

## Seasonal varieties and influential factors of heavy metals in sediments of Wuliangsu Hai Lake

Weidong Tian, Guoxia Pei, Shengnan Zhao, Xiaohong Shi, Hanmeng Zhang, Biao Sun, Shuang Song, Chi Sun and Hong Ma

### ABSTRACT

Wuliangsu Hai Lake, as a typical shallow lake in Hetao irrigation district, is located in Northern China. We took sediment samples in spring, summer, autumn, and winter, respectively. The total arsenic (As), total mercury (Hg) and other parameters (temperature, pH, EC, particle size of sediments and organic matter in sediments) were measured. Based on the temporal variations, seasonal comparisons and factor analysis, the following conclusions were obtained. (1) The seasonal characteristics of Hg and As were: summer > spring > autumn > winter, and spring > summer > autumn > winter. (2) The higher concentration of Hg and As during summer was considered to be caused by the higher organic matter and humus content, which made heavy metals strongly adsorbed and complexed, and changes in the organic matter content would enhance the binding state of the less active organic matter then deposit in sediment. (3) The speciation of mercury and arsenic was also the reason, in summer, the Hg<sup>0</sup> in the atmosphere was oxidized to Hg<sup>2+</sup>, entering into water through rainwater washing and dry deposition; then, soluble Hg<sup>2+</sup> was quickly adsorbed and fixed in sediment, a series of transformations reduces its activity. The As<sup>3+</sup> would be oxidized to As<sup>5+</sup> which would form precipitated. Therefore, the content of Hg and As, environmental risk and potential ecological risk of mercury in sediments were higher in summer.

**Key words** | arsenic, controlling factors, mercury, seasonal varieties, Wuliangsu Hai Lake

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### INTRODUCTION

The pollution of mercury (Hg), is receiving worldwide attention for its strong bio-toxicity, volatility and long-distance transportability (Obriest *et al.* 2017). Selin (2018) put forward in Science that the global high consistence of Hg was mostly caused by Hg left over from human behavior in the past, and its recovery would take decades to centuries, thus the Hg we emit today will become mercury pollution in the future. Then policy recommendations for global Hg pollution emissions were proposed. The Minamata Convention came into force in August 2017, and currently 128 contracting parties are committed to taking action to protect human health and the environment from anthropogenic Hg emissions and their effects. As a contracting state, China implemented a series of measures to reduce Hg pollution

(Ye *et al.* 2018). Arsenic (As) is a highly toxic element, and its pollution is characterized by durability, mobility, high biological enrichment, and strong toxicity (Joseph *et al.* 2019). As and its soluble compounds are highly toxic and have been classified as primary carcinogens by the U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) (Straif *et al.* 2009). According to the investigation by the Ministry of Environmental Protection, the heavy metal pollution rate in the sediments of rivers and lakes in China is as high as 80.1%, among which the pollution of Hg and As is particularly serious (Lu *et al.* 2017).

Wuliangsu Hai Lake (40°36'–41°03'N, 108°43'–108°57'E) is located in Urad Front Banner, Bayan Nur,

Inner Mongolia. Wuliangsu Hai is a shallow lake with a mean depth of 1–1.5 m, maximum depth of 2.5–3.0 m and a volume of  $3\text{--}4 \times 10^8 \text{ m}^3$ ; it provides food (fish and crustaceans) for people and biomass (reed) for the paper industry, and acts as an important water reservoir (Song *et al.* 2019). Local mean annual air temperature is  $7.5^\circ\text{C}$ , annual precipitation and potential evapotranspiration are around 225 mm and 2,140 mm, ([www.ntsg.umd.edu/project/modis/mod16.php](http://www.ntsg.umd.edu/project/modis/mod16.php)). Hg pollution in Wuliangsu Hai Lake is relatively severe. According to the surface water detection in 2015, the average concentration of Hg in the surface water of Wuliangsu Hai Lake was  $1.17 \mu\text{g/L}$ . The average value of Hg in the surface sediments of the whole lake was  $0.169 \text{ mg/kg}$ , which was tens to hundreds of times compared with the background value (Liu *et al.* 2017). The ratio of acid-extractable mercury in heavy metal form in the sediments of Wuliangsu Hai Lake was 8.33%, Fe-Mn oxide bound mercury was 13.89%, and organic compounds and mercury sulphides was 27.78%. Thus it had strong biological activity and potential migration ability (Ding *et al.* 2016), which could cause secondary pollution by entering the water phase through exchange between water-sediment interfaces. The content of As in the surface water of Wuliangsu Hai Lake was between 2.27 and  $11.98 \mu\text{g/L}$ , with an average of  $6.67 \mu\text{g/L}$ , and the average carcinogenic risk was  $1.27 \times 10^{-5}/\text{a}$ , far exceeding the maximum acceptable value recommended by the Swedish Environmental Protection Agency and Netherlands Ministry of Construction and Environment. The average value of As in the surface sediments of Wuliangsu Hai Lake was  $27.16 \text{ mg/kg}$ , much higher than the background value of  $9.68 \text{ mg/kg}$  (Ding *et al.* 2016). According to the standard of Critical Value of Ecological Hazard (TEL), the monitoring value of As was about 2–6 times compared with the critical value (Ding *et al.* 2016).

Research on heavy metals in rivers and lakes has been reported since the 1980s at home and abroad. It was found that there were seasonal characteristics in heavy metal content of each medium in the water environment (Salem *et al.* 2014). Wuliangsu Hai Lake is located in the cold areas of the Mengxin Plateau Lake District. It has the seasonal characteristics of long and cold winter, windy and drought spring, short and cool summer, as well as sharply cooling autumn. The seasonal characteristics of

heavy metal pollutants in the lake environment in cold and arid regions are more obvious. In addition, the research results showed that Wuliangsu Hai Lake was in a comprehensive pollution state of eutrophication, salinization and organics (Yang *et al.* 2016). In winter, the pollution of water under ice increased sharply, and the states of water before and after icing were eutrophic and heavily eutrophic respectively, which indicated that the icing process deteriorated the eutrophication of lake water. Changes in the contents of nitrogen, phosphorus and organic matter in different seasons may cause a variation in oxygen consumption rate, causing certain changes in the oxidation-reduction potential, dissolved oxygen content and pH value at the bottom of the lake. And the change of salt content has a certain influence on the adsorption and desorption of heavy metal elements in sediments.

