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## ABSTRACT

Surface sediment samples were collected from a source water reservoir in Zhejiang Province, East of China to investigate pollution characteristics and potential ecological risk of heavy metals. The BCR sequential extraction method was used to determine the four chemical fractions of heavy metals such as acid soluble, easily reducible, easily oxidizable and residual fractions. The heavy metals pollution and potential ecological risk were evaluated systematically using geoaccumulation index ($I_{geo}$) and Hakanson potential ecological risk index ($H'$). The results showed that the sampling sites from the estuaries of tributary flowing through downtowns and heavy industrial parks showed significantly ($p < 0.05$) higher average concentrations of heavy metals in the surface sediments, as compared to the other sampling sites. Chemical fractionation showed that Mn existed mainly in acid extractable fraction, Cu and Pb were mainly in reducible fraction, and As existed mainly in residual fraction in the surface sediments despite sampling sites. The sampling sites from the estuary of tributary flowing through downtown showed significantly ($p < 0.05$) higher proportions of acid extractable and reducible fractions than the other sampling sites, which would pose a potential toxic risk to aquatic organisms as well as a potential threat to drinking water safety. As, Pb, Ni and Cu were at relatively high potential ecological risk with high $I_{geo}$ values for some sampling locations. Hakanson potential ecological risk index ($H'$) showed the surface sediments from the tributary estuaries with high population density and rapid industrial development showed significantly ($p < 0.05$) higher heavy metal pollution levels and potential ecological risk in the surface sediments, as compared to the other sampling sites.

## Introduction

Rapid population growth and economy development have resulted in serious pollution of water environment such as rivers and lakes or reservoir in many developing countries including China. Sediments, as sources and sinks of various pollutants like pesticides and heavy metals, are sensitive indicators that can reflect the spatial and temporal variations of the pollutant sedimentation in water body.[1] Sediment pollution has been one of the most serious environmental problems in aquatic ecological system,[2,3] which has seriously affected water quality and posed a potential toxic risk to aquatic organisms. [4] Heavy metals (HMs) are greatly harmful to organisms and ecological systems due to its degradation-resistance, bioaccumulation, and bio-amplification.[5–7] Sediments function as a sink for HMs from diverse sources, reflecting the natural soil composition of the surrounding areas, as well as human activities.[8] The heavy metals in the lakes or reservoirs are mostly concentrated in sediments by flocculation and sedimentation and thereby contaminated the sediments.[9] The lake sediments conserve valuable historic information on past and present water environment conditions and inputs of pollutants such as HMs.[10] Therefore, the research on heavy metal pollution and environmental risk assessment of the sediments from lake or river affected by urbanization and industrialization is of great significance and attract many researchers all over the world.[11,12]

However, the total amount analysis of the heavy metals cannot fully reflect environmental behavior and ecological effect of heavy metals in the sediments. [13,14] The migration and transformation process, biological toxicity, and bioavailability of heavy metals in the sediment mainly depend on the fractionation of heavy metal,[15,16] while the forms of heavy metals is closely associated with the toxic effects and ecological risk of the sediments.[17] The speciation of metals in sediments is therefore a critical factor in assessing the potential environmental impacts.[18] Single and sequential extraction methods have been widely applied to characterize the

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chemical forms in which trace metals are present in soils, sediments and sludges.[19] The use of sequential extractions identifies detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals.[20] The BCR method is widely applied to fractionation studies of soil and sediment heavy metals, and a certified reference material for a three-step sequential extraction schemes are prepared by Standards Measurements and Testing.[21]

As an important drinking water source, Qingshan Reservoir is located in the junction of Hangzhou-Jiaxin-Huzhou Plain and the western mountainous area in Zhejiang Province, East of China. It is the trunk of Dongtiao River and the downstream of Nantiao River. This lake is a large comprehensive reservoir mainly for flood control and also the important back-up water source for Hangzhou. In recent years, with the rapid economic development of the basins areas, Qingshan Reservoir watershed faces increasing discharge load into the tributaries from municipal domestic sewage, industrial wastewater, and agricultural non-point source pollution.[22] These pollutions have resulted in the constant deterioration of the water quality in the lake and greatly threaten the drinking water safety of local residents. At present, contamination status and ecological risk of heavy metals in the sediments of Qingshan Reservoir has been rarely reported. In the present study, the sediments sampled from different estuaries of the major tributaries into the Qingshan Reservoir were firstly analyzed for total amount and different species of heavy metals such as acid soluble, easily reducible, easily oxidizable, and residual fractions. Ecological risks of surface sediment heavy metals pollution were also assessed using geoaccumulation index ($I_{geo}$) and Hakanson potential ecological risk index ($H'$). The present research will provide basic data and scientific evidences for anthropogenic impacts on aquatic environment of the Qingshan Reservoir.

