Occurrence and Ecological Risk Assessment of Heavy Metals from Wuliangsuhai Lake, Yellow River Basin, China

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Abstract: As one of the eight largest freshwater lakes in China, Wuliangsuhai Lake is an extremely rare large lake with biodiversity and environmental protection functions in one of the world’s arid or semi-arid areas and it plays a pivotal role in protecting the ecological security of the Yellow River Basin. Heavy metals in sediment interstitial water, surface sediments, and sediment cores of Wuliangsuhai Lake were investigated and analyzed, and the pollution degree evaluated based on multiple assessment methods. The bioavailability of heavy metals of the surface sediments was evaluated by calculating the ratio of chemical fractions of heavy metals. The toxicity assessment of sediment interstitial water indicated that Ni, Zn, As, and Cd would not be toxic to aquatic ecosystems, however, Hg and Cr in some regions may cause acute toxicity to the benthos. The ecological assessment results of the surface sediments indicated that some areas of the lake are heavily polluted and the main polluting elements are Cd and Hg. Cd has the highest bioavailability because of its high exchangeable fraction ratio. In addition, exogenous pollution accumulated within 20 cm of the sediment cores, and then, with the increasing of the depth, the pollution degree and ecological risk decreased.

Keywords: heavy metals; sediment interstitial water; sediment; chemical fraction; ecological risk; Wuliangsuhai Lake

1. Introduction

One of the eight largest freshwater lakes in China, Wuliangsuhai (WLSH) Lake is a type of furiotile lake. Since the mid-19th century it has been under the influence of geological movement and it is one of the most important and the largest lakes in the Yellow River Basin. WLSH Lake is an extremely rare large lake with abundant biodiversity and multi-environment functions in one of the world’s desert or semi-desert areas [1,2]. Its environment and ecology has a significant impact on maintaining the ecological balance and protecting the diversity of species in northwestern China. WLSH Lake not only contains tremendous resources of aquatic plants, fisheries, birds, and tourism, but it is also an important ecological barrier in northern China [3,4]. During the dry season it is also a major water supply reservoir ensuring the continuous flow of the Inner Mongolia section of the Yellow River, and during the ice-flood season of the Yellow River or local rainstorms and flood seasons, it acts as a detention reservoir. It therefore has a huge and irreplaceable role in maintaining the water system of Yellow River. WLSH Lake is an extremely rare multi-function lake with high ecological benefits in a semi-desert area. At present, nearly half of the surface water of the lake is covered with reeds, and the rest with...
aquatic plants, making WLSH Lake a typical macrophytic eutrophic lake. The ecological security of WLSH Lake is important for the stability of Hetao area. It accepts more than 90% of the farmland drainage of the Hetao area [5], and then discharges into the Yellow River after the biochemical processes of the lake, which play a key role in improving the water quality and regulating the water volume of the Yellow River, and controlling the salinization of the Hetao area. These processes have reduced the direct impact of farmland drainage on the water quality of the Yellow River.

In recent years, with the acceleration of industrialization and urbanization of Bayannaoer City, large quantities of industrial wastewater, urban domestic sewage, and agricultural waste water are being poured into the lake [6,7]. Meanwhile, the heavy metals carried by them are entering the aquatic ecosystem through a series of geochemical processes such as direct discharge, atmospheric deposition, surface runoff, and soil erosion. Considerable attention has been given to heavy metals in aquatic ecosystems because it is difficult for them to be degraded by microorganisms after entering the aquatic environment, and they can accumulate in the living body through food chains, destroying the normal physiological metabolic activities of aquatic organisms, and high concentration are a potential risk to human health [8–10]. The ecological environmental problems of WLSH Lake not only affect the function of the lake, but also directly affect the regional food security and threaten the safety of water supply in the middle and lower reaches of the Yellow River. Therefore, investigating and assessing the current of heavy metal pollution in WLSH Lake is important for ecological protection and high-quality development in the Yellow River Basin. Some scholars have studied different aspects of the heavy metals in WLSH Lake from [11–13]. However, there are little research on the comprehensive monitoring and assessment of heavy metals in this lake.

In aquatic systems, sediment serves as an important sink of heavy metals. After heavy metals enter the water, except for the small amount that dissolves in the overlying water, most can be absorbed into the sediment by complexation interaction with the organic matter, clay minerals, and sulfides in the sediment. Meanwhile, heavy metals in the sediment are more likely to be resuspended in the sediment interstitial water when environmental factors (e.g., wind–wave disturbance, pH, ORP, DO, and microbial activity) change [14]. Meanwhile, because of differential concentrations, heavy metals in sediment interstitial water can be re-released into the overlying water by diffuse flux [15,16]. Therefore, investigating the concentrations of heavy metals in the sediment interstitial water and surface sediments is of great significance for the study of lake water quality and aquatic organisms. Moreover, the vertical concentrations of heavy metals in sediment cores have been used to study the degree of accumulation, exogenous sources, and further trends [17–20].

