Heavy Metal Concentration Distribution and Ecological Risk Assessment of Songhua River Sediments

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Keywords: Heavy Metal, Ecological Risk Assessment, Songhua River

Abstract: Contamination level, ecological risk of heavy metals in sediments form Songhua River were investigated in this study. The results founded that the total concentration of Cr, Ni, Cu, As, Cd and Pb were in the range of 32.38-60.77,12.51-46.49,13.6-34.81,29.6-107.11,0.5-1.93 and 26.07-72.38mg/kg, respectively. The correlation and principal component analysis results showed that Cr, Ni, Cu and Pb may have similar pollution sources or common bioaccumulation. The geo-accumulation index (I_{geo}) showed that Cd and As contributed a very high ecological risk in this study.

1. Introduction

Heavy metal pollutants featuring extensive sources, long time with residual toxicity, difficulty in biodegradation, have posed potential threats to living beings in the river and human beings (Alkarkhi et al., 2009). While sediment is an important composition of the river ecosystem, which has always exchanged material and energy with the river water as a carrier (Malvandi, 2017;). Most heavy metals discharged into water can be absorbed by river sediment with a strong accumulative effect presented, which may directly and indirectly threat human beings and ecosystems through a series of physical, chemical and biological effects(Da et al., 2015).

Songhua River Basin is an energy production base with developed heavy industry in China, possessing an important position in the country's economic development(Ren et al., 2013). Songhua River, one of the seven greatest water systems in China, is the most important tributary of Sino-Russian Heilong Boundary River, which exerts a great influence on the water quality of the Heilong Boundary River(Cui et al., 2016). The whole basin of Songhua River is composed of the main stream of the Songhua River, the Second Songhua River and the Nen River Valley. The Songhua River was once polluted severely by heavy metal in the history(Zhang et al., 2015). Along with the rapid economic development in the Songhua River Basin in recent years, elements of heavy metals can be assessed to the Songhua River through precipitation and direct surface runoff due to water pollution and air pollution resulted from intensive human activities, which may result in heavy metal pollution in the Songhua River.

The main objectives of the research are (1) to analyze the spatial distribution of heavy metals in the Songhua River Basin; (2) to analyze the correlation among heavy metals to determine the sources of pollution among heavy metals with Pearson and PCA; and (3) to perform ecological risk assessment of heavy metal with the geo-accumulation index (I_{geo}) .

2. Materials and methods

2.1 Samples collection and preparation

Sixteen surface sediments were collected from Songhua River during September 2016(Fig1). Three random replicates of surface sediment (5cm form the top) were collected by spade at each sample sites. Each samples were saved in clean polyethylene bags and brought back to the lab. And

  DOI: 10.25236/icemeet.2019.145

then, the sediment samples were freeze-dried and crushed in an agate mortar, passed through a nylon 100-mesh sieve. All samples must be carefully handled to avoid loss of trace elements during analysis.

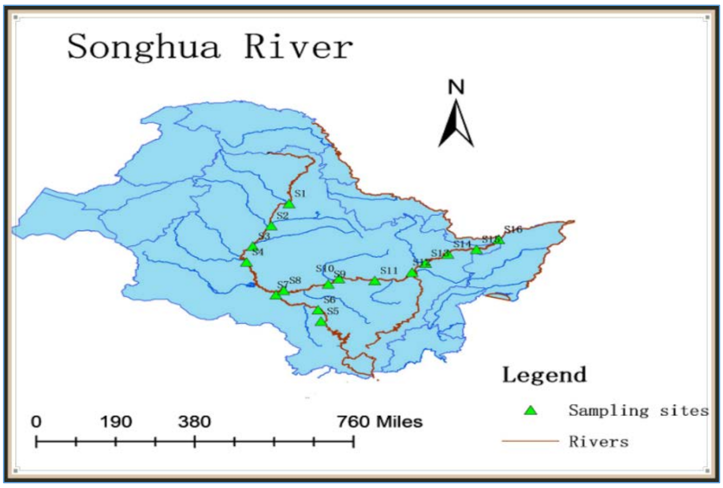

Fig.1. Sampling sites form Songhua River

2.2 Analysis of samples

Total concentrations of Cr,Ni,Cu,As,Cd and Pb in the sediments were analyzed using Inductively Coupled Plasma- Mass Spectrometry (Agilent 7500 ICP-MS) .All devices are cleaned by rinsing with pure water and kept in 0.2mol HNO_3 for 24 hours or more before sampling. All solutions are prepared using ultra-pure.Each samples were used standard reference materials (GBW-7) form the Center of National Standard Reference material of China to ensure the precision of the data.

