Hindawi
Journal of Chemistry
Volume 2022, Article ID 2857700, 12 pages
https://doi.org/10.1155/2022/2857700

Research Article

Characteristics of Water Pollution and Evaluation of Water Quality in Subsidence Water Bodies in Huainan Coal Mining Areas, China

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Received 22 April 2022; Accepted 8 June 2022; Published 15 July 2022

Academic Editor: Jun Wu

The subsidence water bodies in coal mining areas are vulnerable to being polluted by the surrounding mining production wastewater, domestic sewage, and agricultural return flow. Therefore, it is important to grasp the water quality condition of the above water bodies. A total of 16 surface water samples from 7 different subsidence water bodies in the Huainan mining area were collected and focused on the selection of 22 water quality indicators for water pollution characteristics analysis. The result of correlation analysis showed that Cr and Zn came from the same source of pollution. Three principal factors were selected by factor analysis, which could explain 82.294% of the total variance. Principal factor 1 indicated a mixture of pollution related to nitrogen and phosphorus nutrients, organic pollutants, and heavy metals; principal factor 2 showed heavy metal pollution; and principal factor 3 presented the pollution from heavy metals and cations. Results of cluster analysis showed that the water quality status of 16 sampling points could be divided into 4 clusters. The results of the heavy metal pollution index method showed that the heavy metal pollution was most serious in sample 9 (S9), S15, and S16, and the main elements of pollution were Ni, Fe, and Mn. Single-factor evaluation, comprehensive pollution index, the universal exponential formula of logarithmic power function, and membership degree method were used to evaluate the five important water quality indicators, namely total nitrogen, ammonia nitrogen, total phosphorus, dissolved oxygen, and chemical oxygen demand. The results showed that the total nitrogen pollution in the study area was more serious, most of the sites exceed class V standards of the surface water, S14 and S16 were heavily polluted. Based on the comparison of the different methods, the surface water quality in the study area can be reflected more comprehensively.

1. Introduction

In China, the proportion of coal in total energy consumption has been reduced from 70.7% (1978) to 56.8% (2020) [1], but the consumption of coal still occupies a large proportion. Long-term mining activities result in surface subsidence, which has caused irreversible impacts on the geological environment of coal mining areas [2]. The area of subsidence water bodies is expanding and has become a special kind of surface water body [3]. At present, the coal mining subsidence area is about 7262.17 hm^2 and more than 70% is subsidence water bodies [4]. They are easily polluted and the ecological environment is easily damaged. Therefore, it is important to choose a scientific method to assess the water quality of subsidence water bodies to realize the sustainable development of mining areas.

In the 1980s, the environmental problems caused by the subsidence of coal mining areas in Huainan were noticed [5]. Early studies evaluated the water ecological environment states by employing the frequently used water quality indicators (transparency, total phosphorus, total nitrogen, permanganate index, etc.), conducted water resources investigation and research on eutrophication characteristics in the subsidence areas, and analyzed the functional uses of the water body [6, 7].

Pei et al. used the comprehensive nutrition state index method to assess the eutrophication state of the subsidence water bodies of Yangzhuang village in Panji, and the result was mild-moderate eutrophication [8]. Qu et al. concluded that the nitrogen to phosphorus ratio (N:P = 25–117) of the subsidence water bodies was high with obvious seasonal variation, and the N:P was lower in the growing season than in other seasons [9]. Subsequently, heavy metal contamination of the water bodies raised concerns. Wang et al. determined Cd, Cu, Pb, and Zn in different tissues of crucian carp, and concluded that the aquatic ecosystem was not contaminated by them, the metal concentrations were lower than the regulations for cultured fish [10]. In risk assessment, Chen et al. evaluated the health risk of heavy metals (Cu, Ni, Pb, Cd, Co, Cr, As, Hg, etc.) in the subsidence water bodies based on the Monte Carlo method; the results showed that the total carcinogenic risk values for two exposure pathways of Cr, Ni, and As were greater than the maximum acceptable level, and the highest carcinogenic risk was found in the water body of Xinji'er mine [11].

In recent years, various water quality evaluation methods have been put forward, it is helpful to identify the pollutant characteristics and clarify the water quality objectives. Liu et al. selected four evaluation methods, including single-factor evaluation, comprehensive pollution index, graded evaluation, and comprehensive water quality identification index method to compare, and concluded that the evaluation results of the comprehensive water quality identification index were reliable and applicable to the water quality evaluation of coal mine subsidence water bodies [12]. In the evaluation process of groundwater quality in Urumqi city, Wang et al. calculated the weight of water quality indexes by the fuzzy synthesis evaluation coupled grey relational analysis (GRA-fuzzy), and concluded that it was better than the single-factor evaluation and Nemero synthesis index evaluation method [13]. Liu and Zheng thought that the modified comprehensive water quality identification index (WQI) method not only overcame the shortcomings of single-factor evaluation but also took into account the impact of multiple indicators [14]. In addition, there were other water quality evaluation methods, such as the fuzzy comprehensive evaluation method [15], T-S fuzzy neural network method [16], and grey correlation analysis method [17].

The above studies have achieved some results, but the selection of subsidence water bodies was not comprehensive enough, and usually only the several typical water bodies were analyzed [18, 19]. In addition, the single evaluation method, that was frequently used, was not conducive to the mutual verification and comparison between evaluation results. Therefore, to understand the pollution situation of Huainan subsidence water bodies more scientifically and reasonably, a more comprehensive water quality evaluation was needed.

The research objectives of this article were (1) to analyze water pollution characteristics of subsidence water bodies based on water quality monitoring data to understand the pollution status of subsidence water bodies; (2) to use the factor analysis model to identify pollution sources; and (3) to provide a scientific basis for water resources development and pollution prevention by comparing four water quality evaluation results.

2. Materials and Methods

2.1. Study Area and Locations of the Samples. Huainan mining area is located on both sides of the Huai River in northern Anhui Province, and spans the cities of Huainan and Fuyang, with an area of about $3200\,km^2$. The advantageous geographical location and convenient transportation provide convenient conditions for the mining and transportation of coal resources [20]. The prospective coal reserve reaches 44.4 billion tons, and the proven reserve reaches 15.3 billion tons [21]. Due to the ground subsidence caused by coal mining, the cumulative area of the subsidence area was about $316.81\,km^2$ by the end of 2019 [22]. With the continuous mining of coal, the subsidence area is increasing and the area of subsidence water bodies is expanding. According to the spatial distribution of subsidence water bodies, 7 subsidence water bodies were selected, 16 sampling points were set up, and the specific points were shown in Figure 1 (Due to the short distance, some points may be blocked). In addition to the consideration of physical and chemical parameters and nutrient indexes (pH, total hardness, ammonia nitrogen, NO_3^-, TN, and TP), oxygen-consuming organic matter index (DO, COD, and TOC), cations and anions (K^+, Na^+, Mg^{2+}, Cl^-, and F^-), this study selected 8 heavy metal indexes (Cu, Zn, Cr, As, Pb, Ni, Fe, and Mn) that were more concerned in subsidence water bodies to evaluate the water quality of the study area, and a total of 22 indexes were selected.