## Materials and methods

### Study site description

The study area is located in Qingshan Reservoir, one of local drinking water sources, situated in Zhejiang province (30°15′N, 119°45′E) of East China. It is built for flood protection, agricultural irrigation, aquaculture and drinking water source for Hangzhou City by intercepting Nantiao River Lake using dam. The Qingshan Reservoir has a surface area of 20.2 km² with mean depths of 25 m and a total water capacity of $2.13 \times 10^9$ m³. It has become the largest artificial reservoir and the largest flood-control and water-storage project in Hangzhou. Qingshan Reservoir has four main tributaries, namely, Shuangxiu River, Jin River, Heng River, and Ling River. The water quality of many parts of the lake has deteriorated over the recent two decades as a result of increased anthropogenic inputs. Heng River flows through the Lin'an Industrial Zone and thus gives access to a certain amount of industrial wastewater and domestic sewage. Jin River and Nantiao River flow across downtown with dense population and heavy industrialization and is affected by seriously industrial and domestic pollution, which has resulted in poor water quality in the estuary. Shuanglin River located in the North of Qingshan Reservoir flows across rural areas and receives mainly agricultural non-point source pollution. As a result, the water quality in the estuaries of the four tributaries is apparently different.[23]

### Sediment sampling and pretreatment

To investigate and verify the influences of different pollution sources to the heavy metal accumulation in the surface sediment of Qingshan Reservoir, eight representative sampling locations covering different levels of urbanization and industrialization effects were selected as show in Figure 1. S1 and S2 lied in the estuaries of Nantiao River and Jin River, respectively. S3 is situated near discharging point of effluent from the municipal wastewater treatment plant. S4 is located in the estuary of Shuanglin River and surrounded by rural areas on the north of Qingshan Reservoir. S6 and S7 were located in the estuaries of Heng River and Ling River. S5 and S8 were situated in the center of Qingshan Reservoir, while S8 is closer to the downstream than S5. In 10 November 2011, the sampling locations were positioned by global positioning system. The surface sediment samples were collected from the eight sampling sites in Qingshan Reservoir using bottom sampler with three samples from each sampling site. In total, 24 surface sediment samples were obtained. The samples collected were mixed evenly and the large stones and foreign materials were removed. Then the samples were put into polyethylene valve bags and placed in a refrigerated box. The refrigerated box was quickly brought back to the lab. Each sample was subsequently vacuum freezing-dried and finely ground (2 mm) for analysis of total amount and different fractions of heavy metals and other chemical analysis.

### Sediment samples analysis

pH value in the sediment samples was determined at a sediment and water ratio of 1:2.5 with a pH electrode (E-201-C, Shanghai Precision & Scientific Instrument Co. Ltd., China). Oxidation-reduction potential (ORP) for the surface sediments were measured in situ by the ORP depolarization automatic analyzer with a Pt electrode (FJA-6, Nanjing Chuan-Di Instrument & Equipment Co., Ltd., China). Total organic carbon (TOC) in the sediments was analyzed by means of dry combustion method by [24] with a TOC Analyzer (TOC-V$_{CPH}$, Shimadzu Scientific Instruments, Japan).
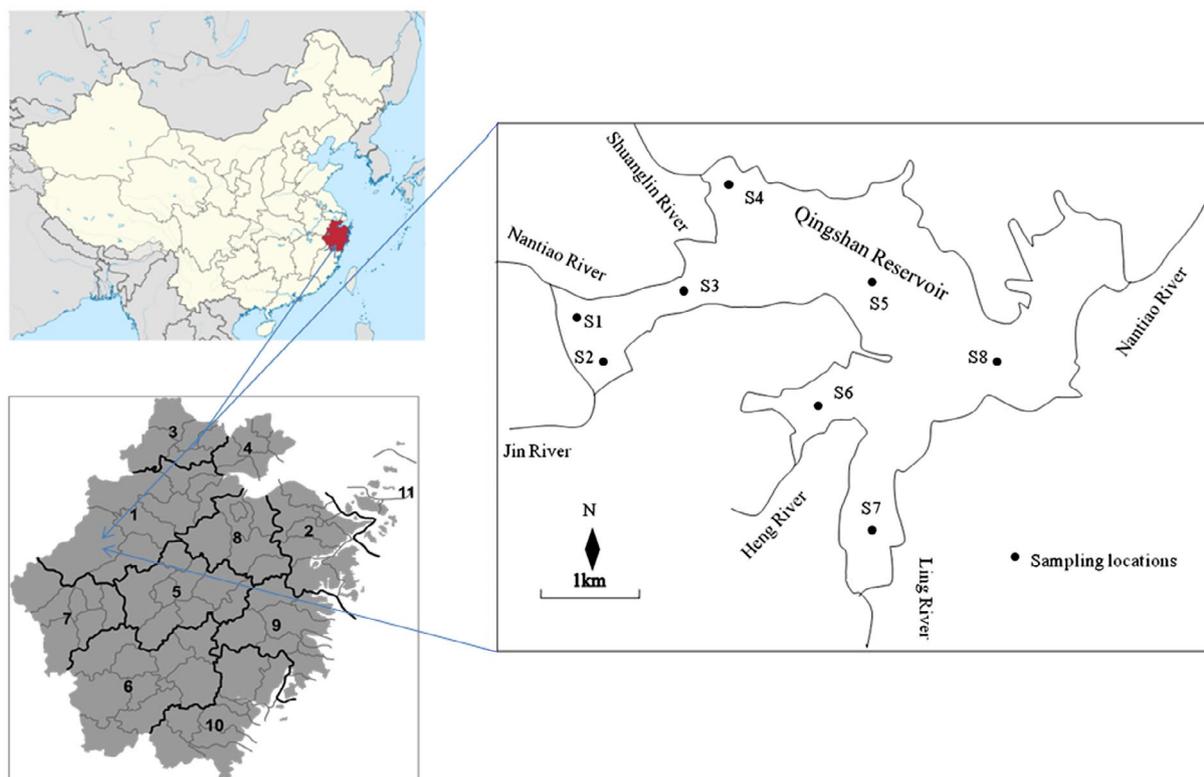
**Figure 1.** Study area and sediment sampling locations in the Qingshan Reservoir.