Weigh 0.100g of the freeze-dried, 100 mesh sieve sample into the digestion tube, add 5mL concentrated HNO_3,2mLH_2O_2, 3mLHF cover the lid, disintegrate the digestion tube in a microwave digestion device, and cool to room temperature after digestion Remove the lid of the digestion tube, place the digestion tube in a water bath, and heat at a constant temperature for 30 minutes until no red matter is present. Then pour the digestion solution into the crucible and place it on the hot plate to catch the acid. After the acid is completed, transfer the digestion solution to a 50 mL colorimetric tube, dilute to the mark with ultrapure water, shake well, and the solution is passed through a 0.45 μm mixed membrane and stored at 4℃ .

2.3 Risk assessment and statistical methods

Geo-accumulation index.

The index (I_{geo}) was proposed by muller (Muller, 1969), was used to evaluate the degree of metal pollution in the sediments. The calculation formula of I_{geo} is defined as:

$$I_{geo} = \log_2\left(\frac{C_n}{K \times B_n}\right)$$

Where C_n is the actual concentration of metal in sediment (mg/kg). B_n is the background values of geochemistry (Cr=45,Cu=23,As=6.41,Ni=57,Cd=0.39,Pb=15mg/kg.), K is the background correlation coefficient (k=1.5). According to I_{geo}, the sediments were categorized into seven levels.(1) $I_{geo} \leq 0$, no risk(2) $0 < I_{geo} \leq 1$,low risk (3) $1 < I_{geo} \leq 2$,partial pollution (4)$2 < I_{geo} \leq 3$,moderation pollution(5)$3 < I_{geo} \leq 4$,strongly pollution(6) $4 < I_{geo} \leq 5$,Strongly to extremely pollution(7)$5 < I_{geo}$,strongly pollution.

2.4 Statistical analysis

In order to improve accuracy and reduce random deviation, the analysis of all samples was repeated three times and the test results were averaged. The Pearson correlation coefficient was used to analyze the relationship between each metal. The principal components analysis(PCA) was used to explore the possible sources of metals. Statistical analysis were handled using Origin8.0 and

SPSS16.0 statistical software on computer. The spatial distribution of sample were conducted by ArcGIS10.2 for windows.

3. Results and discussion

3.1 Metals concentration of sediments

The total concentration of metal in the sediment form Songhua river are given in Fig2.The total concentration of Cr, Ni,Cu,As,Cd and Pb were in the range of 32.38-60.77, 12.51-46.49, 13.6-34.81, 29.6-107.11, 0.5-1.93 and 26.07-72.38mg/kg, respectively. The order of the average concentrations of the metals in the sediment was As>Cr>Pb>Ni>Cu>Cd. The highest level of Cr and Ni in the sediment were occurred S5 with concentration 60.77 and 46.49mg/kg, and the highest concentration of Cu and Pb existed S6 with 34.81 and 72.38mg/kg, respectively. Moreover, for As, it was observed that the highest concentration occurred in S10 with 107.11mg/kg. Generally, The most serious pollution in the Second Songhua River (S5-S7), which have a large number of petrochemical and other industry and some drain outlets may discharge wastewaters into the river.

Table1.Metal concentration in sediments form Songhua River (mg/kg).

