Spatial Distribution and Ecological Risk Assessment of Heavy Metals in Surface Sediment of Songhua River, Northeast China

LIU Baolin^{1, 2}, DONG Deming¹, HUA Xiuyi¹, DONG Weihua³, LI Ming⁴

(1. Key Laboratory of Groundwater Resources and Environment of Ministry of Education, College of New Energy and Environment, Jilin University, Changchun 130012, China; 2. College of Chemistry, Changchun Normal University, Changchun 130032, China; 3. College of Urban and Environmental Science, Changchun Normal University, Changchun 130032, China; 4. Key Laboratory of Songliao Aquatic Environment, Ministry of Education, School of Civil and Environmental Engineering, Jilin Jianzhu University, Changchun 130118, China)

Abstract: The Songhua River, one of the seven major rivers in China, locates in Northeast China with 1897 km long. This study aims to investigate the concentrations, distribution, source apportionment and ecological risk assessment of heavy metals including copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni) and chromium (Cr) in main stream and tributaries of the Songhua River in Jilin Province, Northeast China. Surface sediment samples (0-15 cm) were collected from 39 sampling sites in the Songhua River in July 2012. Concentrations of Cu, Zn, Cd, Pb, Ni and Cr were analyzed. The mean concentrations of heavy metals were (24.0 ± 9.2) mg/kg, (59.3 ± 18.0) mg/kg, (4.0 ± 2.1) mg/kg, (39.0 ± 27.9) mg/kg, (18.5 ± 8.6) mg/kg and (56.1 ± 17.6) mg/kg for Cu, Zn, Cd, Pb, Cr and Ni, respectively. The average contents of Cu, Cd, Pb, Cr and Ni were higher than their background values. Higher concentrations of heavy metals were found in the lower reaches with industrial enterprises and cities along the Songhua River. Zn, Pb and Ni might come from industrial sewage and mineral processing, while Cu and Cd were derived from electroplating wastewater and agricultural non-point source sewage. Cr originated from lithogenic sources. The concentrations of Cu, Zn and Cr were below the effect range low (ERL) at all sites, while Cd, Pb and Ni concentrations were detected ranging from ERL to the effect range median (ERM) at more than 15% of samples. Concentrations of Ni exceeded ERM in more than 50% of samples. The mean toxic units of heavy metals in the Songhua River decreased following the order: Cd (6.7) > Pb (2.2) > Ni (1.6) > Cu (0.7) > Cr (0.5) = Zn (0.5). Potential ecological risk index was found to be higher in middle and lower reaches of the Songhua River, where Cd could impose an extremely high ecological risk.

Keywords: heavy metals; surface sediment; ecological risk assessment; Songhua River; Northeast China

Citation: LIU Baolin, DONG Deming, HUA Xiuyi, DONG Weihua, LI Ming, 2021. Spatial Distribution and Ecological Risk Assessment of Heavy Metals in Surface Sediment of Songhua River, Northeast China. *Chinese Geographical Science*, 31(2): 223–233. https://doi.org/10.1007/s11769-021-1186-8

1 Introduction

Sediment serves as the carrier and reservoir of numerous pollutants migrating and transferring in aquatic environments (Förstner and Wittmann, 1981). Pollutants entering into rivers or lakes via various pathways can be adsorbed by suspended solid, and finally precipitate into sediment, which acts as an ultimate receptor of pol-

Received date: 2020-03-24; accepted date: 2020-07-03

Foundation item: Under the auspices of the National Natural Science Foundation of China (No. 42077343), the Major Science and Technology Program for Water Pollution Control and Treatment in China (No. 2009ZX07207-001-03), the Science and Technology Development Program of Jilin Province (No. 20200403020SF), the Natural Science Foundation of Changchun Normal University (No. 2019009)

Corresponding author: DONG Deming. E-mail: dmdong@jlu.edu.cn

© Science Press, Northeast Institute of Geography and Agroecology, CAS and Springer-Verlag GmbH Germany, part of Springer Nature 2021

lutants. However, sediment can re-suspend and migrate via water movements. In the meantime, the adsorbed pollutants could be released into water, resulting in secondary pollution due to the changes of sediments in granularity, properties and hydrological conditions (Nriagu, 1996).

Heavy metal pollution has received a widespread attention because of their environmental persistence and biological toxicity (Dong et al., 2011; Li et al., 2014b). They have a great impact on biological availability and toxicity of aquatic organisms (Hester and Harrison, 2006). More seriously, some heavy metals could accumulate and transfer in various species in freshwater food webs, leading to an increasing risk of rivers and oceans (Barhoumi et al., 2009; Chouvelon et al., 2019). Heavy metals in environments come from natural sources and anthropogenic sources including industrial activities, burning of fossil fuels, application of pesticides and chemical fertilizers, automobile exhausts, etc. (Nriagu and Pacyna 1988; Bergbäck et al., 2001; Förstner et al., 2004). However, little information is available on the levels, sources and ecological risk of heavy metals in a basin-scale study in China.

