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Evaluation of Water Quality and Heavy Metals in Wetlands along the Yellow River in Henan Province

Zhendong Hong [1], Qinghe Zhao [1], Jinlong Chang [1], Li Peng [1], Shuoqian Wang [1], Yongyi Hong [1], Gangjun Liu [2] and Shengyan Ding [1,*]

[1] Key Laboratory of Geospatial Technology for the Middle and Lower Yellow River Regions, College of Environment and Planning, Henan University, Jinming Road, Kaifeng 475004, China; zdhong@henu.edu.cn (Z.H.); zhaoqinghe@henu.edu.cn (Q.Z.); 104753180157@vip.henu.edu.cn (J.C.); pengli3315@163.com (L.P.); wangshuoqian@henu.edu.cn (S.W.); yhong28@126.com (Y.H.)

[2] College of Science, Engineering and Health, RMIT University, 124 LaTrobe Street, Melbourne 3000, Australia; gang-jun.liu@rmit.edu.au

* Correspondence: syding@henu.edu.cn; Tel.: +86-3712-388-1102

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Abstract: Assessing spatiotemporal variation in water quality and heavy metals concentrations in wetlands and identifying metal contamination source are crucial steps for the protection and sustainable utilization of water resources. Using the water quality identification index (I_{wq}), heavy metal pollution index (HPI), hierarchical cluster analysis (HCA) and redundancy analysis (RDA), we evaluated spatiotemporal variation in water quality and heavy metals concentrations, and their interrelation in wetlands along the middle and lower Yellow River. The average I_{wq} was highest during flood season but the average HPI was lowest in the same season. Meanwhile, the trend in mean HPI across three hydrological seasons was the opposite to that of mean I_{wq}. There was significant variation in wetlands water pollution status across seasons. During the flood season, the wetlands in the affected area with hanging river were seriously polluted. In other seasons, pollution in the artificial wetlands was even more severe. Moreover, serious pollution of wetlands in belt transect #03 (Yuanyang-Zhongmu) was more frequent. Dissolved oxygen and chemical oxygen demand strongly influenced heavy metal concentrations, while other water quality parameters had different influences on heavy metal concentrations in different hydrological seasons. The causes of water pollution were divided into natural factors and human disturbance (with potential relationships between them). The polluted wetlands were greatly affected by the Yellow River during the flood season while they were more impacted by agricultural and domestic sewage discharge in other seasons. However, heavy metal deposition and leaching into riparian wetlands were still affected by diverse channel conditions. If this trend is allowed to continue unabated, wetlands along the middle and lower Yellow River are likely to lose their vital ecological and social functions.

Keywords: water quality; heavy metals; riparian wetlands; middle and lower Yellow River; Henan Province

1. Introduction

Wetlands are among the most productive and vulnerable ecosystems in the world, have fundamental ecological functions, and play an irreplaceable role in the maintenance of biodiversity and human development [1–3]. Despite the relevant departments' efforts to restore natural wetlands for human well-being [4], global change and intense anthropogenic pressure have destroyed more than half of global wetlands during the last century [5]. Riparian wetlands are buffer zones for the water and nutrient budget of the landscape which play an important ecological role. However, because they tend to be quite narrow in width, their importance for landscape ecology, biogeochemistry, and biodiversity is often overlooked [6]. Riparian wetlands are thus often threatened by water resources and hydropower projects that primarily consider human demand, causing changes in the hydrological regimes, eutrophication, nutrient enrichment, salinization, and pollution with organic compounds, pesticides and heavy metals [7–11].

Water is the chief constituent of wetland ecosystems [12] and water quality is not only indicative of water's suitability for maintaining various industrial applications and processes, but also as a potential factor in supporting biodiversity and ecosystem function [13–15]. Water quality is generally expressed as the concentration of inorganic and organic materials in the water, and its degradation can seriously affect wetland ecosystems function [15–17]. Meanwhile, heavy metal pollution is one of the most important factors in the short-term anthropogenic impacts on wetlands [18–20]. Heavy metals, which affect water quality and the trophic structure and function of communities [18,19,21,22], enter wetland ecosystems in different ways. In contrast to chemical pollutants, heavy metals cannot be removed by natural degradation processes. Potential threats to human health and wetland ecosystems make trace element pollution of freshwater ecosystems an ongoing environmental problem. Therefore, it is important to study trace element concentrations, distributions, sources, and health risks to protect water resources and control water pollution.

Wetlands with healthy aquatic environments can provide various ecosystem services; thus, the identification of spatiotemporal alterations and distribution of water quality and heavy metal pollution origins in water of wetlands is important [23]. Previous research on the wetlands along the Yellow River in China, mainly conducted in the headwaters and delta areas [24,25], confirmed that wetlands were suffering from great threats which had resulted in the reduction of area and aggravation of landscape fragmentation. However, research on the wetlands along the middle and lower Yellow River has been rare. The wetlands along the middle and lower Yellow River were, however, seriously degraded by climate change, lateral infiltration through banks elevated above the water surface, and anthropogenic activities. Moreover, China put forward a strategic policy to promote ecological protection and high-quality development in the Yellow River basin in 2019. The main reasons for monitoring wetland water have been to assess water quality and heavy metal concentrations compared to existing standards and to verify whether they are suitable for ecosystem service sustainability. Wetland water research has not only evolved to investigate trends in the aquatic environment, but also to seek their potential drivers and to identify pollution sources [15,16,18,19]. Therefore, there is an urgent need to evaluate the status and spatiotemporal dynamic of water quality and heavy metals in wetlands along the middle and lower Yellow River. Meanwhile, the relationships between water quality and heavy metals and their drivers, which can deepen our understanding of the importance of wetland conservation, deserve further exploration.

Our main objectives were (1) to quantify water quality and heavy metal concentrations and to determine wetlands status; (2) to analyze spatiotemporal dynamics of water quality and heavy metals and their drivers; and (3) to examine the correlations between water quality parameters and heavy metals. This study will be beneficial to conservation and restoration of the degraded wetlands, especially along the middle and lower Yellow River.

2. Materials and Methods

2.1. Study Area

The study area involves ten counties along the middle and lower Yellow River in Henan province, China (Figure 1). It ranges from Gongyi city in the west to Lankao county of Kaifeng city in the east, with most areas consisting of typical alluvial plain (113°5′–114°41′ Long. and 34°0′–34°57′ Lat.). The altitude of the study area gradually decreases from southwest to northeast. It is located at the north–south transitional climate zone with a temperate-subtropical, humid and sub-humid monsoon climate. The average annual temperature is generally 12–16 °C with obvious differences between mountain and plain areas in temperature. The annual average precipitation is about 500–800 mm with approximately half in summer in the form of frequent rainstorms [26,27]. The study area, which is one of the national food production bases, has a long history of agricultural cultivation and the landscape is dominated by agriculture. Most of the study area is located at low elevation and is seriously influenced by the Yellow River. East of Huayuankou in Zhengzhou, the lower Yellow River is characterized by gentle flow, wide and shallow channel controlled by dikes, leading to serious silt deposition and risen river bed, thus forming the "hanging river". Changes in river channel coupling with the irrigation practices have resulted in dramatical dynamics of surrounding landscape, which is especially true for the formation and maintenance of wetlands and the appearance and disappearance of ponds.

