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Influence of Solar Photovoltaic System on the Concentration and Environmental Risks of Heavy Metals in Subsidence Pond Water from Coal Mining Area: A Case Study from Huainan Subsidence Pond

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Abstract: The subsidence pond is an important water resource for coal mining areas in China. In order to take full advantage of the subsidence pond, a floating photovoltaic cover or a pillaring photovoltaic cover were installed on the surface water of the subsidence pond in the Huainan coal field. Different photovoltaic systems (floating/pilling cover) equipped in the subsidence pond may affect the water quality; thus, assessing the metals in the subsidence pond with the solar photovoltaic system is of great importance for environment control. In this research, surface water samples were collected from three different subsidence ponds, with or without the solar photovoltaic system. The concentrations of Pb, Cr, Ni, Cu, As, Mn, and Zn in the water of the subsidence pond were determined using ICP-MS and AFS. Then, the health risk posed by the heavy metal in different subsidence pond waters via the ingestion pathway was evaluated and analyzed using the assessment model recommended by USEPA. The results indicated that the mean concentrations of Pb, Cr, Ni, Cu, As, Mn, and Zn in the water of different subsidence ponds were less than the environmental quality standards for surface water (China, Grade II). Cr showed a higher non-carcinogenic risk than the other metals, and the photovoltaic cover actually decreased the total non-carcinogenic risk in the photovoltaic subsidence pond compared with the natural subsidence pond. Non-carcinogenic risks of single and total heavy metals in the subsidence ponds with or without solar photovoltaic systems were below 1; thus, these risks in different subsidence ponds were considered to be at an acceptable level. However, the potential single carcinogenic risks of Cr, Ni, and As; and the multielement carcinogenic risks of Pb, Cr, Ni, and As exceeded the limits of 1×10^{-6} and 1×10^{-4}, respectively, suggesting that these metals showed single and total potential health risks in the subsidence pond, with or without the solar photovoltaic system. Further, the subsidence pond with the photovoltaic cover showed higher total carcinogenic risks in comparison with the natural subsidence pond. Therefore, a subsidence pond with a solar photovoltaic system should be monitored periodically to ensure the water safety.

Keywords: heavy metals; subsidence pond; solar photovoltaic system; coal mining

1. Introduction

During coal mining, some parts of the ground sink and form a subsidence pond in low-lying areas with a relative a high groundwater level. A subsidence pond is usually considered to be an environmental geologic hazard, which can pose a threat to vegetation and construction [1]. The subsidence pond can receive ground water, surface flow, and precipitation water, which leads to differences in depth, which could amount to several dozen meters. At some sites, the banks and the bottom of the subsidence pond are always coved with coal gangue [2]. Therefore, the subsidence pond is characterized by high temporal and spatial variability. On the other hand, the subsidence pond is regarded as a kind of refuge for freshwater animals. Many subsidence ponds are developed for cultivating fish to improve the local economy [3].

Previous studies have found that over 71% of coal mining areas lack water, and 40% of them have serious water contamination, due to water shortages and water pollution from anthropogenic activity [4]. From 2000, the subsidence pond was considered as a kind of reservoir for storing water in a coal mining area. In recent years, more and more research has supported the view that a larger quantity of water stored in the subsidence pond could be a good choice for satisfying the needs of some cities with water shortages [5]. Chen et al. [6] predicted that the subsidence area would exceed 275.2 km^2, and the catchment area would achieve 195.4 km^2 in 2030 in Huainan City. As the subsidence pond is connected with the lakes and the Huaihe river, it would be possible to convert the subsidence pond into a plain reservoir to meet the demands for water resources in Huainan City. Additionally, the subsidence pond can also be supplied by rain and shallow ground water [7]. With adequate and proper environmental protection solutions, the water in the subsidence pond can be maintained at a high quality for ecological requirements. Therefore, the subsidence pond is a potential water resource in coal mining areas.

With regard to the coal mining activities, the water of the subsidence pond is at the risk of being polluted by the heavy metals that are released by anthropogenic activities. Water leached from the coal gangue dump, farmland drainage, and domestic sewage can all easily flow into the subsidence pond and affect the heavy metals concentrations in the pond water [8]. Chen et al. [3] observed that the non-carcinogenic health risk values of Cu, Ni, Pb, Cd, Cr, V, Fe, Mn, and Zn in surface water from six different subsidence water bodies were less than 1, and the total carcinogenic risk values for Cr, Ni, and As in every subsidence water via two exposure pathways were greater than the maximum acceptable level in the Huainan coal mining area. Tan et al. (2020) [9] found that the As concentration in the subsidence pond water slightly exceeded Class III of China's Environmental Quality Standards for Surface Water. Therefore, if the subsidence pond was proposed for resource utilization in the Huainan coalfield, the heavy metals levels in the pond water should be monitored, and the metal risk also needs to be assessed, to assure water safety to the people.

Nowadays, a solar photovoltaic cover is introduced into the subsidence pond for collecting electricity in the Huainan coalfield. This was an economic way to take full advantage of the subsidence pond water surface. Actually, the solar photovoltaic cover could reduce water evaporation, thus changing the water quality [10]. Lee et al. [11] reported that pH, DO, COD, TN, TP, Chl-a, and BGA could be affected in the agricultural reservoir when it is covered with a floating photovoltaic panel. However, no research has been focused on the effect on heavy metals in the subsidence pond water from effects by the solar photovoltaic cover. Therefore, the objectives of this study are (1) to discover the magnitudes of heavy metal levels from the subsidence pond water covered with the different solar photovoltaic panel; (2) to assess the potential carcinogenic and non-carcinogenic health risks via the ingestion pathway; (3) to discuss the uncertainty during the assessment of health risks for heavy metals in the subsidence pond.

2. Materials and Methods

2.1. Study Area

Huainan city is famous for its coal resources. Fourteen pairs of key state-owned coal mines belong to this city. They cover an area of approximately 5533 square kilometers. The climate is semi-humid and warm, the annual mean temperature is 15.2 °C, and the mean precipitation is 922.6–926.3 mm. Coal mining in Huainan city has proceeded for over 100 years [12]. In 2020, the raw coal production was 57.3 million tons. During this long-term coal mining, a larger subsidence area is produced, which has led to the formation of many subsidence ponds. From 1992 to 2015, the subsidence area in Huainan city enlarged from 67.09 to 220 km^2 [8].

