidly and the production of norfloxacin, ciprofloxacin and enrofloxacin accounts for 98% of the total production of quinolones in China. Based on our results, NOR, CIP and ENR, as representative quinolone antibiotics, were detected in fish samples from the lower reach of Yellow River. In line with the other studies [41,42], the results showed that quinolone antibiotics are easily accumulated in freshwater fish.

In recent years, people have focused on the ecological and environmental problems caused by quinolone antibiotic pollution [43]. Quinolone antibiotics with different concentration levels have been detected in surface water, groundwater, drinking water, medical wastewater and urban sewage [44]. Trace elements of antibiotics in river water pose a great risk to the health of both human and ecological systems [45,46]. Present concentrations of antibiotics in the lower Yellow River are unlikely to cause acute toxicity to organisms. However, some antibiotics may have cumulative effects on lower aquatic organisms in response



to their non-targeting properties [5]. Although previous studies have shown that exposure to antibiotics could lead to serious and harmful influences on aquatic organisms [47–49], the data on chronic effects of low-dose exposure to antibiotics are very limited. This gap extends specifically to the toxic nature within the molecular mechanism of these antibiotics. The residue left behind after using a single antibiotic is considered low; however, the combination of multiple antibiotics sharing the same target may have synergistic effects [50]. Therefore, environmental residue and potentially adverse influences related to antibiotics are among the major environmental concerns in this century.

The content of heavy metals in fish muscle samples is generally higher than that in surface water samples of the lower Yellow River (Table 2), proving that heavy metals have a bioaccumulation effect in aquatic organisms. This is in line with other research and publications [2]. Also, contaminant levels in muscle tissue of common carp (*Cyprinus carpio*) are higher than that of grass carp (*Ctenopharyngodon idellus*). This variation may be related to the habitats occupied by the two fish species [51,52].

#### 4. Conclusions

This study investigated the residual levels and spatial distribution of various pollutants—including heavy metals, antibiotics, and other pollutants—in the lower Yellow River. Based on these findings, the study assessed the ecological risks associated with the targeted contaminants. Results showed the main pollutants present in sampled surface water were COD, BOD<sub>5</sub>, TP, and TN. This finding was related to industrial and agricultural development in the region. Among heavy metals, Hg should be focused on going forward as it has harmful and potentially catastrophic bioaccumulation effects. Antibiotics were detected in all sampled surface water; however, their accumulation in fish samples proved that antibiotics are widespread in the lower Yellow River. Through this study, novel research was conducted to provide new literature that can be used as a reference for studies of pollutants in natural water bodies. Specifically, studies and resulting data on pollutants present in the lower Yellow River can assist the national, regional, and local governments to make informed and up-to-date policies for ecological preservation. Due to the rapid economic development within the study region, ongoing research and monitoring are necessary to assess pollutant content and their risks in water bodies.

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## Abbreviations

mercury-Hg, arsenic-As, copper-Cu, chromium-Cr, zinc-Zn, enrofloxacin-ENR, ciprofloxacin-CIP, Norfloxacin-NOR, chemical oxygen demand-COD, five-day biochemical oxygen demand-BOD<sub>5</sub>, total phosphorus-TP, total nitrogen-TN, Environmental Quality Standard for Surface Water-EQSSW, high-performance liquid chromatography-mass spectrometry-HPLC-MS, limit of detection-LOD.

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