Distribution and Assessment of Heavy Metals in the Overlying Water-Sediment-Plant-Fish System in the Wuliangsuhai Lake by Using Inductively Coupled Plasma Mass Spectrometry

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Abstract　Heavy metal (HM) contamination has become a widespread global problem and posed threat to the aquatic environment due to their toxicity，persistence and bioenrichment in the food chain. In this study，overlying water，sediment，*Potamogeton pectinatus L.* (*P. pectinatus*)，*Phragmites australis* (*P. australis*)，and four types of fish in Wuliangsuhai Lake，China，were analyzed for HMs. The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine the contents of HMs in collected samples in order to investigate their spatial distribution，enrichment characteristic，risk assessment and the possible sources. The results showed that：(1) The mean levels of Cr，Ni，Cu，Mn，Pb and Zn mainly followed an order of sediment ＞*P. pectinatus* (submerged plants)＞*P. australis* (emergent plants)＞fishes＞overlying water，but for As，the concentration in overlying water was higher than that in *P. australis* and fishes. The content of Cd，in *P. australis* was almost 50 times higher than that in normal plants and in fish was 3.3 times higher than the permissible threshold standards in China，leading to potential hazards to fish and human health via food chain bioaccumulation. (2) In sediment As and Cd experienced moderately severe enrichment. For *P. pectinatus*，the higher bioconcentration factor (BCF) and the lower biota-sediment accumulation factor (BASF) indicated that this species was more likely to accumulate HMs from overlying water and could remove HMs from Wuliangsuhai Lake as a hyperaccumulator. (3) In sediment，the E_i^r and R_I values suggested that Cd posed a considerable high ecological risk and a very high risk to the surroundings. Because of the high HM contamination levels in the northwest part of the lake，the inlet and outlet of the lake were identified as priority regions for metal pollution monitoring and management. (4) The results of source identification indicated that Zn and Cd were derived from mining and industrial wastewater，while As was related to nonpoint source pollution from agriculture. These results will provide important information for improving the aquatic environment，minimizing the potential risks posed by the HMs pollution in Wuliangsuhai Lake and managing the water quality of the Yellow River.

Keywords　Heavy metals；Enrichment factors；Risk assessment；The Wuliangsuhai Lake；Inductively coupled

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Introduction

Heavy metal（HM）contamination of lake systems has been considered as a long recognized and persistent environmental problem and posed a large threat to environmental quality and human health[1]. Sediments act not only as a major sink of HMs in aquatic ecosystems but also as a secondary pollution source impacting the water quality when the physical and chemical properties of the water change[2]. Anthropogenic HMs in sediments have been considered to have higher mobility，bioavailability and adverse effects compared with metals of natural origin[3]. Aquatic plants are considered as natural sinks for metals because they can adsorb and accumulate large amounts of metals from sediments and water[4]. Therefore，there has been increasing interest in the study of metal-accumulating plants as phytoremediators[5]，which were harvested and disposed to prevent recycling of accumulated metals when the plants decomposed[4]. Fish are often used as the most suitable bioindicator to investigate ecological environments and potential health risks via dietary exposure since they occupy a high trophic level[1].

Wuliangsuhai Lake is located at the end of the Hetao region near the plain in northern Inner Mongolia，China，and is the largest freshwater lake in the Yellow River basin and a typical macrophytic lake in a cold and arid region. In recent years，Wuliangsuhai Lake has suffered from multiple types of pollution from farmland irrigation，industrial sewage，papermaking facilities，metal smelting activities，small fertilizer plants and municipal wastewater，etc.，resulting in frequent pollution incidents and affecting the Yellow River water quality[6]. In particular，with the superfluous growth of *P. pectinatus* and *P. australis*，Wuliangsuhai Lake has evolved into a macrophytic lake suffering from severe eutrophication. To date in Wuliangsuhai Lake，researches have primarily focused on analyzing eutrophication[7] rather than the heavy metal transmission in the overlying water-sediment-plant-fish system，which is essential to understand HM geochemical cycling. Based on the discussion above，the goals of our study are（1）to investigate the distribution of HMs in the overlying water，sediments，plants（*P. pectinatus* and *P. australis*）and fishes（crucian，carp，catfish and mullet）in Wuliangsuhai Lake；（2）to determine the potential ecological risk of HMs；and（3）to identify the contributing sources of HMs in sediment samples with multivariate statistical methods.