In addition, the total content of heavy metals in the sediment can provide information about the pollution level, but it cannot reflect the potential ecological risk. The environmental behaviors and ecological effects of heavy metals in different chemical fractions are also different [21,22]. The migration and transformation, toxicity, bioavailability and potential ecological risk of heavy metals in sediment greatly depend on their different chemical fractions. According to the BCR sequential extraction procedure [23], the heavy metals in the sediments can be classified into four chemical fractions. Under certain conditions, these fractions are easily released into the overlying water, thus causing secondary pollution [24,25]. Therefore, when evaluating the ecological risk of heavy metals in sediments, the chemical fractions, especially the bioavailable fractions, should be taken into consideration.

In order to provide more comprehensive information about the heavy metals of the WLSH Lake, this study (1) describes the contents of heavy metals in interstitial water and surface sediments of WLSH Lake, (2) quantified the percentages of chemical fractions of heavy metals at each sampling site; (3) investigated the vertical distribution of heavy metals in sediment, and (4) comprehensively assessed the pollution degree and ecological risk by the methods of enrichment factor (EF), geo-accumulation index ($I_{geo}$), toxic units ($\Sigma TUs$) and toxic-risk index (TRI), risk-assessment code (RAC), and potential ecological
risk index (RI) and to calculate the modified potential ecological risk index (MRI) based on the chemical fractions.

2. Materials and Methods

2.1. Study Area

As the eighth largest freshwater lake in China, Wuliangsuhai Lake is the most typical shallow grassy lake in an arid area, and is also an important site for water conservation, storage, and water diversion in the middle and upper reaches of the Yellow River. Wuliangsuhai Lake (108°43′–108°57′E, 40°27′–40°03′N) belongs to the lake area of Neimenggu-Xinjiang Plateau, located in the city of Bayannaoer, in the Inner Mongolia Autonomous Region. It is also in the arid and semi-arid area of northern China. The area where the basin is located has strong solar radiation, rare rainfall, strong evaporation, a large difference between dry and wet periods, a large temperature difference between day and night, and frequent wind and sand weather. The region where the lake is located has four obvious seasons, and the temperature varies greatly. There is less rainfall and more evaporation in the lake basin.

This lake covers 285.38 km², including a reed area of 118.97 km² and a clear water area of 111.13 km². In the clear water area there is a 85.7 km² dense area of submerged plants and the rest is swamp area. The lake is long from north to south and narrow from east to west, with a length of 35–40 km, and a width of 5–10 km. The lakeshore is 130 km long and the water storage is 2.5 to 300 million m³. Most of the lake water depth is between 0.5 and 2.5 m, and the average annual water depth is 0.7 m.

2.2. Sample Collection and Sample Preparation

According to the characteristics of water system of WLSH Lake, the village distribution, land use, and administrative region, 23 sampling sites were selected (Figure 1). In August 2021, sediment samples were collected, and then eight sites were selected for collecting the core samples of the sediments. All surface sediment samples were collected using a Peterson grab bucket. At every sampling site, 5 cm of the surface sediment and four subsamples were collected. These were then mixed on the spot and put into a sterile sampling bag. The core samples (S1, S2, S5, S6, S8, S10, S16, and S18) were collected by column sampler (04.23 BEEKER, Eijkelkamp, Giesbeek, The Netherlands), and all the samples were segmented into 5 cm layers, with each layer being placed in the sterile sampling bag. At every core sampling site, three 3 sub-samples were collected and analyzed separately. All of the samples were kept at temperatures below −4 °C and transported to the laboratory within three days. In the laboratory, from each sampling site, approximately 250 g of well-mixed fresh sediment sample was dispensed into several 100 mL centrifuge tubes, and then centrifuged in 10,000 rpm for 10 min. Then, all the filtrate was mixed and filtered with 0.45 µm glass fiber filters. The obtained interstitial water was stored at −4 °C and analyzed within three days. After centrifugation, the sediment samples were dried by cold-drying and then the samples were sieved through a 40-mesh nylon sieve to remove rocks, organic debris, and other debris and a portion of each sample (about 50 g) was ground in a mortar and then sieved through a 100-mesh nylon sieve. The prepared samples were stored in self-sealing bags at 4 °C for further analysis.

2.3. Analytical Methods

Heavy elemental analyses were performed at the Zhengzhou Key Laboratory of Water Resource and Water Environment. As is metalloid, but for convenience of description, in this study, As is classified as heavy metal. Heavy metals in sediment interstitial water were digested by HNO₃. The total content of heavy metals in the sediments was digested by a mixture of acid (6 mL HNO₃ + 3 mL HF + 1 mL H₂O₂) using a microwave digestion platform (Milestone, ETHOS UP). Chemical fractions of heavy metals in the sediments were extracted according to the BCR sequential extraction method, and the specific extraction steps are shown in Supplementary Materials. The digestion method of the residual fraction refers to the total content. Finally, the concentrations of all heavy metals were analyzed.
using inductively-coupled plasma-mass Spectrometry (ICP-MS, Agilent 8800, Agilent Technologies, Santa Clara, CA, USA) according to HJ 700-2014 of the Ministry of Ecology and Environment of China.