2.2. Collection of Water Samples and Test. The water samples from the subsidence water bodies were collected on February 18–19, 2021. Standard water sampling bottles were used to hold the water samples, and the collected samples were pretreated according to different measurement indexes by selecting the corresponding pretreatment methods. Then they were stored away from light and transported to the laboratory for testing. At each sampling point, pH, water temperature, and dissolved oxygen (DO) were measured on-site using an HQ40D portable multi-parameter water quality analyzer. Chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), ammonia nitrogen, nitrate ion (NO_3^-), total hardness, K^+, Na^+, Mg^{2+}, F^-, Cl^-, Cu, Zn, Cr, As, Pb, Ni, Fe, and Mn were brought back to the professional testing institution for testing. The testing standards of the water quality indexes involved in this article were shown in the supplementary materials (Section 2.2).

2.3. Water Quality Assessment Methods

2.3.1. Single-Factor Evaluation Method. The single-factor evaluation method determines the comprehensive water quality category according to the category of the single index with the worst water quality among all the water quality indexes involved in the evaluation [23]. The selected indicators (COD, TN, TP, ammonia nitrogen, and DO) were compared with Environmental quality standards for surface water (GB3838-2002) [24], and the thresholds for the five

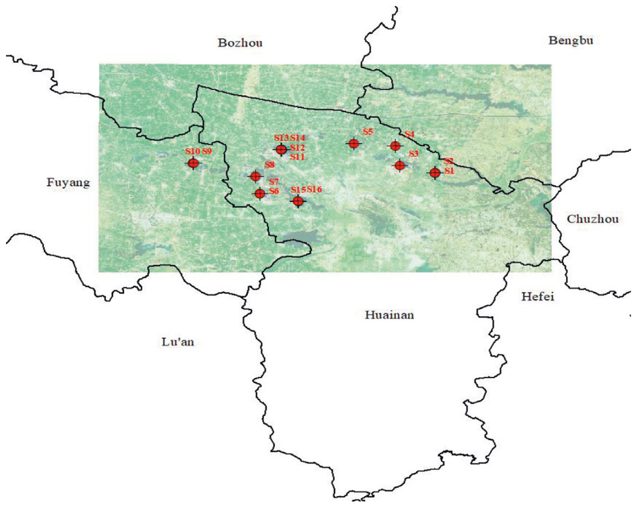

FIGURE 1: Sampling points located in the coal mining subsidence water area of Huainan, China.

levels of standards were shown in Table S1 (supplementary Table 1). In this study, the class V standard was selected as the reference standard and calculated by equation (1):

$$P_i = \frac{C_i}{C_0}, \quad (1)$$

where C_i is i^{th} pollutant concentration value (mg/L), C_0 is i^{th} pollutant evaluation standards (mg/L), and P_i is i^{th} pollutant pollution index.

2.3.2. Comprehensive Pollution Index Method. The comprehensive pollution index method assumes that the contribution of each factor to water quality is basically the same, and calculates the arithmetic mean of the sum of the standard indices of each factor. The method can determine the degree of pollution of the study water bodies [25], which is calculated by equation (2):

$$P = \frac{1}{m}\sum_{i=1}^{m} P_i, \quad (2)$$

where P_i is the pollution index of pollutant *i*.

The comprehensive pollution index corresponding to the classification of water quality is as follows [26]: $P \le 0.25$, clean; $0.25 < P \le 0.4$, relatively clean; $0.4 < P \le 0.5$, light pollution; $0.5 < P \le 0.99$, medium pollution; and $P \ge 1$, heavy pollution.

2.3.3. Universal Exponential Formula of Logarithmic Power Function. The Environmental Quality Standard for Surface Water (GB3838-2002) divides the water quality evaluation criteria into five levels, and the concentration limits of the environmental quality level 5 standards for some indicators were shown in Table S2. After optimizing the parameters, the universal exponential formula of the logarithmic power function was as follows [27]:

$$\mathrm{WQI}_j = 0.0466 * \left(\ln x_j\right)^{2.1029}, \quad (3)$$

where x_j is the "normative value" of the indicator *j* listed in Table S2, calculated by equation (4):

$$x_j = \begin{cases} \left(\dfrac{c_{j0}}{c_j}\right)^2, & c_j \le c_{j0}, \text{For the DO}, \\ \left(\dfrac{c_j}{c_{j0}}\right)^2, & c_j \ge c_{j0}, \text{For the CODcr, dissolved iron}, \\ \left(\dfrac{c_j}{c_{j0}}\right)^{1/2}, & c_j \ge c_{j0}, \text{For Zn, Hg, petroleum, } \textit{Escherichia coli}\text{, volatile phenols, CN}, \\ \dfrac{c_j}{c_{j0}}, & c_j \ge c_{j0}, \text{For the remaining 12 indicators in the original table}, \\ 1, & c_j > c_{j0}, \text{For the DO}, \\ 1, & c_j < c_{j0}, \text{Other indexes except dissolved oxygen}. \end{cases} \quad (4)$$

The formula for the composite index of the *m* indicator is as follows:

$$\mathrm{WQI} = \sum_{j=1}^{m} W_j * \mathrm{WQI}_j, \quad (5)$$

where W_j is the normalized weight of index j.

2.3.4. Membership Degree Method. The membership degree method refers to a pollution indicator that belongs to a certain category of standard degree, in the same category, the greater affiliation of water quality is worse, and the smaller affiliation of water quality is better [28], can be calculated by equation (6):

$$y = \frac{x - x_0}{x_1 - x_0}, \tag{6}$$

where y is the membership degree corresponding to the type of water quality specified in x_1, x is the measured value (mg/L) and x_0 and x_1 are the standard values of two adjacent levels of x ($x_0 < x < x_1$).

2.3.5. Heavy Metal Pollution Index (HPI). The heavy metal pollution index method is a method for comprehensive evaluation of water quality pollution caused by various heavy metals in water bodies based on the weighted arithmetic mean method that can be calculated by equations (7)–(9) [29-31]:

$$W_i = \frac{k}{S_i}, \tag{7}$$

$$Q_i = \frac{100C_i}{S_i}, \tag{8}$$

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

where S_i is the standard value of the concentration of heavy metal i in the water body (μg/L); k is the proportionality constant, taken as 1; C_i is the measured concentration of heavy metal i in the water body (μg/L); Q_i is the quality level evaluation of heavy metal i; HPI is the heavy metal pollution index; n is the number of heavy metal elements involved in the evaluation; W_i is the weight of heavy metal i, which is regarded as an inversely proportional value to S_i in the model.