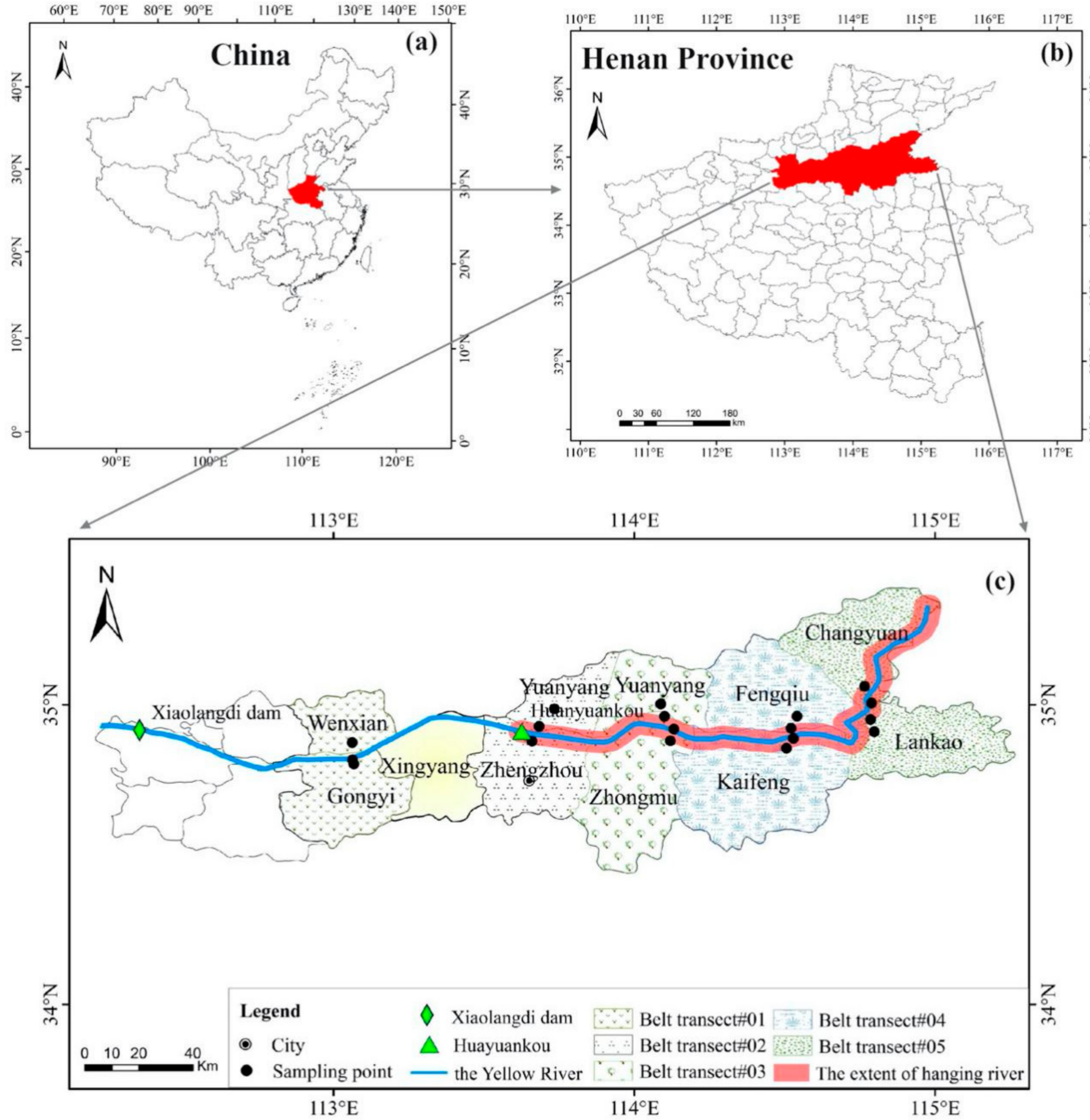

Figure 1. Location of sampling sites (**c**) at the middle and lower Yellow River, Henan (**b**), China (**a**). 18 wetlands were investigated.

2.2. Sample Collection and Analysis

The study area was divided into 5 belt transects, according to the distance from Xiaolangdi dam and the height of the riverbed above the ground level (Table A1). Based on remote sensing images and field investigation, 18 typical riparian wetlands were selected as sample sites, including both natural and artificial wetlands at the north and south Banks of the Yellow River and/or inside and outside the dykes. Water samples were collected from the middle as in depth-wise of the surface water, 50 cm below the water surface at each site. Typical total stream depths were 1m, but where stream depth was is <0.5 m, we sampled at half the depth of the stream. We sampled water between and 12 April and 20 April 2018 during the pre-flood season (S_B), from 27 to 31 July 2018 during the flood season (S_D) and from 26 October to 1 November 2018 during the post-flood season (S_A). The sampling timing was planned to avoid significant rain events (10 mm over 48 h).

The water samples were stored in prewashed polyethylene bottles and shipped to the lab in a cooled container following dilution with HNO_3 or H_2SO_4, depending on the analysis to be conducted. In situ measurements of dissolved oxygen (DO) were performed on each water sample with an SX736 multi-probe. Duplicate co-located samples were collected at each monitoring site and the percent difference in results between duplicates was always less than 10%.

We analyzed 12 chemical and heavy metal parameters. Ammonia nitrogen (NH_3-N) was determined by Nessler's reagent method, total phosphorus (TP) by the ammonium molybdate method, total nitrogen (TN) by the alkaline persulfate digestion method [28], and chemical oxygen demand (COD) by the dichromate reflux method [29]. Heavy metals including lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd) and chromium (Cr) were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The determination of arsenic (As) and mercury (Hg) concentrations in water samples was conducted by atomic fluorescence spectrophotometry (DB51/T836-2008). All water quality parameters were determined within one week of sample collection.

2.3. *Quantifying Water Quality*

The comprehensive water quality identification index (I_{wq}) and heavy metal pollution index (HPI) provide substantial information for water quality assessment. The I_{wq} is based on single-factor water quality identification index (P_i), so P_i is calculated firstly [30]. I_{wq} and HPI both are simple, easy to understand [31,32] and can eliminate the variations between different water quality parameters that are used individually [33].