Figure 1. Locations of Wuliangsuhai Lake and sampling sites.

2.4. Quality Assurance and Quality Control (QA/QC)

The containers used in the study were soaked in 20% HNO$_3$ solution ($v/v$) for 24 h before use, and then rinsed with ultra-water (Milli-Q, $\rho > 18$ MΩ-cm) to prevent container contamination. In order to ensure the accuracy and precision of the results, standard samples were used between every 20 samples. Each sample was determined three times in parallel, and the results expressed as the average value of the three parallel tests (error range < 5%). Soil reference materials (aquatic sediment standard materials (GSD7)) were used to control the quality during the determination process in the study, and the results of recovery of each heavy metal are shown in Table S1. During the experiment, blank samples were determined to eliminate the influence of background values.

2.5. Pollution Assessment Methods

2.5.1. Enrichment Factor (EF)

The enrichment factor (EF) is an important index to quantitatively evaluate accumulation degree and pollution sources [26]. In order to reduce the influence of particle size on heavy metal pollution assessment, a standard metal is generally used to normalize the original data. Aluminum (Al) in the environment mainly comes from natural rock with poor mobility, and is often selected as the standard metal. The EF is calculated as follows:

$$EF = \frac{C_i / C_{Al}}{B_i / B_{Al}}$$

where $C_i$ represents the measured concentration of metal $i$, $C_{Al}$ represents the measured concentration of Al, $B_i$ is the background value of metal $i$, and $B_{Al}$ is the background value of Al. EF $> 1$ indicates anthropogenic contamination. According to the calculated values, EF can be divided into five categories, which are shown in Table S2.

In this study, the background values of Henan Province soil were used to evaluate the pollution degree and ecological risk of heavy metals in WLSH Lake.

2.5.2. Geo-Accumulation Index ($I_{geo}$)

The geo-accumulation index ($I_{geo}$) was proposed by Müller [27], and can evaluate the pollution degree of heavy metals in various environmental media, especially sediments.
and soils. The pollution degrees of heavy metals are classified into seven levels based on $I_{geo}$, and the equation for $I_{geo}$ is presented as follows:

$$I_{geo} = \log_2 \frac{C_i}{1.5 \times B_i}$$

(2)

where, the meanings of $C_i$ and $B_i$ are consistent with EF. In order to minimize the variation of background values caused by petrogenesis, a constant of “1.5” is introduced. The classification of $I_{geo}$ is shown in Table S3.

2.5.3. Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) is widely used to evaluate the pollution levels and ecological hazard degrees of heavy metals in sediments [28]. The equation for RI is as follows:

$$RI = \sum E_i = \sum T_i \times C_i / B_i$$

(3)

where, the meanings of $C_i$ and $B_i$ are consistent with EF, $C_i$ is the pollution index of metal $i$, $E_i$ is the potential ecological risk coefficient of metal $i$, $T_i$ is the toxicity response coefficient of metal $i$, and, in this study, the $T_i$ for Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb were 2, 5, 5, 1, 10, 30, 40, and 5, respectively. RI is the total potential ecological risk of all the investigated heavy metals. The classification and standard values of RI are shown in Table S4.

2.5.4. Toxic Units ($\Sigma$TUs) and Toxic-Risk Index (TRI)

Sediments quality guidelines (SQGs) can be used to assess potential ecological risks caused by heavy metals in sediments. SQGs include threshold effect levels (TELs) and probable effect levels (PELs) [29]. Adverse biological effects rarely occur at concentrations lower than the TEL, but often occur at concentrations higher than the PEL. Based on the ratio of measured values to PEL, $\Sigma$TUs can be used to evaluate the toxic effects of sediments, and the equation is as follows:

$$\sum TUs = \sum \frac{C_i}{C_{PEL}}$$

(4)

After considering TEL and PEL, the comprehensive toxic effects of heavy metal in sediments, that is, TRI, is calculated using the following equation:

$$TRI = \sum TRI_i = \sum \sqrt{\left(\frac{C_i}{C_{PEL}}\right)^2 + \left(\frac{C_i}{C_{TEL}}\right)^2}$$

(5)

where the meaning of $C_i$ is consistent with EF, $C_{PEL}$ and $C_{TEL}$ are the corresponding PEL, and TEL of metal $i$, respectively.

