

Assessment of heavy metal pollution in stream sediments for the Baoji City section of the Weihe River in Northwest China

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ABSTRACT

The concentrations of Pb, Zn, Cu, Cd and Cr in the stream sediment in the Baoji City section of the Weihe River, Northwest China, were determined to evaluate their contamination levels, spatial distribution and potential ecological risk. The average concentrations of the heavy metal sediments were 52.92 mg kg^{-1} for Pb, 99.04 mg kg^{-1} for Zn, 17.43 mg kg^{-1} for Cu, 0.79 mg kg^{-1} for Cd and 86.97 mg kg^{-1} for Cr. The result of the assessment indicates that the pollution by Cd is serious, Zn and Cr are moderate and Cu is relatively light or unpolluted. The correlation analysis showed that the five heavy metals are significantly associated with each other. The hierarchical cluster analysis suggested that Zn, Cr and Pb might have identical anthropogenic and natural sources in stream sediments while Cu and Cd might have the same source in the Baoji City section of the Weihe River.

Key words | ecological risk assessment, geoaccumulation index, heavy metal, stream sediment

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INTRODUCTION

Heavy metals are discharged into the river from numerous sources. They may be transported as either dissolved species in water or as an integral part of sediments; the latter may be ultimately stored in riverbed sediments. The stream sediment can be an important carrier and pollution indicator of aquatic environment contaminants (Farkas *et al.* 2007; Zhu *et al.* 2012), and plays an important role in the assessment of metal contamination in natural waters. Anthropogenic activities have resulted in the potential accumulation of pollutants, especially heavy metals, in stream sediment. When heavy metals are discharged into the aquatic environment, they are deposited in aquatic sediments (Moore *et al.* 2009) and then released into the water phase by physicochemical processes (Kaplan *et al.* 2007). They may accumulate in microorganisms and aquatic flora and fauna, and finally enter the food chain and cause harm to human health.

In recent years, the Weihe River has become a seasonal river with an unpleasant colour and smell. A number of studies have been carried out to study the Weihe water pollution and to propose pollution control strategies. However, most of the previous studies focused on the organic pollutions such as nitrogen and phosphorus. Relatively less attention was paid to the heavy metal contaminants in

stream sediments (Zhang *et al.* 2012; Wang *et al.* 2013). In particular, few studies were found to investigate the heavy metal pollution and its potential ecological risk for the Baoji City section of the Weihe River.

The objective of this study was to assess the extent of heavy metal pollution in the Baoji City section of the Weihe River. Focus was placed on examining heavy metals of Pb, Zn, Cu, Cr and Cd in the sediments and their contamination levels and assess the potential ecological risk for the purpose of providing useful information for reducing pollution and aiding the decision making of the government.

MATERIALS AND METHODS

Study area and sediment sampling

The Weihe River is a major river in China's western-central Gansu and Shaanxi provinces. It is the largest tributary of the Yellow River with a length of 818 km and a catchment area of 135 km^2 . The Baoji City section of the Weihe River lies at $33^{\circ}35' - 35^{\circ}06'$ latitude and $106^{\circ}18' - 108^{\circ}03'$ longitude. It is surrounded by areas of urban residences, industrial

estates and agricultural zones. The sediment samples were collected by a multi-sampler in June 2012. The coordinates of the six sampling locations were recorded by global positioning system (GPS): No. 1, 34°21'57.49"N, 107°7'18.72"E; No. 2, 34°21'55.12"N, 107°8'2.18"E; No. 3, 34°21'10.55"N, 107°9'57.42"E; No. 4, 34°21'2.66"N, 107°10'53.94"E; No. 5, 34°21'16.81"N, 107°12'21.31"E; and No. 6, 34°21'32.33"N, 107°13'52.36E. Five samples were collected from each sampling location. Only the top portions (0–10 cm) of the sediments were sampled.

Sample preparation and analysis

The sediment samples were first air-dried at room temperature, stones and plant roots were removed, and it was then ground with an agate mortar, and finally passed through a 0.15 mm nylon screen sieve. The samples from the same sampling location were mixed as one analytical sample. For trace metal determination, the samples were wet-digested with a concentrated acid mixture (HNO₃–HF–HClO₄). The dry sample of 0.5 g was added to a 200 ml volumetric beaker with a mixture of concentrated acids of 10.0 ml HNO₃, 10.0 ml HF and 10.0 ml HClO₄. The mixtures were then boiled at 180–230 °C until they were nearly dried. After cooling, 5.0 ml HNO₃, 5.0 ml HF and 5.0 ml HClO₄ were added and the mixture was boiled again until dense white fumes appeared. After cooling, 15 ml of distilled water was added and the mixture was boiled for 5 min. The solution was cooled and transferred from the beaker to a volumetric flask (50 ml). The wall of the beaker was washed 2–3 times with dilute nitric acid (10%). Thereafter, the volumetric flask was diluted to 50 ml with dilute nitric acid (10%). The total metal concentrations of Pb, Zn, Cu, Cr and Cd were determined by a flame atomic absorption spectrophotometer (AAS, SHIMADZU AA-6800).