The Songhua River Basin is one of the regions with a dense population and rapid economic development in China. Its drainage area is 54 560 000 km², accounting for 69.3% of the total area of Northeast China. In recent years, the occurrence, behavior and ecological effects of heavy metals have been studied in the sediment of the Songhua River (Zhang et al., 2010; Li et al., 2017; Li et al., 2020), which have provided supports for understanding the pollution of sediments in the Songhua River Basin. However, these studies considered a small reach only and can not meet the theoretical and practical requirements for future exploitation and utilization towards the vast Songhua River. There are a lot of manufacturing activities along the Songhua River, including mining, petroleum processing, pharmaceutical industries, etc., which are considered to be the predominant sources (Gao et al., 2010). Jilin Province is known for its large-scale agricultural activities, which produce a large amount of non-point wastewater entering into rivers. Moreover, a large amount of domestic sewage is discharged into the Songhua River, leading to a declining tendency of the water quality (Li et al., 2017). This investigation on heavy metal contamination of sediment in watershed-scale will provide a detailed database to

policy planners for management and rejuvenation of the Songhua River. In addition, the methods used in this study were suitable for further analysis of the threats that human activities have posed on heavy metal pollution.

The major purposes of this study are: 1) investigating the distribution characteristics of heavy metals in surface sediments of the Songhua River using a geostatistical method; 2) evaluating potential ecological risks of the heavy metals referring to the standards of sediment quality; 3) analyzing the sources of heavy metals using factor analysis and multivariate statistical analysis.

2 Materials and Methods

2.1 Study area

The Songhua River traverses the central and eastern part of Northeast China with an overall length of 1897 km. The Songhua River Basin has a temperate continental monsoon climate with annual precipitation of about 500-1000 mm concentrated in summer. The soil consists of sand, loam and clay. There are abundant mineral resources distributed in the basin (e.g., gold, nickel, iron, copper, silica, etc.) (Liu et al., 2015). The Songhua River in Jilin Province flows through Jilin, Yushu, Fuyu and Songyuan cities. The Songhua River Basin serves 21.77 million people, accounting for 79% of the total population of Jilin Province (Statistics Bureau of Jilin Province, 2016). Jilin is famous for its large-scale manufacturing activities, including petroleum processing, chemical industry, electroplating, etc. Yushu, Fuyu and Songyuan cities are known for the grain production and processing.

2.2 Sample collection and analysis

The present study was conducted in July 2012 at 39 sites considering 790 km river stretch in Jilin Province from Lake Tianchi in Changbai Mountain to Fuyu County covering over 40% of the river length (Fig. 1). There are 16 sites from the mainstream and 18 sites from the main tributaries, including 6 sites at the Gudong River, 6 sites at the Huifa River, 4 sites at the Yinma River, 1 site at the Yitong River and 1 site at the Lalin River. We also collected 5 sediment samples from the Hunjiang River located in the Songhua River Basin. Three sampling sites were chosen in the distance of 1/4, 1/2, 3/4 width of each site from the river for obtaining

the mean concentrations of heavy metals. According to Hao et al. (2009), the average sedimentation rate in the Songhua River was determined to be 0.7 cm/yr. The surface sediment was sampled at the depth of 0-15 cm, which could be representative of 20 vr of sedimentary history in the Songhua River. The sediment samples were collected using a self-made grab sampler, and then enclosed in polythene bags and taken back to the laboratory from Jilin University. After the sediments were airdried at room temperature, they were ground and then sieved by a 100-mesh nylon screen. The homogenized sediment was digested using the ternary acid mixture (HNO₃-HClO₄-HF). The process of digestion was as follows: 10 mL of nitric acid was added in a 50 mL polytetrafluoroethylene (PTEE) beaker in which approximate 0.5 g of dried sample was previously added. Each beaker was heated on a low temperature to resolve organic matter. When the mixture was viscous, 10 mL of hydrofluoric acid was added to remove the silicon. At last, the beaker was continued to heat until the white smoke ran out after 5 mL of perchloric acid was added. After the digestion, the beaker was washed by dilute nitric acid, and then the eluent was diluted to 50 mL. Heavy metals were measured by a Shimadzu atomic absorption spectrophotometer (AA6300, Shimadzu, Japan).

2.3 Quality control (QC)

The sediment certified reference materials GBW07311 (GSD-11) and GBW07366 (GSD-23) were used to ensure the precision and accuracy. The limits of detection (LODs) were 0.9 mg/kg, 0.5 mg/kg, 0.2 mg/kg, 1.9 mg/kg, 4.8 mg/kg and 4.6 mg/kg for copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni) and chromium (Cr), respectively. Recoveries of Cu, Zn,

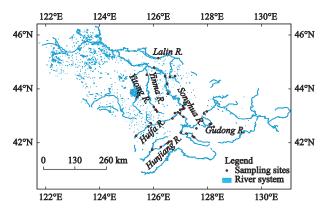


Fig. 1 Map showing the sampling sites along the Songhua River

Cd, Pb, Ni and Cr were 95%–104%, 94%–105%, 92%–99%, 86%–102%, 96%–104% and 90%–105%, respectively. QC was conducted by reagent blank and sample blank. All the analyses were carried out in triplicate, and the standard deviations were within $\pm 5\%$ of the mean values.

2.4 Sediment quality guidelines

MacDonald et al. (2000) has developed two kinds of sediment quality guidelines to evaluate the ecological risks from heavy metals in the sediments to freshwater ecosystem: 1) the effect range low (ERL) / effect range median (ERM) and 2) the threshold effect level (TEL) or probable effect level (PEL). Low range effects (i.e., ERLs or TELs) are neglected due to the extremely low impacts on zoobenthos. However, median range effects (i.e., ERM or PEL) referring to the concentration higher than the threshold, has the possibility of causing adverse effect on zoobenthos. Therefore, the ratios between detectable concentrations and ERM or PEL can be used to evaluate the toxic effects of heavy metals (Pedersen et al., 1998).