2.5.5. Risk-Assessment Code (RAC)

In this study, the risk-assessment code (RAC) proposed by Singh et al. [30] has been used to assess the risk of secondary release of heavy metals from sediments in WLSH lake. The calculation equation of the RAC is as follows:

$$RAC = \frac{C_e}{C_t} \times 100\%$$

(6)

where $C_e$ is the content of exchangeable and carbonate-bound heavy metal and $C_t$ is the total content of heavy metal. According to RAC values, the bioavailability of heavy metal can be classified into five levels, which are shown in Table S5.
2.5.6. Modified Potential Ecological Risk Index (MRI)

Different fractions of heavy metals have different potential ecological risks to the environment. A modified potential ecological risk index (MRI) was applied to assess the potential ecological risks of heavy metals. The MRI was calculated as follows:

\[ \Omega = A \varnothing + B \]  
\[ \tilde{C}_i = C_i \Omega \]  
\[ \tilde{C}_j = \tilde{C}_i / B_i \]  
\[ \tilde{E}_i = T_i \tilde{C}_j \]  
\[ MRI = \sum \tilde{E}_i \]

where, \( \tilde{C}_i, \tilde{C}_j, \tilde{E}_i, \) and MRI are the modified forms of \( C_i, C_j, E_i, \) and RI, respectively, \( \Omega \) is the modified indicator, \( A \) is the ratio of exchangeable fraction to the total, the value of \( B \) is equal to 1-\( A \), and \( \varnothing \) is the toxicity coefficient corresponding to different percentage of exchangeable fractions. Table S5 shows the values of \( \varnothing \) obtained according to the values of RAC and expert consultation.

2.6. Statistical Analysis

A geographic information system (GIS) was used to analyze the spatial distribution of heavy metals in sediment interstitial water and sediments from the WLSH Lake. The inverse distance (IDW) method was applied to map the spatial distribution of pollutants based on ArcGIS 10.2 software (ESRI, Inc., Redlands, CA, USA).

3. Results and Discussion

3.1. Heavy Metals in the Sediment Interstitial Water

The material exchange across the sediment–water interface is mainly through sediment interstitial water, and the growth environment of the benthos and its toxicity is closely related to sediment interstitial water. Therefore, sediment interstitial water plays an important role in the geochemical cycling of heavy metals in lake systems [31,32]. In this study, the concentrations of Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb in the sediment interstitial water of WLSH Lake were investigated and analyzed. The spatial distribution characteristics of heavy metals in the sediment interstitial water are illustrated in Figure 2.

As shown in Figure 2, there was a large difference in the spatial distribution of each metal in the sediment interstitial water of WLSH Lake. The concentrations of heavy metals in the western bank were generally higher than these in the eastern bank. The eight heavy metals could be roughly classified into two types. The first was those whose concentrations were generally higher in the estuary of the lake than in the center of the lake, with the highest value occurring in the estuary of the Ninth Drain in the west lake. Heavy metals of this type included Cr, Cu, Zn, and Hg. Concentrations of the second type, which included Ni, As, Cd, and Pb, were higher in the middle of the lake.

This study evaluated the toxicity of heavy metals in interstitial water of WLSH Lake to the aquatic ecosystem based on the National Recommended Water Quality Criteria by EPA [33]. This criteria includes criterion continuous concentration (CCC) and criterion maximum concentration (CMC). Chronic toxicity may occur to aquatic ecosystem if the concentration of a heavy metal in the water exceeds its corresponding CCC value. Acute toxicity may occur when the concentration exceeds its corresponding CMC value. The concentration of heavy metals in the sediment interstitial water of WLSH Lake and EPA water quality standard are shown in Table 1.
Figure 2. Spatial distributions of Cr (a), Ni (b), Cu (c), Zn (d), As (e), Cd (f), Hg (g), and Pb (h) in sediment interstitial water from the Wuliangsuhai Lake.

Table 1. Descriptive statistics of heavy metal concentrations in the sediment interstitial water of Wuliangsuhai Lake and EPA water quality criteria (µg/L).

|      | Cr   | Ni   | Cu   | Zn   | As   | Cd   | Hg   | Pb   |
|------|------|------|------|------|------|------|------|------|
| Min  | 0.10 | 5.53 | 5.67 | 0    | 3.96 | 0    | 0.04 | 0    |
| Max  | 30.04| 31.42| 34.41| 34.38| 72.69| 0.23 | 4.23 | 5.19 |
| Mean | 8.44 | 10.69| 15.43| 6.56 | 16.28| 0.08 | 0.58 | 0.82 |
| SD   | 7.91 | 5.70 | 8.12 | 9.95 | 16.44| 0.07 | 0.93 | 1.25 |
| CMC  | 13   | 470  | 13   | 120  | 340  | 2    | 1.4  | 65   |
| CCC  | 9    | 52   | 9    | 120  | 150  | 0.25 | 0.77 | 2.5  |

1 SD: standard deviation. 2 CMC: criterion maximum concentration. 3 CCC: criterion continuous concentration.

Comparing the concentrations of heavy metals in the sediment interstitial water with the standard concentrations, the results showed that the average concentrations of Ni, Zn, As, and Cd were less than the corresponding CCC values, that is, they would not cause toxicity to the aquatic ecosystem. The average concentration of Cu was higher than that of CCC-Cu, indicating that Cu in interstitial water of WLSH Lake may cause chronic toxicity to the benthos, which should be paid attention to. The average concentrations of Cr and Hg in the middle of the lake were less than the CCC value, while those in estuary were higher than the CMC, indicating that Cr and Hg in the estuary may cause acute toxicity to the aquatic ecosystem.

