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Original Research

Seasonal and Spatial Variations of Heavy Metal Pollution in Water and Sediments of China's Tiaozi River

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Abstract

The objectives of this study were to investigate the seasonal and spatial variations of heavy metal pollution in the overlying water and surface sediments of the Tiaozi River, a tributary of the Liao River, which is one of the seven major rivers and one of the most heavily-polluted rivers in China. Water and sediment samples were collected over four seasons, analyzed for heavy metals (Pb, Cu, Ni, Mn, Cd, and Zn), and assessed with an integrated water quality index (WQI) and a geoaccumulation index (I_{geo}). Results indicated that the maximum concentrations of all the metals in water and sediments occurred in winter and the minimum in summer. Assessment of the pollution indicated that the water was uncontaminated by heavy metals, but the sediments were slightly contaminated with Cu, Ni, Cd, and Zn. Therefore, the pollution of Cu, Ni, Cd, and Zn in the Tiaozi River Basin should be taken into account during the formation of regional management strategies for the water environment.

Keywords: heavy metal, seasonal variation, spatial distribution, Tiaozi River, Liao River

Introduction

Heavy metals are widespread persistent pollutants that are of environmental concern due to their non-degradability, bioaccumulation, and potential toxicity to living organisms [1, 2]. Surface water pollution by heavy metals is of great concern worldwide [3]. Once heavy metals are released into the aquatic environment, most of them are bound to particulate matter and eventually deposited into sediments. However, some of the sediment-bound metals may be desorbed from sediments and released back to waters when environmental conditions change. Seasonal variations may lead to environmental conditions affecting heavy metals partitioning between water and sediments. Most studies have focused on heavy metals in the sediments, rather than in bulk river water [4-7]. However, variation of the concentrations of heavy metals in the water and sediments can provide direct information for evaluating the status of heavy metal pollution and baseline data to help further develop an efficient strategy in their control and reduction in river systems [8].

The Liao River in northeast China is one of the seven major rivers in China. The river basin is one of the most important heavy-industry bases in China, including chemical, petrochemical, pharmaceutical, metallurgical, dyeing, heavy machinery, and automobile manufacturing. Due to the discharge of wastewater from these industrial sectors, the Liao has become one of the most heavily-polluted rivers in China [9]. Since 2008, some efforts, such as the development of pollution source control technology, have been

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made for pollution control in the Liao basin. Monitoring results for water bodies indicated that water quality, in terms of indexes COD, BOD and NH_3-N, has been improved year by year. However, there have been more concerns regarding the level and ecological risk of persistent toxic substances, such as persistent organic pollutants and heavy metals in the river. Previous studies on the pollution of heavy metals in surface sediments of some tributaries in the lower reaches of the Liao have been investigated, and they indicate that the sediments adjacent to big cities and mining areas were contaminated by heavy metals, and the primary characteristic heavy metals were different in different tributaries [10]. For example, Cd and Pb showed more severe enrichment in Daliao River sediments, while Cd and Zn showed more severe enrichment in sediments in the upper reaches of the Hun River [11, 12].

The Tiaozi River is one of the upper tributaries of the Liao system and a transboundary river between Jilin and Liaoning provinces. It receives domestic, agricultural, and industrial wastewater from Siping, a mid-sized city in the east Liao River basin. The Tiaozi is regarded as one of the most severely polluted tributaries in the upstream Liao [13]. However, few data of heavy metals in the river can be acquired and few studies regarding space-time distribution and assessment of heavy metal contamination in the river have been reported.

The aim of this study was to assess the level of contamination and analyze the seasonal and spatial variation of heavy metals in the Tiaozi by measuring the concentrations of Pb, Cu, Ni, Mn, Cd, and Zn in both the river water and sediments collected from three sites over four seasons. Results obtained for this study will provide useful information for managing the heavy metal pollution in the Tiaozi, as well as the Liao.