The total concentrations of heavy metals such as lead (Pb), zinc (Zn), nickel (Ni), arsenic (As), chromium (Cr), Manganese (Mn) and copper (Cu) were determined using inductively coupled plasma atomic emission spectrometry (ICP-OES) (Agilent 720ES), after the sediment sample was digested by an acid mixture (5 mL $HNO_3$ + 5 mL $HF$ + 3 mL $HClO_4$). Chemical fractionation of heavy metals in the sediments was conducted using BCR sequential extraction method by [21] with minor modifications. Briefly, 1 g of sediment sample was shaken for 16 h with 0.11 mol $L^{-1}$ acetic acid at 200 rpm. After shaking, solution was centrifuged at 4000 rpm for 15 min. The supernatant is regarded as exchangeable acid-and water soluble fraction. The residue was shaken for 16 h, pH 2 at 200 rpm with 0.5 mol $L^{-1}$ hydroxilammonium chloride. After shaking, solution was centrifuged at 4000 rpm for 15 min. The supernatant was regarded as reducible fraction. The residue was digested with $H_2O_2$ at room temperature, evaporated, re-digested and re-evaporated. After shaking for 16 h at 200 rpm with 1.0 mol $L^{-1}$ ammonium acetate, the solution was centrifuged at 4000 rpm for 15 min. The supernatant is considered as oxidizable fraction. The remaining residue was digested with Aqua Regia, and evaporated, re-digested, re-evaporated, and finally filtrated with blue ribbon filter paper. The supernatant was residual fraction. The solutions of the digested samples from different fractions of heavy metals were analyzed using ICP-OES.

Quality assurance and quality control were assessed using duplicates, method blanks, and standard reference materials (GBW08303, National Research Centre for Certified Reference Materials), with each batch of samples (1 blank and 1 standard for each 10 samples). The recoveries of samples spiked with standards varied, but all fell within the range from 95.7 to 102%, and the precision was under 3% RSD (relative standard deviation). The limits of detection (LOD) were: 0.230 µg $g^{-1}$ for As, 0.015 µg $g^{-1}$ for Ni, 0.542 µg $g^{-1}$ for Mn, 0.035 µg $g^{-1}$ for Cr, 0.350 µg $g^{-1}$ for Pb, 0.015 µg $g^{-1}$ for Cu, and 0.068 µg $g^{-1}$ for Zn.

### Ecological risk assessment of heavy metals

Index of geoaccumulation and potential ecological risk index are the two methods that mostly used as quantitative determination of the potential hazardous trace elements pollution and their potential ecological risk in aquatic sediment.[25,26] In this study, the two methods were also applied to assess the environmental and eco-toxicological impacts of heavy metals in the sediment samples from the estuaries of the main tributaries into the Qingshan Reservoir.