Table1	Mean	Median	Max	Min	CV%	Kurtosis
Cr	42.87	42.74	60.77	32.38	19.16	0.779
Ni	23.18	19.69	46.49	12.51	42.64	2.735
Cu	22.06	21.27	34.81	13.6	27.71	-0.160
As	62.34	65.56	107.11	29.6	46.01	-1.712
Cd	1.28	1.29	1.93	0.5	23.62	3.059
Pb	38.7	35.97	72.38	26.07	29.02	4.809

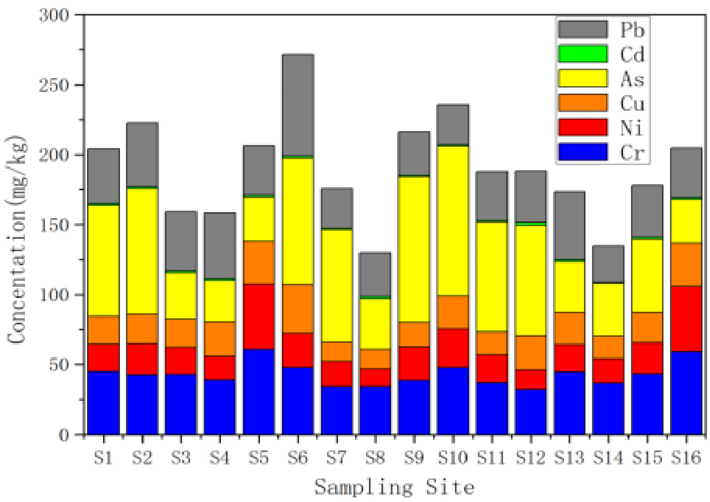

Fig. 2. Total concentration of metals in sediments form Songhua River.

3.2 Correlation and principal component analysis

Table 2 Correlation analysis of heavy metals in sediments of Songhua River.

	Cr	Ni	Cu	As	Cd	Pb
Cr	1					
Ni	0.929**	1				
Cu	0.743**	0.639**	1			
As	-0.235	-0.169	-0.100	1		
Cd	-0.048	-0.119	0.280	-0.009	1	
Pb	0.216	-0.018	0.630**	0.030	0.345	1

**Correlation is significant at P<0.01

The Pearson coefficient analysis of the 6 metals in the sediments are shown in Table2.It can discover that Cr-Ni,Cr-Cu,Ni-Cu,Pb-Cu these metals have a significantly positive correlation at $P<0.01$.This result implies that Cr,Ni,Cu and Pb may have similar pollution sources or common bioaccumulation. However, it can be clearly obtained the As and Cr showed negative correlations with all metals in sediments, indicating that there may be some differences in the sources of contamination between these two metals and other metals.

Table3 Principal component analysis of metals in sediment form Songhua River.

Element	Component	
	1	2
Cr	**0.933**	-0.286
Ni	**0.846**	-0.449
Cu	**0.919**	0.277
As	-0.254	0.252
Cd	0.152	**0.753**
Pb	0.466	**0.734**
Eigen value	2.737	1.529
Total variance %	45.612	25.486
Cumulative %	45.612	71.097

The principal component analysis method can determine the source of metal contamination, and the results of the PCA analysis are shown in Table 3.From the results we have obtained, Eigen values of two PCs in the sediments were more than 1, explaining 71.1% of the total variance. The total variance of PC1 is 45.61% in the sediment samples, and there is a very high load on Cr, Ni, and Cu, indicating that these metals have similar sources. The total variance of PC2 is 25.49%, and there is a higher load on Cd and Pb.

It is well known that Cd is mainly the raw material of the battery, and it is also the identification element of pesticides and fertilizers. As is mainly derived from human activities such as pesticides and chemical fertilizers, Pb is the identification element of motor vehicle pollution. The ecological risks mainly come from As,Cd and Pb in Songhua River, so it is inferred that PC2 is mainly originated form anthropogenic activities. In addition, the contents of Cr, Ni, and Cu were lower than background values and there is almost no ecological risk, so it is inferred that PC2 comes from natural sources.