Materials and Methods

Study Area and Sample Collection

Water and sediment samples were collected from three sites along the Tiaozi, as shown in Fig. 1, during autumn, winter, spring, and summer from 2012 to 2013. Huihekou (Site A) is located upstream of the main Tiaozi River and is near the municipal wastewater treatment plant of Siping. Both Yihetun (Site B) and Linjia (Site C) are monitoring sites within the provincial boundary. Overlying water samples (approximately 0.5 m below the surface) were collected using polyethylene bottles, and surface sediment samples (< 10 cm depth) were collected using a plastic ladle. Each sample was a composite of two individual, parallel samples. Once collected, the samples were immediately

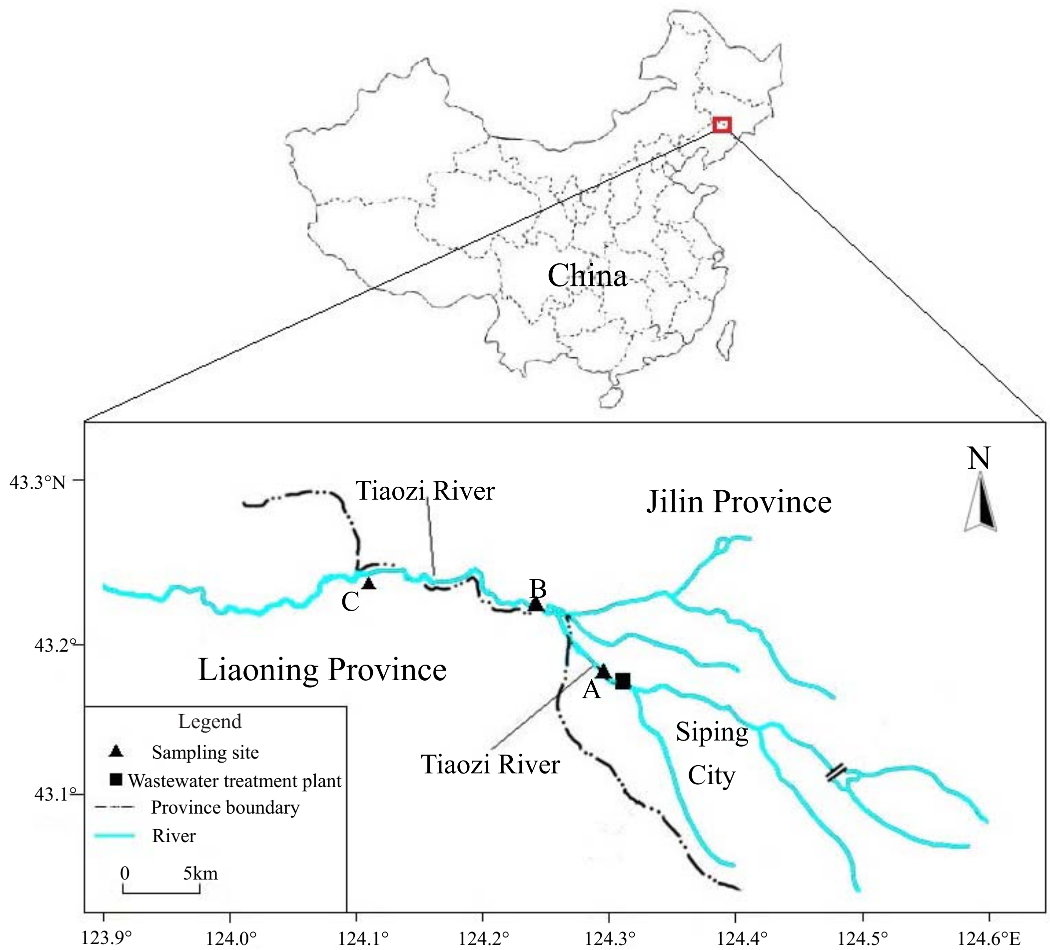

Fig. 1. Location of the sampling sites – A: Huihekou, B: Yihetun, C: Linjia.

Table 1. Geoaccumulation index (I_{geo}) and classification of pollution status.

I_{geo}	Class	Pollution status
< 0	0	Unpolluted
0~1	1	Slightly polluted
1~2	2	Moderately polluted
2~3	3	Moderately to heavily polluted
3~4	4	Heavily polluted
4~5	5	Heavily to extremely polluted
> 5	6	Extremely polluted

transported to the laboratory. Prior to analysis, water samples were filtered through a 0.45 µm membrane filter, and sediment samples were freeze-dried, crushed using a mortar and pestle, and then sieved through a 60-mesh nylon sieve. Unfortunately, as a result of the frozen river in winter, a sediment sample in Site A and a water sample in Site C could not be obtained.