The index of geoaccumulation ($I_{geo}$) was first proposed by Müller since the late 1960s and calculated as follows [27]:

$$I_{geo} = \log_2 C_n/KB_n \tag{1}$$

where $C_n$ refers to the measured content of heavy metal $n$ in sediments, which $B_n$ represents the background concentration of heavy metal $n$. $K$ is set to be a constant

**Table 1.** Grading standard of potential ecological risk according to $E_r^i$ and H'.

| Potential ecological risk factor ($E_r^i$) | | Potential ecological risk index (H') | |
|---|---|---|---|
| Threshold range of single metals $E_r^i$ grade | | Threshold range of seven metals H' grade | |
| <40 | Low | <150 | Low |
| 40–80 | Moderate | 150–300 | Moderate |
| 80–160 | High | 300–600 | High |
| 160–320 | Very high | >600 | Very high |
| >320 | Dangerous | | |

in view of the background value fluctuation caused by diagenesis (generally $K = 1.5$). Qingshan reservoir was built by dam construction at the depression of the original mountain area. Owing to it is geographically near to Hangzhou-Jiaxing-Huzhou plain, its surface sediments show the basically same geochemical characteristics with the soil in this area. This research thereby employed the environment background values of the surface soil in Hangzhou-Jiaxing-Huzhou plain in Zhejiang province as the background concentrations of heavy metals in the sediments.[28] The background concentrations of As, Cr, Cu, Mn, Ni, Pb, and Zn are 7.59, 77.6, 30.8, 60.9, 32.4, 30.4, and 92.7 mg kg⁻¹ respectively. The heavy metal pollution was classified into seven levels according to the $I_{geo}$ value as follows: rank 1: $I_{geo} \leq 0$ practically uncontaminated, rank 2: $0 < I_{geo} \leq 1$ uncontaminated to moderately contaminated, rank 3: $1 < I_{geo} \leq 2$ moderately contaminated, rank 4: $2 < I_{geo} \leq 3$ moderately to strongly contaminated, rank 5: $3 < I_{geo} \leq 4$ strongly contaminated, rank 6: $4 < I_{geo} \leq 5$ strongly to extremely contaminated, and rank 7: $I_{geo} > 5$ extremely contaminated.

The method of potential ecological risk index was put forward by Hakanson [29]. It is designed to assess the potential ecological risk of heavy metals in sediments according to the toxicity of heavy metals and the response of the environment. Hakanson potential ecological risk index (H') was calculated by following equation:

$$H' = \sum_1^n E_r^i = \sum_1^n T_r^i \times C_f^i = \sum_1^n T_i^r \times C_s^i / C_n^i \quad (2)$$

where $E_r^i$ is the potential ecological risk of element (i), $T_i^r$ is the toxic response factor of heavy metal (i) (As,10; Cr,

2; Cu, 5; Ni, 5; Pb, 5; and Zn, 1), $C_f^i$ is the contaminative factor of element (i), $C_s^i$ is the measured concentration of heavy metal (i) in surface sediments, and $C_n^i$ represents the background value of heavy metal (i). The Grading standard of potential ecological risk according to $E_r^i$ and H' was showed as Table 1.[25,30]

## Data statistics and analysis

All analyzes were performed using three replicates. Data were subjected to ANOVA. Duncan's new multiple range test was used to assess differences between the sampling locations means. Differences in total amounts and fractions of heavy metals between the surface sediments from different samplings locations were declared as significant at the 5% level. Standard errors were calculated for mean values of all determinations. Correlations of the concentrations of total and fractions of heavy metals to sediment chemical parameters were performed by a regression analysis. All statistical analyzes were performed with SPSS version 12.0 software (SPSS Inc.).

## Results and discussion

### The major physiochemical parameters and total concentrations of heavy metal

The major physicochemical parameters and the total contents of theavy metals in the sediment samples are analyzed. As shown in Table 2, the sediment samples show relatively low pH values, but there were no significant ($p > 0.05$) differences between the eight sampling locations. The ORP varied from −89.2 to −25.6 mV, and the sediment samples from the estuaries of Nantiao River (S1) and Jin River (S2) showed significantly ($p < 0.05$) lower ORP, as compared with the other sampling locations. The TOC contents of the sediment samples range from 9.39 to 20.89 mg kg⁻¹, and the highest TOC was detected in the estuary of Jin River as affected the heavy urbanization and industrialization (Table 2). The surface sediments samples for S5 and S8 located in the center of the lake showed relatively low TOC as compared with the other sampling sites, indicating that the sources of sediment and pollution are mainly from the tributaries