Generally, the critical pollution index of the HPI value is set at 100 [32]. However, Edet and Offiong divided the degree of heavy metal pollution into three levels (high, medium, and low): when HPI > 30, the degree of pollution is high; when 15 ≤ HPI ≤ 30, the degree of pollution is moderate; and when HPI < 15, the degree of pollution is low [33].

2.4. Statistical Analysis Methods. IBM SPSS 23.0 software was used for statistical analysis of the data, including Pearson correlation analysis, one-way ANOVA, factor analysis, and cluster analysis.

3. Results and Discussion

3.1. Characteristics of Water Quality Factors

3.1.1. Physical and Chemical Parameters and Nutrient Indexes. The physicochemical parameters and nutrient indicators measured in this study included pH, total hardness, ammonia nitrogen, NO_3^-, TN, and TP. The pH of 16 sampling sites ranged from 7.25–8.84, which belonged to medium alkaline water bodies (pH = 6–10) [34], and met the pH standard limits (6–9) in the Environmental Quality Standards for Surface Water (GB3838-2002), and most of the sampling sites could also meet the requirements of the pH value of the Water Quality Standard for Fisheries (GB11607-89; pH = 6.5–8.5) [35] and the total hardness ranged from 155 to 260 mg/L with an average value of 199 mg/L. Moreover, the content of ammonia nitrogen ranged from 0.338 to 1.060 mg/L, and all of them reached the water quality standard of surface water category IV (1.5 mg/L). The content of NO_3^- ranged from 0.016 to 5.640 mg/L and all sampling sites reached the standard limit (10 mg/L). The content of TN and TP at each sampling point was shown in Figure 2. As seen in Figure 2(a), the content of TN ranged from 1.87 to 5.46 mg/L and exceeded the surface water class V standard (2.0 mg/L) at all sites except for S15. In the end, the content of TP ranged from 0.06 to 0.74 mg/L in Figure 2(b), except for S8, S14, and S16 which exceeded the surface water class V standard (0.4 mg/L), and all other sampling points could meet the class V standard of surface water. Overall, the total nitrogen index exceeded the standard more seriously.

3.1.2. Oxygen Consuming Organic Matter Index. The content of DO and COD at each sampling point was shown in Figure 3. DO is an important indicator of the self-purification ability of water bodies. Generally speaking, the higher the dissolved oxygen in water, the better the water quality. However, due to the overgrowth of algae, DO may be oversaturated [20], which can have adverse effects on fish. The content of DO in the study area ranged from 7.15 to 15.29 mg/L (water temperature was 11.2–15.6°C), and the average content of DO was 10.6 mg/L, which could meet the surface water class I standard (7.5 mg/L) except for sampling site S1. COD indicator can represent the pollution degree of water bodies by organic matter to a certain extent. The greater the COD, the more serious the pollution of water bodies by organic matter. The content of COD measured in this study ranged from 16 to 49 mg/L, with an average value of 30.56 mg/L. Except for S14 and S16, which exceeded the surface water class V standard (40 mg/L), the other sampling sites met the standard. TOC is an indicator of organic content directly expressed as the amount of carbon in the water sample, and the higher the TOC value, the higher the organic content in the water. The content of TOC measured in the study area ranged from 0.8 to 12.1 mg/L, with an average value of 8.31 mg/L.

3.1.3. Heavy Metal Index. Heavy metal pollutants have the characteristics of easy accumulation, difficult decomposition, and strong toxicity [36, 37]. Heavy metals entering the water environment will cause serious and lasting environmental pollution to rivers and lakes, and enrich the environment through the food chain in organisms step by step [38], which will also be harmful to humans. In this study, the contents of eight heavy metals, including Cu, Zn, Cr, As, Pb, Ni, Fe, and Mn, were detected to study the heavy metal pollution in subsidence water bodies. The contents of Cu, Cr, and Pb were 0.97–2.46 μg/L, 0.12–1.08 μg/L, and 0.18–1.19 μg/L, respectively,

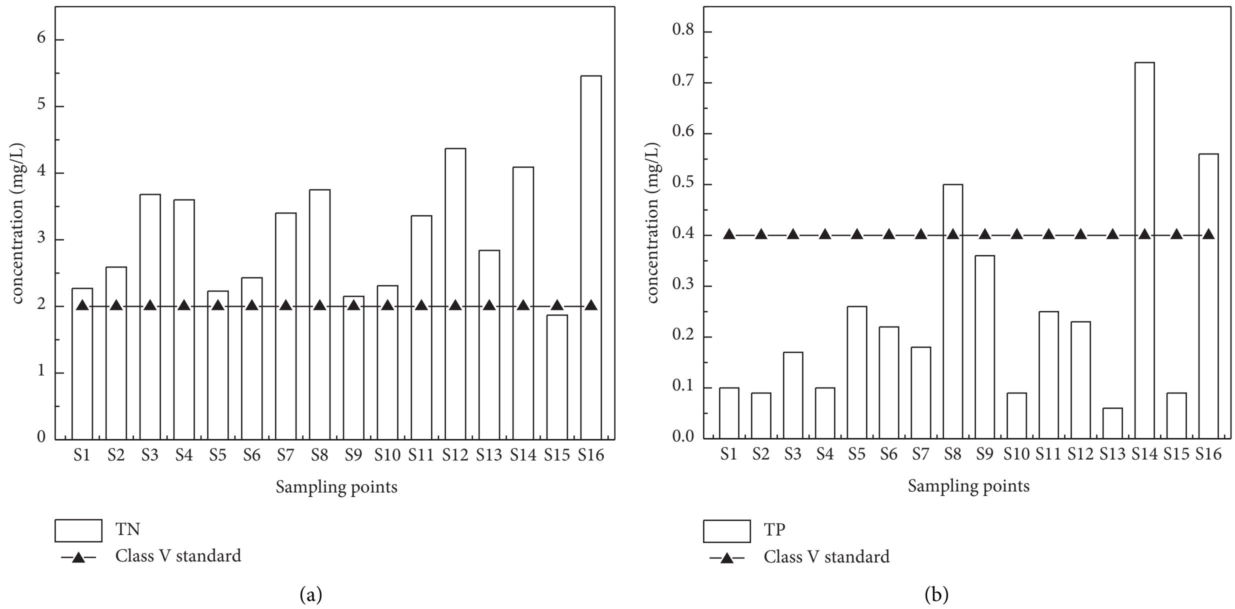

FIGURE 2: The content of TN (a) and TP (b) at each sampling point in the Huainan coal mining subsidence water bodies.