3.2. Heavy Metal in the Surface Sediments

3.2.1. Contents of Heavy Metals in the Surface Sediments

The descriptive statistics of the heavy metals concentrations in the surface sediments of WLSH Lake as well as the background values (the soil background values of Inner Mongolia from CNEMC, 1990), and the corresponding values based on SQGs are summarized in Table 2. According to the background values of WLSH Lake, they indicated that the concentrations of heavy metals except Cr and Zn in the surface sediments of this study...
were higher than their corresponding background values. Cd and Hg, in particular, had average values 10.19 and 4.25 times higher, respectively, than their background values.

Table 2. Descriptive statistics of heavy metal concentrations in the surface sediments of Wuliangsuhai Lake (mg/kg).

|     | Cr   | Ni   | Cu   | Zn   | As   | Cd   | Hg   | Pb   |
|-----|------|------|------|------|------|------|------|------|
| Min | 18.76| 18.36| 4.77 | 22.65| 3.89 | 0.35 | 0.01 | 16.03|
| Max | 45.27| 31.06| 65.44| 68.11| 17.26| 0.92 | 0.51 | 53.93|
| Mean| 32.76| 25.90| 18.01| 38.69| 10.13| 0.54 | 0.17 | 29.17|
| SD  | 8.72 | 3.58 | 12.67| 10.42| 3.30 | 0.15 | 0.11 | 10.24|
| TEL | 43.4 | 22.7 | 31.6 | 121  | 9.8  | 0.99 | 0.18 | 35.8 |
| PEL | 111  | 48.6 | 149  | 459  | 33   | 5    | 1.1  | 128  |
| BV  | 41.4 | 19.5 | 14.1 | 59.1 | 7.5  | 0.053| 0.04 | 17.2 |

1 TEL: threshold effect level. 2 PEL: probable effect level. 3 BV: background value.

The average concentrations of Cr, Ni, Cu, Zn, Cd, Hg, and Pb were lower than their corresponding TEL values. Furthermore, the maximum concentrations of Cr, Cu, As, Hg, and Pb exceeded the corresponding TEL values by 1.04, 2.07, 1.76, 2.83, and 1.51 times, respectively. In addition, the maximum concentrations of all the heavy metals were lower than their corresponding PEL values. Thus the adverse biological effects in some regions were probable but would not be frequent.

Comparing the heavy metal concentrations in the surface sediments of WLSH Lake with the published literature of other freshwater lakes in China and abroad (Table 3), revealed that compared with algae lakes (e.g., Taihu Lake and Chaohu Lake), the heavy metal concentrations in WLSH Lake were not high. Nevertheless, compared with other lakes in the Neimenggu-Xinjiang Plateau (e.g., Hulun Lake), the average concentrations of Cd and Hg in WLSH Lake were relatively high. In general, the pollution degrees of heavy metals in sediments from the lakes in economically developed areas (e.g., Taihu Lake (Jiangsu Province) and Dongting Lake (Hunan Province)) were higher than those in economically developing areas in China. Obviously, the heavy metal concentrations in lake sediments were related to the intensity of human activities.

Table 3. Comparison the concentrations of heavy metals in the surface sediments of Wuliangsuhai Lake and other freshwater lakes in China and abroad.

|                        | Cr   | Ni   | Cu   | Zn   | As   | Cd   | Hg   | Pb   |
|------------------------|------|------|------|------|------|------|------|------|
| Wuliangsuhai L., China | 32.76| 25.90| 18.01| 38.69| 10.13| 0.54 | 0.17 | 29.17|
| Taihu L., China [34]   | 68.09| 36.23| 34.14| 105.5| 9.82 | 0.14 | 0.11 | 33.55|
| Chaohu L., China [35]  | 81.9 | 37.2 | 28.9 | 152  | 11.99| 0.44 | 0.134| 52.4 |
| Baiyangdian L., China [36]| 30.13–86.00| 22.00–40.00| 16.13–204.02| 41.63–263.00| NA | 0.19–2.47| NA | 25.33–99.26 |
| Hulun L., China [37]   | 31.37| 15.61| 16.17| 48.43| 10.36| 0.09 | 0.019| 20.87|
| Dongting L., China [38] | 88.29| 41.65| 47.48| 185.25| 29.71| 4.65 | 0.157| 60.99|
| Erie L., USA [39]      | 46.4 | 28.3 | 27.3 | 123.4| 11.7 | 2.8  | NA   | 75.5 |
| Jinzai L., Japan [40]  | 42   | 11   | 34   | 215  | 14   | NA   | NA   | 24   |
| Veeranam L., India [41] | 88.20| 63.61| 94.12| 180.08| NA  | 0.81 | NA   | 30.06|
| Gökçekaya L., Turkey [42]| 239.67| 132.38| 107.88| 287.11| 17.02| 0.027| 0.027| 92.92|

NA: not applicable.

3.2.2. Chemical Fractions of Heavy Metals in the Surface Sediments

The heavy metals in sediments exist in different fractions, mainly including the exchangeable fraction, the reducible fraction, the oxidizable fraction, and the residual fraction. Among these, the first three fractions are referred to as extractable fractions. They can be used by organisms and are potentially harmful to the ecological environment.