2.3.1. Single-Factor Water Quality Identification Index (P_i)

The P_i consists of integer and decimal fractions and P_i can be expressed by the formula:

$$P_i = C_1 \times C_2 \times C_3 \tag{1}$$

where C_1 is the integer and shows the grade of water quality; C_2 is the decimal fraction and shows the degree of monitoring data in interval of C_1 class water quality changing; C_3 is the comparison difference of water quality grade and function goal grade.

According to the Surface Water Environment Quality Standards of China, when the water quality grade is between class I and V, for the general indicators (TN, COD, TP and NH_3-N) and DO, $C_1 \times C_2$ is calculated by the following Equations (2) and (3), respectively:

$$C_1 \times C_2 = a + \frac{E_i - E_{ls}}{E_{us} - E_{ls}} \tag{2}$$

$$C_1 \times C_2 = a + 1 - \frac{E_i - E_{ls}}{E_{us} - E_{ls}} \tag{3}$$

where E_i is the monitoring value of ith target; E_{us} is the upper limit of ith target in water quality standard interval of class a; E_{ls} is the lower limit of ith target in water quality standard interval of class a; a = 1, 2, 3, 4, 5, based on monitoring data and national standards.

When the water quality is worse than or equal to class V, for the general indicators (TN, COD, TP and NH_3-N) and DO, $C_1 \times C_2$ is calculated by the following Equations (4) and (5), respectively:

$$C_1 \times C_2 = 6 + \frac{E_i - E_{vus}}{E_{vus}} \tag{4}$$

$$C_1 \times C_2 = 6 + \frac{E_{vls} - E_i}{E_{vls}} \times m \tag{5}$$

where E_{vus} is the upper limit of ith target in water quality standard interval of class V; E_{vls} is the lower limit of ith target in water quality standard interval of class V; m is the correction coefficient, m = 4 in this study [30].

$$C_3 = C_1 - f_l \tag{6}$$

where f_l is the goal grade of water environment functional area. Note: when $C_3 > 9$, $f_l = 9$.

2.3.2. Comprehensive Water Quality Identification Index (I_{wq})

I_{wq} is used to evaluate general water quality both qualitatively and quantitatively. Water quality parameters (e.g., TP, TN, COD, DO and NH_3-N) were selected in this study to conduct a comprehensive evaluation of water quality in water body using I_{wq}, which is calculated by the following formula:

$$I_{wq} = X_1 \times X_2 X_3 X_4 \tag{7}$$

$$X_1 \times X_2 = \frac{1}{m} \sum (P_1 + P_2 + \cdots + P_m) \tag{8}$$

where $X_1 \times X_2$ shows comprehensive water quality index; P_m is single factor water quality index (that is $C_1 \times C_2$ in single factor water quality identification index), and each indicator is weighted evenly; m is the number of indicators; X_3 is the number of indicators which are worse than water quality standards graded among all indices; X_4 represents the comparison results of water quality categories and function zoning category.

Surface water quality grades can be determined based on $X_1 \times X_2$ of I_{wq} (Table 1). According to the Surface Water Environment Quality Standards of China, the water quality in this study area should meet class III.

Table 1. Comprehensive water quality grade evaluation standards.

Judging Basis	The Water Quality Grade
$1.0 \leq X_1 \times X_2 \leq 2.0$	class I
$2.0 < X_1 \times X_2 \leq 3.0$	class II
$3.0 < X_1 \times X_2 \leq 4.0$	class III
$4.0 < X_1 \times X_2 \leq 5.0$	class IV
$5.0 < X_1 \times X_2 \leq 6.0$	class V
$6.0 < X_1 \times X_2 \leq 7.0$	Inferior, but not black and foul
$X_1 \times X_2 > 7.0$	Inferior, black and foul

2.4. Quantifying Heavy Metal Pollution

The HPI can objectively reflect the quality of water and its suitability for drinking purposes with respect to metals pollution [34]. Heavy metals (e.g., As, Hg, Cd, Cr, Cu, Pb and Zn) were selected in this study to conduct a comprehensive evaluation of heavy metal pollution in the water body using HPI. The pollution critical index (HPI_c) is 100. HPI > 100 indicates that the level of heavy metal pollution in a water body exceeds its maximum acceptable level [34,35].

HPI is based on a weighted arithmetic quality mean method as follows [31]:

$$HPI = \sum_{i=1}^{n}(Q_i W_i) / \sum_{i=1}^{n} W_i \tag{9}$$

$$W_i = k/S_i \tag{10}$$

$$Q_i = 100\left(\frac{C_i}{S_i}\right) \tag{11}$$

where W_i (weight unit) is calculated as $1/S_i$ where S_i is the recommended standard of the relevant metal. Generally, the proportionality constant (k) determined by the condition is set at 1 for simplicity of calculation [34]. n is the number of estimated metals; Q_i is the individual quality rating of ith metal and C_i is the measured value of the ith metals in μg/L. The standard allowable value (S_i) for each parameter was taken from the criteria for class III of the water quality standard (GB3838-2002) [36].

2.5. Multivariate Analyses

Four multivariate statistical methods including the principal components analysis (PCA), hierarchical cluster analysis (HCA), Pearson's correlation analysis, and redundancy analysis (RDA) were utilized in this study. Prior to the multivariate analyses, the water quality and heavy metal parameters were required to conform to a normal distribution [37,38]. Therefore, the normality of the distribution of each variable was checked by analyzing its kurtosis and skewness [39]. The results showed that all parameters were normally distributed and in line with the standard of the statistical analysis. All the tests were conducted using SPSS® software for Windows 22.0 and Canoco® software for Windows 5.0, and the graphics were generated in Origin for Windows 9.1®.

Firstly, Kaiser Meyer Olkin (KMO) and spherical Bartlett tests were used to analyze the suitability of the water quality and heavy metal parameters for PCA. The KMO index compared the values of correlations between variables and those of the partial correlations [40]. Generally, this index should be greater than 0.5 for a satisfactory factor analysis. Bartlett Test of Sphericity was used to check the null hypothesis that the intercorrelation matrix comes from a population in which the variables are uncorrelated [41]; the null hypothesis was rejected at the significance level of 0.05. PCA was used to identify the parameters which explained the majority of contamination status. PCA selected a small number of important variables through linear transformation of multiple variables, and several principal components were used to explain water quality and heavy metals concentrations, it becomes more meaningful [39,42].

HCA includes both the variable HCA and the case HCA [28,43]. The variations in water quality and heavy metal parameters were addressed using spatiotemporal matrices. Clustering was based on the similarity between observations and successively by case HCA which is the most widely used clustering method for delineating differences or similarities among sampling sites [44,45].