1　Materials and methods

1.1　Sample collection and analysis

In October 2016，samples were collected from 19 different sites in Wuliangsuhai Lake：S1-S17，A and Z from the overlying water（the inlet and outlet of the lake，respectively）

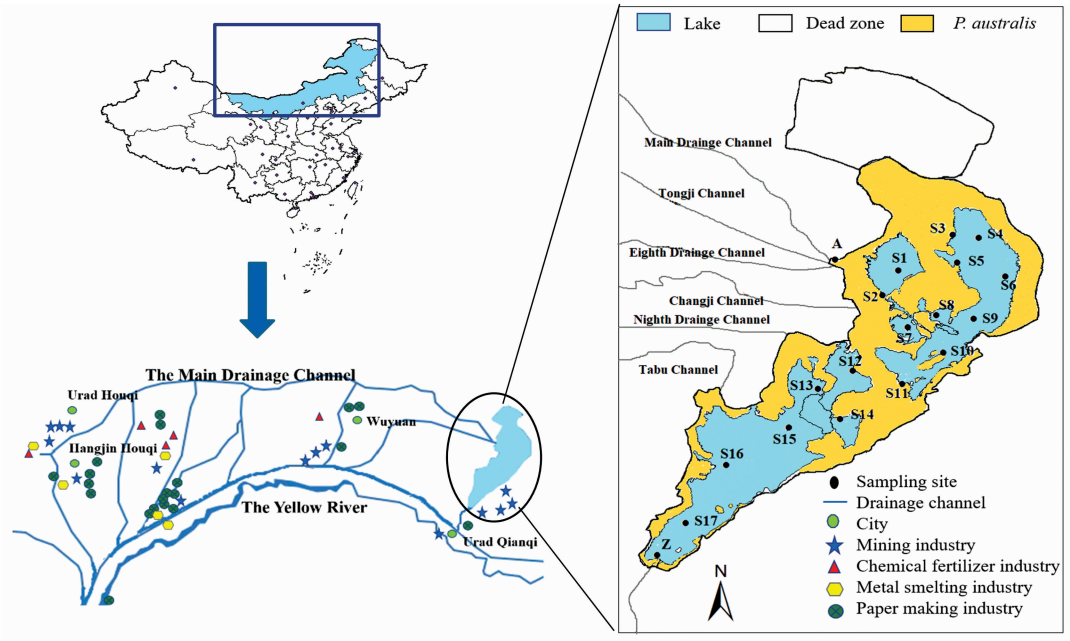


Fig. 1　Map of Wuliangsuhai Lake and the sampling locations

The data sets of Chinese Map and Wuliangsuhai Lake are provided by Data Center for Resources and Environmental Sciences，Chinese Academy of Sciences（http://www.resdc.cn）；the date set of Hetao irrigation system was cited from Liu et al.[6] and modified by Photoshop

(Fig. 1). Seventeen sediments (S1—S17) were also gathered by a gravity corer. Ten *P. pectinatus* (S1, S4—S10, S13, and S17) and 8 *P. australis* samples (S2, S3, S7—S10, S15, and S16) were acquired from where they were growing. 43 freshly caught lake fish ($n=10\sim15$ individuals per species) were purchased from the fishermen of Wuliangsuhai Lake fishery, in which four species of fish were crucian, carp, catfish and mullet highly consumed by local residents.