Sample Pretreatment and Chemical Analysis

Pb, Cd, Ni, Cu, Zn, and Mn were determined in water samples based on the liquid-liquid extraction procedure, in which 100 mL water sample was placed in a beaker and digested with HNO_3 (5 mL) on a temperature-controlled hot plate. Once the solution had evaporated, leaving a residue of 10 mL, a further aliquot of HNO_3 (5 mL) and HF (1 mL) was added to the solution and continuously heated until the volume was reduced to approximately 10 mL. The solution was then allowed to cool, transferred to a 50 mL volumetric flask, and diluted with a further 0.2% HNO_3 solution to volume in preparation for analysis [14].

Heavy metals in sediment samples were determined according to Lin et al. [15], where 0.5 g sediment sample was placed in a polytetra-fluoroethylene (PTFE) beaker. Sample digestion was then performed on a hot plate by adding a tiny bit of water to wet the sample, followed by 10 mL HNO_3, 5 mL HF, and 3 mL $HClO_4$. Once the solution became clear with no brown-colored vapor visible, the residue was redissolved with 0.2% HNO_3 (10 mL), transferred to a 50 mL volumetric flask, and diluted with a 0.2% HNO_3 solution to volume for heavy metal analysis.

The final metal concentrations in extracts were determined using Flame AAS (PerkinElmer, AA 700). The graphite furnace method was used for Cd analysis. The accuracy and precision of the analytical methodology were assessed by triplicate analyses of a standard reference solution (GSB04-1767-2004, National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials, China) and a standard reference material for stream sediment (GBW07302a, Geophysiochemistry Prospecting Institute of Academy of Geological Science of China). The relative deviation for Mn did not exceed 10%

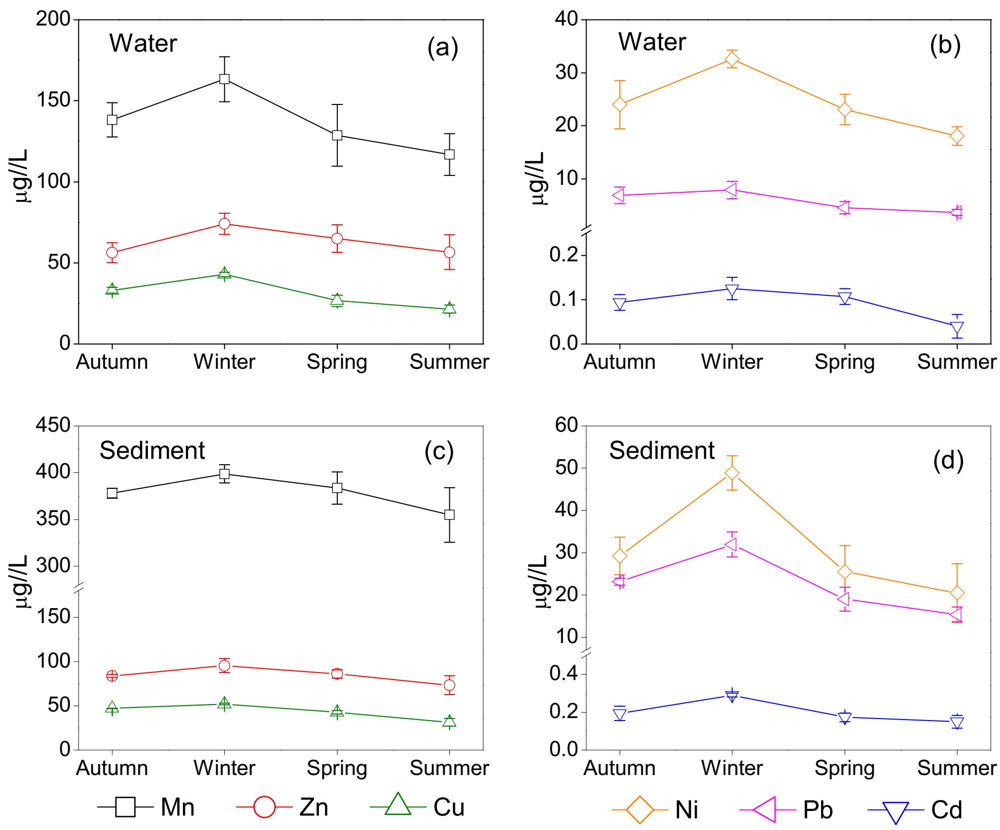

Fig. 2. Seasonal variations of heavy metal concentrations in the water and sediments: (a) Mn, Zn, and Cu in the water; (b) Ni, Pb, and Cd in the water; (c) Mn, Zn, and Cu in the sediments; and (d) Ni, Pb, and Cd in the sediments.

and those for Pb, Cu, Ni, Cd, and Zn did not exceed 5%. The recovery values, ranging from 83% to 117%, were obtained for the analyzed heavy metals in the water and sediments.