Finally, Pearson's correlation analysis and RDA were used to identify relationships among individual parameters. RDA is a direct gradient analysis method that statistically evaluates the relationship between one or a set of variables and another set of multivariate data [46]. It has been successfully used in various environmental studies, including for correlations among sampling sites and environmental conditions and outcomes. The advantages and disadvantages of RDA relative to other related multivariate analytical techniques have been discussed extensively [47–49]. In this study, the standard deviation (SD) of the average parameter concentrations in this study were 1.2 (S_D), 1.0 (S_A) and 1.2 (S_B), respectively, suitable for a regression analysis by a linear model. Therefore, heavy metal elements and water quality parameters are used as the response variables in RDA and the individual and comprehensive effects of environmental factors on these response variables respectively. RDA yields directional indices of the shared variance between two data sets, which can be regarded as predictive of the other. RDA biplot diagrams explain the relationships between them. In the diagrams, the arrows indicate the correlations among parameters: a longer arrow indicates that the corresponding parameter was more important; a small angle between two arrows indicates that the correlation between the two corresponding parameters was strong [50].

3. Result and Discussion

3.1. Comprehensive Water Condition

3.1.1. Water Quality Status

The mean I_{wq} value was 5.033, 5.032 and 2.995 the in S_D, S_A and S_B, respectively. A bar chart shows that the I_{wq} value in S_B was obviously lower than that in S_D and S_A (Figure 2a). Based on the I_{wq} classification, the water quality was rated as "class II" in S_B, but "class V" during other seasons (Table 1). There were six sample sites where the I_{wq} value was highest in S_D and lowest in S_B. 83% of which were natural wetlands within the dike. However, there were 10 sample sites where the I_{wq} maximum value occurred in S_A and the minimum value occurred in S_B, all of which were artificial wetlands. Only two natural wetlands did not follow this order.

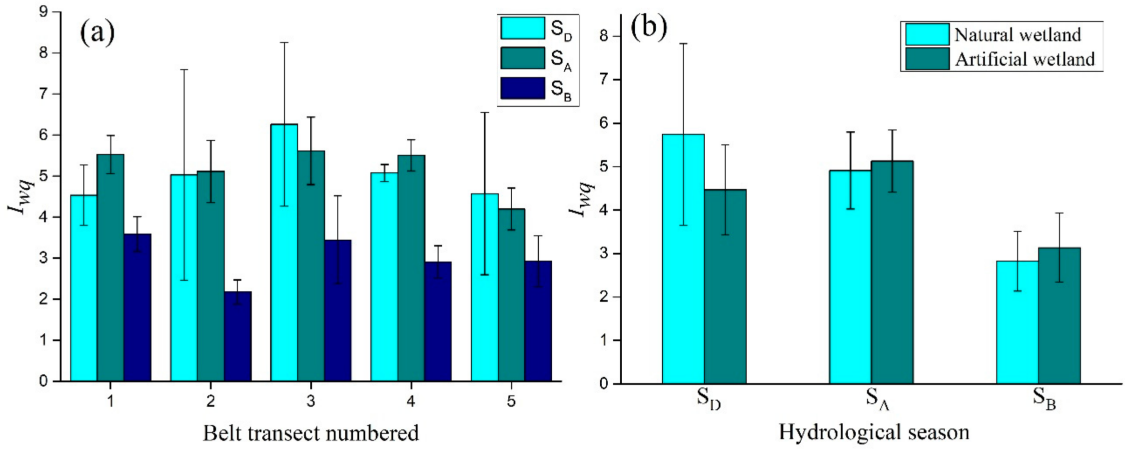

Figure 2. I_{wq} values in different sampling belt transects (**a**) and wetland types in three seasons (**b**).

The water quality met the standard (I_{wq} value $\leq$ 4) in S_B. In S_D and S_A, water quality of major wetlands was worse than class III standard. The average I_{wq} value of belt transect #03 and #05 in S_A were slightly better than in S_D, while the other three sample belts were the opposite. The mean I_{wq} value of two wetland types in the three sampling periods in this study area is shown in Figure 2b. The water quality situation of natural wetlands was slightly better than that of artificial wetlands in S_A and S_B. The water quality situation of artificial wetlands was obviously better than that of natural wetlands in S_D.

Overall, water pollution was most serious in S_B, followed by the S_A. We expected to observe a higher concentration of water quality parameters during low-flow periods [15–17]. Meanwhile, because the selected wetlands were in a major agricultural province, the increased runoff in summer and the fertilization and sewage discharge from farmlands around the wetlands in S_B and S_A may be the main cause of pollution [51–53]. Water quality was excellent in S_B, possibly due to the effects of a constructed reservoir on control of river water and sediment [54]. More river runoff would increase the quantity of eroded material and cause more serious water pollution in S_D. Because most of the selected natural wetlands were close to a river channel, their water quality was worse than that of artificial wetlands in S_D. In S_A and S_B, artificial wetlands were strongly disturbed by human activities, while natural wetlands were less disturbed. The water body of riparian wetlands had some self-purification ability, and the water quality of natural wetlands was slightly better than that of artificial wetlands.

3.1.2. Heavy Metal Pollution

The mean HPI value was highest in S_B (Table 2). All HPI values were lower than HPI_c in S_D, indicating that heavy metals were not polluting the wetlands. Other than two sites, heavy metal concentrations were lower than the pollution threshold in S_A. However, the HPI value of the polluted sample sites exceeded the HPI_c values 2–3 times over, indicating serious heavy metal pollution. The HPI of the sample site (1-S-I-I) with severe human disturbance was close to exceeding the standard, and was obviously higher than that in the adjacent natural wetland (1-S-I). The HPI value of all sample sites exceeded the HPI_c value by an order of magnitude or more in S_B, primarily because Hg content was very high.

Table 2. The Heavy metal Pollution Index in different hydrological seasons.

SN	HPID	HPIA	HPIB
1-N-O-2	6	0.1626	10,265
1-S-I	20	75	47,192
1-S-I-I	37	99	2780
2-N-O	55	0.0495	64,977
2-N-I	25	0.0493	7885
2-S-I	37	0.0045	30,030
3-N-O	29	0.0875	78,995
3-N-I	28	37	49,507
3-S-O	32	0.0233	4796
3-S-I-2	0.1526	0.0626	10,910
4NO	42	7	7197
4-N-I	30	0.0485	33,280
4-S-O	49	62	40,775
4-S-I-2	19	306	69,830
5-N-O	19	33	42,339
5-N-I	31	205	55,055
5-S-O	45	0.0575	7660
5-S-I	41	0.1054	39,456

Notes: SN—Sampling site number; HPI—Heavy metal pollution index (the subscripts D, A and B represent the hydrological seasons: flood season, post-flood season, pre-flood season, respectively).

Moreover, there were some differences in the temporal pattern of HPI. There were 11 sampling sites whose HPI value was highest in S_B and minimum value appeared in S_A, among which artificial wetlands accounted for 64% and five of all were within the dike. Meanwhile, there were seven sampling sites whose maximum HPI value appeared in S_B and minimum value appeared in S_D, among which artificial wetlands account for 57%. Five of these were within the dike. In terms of wetlands types, HPI also showed some seasonal variation. The mean HPI value in natural wetlands was higher than that in artificial wetlands in S_D and S_A while it was the opposite in S_B.