The collected plant, sediment and fish samples were digested with HNO_3-H_2O_2 (guaranteed reagent, GR), HNO_3-H_2O_2-HF (GR) and HNO_3 (GR), respectively. Then, the heavy metals concentrations were measured by using inductively coupled plasma mass (ICP-MS) spectrometry (Agilent Technologies, USA), and the operating parameters were listed in Table 1.

Table 1 Operating parameters of ICP-MS

Parameters	Numerical Value
RF power/W	1 550
Nebulizer gas flow/($L\cdot min^{-1}$)	0.9(0.6～1.0)
Auxiliary gas flow/($L\cdot min^{-1}$)	0.25(0.3～1.0)
Sampling depth/mm	8(7～10)
Peristaltic pump speed/(rps)	0.1(0.1～0.3)
Sample cone/mm	1.0
Skimmer cone/mm	0.7

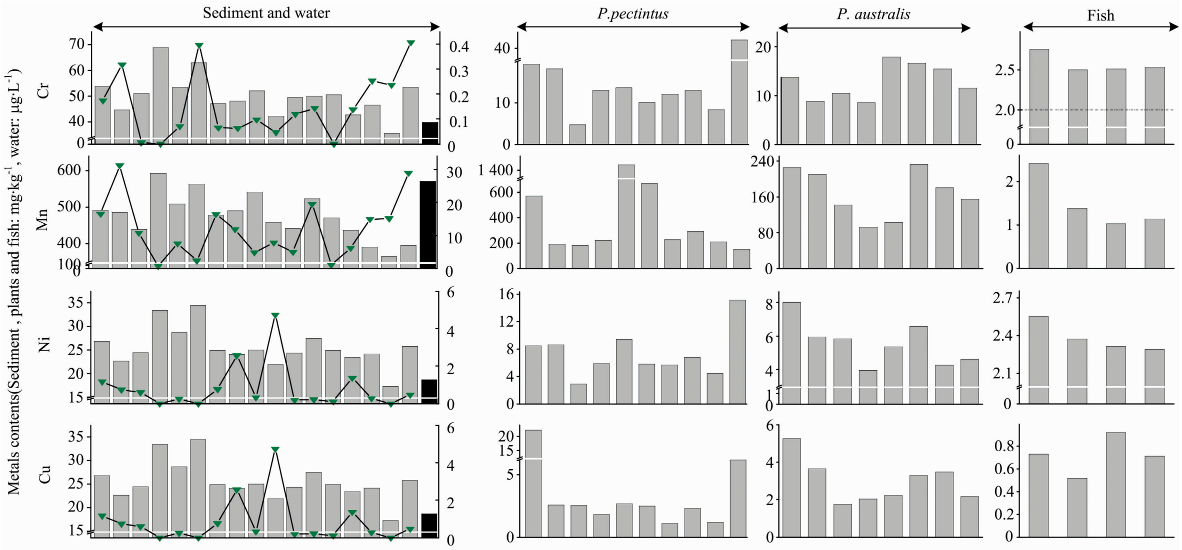
1.2 Data analysis method

The enrichment factor (EF), bioconcentration factor (BCF) and the biota-sediment accumulation factor (BASF) were used to determine the enrichment characteristics of the HMs, which were referenced from Ref. [8] and [9]. In sediment, the potential ecological risk index (R_I) was used to evaluate the potential ecological risk of metal contaminants. The R_I grading standard was modified by using the weighted average method[10]. Data analysis was performed using the SPSS 22.0 software package for Windows. Principal component analysis (PCA) was used to determine the relationship among HMs in sediments and their possible sources. The spatial distribution patterns of the R_I value at each site were obtained by using geostatistical analysis in geographic information system (GIS) software (Arc GIS, version 10.2)