Subsidence ponds in the Hainan coalfields can be categorized into three kinds: a new subsidence pond (formed fewer than 10 years ago), a middle aged subsidence pond (formed 10–20 years ago), and an old aged subsidence pond (formed more than 20 years ago). Usually, the depth of the subsidence pond is between 3 and 10 m, and the maximum depth may reach 20 m in some old subsidence ponds. Since 2016, a solar photovoltaic system was installed on the surface of a subsidence pond. As the water depth exceeded 3 m, a floating photovoltaic cover was installed in the subsidence pond (Figure 1a). The pillaring photovoltaic cover was equipped in the subsidence pond, as the water depth was below 3 m (Figure 1b). So far, more than 150 MW of solar photovoltaic system have been installed in the subsidence pond in the Huainan coalfield.

(**a**) (**b**)

Figure 1. Subsidence pond with different photovoltaic cover systems: (**a**) subsidence pond with a floating photovoltaic cover; (**b**) subsidence pond with a pillaring photovoltaic cover.

2.2. Collection of Water Samples

Water samples were collected at the end of June 2021. As shown in Figure 2, the surface water samples were taken from a subsidence pond without a photovoltaic cover (non-photovoltaic subsidence pond, NPP) near Xieyi coal mine, a subsidence pond with a floating photovoltaic cover near Panyi coal mine (floating photovoltaic subsidence pond, FPP) and a subsidence pond with a pillaring photovoltaic cover (pillaring photovoltaic subsidence pond, PPP) near Li Yingzi coal mine. Six water samples for each subsidence pond were collected, using a vertical water sampler or a sampling pump under the pressure of manpower [3]. Water samples were collected at points along a certain distance along the shore of the subsidence pond. Eighteen water samples were gathered for these three subsidence ponds.

2.3. Analytical Methods

Water samples were filtered via a 0.45 mm membrane, then acidified with ultra-pure nitric acid and preserved at 4 °C before analysis. Heavy metals in the water samples were analyzed in accordance with Chinese national standard testing methods [3]. As was determined via atomic fluorescence spectrometry (AFS9700, China). Pb, Cr, Ni, Cu, Mn, and Zn were determined using ICP-MS (NexION300X, PerkinElmer, Waltham, MA, USA). Quality control and assurance were carried out in accordance with the standard procedure, which included duplicate samples and reagent blanks. The certificated reference material

(GSB-1767-2004) was used to check the quality of assurance for heavy metals analysis. The recovery percentage ranges for the analyzed metals were within the acceptable range. A calibration blank and an independent calibration verification standard were analyzed every 10 samples, to confirm the calibration status of the ICP-MS. The precision obtained in most cases was better than 5% relative standard deviation.

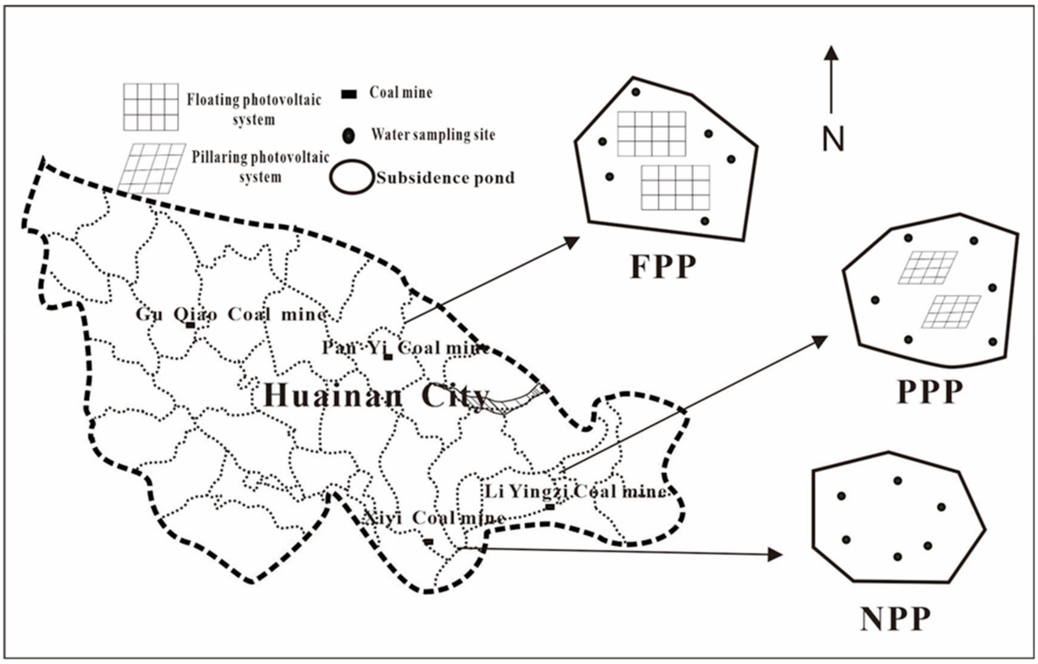

Figure 2. Study area and water sampling sites in different subsidence ponds in Huainan coalfield.

2.4. Health Risk Assessment

In order to evaluate the health risk for environmental pollution, the assessment model recommended by USEPA is adopted in this study. The heavy metals in the subsidence pond water may enter the human body through three pathways: dermal absorption, ingestion, and inhalation. Actually, ingestion is the predominant pathway for the water from the subsidence pond [13]. Therefore, only the ingestion pathway was mainly considered in the health risk.

CDI, called the chronic daily intake (mg kg^{-1} day^{-1}) of a heavy metal in subsidence water through the ingestion pathway, was calculated as Equation (1) [14]. HI was defined as the hazard index for the total non-carcinogenic risk, and was calculated as Equation (2). CR was regarded as the cancer risk, and calculated as Equation (3) [15]:

$$CDI_{ingestion} = (C \times IR \times EF \times ED)/(BW \times AT) \tag{1}$$

$$HI = \sum HQ = CDI_{ingestion}/RfD \tag{2}$$

$$CR = CDI_{ingestion} \times SF \tag{3}$$

where C represents the heavy metal concentration in the subsidence pond water, in mg L^{-1}; IR represents the daily ingestion rate, in L day^{-1}; EF denotes the exposure frequency, in days $year^{-1}$; ED means exposure duration, which is 70 years for a carcinogen and 30 years for a non-carcinogen; BW and AT are the body weight and average exposure time, respectively, and AT equals ED multiplied by 365; SF represents the cancer slope factor (mg kg^{-1} day^{-1}).

HQ means the hazard quotient, and RfD is the reference dose (mg kg^{-1} day^{-1}). HQ > 1 suggests an adverse effect on human health [16]. HI represents the total non-cancer ingestion risk from the subsidence pond. HI > 1 suggests a possibility of adverse health effects, where HI < 1 denotes no significant risk of negative health effects for the heavy metals through the ingestion pathway [15].