Figure 3 illustrates the percentages of chemical fractions for each heavy metal in the sediment from WLSH Lake. As shown in Figure 3, Ni, Cu, Cd, and Hg were mainly in the extractable fraction. The percentage of Cd in the exchangeable fraction ranged...
from 28.69 to 50.83%, and the lakeshore in the northwest had relatively high levels. The percentages of the reducible and oxidizable fractions ranged from 17.45 to 38.48% and 6.76 to 14.61%, respectively. In the extractable fraction, Hg was mainly in the oxidizable fraction, and ranged from 21.75 to 33.67%, followed by the reducible fraction, with the average value of 13.55%. Moreover, Ni and Cu were mainly in the reducible fraction, and the amounts of the acid-soluble and reducible fractions were relatively lower.

![Figure 3. Percentages of the chemical fractions for (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Cd, (g) Hg, and (h) Pb in 23 sediment samples from Wuliangsuhai Lake.](image)
The residual fraction is extremely stable and hardly used by organisms [25]. The percentages for chemical fractions of Cr, Zn, As, and Pb in the surface sediments of WLSH Lake were mainly in the residual fraction, especially for As and Pb, which were 94.05% and 81.57%, respectively. In contrast, to the residual fraction, the greater the proportion of the extractable fraction of the heavy metals, the greater their bioavailability, the more likely they are to be released to cause secondary pollution, and the more likely to pose a potential threat to the environment. In this study, the potential bioavailability of the eight metals was ranked as Cd > Cu > Ni > Hg > Cr > Zn > Pb > As.

3.2.3. Pollution Assessment of Heavy Metals in the Surface Sediments

After normalization with the element Al, the EF value of each heavy metal was calculated by comparing the measured concentration to its corresponding background value, and the results are shown in Table 4. The average EF value of Cd was 3.51, showing that it reached moderate enrichment; the average EF value of Hg was 1.94, showing that Hg was in minimal enrichment, however, the EF value of Hg at S7 was as high as 10.62, reaching significant enrichment. The EF values at some sampling sites of Ni, Cu, and As approximated 1, indicating that the metals were considered to be partly contaminated. The EF values of Pb, Cr, and Ni in all sampling sites were lower than 1, indicating that these metals may not be contaminated by anthropogenic sources. The average enrichment degree decreased in the order of Cd > Hg > Pb > As > Cu > Ni > Cr > Zn.

Table 4. The EF value of each heavy metal in the surface sediments of Wuliangsuhai Lake.

|       | Cr | Ni | Cu | Zn | As | Cd | Hg | Pb |
|-------|----|----|----|----|----|----|----|----|
| Min   | 0.20 | 0.25 | 0.20 | 0.12 | 0.16 | 2.36 | 0.03 | 0.42 |
| Max   | 0.42 | 1.18 | 3.13 | 0.49 | 1.31 | 5.64 | 10.62 | 0.78 |
| Mean  | 0.27 | 0.52 | 0.53 | 0.23 | 0.55 | 3.51 | 1.94 | 0.56 |

Figure 4a–h illustrates the spatial distribution characteristics of $I_{geo}$ values of each heavy metal, and Figure 4i was the violin plot of $I_{geo}$. As shown in Figure 4, the concentrations of Ni, As, and Hg showed similar spatial distribution. The highest concentrations of those metals were near the lake entrance in the northeastern lake owning to the large amount of drainage water from the Hetao irrigation area and industrial wastewater and domestic sewage from upstream, all discharged into the lake through lake entrance. In addition, dense emerged plants slowed the water flow. As a result, heavy metals in water were absorbed by sediments and accumulated. Moreover, the sampling sites with the highest Cd and Pb contents were located in the estuary near the Total Drain. This may have been because that the mobility of Cd and Pb is strong, and long-term closure of the water gate makes the sedimentary environment relatively stable, which is conductive to the accumulation of Cd and Pb. The high value area of heavy metals except Hg was in the northern lake. The reason for this is that mixed sewage is discharged from the northern lake, and then is diverted to the south after being blocked by the reeds. During the diversion, it is mixed with the waste water from the Total Drain, which makes a high content of heavy metals in the northern part of WLSH Lake. As shown in Figure 4i, the mean $I_{geo}$ values of the heavy metals ranked as Cd > Hg > Pb > Ni > As > Cu > Cr > Zn, and the mean $I_{geo}$ values of Ni, As, Cu, Cr, and Zn were all less than 0. According to $I_{geo}$ classification, the mean $I_{geo}$ of sediments in WLSH Lake indicated that it was unpolluted by Cr, Ni, Cu, Zn, or As, unpolluted to moderately polluted by Pb (0.10), moderately polluted by Hg (1.08), and moderately to strongly polluted by Cd (2.73). The maximum value of $I_{geo}$-Cd was 3.37, showing that it was strongly polluted. The $I_{geo}$ values of Cr and Zn in all sampling sites were less than 0, indicating that the heavy metal pollution in the surface sediments of WLSH Lake was mainly caused by other metals. The sampling sites with $I_{geo}$ values greater than 0 for Ni, Cu, and As accounted for 17.4%, 21.7%, and 30.4% respectively.
Figure 4. I_{geo} assessment results of heavy metals in the surface sediments (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Cd, (g) Hg, and (h) Pb from Wuliangsuhai Lake. (i) violin plot of I_{geo}.