Assessment Methods and Data Analysis

An integrated water quality index (WQI) was used to establish the heavy metal contamination in the overlying water [16]. The WQI treats all the heavy metals from a site as a whole and determines the effect of their interactions on the environment. The WQI formula is expressed as follows:

$$A_i = \frac{C_i}{C_{si}}, \quad WQI = \frac{1}{n}\sum_{n}^{1} A_i \qquad (1)$$

...where A_i is the pollution index of heavy metal i, C_i is the measure concentration of heavy metal i, C_{si} is the water quality criteria of heavy metal i, and n is the number of heavy metals. A result of WQI ≤ 1 is considered unpolluted, 1 < WQI ≤ 2 is slightly polluted, 2 < WQI ≤ 3 is moderately polluted, and WQI > 3 is heavily polluted. In this study, the third type standard values for surface waters in China (GB 3838-2002) were employed to evaluate Pb, Cd, Cu, and Zn pollution, and centralized drinking water source standard values (GB 3838-2002) were used to assess Mn and Ni pollution. The standard value of Pb, Cd, Cu, Zn, Mn, and Ni is 50, 5, 1000, 1000, 100, and 20 μg/L, respectively [17].

The geoaccumulation index (I_{geo}) introduced by Muller was conducted as the quantitative measure of heavy metal pollution in aquatic sediment [18]. The formula of I_{geo} is expressed as follows:

$$I_{\text{geo}} = \log_2\left[\frac{C_{\text{n}}}{1.5 \times B_{\text{n}}}\right] \qquad (2)$$

...where C_n is the concentration for metal n, B_n is the background value (average shale) for metal n, and factor 1.5 is the background matrix correlation factor due to lithogenic variation. In the Liao Plain, the background value of soil of Mn, Zn, Cu, Ni, Pb, and Cd is 423.6, 55.4, 20.8, 24.6, 19.9, and 0.11 mg/kg, respectively [19]. The seven classes of the I_{geo} were suggested by Muller, as shown in Table 1 [20]. All the data calculations and statistical analysis were performed using Microsoft Excel 2010 software.

Results and Discussion

Seasonal and Spatial Variations of Heavy Metals in the Water and Sediments

The mean concentrations of heavy metals in the water and sediments in the Tiaozi varied seasonally and spatially and are shown in Figs. 2 and 3, respectively. The average of Mn, Zn, Cu, Ni, Pb, and Cd concentrations in the overlying water was found to be 134.36, 61.96, 29.91, 23.70, 5.55, and