An acceptable risk levels for the carcinogenic risk (CR) were proposed, according to the USEPA. If the CR is lower than or equal to 10^{-6}, it is considered as being negligible. When the risk is higher than 10^{-4}, it is regarded as being unacceptable. If the risk is between 1×10^{-6} and 1×10^{-4}, it should be discussed in the light of the circumstances. A single heavy metal for the carcinogenic risk limit is set to 1×10^{-6}, but the limit for multiple heavy metals for carcinogenic risk is defined as 1×10^{-4} [17].

2.5. Data Analysis

A descriptive statistical analysis of the results, including the standard deviation, mean, minimum and maximum values, and coefficient of variations (CV%) were conducted using SPSS 19.0 software. The Spearman correlation was employed to find the relations between the different heavy metals in the water of the different subsidence ponds. Principal component analysis (PCA) was adopted to assess the probable sources of heavy metals in subsidence water, with or without a photovoltaic cover. The factor with an eigenvalue > 1, defined as a principal component, could be recognized as being effectively indicated in the original data.

3. Results and Discussion

3.1. Heavy Metals Concentrations in Different Subsidence Ponds

The concentrations of heavy metals in different subsidence ponds are shown in Table 1. Mn and Zn presented relatively higher mean levels, while Pb and As displayed relatively lower mean values in different subsidence ponds. Actually, the mean concentrations of heavy metals in the water of different subsidence ponds followed the same decreasing order: Mn > Zn > Cr > Ni > Cu > As > Pb. The coefficient of variance (CV) gave the degree of variability for the heavy metals in the water of the subsidence ponds. Cr concentrations in NPP and PPP, and Mn concentrations in FPP had maximum CV values compared to other heavy metals, which suggested that Cr and Mn were more variable, and probably ascribed to anthropogenic activities such as photovoltaic cover [18]. Similar results were also reported by Chen et al. who found that Cr had a high variability (CV: 58%), and that Mn presented a relatively high coefficient of variance (24%) in the water of the subsidence ponds near Zhuji coal mine, Pandong coal mine, Xinji'er coal mine, Zhangji coal mine, Panyi coal mine, and Xinjiyi coal mine in Hainnan coal fields, which were ascribed to human activities [3]. The maximum CV for Cd in this study was lower, and the maximum CV for Mn was greater than the values from Chen et al., suggesting that Cr and Mn always presented a high degree of variability in the waters of different subsidence ponds near the coal mines in Huainan coalfield.

With regard to the water quality standards of China (GB3838-2002) (Grade II) [19], according to the WHO (2017) [20] and USEPA (2009) [21], the mean concentrations of Pb, Cr, Ni, Cu, and As in the water from the different subsidence ponds were lower than these limits. Only the mean concentrations of Mn in different subsidence ponds exceeded the USEPA standards (2009) [22], but they were lower than the standards of the WHO (2017) [20]. The mean Zn concentration in PPP was higher than the standards of the WHO (2017) [20], but they did not exceed the China limit (GB3838-2002) (Grade II) [19]. Further, comparing the mean heavy metal concentrations calculated from FPP and PPP with the regulated values, the mean Mn concentration (82.25 ug/L) from the FPP and PPP was over the USEPA (2009) [22] limit and below the WHO (2017) limit [20]. The mean Zn concentration (50.43 ug/L) from the FPP and PPP was close to the WHO (2017) limit [20] and was less than the China (GB3838-2002) (Grade II) limit [19]. The mean concentrations of Pb, Cd, Ni, Cu, and As from FPP and PPP were lower than those regulated values.

When comparing the heavy metals in the water of the subsidence pond with the other coal mining areas, all of the heavy metals concentrations in the water of the subsidence ponds in this study were higher than those values in the subsidence pond from Huaibei [9]. Low levels of Pb, Ni, and Mn were observed in this research, compared with those values in the water of ponds from Jining City [2], Karanpura coal mine [23], and Okpara coal mine [18]. The Cu and As concentrations of this study were higher than those values of Karanpura coal mine [23] and Okpara coal mine [18], but lower than the values of Jining City [2]. The Cr concentration in the natural subsidence pond of this study was less than the subsidence pond in Jining City [2], while the Cr concentrations in the subsidence ponds with floating/pillaring photovoltaic covers were over the Cr concentrations in the subsidence ponds from Karanpura coal mine [23] and Okpara coal mine [18]. While the Ni concentrations in the natural subsidence pond and the pond with a pillaring photovoltaic cover in this study were lower than those values in Karanpura coal mine [23] and Okpara coal mine [18], the concentration of Ni in the subsidence pond with a floating photovoltaic cover exceeded the value of the pond in Karanpura coal mine [23], and was below the value observed in the pond of Okpara coal mine [18]. Based on our result, comparing with other natural subsidence ponds from different sites, Pb, Ni, and Mn in the subsidence ponds with photovoltaic panels presented low levels, Cu and As showed comparable concentrations with other sites, but Cr posed high levels in the subsidence pond with photovoltaic panels, denoting that Cr possessed more environmental sensitivity than other metals in the subsidence pond with a solar system in Huainan coalfield.

Table 1. The statistics of heavy metals concentrations in different subsidence ponds (ug/L).

Subsidence Pond/Criterion		Pb	Cr	Ni	Cu	As	Mn	Zn
NPP	Range	1.39–2.78	26.65–63.05	10.55–20.70	3.21–6.42	1.36–3.40	44.87–138.07	33.81–68.60
	Average	1.93	38.30	13.73	4.43	2.27	84.34	49.74
	C.V. [a] /%	27.23	44.07	29.24	27.86	32.11	37.89	23.61
FPP	Range	1.14–2.13	23.52–62.17	12.46–26.94	4.14–7.25	1.44–2.30	34.31–160.78	35.71–63.34
	Average	1.62	42.11	19.61	5.85	1.82	69.94	49.98
	C.V./%	27.39	36.78	26.47	20.58	16.14	65.13	21.81
PPP	Range	0.85–0.99	19.70–57.35	9.26–19.05	3.06–5.89	1.36–2.34	67.17–131.32	38.75–63.15
	Average	1.47	43.32	14.16	4.76	1.74	94.56	50.88
	C.V./%	32.06	37.28	27.01	25.09	26.23	23.92	15.24
Average values for the water from FPP and PPP	Average	1.55	42.71	16.89	5.30	1.78	82.25	50.43
Environmental quality standards for surface water (GB3838-2002) (China, Grade II) [b] [19]		10	50	20	1000	50	-	1000
WHO (2017) [17]		10	50	20	2000	10	400	50
USEPA (2009) [21]		-	100	70	1300	30	50	-
Subsidence Pond in Huaibei coal mine area [9]		0.06	0.73	0.81	0.53	-	0.67	0.98
Subsidence pond in Jining City [c] [2]		117.9	42	-	183.1	433.2	-	
Subsidence pond in Karanpura coal mine area [23]		-	2.04	15.49	2.36	0.67	1161.2	46.8
Subsidence pond in Okpara coal mine area [18]		6.47	0.97	53.1	1.34	0.48	3350	253.85

[a] C.V. means coefficient of variation; "-" means not available; [b] Environmental quality standards for surface water (GB3838-2002) (China, Grade II): mainly suitable for centralized drinking water surface water source level 1 protection zone, habitat of precious aquatic organisms, spawning ground of fish and shrimp, feeding ground of young fish, etc.; [c] The subsidence ponds in Huaibei coal mine area, Jining City, Karanpura coal mine area, and Okpara coal mine area were not equipped with a solar system.