At present, some progress has been made in the study of heavy metals in Wuliangsu Hai sediments, but most of them are based on the current situation (Lv *et al.* 2017). Wuliangsu Hai Lake has four distinct seasons. In different seasons, the external environmental conditions (including temperature, redox, acidity, and salinity) of the lake will inevitably affect the migration or transformation of heavy metals at the sediment-water interface by changing the occurrence form of heavy metals, which makes heavy metals in different seasons have a certain regularity. Therefore, it is necessary to study the seasonal changes of heavy metals in Wuliangsu Hai sediments, so as to reveal the seasonal changes of heavy metals in the sediments, which is of great significance to the control and treatment of environmental pollution in Wuliangsu Hai.

The grain size, pH value, electrical conductivity and organic matter content of Wuliangsu Hai sediments in different seasons were determined, the seasonal and spatial distribution characteristics of Hg and As contents in Wuliangsu Hai sediments were analyzed; what's more, the quality assessment and environmental risk assessment were carried out for the seasonal pollution degree, combined with the physical and chemical properties of deposition, the main factors affecting the seasonal characteristics are explored, to understand the seasonal variation of Hg and As in Wuliangsu Hai sediment more comprehensively, and to provide a scientific theoretical basis for Hg and As pollution remediation and treatment in Wuliangsu Hai and other similar lakes.

Our hypotheses were: (1) the characteristics of Hg are different in different seasons, and the same with As, probably during Summer, they are higher; (2) through making heavy metals strongly adsorbed and complexed, the larger organic matter content and higher humus content are some of the reasons; and (3) the speciation of mercury and arsenic were also reasons.

## MATERIALS AND METHODS

The 2 km × 2 km square grid was spatially set in Wuliangsu-hai, and the sample collection points were set at the intersection of the square grid, and considering the dynamic characteristics of the lake, we selected sample points from the water area. Ten sampling points were selected in the study (Figure 1), and we took the samples in July 2017 (summer), October 2017 (autumn), January 2018 (winter) and April 2018 (spring), respectively. Before sampling, water sample collectors and sample bottles were cleaned, immersed for 24 h in 10% nitric acid, and then rinsed with ultrapure water. About 30 cm sediment core was collected by a gravity column-shaped mud collector, stratified by 5 cm on the spot, and then placed in a low temperature freezer (−4 to 4 °C). The glassware used in the experiment were

immersed in 1:3 (volume ratio) nitric acid for more than 24 h, and repeatedly washed with ultrapure water (Liu *et al.* 2017).

Measurement of total amount of Hg and As: The sediment samples of 0.2–2.0 g over 100 mesh sieve were all treated with 1:1 aqua regia digestion method and measured by model atomic fluorescence spectrometer (AFS-933) and the relative standard deviation (RSD) was less than 10.0%.

Particle size of sediments: Took a proper amount of sediments over 24 mesh sieve, and conducted particle size testing with laser particle size analyzer (HELOS-RODOSM, Germany).

Organic matter in sediments: The sediment samples of 0.1–0.5 g over 100 mesh sieve were taken in the test tube, and measured using potassium dichromate – external heating method.

pH and EC of sediments were measured by SG8 portable pH meter and SG7 conductivity meter produced by Mettler Toledo, respectively.

## Statistical analysis

Based on the background value of heavy metals in Hetao Irrigation District, the pollution condition and ecological risk of heavy metals in surface sediments of Wuliangsu-hai

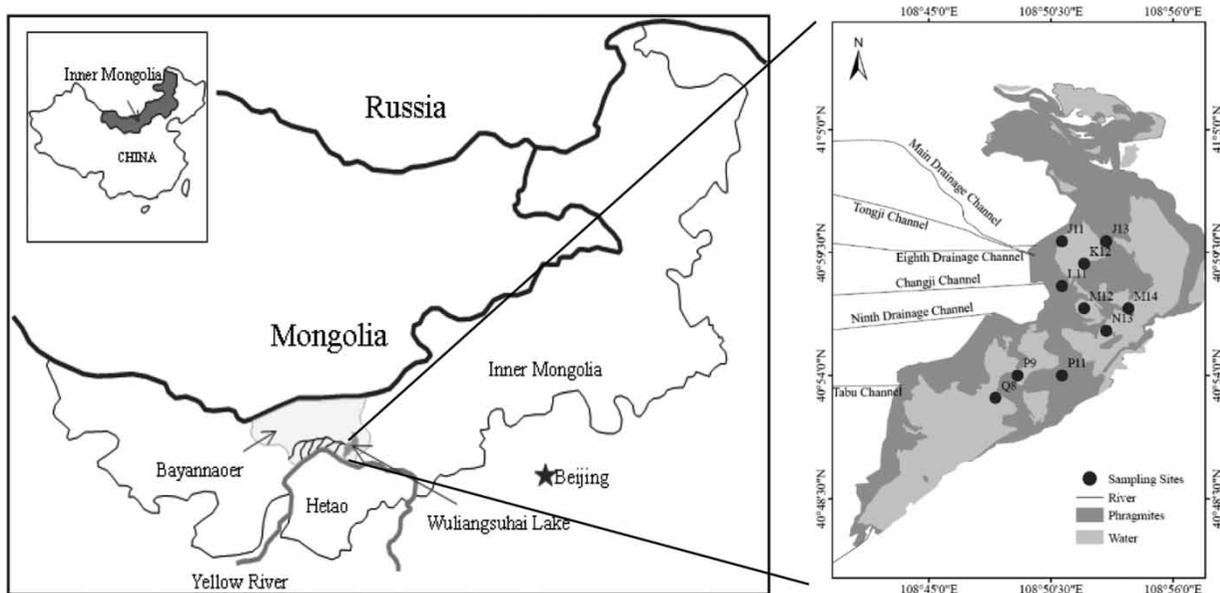


Figure 1 | Sampling sites.