2 Results and discussion

2.1 The concentration distributions of HMs in overlying water-sediment-plant-fish

In this study, the mean levels of Cr, Ni, Cu, Mn, Pb and Zn mainly followed an order of sediment > *P. pectinatus* (submerged plants) > *P. australis* (emergent plants) > fishes > overlying water (Fig. 2), but we found that the concentration distribution of As in overlying water was higher than that in *P. australis* and fishes possibly because As and P are cognate elements with similar physical and chemical properties and that P from agricultural runoff competed with As for adsorption points on the oxide surfaces of solid-liquid interfaces, causing As to desorb and ultimately drain into the channel[6]. Additionally, it was interesting that the order of the Cd content—*P. australis* > fishes > *P. pectinatus* > sediment (Cd was not detected in the overlying water)—was different from that of the other elements, and the content of Cd in *P. australis* was almost 50 times higher than that in normal plants (0.05 to 0.2 mg kg^{-1} [5]); in four types of fish, Cd was 3.3 times higher than the permissible threshold standards in China, leading to inhibition of plant growth, excessive accumulation of Cd in plants, and potential hazards to fish and human health via food chain bioaccumulation[11].



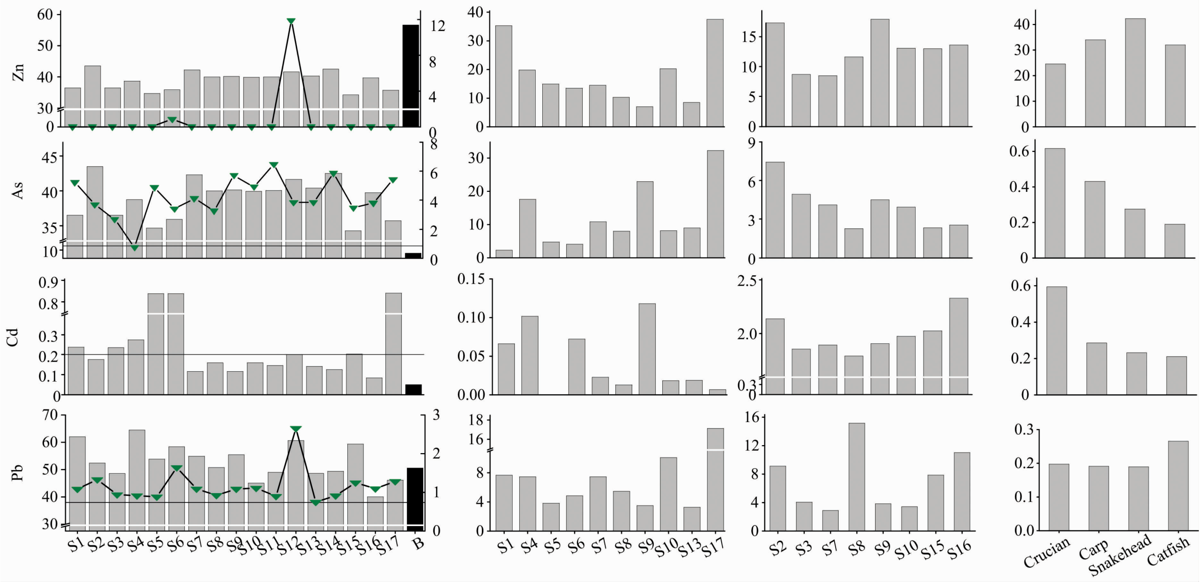


Fig. 2　HM contents in overlying water-sediment-plant-fish in Wuliangsuhai Lake

Water contents ($\mu g \cdot L^{-1}$) were shown in a line graph; contents ($mg \cdot kg^{-1}$) in sediment, *P. pectinatus*, *P. australis* and fish were shown in a bar graph; and their respective Chinese national quality values (solid lines) are shown for the collected samples