2.5 Toxic unit (TU) and potential ecological risk index (PERI)

The estimation of the potential toxicity of heavy metal in sediment was performed using toxic unit (*TU*, Pedersen et al., 1998), which was calculated using Equ. 1.

$$TU = C_i / PEL \tag{1}$$

where C_i is the concentration of heavy metal i; PEL is the probable effect level. we use $\sum TU$ to represent the ecological risk of all the studied heavy metals at each sampling site.

The ecological risk of individual metal (E_r^i) and potential ecological risk index (PERI) was also employed to assess ecological risk of heavy metals in sediment (Hakanson, 1980) and could be defined as Equs. 2 and 3.

$$E_r^i = T_r^i \times \left(\frac{C_i}{C_0}\right) \tag{2}$$

$$PERI = \sum_{i=1}^{n} T_r^i \times \left(\frac{C_i}{C_0}\right) \tag{3}$$

where n is the number of heavy metals, C_0 is the background value of heavy metal, T_r^i is the biological toxicity factor r of individual metal i, which was defined as 5 for Cu, Pb and Ni, 1 for Zn, 2 for Cr, and 30 for Cd

(Suresh et al., 2012). The evaluation standard was illustrated as follows (Li et al., 2016): $E_r^i < 40$, low risk level; 40–80, moderate risk level; 80–160, considerable level; 160–320, high level; >320, very high risk level. *PERI* <150, low risk level; 150–300, moderate risk level; 300–600, considerable level; and > 600, high risk level.

2.6 Statistics analysis

Pearson correlation analysis and factor analysis were applied to investigate the correlations and the common pollution sources among the heavy metals. The significant components and associate loadings were extracted by principal component analysis (PCA) in which the method of varimax was used. PCA leads to a reduction of initial dimension of data (Islam et al., 2018) and has been widely used to identify the sources of heavy metals (Amano et al., 2011; Bai et al., 2011; Wang et al., 2012; Hu et al., 2013; Li et al., 2013a;b). Hierarchical clustering analysis (HCA) and PCA are often employed to confirm results and provide grouping of variables (Li et al., 2015). In this study, HCA was used to understand the

relationships among heavy metals on the same dataset as PCA. Analysis was performed by Excel and SPSS (version 20.0).

3 Results and Discussion

3.1 Spatial distribution of heavy metals in surface sediment

The concentrations of heavy metals in surface sediments of the Songhua River were summarized in Table 1. The mean concentrations of the heavy metals decrease with Zn (59.3 mg/kg) > Ni (56.0 mg/kg) > Pb (39.0 mg/kg) > Cu (24.0 mg/kg) > Cr (18.5 mg/kg) > Cd (4.0 mg/kg). The mean concentrations of metals were higher than background values (Table 1) except Zn, and higher than ERM except Pb, whereas Cd, Pb, and Ni were higher than PEL.

Spatial distribution of Cd, Pb, Zn, Cu, Cr and Ni in surface sediment of the Songhua River was shown in Fig. 2. Cu and Zn, two micronutrients for aquatic organisms in natural water, are toxic when their concentrations exceed the limits (Hall et al., 1997). The concentrations

 Table 1
 Descriptive statistics of heavy metal concentrations in surface sediments of the Songhua River

	Cd	Pb	Zn	Cu	Cr	Ni	
Minimum / (mg/kg)	2.0	2.4	17.0	8.5	9.7	17.5	
Maximum / (mg/kg)	11.0	86.4	98.5	49.4	39.6	90.8	
Mean / (mg/kg)	4.0	39.0	59.3	24.0	18.5	56.0	
S.D. / (mg/kg)	2.1	27.9	18.0	9.2	8.6	17.6	
CV / %	52.3	71.6	30.4	38.3	46.6	31.5	
$ERL^a / (mg/kg)$	5.0	35.0	120.0	70.0	80.0	30.0	
ERM / (mg/kg)	9.0	110.0	270.0	390.0	145.0	50.0	
TEL / (mg/kg)	0.6	18.0	123.0	35.7	37.3	35.0	
PEL / (mg/kg)	3.5	36.0	315.0	197.0	90.0	91.3	
Compared with TEL and PEL	the ratio of samples to the total samples in each guideline						
< TEL / %	0	35.9	100	92.3	94.9	12.8	
\geq TEL $<$ PEL $/$ %	61.5	2.6	0	7.7	5.1	87.2	
≥ PEL (%)	38.5	61.5	0	0	0	0	
Compared with ERM and ERL	the ratio of samples to the total samples in each guideline						
< ERL / %	79.5	38.5	100	100	100	7.7	
≥ ERL < ERM (%)	18.0	61.5	0	0	0	23.1	
$\geq ERM / \%$	2.5	0	0	0	0	69.2	
Background value ^b (mg/kg)	0.14	24.0	71.0	17.7	17.3	22.0	

Notes: S.D., standard deviation; CV, coefficients of variation; TEL, threshold effect level; PEL, probable effect level; ERL: effects range low; ERM, effects range median. ^a Threshold effect level or probable effect level for freshwater ecosystem (MacDonald et al., 2000). ^b Background value of sediment in the Songhua River (Li and Zheng, 1989)

trations of Cu ranged from 8.5 to 49.4 mg/kg, which were lower than TEL at most sampling sites. The concentrations of Cu in sediment samples from certain subareas (e. g., the Hunjiang River and the middle reach of the Songhua River) were much higher than those from other subareas (Fig. 2a). The concentrations of Zn ranged from 17.0 to 98.5 mg/kg, which were higher than TEL especially in the downstream and posed a toxic effect to aquatic organisms (Fig. 2b).