The potential ecological risks of heavy metals in the surface sediments of WLSH Lake were calculated based on Equation (3). Figure 5a shows the $E_i^r$ value of each metal, and Figure 5b illustrates the spatial distribution characteristics of RI. The mean $E_i^r$ value were
ordered as follows: Cd > Hg > As > Pb > Ni > Cu > Cr > Zn. The $E_i^T$ values of Cr, Ni, Cu, As, and Pb were less than 40 at all sampling sites, indicating that these metals were at low risk. The mean $E_i^T$ values of Cd and Hg were 307.89 and 171.42, corresponding to high risk. The maximum $E_i^T$ values of Cd and Hg were 519.20 and 505.51, respectively, corresponding to very high risk. With respect to Cd, 62.5% of the sampling sites were at considerable risk, and the rest were at high to very high risk. The average RI value of the surface sediments in WLSH Lake was 516.34. According to the classification of RI, the surface sediments of WLSH Lake posed a considerable risk. Due to the high enrichment and strong toxicity, Cd and Hg had the highest contribution rate to RI. The RI values at S1, S2, S7, and S15 sampling sites were all higher than 600, corresponding to very high risk. These sampling sites were located in the central lake. Overall, the ecological risks in the central lake were higher than these in lakeshore. The spatial distribution characteristics of RI were similar to those of Zn, Cd, Hg, and Pb.

The $\Sigma TUs$ and TRI distributions and values of individual metals are shown in Figure 5e–h. Previous studies have shown that when $\Sigma TUs < 4$, the sediment will not cause the death of amphipod *C. volutator* (Pallas), nor will it cause the acute toxicity to *V. fischeri*. However, when $\Sigma TUs$ is higher than 4, significant toxicity will occur [19,43]. Therefore, $\Sigma TUs$ of 4 is the vital threshold to identify whether heavy metals in sediment will have toxic effects. However, there was no site with $\Sigma TUs$ values higher than 4.0. The results of $\Sigma TUs$ showed that the potential eco-toxicity of Ni, As, and Cr was higher than that of other metals, but this is not consistent with the actual pollution situation. This may because of the high PEL value, which cause misjudgment of potential eco-toxicity. Thus, $\Sigma TUs$ is not suitable for WLSH Lake. Based on TRI results, TRI values ranged from 2.96 to 6.34, with the highest value in the center lake and the lowest in the midwestern lakeshore. Spatially, the TRI of the study area increased from the west to the middle, and then decreased from the middle to the east. This method takes the PEL and TEL into consideration, which can provide more reference information for actual pollution estimation.

The exchangeable fraction of heavy metals in sediments is the most sensitive to environmental changes. The exchangeable fraction is easily released under neutral or acidic conditions, due to its weak bonding force, so it has the ability of rapid desorption and high bioavailability. As shown in Figure 5g, the bioavailability of heavy metals in this study varied greatly, and the bioavailability of each heavy metal had spatial differences. In general, the heavy metals in the surface sediments of WLSH Lake can be classified into three groups: the RAC values of Cr, Zn, As, and Pb in all sampling sites were less than 10%, corresponding to no to low risk; the RAC values of Cu, Ni, and Hg were less than 30%, corresponding to low to medium risk; the RAC values of Cd ranged from 28.69% to 50.83%, with an average value of 35.50%, indicating that Cd in the surface sediments of WLSH Lake was at high risk, while Cd in S4 sampling site was at very high risk. The results showed that a high proportion of Cd in the surface sediments existed in the fraction of active adsorption. The assessment results were similar to those based on the total contents, but there were some differences, indicating that the chemical fractions had an impact on the ecological risk of sediments.

In this study, MRI, which is a modified index of RI, takes the toxicity and concentration of F1 fraction into consideration. Compared with RI, in some cases, MRI can better assess the actual ecological risk of sediments. As shown in Figure 5h, the MRI values of 23 sampling sites were all higher than the corresponding RI values. Both RI and MRI of S1, S2, S7, S12, and S15 were at very high risk. Moreover, RI of S4, S5, and S18 were at high risk, while the MRI values of these sampling sites were at very high risk. Compared with other sampling sites, MRI values were significantly higher than RI values at heavily polluted sites, showing that the percentage of F1 has a great influence on the MRI values. Since most of exchangeable heavy metals were mainly from anthropogenic sources, MRI can be considered to be more suitable for assessing the ecological risk of heavy metals in sediments which are under the influence of human activities.
Figure 5. Risk assessment by RI (a,b), ΣTUs (c,d), TRI (e,f), RAC (g), and MRI (h).
The above assessment results indicated that the heavy metals in the surface sediments of WLSH Lake were at considerable risk, with the pollution degree in the central part of northern lake being the highest. The enrichment degree, potential ecological risk, and biological toxicity of most heavy metals were higher in the central part of northern lake, while the southern lakeshore region was less polluted. Compared with other heavy metals, Cd was the primary pollutant in the surface sediments of WLSH Lake. The average concentration of Cd in the surface sediments of WLSH Lake was 10.1 times that of the corresponding value, reaching significant enrichment in some regions. This may be because there is a large amount of farmland around WLSH Lake, and the use of phosphate fertilizers causes the increase of Cd contents in the sediments. In addition, the plastic films used in greenhouses also contain Cd, further increasing the Cd loading in the sediments. Moreover, both industrial wastewater and domestic sewage are drained into the lake, leading a high risk of heavy metals.