3.2. Heavy Metals Distribution in Different Subsidence Ponds

The heavy metals concentrations in the water of the subsidence pond are easily affected by the surrounding soil, acid mining wastewater, the nearby coal gangue, and the coal power plant [23]. Previous findings have observed that heavy metals concentrations in a subsidence pond water vary with the subsidence periods. Ni concentrations were higher in a middle-aged subsidence pond. Cr showed lower concentrations in an older subsidence pond [3]. Heavy metal concentration in the subsidence pond also changed with the month. Wei et al. [24] found that Cd, As, Pb, and Cu concentrations in the water of a subsidence pond were high in April and June, but Ni, Cr, and Mn were high in August and October, and Zn and V were not changed between the months.

In this study, the mean concentrations of heavy metals in the water of the subsidence ponds varied with the photovoltaic system (Figure 3). Cr, Ni, Cu, and Zn showed higher mean concentrations in FPP and PPP than NPP. Pb and As showed lower mean concentrations in FPP and PPP compared with NPP. The mean Mn concentration in FPP was below the value in NPP, while the Mn mean concentration in PPP was higher than in NPP. The mean concentrations of Pb, Ni, and Cu in FPP exceeded those metal concentrations in PPP, While Cr, As, Mn, and Zn showed the reverse trend, where higher levels of those metals were observed in PPP than in FPP. Thus, the photovoltaic cover could be an important factor affecting the heavy metal levels in the subsidence pond.

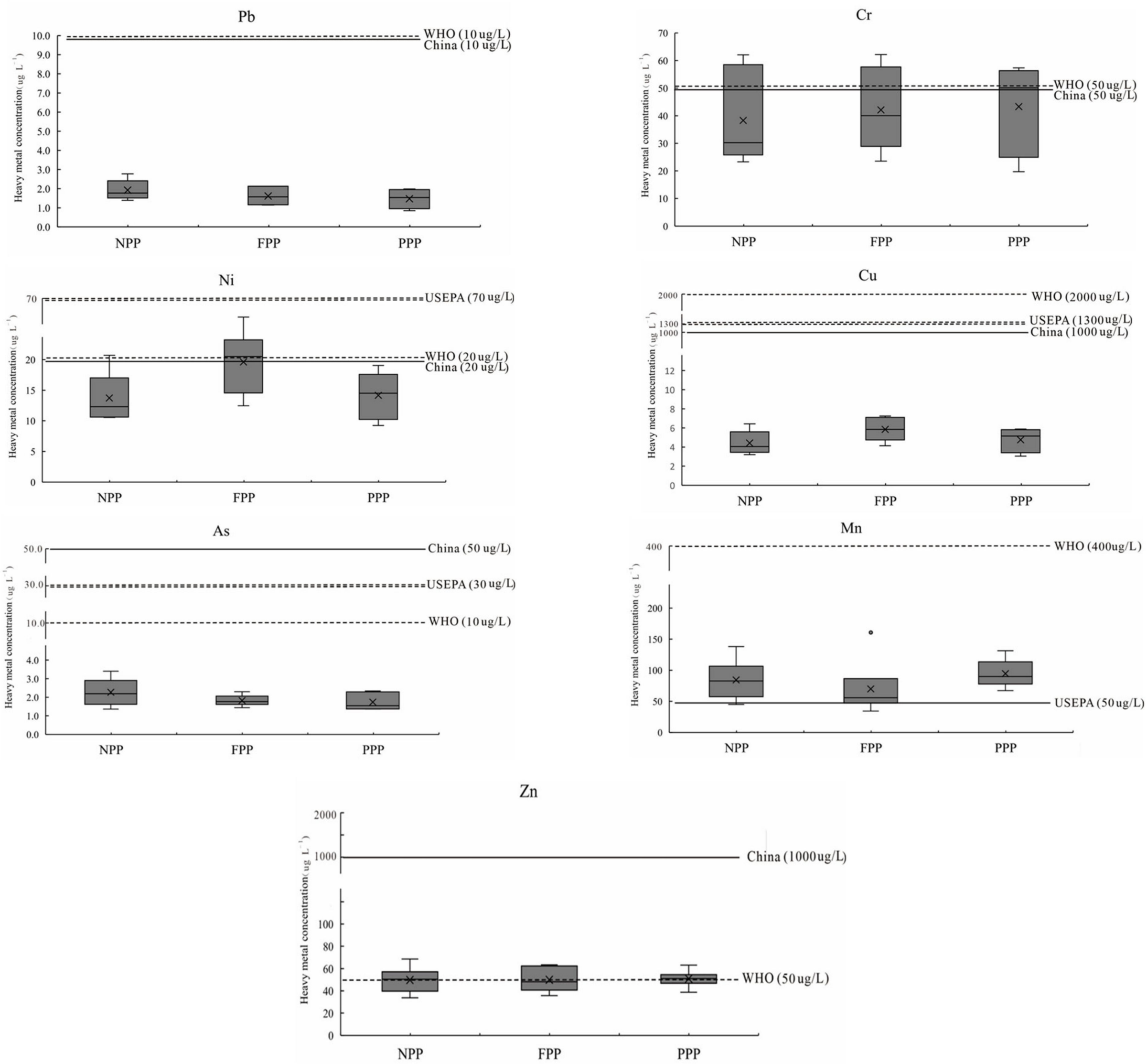

Figure 3. Heavy metals concentration variation in different subsidence ponds.

Previous research has reported that the water quality can be influenced by the photovoltaic system. Taboada et al. [10] found that a reduction in water evaporation was greater than 90% in the pond installed with a floating photovoltaic cover. The average light intensity and pH were lower in the pond with the pillaring photovoltaic system, and dissolved oxygen showed an inverted "U"-shaped change trend [25]. The floating photovoltaic system covering the pond decreased in WT and DO, and reduced in Chl-a, N, SS, and BOD, and promoted average P [26]. Our study also confirmed that different photovoltaic covers could change the heavy metals concentrations in the subsidence pond. From this study and from previous works mentioned above, it could be postulated that different photovoltaic covers may affect different water quality indices, such as DO, temperature, P, and pH, etc., which changed the heavy metals levels in the subsidence pond with the different photovoltaic panels.