Ni and Cr are frequently associated with rocks. There are high concentrations of Ni and Cr in the earth's crust. In this study, Cr concentrations ranged from 9.7 to 39.6 mg/kg, which were higher in the midstream sediment of the Songhua River (Fig. 2c). However, the concentrations of Cr did not exceed its TEL, which had little effect on aquatic organisms. Ni concentrations ranged from 17.5 to 90.8 mg/kg, exceeding TEL in most samples in middle and lower reaches of the Songhua

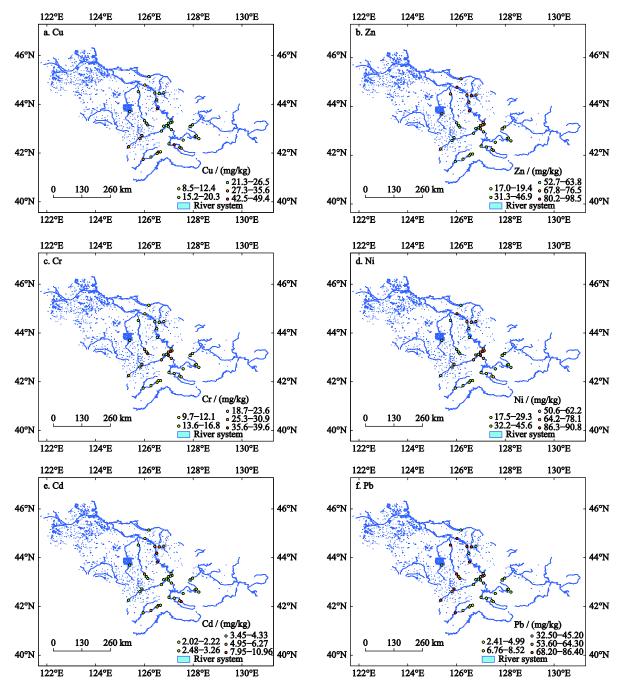


Fig. 2 Spatial distributions of Cu, Zn, Cr, Ni, Cd, Pb in surface sediments of the Songhua River

River, which could probably be toxic to aquatic organisms (Fig. 2d). Cr and Ni had similar spatial distributions. High concentrations of Cr and Ni were found in the sediment samples located in the middle reach of the Songhua River, where there were a larger amount of mining industries distributed (Liu et al., 2014).

The concentrations of Cd ranged from 2.0 to 11.0 mg/kg, which were higher than background value and TEL in all sampling sites. Furthermore, Cd concentrations in downstream sediments were extremely high (Fig. 2e), which had a great adverse effect on aquatic organisms. Comparing to other elements, Pb could threaten the survival of aquatic organisms even at a low concentration (Sadiq et al., 2003). The concentrations of Pb ranging from 2.4 to 86.4 mg/kg were found to be higher in middle and lower reaches (Fig. 2f). Pb concentrations exceeded TEL in all the downstream, resulting in high ecological risks. High levels of Cd and Pb were found in the sediments located in urban river of Jilin, which was recognized as well-developed manufacturing cities

(Dong et al., 2018). High concentrations of Cd and Pb were likely to be related to the industrial wastewater discharge. Moreover, high concentrations of Pb were found in the sediments located in the Huifa River, which was likely to be related to local mining activities.

A comparison was made on mean concentrations of six heavy metals in sediments of the rivers in China. As shown in Fig. 3, the highest mean concentrations of Cu, Zn, Cd, Pb and Ni were observed in samples collected from the Xiangjiang River at 101 mg/kg, 443 mg/kg 13.7 mg/kg, 215 mg/kg and 57.1 mg/kg, respectively (Chai et al., 2017). The concentration of Ni in the Xiangjiang River is comparable to that in the Songhua River in Jilin Province at 56 mg/kg (this study). The highest mean concentrations of Cr were found in samples collected from the Songhua River (Harbin region) at 121 mg/kg (Li et al., 2017), and the Xiangjiang River at 120 mg/kg (Chai et al., 2017). The Lowest concentrations of Cu and Ni were observed in samples collected from the Songhua River Harbin region at 13.3 mg/kg

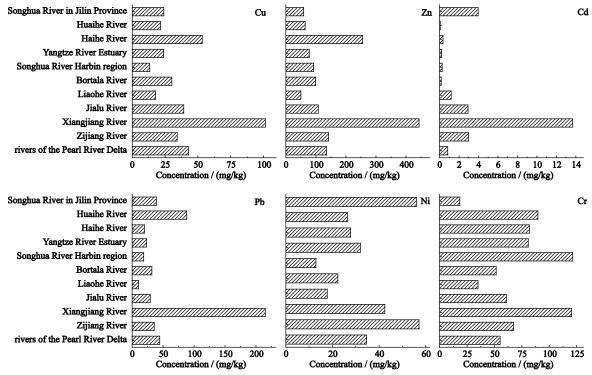


Fig. 3 Mean concentrations of Cu, Zn, Cd, Pb, Ni and Cr in sediments collected from China. The data for the Songhua River in Jilin Province were from this study. The data for the Huaihe River were from Yang et al. (2017). The data for the Haihe River were from Tang et al. (2013). The data for the Yangtze River Estuary were from Wang et al. (2014). The data for the Songhua River Harbin region were from Li et al. (2017). The data for the Bortala River were from Zhang et al. (2016). The data for the Liaohe River were from Ke et al. (2017). The data for the Jialu River were from Fu et al. (2014). The data for the Xiangjiang River were from Chai et al. (2017). The data for the Zijiang River were from Zhang et al. (2018)