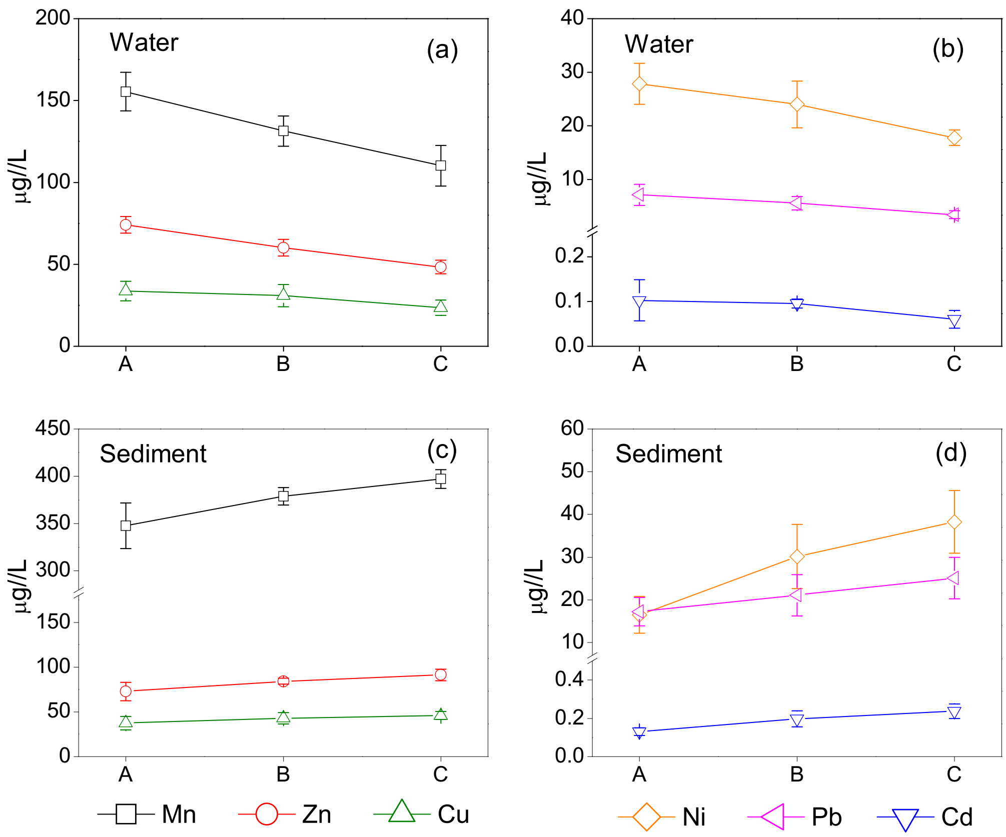

Fig. 3. Spatial variations of heavy metal concentrations in the water and sediments: A, Huihekou; B, Yihetun; C, Linjia; (a) Mn, Zn, and Cu in the water; (b) Ni, Pb, and Cd in the water; (c) Mn, Zn, and Cu in the sediments; (d) Ni, Pb, and Cd in the sediments.

Table 2. Maximum, average, and standard values of heavy metal concentrations in Tiaozi River water (μg/L).

Heavy metal	Maximum	Average	Standard value
Zn	80.58	61.96	1000
Cu	44.33	29.91	1000
Pb	9.56	5.55	50
Cd	0.15	0.09	5
Mn	177.21	134.36	100
Ni	34.23	23.70	20

0.09 μg/L, respectively. The mean contents of Mn, Zn, Cu, Ni, Pb, and Cd in the surface sediments were 377.08, 83.56, 42.48, 29.39, 21.50, and 0.19 mg/kg, respectively. Both the mean concentrations of metals in the water and sediments followed the order: Mn > Zn > Cu > Ni > Pb > Cd.

The maximum mean concentrations for heavy metals in both matrices occurred in winter, with all the minimum concentrations measured in summer and the mean concentrations between spring and autumn relatively similar. The mean concentrations of Mn, Zn, Cu, Ni, Pb, and Cd in the water in winter were approximately 1.4, 1.3, 2.0, 1.8, 2.2, and 3.1 times higher than in summer, respectively. The lowest metal concentrations in water and sediments may be attributed to dilution by rainwater in summer [11, 21].

The mean concentrations of all six metals in the overlying water at the three sampling sites decreased downstream in the order of A > B > C. The mean aqueous concentrations of Mn, Zn, Cu, Ni, Pb, and Cd at site A were 1.4, 1.5, 1.4, 1.6, 2.1, and 1.7 times higher than at site C, respectively. However, the mean concentrations of all the metals in the sediments increased upstream in the order of A < B < C. The mean concentrations of Mn, Zn, Cu, Ni, Pb, and Cd in the sediments at site C were 1.1, 1.3, 1.2, 2.3, 1.5, and 1.8 times higher than that at site A, respectively. This spatial distribution of heavy metal concentrations may be associated with wastewater discharge.

The Tiaozi, as an urban river, receives effluent discharged by Siping's domestic wastewater plant. The removal of some pollutants by the current wastewater plant is not adequate and, as site A is the closest to the wastewater plant and industrial areas, this could lead to elevated heavy metal concentrations [13]. However, the characteristics of the spatial distribution of heavy metals between the water and sediment phases showed a conflicting trend. It could be inferred that the most influential factors on heavy metal concentration in the Tiaozi sediments are the physicochemical characteristics of the sediment, such as particle size, clay mineral content, and fraction of organic matter, rather than the discharge of the upper water. The adsorption of heavy metals is known to be particularly affected by particle characteristics [22]. It is widely accepted that the contents of heavy metals are positively correlated with the concentration of organic matter in sediment, as organic matter can act as an important reservoir for heavy metals due to its strong complex capacity with metallic contaminants [23]. The concentrations of total organic carbon in the sediments in the samples for sites A, B, and C were 0.41%, 0.74%, and 1.11%, respectively. Therefore, it can be concluded that the spatial distribution of heavy metals in the surface sediments of the Tiaozi was largely influenced by the properties of sediment in different sampling sites.