3.3 Assessment of risks

The geo-accumulation index (I_{geo}) of the 6 metals in the sediment are shown in Fig4.According to the evaluation results, the I_{geo} index of heavy metals were in the order of: As>Cd>Pb>Cu>Cr>Ni. Briefly, the Cu,Cr and Ni showed non-pollution ($I_{geo}<0$) in all of the sediments. Cd showed slight pollution at most of sampling sites, but showed non-pollution in few sites. Pb shows slight pollution in all sampling sites. In general, As pollution is the most serious ($1.62 < I_{geo} <3.48$), all sites in the Songhua River showed moderate pollution. The sum of I_{geo} index of the 6 metals in the all sediment are shown in Fig4.In short, most of the sites in the Nen River and Songhua Rivers was founded non-pollution level.it can be seen that S6-S7 shows a higher ecological risk. Both S6 and S7 are the Second Songhua River shows that has more serious pollution than the Nen River and the main stream of Songhua Rivers, therefore, further study should be paid more attention to the Second Songhua River.

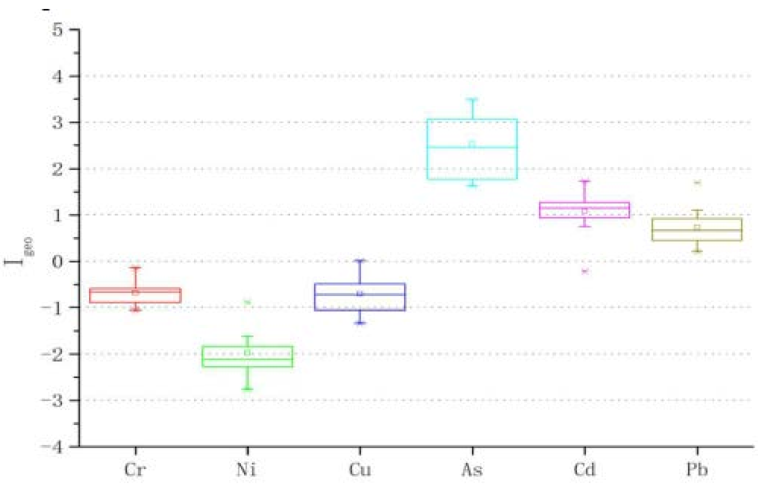

Fig.3. Geo-accumulation index of metals in sediments

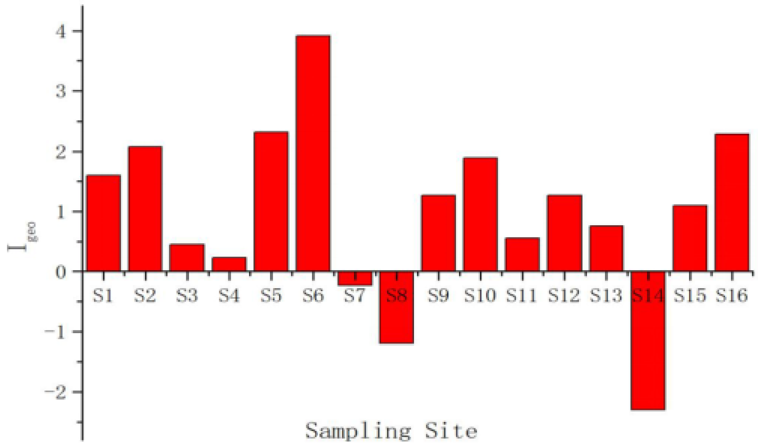

Fig.4.Geo-accumulation index of metals

4. Conclusion

Six trace metals (Cr,Ni,Cu,As,Cd and Pb) were collected in the sediments form Songhua River in China. The total concentration of Cr,Ni,Cu,As,Cd and As were in the range of 32.38-60.77,12.51-46.49,13.6-34.81,29.6-107.11,0.5-1.93 and 26.07-72.38 mg/kg, respectively. The concentration of Cd and As in the sediment were higher than background values, suggesting these pollution of metals may come from anthropogenic activities.

The correlation and principal component analysis results showed that Cr,Ni,Cu and Pb may have similar pollution sources or common bioaccumulation. The assessment of geo-accumulation index (I_{geo}) showed that Cd and As contributed a very high ecological risk in this study, and the metal pollution level in the Second Songhua River were higher than the Nen River and main stream Songhua River.

Acknowledgement

National Water Pollution Control and Management Science and Technology Major Project (2015ZX07201-008-02).

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