**Table 2.** Physiochemical parameters and total contents of heavy metals in the surface sediments from different sampling sites.

| Sampling locations | Heavy metals (mg kg⁻¹) | | | | | | | pH (1:2.5) | ORP (mV) | TOC (mg kg⁻¹) |
|---|---|---|---|---|---|---|---|---|---|---|
| | As | Cr | Cu | Mn | Ni | Pb | Zn | | | |
| S1 | 26.52 c* | 83.92 c | 62.76 a | 1488.47 a | 47.61c | 78.49 b | 232.31 a | 4.13 a | −89.2 a | 17.44 b |
| S2 | 30.64 c | 93.46 bc | 47.08 bc | 1150.72 b | 65.17 b | 101.2 a | 205.54 a | 4.22 a | −81.2 a | 20.89 a |
| S3 | 23.25 d | 53.62 e | 44.55 c | 1173.60 b | 45.36 c | 68.99 c | 210.81 a | 4.08 a | −53.1 b | 16.74 b |
| S4 | 19.75 d | 50.83 e | 44.28 c | 868.48 c | 34.34 d | 29.34 d | 156.06 b | 4.11 a | −37.9 c | 12.20 c |
| S5 | 26.45c | 60.24 d | 33.39 d | 753.01 d | 31.06 d | 27.39 d | 150.74 b | 4.09 a | −31.4 d | 10.85 d |
| S6 | 43.60 a | 120.89 a | 61.67 a | 1043.33 b | 75.30 a | 82.12 b | 211.23 a | 4.13 a | −59.4 b | 16.90 b |
| S7 | 38.79 b | 96.98 b | 54.55 b | 1017.35 b | 61.89 b | 75.22 b | 178.76 b | 4.08 a | −49.6 b | 13.41 c |
| S8 | 11.44 e | 43.37f | 29.27 d | 616.85 e | 28.23 d | 23.42 d | 125.44 c | 4.09 a | −25.6 d | 9.39 d |

*Values represent means for three replicates. In each column, values followed by different letters are significantly different at $p < 0.05$ by a Duncan's multiple range test.

of the Qingshan Reservoir. The sampling location S3 had significantly ($p < 0.05$) higher TOC than S5 and S8, which may attribute to the effluent discharge from the municipal wastewater treatment plant.[31]

The surface sediment samples showed significant ($p < 0.05$) differences in the total heavy metal contents between different sampling locations (Table 2). The sediments from sampling sites S1 and S2 have significantly ($p < 0.05$) higher total average contents of heavy metal than those from the sampling locations S5 and S6, indicating that densely-populated downtowns and rapid urbanization may greatly contribute to the discharge of heavy metals into Qingshan Reservoir. In addition, the sediments from the sampling sites S6 and S7 also suffered severe heavy metal pollution (Table 2). Especially, the sediment for S6 showed the highest total concentrations of As, Cr and Ni among the eight sampling locations. Since S6 is located in the estuary of Heng River that flows through Lin'an Industrial Zone, it can be proved that the heavily industrial development has been resulted in the serious heavy metal pollution in the sediments of Qingshan Reservoir to some extent. Similar results also showed that urbanization and industrialization with improper environmental planning may be related to the increasing heavy metals contamination in aquatic environments.[32,33] Xiao et al. found a "hot area" of heavy metal pollution being observed in the upper and middle reaches of the urban river area.[34] Our present results verified that the heavy metals and Arsenic in the sediment of Qingshan Reservoir exhibit obvious spatial heterogeneity, which can be a good indicator of the pollution load and economic development of the Qingshan Reservoir watershed.

Organic matter (OM) could control and affect the enrichment and accumulation of heavy metals in the sediment or soil, since SOM could act as a major sink for heavy metals due to its strong complexing capacity for metallic contaminants.[35] Correlation analysis also showed that there existed significant ($p < 0.05$) relationship between average total concentrations of heavy metals and TOC in the sediment samples, although the correlations of individual element accumulation to TOC did not displayed the consistence (data not listed).