Table 3. The integrated water quality index (WQI) of heavy metals in Tiaozi River water.

Season	Sampling site	WQI
Autumn	A	0.5
	B	0.5
	C	0.4
Winter	A	0.6
	B	0.5
	C	-
Spring	A	0.5
	B	0.4
	C	0.4
Summer	A	0.4
	B	0.4
	C	0.3

A: Huihekou, B: Yihetun, C: Linjia. '-': No data.

Pollution Assessment of Heavy Metals in the Water

Based on Surface Water Quality Standards

The mean and maximum concentrations of Pb, Cd, Cu, Zn, Mn, and Ni in the Tiaozi are listed in Table 2. In this study, the third type standard values for surface waters in China (GB 3838-2002) were employed to evaluate Pb, Cd, Cu, and Zn pollution, and centralized drinking water source standard values (GB 3838-2002) were used to assess Mn and Ni pollution. The standard values of Pb, Cd, Cu, Zn, Mn, and Ni are 50, 5, 1000, 1000, 100, and 20 μg/L, respectively [17]. The results show that both the mean and maximum concentrations of Pb, Cd, Cu, and Zn were lower than their standard values, but the mean and maximum value of Mn and Ni were higher than the standard value of a centralized drinking water source. The standard value of centralized drinking water source is strict to the urban river, so the level of heavy metal pollution in Tiaozi water was not considered serious.

Based on the Integrated Water Quality Index

The WQI of the heavy metals in each water sample was calculated by equation (1) and listed in Table 3. The WQI