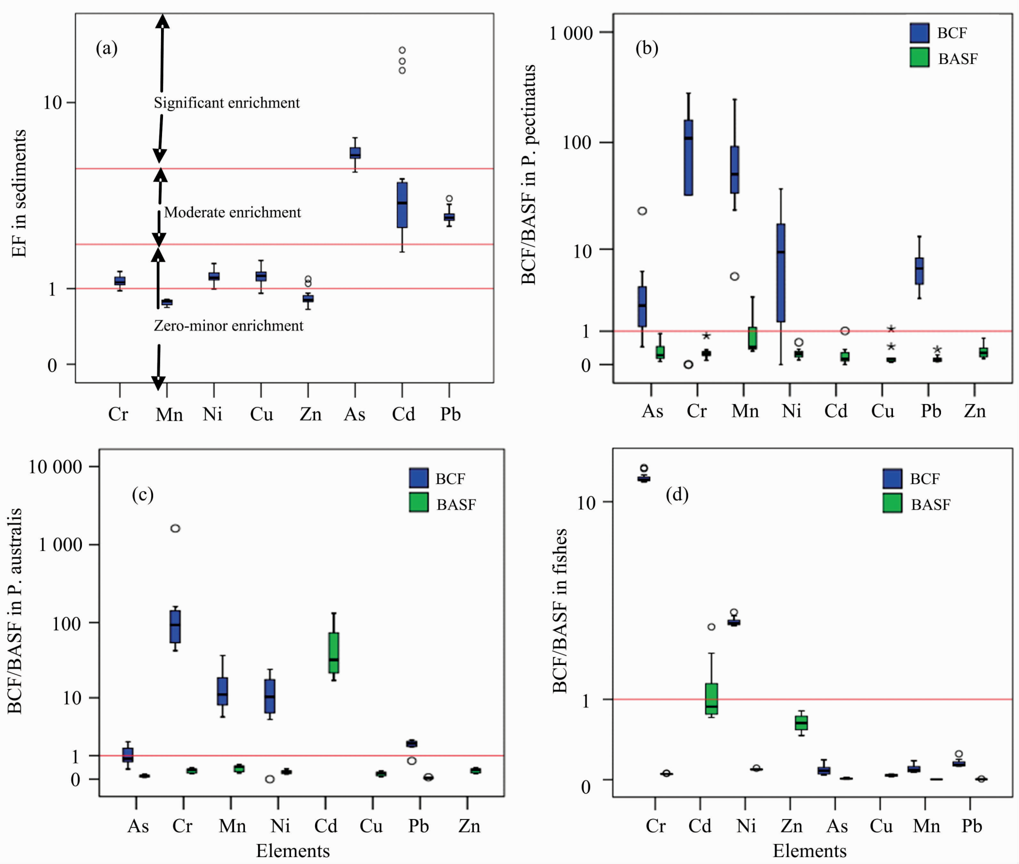


Fig. 3　Box-Whisker plots of the EFs in surface sediments and BCF/BASF in plants and fishes

(a): EFs in sediment; (b): BCFs/BASFs in *P. pectinatus*; (c): BCFs/BASFs in *P. australis*; (d): BCFs/BASFs in fish. The box shows the 25th and 75th percentiles, and the whiskers represent the smallest and the largest values. The red line represents the values of 2 and 5, the dotted line shows EF=1 in Fig. 3(a), and the red lines stand for a value of 1 in Fig. 3(b)—(d)

According to the EF grading criteria, As and Cd experienced moderately severe enrichment and might originate from industrial and agricultural nonpoint source pollution [Fig. 3(a)]. Based on the BCF and BASF, we found that in *P. pectinatus* and *P. australis* [Fig. 3(b), (c)], the BCF of all metals was greater than 1, but the BASFs were lower than 1, except Cd, demonstrating that *P. pectinatus* was more likely to accumulate HMs from overlying water because its leaf surface had a special porous structure that increased the area available for adsorption and promotes the adsorption of metal ions[11]. Finally, in the crucian, carp, catfish and mullet, the BCFs and BASFs were almost less than 1 (except for the BCFs of Cr and Ni and the BASF of Cd) [Fig. 3(d)]. These results indicated that these fish species tended to restrict their uptake of metals from water and sediments to guarantee their growth; however, the bioaccumulation level of metals in fish might not cause any adverse effects in the fish itself but might pose a hazard to their predators, such as piscivorous birds, mammals and human[1].