### The distribution characteristics of heavy metal fractions in sediment

Figure 2 described the proportions of acid extractable fraction, reducible fraction, easily oxidizable fraction, and residual fractions of the total As, Cr, Cu, Pb, and Ni in the 24 sediment samples respectively. The sum of the extracted four fractions agrees to within 10% with the independently determined total metal concentrations, supporting the overall accuracy of the extraction procedure. In the sediment samples from different sites, arsenic (As) mainly existed in residual fraction, with a proportion of 66.8–75.8% in the total As, while the proportions of the other three fractions of As are lower than 35%. The residue fraction is very stable and nearly nontoxic and it is difficult to be transformed for this fraction. [13,14] Present results suggest the weak migration and release potential of As. Due to high As concentration for S6 and S7, however, As still exhibited certain potentially biological toxicity and high mobility,[36,37] especially in the sediments with low pH and ORP (Table 2). The residual fraction of Cr accounts for 39.15–83.47% of the total contents, while the proportions of the acid extractable fraction Cr is relatively low. Cu and Pb were mainly in reducible fraction and the proportions of this fraction in total contents ranged from 55.61 to 77.50% and 74.61 to 85.34% respectively. Mn in the sediment showed the highest amount as acid extractable fraction despite the sampling location, with a proportion range as high as 56.39–69.37%, which reveals that Mn had higher bioavailability and migration ability in the aquatic system. [21,37]

Different sampling locations showed significant ($p < 0.05$) differences in the distribution characteristics of heavy metal fractions in the sediments, especially for As, Cr, Cu and Ni (Figure 2). The acid extractable and reducible fractions of the four heavy metals showed the higher proportions of the total contents for sampling location S6 and S7. The acid extractable and reducible fractions of the four heavy metals are regarded as the most mobile and bioavailable and easily release from the sediment to water body,[38,39] which will influence the aquatic organism health and drinking water safety. When a soil or sediment was under reducing conditions, heavy metals, i.e. Cu and Zn, were transformed from the non-available forms and potentially available forms into the available and readily available forms, increasing their mobility, availability or toxicity.[40] Relatively low pH and ORP (Table 2) in the sediments from Qingshan Reservoir may greatly contribute to high proportions of bioavailable fractions such as acid extractable and reducible fractions in the total heavy metal elements. The above results can imply that the sediments for the two sediment samples from the estuaries of tributaries affected by the heavy industrialization suffered with heavy manmade pollution and high potentially ecological hazard. [41] The sediment samples for S5 and S8 had significantly ($p < 0.05$) higher proportions of residual fraction heavy metals, especially for Cu, Cr, and Ni, as compared with the sampling locations of the major tributaries, indicating that the sediments from the center of Qingshan Reservoir show slight anthropogenic pollution sources.

### Potential ecological risk assessment of heavy metals in the sediments

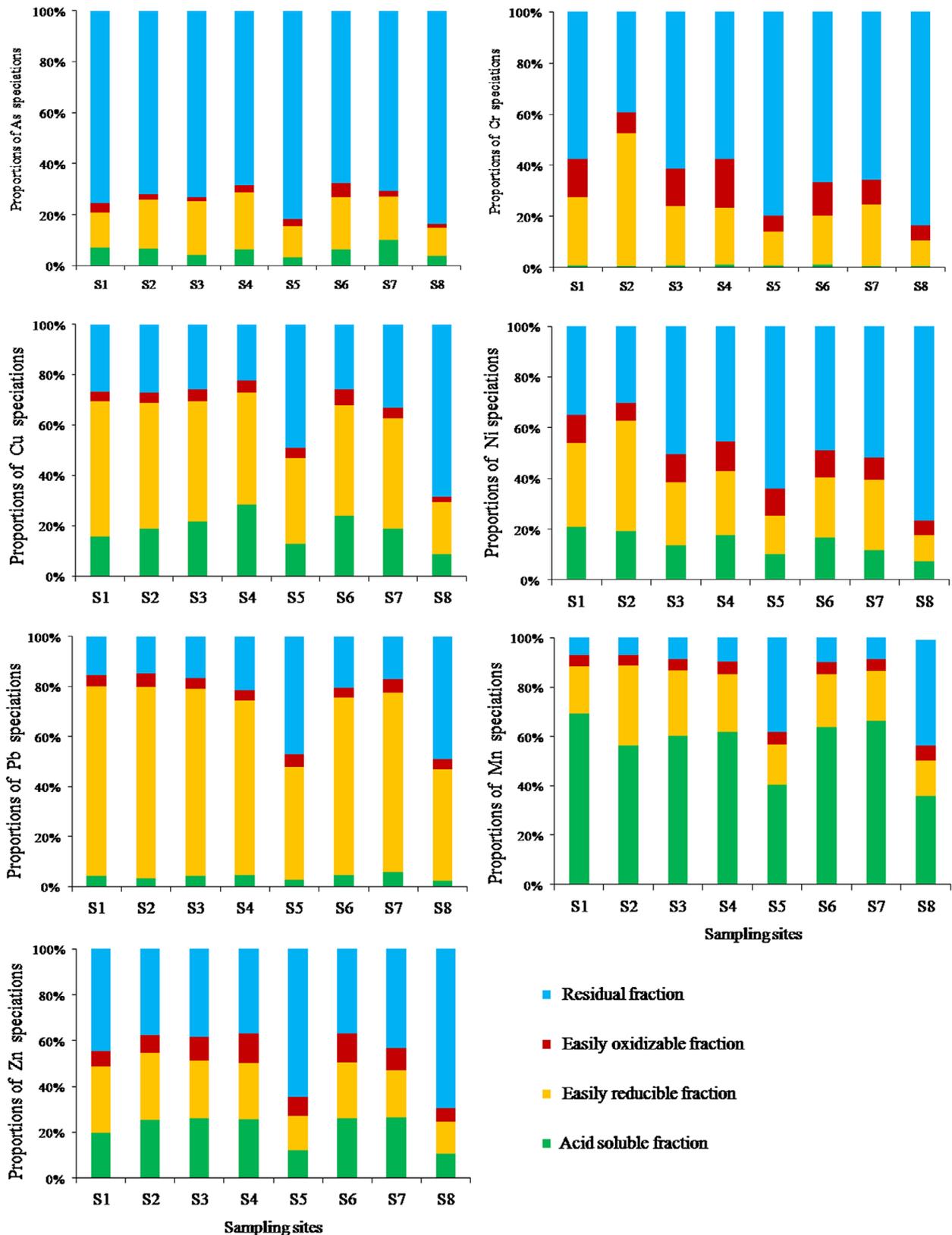Possible enrichment and accumulation of heavy metals and As in the surface sediments was evaluated using