and 12.9 mg/kg, respectively (Li et al., 2017). Concentrations of Zn and Cr in the Songhua River in Jilin Province presented the lowest among the listed rivers in China. Moreover, Tang et al. (2013) reported the lowest concentration of Cd in samples collected from the Huaihe River at 0.1 mg/kg, and Ke et al. (2017) reported the lowest concentration of Pb in samples collected from the Liaohe River at 10.6 mg/kg. The results indicated that the relatively high concentrations of Cd and Ni were observed in the sediments from the Songhua River compared to other rivers in China, which was likely due to the increase in pollution attributable to rapid industrial development during the last few decades (Li et al., 2017).

3.2 Source apportionment of heavy metals

The result of PCA for heavy metal contents was presented in Table 2. Heavy metals could be grouped into two principle components (PCs) accounting for 73.3% of all the data variation. PC1 was loaded with Pb, Zn, and Ni explaining 47.2% of the total variance, suggesting that

they may have similar sources (Omwene et al. 2018; Siddigui and Pandey, 2019). Considering that Pb, Zn and Ni concentrations being higher than background values were mainly distributed in middle and lower reaches, PC1 may be related to anthropogenic sources, for instance, the industries of metal smelting, automobile exhaust, coal, coating material, etc. PC2 explained 26.1% of the total variance and showed a strong loading of Cd and Cu, indicating that they may have common sources. The Songhua River is heavily polluted by Cd, with the concentration greatly exceeding background values in all sampling sites. Cd can be fixed and deposited into sediment in the form of carbonate or hydroxide complex at an alkaline condition (Li et al., 2014a). Cd was always considered as the marker of unreasonable agricultural management (Satpathy et al., 2014; Mustafa and Komatsu, 2016). PC2 indicated electroplating wastewater and agricultural non-point source sewage (Bai et al., 2011). Cr had relatively strong correlation with conservative element Fe (Table 3), sug-

Table 2 Total variance explained by principle component analysis of heavy metals in surface sediments of the Songhua River (two principal components are elected)

Florens	Compone	ent matrix	Rotated component matrix	
Element	PC1	PC2	PC1	PC2
Cd	0.081	0.791	0.054	0.793
Pb	0.906	0.102	0.902	0.133
Zn	0.842	0.046	0.840	0.074
Cu	0.048	0.879	0.018	0.880
Cr	0.784	0.095	0.780	0.121
Ni	0.825	-0.378	0.837	-0.350
Initial eigenvalue	2.834	1.563	2.832	1.565
Proportion of total variance/%	47.225	26.055	47.201	26.079
Proportion of cumulative variance /%	47.225	73.280	26.079	73.280

Table 3 Correlation analysis of heavy metals in surface sediments of the Songhua River

Element	Cd	Pb	Zn	Cu	Cr	Ni	Fe
Cd	1	0.141	0.104	0.436**	0.006	-0.112	-0.162
Pb		1	0.739**	0.109	0.628**	0.644**	-0.086
Zn			1	0.060	0.464**	0.605	-0.242
Cu				1	0.202	-0.309	0.010
Cr					1	0.567**	0.363*
Ni						1	0.216
Fe							1

Notes: ** Correlation is significant at the 0.01 level (2-tailed); * significant at the 0.05 level

gesting that Cr in the sediment is preferred to bind to the Fe-Mn oxides, which could be related to a lithogenic contribution (Cox and Preda 2005; Hu et al., 2013; Brady et al. 2014; Saleem et al., 2015).

A dendrogram of heavy metal contents was shown in Fig. 4. In this dendrogram, there are two completely different clusters, one consists of Pb, Zn and Ni, while the other includes Cd, Cu and Cr. Different from PCA result, Cr is classified into cluster-2 group, suggesting anthropogenic inputs. These two groups of metals come from different sources, confirming the PCA results.

3.3 Ecological risk assessment of heavy metals in surface sediment

Numerical sediment quality guidelines (SQGs) are usually used to evaluate the degree of adverse impacts from the sediment-associated chemical substances on aquatic organisms (MacDonald et al., 2000; Caeiro et al., 2005). The results of potential effects in sediment were shown in Table 1. Compared with TEL and PEL standards, the concentrations of Cd, Pb and Ni in most samples were higher than TEL. The concentrations of Cd and Pb higher than PEL were found in 38.5% and 61.5% of samples , respectively. However, compared with ERL and ERM standards, Cu, Zn and Cr concentrations in all the samples were lower than ERL. The concentrations of Cd, Pb and Ni in 18.0%, 61.5% and 23.1% of samples were in the range from ERL to ERM, respectively. The concentrations of Cd and Ni in 2.5% and 69.2% of samples were higher than ERM.