Generally, the spatiotemporal variations in metals concentration in water bodies depend on many factors, including climate, soil type, and pH. Compared with the natural environment, human activities such as urbanization and industrialization aggravate the heavy metal pollution in water [9]. High rainfall and water volume in the Yellow River in S_D may accelerate the water flow in wetlands, diluting heavy metal elements. Meanwhile, dense plants in S_D also have a certain adsorption effect on heavy metals. Field investigation shows that there were no industrial sources of heavy metals around the selected wetlands. The flood season was in the period of agricultural cultivation in Henan province, and the content of heavy metal elements in agrochemicals and fertilizers is relatively high. Therefore, the excess concentration of heavy metals in the wetlands could be caused by agricultural activities in the surrounding farmlands in S_D.

Heavy metal elements were deposited in large volumes (mainly Hg) in S_B. The river runoff was relatively small and the wetland plants just germinating, which would cause the heavy metal deposition in the wetlands. The HPI value of artificial wetlands was higher than that of natural wetlands, indicating that the excessive heavy metal concentrations could be caused by human factors, or the vegetation of artificial wetlands would be less than that of natural wetlands. Compared with artificial wetlands, natural wetlands were closer to the river channel and most of them live within the dike of the Yellow River. Heavy metals carried by the Yellow River could be deposited in natural wetlands, resulting in the heavy metal pollution in them being more serious.

3.2. Spatiotemporal Analysis

Most water body parameters had significant spatiotemporal variation. Among them, the water body parameters with large spatiotemporal changes include CV of TN, TP, Hg, Cd, Cr, Cu, Pb, and Zn, all of which were over 100%. COD and As had small spatiotemporal changes compared with the other parameters and the standardized coefficient of variation (CV) were 68.85% and 68.79%, respectively (Table 3).

Table 3. Statistical information of water body parameters in different hydrological seasons in wetlands along the Yellow River.

Parameter/(mg/L)	Mean	Min	Max	SD	CV	Mean in $S_D/S_A/S_B$
DO	4.93	0.06	12.64	3.61	73.30%	2.1/3.38/9.31
NH_3-N	1.41	0.154	5.984	1.37	97.36%	1.150/2.580/0.499
COD	42.97	1.535	121.3	29.59	68.85%	44.729/51.610/32.577
TN	2.15	0.258	10.161	2.53	117.63%	2.596/3.085/0.764
TP	0.27	0	3.108	0.64	236.79%	0.637/0.113/0.062
As	0.009	0.0008	0.0279	0.01	68.79%	0.1358/0.0038/0.0107
Hg	0.011	0	0.0811	0.02	189.32%	0/4.69 × 10^{-5}/0.0347
Cd	0.026	0	0.1415	0.04	163.65%	0.0776/2.06 × 10^{-6}/0
Cr	0.005	0	0.05858	0.01	274.42%	0/0.0102/0.0033
Cu	0.009	0	0.0582	0.02	159.74%	0.0006/0.0245/0.0033
Pb	0.010	0	0.0677	0.02	194.02%	0.0282/0/0.0006
Zn	0.027	0	0.1792	0.03	114.44%	0.0281/3.33 × 10^{-7}/0.0518

Notes: Mean—Mean concentration; Min—Min concentration; Max—Max concentration; SD—Standard deviation of all values; CV—Coefficient of variation of all values.

3.2.1. Water Parameter Seasonality

The mean TP concentration was highest and lowest during flood season and pre-flood season, respectively. The maximum TP value appeared in S_D, while the minimum value appeared in S_A (Table 3). However, the seasonal sequence of average DO concentration was opposite to TP, while the maximum and minimum value were also opposite. The mean NH_3-N, COD, and TN concentrations were highest and lowest in S_A and S_B respectively. Among them, the maximum concentration of NH_3-N appeared in S_A and the minimum appeared in S_B. The maximum COD concentration appeared in S_B, and the minimum appeared in S_D. The maximum value of TN concentration appeared in S_A and the minimum value appeared in S_D. The chemical status of each water body studied in S_B was better than those of other seasons, consistently with the I_{wq} results.

Based on the Surface Water Environment Quality Standards of China, the mean DO concentration only reached class III in S_B, possibly because temperature, microbial metabolism, and organic matter degradation are higher in this season [55,56]. The average concentrations of TN, NH_3-N and TP in the majority of sites exceeded the standard threshold in S_D. Meanwhile, the concentrations of TN and NH_3-N in many sites also exceeded the class III in S_A, while these three parameters all met the standard in S_B. The reason may be the discharge of domestic and industrial water around the wetland (such as the waste water generated by the excrement of the farm and the water discharge from the sewage treatment plant, etc.) and the drainage after the excessive use of chemical fertilizers in the farmland [57–59]. N and P concentrations in wetland water were low in S_B, which may be associated with artificial adjustments of river water and sediment. After the operation of the Xiaolangdi dam, ammonia nitrogen management obviously improved near the dam, and thus, the downstream wetland water quality of ammonia nitrogen pollution might be reduced [54].

Higher COD aids estimation of organic matter pollution. Our results agree with previous findings that the mean concentration of COD exceeded the class III in three seasons [56]. The excessive concentration of COD could be related to the leaching and transport of natural, domestic sewage, agricultural and industrial pollutant, the high surrounding population density, and the extent of construction and other social factors [39,41,45]. The seasonal sequence of average COD concentration was similar to TN and NH_3-N sequence. The excess concentration of COD could be the same as the source of N, which was the discharge of agricultural and domestic sewage around wetlands.

Heavy metal concentrations exhibited distinct seasonal variation (Table 3). The mean Cr concentration was highest and lowest in S_A and S_D, respectively. However, five other elements' concentrations had different seasonal dynamics, and the temporal difference between the maximum and minimum values was also great. Among these, Hg exceeded the standard seriously in S_B, and its difference between seasons was also the greatest. Due to the very high value of a single parameter, the HPI value was affected mainly by this element.

The concentration of As in all selected sample sites was lower than class III allow in all three seasons. The concentration of Hg in all selected sample sites was lower than the detection line in S_D; there were three sample sites that exceeded the standard in S_A, which is 1–3 times higher than the standard. In S_B, the concentration of Hg exceeded the standard and was many times or even hundreds of times of the threshold value in all selected sites. It is worth noting that Hg concentration was low in almost all wetlands water in S_D and S_A. In S_D, except for one wetland in belt transect #03, the concentration of Cd from other wetland water exceeded the standard threshold, and the highest concentration was 28 times exceeded than the III class standard of water quality. The concentration of Cd was below the standard in the other two hydrological seasons. In S_D, Pb concentration exceeded the standard at three sites in belt transect #01, #02 and #03, respectively, while it was normal in two other hydrological seasons. In S_D, Cr concentration was lower than the detection line in all sites. However, Cr concentration in two sites exceeded the standard in S_B and S_A. The Cu and Zn concentrations all were lower than the standard values.