3.3. Heavy Metals in the Sediment Cores

3.3.1. Contents of Heavy Metals in the Surface Sediments

The contents of heavy metals in eight sediment cores are shown in Figure 6. The contents of heavy metals in sediment cores decreased with the depth. When the depth of the sediment reached 40 cm, the contents tended to gradually stabilize. Therefore, this study regarded the sediment layers blow 45 cm as the “unpolluted layer of the lake”. Meanwhile, the sedimentation rate of the WLSH Lake is 9–13 mm/a [44] (The effect of lake disturbance on sedimentation rate was not considered). Based on this, the sediment profile of 40 cm corresponded to the 1970s. In this study, the “unpolluted sediment layer of the lake” was 45–80 cm, which can be considered as the “background layer” before industrialization.

![Figure 6. Profile of heavy metals from sediment cores in Wuliangsuhai Lake: (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Cd, (g) Hg, (h) Pb.](image)

3.3.2. Pollution Assessment of Heavy Metals in Sediment Cores

Figure 7 illustrates the average values of RI, \( \Sigma \) TUs, and TRI of eight sediment cores. As shown in Figure 7a, the primary pollutant of sediment cores was Cd, and the contribution rate of Cd to RI in each layer was the highest. The RI values in the surface sediments (0–20 cm) were much higher than those of bottom sediments (depth > 20 cm). The RI value of sediments at the depth of 0–5 cm was 2.69 times that of the sediments at the depth of 75–80 cm, indicating that the surface sediments were greatly disturbed by human activities. It can be seen from Figure 7b,c that the vertical distribution characteristics of \( \Sigma \) TUs and TRI were similar. The values of \( \Sigma \) TUs and TRI of sediments at depth of 0–20 cm were greater...
than those at depth > 20 cm. However, the variation trend of TRI with depth was more obvious than that of ΣTUs. Ni had the highest contribution rate to ΣTUs and TRI, and the contribution rates at the bottom sediments (depth > 20 cm) were higher than those at the surface sediments (0–20 cm), which also demonstrated that the Ni contents had little differences in each layer. In the surface sediments, the contribution rates of Cd to ΣTUs and TRI were 6.26% and 9.38%, respectively, showing that TRI was more sensitive to the changes in metal contents. Combined with the three assessment results, it was indicated that the ecological risk and biological toxicity at the surface sediments (0–20 cm) were higher than those at the bottom sediments. As the depth increased, the ecological risk and biological toxicity gradually decreased.

Figure 7. The assessment results of (a) RI, (b) ΣTUs, and (c) TRI of sediment cores from Wuliangsuhai Lake.

4. Conclusions

In this work, eight heavy metals (Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb) in sediment interstitial water, surface sediments, and sediment cores from Wuliangsuhai Lake were investigated. The chemical fractions of heavy metals were obtained using the BCR extraction procedure. Then, the pollution assessment of these heavy metals was studied using enrichment factor, geo-accumulation index, potential ecological risk, SQGs, and modified potential ecological risk based on risk assessment code. Comparing the concentrations of heavy metals in the sediment interstitial water with the National Recommended Water Quality Criteria by EPA, indicated that Ni, Zn, As, and Cd would not be toxic to aquatic ecosystems, however, Hg and Cr in some regions may cause acute toxicity to the benthos. The mean concentrations of Ni, Cu, As, Cd, Hg, and Pb in the surface sediment exceeded the geochemical background values. Cr, Zn, Cd, and Pb exhibited similar spatial distributions in concentrations, with the highest value appearing at the estuary near the Total Drain. In contrast, the highest concentration values of Ni, As, and Hg were at the northeast of lake. Based on the pollution assessment results, Cd is the primary pollutants in WLSH Lake, which deserves attention. The bioavailability and mobility of heavy metals followed a decreasing order of Cd > Ni > Cu > Hg > Zn > Pb > As > Cr. The concentrations and ecological risk of heavy metals in sediment decreased with the increase in depth.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14081264/s1, Text S1: Steps of BCR, Table S1: Results of the recovery test of standard samples (GSD7), Table S2: Classification of EF, Table S3: Classification of Igeo, Table S4: Indices and grades of potential ecological risk, Table S5: Classification of RAC and values of \( \partial \).

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