2.2 Risk analyses in the overlying water-sediment-plant-fish system

The contents of As, Cd and Pb in sediments were 6.4, 5.8 and 3.1 times higher than the soil background values and exceeded the standard limits of 100%, 18% and 18% at all sites (Fig. 2), respectively, demonstrating that they could affect lake sediment quality.

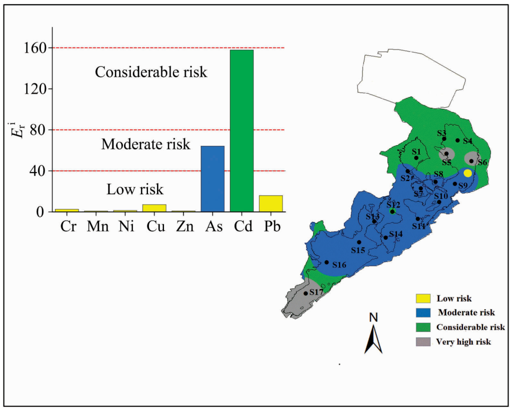


Fig. 4 Evaluation on potential ecological risk of HM pollution in sediments of the Wuliangsuhai Lake

Based on the ecological risk grades of a single metal, the E_r^i values of the sediment at S6 were higher than those at the other sites, indicating higher HM pollution (Fig. 4). In all sediments, because the E_r^i values were lower than 40, Cr, Mn, Ni, Cu, Pb and Zn posed low ecological risk. However, moderate risks posed by As were found in all sediments. At S5, S6 and S17, Cd showed rather higher E_r^i values (>500), indicating very high ecological risk. However, in other sediments, Cd posed considerable risk. R_I represents the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk posed by HMs[9]. The results showed that the R_I values at all sites were higher than 105, indicating moderate to considerable ecological risk. Furthermore, the sediment at S6 posed the highest risk compared with the sediments at the other sites. The areas with higher potential ecological risks posed by HMs were mainly distributed in the northwest and southwest areas of the lake (Fig. 4), but the eastern area of the lake had low risk, which was mainly caused by natural conditions and human activities.

2.3 Source identification for HMs in the overlying water-sediment-plant-fish system

The results of principal component analysis (PCA) revealed that there were three principal components (PCs) for the sediment samples, with an explanation of 86.33% (PC1 30.3%; PC2 27.17%; PC3 25.94%) of the total variance (Fig. 5). In Fig. 5(c) and (d), we found that sites S4, S6, S7 and S17 apparently had a high correlation with PC1, PC2 and PC3, indicating that the HM contents at these sites were high, which was in agreement with the R_I assessment showing a very high risk at S6 and S17. Fig. 5(a) and (b) showed that PC1 had high loadings for Pb ($r=0.97$), Cu ($r=0.818$), Mn ($r=0.781$), Ni ($r=0.76$) and Cr ($r=0.743$), which are abundant elements in nature. Clay minerals were derived from weathered rock basins and reach lake water by leaching in surface runoff, finally accumulating in sediments[6]. The sediments in Wuliangsuhai Lake were mainly formed from clay; therefore, Cu, Fe, Mn and Cr were the main components of the sediments and weathered products. The ecological risks posed by Cr, Cu and Pb were all low in this study, indicating that the impacts from human activities on these elements were small. Therefore, PC1 was mainly associated with natural weathering and deposition.

PC2 had high positive loadings for Zn ($r=0.847$), Cd ($r=0.625$), and pH ($r=0.876$), which were deemed to have primarily anthropogenic sources. We found that around Wuliangsuhai Lake, there were dozens of chemical fertilizers and mineral processing enterprises, such as the Huafeng zinc oxide operation, the Tanyaokou pyrite operation, mining plants, the Bameng Ring Farm mine, the Urals fertilizer plants, the chemical plants in Wuyuan and the fertilizer plants in Linhe (Fig. 1). These operations were located in drainage channels that empty into the lake, and industrial wastewater and municipal sewage were the main potential sources of pollution by HMs, such as Cd and Zn[12]. Therefore, PC2 in sediments was mainly an industrial sewage and waste source. In this study, the weakly alkaline conditions (pH 7.8～8.7) were unfavorable for HM release from sediments. In addition, Cd had low stability and was easily released from sediments to water with environmental changes (pH, redox potential, temperature, etc.) to become bioavailable[13]. The sources, including those of Zn and Cd, and the correlations with pH were mainly characterized by PC2.