**Table 1** | The assessment of geoaccumulation index, potential ecological risk index for heavy metal

Evaluation index	Formula	Parameter meaning
Geoaccumulation index	$I_{geo} = \log_2 [C_i/1.5B_i]$	$C_i$ : the measured concentration (mg/kg) $B_i$ : geochemical background value (mg/kg) 1.5, the background matrix correction factor due to lithogenic effects
Potential ecological risk index	$RI = \sum T_i \times C_i/B_i$	$C_i$ : the measured concentration (mg/kg); $B_i$ : geochemical background value (mg/kg) $T_i$ : the toxic response factor for the heavy metal The toxic response factors for common Hg, As were 40, 10 respectively

Lake were evaluated by the Geo-accumulation Index method (Muller 1979) and Potential Ecological Risk Index method (Hakanson 1980). The specific calculation methods are shown in Table 1.

Grading standard of Geo-accumulation Index:  $I_{geo} < 0$  is for no pollution,  $I_{geo} = 0$  for mild to moderate pollution,  $1 \leq I_{geo} < 2$  for moderate pollution,  $2 \leq I_{geo} < 3$  for moderate to severe pollution,  $3 \leq I_{geo} < 4$  for severe pollution,  $4 \leq I_{geo} < 5$  for severe to extremely severe pollution,  $I_{geo} \geq 5$  for extremely severe pollution. Grading standard of potential ecological risk:  $RI \leq 150$  is for mild risk,  $150 < RI \leq 300$  for moderate risk,  $300 < RI \leq 600$  for severe risk,  $600 < RI \leq 1200$  for very severe risk,  $RI > 1200$  for extremely severe risk (Hakanson 1980).

## RESULTS

### Characteristics of physical and chemical properties of sediments in Wuliangshuai Lake in different seasons

The particle size of lake sediments is mainly related to lake formation, deposition and hydrodynamic conditions. There was little difference in sediment particle compositions in Wuliangshuai Lake in different seasons, and with the same regularity: most of them were silt (mass fraction: 52.11%–57.83%), and the mass fractions of clay and sand were similar (12.91%–29.76% and 16.53%–34.98%, respectively). It could be seen that the particle size distribution of sediments in Wuliangshuai Lake was dominated by silt. In spring, the average particle size of the whole lake varied from 2.59 to 110.88  $\mu\text{m}$ , mainly at the level of very fine silt to medium silt. In summer, it ranged from 25.75 to 146.47  $\mu\text{m}$ , mainly at the level of medium silt to fine sand. In autumn, it

ranged from 30.8 to 125.92  $\mu\text{m}$ , mainly at the level of medium silt to fine sand. In winter, it varied from 27.26 to 141.07  $\mu\text{m}$ , mainly at the level of medium silt to fine sand.

The pH of sediments is a comprehensive indicator reflecting the sedimentary environment, which directly affects the morphological distribution, solubility and eco-environmental effects of heavy metals in sediments (Schroeder et al. 2019). The pH values of sediments in Wuliangshuai Lake in different seasons ranged from 7.677 to 9.69, which was weakly alkaline.

Salinity of sediments can also affect morphological distribution and bioavailability of heavy metals (Hariri & Abu-Zied 2018). The salinization status of Wuliangshuai Lake could be indirectly explained by EC: the EC of sediments in different seasons ranged from 103.6 to 3,960  $\mu\text{S}/\text{cm}$ . The average value of EC was relatively large in summer and small in spring.

Organic matter in sediments controls the ecotoxicity and environmental migration behavior of heavy metals by adsorption, complexation, etc (He et al. 2019). Organic matter in the sediments of Wuliangshuai Lake in different seasons ranged from 0.036% to 7.773% (Table 2).

### Seasonal distribution characteristics of mercury and arsenic in surface sediments of Wuliangshuai Lake

The content of Hg in the surface sediments of Wuliangshuai Lake ranged from 0.013 to 0.135 mg/kg, with an average of 0.054 mg/kg (Table 3). It was higher than the soil background value of 0.02485 mg/kg in Hetao Irrigation District, with over-standard rate reaching 80% and coefficient of variation reaching 63.2%. This showed that Wuliangshuai Lake was heavily polluted, with great variability in overall

**Table 2** | EC of sediments from Wuliangsu Hai Lake

	Summer	Autumn	Winter	Spring
Organic matter (%)	0.036–7.77	0.26–5.65	0.24–6.11	1.08–6.50
pH	8.278–9.69	8.60–9.52	7.72–8.76	7.67–8.65
Conductivity ( $\mu\text{s}/\text{cm}$ )	247–3,960	266–2,400	145.1–2,870	103.6–2,210
Particle compositions /%				
<4 $\mu\text{m}$	4.24–21.84	4.14–24.93	3.87–29.84	2.65–58.90
4–64 $\mu\text{m}$	29.43–80.92	23.91–69.17	26.99–83.29	16.18–72.40
>64 $\mu\text{m}$	6.18–60.68	16.03–71.35	7.94–48.89	0–55.37

**Table 3** | Contents of Hg and As in surface sediment of Wuliangsu Hai Lake

	Season				Soil background value of Hetao Irrigation District/(mg/kg)
	Summer	Autumn	Winter	Spring	
Hg					
Range (mg/kg)	0.013–0.196	0.02–0.133	0.019–0.063	0.014–0.135	0.02485
Mean (mg/kg)	0.11	0.055	0.036	0.057	
SD	0.031	0.035	0.015	0.045	
As					
Range (mg/kg)	2.25–15.18	3.53–14.26	5.20–9.62	5.77–13.95	9.68
Mean (mg/kg)	8.10	7.52	7.39	9.67	
SD	2.13	2.00	2.41	3.12	

spatial distribution. There is some man-made Hg pollution if the coefficient of variation is greater than 50%.