**Figure 2.** Distribution of heavy metal fractions in the surface sediments of the Qingshan Reservoir.

geoaccumulation indices ($I_{geo}$).[27] The $I_{geo}$ values and pollution ranks of heavy metals at each sampling site were displayed in Table 3. The results indicated that the surface sediments of Qingshan reservoir suffered from heavy metal pollution to a varying extent, except for the sampling site S4, S5, and S8, which showed practically uncontaminated level. The sampling site S6 showed significantly ($p < 0.05$) higher heavy metal pollution ranks, as compared with the other sampling locations. Especially, the pollution ranks for As, Ni, Pb, and Cu belonged to a moderate level with the $I_{geo}$ values of 1.43, 1.27, 1.03, and 1.01, respectively. Ni for S7 also showed

**Table 3.** Geoaccumulation index ($I_{geo}$) and its classification of heavy metals in the surface sediments of the Qingshan Reservoir.

| Sampling sites | Geoaccumulation index ($I_{geo}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | As | Cr | Cu | Mn | Ni | Pb | Zn |
| S1 | −0.12 (1) c* | −0.48 (1) a | 0.43 (2) c | 0.16 (2) c | 0.45 (2) b | 0.78 (2) c | 0.12 (2) b |
| S2 | −0.14 (1) c | −0.48 (1) a | 0.46 (2) c | 0.33 (2) b | 0.62 (2) b | 1.53 (3) a | 0.14 (2) b |
| S3 | −0.12 (1) c | −0.73 (1) b | 0.04 (2) d | 0.01 (2) d | 0.23 (2) c | 0.30 (2) d | 0.07 (2) c |
| S4 | −0.34 (1) d | −0.74 (1) b | −0.05 (1) e | −0.19 (1) f | −0.13 (1) d | 0.42 (2) d | −0.05 (1) d |
| S5 | −0.38 (1) d | −1.03 (1) c | −0.36 (1) f | −0.07 (1) e | −0.33 (1) e | −0.17 (1) e | −0.17 (1) e |
| S6 | 1.43 (3) a | −0.32 (1) a | 1.01 (3) a | 0.70 (1) a | 1.27 (3) a | 1.03 (3) b | 0.27 (2) a |
| S7 | 0.87 (2) b | −0.47 (1) a | 0.50 (2) b | 0.36 (1) b | 1.18 (3) a | 0.83 (2) c | 0.22 (2) a |
| S8 | −1.02 (1) e | −1.20 (1) c | −0.45 (1) f | −0.10 (1) e | −0.39 (1) e | −0.24 (1) e | −0.24 (1) e |

*Values represent means or three replicates. Data in the parentheses show the pollution ranks. In each column, values followed by different letters are significantly different at $p < 0.05$ by a Duncan's multiple range test.