Fig. 5a showed the \sum TU distribution of heavy metals in the Songhua River. \sum TU exceeded 5 at all the sampling sites, which was above the moderate toxicity level (Pedersen et al., 1998). Higher toxicity was observed in middle and lower reaches of the Songhua River. Based on the composition of heavy metals (Fig. 5b),

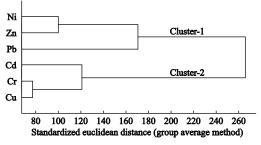


Fig. 4 Hierarchical clustering analysis of heavy metals in surface sediments of the Songhua River

Cd accounted for a very high percentage of \sum TU in all the samples of the Songhua River. Pb and Ni were also the main components in middle and lower reaches due to the mining and discharge of chemical sewage. The average toxicity of heavy metals in sediments of the Songhua River appeared in the order as Cd (6.7) > Pb (2.2) > Ni (1.6) > Cu (0.7) > Cr (0.5) = Zn (0.5). The contributions of \sum TU decreased in the order of Cd (55.0%), Pb (18.0%), Ni (13.1%), Cu (5.7%), Cr (4.1%) and Zn (4.1%) (Fig. 6).

The average E_r of the heavy metals decreased in following sequence: Cd (849) >> Ni (12.7) > Pb (8.1) > Cu

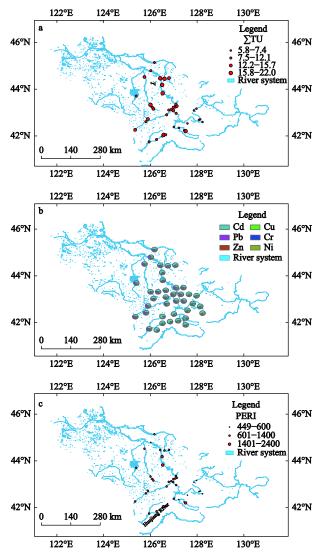


Fig. 5 Spatial distribution of the sum of the toxic units (a), composition of toxic units of all heavy metals (b) and potential ecological risk index (PERI) (c) in surface sediments of the Songhua River

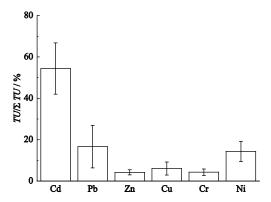


Fig. 6 Contributions of heavy metals to the sum of toxic units in surface sediments of the Songhua River

(6.8) > Cr (2.1) > Zn (0.8). The average E_r of Ni, Pb, Cu, Cr and Zn was less than 40, indicating a low ecological risk. The E_r of Cd was greater than 320 in all the sediment samples, suggesting a very high risk to aquatic organism. The result of PERI of heavy metals in surface sediment of the Songhua River was shown in Fig. 5c. PERI values of heavy metals indicated high-risk grades in 74% of sediments collected from middle and lower reaches and most of tributaries of the Songhua River, where Cd imposed a very high risk, probably due to the wastewater input from upstream and nearby urban and industrial discharge and agro-runoff. Further research on the remediation of Cd in surface sediments of the Songhua River should be conducted. The Gudong River, an important tributary in the upper reaches of the Songhua River, showed a considerable risk of heavy metals with PERIs less than 600. In addition, the PERI was found to be higher in mainstream than in tributaries of the Songhua River (P < 0.05), indicating that surface sediments from mainstream were seriously polluted by heavy metals.

4 Conclusions

The basin-scale study provides information on the distribution, sources, and ecological risks of six heavy metals in the surface sediment of the Songhua River. The mean concentrations of studied heavy metals exceeded their geochemical background levels in the Songhua River except Zn. The spatial distribution of heavy metals was in close relationship with the emission characteristics along the Songhua River. Lower pollution levels and ecological risks of heavy metals were observed in sediments from upper reaches of the Songhua River and the

Gudong River. Higher concentrations of Zn, Ni, Cd and Pb were found in middle and lower reaches of the Songhua River, indicating a great adverse effect on aquatic organisms. Source apportionment found that industrial sewage and mineral processing dominated higher concentrations of Pb, Zn and Ni in sediments. High concentrations of Cd were observed in the whole basin, which can be associated with electroplating and agricultural non-point sewage. Cr may originate from geogenic sources, as the low concentrations are comparable to its background value. The ecological risk of an individual metal demonstrated that Cd was at an extremely highrisk level in surface sediment of the Songhua River, while the other studied metals were at low risk levels. PERI also revealed that Cd was the most serious ecological risk factor. The ubiquitous presence of heavy metals revealed their widespread distribution in the sediments of the Songhua River. This study could provide a large amount of detailed information to understand the contamination levels of heavy metals and establish rational ecological protection measures in the Songhua River.

References

Amano A, Kuwae M, Agusa T et al., 2011. Spatial distribution and corresponding determining factors of metal concentrations in surface sediments of Beppu Bay, southwest Japan. *Marine Environmental Research*, 71(4): 247–256. doi: 10.1016/j.marenvres.2011.01.009

Bai J, Cui B, Chen B et al., 2011. Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland, China. *Ecological Modelling*, 222(2): 301–306. doi: 10.1016/j.ecolmodel.2009.12.002

Barhoumi S, Messaoudi I, Deli T et al., 2009. Cadmium bioaccumulation in three benthic fish species, *Salaria basilisca*, *Zosterisessor ophiocephalus* and *Solea vulgaris* collected from the Gulf of Gabes in Tunisia. *Journal of Environmental Sciences*, 21: 980–984. doi: 10.1016/S1001-0742(08)62371-2

Bergbäck B, Johansson K, Mohlander U, 2001. Urban metal flow—a case study of Stockholm. *Review and conclusions*. *Water, Air, and Soil Pollution: Focus*, 1(3–4): 3–24. doi: 10.1023/A:1017531532576

Brady J P, Ayoko G A, Martens W N et al., 2014. Enrichment, distribution and sources of heavy metals in the sediments of Deception Bay, Queensland, Australia. *Marine Pollution Bulletin*, 81: 248–255. doi: 10.1016/j.marpolbul.2014.01.031