The content of As in the surface sediments of Wuliangsu Hai Lake ranged from 4.257 to 13.948 mg/kg, with an average of 8.197 mg/kg. Compared with soil background value of 9.68 mg/kg in Hetao Irrigation District, 20% of the sampling points exceeded the background value.

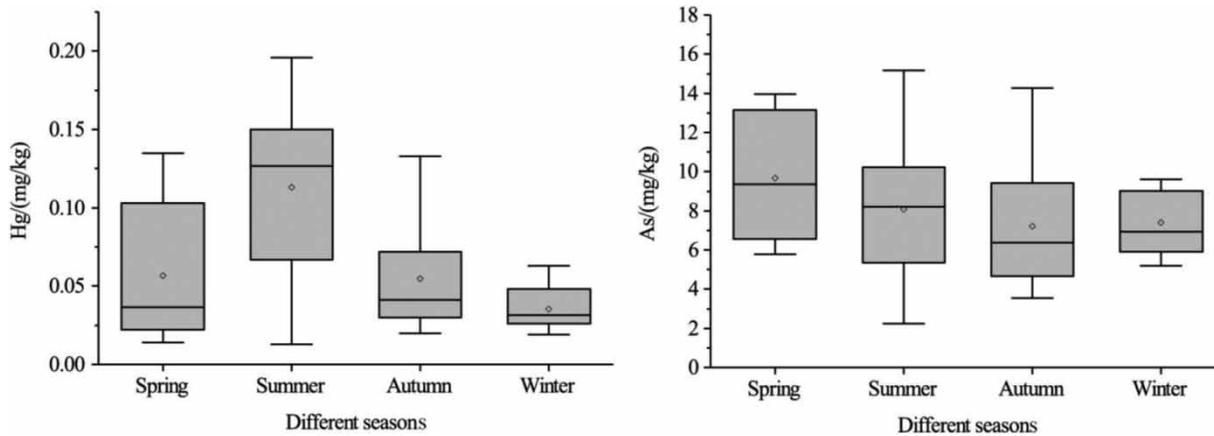
In general, the over-standard rate of Hg in the surface sediments of Wuliangsu Hai Lake was higher than that of As.

Hg and As had certain seasonal characteristics in the surface sediments of Wuliangsu Hai Lake. As shown in Figure 2, the seasonal characteristics of heavy metal Hg were: summer > spring > autumn > winter, with average values being 0.11 mg/kg, 0.057 mg/kg, 0.055 mg/kg, and 0.036 mg/kg, respectively. Compared with the soil background value of Hetao Irrigation District, 90% of the sampling points exceeded the background value in summer, 60% in spring, 90% in autumn, and 80% in winter. The maximum value

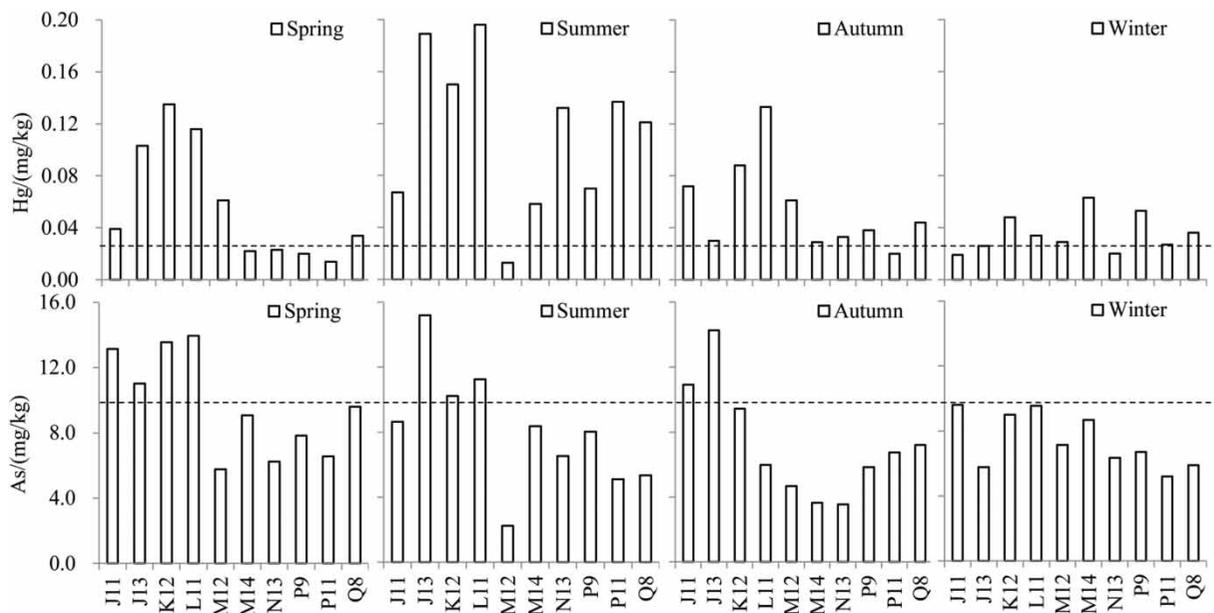
0.196 mg/kg was at point L11 in summer, 7.97 times the soil background value in Hetao Irrigation District.

The seasonal characteristics of As were: spring > summer > autumn > winter, with average values being 9.67 mg/kg, 8.10 mg/kg, 7.52 mg/kg, and 7.39 mg/kg, respectively. Compared with the soil background value of Hetao Irrigation District, 40% of the sampling points exceeded the background value in spring, 30% in summer, and 20% in autumn. The maximum value of 15.18 mg/kg was at point J13 in summer, 1.57 times the soil background value (9.68 mg/kg) in Hetao Irrigation District.