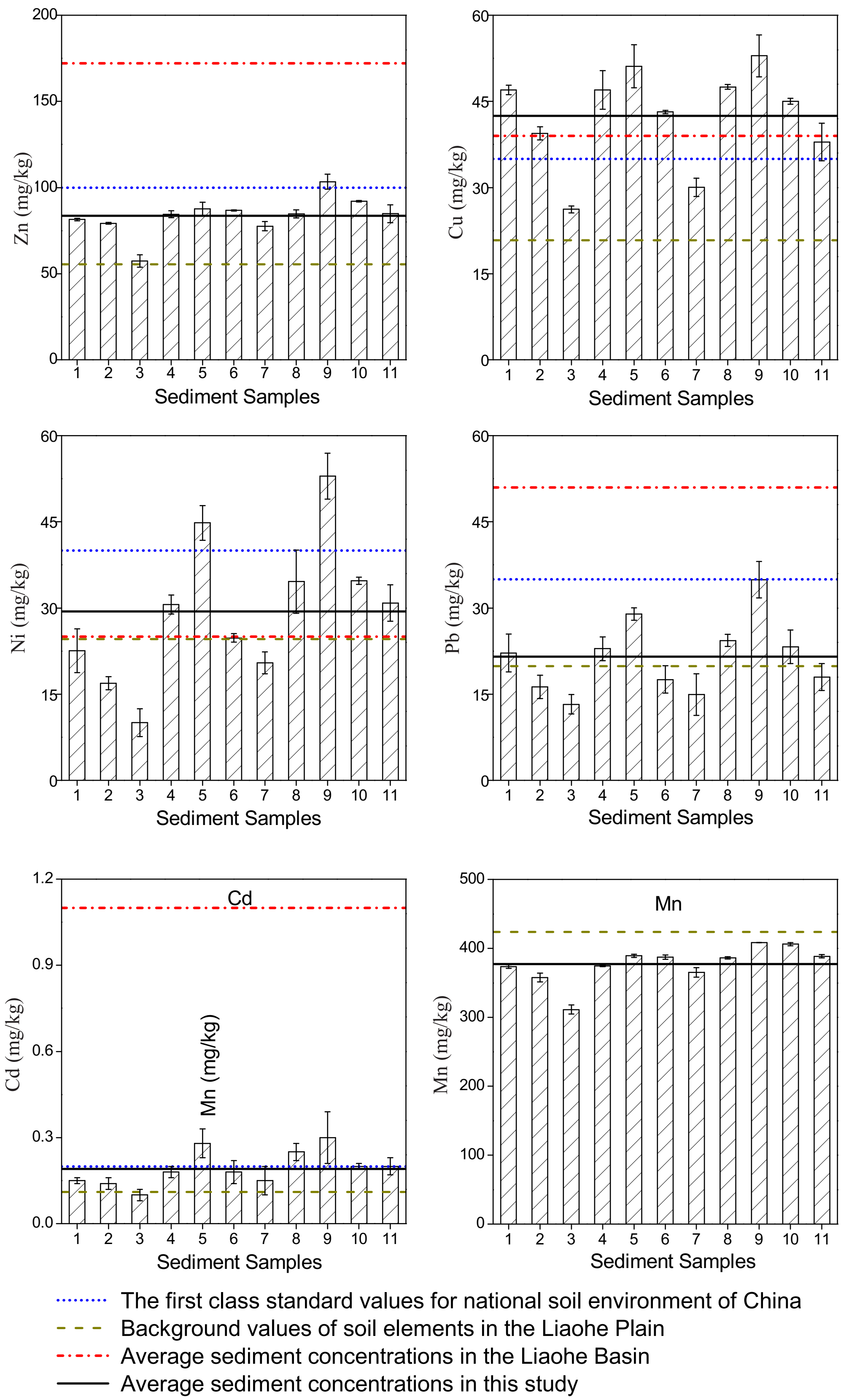

Fig. 4. Heavy metal contents in Tiaozi River sediments and comparison with assessment values. Sediment samples are represented by the numbers on the X-axis: 1 – Huihekou in autumn; 2 – Huihekou in spring; 3 – Huihekou in summer; 4 – Yihetun in autumn; 5 – Yihetun in winter; 6 – Yihetun in spring; 7 – Yihetun in summer; 8 – Linjia in autumn; 9 – Linjia in winter; 10 – Linjia in spring; and 11 – Linjia in summer.

Table 4. Mean concentrations of heavy metals in Tiaozi River surface sediments and a comparison with other water bodies in the Liao River Basin (mg/kg).

Water bodies	Zn	Cu	Ni	Pb	Cd	Mn	Reference
Tiaozi River	83.56	42.48	29.39	21.50	0.19	377.08	This study
Hun River	885.51	288.67	40.48	63.96	13.11	-	[12]
Dahuofang Reservoir	137.49	65.20	-	36.69	2.38	-	[26]
Daliao River and its estuary	47.23	11.2	15.01	19.61	0.62	311	[11]

Table 5. The geoaccumulation index (I_{geo}) value and classification of heavy metals in Tiaozi River sediments.

Site	Season	Mn		Zn		Cu		Ni		Pb		Cd	
		I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class
A	Autumn	-0.77	0	-0.03	0	0.59	1	-0.71	0	-0.43	0	-0.14	0
	Winter	-	-	-	-	-	-	-	-	-	-	-	-
	Spring	-0.83	0	-0.07	0	0.34	1	-1.13	0	-0.88	0	-0.24	0
	Summer	-1.03	0	-0.54	0	-0.25	0	-1.88	0	-1.18	0	-0.72	0
B	Autumn	-0.76	0	0.02	1	0.59	1	-0.27	0	-0.38	0	0.13	1
	Winter	-0.71	0	0.07	1	0.71	1	0.28	1	-0.04	0	0.76	1
	Spring	-0.71	0	0.06	1	0.47	1	-0.57	0	-0.77	0	0.13	1
	Summer	-0.80	0	-0.10	0	-0.06	0	-0.85	0	-1.00	0	-0.14	0
C	Autumn	-0.72	0	0.03	1	0.61	1	-0.09	0	-0.29	0	0.60	1
	Winter	-0.64	0	0.31	1	0.76	1	0.52	1	0.23	1	0.86	1
	Spring	-0.65	0	0.15	1	0.53	1	-0.09	0	-0.36	0	0.28	1
	Summer	-0.71	0	0.03	1	0.28	1	-0.26	0	-0.73	0	0.28	1

A: Huihekou, B: Yihetun, C: Linjia. '-': No data.

ranged from 0.3 to 0.6, which is below the threshold of < 1, indicating that Tiaozi water was not polluted by heavy metals. The results based on the above two methods for the Tiaozi reveal that it was unpolluted by heavy metals.