3.3. Heavy Metals Source Analysis in Different Subsidence Ponds

A Spearman correlation analysis was conducted to evaluate the degree of interrelation between the heavy metals. Table 2 listed the correlation matrices for heavy metals in the water from different subsidence ponds. Cr was significantly and positively correlated with Ni and Cu at a 0.01 or 0.05 level in the different subsidence ponds. Cr also showed a strong correlation with As and Zn at the 0.05 or 0.01 level in the subsidence ponds with a floating cover. Ni was correlated with As in the subsidence pond with a floating/pillaring photovoltaic cover ($p \leq 0.05$). Cu was correlated with As and Zn, and As was correlated with Mn and Zn in the subsidence pond with a floating photovoltaic cover ($p \leq 0.05$ or $p \leq 0.01$). Mn was related with Zn in the subsidence pond with a pillaring photovoltaic cover ($p \leq 0.05$). Usually, the positive correlations between the heavy metals are most likely related to their common source [27]. Therefore, Cr, Ni, and Cu had the same origin in different subsidence ponds. As and Ni originated from the same source in the subsidence ponds with floating/pillaring photovoltaic covers. Cu, As, Mn, and Zn had the same source in the subsidence pond with a floating photovoltaic cover. Zn and Mn originated from the same source in the subsidence pond with a pillaring photovoltaic cover.

Table 2. Correlation coefficient matrix of heavy metals in different subsidence ponds.

Subsidence Pond	Elements	Pb	Cr	Ni	Cu	As	Mn	Zn
NPP	Pb	1						
	Cr	−0.630	1					
	Ni	−0.383	0.897 *	1				
	Cu	−0.57	0.940 **	0.984 **	1			
	As	0.079	0.340	0.579	0.457	1		
	Mn	−0.338	0.771	0.744	0.705	0.499	1	
	Zn	0.412	0.042	−0.001	−0.109	0.330	0.515	1
FPP	Pb	1						
	Cr	0.783	1					
	Ni	0.404	0.836 *	1				
	Cu	0.564	0.902 *	0.952 **	1			
	As	0.531	0.902 *	0.844 *	0.869 *	1		
	Mn	0.274	0.767	0.797	0.705	0.898 *	1	
	Zn	0.735	0.933 **	0.751	0.885 *	0.923 **	0.683	1
PPP	Pb	1						
	Cr	0.071	1					
	Ni	0.180	0.909 *	1				
	Cu	0.092	0.971 **	0.965 **	1			
	As	−0.089	0.703	0.891 *	0.807	1		
	Mn	−0.399	0.673	0.476	0.642	0.472	1	
	Zn	−0.103	0.766	0.711	0.781	0.723	0.895 *	1

* means significant at $p \leq 0.05$, ** means significant at $p \leq 0.01$.

The principal components can indicate a lesser number of variables, including the essence of total variation [28]. The relations between the principal components and the heavy metals in the different subsidence ponds are shown in Table 3. The results could suggest possible sources that influence the variation of heavy metals in the subsidence ponds, with or without the solar photovoltaic systems. Two principal components were extracted, based on an eigenvalue > 1 for NPP and PPP, which explained 83.05% and 87.95% of the total variance for these two subsidence ponds, respectively. However, there is only one principal component explaining 80.3% of the total variance for FPP. As a result, subsidence ponds with or without solar photovoltaic covers have different origins for heavy metals.

Table 3. Loading matrix of principal component analysis of heavy metals in the water of different subsidence ponds.

Variable	NPP		FPP	PPP	
	PC1	PC2	PC1	PC1	PC2
Pb	−0.538	0.678	0.670	−0.040	0.925
Cr	0.955	−0.158	0.978	0.940	0.128
Ni	0.958	−0.011	0.903	0.929	0.313
Cu	0.958	−0.171	0.947	0.967	0.173
As	0.562	0.532	0.961	0.860	0.066
Mn	0.854	0.344	0.828	0.765	−0.535
Zn	0.109	0.896	0.946	0.902	−0.210
Eigenvalue	4.095	1.719	5.621	4.821	1.335
Contribution value/%	58.495	24.555	80.300	68.877	19.072
Cumulative contribution rate/%	58.495	83.050	80.300	68.877	87.949

PC1 showed strong positive correlations with Cr, Ni, Cu, As, and Mn, and explained 58.50%, 80.30%, and 68.89% of the total variance for NPP, FPP, and PPP, respectively. Actually, the subsidence ponds are near the coal mine, coal power plant, and coal gangue pile. Cr, Ni, Cu, As, and Mn could be released during coal processing, acid mining drainage, and coal combustion [9]. Furthermore, some metals could also be released by the immersed coal gangue at the bottom of the subsidence pond [29]. Leachate from the coal gangue pile also discharged some heavy metals into the subsidence pond. Thus, PC1 represented the heavy metal source from coal exploitation, coal processing, and coal comprehensive utilization.

PC2 in NPP accounted for 24.56% of the total variance, and displayed strong positive correlations with Pb and Zn. PC2 in PPP accounted for 19.07% of the total variance, and exhibited a strong positive correlation with Pb. Pb mainly originated from pesticides and agricultural machinery, and vehicle and exhaust emissions [30]. Zn is widely used in automotive tires and brake pads, and is a major additive in motor vehicle lubricants [31,32]. There is much cropland distributed around the subsidence pond, which may result in agricultural effluent and extra pesticides discharging into the subsidence pond. The coal is transported by a giant truck, leading to another important source for heavy metal enrichment in the subsidence pond as well. Therefore, PC2 for NPP and PPP could be recognized as a heavy metal source from agricultural production and the traffic. In addition, As, correlated with Ni, was observed only in subsidence ponds with floating and pillaring photovoltaic covers. As is always found in coal or coal combustion, and Ni is mainly derived from diesel and gasoline, and lubricating oil and metal plating, etc. [33]. Thereby, As correlated with Ni may denote another important heavy metal source from the solar photovoltaic system.