The spatial distribution characteristics of Hg in the four seasons were similar. The spatial distribution of different seasons is shown in Figure 3: the content of high value areas was 0.103–0.135 mg/kg in spring, 0.15–0.189 mg/kg in summer, 0.088–0.133 mg/kg in autumn and 0.026–0.063 mg/kg in winter. The high value areas were mainly located at points J13, K12 and L11 where the water inlet



**Figure 2** | Hg and As seasonal characteristics in the surface sediments of Wuliangsu Hai Lake.



**Figure 3** | Content of Hg and As in surface sediment of Wuliangsu Hai Lake.

is concentrated. The content at points P9, P11 and Q8 in the southern part of the lake was relatively low.

The high value areas of As in different seasons were similar to those of Hg. They were mainly located at points J11, J13, K12 and L11, where the water inlet is concentrated. The content of high value areas was 11.02–13.95 mg/kg in spring, 8.65–15.18 mg/kg in summer, 5.98–14.26 mg/kg in autumn, and 5.78–9.62 mg/kg in winter. The low value areas were mainly located at points M12, M14 and N13 in the central area of the lake.

### Environmental risk assessment of mercury and arsenic in different sediments in Wuliangsu Hai Lake

The geo-accumulation index ( $I_{geo}$ ), commonly referred to as the Muller index, considers not only the influence of background values caused by natural geological processes, but also the effects of human activities on heavy metal pollution. Therefore, the index not only reflects the natural variation characteristics of heavy metal distribution, but also can determine the impact of human activities on the

environment. It is an important parameter to distinguish the influence of human activities. This study took the soil background value of Hetao Irrigation District (Table 1) as reference and used the Igeo method to evaluate the heavy metal pollution status of surface sediments in Wuliangshuai Lake. The evaluation results are shown in Figure 4.

In spring, the Igeo of Hg in sediments was between -1.41 and 1.86, and 30% of the values in monitoring points were between 1 and 2, indicating moderate pollution, with the highest value of point K12 being 1.86; 20% were between 0 and 1, indicating mild pollution; 50% were less than 0, indicating no pollution.

In summer, the Igeo of Hg in sediments was between -1.52 and 2.39, and 30% of the values in monitoring points were between 2 and 3, indicating moderate to severe pollution, with the highest value of point L11 being 2.39; 30% between 1 and 2, indicating moderate pollution; 30% between 0 and 1, indicating mild pollution; 10% were less than 0, indicating no pollution.

In autumn, the Igeo of Hg in sediments was between -0.90 and 1.84, and 20% of the values in monitoring points were between 1 and 2, indicating moderate pollution; 40% were between 0 and 1, indicating mild pollution; 40% were less than 0, indicating no pollution.

In winter, the Igeo of Hg in sediments was between -0.97 and 0.76, and 30% of the values in monitoring points were between 0 and 1, indicating mild pollution; 70% were less than 0, indicating no pollution.

The Igeo of As in the sediments of the four seasons were almost all less than 0, indicating no pollution, and only the

value of point J13 in summer was 0.06, indicating mild pollution.

In summary, Hg pollution in surface sediments reached the highest level in summer, reduced in autumn, hit the bottom in winter, and began to increase in spring.

The Potential Ecological Risk Index (RI) comprehensively reflects the pollution level and potential ecological hazard of Hg and As in sediments. The study adopted the Hakanson Potential Hazard Index Method to conduct potential ecological risk assessment of heavy metal content in surface sediments of Wuliangshuai Lake.

The total RI of the whole lake ranged from 23.47 to 330.58, with an average of 114.25. Overall, the potential ecological risk of surface sediments at the sampling points fell into the moderate level, with individual points reaching the severe level. As shown in Figure 5, in summer, the range of RI varied from 23.47 to 330.58, with an average of 192.69, and 20% of the sampling points were at very high level, 40% at high level, 30% at moderate level, and 10% at low level. In spring, the range of RI varied from 29.57 to 233.69, with an average of 102.27, and 30% were at high level, 30% at moderate level, and 40% at low level. In autumn, the range of RI varied from 39.51 to 222.62, with an average of 96.63, and 20% were at high level, 70% at moderate level, and 10% at low level. In winter, the range of RI varied from 39.11 to 111.49, with an average of 65.41, 50% were at moderate level, and 50% at low level. The total RI of surface sediments in the whole lake was most severe in summer and mildest in winter, among which Hg contributed the most. Together with its high biological toxicity, we should deeply discuss and pay attention to this element.

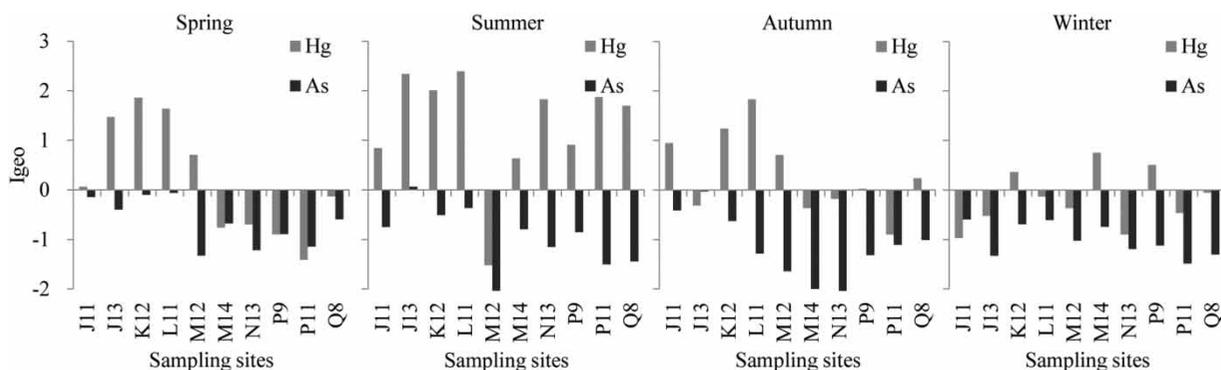
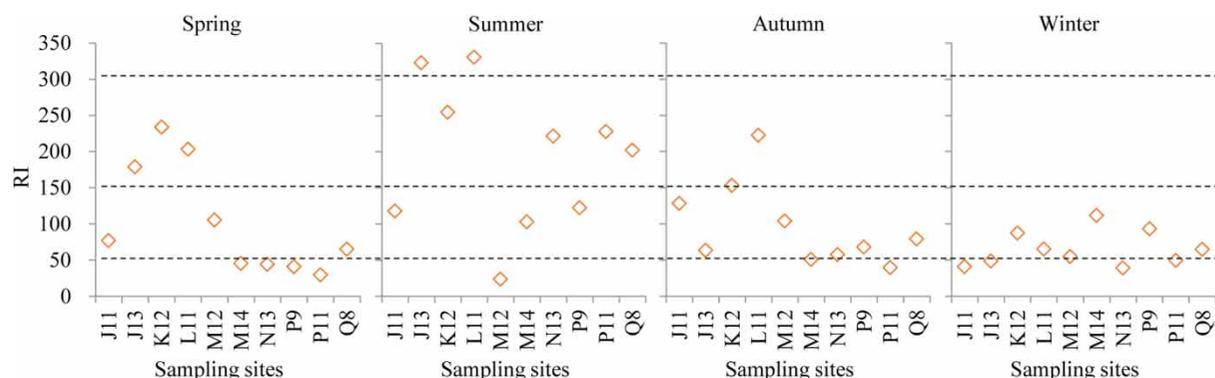