High Cd concentration was almost certainly a result of anthropogenic activities, especially wastewater discharge from industry and the overuse of agrochemicals and fertilizers [60–62]. Excessive Pb in wetland water is associated with anthropogenic origin, and travels via the freshwater input from rainfall and freshwater from rivers [63]. If humans ingest the water or fauna from these wetlands, the Pb can be harmful to human health [64]. Regarding seasonal difference, the main factor may be human-caused. For example, all sites with higher Cr concentration were artificial wetlands. High Hg concentration in wetlands could be related to lower water supply and excessive human interference in S_B. The excessive Hg may not only be caused by the human disturbance but also by natural factors such as decreased runoff from the Yellow River and the plants in juvenile stage [64–68].

3.2.2. Analysis of Water Parameters' Spatial Characteristics

KMO had a value of 0.673 greater than 0.5, which can take a satisfactory factor analysis. Meanwhile, the null hypothesis of Bartlett Test of Sphericity was rejected at the significance level of 0.05, but in this study, the value is 0, which is small enough to reject the null hypothesis. In fact, the PCA successfully identified underlying interrelationships amongst the parameters.

In this study, four principal components with eigenvalues greater than 1 were extracted; they explained 71.167% of the total variance in the water dataset (Table 4). The first and second principal components accounted for 51% of the total variance among the original variables, and then the indices with the highest load value > 0.7 were Cu (0.721) and Cd (0.788) [69], indicating that these two water quality parameters can explain more than 50% of the water quality change information of wetlands (Table 4). The contribution of the third and fourth principal components were 11% and

9%, respectively. The parameters with the highest load value were TN and COD, respectively, and their values were 0.591 and 0.755. PC3 and PC4 including organic and nutrient variables can be attributed to anthropogenic pollution sources, may be associated to influences from municipal and industrial point-source discharges, agricultural nonpoint sources, livestock operations, and/or domestic sources [41,69].

Table 4. Principal component loading matrix.

Water Quality Parameters	Principal Component			
	1	2	3	4
DO	−0.603	−0.579	0.327	−0.135
NH_3-N	0.695	−0.089	0.055	0.33
COD	0.398	0.161	0.261	0.755
TN	0.555	0.28	0.591	−0.218
TP	0.269	0.597	0.554	−0.162
As	−0.485	0.462	−0.317	0.423
Hg	−0.662	−0.354	0.363	0.04
Cd	−0.021	0.788	−0.33	−0.179
Cr	0.448	−0.504	−0.298	−0.205
Cu	0.721	−0.546	−0.186	−0.04
Pb	0.036	0.758	−0.096	−0.253
Zn	−0.655	0.105	0.11	0.137
Characteristic root	3.208	2.902	1.32	1.11
% of variance explained	26.736	24.183	11.002	9.246
Cumulative % of variance	26.736	50.919	61.921	71.167

HCA groups sample sites according to their spatial similarities in water quality parameters and heavy metal parameters [70]. By analyzing the principal component load matrix, the change of water quality in wetland landscapes along the Yellow River can be better explained by the COD, TN, Cd and Cu. Then, the wetlands in different hydrological seasons were statistically clustered by four characteristic parameters. We built a dendrogram from the case HCA using Ward's method and grouped the 18 sampling sites into four statistically significant groups at the rescaled squared Euclidean distance (SED) < 5.000 (Figure 4).

Cluster 1 included most sample sites, located in all belt transects in each hydrological season. In S_D, Cluster 2 was consistent with four sites, most of which were inside the dike or on the north side of the Yellow River. TN, TP, COD, NH_3−N and Zn in Cluster 2 sites were obviously higher than in Cluster 1 wetlands, DO was the opposite of the former (Figure 3a). The overall pollution was serious in Cluster 2 sites in S_D. By analyzing the records of the ambient environments, Cluster 2 was found to be in the affected area with hanging river. The Yellow River had great water volume and carried a large amount of material in S_D, which influences the wetlands along the middle and lower Yellow River through the lateral infiltration mechanism, especially the sites within the great dike of the Yellow River. In the north bank of the belt transect #03, the wetlands were also seriously polluted outside the dike. Lateral infiltration was significant in this area due to topography and river situation; still, it was an artificial wetland and the influence of human interference on it cannot be ignored.

In S_A, Cluster 2 contained four sites, two inside and two outside the dike. Three were located at the south side of the Yellow River (Figure 3b). Cr, Hg, Cu, Zn and TP in Cluster 2 were obviously higher than in Cluster 1. The concentration of several heavy metal elements in Cluster 2 was higher than that in Cluster 1. Cluster 2 included only artificial wetlands, except one. There was a high concentration of heavy metals in S_A, mainly due to human disturbance. Belt transect #03 (Yuanyang-Zhongmu) in southern region of the Yellow River are located in Yuanfang of Kaifeng. According to field surveys, the intense human development in the region (large areas of cultivated land, amusement parks, plants, etc.), may have caused the high heavy metal concentrations.

In S_B, Cluster 2 contained three sites, two sites on the south bank inside the dike and one on the north bank on the outside the dike. Cluster 3 was a fish pond with serious human disturbance (Figure 3c). Cluster 2 was mainly characterized by serious organic pollution. Two of the clustering sites were in the belt transects #03 and were artificial wetlands. Their surrounding areas were residential areas and farmland, so the pollution source might be agricultural pollution and domestic wastewater. Another wetland in Cluster 2 was located near the channel and fish pond on the south bank of the Yellow River, and was also contaminated by human disturbance. Cluster 3 was a typical artificial fish pond. An artificial oxygen pump raised its DO concentration. Due to the human disturbance, the content of heavy metal elements was much higher than that of other wetlands.

Water quality differed among hydrological seasons. The covariability of water quality parameters in three seasons was diverse, which indirectly indicates that water pollutants come from different sources. Overall, the affected area with hanging river was seriously polluted, and the pollutants may be accumulated through natural factors (the Yellow River lateral infiltration) in S_D. The artificial wetlands were seriously polluted in S_B and S_A, mainly by agricultural and domestic wastewater. There was frequent serious pollution of wetlands in belt transect #03.