All the reagents were of guarantee reagent (GR) grade and double-distilled water was used throughout the study.

The accuracy of instrumental methods and analytical procedures was validated using the certified reference materials obtained from the National Research Center for CRMs (Beijing, China): trace elements in river Sediments (GBW08301) (Ji 1996). Accuracy of the analytical method was given as a percentage recovery for each of the elements: Pb, 98%; Zn, 99%; Cu, 102%; Cr, 98%; and Cd, 103%. The limits of detection for the metals' analysis by AAS in the flame mode are as follows: Pb, 0.03 mg l⁻¹; Zn, 0.005 mg l⁻¹; Cu, 0.008 mg l⁻¹; Cr, 0.007 mg l⁻¹; and Cd, 0.002 mg l⁻¹. The error of the device is about 0.5%. Furthermore, each analytical batch contained at least a method blank. Standard solutions were analysed after every 10 sample solutions as a check on instrument performance. In addition, the error of artificial measurement is about 1–1.5%.

The heavy metal concentrations in stream sediment are given as mg kg⁻¹ dry weight. All statistical analyses were performed using the SPSS software package (version 19.0), Microsoft Excel 2003 and Origin 7.5. The geoaccumulation index, contamination degree, ecological risk index, correlation analysis and hierarchical cluster analysis were also calculated based on the data.

RESULTS AND DISCUSSION

Concentrations of sediment heavy metals

Descriptive statistical results of the heavy metal (Pb, Zn, Cu, Cd and Cr) concentrations are shown in Table 1. The regional variation (the median concentration) is 45.36–62.34 mg kg⁻¹ (51.53 mg kg⁻¹) for Pb; 84.35–112.65 mg kg⁻¹ (99.65 mg kg⁻¹) for Zn; 15.03–20.98 mg kg⁻¹ (17.34 mg kg⁻¹) for Cu; 0.62–0.93 mg kg⁻¹ (0.81 mg kg⁻¹) for Cd; and 72.08–98.79 mg kg⁻¹ (89.35 mg kg⁻¹) for Cr. All the heavy metals except for Cu significantly exceeded the background concentration of national and Shaanxi

Table 1 | Heavy metal concentration in stream sediment of the Weihe River in Baoji City (mg kg⁻¹ dry weight)

Element	Range	Median	Variance	CV ^a (%)	Background values of China ^b	Background values of Shaanxi ^b
Pb	45.36–62.34	51.53	38.532	11.73	26	21.4
Zn	84.35–112.65	99.65	102.666	10.23	74.2	69.4
Cu	15.03–20.98	17.34	4.422	12.05	22.6	21.4
Cd	0.62–0.93	0.81	0.014	15.19	0.097	0.094
Cr	72.08–98.79	89.35	110.233	12.07	61	62.5

^aCV: coefficient of variation;

^bChina Environment Protection Agency, The Total Station of China Environment Monitoring (1990).

provincial levels. Compared with the Chinese soil background value, the lowest concentration of Cd is about 6.4 times higher than the background value while Pb is twice higher, Zn is 1.2 times higher and Cr is 1.1 times higher than the reference value. Only Cu is slightly lower than the background value.

Geoaccumulation index of heavy metals in sediments

The geoaccumulation index (I_{geo}) was applied to assess the contamination levels of heavy metals in stream sediments by previous researchers. I_{geo} is computed by Equation (1) (Müller 1969):

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{1.5 \times B_n} \right] \quad (1)$$

where C_n is the concentration of heavy metals in soil, mg kg^{-1} ; B_n is the geochemical background concentration of heavy metals, mg kg^{-1} ; China background values were selected as the background (Pb, 26; Zn, 74.2; Cu, 22.6; Cd, 0.097; and Cr, 61). The value of 1.5 is the background matrix correction factor due to lithogenic effects. I_{geo} is classified into seven grades by Müller (1969): unpolluted ($0 < I_{\text{geo}}$), unpolluted to moderately polluted ($0 \leq I_{\text{geo}} < 1$), moderately polluted ($1 \leq I_{\text{geo}} < 2$), moderate to strongly polluted ($2 \leq I_{\text{geo}} < 3$), strongly polluted ($3 \leq I_{\text{geo}} < 4$), strongly to extremely polluted ($4 \leq I_{\text{geo}} < 5$) and extremely polluted ($I_{\text{geo}} \geq 5$). Figure 1 displays box-and-whisker plots of the index of geoaccumulation of Pb, Zn, Cu, Cd and Cr derived from this study.