3.4. The Health Risks of Heavy Metals in Different Subsidence Ponds

3.4.1. Non-Carcinogenic Health Risks

The non-carcinogenic health risks posed by heavy metals in the water of different subsidence ponds via ingestion are shown in Table 4. Hazard quotient (HQ) and hazard index (HI) calculated for the heavy metals varied in subsidence ponds with or without different solar systems. The HQs of Pb and As in the subsidence ponds without solar systems were higher than those in the subsidence ponds with solar systems. The HQs of Cr, Ni, Cu, and Zn in the subsidence ponds without solar systems were lower than those in the subsidence ponds with solar systems. In contrast, the HQ of Mn in the subsidence pond without a solar system was higher than in the subsidence pond with a floating cover, but lower than in the subsidence pond with a pillaring cover. Pb, Ni, Cu, and As in the subsidence pond with a floating cover showed higher values of HQ than those values in the subsidence pond with a pillaring cover, but other heavy metals showed the reverse trend of change. Actually, the HQs of heavy metals for adults exceeded the values for children, irrespective of the different subsidence ponds. The HQs of heavy metals in different subsidence ponds ranged from 3.88×10^{-4} to $1.87 \times 10^{-4} < 1$, and the HIs for the total heavy metals in different subsidence ponds ranged from 8.44×10^{-2} to $3.18 \times 10^{-2} < 1$, suggesting no significant non-carcinogenic risks posed by single and total heavy metals in the subsidence pond, with or without a solar system.

Table 4. Calculated HQs and HIs for adults and children due to oral exposure to heavy metals in the water of different subsidence ponds.

Element	NPP		FPP		PPP	
	Adult	Child	Adult	Child	Adult	Child
Pb	1.79×10^{-2}	4.82×10^{-3}	1.50×10^{-2}	4.05×10^{-3}	1.37×10^{-2}	3.69×10^{-3}
Cr	1.66×10^{-1}	4.48×10^{-2}	1.82×10^{-1}	4.92×10^{-2}	1.87×10^{-1}	5.06×10^{-2}
Ni	8.91×10^{-3}	2.41×10^{-3}	1.27×10^{-2}	3.44×10^{-3}	9.19×10^{-3}	2.48×10^{-3}
Cu	1.44×10^{-3}	3.88×10^{-4}	1.90×10^{-3}	5.13×10^{-4}	1.55×10^{-3}	4.18×10^{-4}
As	9.81×10^{-2}	2.65×10^{-2}	7.88×10^{-2}	2.13×10^{-2}	7.53×10^{-2}	2.03×10^{-2}
Mn	2.38×10^{-2}	6.43×10^{-3}	1.97×10^{-2}	5.33×10^{-3}	2.67×10^{-2}	7.21×10^{-3}
Zn	2.15×10^{-3}	5.81×10^{-4}	2.16×10^{-3}	5.84×10^{-4}	2.20×10^{-3}	5.95×10^{-4}
HI	3.18×10^{-1}	8.59×10^{-2}	3.12×10^{-1}	8.44×10^{-2}	3.16×10^{-1}	8.53×10^{-2}

HQ levels calculated from heavy metals for different subsidence ponds and different populations followed the order of Cr > As > Mn > Pb > Ni > Zn > Cu, denoting Cr posed a higher non-carcinogenic risk than other metals in the subsidence pond, with or without the solar systems. The HI values in the subsidence pond without a solar system were higher than those values in the subsidence pond with a solar system, suggesting that installation with a photovoltaic cover actually decreased the total non-carcinogenic risk from heavy metals via oral exposure in the subsidence pond.

3.4.2. Carcinogenic Health Risk

Pb, Cr, Ni, and As were classified as possible carcinogens by the International Agency for Research on Cancer [34]. The SFs (cancer slope factors) of Pb, Cr, Ni, and As were 0.009 mg kg^{-1} day^{-1}, 0.5 mg kg^{-1} day^{-1}, 0.84 mg kg^{-1} day^{-1}, and 1.5 mg kg^{-1} day^{-1}, respectively, according to USEPA [15]. As no SFs of Cu, Mn, and Zn were found, only oral intakes of Pb, Cr, Ni, and As were evaluated for cancer risks in this study.

From Figure 4, cancer risks from the heavy metals distributed in the different subsidence ponds and different populations followed the order of Cr > Ni > As > Pb; thus, Cr has the highest cancer risk, and Pb has the lowest cancer risk. Further, the cancer risks of Pb and As in the subsidence ponds without a solar system were higher than those in the subsidence ponds with a solar system, but relatively lower cancer risks of Cr and Ni were observed in the subsidence ponds without solar systems, compared with the other subsidence ponds. The highest cancer risks of Cr and Ni were observed in the subsidence ponds with a pillaring cover and a floating cover, respectively. Additionally, the cancer risks for adults were greater than those risks for children in the different subsidence ponds. Therefore, the cancer risks in the subsidence ponds varied with different heavy metals, different populations, and different photovoltaic covers.

The permissible limits are 1×10^{-4} and 1×10^{-6} for multielement carcinogens and single carcinogens, respectively [21,22]. The single cancer risks of Cr, Ni, and As in different subsidence ponds exceeded the limits of 1×10^{-6}. The multielement cancer risks of Pb, Cr, Ni, and As in different subsidence ponds decreased in the order of FPP > PPP > NPP, and their risks were all higher than 1×10^{-4}, suggesting that the subsidence ponds with or without solar systems both showed potential cancer risks from single heavy metals such as Cr, Ni, and As. Different subsidence ponds also posed potential total carcinogenic health risks from Pb, Cr, Ni, and As, and the photovoltaic covers actually increased the total carcinogenic health risk. Previous studies have reported that Cr and Ni concentrations in Huainan coal are higher than the average global values and China values in coals [35], which should be a concern. Wang et al. [36] found that As was a potential carcinogenic risk in the Huainan coal field. Chen et al. [3] observed that the total carcinogenic risks in the subsidence water body, summed for Cr, Ni, and As via oral pathways, were greater than the maximum acceptable level (1×10^{-4}) in Huainan coal field. The cancer risk from As via the oral pathway was greater than 1 as well [3]. By comparison, our study also found similar results and demonstrated that the subsidence ponds with a solar system would pose a higher cancer risk than a natural subsidence pond. Therefore, subsidence ponds with photovoltaic covers should be periodically monitored for the assurance of water safety.

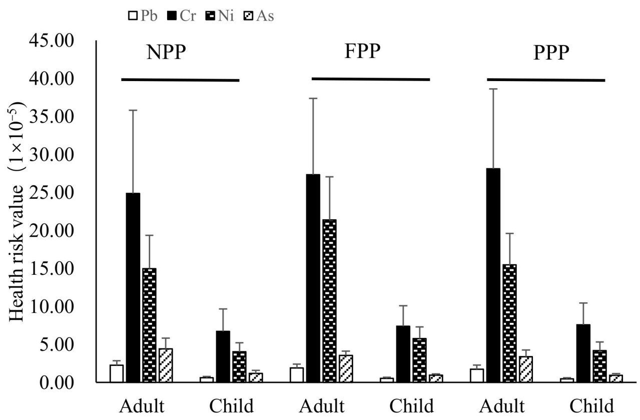

Figure 4. Cancer risks of Pb, Cr, Ni, and As from ingestion pathways in the water from the different subsidence ponds (only Pb $\times 10^{-7}$).