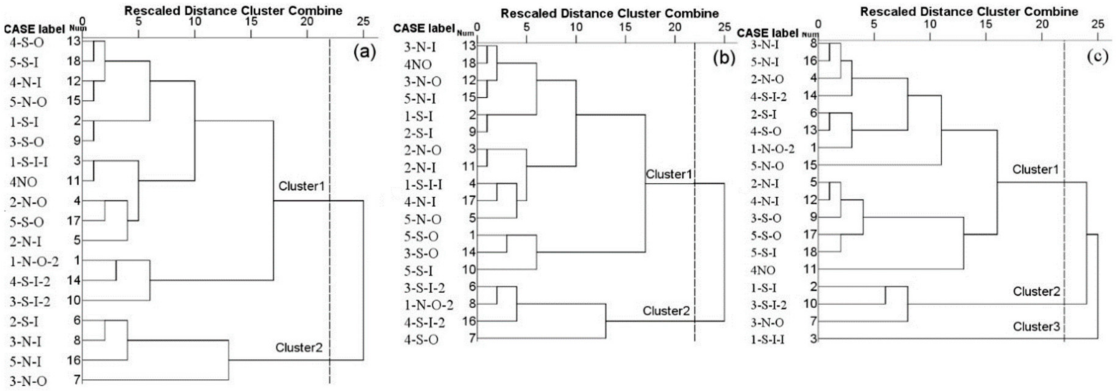

Figure 3. Dendrogram from cluster analysis based on water quality parameters for 18 sites during the flood (**a**), post-flood (**b**) and pre-flood (**c**) seasons.

3.3. Correlations of Heavy Metals with Water Quality

3.3.1. Pearson Correlation Analysis

COD was significantly positively correlated ($p < 0.05$) with NH_3-N and TN, and there was a highly significant positive correlation ($p < 0.01$) between TN and TP, indicating that there was covariance between organic pollution and inorganic pollution during the flood season (Table 5). Meanwhile, the correlation of nitrogen and phosphorus concentrations in water was extremely significant ($p < 0.01$). Both these elements may cause serious eutrophication in water. If the discharge of domestic sewage and agricultural waste can be controlled eutrophication in S_D may be avoided by reducing pollutant inputs. There was no significant correlation ($p > 0.05$) between water quality parameters in S_A. However, there was a significant positive correlation ($p < 0.05$) between COD and TP in S_B, indicating that COD increases with increasing TP, which indirectly proves that COD is driven by domestic sewage and agricultural sewage.

Table 5. Pearson correlation coefficients matrix between the water quality parameters.

Period	Parameter	DO	NH_3-N	COD	TN	TP
S_D	DO	1				
	NH_3-N	−0.255	1			
	COD	−0.02	0.520 *	1		
	TN	0.071	0.366	0.480 *	1	
	TP	−0.047	0.256	0.414	0.895 **	1
S_A	DO	1				
	NH_3-N	0.035	1			
	COD	−0.424	0.065	1		
	TN	0.244	−0.098	−0.162	1	
	TP	0.086	−0.046	0.288	−0.046	1
S_B	DO	1				
	NH_3-N	−0.389	1			
	COD	−0.165	0.26	1		
	TN	0.365	0.001	0.376	1	
	TP	−0.201	0.368	0.565 *	0.43	1

Notes: The S_D, S_A, and S_B represent the three hydrological seasons, respectively flood season, post-flood season, and pre-flood season. *: significance level = 0.05 (Two-tailed), **: significance level = 0.01 (Two-tailed).

According to the Pearson correlation analysis (Table 6), only As and Zn were significantly correlated with water quality (though As and water quality had no significant correlation in S_A), as was negatively correlated with TN in S_D. And it was also significantly negatively correlated ($p < 0.05$) with DO, while extremely significantly positively correlated ($p < 0.01$) with COD and TP in S_B. Zn was negatively correlated with DO and positively correlated with NH_3-N in S_D. Zn was also positively correlated with TP in S_A and TP was positively correlated with NH_3-N in S_B. Heavy metal elements were difficult to degrade in water, but the concentration of some heavy metal elements in water decreased with increasing dissolved oxygen content in some wetlands, which may be partly due by aerobic microorganism activities [71]. Although the correlation between heavy metals concentrations and various water quality indexes was different, all of them were positively correlated, except DO. In other words, these heavy metals and water quality likely covaried with each other [72]. Compared with S_B, the TP and As, DO and Zn show significant negative correlation, while the correlation between COD, TP and heavy metals became insignificant in S_D (Table 6). River surface runoff, rainfall, and agricultural irrigation increased in S_D. Zn and TP in agrochemicals and fertilizers enter into the wetland system through irrigation water or rainfall/agricultural runoff [54,61]. Because of temperature and hydrological conditions in S_D, DO concentrations often decreased greatly. As is also not deposited in wetlands water. Thus, DO and Zn show significant negative correlation and water quality results from S_B can differ from the "first flush" effects on the metal concentrations.

Table 6. Pearson correlation coefficients between the water quality parameters and heavy metals.

Period	S_D		S_A		S_B	
Parameters	**As**	**Zn**	**As**	**Zn**	**As**	**Zn**
DO	−0.128	−0.571 *	−0.050	0.187	−0.513 *	−0.133
NH_3-N	−0.068	0.540 *	0.219	−0.294	0.360	0.589 *
COD	0.125	0.001	0.081	−0.141	0.640 **	0.204
TN	−0.496 *	0.039	−0.141	−0.110	0.155	−0.034
TP	−0.417	−0.036	−0.060	0.698 **	0.658 **	0.117

Notes: Relationships without significant correlations are not listed. *: significance level = 0.05 (Two-tailed); **: significance level = 0.01 (Two-tailed).

3.3.2. Redundancy Analysis

The results show that the first two axes explained 82.3% variation of water quality data. Among the five water quality parameters, COD (IF = 1.3) and DO (IF = 0.9) had significant impacts on the concentration of heavy metals in S_D. Pb and As were in the first quadrant, which contributed to the potential factors of DO and COD with their response values to the heavy metals greater than 0. Zn was in the third quadrant, which contributed to the potential factors of TP, NH_3-N, and TN. In contrast, NH_3-N had the largest influence on Zn, while TP had the smallest. The arrow direction of COD was opposite to that of Cd and Cu and the included angle was obtuse, indicating that there was a negative correlation between them, but it was not significant (Figure 4a).