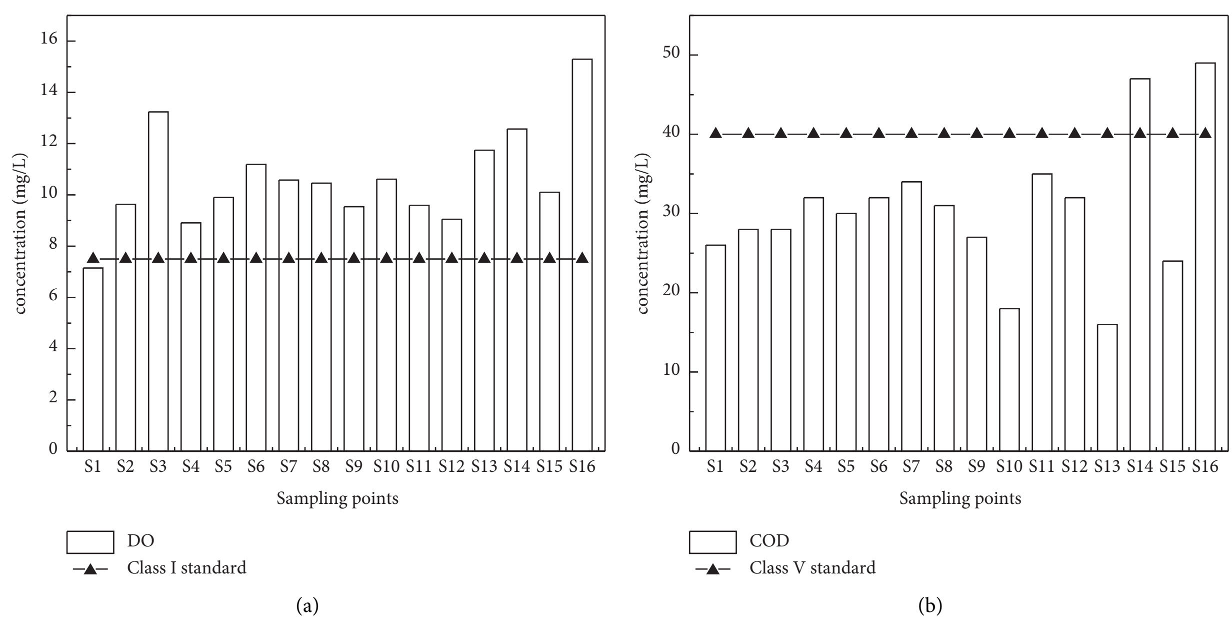

FIGURE 3: The content of DO (a) and COD (b) at each sampling point in the Huainan coal mining subsidence water bodies.

and all sites reached the surface water class I standard (10 μg/L). The contents of Zn and As were 3.93–17.4 μg/L and 2.14–14.6 μg/L, respectively, and all sampling sites reached the standard of surface water class I (50 μg/L). The content of Ni was 1.12–6.99 μg/L, all of which were lower than the standard limit of specific items for centralized surface water sources of living drinking water (20 μg/L).

The pollution of Fe and Mn was more serious. The content of Fe and Mn was shown in Figure 4. The content of Fe was 34.9–666 μg/L, except for S9 and S10, the rest of the sampling points were lower than the standard limit value of the supplementary project of the centralized surface water source of drinking water (300 μg/L), and the content of Fe at S9 reached 666 μg/L that seriously exceeded the standard. The content of Mn was 18.5–120 μg/L. Except at S4 and S11, the rest of the sites were lower than the standard limit value of the supplementary project of a centralized surface water source for drinking water (100 μg/L). In summary, the concentration of Cu, Zn, Cr, As, Pb, and Ni in the study area was low, but the pollution caused by heavy metal Fe from the Xieqiao coal mine (S9–S10) was more serious.

3.1.4. Other Pollution Indicators. In addition to physico-chemical indicators, nutrients, oxygen-consuming organic matter indicators, and heavy metal indicators, K^+, Na^+, Mg^{2+},

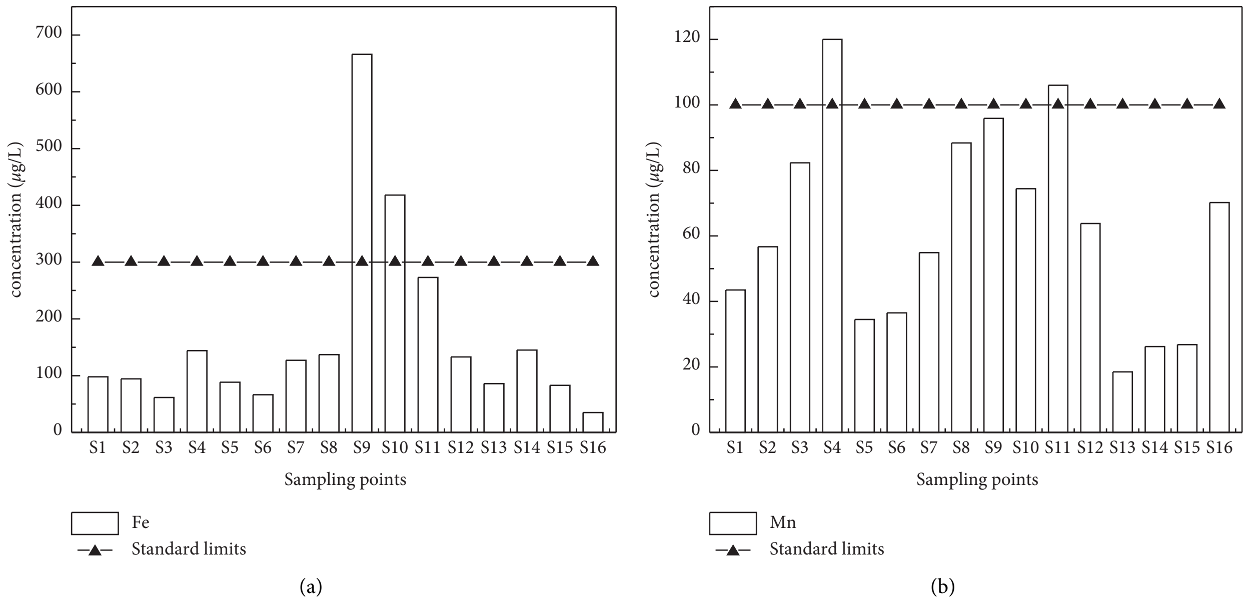

Figure 4: The content of Fe (a) and Mn (b) at each sampling point in the Huainan coal mining subsidence water bodies. (The standard limits of Fe and Mn in the figure refer to the standard limits of supplementary items of centralized surface water sources for drinking water.)