Pollution Assessment of Heavy Metals in Sediments

Based on Standard Values and Comparison with other Water Bodies

The concentrations of heavy metals in each of the sediment samples was compared with the first-class standard values for national soil environment of China (GB15618-1995) (the values of Zn, Cu, Ni, Pb, and Cd are 100, 35, 40, 35, and 0.2 mg/kg, respectively) [24], the background values of soil elements in the Liao River Plain (the values of Zn, Cu, Ni, Pb, Cd, and Mn are 55.4, 20.8, 24.6, 19.9, 0.11, and 423.6 mg/kg, respectively) [19], and the average sediment concentrations in the Liao River Basin (the concentrations of Zn, Cu, Ni, Pb, and Cd are 172, 39, 25, 51, and 1.1 mg/kg, respectively) [25]. Heavy metal concentrations in Tiaozi sediments and a comparison of these assessment values are listed in Fig. 4. Only the mean concentration of Cu was higher than its first-class standard value of Chinese soil environment. The mean concentrations of Cu, Zn, Ni, Pb, and Cd were each higher than their background value in the Liao River Plain soils. This indicates that Cu accumulation in Tiaozi surface sediments is moderate, the accumulation of Zn, Ni, Pb, and Cd is slight, and there is no exogenous Mn input into the Tiaozi sediments. Among the six heavy metals, the only metals with a mean concentration higher than the average concentration in the Liao basin sediments were Cu and Ni. The mean concentrations of Zn, Pb, and Cd were lower than average concentrations in the Liao basin sediments.

The mean concentrations of heavy metals in Tiaozi surface sediments were also compared with those from other water bodies in the Liao basin reported since 2011 (Table 4). The mean concentrations of Zn, Cu, Ni, Pb, and Cd were far lower than those in the Hun River and Dahuofang Reservoir, but Zn, Cu, Ni, Pb, and Mn were slightly higher than those in the Daliao River and its estuary. It has been reported that the concentrations of heavy metals in the Hun were much higher due to mining and agricultural intensification in central Liaoning Province, but the concentrations of heavy metals in the Daliao and its estuary are comparatively low in the Liao basin [11, 12]. So it can be concluded that the levels of studied heavy metals in the Tiaozi were in low-to-moderate class in the Liao basin.

Based on the Geoaccumulation Index

The I_{geo} of the six heavy metals at each sampling site in each season were calculated by equation (2). The I_{geo} value and corresponding classification are listed in Table 5. All the I_{geo} values were <1, with the majority below 0. Therefore, the heavy metal pollution status of Tiaozi sediment may be considered as either class 0 (unpolluted) or class 1 (slightly polluted). Overall, the heavy metal most frequently tested in the sediment to reach class 1 was Cu, which accounted for 81.8% of the total. The proportion of both Cd and Zn in the sediment samples belonging to class 1 accounted for 63.6% of their total. The pollution status of the six heavy metals decreased in the order Cu (slightly polluted) > Cd (slightly polluted) = Zn (slightly polluted) > Ni (unpolluted) > Pb (unpolluted) > Mn (unpolluted).

With regard to the sampling sites, the classification for Cu, Cd, and Zn at site C was slightly polluted across the four seasons; site B was considered slightly polluted in spring, autumn, and winter and unpolluted in summer; at site A, only Cu was at slightly polluting levels in spring and autumn, with the other metals considered to be nonpolluting over the four seasons. The pollution levels of the sediments in the three sampling sites by heavy metals decreased in the order of C > B > A. As for the season, the number of the I_{geo} values belonging to class 1 in spring, summer, autumn, and winter accounted for 38.9%, 16.7%, 38.9%, and 66.7% of their total, respectively. The pollution level of the sediments in the four seasons by heavy metals decreased in the order of winter > autumn=spring > summer.

The results based on the above two methods for Tiaozi sediments reveal that it was slightly polluted by Cu, Ni, Cd, and Zn in some sites, especially, with the pollution of Cu being the most severe. Cu-containing effluents are mainly from electroplating, metallurgical, and machine factories [10]. The production of auto parts, special vehicles, and machinery equipment are leading industries in Siping, so Cu, as well as other metal pollution in Tiaozi River sediments, may be associated with the early emissions of wastewater from these industries. More research is required to further elucidate the pollution sources of heavy metals in the region.

Conclusions

Concentrations of Mn, Zn, Cu, Ni, Pb, and Cd in the overlying water and surface sediments of the Tiaozi River were highest in winter and lowest in summer. The contents of the six heavy metals in the water decreased from upstream to downstream, whereas those in the sediments increased from upstream to downstream. The water in Tiaozi River was unpolluted with the heavy metals, but the surface sediments were slightly polluted by Cu, Ni, Cd, and Zn. Further source identification of slightly polluted Cu, Ni, Cd, and Zn is highly recommended for the study area. In addition, more studies on chemical speciation and bioavailability of heavy metals are required to accomplish a comprehensive ecological risk assessment.

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