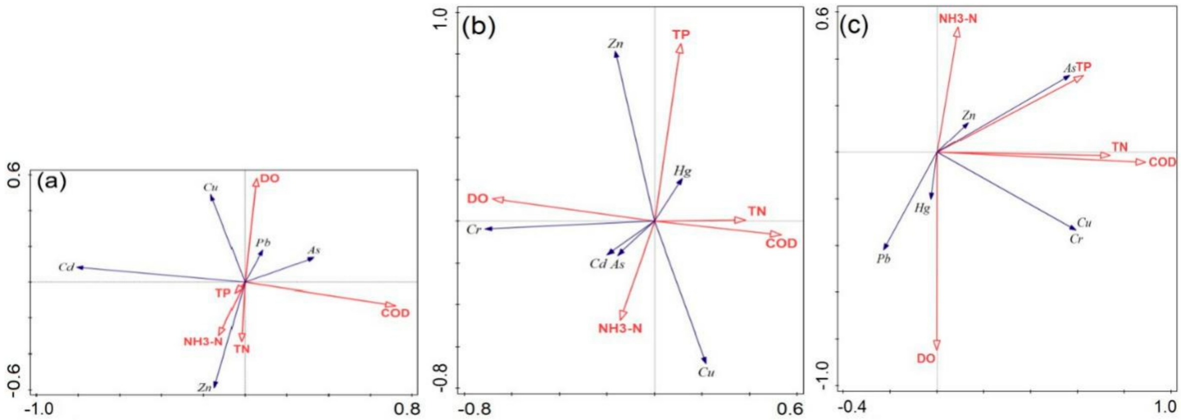

Figure 4. The ordination biplot based on RDA of the relationships among the water quality parameters and heavy metals during the flood (**a**), post-flood (**b**) and pre-flood (**c**) seasons. Positive correlations were represented by red and blue arrows in the same direction, and the projected length between two arrows was the degree of their correlation.

The first two axes explained 96.89% of variation in water quality data. Among the water quality parameters, DO (IF = 3.2), COD (IF = 1.8) and TP (IF = 1.0) had significant influences on the content of heavy metal elements in S_A. Hg and Cu were in the first and fourth quadrant, respectively; TP, TN, and COD may have influenced Hg, among which TP had the most significant influence. The Zn was located in the second quadrant and the Cr, Cd, As in the third quadrant, DO and NH_3-N had certain potential influences on them, among which DO and NH_3-N had the most significant influences on Cr and As, respectively (Figure 4b).

The results show that the first two axes explain 86.81% of variation in water quality. COD (IF = 1.8), DO (IF = 1.3), TN (IF = 1.3) had significant impacts on the content of heavy metal elements in S_B. The Zn and As were in the first quadrant and the Cu and Cr in the fourth quadrant; TP, TN, COD and NH_3-N may have influenced them. TP had the most significant impact on As and COD had a greater impact on these heavy metal elements. The Hg and Pb were in the fourth quadrant DO influenced them and Hg was relatively affected by DO (Figure 4c).

Part water quality parameters and heavy metals concentrations were correlated with each other, may indicate a common origin of pollutant. Correlations between metals may reflect their common source and similar migration behavior [45]. Previous research results indicate that reduced river flows and increased pollution values and agriculture-driven water depletions have caused a critical situation in water quality of the downstream Yellow River [24,54]. The wetland water in S_B is rich in heavy metals and the release of heavy metals can change the physical conditions of freshwater environments, threatening aquatic organisms and reducing the richness and diversity of benthic species [73,74]. However, studies of the relationship between water chemical parameters and heavy metal content are less frequent. We showed that there were diverse potential relationships between multiple factors, that sources of various pollution types may be similar. Among them, DO had a great influence on heavy metal concentrations. DO concentration is an essential parameter that maintains the equilibrium of aquatic ecosystems. It is commonly used to assess water resource quality. Generally, a high DO concentration in the natural state indicated a better water state [55,56]. Prior research had shown DO exhibited weak negative correlations with the heavy metals, proving that it could not be the potential factors of influence on the heavy metals in natural river [45]. In contrast, because artificial oxygen pumps raised wetland water DO concentration in our study area, DO had potential positive influences on heavy metals including Pb, As, Cr, Cd and Hg in different hydrological seasons, indirectly proving that heavy metal pollution is caused by human interference. The effects of environmental parameters on wetland habitats are significant [12]. High concentrations of heavy metals in the surrounding environment can result in reduced relative abundance and diversity of organisms by affecting the balance of the food web, resulting in a considerable potential risk to the wetland ecosystem [75]. The lack of necessary infrastructure and proper management caused environmental pollution at the study region [62] and our study can provide suggestions for water treatment and management.

4. Conclusions

The mean I_{wq} value was highest and lowest during the flood and pre-flood seasons respectively. However, the mean HPI value was lowest in the flood season and highest in the pre-flood season. The excessive I_{wq} value may be due to the pollution of agricultural and domestic wastewater. The main reason for the excessive HPI value may be the small water volume in the Yellow River and the low precipitation in study area, which lead to slow flow of wetlands water and the deposition of heavy metal elements.

There were significant spatiotemporal differences in water quality parameters and heavy metal concentrations in wetlands along the middle and lower Yellow River. TN, COD, Cu, and Cd explain the spatiotemporal changes of water body status. The spatiotemporal difference of water quality parameters may be mainly caused by the discharge of agricultural and domestic sewage around the sample sites. Excepting Hg, the heavy metals likely originate from human sources (mainly agricultural influence) and the seasonal difference of heavy metal concentrations was caused by different degrees of human activity across the year. Due to human disturbance and a decrease in runoff from the Yellow River, Hg element was deposited in wetland waters during the pre-flood season. During flood season, the affected area with hanging river was seriously polluted and the pollutants may be accumulated mainly through natural factors (the Yellow River lateral infiltration mechanism) [76]. The artificial wetlands were seriously polluted during the post-flood and pre-flood seasons. Sites along belt transect #03 were divided into a cluster with serious pollution, indicating that this belt transect was seriously polluted.

There was a potential correlation between the water quality parameters and heavy metal elements, but their mean concentration was distributed in reverse during different hydrological season. Among them, dissolved oxygen had a great influence on heavy metal concentrations. There were diverse potential relationships between multiple factors, suggesting that sources of various pollution types may be similar.

Author Contributions: Z.H. conceived and designed this research; Q.Z. and S.D. also contributed to research idea. Z.H. performed the research and analyzed the data and wrote the paper. Q.Z. and S.D. helped build the idea further and offered critical editing support. J.C., L.P., S.W., Y.H. took part in the experiment. G.L. offered editing support. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

We added the more detailed characterization of environmental settings of the studied wetland in Table A1.

Table A1. The location of Xiaolangdi dam and transects.

Transect Number	Location	Geographic Information	Distance to Xiaolangdi Dam
belt transect #01	Wenxian-Gongyi	113°5′41″ to 113°6′33″ E 34°0′ to 34°51′ N	70 km
belt transect #02	Yuangyang-Zhengzhou	113°40′40″ to 113°44′92″ E 34°54′8″ to 35°0′21″ N	140 km
belt transect #03	Yuangyang-Zhongmu	114°8′7″ to 114°12′10″ E 34°51′34″ to 34°59′58″ N	190 km
belt transect #04	Fengqiu-Kaifeng	114°27′36″ to 114°30′22″ E 34°51′43″ to 34°57′54″ N	230 km
belt transect #05	Changyuan-Lankao	114°30′52″ to 114°41′6″ E 34°50′58″ to 34°57′34″ N	260 km

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