Cl^-, and F^- were also detected in this study. Among them, the pollution of $Cl^-$and F^- was more serious. The content of Cl^- and F^- was shown in Figure 5. Chlorine (Cl) is one of the common elements in coal. During coal combustion, Cl in coal is released in the form of hydrogen chloride or granular Cl [39]. The content of Cl^- in each sampling site ranged from 78.3 to 341 mg/L, among which the Cl^- in S1, S2, S4, S5, S9, S10, and S13 was lower than 100 mg/L. As shown in Figure 5(a), except for S15 and S16, the content of Cl^- at all sampling sites was less than the standard limit (250 mg/L), but the content of Cl^- greater than 50 mg/L is generally considered to be contaminated [20], and it can be seen that the monitoring area has been contaminated by Cl^-, especially S15 and S16 of Xinji'er mine. The concentration of F^- was between 1.10 and 5.45 mg/L. As can be seen in Figure 5(b), only five locations (S4, S7, S9, S10, and S16), reached the surface water class V standard (1.5 mg/L), while the other sampling sites exceeded the standard, among them the Guqiao coal mine (S11–S14) was more seriously polluted. F is an essential trace element for the human body, but it can lead to serious bone diseases if the specific limit value is exceeded [40]. Industrial and civil coal burning, coal gangue, slime, and other solid wastes may lead to fluorine pollution, which belongs to coal fluorine pollution [41].

Based on the above detection results, the pollution of TN in the subsidence water bodies of the study area was serious for all the sample points. At S14 (Guqiao mine) and S16 (Xinji'er mine east), the concentration of TP exceeded the standard and the concentration of COD was high. The content of F^- exceeded the standard at S14, and the content of Fe exceeded the standard seriously at S9 (Xieqiao mine).

3.2. Correlation Analysis. Pearson correlation analysis was performed on 20 water quality indicators (data of Fe and Cl^- that did not satisfy the normal distribution were removed). As seen from the results of the correlation analysis conducted between heavy metals in Figure 6(a), it can be concluded that Pb and Cu have a significant correlation ($P < 0.05$); in addition, there were significant correlations between Cr and Zn ($P < 0.01$) and Cr and Pb ($P < 0.05$). It indicated that Cr and Zn may be contaminated from the same source.

Pearson correlation analysis results of heavy metals with physicochemical properties were showed in Figure 6(b). It revealed that NO_3^- showed a significant positive correlation with Pb and Mn at the 0.05 level. Moreover, heavy metal showed a significant correlation with physicochemical indexes TN, TP, DO, COD, pH, Na^+, and F^-. And they showed an extremely significant positive correlation with TN, TP, and COD at the 0.01 level. Ni was significantly correlated with Na^+, K^+, and ammonia nitrogen, among them Ni showed an extremely significant positive correlation with Na^+ and K^+ at the 0.01 level.

3.3. One-Way ANOVA. To investigate whether there is variability in pollutant concentrations between water bodies with different subsidence times, the 16 sampling sites were divided into three categories according to the age of the subsidence water bodies as older water bodies (S1, S2, S3, S6, S7), middle water bodies (S5, S9, S10, S15, S16), and newer water bodies (S4, S8, S11, S12, S13, S14). After the homogeneity of variance test (Table S3), the one-way ANOVA between different subsidence ages of water bodies was performed for each water quality evaluation index that met the conditions. The results were shown in Table S4, from which it could be concluded that there were significant differences ($P < 0.05$) in Mg^{2+}, F^-, and ammonia nitrogen. Further analysis by multiple comparisons showed that Mg^{2+} differed significantly between medium and new water bodies, F^- differed significantly between new and old

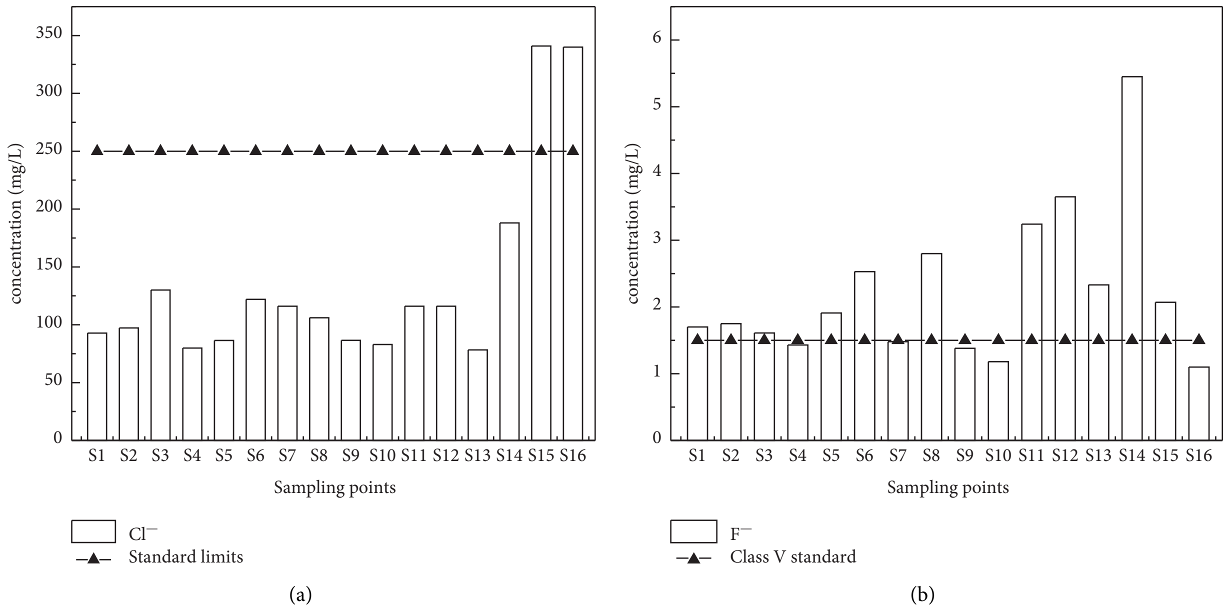

Figure 5: The content of Cl^- (a) and F^- (b) at each sampling point in the Huainan coal mining subsidence water bodies. (The standard limits of Cl^- in the figure refer to the standard limits of supplementary items of centralized surface water sources for drinking water).

water bodies, new and medium water bodies, and ammonia nitrogen differed significantly between old and medium water bodies.

3.4. Identification of Pollution Sources in Subsidence Water Bodies. The data were tested to decide whether they conformed to normal distribution by the one-sample Kolmogorov–Smirnov method. When the distribution of the variables did not conform to the normal distribution, the data needed to be logarithmically transformed, and the data that still did not obey the normal distribution after transformation should be excluded. The article used the KMO to verify the feasibility of the selected water quality factors for factor analysis, and the KMO test value of 0.695 ($P < 0.05$), which was greater than 0.6, so it met the analysis requirements. This article finally selected TN, COD, TP, As, Ni, Na, Cu, Pb, and Cr as the water quality factors for factor analysis.