3.4.3. Uncertainty Analysis

A complete health risk assessment should include contaminants in the air, soil, and water, through ingestion, inhalation, and skin contact [37]. In this research, only Pb, Cr, Ni, Cu, As, Mn, and Zn were evaluated in the water of different subsidence ponds via oral pathways for health risks. The sampling area may be small, and did not fully represent the whole area. Meanwhile, some errors may exist for the selection of the parameters in health risk models. In addition, considering the high mobility of residents in this coal mining area, the people exposed to the subsidence pond water varied with time, lifestyle, weight, and physical fitness, etc. [23,38]. Notwithstanding, considering the single measurements and the relatively low number of water samples analyzed in this research, the results of the current assessment should be recognized as a preliminary evaluation.

Global warming affects the living conditions of human beings. With rapid economic development, coal resources, and oil and natural gas are thoroughly explored for energy to support the industry. Traditional fossil energy could lead to global warming and environmental pollution, whereas solar photovoltaic power generation is an alternative solution to solve the problem. Based on the research of this study, the floating/pillaring photovoltaic cover installed in the subsidence pond takes full advantage of the surface water without causing heavy metal pollution. Previous works have found that a larger area of photovoltaic cover could change the temperature and pH of the water, and thus an appropriate size for photovoltaic deployment on subsidence water may be a key factor in balancing between water quality and energy capture.

4. Conclusions

The mean concentrations of heavy metals in the water of a subsidence pond with or without a solar system followed a decreasing order of Mn > Zn > Cr > Ni > Cu > As > Pb. Generally, the mean Pb, Cr, Ni, Cu, As, Mn, and Zn concentrations in different subsidence ponds were below the environmental quality standards for surface water (GB3838-2002) (China, Grade II). Coal mining was a dominant factor influencing the heavy metal levels in the subsidence pond, while As correlated with Ni in the water of the subsidence pond with different photovoltaic panels may suggest another important heavy metal origin. The non-carcinogenic risks of single and total heavy meals in different subsidence ponds via oral intake were lower than 1, indicating that those risks were at low levels. However, the single carcinogenic risks of Cr, Ni, and As, and the multielement carcinogenic risks of Pb, Cr, Ni, and As exceeded the limits of 1×10^{-6} and 1×10^{-4}, respectively, suggesting that a photovoltaic cover could promote the potential carcinogenic risks of the heavy metals in the subsidence pond. This study put forward a preliminary view on the health risks of the subsidence pond water with different solar photovoltaic panels.

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References

1. Yao, E.N.; Gui, H.R. Four trace elements contents of water environment of mining subsidence in the Huainan diggings, China. Environ. *Monit. Assess.* **2008**, *146*, 203–210. [CrossRef] [PubMed]
2. Wang, W.J.; Zhang, J.; Zhang, Y.J. Investigation on heavy metals pollution in coal-mining subsided water of Jining City. *Occup. Health* **2013**, *29*, 5–7. (In Chinese with English abstract)
3. Chen, G.Z.; Wang, X.M.; Wang, R.W.; Liu, G.J. Health risk assessment of potentially harmful elements in subsidence waterbodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. *Ecotoxicol. Environ. Saf.* **2019**, *171*, 737–745. [CrossRef] [PubMed]
4. Gui, H.R.; Yao, E.Q.; Song, X.M.; Yuan, Z.H.; Zhang, G. *Research on Recycling Technology of Coal Mine Water*; University of Mining and Technology Press: Xuzhou, China, 2011. (In Chinese with English abstract)
5. Liu, F.; Lu, L. Progress in the study of ecological restoration of coal mining subsidence areas. *J. Nat. Resour.* **2009**, *24*, 612–620.
6. Chen, Y.C.; Yuan, L.; Xu, C. Investigation on using mining subsidence area to build a reservoir in Huainan Coal Mining Area. *J. China Coal. Soc.* **2016**, *41*, 2830–2835.
7. Yan, J.P.; Cheng, F.K.; Gong, C.G.; Gu, D.M.; Fan, T.Y.; Liu, J.; Meng, H.; Yu, H.J.; Zhang, B. Plain reservoir construction and water resources protection and utilization of Linhuan mining area in Huaibei. *Coal. Sci. Technol.* **2015**, *43*, 158–162.
8. Ouyang, Z.Z.; Gao, L.M.; Yang, C. Distribution, sources and influence factors of polycyclic aromatic hydrocarbon at different depths of the soil and sediments of two typical coal mining subsidence areas in Huainan, China. *Ecotoxicol. Environ. Saf.* **2018**, *163*, 255–265. [CrossRef]