**Table 4.** Potential ecological risk index of heavy metals in the sediments from eight sampling sites in the Qingshan Reservoir.

| Sampling sites | $E_r^i$ | | | | | | | $H'$ |
|---|---|---|---|---|---|---|---|---|
| | As | Cr | Cu | Mn | Ni | Pb | Zn | |
| S1 | 31.25 cd* | 12.65 b | 17.72 c | 7.89 b | 14.06 c | 28.63 c | 2.27 a | 155.6 d |
| S2 | 35.94 c | 13.12 b | 20.29 c | 9.44 b | 17.35 c | 52.3 a | 2.51 a | 187.2 c |
| S3 | 30.63 cd | 8.56 c | 12.58 d | 6.93 b | 7.00 d | 21.08 d | 1.95 ab | 136.3 d |
| S4 | 21.17 e | 8.13 c | 10.11 d | 7.71 b | 6.06 d | 13.62 e | 1.68 b | 113.5 ef |
| S5 | 15.08 f | 6.12 d | 15.13 c | 3.51 c | 7.44 d | 8.46 f | 1.63 b | 123.6 e |
| S6 | 64.27 a | 18.61 a | 41.21 a | 25.43 a | 44.68 a | 40.83 b | 2.97 a | 445.8 a |
| S7 | 40.37 b | 16.76 a | 29.83 b | 22.67 a | 35.92 b | 31.14 c | 2.22 a | 235.7 b |
| S8 | 14.84 f | 5.86 d | 5.47 e | 2.40 c | 5.87 d | 12.73 e | 1.50 b | 97.23 f |

*Values represent means for three replicates. In each column, values followed by different letters are significantly different at $p < 0.05$ by a Duncan's multiple range test.

an approximately moderately-polluted level. The above results indicated that urbanization and industrialization have result a marked geoaccumulation of As and Ni in the surface sediment. For the sampling site S2, only the pollution rank of Pb in the sediment fell in a moderately-contaminated classification. The index of geoaccumulation ($I_{geo}$) for Cr was all negative despite the sampling locations, suggesting that the eight sampling sites have not been significantly ($p < 0.05$) contaminated by the heavy metal.[42]

Potential ecological risk assessment was applied to detect the potential ecological risk level of heavy metals in the sediments from the Qingshan Reservoir. The results of ecological factor ($E_r^i$) for individual element and comprehensive potential ecological risk index ($H'$) of the investigated heavy metals in the sediments samples were presented in Table 4. The $E_r^i$ values for Cr, Mn, and Zn in the surface sediment samples were lower than 40, despite the sampling locations, indicating that those heavy metals caused low potential ecological risks for the Qingshan reservoir. As and Ni had the highest $E_r^i$ values for S6, indicating the sampling site was at very high ecological risk degree. In addition, Pb may cause moderate ecological risk degree for S2 with the $E_r^i$ value > 40 (Table 4). From the viewpoint of pollution level in every sampling site, S3, S4, S5, and S8 were at low ecological risk with the potential ecological risk index ($H'$) below 150. S6 displayed the significantly higher comprehensive potential ecological risk with $H'$ value of 445.8, which was significantly ($p < 0.05$) higher as compared with the other sampling sites. Risk index ($H'$)

could characterize sensitivity of local ecosystem to the toxic metals and represent ecological risk resulted from the overall contamination.[30] Our present results also indicated that the potential ecological risk assessment could well reflect the impact of the degree of industrialization and urbanization on pollution load into the Qingshan Reservoir.

## Conclusions

There displayed distinct spatial distribution patterns of the total concentrations of heavy metals in the surface sediments in Qingshan reservoir. As a whole, the sampling sites from the estuaries of tributary flowing through downtowns and heavy industrial parks showed significantly ($p < 0.05$) higher concentrations of heavy metals in the surface sediments, as compared to the other sampling sites. The present results indicated that the industrialization and urbanization were important driving factors leading to accumulation and enrichment of heavy metals in surface sediments of Qingshan reservoir. The fractionation analysis results suggested that the contents and proportions of acid extractable and easily reducible fractions of Cu, Mn, and Pb were high for the sampling sites with high total concentration of heavy metal contents, especially in the sediments with relatively low pH and ORP, which may pose a severe threat to the aquatic organism and the drinking water safety. The ecological risk assessment of heavy metals indicated that the surface sediments from the estuaries of the tributaries flowing downtowns and heavy

industrial parks showed high heavy metal pollution levels and potential ecological risk, especially for As and Pb. Based on these results, pollution control of heavy metal such as discharge reduction and advanced treatment of industrial wastewater and municipal sewage should be strengthened to decrease the further enrichment and accumulation of these heavy metals in the sediment and relieve the ecological risk to aquatic ecosystem and human being health in the Qingshan Reservoir watershed. Further monitoring and supervising schemes that focus on sediment and water contamination from heavy metals especially As, Pb and Ni are necessary and exigent for local government authorities.

## Acknowledgment

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

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