Figure 4 | The index of geoaccumulation evaluation results for Hg, As in surface sediments of Wuliangshuai Lake.



**Figure 5** | Potential ecological risk index (RI) for Hg and As in surface sediments of Wuliangsu Hai Lake.

Figure 6 shows the single Hg and As RI of surface sediments in Wuliangsu Hai Lake. Seasonal variations of Hg RI are: summer (184.33) > spring (92.27) > autumn (89.18) > winter (57.77), and those of As RI are: spring (10.00) > summer (8.36) > autumn (7.77) > winter (7.64).

In summer, the single potential ecological risk of Hg at points J11, J13, L11, M14, N13, and P9 was at severe level, K12 even at very severe level, P11 and Q8 at moderate level, and only M12 at mild level.

In autumn, the single potential ecological risk of Hg at point L11 was at very severe level, J11, K12 and M12 at severe level, M12 at mild level, and the other five sampling points at moderate level.

In winter, Hg pollution in surface sediments at points M14 and P9 were at severe level, J11 and N13 at mild level, and the other sampling points at moderate level.

In spring, Hg pollution in surface sediments at points J13, K12 and L11 was at very severe level, M12 was at severe level, J11 and Q8 were at moderate level, and the other sampling points were at mild level.

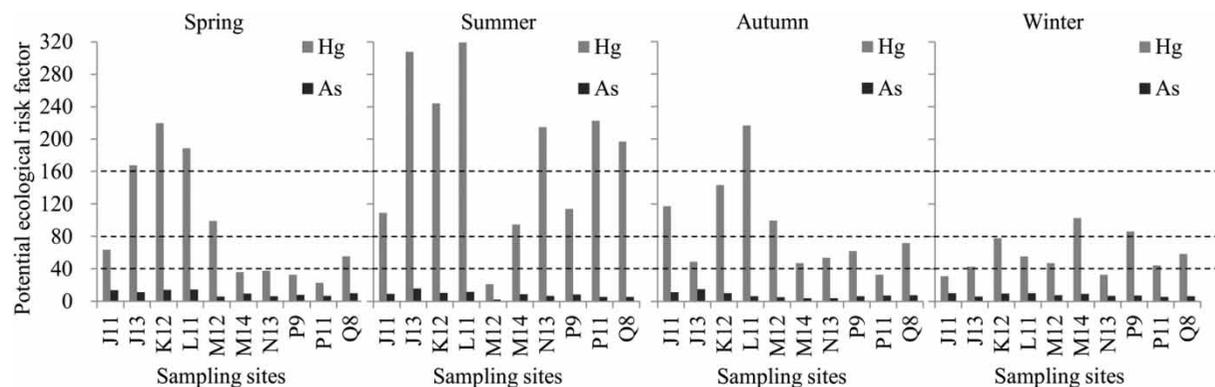
The single potential ecological risk of As in surface sediments of Wuliangsu Hai Lake in the four seasons was basically at a mild level.

In general, from the analysis of the potential ecological risk of a single element, some time in spring was in severe ecological pollution, while most of the time was in mild-moderate pollution; Hg pollution in summer was at severe-very severe level, and in autumn and winter at moderate-severe level.

## DISCUSSION

### Spatial distribution characteristics of mercury and arsenic in sediments of Wuliangsu Hai Lake

The general trend of spatial distribution of Hg and As in the sediments of Wuliangsu Hai Lake was: the total amount of Hg and As gradually decreased from the inlet estuary to the southern part of the lake. The study on Chaohu Lake (Yu



**Figure 6** | Potential ecological risk factor of Hg and As in surface sediment of Wuliangsu Hai Lake.

*et al.* 2013) and Dongping Lake (Lu *et al.* 2017) also shows that the content of Hg and As in the sediment at the entrance of the lake is higher than that in other areas of the lake. The content of Hg at points J11, J13, K12, L11, M12, M14 and N13 was larger than that at P9, P11 and Q8, and points J11, K12 and L11 had a larger content of As. This was because points with higher Hg content were located in the northern part of Wuliangsu Hai Lake; the agricultural waste water, industrial sewage, etc. in the Hetao Irrigation District entered the lake from the northern part, with more reeds, aquatic plants and other plants in that part, and Hg in water was mainly in the form of particles, with the sedimentation of particles in the water, Hg preferentially deposited, resulting in larger Hg content and more serious pollution. While points P9, P11 and Q8 were located in the southern part of the lake, and the waters were relatively open, with fewer reeds, aquatic plants and other plants, causing lower Hg content. Overall, points J11, K12, and L11 were located near the drains of Wuliangsu Hai Lake. From the distribution map of reeds, these three points were surrounded by reeds, an emergent aquatic plant, which could easily be absorbed by the particles and colloids in water, and then deposited, resulting in larger content of arsenic. The geographical difference in spatial distribution was not very large, with relatively even distribution, indicating that human pollution was not the main reason.