9. Li, J.; Gui, H.R.; Hu, R.J.; Chen, L.W.; Xia, Y.T.; Fan, H.X.; Yu, H.; Wang, M.C. Analysis of heavy metal sources and health risk assessment of typical coal mine collapsed lakes in Huaibei coalfield, Anhui Province, China. *Pol. J. Environ. Stud.* **2020**, *29*, 3193–3202. [CrossRef]
10. Taboada, M.E.; Cáceres, L.; Grabera, L.; Galleguillos, H.R.; Cabeza, L.F.; Rojas, R. Solar water heating system and photovoltaic floating cover to reduce evaporation: Experimental results and modeling. *Renew. Energy* **2017**, *105*, 601–615. [CrossRef]
11. Lee, I.J.; Joo, J.C.; Lee, C.S.; Kim, G.Y.; Woo, D.Y.; Kim, J.H. Evaluation of the water quality changes in agricultural reservoir covered with floating photovoltaic solar-tracking systems. *J. Korean Soc. Environ. Eng.* **2017**, *39*, 255–264. [CrossRef]
12. Fang, T.; Liu, G.J.; Zhou, C.C.; Lu, L.L. Lead in soil and agricultural products in the Huainan coal mining area, Anhui, China: Levels, distribution, and health implications. *Environ. Monit. Assess.* **2015**, *187*, 152. [CrossRef] [PubMed]
13. Saha, N.; Rahman, M.S.; Ahmed, M.B.; Zhou, J.L.; Ngo, H.H.; Guo, W.S. Industrial metal pollution of water and probabilistic assessment of human health risk. *J. Environ. Manag.* **2017**, *185*, 70–78. [CrossRef] [PubMed]
14. Cao, S.Z.; Duan, X.L.; Ma, Y.Q.; Zhao, X.G.; Qin, Y.W.; Liu, Y.; Li, S.; Zheng, B.H.; Wei, F.S. Health benefit from decreasing exposure to potentially harmful elements and metalloid after strict pollution control measures near a typical river basin area in China. *Chemosphere* **2017**, *184*, 866–878. [CrossRef]
15. USEPA. Risk assessment guidance for superfund. In *Part A: Human Health Evaluation Manual; Part E, Supplemental Guidance for Dermal Risk Assessment; Part F, Supplemental Guidance for Inhalation Risk Assessment*; United States Environmental Protection Agency: Washington, DC, USA, 2011; Volume 1.
16. USEPA. Risk assessment guidance for superfund. EPA/540/R/99/005 office of superfund remediation and technology innovation. In *Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment)*; United States Environmental Protection Agency: Washington, DC, USA, 2014; Volume 1.
17. RAIS. *(Risk Assessment Information System) in the Risk Exposure Models for Chemicals User's Guide*; Risk Assessment Information System: Washington, DC, USA, 2017.
18. Nganje, J.N.; Adamu, C.I.; Ugbaja, A.N.; Ebieme, E.; Sikakwe, G.U. Environmental contamination of trace elements in the vicinity of Okpara coal mine, Enugu, Southeastern Nigeria. *Arab. J. Geosci.* **2011**, *4*, 199–205. [CrossRef]
19. PRC. *GB3838-2002*; National Standard Environmental Quality Standards for Surface Water, China. State Environmental Protection Administration: Beijing, China, 2002.
20. WHO. *Guidelines for Drinking Water Quality*, 4th ed.; World Health Organization: Geneva, Switzerland, 2017.
21. USEPA. *Risk Assessment Guidance for Superfund: Human Health Evaluation Manual (Part E), Supplemental Guidance for Dermal Risk Assessment*; Office of Superfund Remediation and Technology Innovation U.S.: Washington, DC, USA, 2009.
22. USEPA. *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment)*; EPA: Washington, DC, USA, 2009; pp. 1–68.
23. Neogi, B.; Tiwari, A.K.; Singh, A.K.; Pathak, D.D. Evaluation of metal contamination and risk assessment to human health in a coal mine region of India: A case study of the North Karanpura coalfield. *Hum. Ecol. Risk. Assess.* **2018**, *24*, 2011–2023. [CrossRef]
24. Wei, Y.; Fan, Z.J.; Sun, L.; Liu, G.J. Study on sustainable utilization of water resources in coal mining subsidence area: A case study in Huainan City, China. *J. Muc. Univ. China* **2016**, *25*, 10–14. (In Chinese with English abstract)
25. Li, P.D.; Gao, X.Q.; Jiang, J.X.; Yang, L.W.; Li, Y.J. Characteristic Analysis of Water Quality Variation and Fish Impact Study of Fish-Lighting Complementary Photovoltaic Power Station. *Energies* **2020**, *13*, 4822. [CrossRef]
26. Doabi, S.A.; Karami, M.; Afyuni, M.; Yeganeh, M. Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province. *Iran. Ecotoxicol. Environ. Saf.* **2018**, *163*, 153–164. [CrossRef] [PubMed]
27. Wang, X.M.; Chu, Z.X.; Zha, F.G.; Liu, S.M.; Guijian Liu, G.J.; Dong, Z.B. Determination of Heavy Metals in Water and Tissues of Crucian Carp (*Carassius auratus Gibelio*) Collected from Subsidence Pools in Huainan Coal Fields (China). *Anal. Lett.* **2015**, *48*, 861–877. [CrossRef]
28. Viswanath, N.C.; Kumar, P.G.D.; Ammad, K.K.; Kumari, E.R.U. Ground water quality and multivariate statistical methods. *Environ. Process.* **2015**, *2*, 347–360. [CrossRef]
29. Liu, X.H.; Yu, J.C.; Sun, L.H.; Gui, H.R. Application of positive matrix factorization to identify potential sources of trace metals in water from subsidence area. *Fresen. Environ. Bull.* **2016**, *25*, 5953–5959.
30. Fei, Z.J.; Wang, Z.H.; Tang, Y. Characteristics and source analysis of heavy metals in water of Aha lake during the rain and dry seasons. *Earth. Environ.* **2021**, *49*, 42–50.
31. Gao, J.J.; Tian, H.Z.; Cheng, K.; Lu, L.; Wang, Y.X.; Wu, X.; Zhu, C.Y.; Liu, K.Y.; Zhou, J.R.; Liu, X.G.; et al. Seasonal and spatial variation of trace elements in multi-size airborne particulate matters of Beijing, China: Mass concentration, enrichment characteristics, source apportionment, chemical speciation and bioavailability. *Atmos. Environ.* **2014**, *99*, 257–265. [CrossRef]
32. Weerasundara, L.; Amarasekara, R.W.K.; Magana-Arachchi, D.N.; Ziyath, A.M.; Karunaratne, D.G.G.P.; Goonetilleke, A.; Vithanage, M. Microorganisms and heavy metals associated with atmospheric deposition in a congested urban environment of a developing country: Sri Lanka. *Sci. Total Environ.* **2017**, *584–585*, 803–812. [CrossRef] [PubMed]
33. Fang, F.M.; Lin, Y.S.; Wang, H.D.; Xie, H.F. Source exposure characteristics and its environmental effect of heavy metals in urban surface dust. *Acta Ecol. Sin.* **2011**, *31*, 7301–7310.
34. IARC. *Agents Classified by the IARC Monographs*; International Agency for Research on Cancer: Lyon, France, 2013; pp. 1–108.
35. Chen, J.; Liu, G.J.; Jiang, M.M.; Chou, C.L.; Li, H.; Wu, B.; Zheng, L.G.; Jiang, D.D. Geochemistry of environmentally sensitive trace elements in Permian coals from the Huainan coalfield, Anhui, China. *Int. J. Coal. Geol.* **2011**, *88*, 41–54. [CrossRef]

36. Wang, X.M.; Dong, Z.B.; Liu, G.J. Health risk of some trace elements in the water of the subsidence pool in Huainan. *Adv. Mater. Res.* **2012**, *347–353*, 2021–2027. [CrossRef]
37. Qiu, H.L.; Gui, H.R.; Song, Q.X. Human health risk assessment of trace elements in shallow groundwater of the Linhuan coal-mining district, Northern Anhui Province, China. Hum. *Ecol. Risk. Assess.* **2018**, *24*, 1342–1351. [CrossRef]
38. Wu, D.S. Leaching behavior of coal spoils and environmental impacts. *Earth. Env.* **2004**, *32*, 55–59. (In Chinese with English abstract)