Caeiro S, Costa M N, Ramos T B et al., 2005. Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. *Ecological Indicators*, 5(2): 151–169. doi:

- 10.1016/j.ecolind.2005.02.001
- Chai L, Li H, Yang Z et al., 2017. Heavy metals and metalloids in the surface sediments of the Xiangjiang River, Hunan, China: distribution, contamination, and ecological risk assessment. *Environmental Science and Pollution Research*, 24(1): 874–885. doi: 10.1007/s11356-016-7872-x
- Chouvelon T, Strady E, Harmelin-Vivien M et al., 2019. Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton –zooplankton –small pelagic fish marine food web. *Marine Pollution Bulletin*, 146: 1013–1030. doi: 10.1016/j.marpolbul.2019.07.047
- Cox M E, Preda M, 2005. Trace metal distribution within marine and estuarine sediments of western Moreton Bay, Queensland, Australia: relation to land use and setting. *Geographical Research*, 43(2): 173–193. doi: 10.1111/j.1745-5871.2005. 00312.x
- Dong J, Yu M, Bian Z et al., 2011. Geostatistical analyses of heavy metal distribution in reclaimed mine land in Xuzhou, China. *Environmental Earth Sciences*, 62(1): 127–137. doi: 10.1007/s12665-010-0507-5
- Dong W, Liu B, Song Y et al., 2018. Occurrence and partition of perfluorinated compounds (PFCs) in water and sediment from the Songhua River, China. *Archives of Environmental Contamination and Toxicology*, 74: 492–501. doi: 10.1007/s00244-017-0474-x
- Förstner U, Heise S, Schwartz R et al., 2004. Historical contaminated sediments and soils at the river basin scale: examples from the Elbe River Catchment Area.. *Journal of Soils and Sediments*, 4(4): 247–260. doi: 10.1007/BF02991121
- Förstner U, Wittmann G T W, 1981. *Metal pollution in the aquatic environment*. Berlin: Springer–Verlag. doi: 10.1007/978-3-642-69385-4
- Fu J, Zhao C, Luo Y et al., 2014. Heavy metals in surface sediments of the Jialu River, China: their relations to environmental factors. *Journal of Hazardous Materials*, 270: 102–109. doi: 10.1016/j.jhazmat.2014.01.044
- Gao Y, Li W, Zhang D et al., 2010. Bio—enhanced activated carbon filter with immobilized microorganisms for removing organic pollutants in the Songhua River. *Water Science and Technology*, 62(12): 2819–2828. doi: 10.2166/wst.2010.666
- Hakanson L, 1980. An ecological risk index for aquatic pollution control. *A sedimentological approach. Water Research*, 14(8): 975–1001. doi: 10.1016/0043-1354(80)90143-8
- Hall L W Jr, Scott M C, Killen W D, 1997. A screening level probabilistic ecological risk assessment of copper and cadmium in the chesapeake bay watershed. Chesapeake Bay Program, Annapolis, MD: US EPA.
- Hao L, Liu H, Lu J et al., 2009. Vertical distribution of ¹³⁷Cs and ²¹⁰Pb and sedimentation rate in Songhua Lake. *Journal of Jilin University (Earth Science Edition)*, 39(3): 470–473. (in Chinese)
- Hester R E, Harrison R M, 2006. Risk assessment of metals in the environment. *Issues in Environmental Science & Technology*, 22: 102–131. doi: 10.1039/9781847552440-00102

- Hu B Q, Li J, Zhao J T et al., 2013. Heavy metal in surface sediments of the Liaodong Bay, Bohai Sea: distribution, contamination, and sources. *Environmental Monitoring and Assessment*, 185(6): 5071–5083. doi: 10.1007/s10661-012-2926-0
- Islam M S, Hossain M B, Matin A et al., 2018. Assessment of heavy metal pollution, distribution and source apportionment in the sediment from Feni River estuary, Bangladesh. *Chemo-sphere*, 202: 25–32.
- Ke X, Gui S F, Huang H et al., 2017. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. *Chemosphere*, 175: 473–481. doi: 10.1016/j.chemosphere.2017.02.029
- Li Jian, Zheng Chunjiang, 1988. Databook of environmental background value. Chinese Environmental Science Press, Beijing, China, 342–348. (in Chinese)
- Li F, Huang J, Zeng G et al., 2013a. Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. *Journal of Geochemical Exploration*, 132: 75–83. doi: 10.1016/j.gexplo.2013.05.007
- Li K Y, Cui S, Zhang F X et al., 2020. Concentrations, possible sources and health risk of heavy metals in multi-media environment of the Songhua River, China. *International Journal of Environmental Research and Public Health*, 17(5): 1766. doi: 10.3390/ijerph17051766
- Li N, Tian Y, Zhang J et al., 2017. Heavy metal contamination status and source apportionment in sediments of Songhua River Harbin region, Northeast China. *Environmental Science* and *Pollution Research*, 24(4): 3214–3225. doi: 10.1007/ s11356-016-7132-0
- Li R Y, Li R L, Chai M W et al., 2015. Heavy metal contamination and ecological risk in Futian mangrove forest sediment in Shenzhen Bay, South China. *Marine Pollution Bulletin*, 101(1): 448–456. doi: 10.1016/j.marpolbul.2015.09.048
- Li X, Wang Y, Li B et al., 2013b. Distribution and speciation of heavy metals in surface sediments from the Yangtze estuary and coastal areas. *Environmental Earth Science*, 69(5): 1537–1547. doi: 10.1007/s12665-012-1988-1
- Li Y, Zhang H, Chen X et al., 2014a. Distribution of heavy metals in soils of the Yellow River Delta: concentrations in different soil horizons and source identification. *Journal of Soils* and Sediments, 14: 1158–1168. doi: 10.1007/s11368-014-0861-0
- Li Z Y, Ma Z W, Van der Kuijp T J et al., 2014b. A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment*, 468–469: 843–853. doi: 10.1016/j.scitotenv.2013.08.090
- Liu B, Bi S, Dong D et al., 2014. Background values of certain heavy metal elements in the sediments of the upper reach of Songhua River. *Journal of Jilin Agricultural University*, 36(4): 454–459. (in Chinese)
- Liu B, Diao G, Han X et al., 2015. Spatial distribution and ecological risk assessment of heavy metals in surface sediments from Songhua River. Science Technology and Engineering, 15(8): 140–145. (in Chinese)