As seen in Table 1, the first three factors were extracted according to the standard with an eigenvalue greater than 1. The three factors explained 35.511%, 24.868%, and 21.915% of the total variance, respectively, and the cumulative explained 82.294% of the total variance.

To make the obtained principal factors easier to interpret, the rotated factor loading matrix was analyzed. The factor loadings reflected the correlation degree between the main factors and the variables, detailed information was in Table S5. When the factor loadings were greater than 0.75, it indicated a strong correlation, 0.5–0.75 indicated moderate correlation, and 0.3–0.5 indicated weak correlation [42].

The variables with the high factor loadings greater than 0.75 were selected as the main correlation factors. Principal factor 1 mainly reflected TN, TP, COD, and As; principal factor 2 mainly reflected Cu, Pb, and Cr; and principal factor 3 mainly reflected Ni and Na^+. The three principal factors were strongly correlated with their respective main variables. Figure 7 was the three-dimensional graph of factor loadings, through the factor loadings graph, it was conducive to the intuitive display of the relationship between water quality variables.

The meaning of each principal factor was explained as follows: the contribution of the principal factor 1 was the largest, which had the greatest influence. The principal factor 1 was related to nitrogen and phosphorus nutrients, organic pollutants, and heavy metal pollutants, which were mixed pollution. Nitrogen and phosphorus fertilizers in agricultural production in the surrounding areas were used to improve the yield, but it also brought negative effects causing nitrogen and phosphorus loss to pollute the environment of surrounding water bodies. Especially during the rainy period, nitrogen and phosphorus flowed into the subsidence water bodies with surface water led to the increase of nitrogen and phosphorus nutrients [43]. The principal factor 2 was closely related to heavy metal pollution, which might come from coal gangue leaching, and the leaching water contains some toxic heavy metal elements [20]. The principal factor 3 was influenced by both heavy metals and cations.

The results of the factor scores were shown in Table S6. The higher the factor score, the more serious the sampling site was affected by this pollution. Among all sampling sites, S16 and S14 were the two most seriously polluted by TN, COD, TP, and As. S9 and S11 were subjected to the most

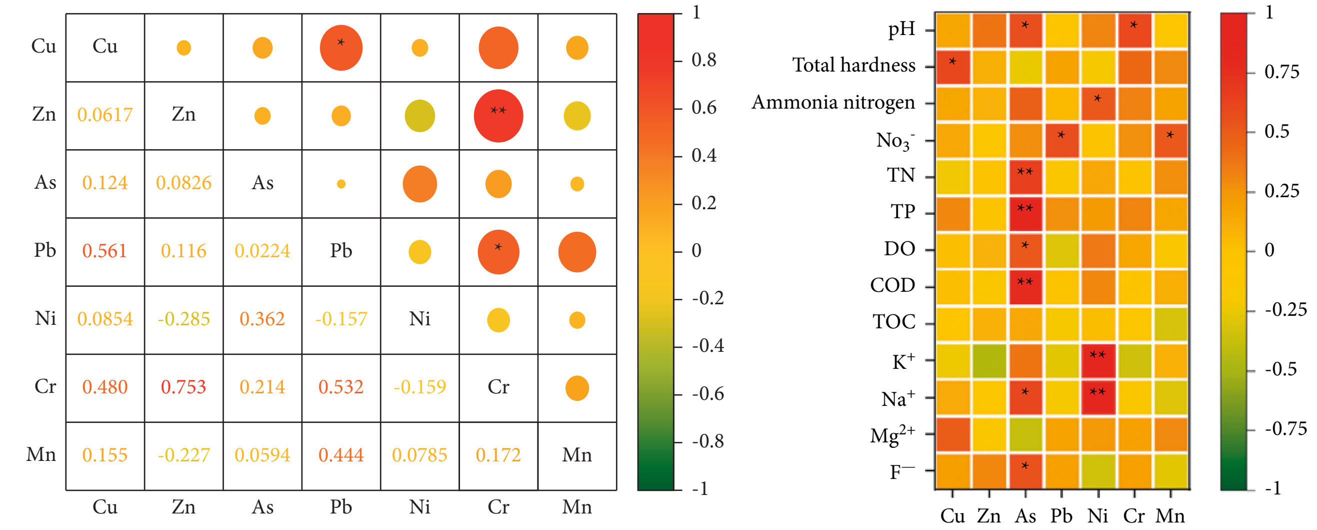

Figure 6: Heat map of correlation coefficient of heavy metal content in subsidence water bodies (a); heat map of correlation coefficients between heavy metals and other water quality parameters in subsidence water bodies (b).

Table 1: Characteristic value and variance contribution of factor analysis of water quality indicators.

Factors	Characteristic value	Variance contribution rate/%	Cumulative variance contribution rate/%
1	3.196	35.511	35.511
2	2.238	24.868	60.379
3	1.972	21.915	82.294

Extraction method: a principal component analysis.

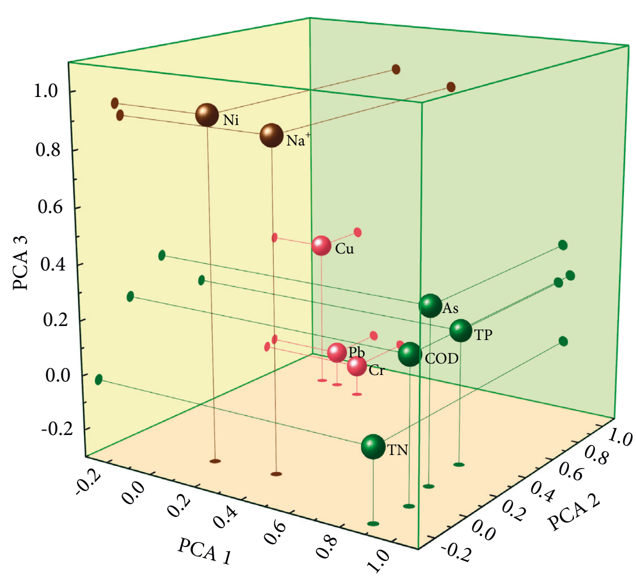

Figure 7: Three-dimensional diagram of the component plot.

serious pollution of Cu, Pb, and Cr. S15 and S16 were subjected to the most serious pollution of Ni and Na^+. The composite factor scores of S14 and S16 were higher, and it indicated that the water quality pollution was more serious in these two sampling points.