### Analysis of influencing factors of distribution characteristics of heavy metals in sediments

Firstly, factor analysis was carried out on various physical and chemical indicators in the sediments of Wuliangsu Hai Lake, and it was found that there was a strong correlation between physical and chemical indicators (Hariri & Abu-Zied 2018). At the same time, the data distribution of different seasons went through the KMO test and Bartlett test (Zhao & Li 2013). The KMO test values of spring, summer, autumn, and winter were 0.512, 0.584, 0.505, and 0.546, respectively, all greater than 0.5. The concomitant probabilities of the four seasons in the Bartlett spheroid test were all 0.000, obviously less than the significance level of 0.05 (Zhao & Li 2013). Therefore, the data of the four seasons could be analyzed by principal component analysis.

In spring, the contribution rate of the first principal component was 40.61%, with pH, organic matter, electrical

conductivity, 0–4  $\mu\text{m}$ , and 64–800  $\mu\text{m}$  having higher load on the component. The second principal component had a higher load in 4–64  $\mu\text{m}$ . In summer, the contribution rate of the first principal component was 45.07%, which was characterized by higher load in pH, organic matter, and electrical conductivity. The contribution rate of the third principal component was 12.73%, and the load in 0–4  $\mu\text{m}$  was 0.750. Clay was also the main factor affecting the content of mercury and arsenic. In autumn, the contribution rate of the first principal component was 37.24%, with pH, electrical conductivity, and organic matter having higher loads on this component, and the contribution rate of the second principal component was 21.70%, with 0–4  $\mu\text{m}$ , 4–64  $\mu\text{m}$ , 64–800  $\mu\text{m}$  having higher load on it. In winter, the contribution rate of the first principal component was 40.87%, with pH, organic matter, electrical conductivity, 0–4  $\mu\text{m}$  having higher load on the component, the contribution rate of the second principal component was 30.38%, with the load in 4–64  $\mu\text{m}$  being  $-0.825$ , and the silt was in easily complexing reaction with mercury and arsenic.

The results of principal component analysis of these four seasons showed that the first principal components of the four seasons had higher loads in pH, organic matter and electrical conductivity, illustrating that these three indicators were major factors affecting the differences of mercury and arsenic content distribution in Wuliangsu Hai Lake (Table 4). This is consistent with the study of Dishui Lake by Liu *et al.* (2016).

Organic matter decisively controls the ecological toxicity and environmental migration behavior of heavy metals in sediments through adsorption, complexation, etc. The organic matter in sediments mainly exists in the form of humus. In general, the content of humus in sediments accounts for 70–80% of the total organic matter, and some areas even reach 99% (Mao *et al.* 2011). The humus takes carbon chain as skeleton and  $-O-$  as well as  $-N-$  as cross-linking group, with hydrogen-containing bond and a large amount of oxygen-containing functional groups. It has the characteristics of large molecular weight, large superficial area, and high cation exchange amount. Therefore, the adsorption and complexation of heavy metals by organic matter are mainly accomplished in three ways: surface complexation, ion exchange and surface precipitation of humus and metal ions. The humus is mainly composed of humic acid soluble in alkali and deposited in acid, fulvic acid

**Table 4** | The PCA results in different season

	Spring				Summer			Autumn			Winter	
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2
Eigenvalue	3.66	1.86	1.24	1.04	4.06	1.71	1.15	3.35	1.95	1.65	3.68	2.73
Contribution rate /%	40.61	20.67	13.74	11.51	45.07	19.04	12.73	37.24	21.70	18.37	40.87	30.38
Cumulative contribution rate /%	40.61	61.28	75.02	86.54	45.07	64.11	76.84	37.24	58.93	77.30	40.87	71.25
pH	-0.84	0.02	0.02	0.54	-0.93	-0.15	0.06	-0.90	0.16	-0.03	-0.94	-0.18
Organic matter	0.78	0.32	-0.26	0.18	0.74	0.03	-0.46	0.84	-0.23	0.06	0.75	0.40
Conductivity	0.59	0.05	-0.04	0.34	0.77	0.35	-0.12	0.80	-0.22	-0.19	0.71	0.31
0–4 μm	-0.70	0.54	-0.30	-0.31	-0.09	0.46	0.75	0.04	0.61	0.62	-0.62	0.60
4–64 μm	0.04	-0.71	0.67	-0.08	-0.58	0.68	-0.44	0.36	0.73	-0.53	0.48	-0.83
64–800 μm	0.82	-0.13	-0.14	0.44	0.58	-0.79	0.19	-0.34	-0.91	0.22	-0.21	0.74

soluble in acid and alkali, and humic acid insoluble in acid and alkali. The strong adsorption and fixation ability of organic matter to heavy metals mainly lies in that the chelate formed by the chelation of heavy metals and humic substances had extremely small solubility, and the humic substance was poorly soluble organic matter (Wu et al. 2009), so it was easy to form precipitates. In addition, changes in the organic matter content would affect the binding form of heavy metals in the sediment, which would increase the binding state of the less active organic matter and tend to deposit in the sediment (Mao et al. 2011).

Forty two percent of the surface area of WL is open and the rest is covered by dense reed (*Phragmites australis*) stands (Song et al. 2019). There are also a lot of algae in Wuliangshuai, and the lake has a huge biomass and a large organic matter. The seasonal characteristics of organic matter content in sediments of Wuliangshuai Lake were: summer (4.63%) > spring (4.52%) > autumn (3.80%) > winter (2.35%). High organic matter content and high humus content make heavy metals strongly adsorbed and complexed; therefore, the seasonal characteristics of heavy metal Hg were: summer > spring > autumn > winter, and that of As were: spring > summer > autumn > winter.