PC3 had high positive loadings for As ($r=0.84$), organic matter (OM) ($r=0.867$), and TOC ($r=0.811$). The heavy use and low efficiency of chemical fertilizers have resulted in large amounts of phosphate residues in agricultural runoff. As mentioned above, phosphorus competes with As for adsorption to sediments; thus, phosphate in agricultural runoff will compete for the adsorption sites on oxide surfaces, causing As to desorb from oxide surfaces and ultimately drain into the channel. Huang et al. (2008)[14] showed that the average content of TP in the Hetao Irrigation District was 1.99 $mg \cdot kg^{-1}$, exceeding Grade V (0.2 $mg \cdot kg^{-1}$ in lakes) of the Surface Water Quality guidelines in China (GB 3838—2002). It was likely that an increasing amount of As in the water and soil would be released into the channel and the lake, that is, the As pollution was partly caused by agricultural nonpoint source pollution and agricultural runoff.

Overall, PC1 was the result of natural weathering and deposition, and PC2 was primarily due to anthropogenic sources, and PC3 was mostly a result of agricultural nonpoint sources.

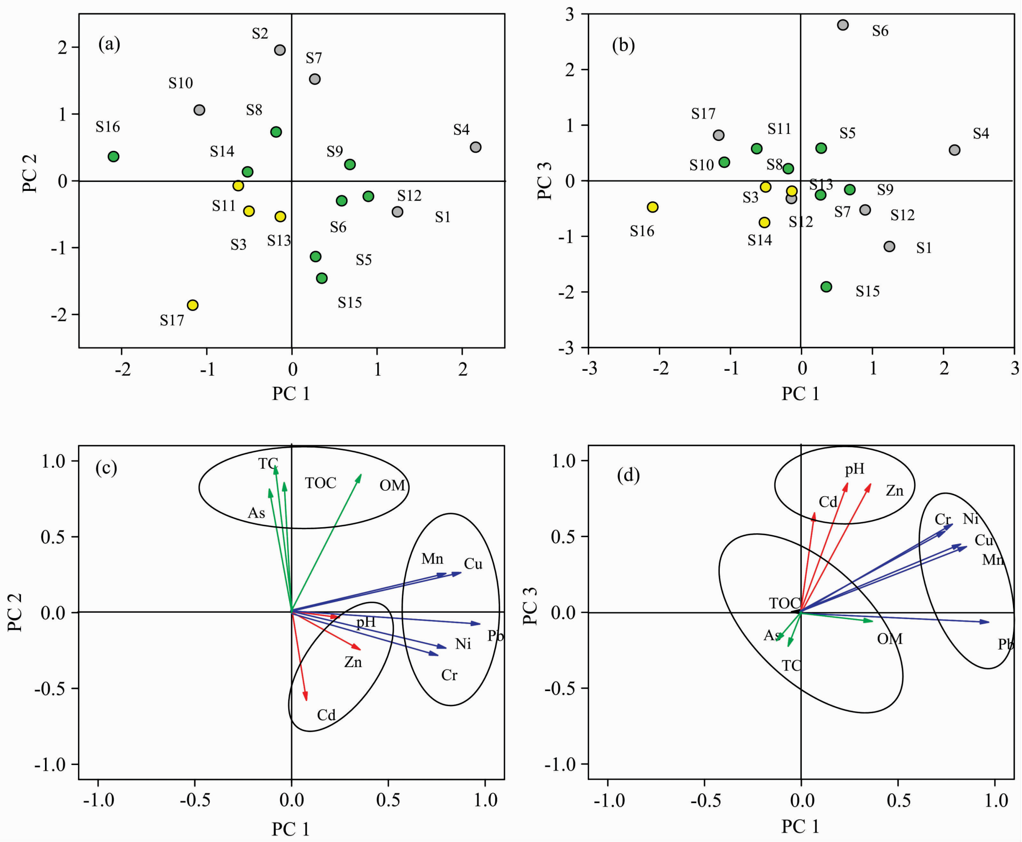


Fig. 5　Loading and score diagram from the PCA of HMs and other factors in Wuliangsuhai Lake

(a), (b): The arrows with different colors represent the variables belonging to diverse components; (c), (d): yellow, green and gray dots represent relatively lower, intermediate and relatively higher levels of scores for the sampling sites, respectively

3　Conclusions

This study remedies the insufficient amount of data on heavy metals in the overlying water-sediment-plant-fish systems. In the present study, the contents of heavy metals in sediments were higher than those in *P. pectinatus*, *P. australis*, fishes and overlying water. For *P. pectinatus*, its higher