Figure 1 indicates that the stream sediments of the Weihe River can be categorised as follows: unpolluted with Zn, Cu and Cr ($I_{\text{geo}} < 0$), unpolluted to moderately polluted with Pb ($0 < I_{\text{geo}} < 1$), and moderately to strongly polluted with Cd ($2 < I_{\text{geo}} < 3$). In conclusion, based on the I_{geo} classification, the magnitude of heavy metal

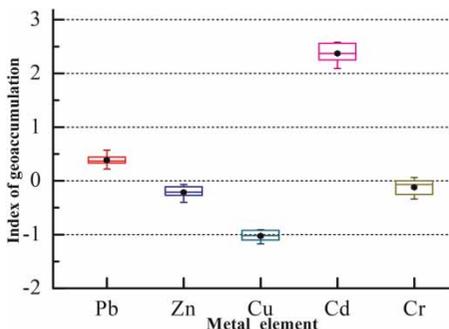


Figure 1 | Box-and-whisker plots of the index of geoaccumulation ($n = 6$).

pollution of the bed sediments of the Weihe River in the Baoji City section yields the following ranking: $\text{Cd} > \text{Pb} > \text{Cr} \geq \text{Zn} > \text{Cu}$.

Contamination factor and contamination degree of analysed metals

The effect and degree of the heavy metal pollution over sediments were described by the factor (C_f) and degree (C_d) of contamination. C_f can be calculated from Equation (2) and C_d from Equation (3) (Håkanson 1980; Sany *et al.* 2012). They represent the degree of pollution of the heavy metal for the environment.

$$C_f = \frac{C_{0-1}^i}{C_n^i} \quad (2)$$

$$C_d = \sum_{i=1}^5 C_f \quad (3)$$

where C_f is the contamination factor; and C_{0-1}^i is the mean content of the substance in question (i) from surface sediment (0–1 cm) at the accumulation area. In the current case, it is the measured concentration of the examined metal in the sediment (0–10 cm), mg/kg . C_n^i is the background value for the compound estimated. In the current case, China background values were selected as the background (Pb, 26; Zn, 74.2; Cu, 22.6; Cd, 0.097; and Cr, 61), mg/kg ; C_d is the contamination degree. The C_f accounts for contamination of a single element, and is applied to evaluate the anthropogenic contribution of heavy metals in surface sediments, which is classified into four groups: $C_f < 1$, low contamination factor; $1 \leq C_f < 3$, moderate contamination factor; $3 \leq C_f < 6$, considerable contamination factor; and $C_f \geq 6$, very high contamination factor. The C_d of the sampling sites was defined by Håkanson (1980). It is the sum of all contamination degrees, and represents the integrated pollution degree of the environment. C_d is as follows: $C_d < 8$, low degree of contamination; $8 \leq C_d < 16$, moderate degree of contamination; $16 \leq C_d < 32$, considerable degree of contamination; and $C_d \geq 32$, very high degree of contamination indicating serious anthropogenic pollution. Figure 2 shows C_f of each heavy metal examined and also C_d for each sampling site.

As shown in Figure 2, $C_f > 6$ for Cd, indicating high contamination factor, $1 < C_f < 3$ for Pb, Zn and Cr, meaning moderate contamination factor and $C_f < 1$ for Cu, implying low contamination factor. The C_d is $11 < C_d < 17$, which

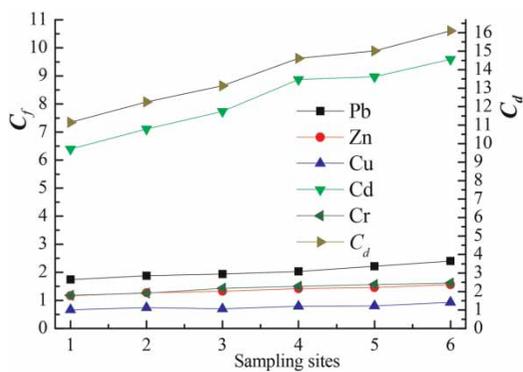


Figure 2 | Distribution histogram graphs of C_f -values and C_d -values in different sampling locations.

shows a considerable degree of contamination except for sample location 6. The C_d has an increasing tendency from upstream to downstream. Based on the C_f classification, the contamination degree follows the ranking of $Cd > Pb > Cr \geq Zn > Cu$, which is in high agreement with the evaluation by I_{geo} .