### Environmental risk of mercury and arsenic in the sediments of Wuliangshuai Lake

The main forms of mercury in lake sediments were  $\text{Hg}^{2+}$ ,  $\text{Hg}^0$ ,  $\text{HgS}$ ,  $\text{CH}_3\text{Hg}(\text{SR})$  and  $(\text{CH}_3\text{Hg})_2\text{S}$ , mainly in the form

of divalent mercury (Joseph et al. 2019). In winter, the lake froze with an ice thickness of about 50–60 cm, which isolated the sediments from the air and made them in a reduced state. The  $\text{Hg}^{2+}$  in sediments was reduced to  $\text{Hg}^0$ , so that the sediment lowered and the mercury migrated into the lake water. In summer, the lake ecosystem was in an oxidized state, making  $\text{Hg}^{2+}$  relatively stable in sediments. In addition, according to the previous pollution source analysis and survey statistics, the source of mercury was mainly atmospheric deposition and the mercury in the atmosphere was mainly from burning coal, accounting for 60% of anthropogenic release (Yin & Jia 2014). The presence of mercury in the atmosphere mainly includes  $\text{Hg}^0$ , water-soluble inorganic mercury compounds and organic mercury compounds, 90% of which exist as  $\text{Hg}^0$ . In summer, the  $\text{Hg}^0$  in the atmosphere was oxidized to  $\text{Hg}^{2+}$  by strong oxidants such as  $\text{O}_3$ ,  $\text{O}_2$ , and  $\text{NO}_2$  in the air, and  $\text{Hg}^{2+}$  entered water by rainwater washing and dry deposition. After entering into water, soluble  $\text{Hg}^{2+}$  was quickly adsorbed and fixed by the sediments, and a series of transformations reduced its activity (Yin & Jia 2014). Compared with winter, although the Hg content in the air was lower, the effect of atmospheric deposition on this cycle was largest. There was little seasonal variation of dry deposition; however, due to rainwater, the wet deposition in summer was obviously higher than in winter. Wet deposition played a dominant role in the whole year, accounting for 70% of the deposition. Therefore, the Hg content, environmental risk and potential ecological risk of mercury in sediments were higher in summer than that in winter.

The main source of As in the sediments of Wuliangshuai Lake was the arsenic-containing compound released into the air from burning coal (Yin & Jia 2014). Similar to the deposition principle of mercury, arsenic compounds in the atmosphere entered the lake water through dry and wet deposition and deposited in lake sediments. Major valence states of As are trivalent and Arsenite, and the solubility of trivalent arsenic compounds is 4 to 10 times higher than that of Arsenite (Bo & Luo 2009). When summer came, the migration of As from the air into the lake increased, the trivalent arsenic would be oxidized to Arsenite arsenic, causing As to migrate from water to sediments; and the Arsenite arsenic would form  $\text{FeAsO}_4$ ,  $\text{Ca}_3(\text{AsO}_4)_2$ ,  $\text{Mg}(\text{AsO}_4)_2$  and other poorly soluble arsenate with Fe, Al, Ca, and Mg in the water, and then precipitated (Zhao & Li 2013), resulting in increased arsenic content in the sediments. In winter, as the redox potential decreased, the trivalent arsenic in the lake was not easily oxidized. On the contrary, the Arsenite arsenic was easily reduced to trivalent. The compound formed by trivalent arsenic is easily soluble in water, resulting in lower arsenic content in the sediments. Therefore, the arsenic content and potential ecological risk in summer were higher than in winter.

The results of the evaluation of the Igeo method showed that most of the sampling points in the surface sediments were polluted by mercury to mild and even moderate level; and the results of the RI method showed that the total potential ecological risk of mercury and arsenic was at mild-moderate level, with individual points at severe level. However, some individual sampling points with no Hg pollution in the Igeo method were evaluated to mild pollution in the RI method, which indicated that the RI evaluation system was more sensitive to the impact of pollutant enrichment, and it also considered the potential ecotoxicity effects of different elements. Overall, the two evaluation results were not completely consistent, and the RI assessment was higher. According to the potential ecological risks of these four months, the pollution of sampling points in the north-western part of the lake was more serious than that of the southeastern part; the potential ecological risk in summer was the most serious compared with the other three seasons; it began to decrease in autumn, and hit the bottom in winter. Therefore, Hg and As pollution were affected by seasonal changes as well as regional variations.

## CONCLUSION

The content of Hg in the surface sediments of Wuliangshuai Lake ranged from 0.013 to 0.135 mg/kg, with an average of 0.054 mg/kg, and the content of As varied from 4.257 to 13.948 mg/kg, with an average of 8.197 mg/kg, 80% and 20% of sampling points exceeded the soil background value of the Hetao Irrigation District, respectively. The seasonal characteristics of Hg were: summer > spring > autumn > winter, and that of As were: spring > summer > autumn > winter, mainly affected by pH, organic matter and electrical conductivity of sediments. In terms of spatial distribution, the content of mercury and arsenic in the entrance of Wuliangshuai Lake was relatively high, and the content in the lake area and the southern part of the lake were similar and both decreased. In combination with the Igeo method and RI method, it could be seen that Hg and As pollution in summer was more serious than that in the other three seasons. The overall ecological risk of surface sediments at the sampling points was moderate, with some individual points reaching severe level. Due to the high RI of Hg in sediments of Wuliangshuai Lake, some times in spring were in severe ecological pollution, while most time was in mild-moderate pollution; Hg pollution in summer was at severe-very severe level, and in autumn and winter at moderate-severe level.

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## AUTHOR CONTRIBUTIONS

Data curation, W.T., C.S., H.M. and S.S.; Formal analysis, W.T., S.Z., H.Z.; Methodology, W.T., S.Z. and S.B.; Writing-original draft, W.T.; Writing-review & editing, G.P., and X.S.

## CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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