3.5. Cluster Analysis. Hierarchical clustering of sampling sites was performed based on factor scores. Using the factor scores of sampling points and the spectrum diagram for analysis was shown in Figure S1 (supplementary Figure 1), they were divided into four clusters, cluster 1 had nine sites, with a low integrated score and a better water quality situation relative to other sites. Cluster 2 has five sites, mainly affected by the main factor 1 and main factor 2, indicating that these five monitoring sites polluted by heavy metals, organic pollutants, nitrogen, and phosphorus nutrients were mainly affected by the surrounding mining production, the comprehensive score was high, and the water quality situation was poor. Cluster 3 and cluster 4 have only one component, factor score 3 for the S15 sampling point of cluster 3 was very high and polluted by the heavy metals and cations of the dual impact. For cluster 4, factor score 1 of the S16 sampling point was very high and had a high comprehensive score, indicating that the comprehensive pollution of the S16 place was serious, water quality was poor, and the former evaluation was consistent with it.

3.6. Evaluation of Surface Water Quality in Coal Mining Subsidence Area

3.6.1. Evaluation Results of the Single-Factor Evaluation Method. Five water quality indicators, namely TN, ammonia nitrogen, TP, DO, and COD, were selected to evaluate the water quality of surface water in the Huainan coal mining subsidence area by the single-factor evaluation method. Class V standard in the Environmental Quality Standards for Surface Water (GB3838-2002) was used for the analysis, only S15 reached the surface water V standard, and the rest of the sites exceeded the class V standard. The reasons for exceeding the standard for most of the sampling sites were due to excess of TN concentrations, the specific results were shown in Table S7. Among them, TN and TP exceeded the standard at S8, TN, TP, and COD exceeded the standard at S14 and S16, and only TN exceeded the standard at the remaining sampling points.

3.6.2. Evaluation Results of the Comprehensive Pollution Index Evaluation Method. The integrated pollution index of each sampling point was 0.445–1.282, the specific results were shown in Table S7. The composite pollution index of each point was S10 < S15 < S13 < S1 < S2 < S6 < S5 < S9 < S3 < S4 < S7 < S11 < S12 < S8 < S14 < S16, and the composite pollution index of S10, S15, S13, and S1 were between 0.4 and 0.5, which were light pollution; S2, S6, S5, S9, S3, S4, S7, S11, S12, and S8 had a combined pollution index between 0.5 and 0.99, which were medium pollution; S14 and S16 were greater than 1, which were heavy pollution. Figure 8 showed the average contribution rate of various pollutants at each sampling point in the comprehensive pollution index method, which could be seen that TN has the greatest influence on the water quality situation in the study area, followed by COD.

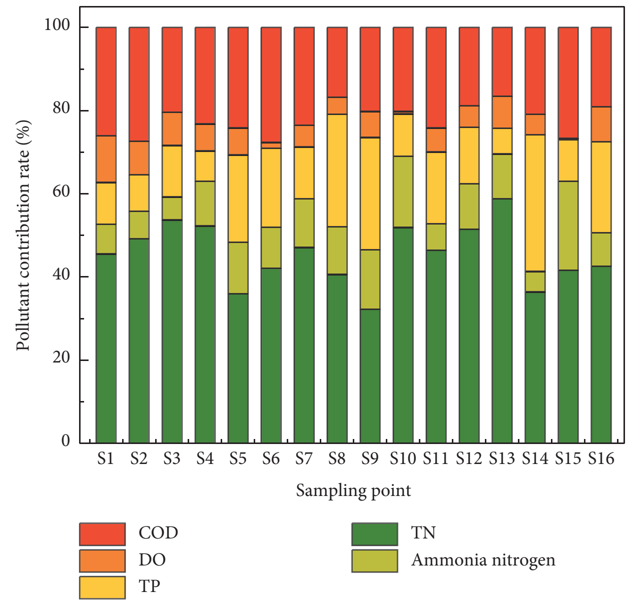

Figure 8: The contribution rate of pollutants at each sampling point for the comprehensive pollution index method.

3.6.3. Evaluation Results of the Universal Exponential Formula of Logarithmic Power Function. The five indexes TN, ammonia nitrogen, TP, DO, and COD were selected to evaluate the surface water by using the universal exponential formula of the logarithmic power function. Equations (3)–(5) were used to calculate the water quality integrated index (WQI) of 16 sampling points, the evaluation results were shown in Table S8. For S14 and S16, the comprehensive pollution index evaluation results were heavy pollution, and the evaluation results of the universal exponential formula of logarithmic power function were class V standard, both indicated that these two sites were serious pollution compared with other sites. At S1, S10, S13, and S15, the comprehensive pollution index evaluation results were light pollution, and the evaluation results of the universal exponential formula of logarithmic power function were class III standard, so it indicated that the pollution level of these four sampling sites was relatively light.

3.6.4. Evaluation Results of the Membership Degree Method. The five indicators of TN, ammonia nitrogen, TP, DO, and COD were selected to evaluate the water quality of the subsidence water bodies by using the membership degree method. The affiliation degree of each index indicated the degree of this measured value belongs to the standard level, the larger the value, the heavier the pollution, the specific results were shown in Table S9. For example, the affiliation degree of ammonia nitrogen at S9 was 0.924, which meant that the ammonia nitrogen concentration was close to the upper limit of surface water class III standard. From the evaluation results, it could be seen that the TN pollution was serious, which was consistent with the results of the single-factor evaluation method and the comprehensive pollution index evaluation method. For S8 and S16, except for the evaluation results of DO were class I standard, the other evaluation results were class IV and V standards. The water quality situation at the above two locations was poor. The concentrations of COD at S2, S3, S5, and S9 belong to the surface water IV standard; their affiliation was higher, belonging to the class IV standard,but the pollution was close to the lower limit of V water.

3.6.5. A Comparison of the Four Methods. The single-factor evaluation method is simple to calculate and intuitively reflects the exceedance of a single water quality index, but it is difficult to ensure the scientificity and reasonableness to determine whether the water quality of the study area meets the standard only by the worst water quality index. In the process of using the single-factor evaluation method, most of the sites in this study area were evaluated as poor class V only because TN exceeded the class V standard.