- MacDonald D D, Ingersoll C G, Berger T A, 2000. Development and evaluation of consensus—based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 39(1): 20–31. doi: 10.1007/s002440010075
- Mustafa G, Komatsu S, 2016. Toxicity of heavy metals and metal-containing nanoparticles on plants. *Biochimica et Biophysica Acta (BBA) Proteins and Proteomics*, 1864(8): 932–944. doi: 10.1016/j.bbapap.2016.02.020
- Nriagu J O, 1996. A history of global metal pollution. *Science*, 272(5259): 223–224. doi: 10.1126/science.272.5259.223
- Nriagu J O, Pacyna J M, 1988. Quantitative assessment of world-wide contamination of air, water, and soils by trace metals. *Nature*, 33(6169): 134–139.
- Omwene P I, Öncel M S, Çelen M et al., 2018. Heavy metal pollution and spatial distribution in surface sediments of Musta-fakemalpaşa stream locaOryza sativated in the world's largest borate basin (Turkey). *Chemosphere*, 208: 782–792.
- Pedersen F, Bjørnestad E, Andersen H V et al., 1998. Characterization of sediments from Copenhagen Harbour by use of biotests. *Water Science and Technology*, 37(6–7): 233–240.
- Sadiq R, Husain T, Bose N et al., 2003. Distribution of heavy metals in sediment pore water due to offshore discharges: an ecological risk assessment. *Environmental Modelling & Software*, 18(5): 451–461. doi: 10.1016/S1364-8152(03)00010-0
- Saleem M, Iqbal J, Shah M H, 2015. Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—a case study from Mangla Lake, Pakistan. *Environmental Nanotechnology, Monitoring & Management*, 4: 27–36. doi: 10.1016/j.enmm.2015.02.002
- Satpathy D, Reddy M V, Dhal S P, 2014. Risk assessment of heavy metals contaminationin paddy soil, plants, and grains (*Oryza sativa* L.) at the East Coast of India. *Biomed Research International*, 1–11. doi: 10.1155/2014/545473
- Siddiqui E, Pandey J, 2019. Assessment of heavy metal pollution in water and surface sediment and evaluation of ecological risks associated with sediment contamination in the Ganga River: a basin-scale study. *Environmental Science and Pollution Research*, 26(11): 10926–10940. doi: 10.1007/s11356-019-04495-6

- Statistics Bureau of Jilin Province, 2016. Available at http://tjj.jl.gov.cn/tjsj/tjnj/2016/ml/indexc.htm.
- Suresh G, Sutharsan P, Ramasamy V et al., 2012. Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. *Ecotoxicology and Environmental Safety*, 84: 117–124. doi: 10.1016/j.ecoenv.2012.06.027
- Tang W Z, Zhao Y, Wang C et al., 2013. Heavy metal contamination of overlying waters and bed sediments of Haihe Basin in China. *Ecotoxicology and Environmental Safety*, 98: 317–323. doi: 10.1016/j.ecoenv.2013.09.038
- Wang F, Wang W X, Huang X P, 2012. Spatial distribution of gut juice extractable Cu, Pb and Zn in sediments from the Pearl River Estuary, Southern China. *Marine Environmental Research*, 77: 112–119. doi: 10.1016/j.marenvres.2012.03.002
- Wang J W, Liu R M, Zhang P P et al., 2014. Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary. *Marine Pollution Bulletin*, 87(1–2): 364–373. doi: 10.1016/j.marpolbul. 2014.07.048
- Yang Y, Jin Q, Fang J M et al., 2017. Spatial distribution, ecological risk assessment, and potential sources of heavy metal (loid)s in surface sediments from the Huai River within the Bengbu section, China. *Environmental Science and Pollution Research*, 24(12): 11360–11370. doi: 10.1007/s11356-017-8732-z
- Zhang Z S, Sun X J, Wang Q C et al., 2010. Recovery from mercury contamination in the Second Songhua River, China. *Water Air and Soil Pollution*, 211(1–4): 219–229. doi: 10.1007/s11270-009-0294-3
- Zhang Z X, Lu Y, Li H P et al., 2018. Assessment of heavy metal contamination, distribution and source identification in the sediments from the Zijiang River, China. *Science of the Total Environment*, 645: 235–243. doi: 10.1016/j.scitotenv.2018. 07.026
- Zhang Z Y, Li J Y, Mamat Z et al., 2016. Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. *Ecotoxicology and Environmental Safety*, 126: 94–101. doi: 10.1016/j.ecoenv.2015. 12.025