BCF and lower BASF indicated that this species was more likely to accumulate heavy metals from water and could remove HMs from Wuliangsuhai Lake as a hyperaccumulator. In sediments, the E_i^r and R_I values suggested that Cd posed a higher ecological risk than the other HMs and very high risk to the lake environment. Because of the high heavy metal contamination levels in the northwest part of the lake, the inlet and outlet of the lake were identified as priority regions for metal pollution monitoring and management. Multivariate statistical analyses showed that Zn and Cd were mainly derived from mining and industrial wastewater, while As was related to nonpoint agricultural sources. Therefore, improving the hydrological conditions and reducing industrial effluent, domestic sewage discharge, and chemical fertilizer and pesticide use are useful ways to improve the aquatic environment of Wuliangsuhai Lake and diminish the influence of farmland drainage on the Yellow River.

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电感耦合等离子体质谱法研究乌梁素海上覆水-沉积物-植物-鱼体系中重金属的分布和评价

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摘要 重金属污染已经成为全球性问题，由于其毒性、持久性和在食物链中的生物富集特点，对水生环境构成严重威胁。本研究选取乌梁素海为研究区域，采用电感耦合等离子体质谱法(ICP-MS)测定、分析了该湖泊中上覆水、沉积物、龙须眼子菜、芦苇和四种鱼类样品中重金属的含量，以探究其空间分布、富集特征、风险评估和可能的来源。结果表明：(1) Cr，Ni，Cu，Mn，Pb和Zn的平均含量大小顺序为：沉积物＞龙须眼子菜(沉水植物)＞芦苇(挺水植物)＞鱼类＞上覆水；但是上覆水中As的浓度高于芦苇和鱼类。芦苇中Cd的含量几乎是普通植物的50倍，且鱼类中Cd的含量是中国允许标准阈值的3.3倍。因此，推测Cd可能通过食物链生物累积对鱼类和人类的健康造成潜在危害。(2) 在沉积物中，As和Cd属于中度严重的富集程度。龙须眼子菜具有较高的生物富集因子(BCF)和较低的生物-沉积物积累因子(BASF)，表明该物种更有可能从上覆水中积累重金属，并可以作为超积累植物去除乌梁素海的重金属。(3) 沉积物中的 E_r^i 和 R_I 值表明，Cd具有相当高的生态风险，可能对周围环境产生高风险。由于湖泊的入口、出口处及西北部重金属污染程度较高，因此应被当作金属污染监测和管理的优先区域。(4) 重金属源解析结果表明，Zn和Cd是来自采矿和工业废水，而As与农业的面源污染有关。本研究结果可为改善水环境质量、减少重金属污染对乌梁素海和黄河水质管理带来的风险提供重要信息。

关键词 重金属；富集系数；风险评价；乌梁素海；电感耦合等离子体质谱法

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