The comprehensive pollution index method considers the degree of comprehensive influence of multiple indicators on water quality pollution and quantifies the water quality situation. The universal exponential formula of the logarithmic power function continuously describes the water quality situation with specific index values, and the evaluation results can visually reflect the different degrees of pollution belonging to a certain level [26]. Overall, the two evaluation results were similar in this study, but the comprehensive pollution index method cannot determine a

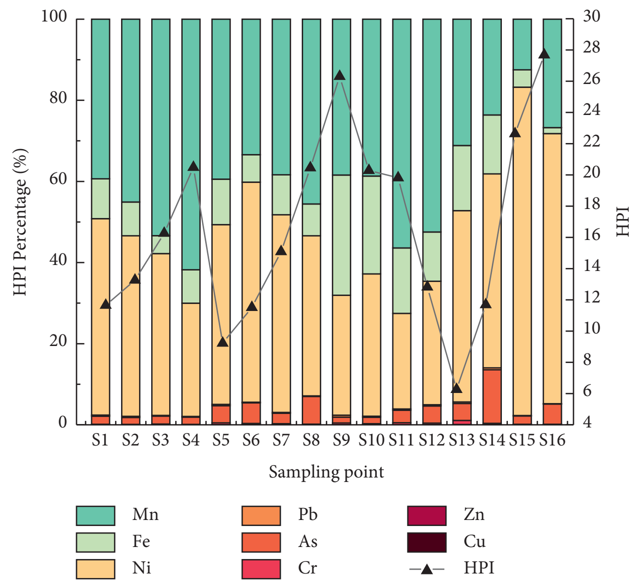

Figure 9: Changes of HPI at different sampling points of the subsidence water bodies and proportion of HPI of different heavy metals.

specific water quality category, and the evaluation results of the universal exponential formula of logarithmic power function were more refined.

The membership degree method could evaluate the specific differences for the same water quality indicator at different sampling points, and be quantitatively compared, the method was better than the single-factor evaluation method and the comprehensive pollution index method [44], but the degree of comprehensive impact of water quality pollution for multiple indicators was not comprehensive consideration.

In the light of the analysis of a single indicator, the membership degree method could give reliable evaluation results and could clearly distinguish the degree of pollution of similar water bodies. Compared with the single-factor evaluation method, its result was more reliable. Evaluation results of the universal exponential formula of logarithmic power function could visually reflect the different levels of pollution belonging to a certain level. Compared with the evaluation results, the comprehensive pollution index method was more reliable.

3.7. Evaluation Results of the Heavy Metal Pollution Index Method. The heavy metal pollution index method (HPI) was used to evaluate the heavy metal pollution in the subsidence water bodies, and the HPI variation of different sampling points and the percentage of various heavy metal HPI were obtained, as shown in Figure 9. The HPI of the sampling points ranged from 6.26 to 27.68, and the HPI of the seven sampling points S1, S2, S5, S6, S12, S13, and S14 were all within 15, which were lightly polluted; the HPI values of the remaining sampling points (S3, S4, S7, S8, S9, S10, S11, S15, and S16) were in the range of 15–30, which were moderately polluted, and there were no heavy pollution points. The overall degree of heavy metal pollution at each sampling point was S13 < S5 < S6 < S1 < S14 < S12 < S2 < S7 < S3 < S11 < S10 < S8 < S4 < S15 < S9 < S16, and the main factors causing heavy metal pollution were Ni, Fe, and Mn. Meanwhile, it could also be seen from Figure 9 that S9, S15, and S16 had the most serious heavy metal pollution.

3.8. Discussion. In the study area, the concentration of TN exceeded 2 mg/L at most sampling points and exceeded the class V standard of the surface water. In the previous study [45], it was also found that the concentration of TN in Huainan coal mining subsidence water bodies was high with an average value of 3.04 mg/L. Among them, the Panyi mine and Guqiao coal mine were also monitored, and the content of TN was 4.07 and 2.77 mg/L, respectively. Fertilization of farmland and aquaculture in the study area may lead to nitrogen runoff into water bodies. Therefore, the subsequent management of Huainan subsidence water bodies needed to pay attention to the impact of agricultural surface source pollution and aquaculture on the subsidence water bodies.

In this study, seven typical subsidence water bodies were selected. Because the scope of each collapsed area is very large, not enough samples were taken. So it would affect the representativeness of water quality. Every water quality evaluation method had its advantages and disadvantages. So, the characteristics of water quality indicators should be fully considered to select the appropriate evaluation methods. By comparing the results of different evaluation methods, more scientific and reasonable evaluation results could be obtained.

4. Conclusions

(1) For all the sample points, the pollution of TN in the subsidence water bodies of the study area was serious. In sampling point S14 (Guqiao coal mine) and S16 (east Xinji'er mine), the concentration of TP exceeded the standard and the concentration of COD was high. The content of F^- exceeded the standard at S14, and the content of Fe exceeded the standard seriously at S9 (Xieqiao mine).

(2) The correlation analysis of water quality indicators showed that the heavy metals Cr and Zn have significantly strong correlation ($P < 0.01$), and the pollution sources of Cr and Zn might be the same. The heavy metal As showed significantly strong positive correlations with TN, TP, and COD ($P < 0.01$). One-way ANOVA showed that Mg^{2+}, F^-, and ammonia nitrogen were significantly different in different water bodies with different subsidence times.

(3) By factor analysis, three principal factors were selected. Principal factor 1 represented mixed pollution related to nitrogen and phosphorus nutrients, organic pollutants, and heavy metal pollutants; principal factor 2 was closely related to heavy metal pollution; and principal factor 3 was influenced by

both heavy metals and cations. The 16 sampling points were divided into 4 clusters according to the score of three main factors. The comprehensive score of S16 of cluster 4 was high, and the water quality was bad.

(4) The single-factor evaluation result showed that using the class V standard as the target standard, only S15 reached the standard, all other sampling points exceeded the class V standard, and most of the sampling points exceeded the standard because of the content of TN. The evaluation results of the comprehensive pollution index method showed that the comprehensive pollution index at S14 and S16 was greater than 1, which was heavy pollution. For S14 and S16 sites, the evaluation result of the universal exponential formula of logarithmic power function was class V, which showed that these two sites were seriously polluted compared with other sites. According to the evaluation results of the membership degree method, it could be seen that the pollution of TN was serious and the water quality at S16 was bad, which was consistent with the previous evaluation results.

(5) The heavy metal pollution was most serious at S9, S15, and S16 in the study area, and the main factors causing heavy metal pollution were Ni, Fe, and Mn.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

The work was funded by the National Natural Science Foundations of China (Grant Nos. 41471422 and 51878004) and Top Notch Talents Program of Universities in Anhui Province (Grant No. 2019gxbjZD24).

Supplementary Materials

Table S1: Threshold values of the five grades for DO, COD, ammonia nitrogen, TN, and TP under Environmental Quality Standard for Surface Water (mg/L). Table S2: c_{jk} specification value, x_{jk}, and logarithm lnx_{jk} of surface water environmental quality classification standard. Table S3: Homogeneity of variance test. Table S4: one-way ANOVA and multiple comparisons. Table S5: Rotated component matrix. Table S6: Factor scores. Table S7: Evaluation results of the single-factor evaluation and the comprehensive pollution index evaluation method. Table S8: Comprehensive evaluation index and grade evaluation of water quality at each sampling point. Table S9: Water quality membership evaluation results. Figure S1: cluster dendrogram. (*Supplementary Materials*)

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