Correlation analysis and hierarchical cluster analysis

In order to establish relationships between metals and determine the common source of metals in stream sediments for the Baoji City section of the Weihe River, Spearman's rank correlation analysis was conducted for heavy metals (Zou *et al.* 2012; Cheng *et al.* 2013). The calculation was performed on the datasets and enabled the identification of possible common characteristics of heavy metals in the sediment. It can also be used to evaluate the potential to control metal mobility. According to the grade classification for the coefficient of correlation (Shufen 2011), the results of Spearman's rank correlation analysis show a significant relationship for Pb–Zn ($r = 0.971$, $p < 0.01$), Pb–Cu ($r = 0.943$, $p < 0.01$), Pb–Cd ($r = 0.941$, $p < 0.01$), Pb–Cr ($r = 0.931$, $p < 0.01$), Zn–Cu ($r = 0.925$, $p < 0.01$), Zn–Cd ($r = 0.989$, $p < 0.01$), Zn–Cr ($r = 0.977$, $p < 0.01$), Cu–Cd ($r = 0.895$, $p < 0.01$), Cu–Cr ($r = 0.828$, $p < 0.05$) and Cd–Cr ($r = 0.980$, $p < 0.01$). Overall, Spearman's rank correlation analysis suggests that these metals are associated with each other and have exhibited identical behaviour during transport in the stream environment. Furthermore, these metals might have identical anthropogenic and natural sources in stream sediments for the Baoji City section of the Weihe River.

The hierarchical cluster analysis of heavy metal concentrations enables us to explore the sources of the heavy metals in the sediments. The samples can be classified into two clusters as shown in Figure 3. Zn, Cr and Pb could be

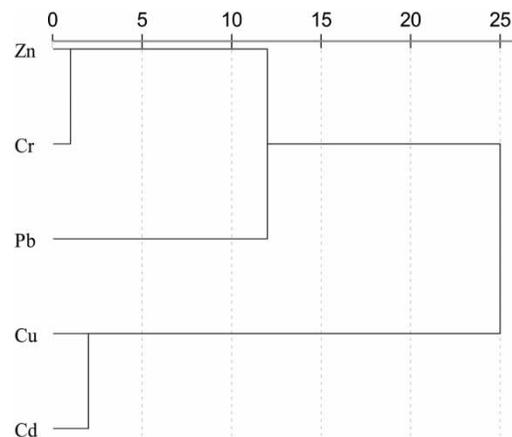


Figure 3 | Dendrogram of hierarchical cluster analysis of heavy metal concentrations.

sorted into a single group, and Cu and Cd into another group. This could suggest that Zn, Cr and Pb have the same source of contamination while Cu and Cd are from another source of contamination in the Baoji City section of the Weihe River.

Discussion

The main purpose of this study was to investigate and assess the sediment contamination for the Baoji City section of the Weihe River. The results of this study are in good agreement with previous studies (Wang *et al.* 2011a, 2011b; Hua *et al.* 2011; Luo *et al.* 2013) for this river concerning metal concentrations in sediments and that Cd pollution is serious. Comparisons of the data with the results of the previous studies suggest that there is a progressive increase over time in surface sediment contamination with these metals. It can be concluded that the input of untreated urban household and industrial wastewaters and agricultural runoff into the Weihe River is responsible for the intense pollution of the water and sediments. Prevention and control of sediment pollution is needed to control the water pollution. Thus, adequate attention is needed from local government in order to protect the lake from further contamination. First, the anthropogenic discharges of various wastewaters into the Weihe River should be reduced. Environmental remediation and treatment of wastewaters along the Weihe River is essential. Secondly, the direct input of agricultural runoff should be prevented as far as possible. Thirdly, the local government should have more strict regulatory policies, laws, management policies and mechanisms in order to prevent the river from being polluted. At the same time, planting wetland emergent plants to absorb the

pollutants and establishing monitoring networks are useful options from an engineering and management point of view in order to remediate the polluted river.

CONCLUSIONS

The surface sediment data show that the total concentration of Pb, Zn, Cu, Cd and Cr is higher than the background concentration of national and Shaanxi provincial levels, and has suffered disproportionate contamination. All heavy metals, except Cu, show significant variation in their concentrations in the sediment with increasing distance from upstream to downstream of the Weihe River. The I_{geo} calculations indicate that Cd is moderately to strongly polluted, Pb is unpolluted to moderately polluted, and Zn, Cu and Cr are all unpolluted in the order of $Cd > Pb > Cr \geq Zn > Cu$. The results of the C_f show that Cd has a high contamination factor; Pb, Zn and Cr all have a moderate contamination factor; while Cu is relatively light. The results of this study show that Cd has higher I_{geo} and C_f compared with other studied elements, which show that Cd pollution is serious. The assessment results of C_d show that C_d is in high agreement with the evaluation by I_{geo} which follows the ranking of $Cd > Pb > Cr \geq Zn > Cu$. The analysis of Spearman's rank correlation matrix coefficients shows that Pb, Cu, Cd and Cr are in various degrees of significant positive correlation, indicating that these metals have similar sources of pollution. At the same time, the hierarchical cluster analysis shows that Zn, Cr and Pb have identical anthropogenic and natural sources while Cu and Cd have another identical source. Results of this study provide baseline data, which can be used by authorities for environmental management.

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