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Heavy Metals in the Surface Sediments in Lanzhou Reach of Yellow River, China

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Abstract The heavy metal pollution and their fractionations in the surface sediments of Yellow River in Lanzhou Reach was monitored for arsenic (As), lead (Pb), Zinc (Zn), chromium (Cr), copper (Cu) and manganese (Mn) with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The mean sediment concentrations (in µg/g dry weight) ranged from 13.68–48.11 (As), 26.39–77.66 (Pb), 89.80–201.88 (Zn), 41.49–128.30 (Cr), 29.72–102.22 (Cu), and 773.23–1459.69 (Mn). Spatial distribution showed that each heavy metal concentration remained almost constant in this reach. Correlation coefficients indicated that metals were not strongly associated with sediment sand content or organic carbon content (f_{oc}). Labile fractions (exchangeable + carbonate + Fe–Mn oxide) had no significant correlations with sand content or f_{oc}, either. Results from the present study are useful for understanding heavy metal distributions in a torrential river sediment environment.

Keywords Heavy metals · Speciation · Sediment · Distribution

The pollution of riverine system by heavy metals has attracted considerable attention of both scientific and regulatory communities. Unlike organic contaminants which can be decomposed during natural processes, heavy metals in the river environment can be enriched by organisms and be converted to organic complexes. After being introduced into the aquatic environment via various sources and paths, metals are adsorbed onto inorganic and organic particulates and are incorporated into sediment resulting in elevated levels of heavy metals in bottom sediment (Jeon et al. 2003; Schmitt et al. 2003; Ochieng et al. 2007). Metals cannot always be fixed by sediments permanently. Some of the sediment-bound metals may remobilize and be released back to waters via the variation of environmental conditions such as acidification, redox potential conditions, the organic ligand levels, etc., and impose adverse effects on living organisms.

It is accepted that total heavy metal content itself is not a good measurement of bioavailability and not a very useful tool to determine the potential risks from soil and sediment contamination. The environmental impact of heavy metal contaminants strongly depends on the metals speciation, mobility, and bioavailability. Sequential extraction method, based on the process known as fractionation where a sequential series of selective extractants with an increasing extractant power is employed to selectively dissolve or solubilize the different solid phase forms or mineralogical fractions, has often been used to study the speciation and possible associations between metals and soil or sediment components. The early methods proposed by Tessier et al (1979) and Kersten and Forstner (1986), and many modified procedures including the BCR method (Ure et al. 1993), were developed with the different sequences of reagents or the modified operational conditions.

Although heavy metal distributions in sediment core samples were often investigated, in this study, only surface sediment samples (0–20 cm depth) were collected for heavy metal analysis, due to the fact that the bioavailable

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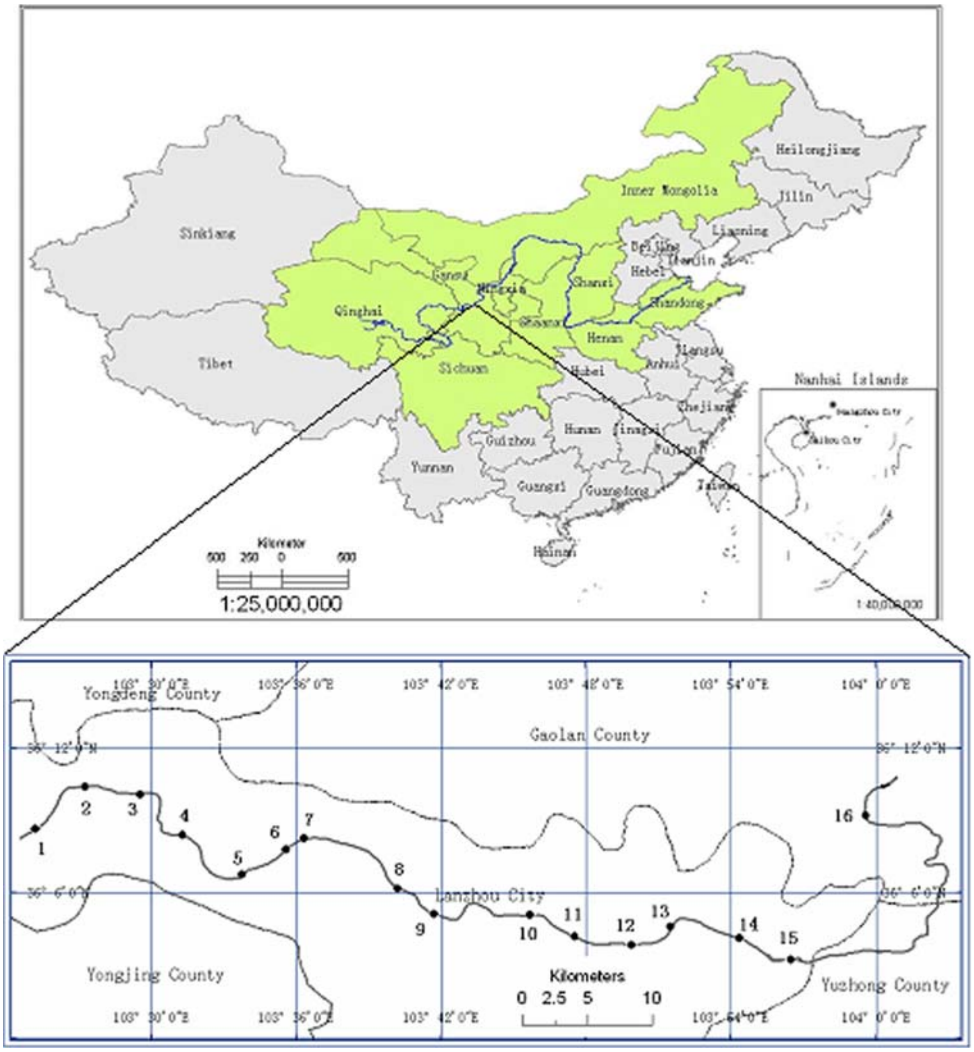


Fig. 1 Sampling sites in the study area

phases decreased by depth (Kwon and Lee 2001). Sixteen surface sediment samples from Lanzhou Reach of Yellow River were taken in July 2004 (Fig. 1), and analyzed for heavy metal levels and speciation. This reach covered a range of 83 km long, including industrial area, domestic inhabitation area, and landscape area.

Materials and Methods

Surface sediments were grab sampled along the river with a stainless steel container. Samples were transported to the laboratory, freeze dried and ground with a mortar and pestle then passed through a sieve with 1 mm opening. Some physicochemical properties of sediments are listed in Table 1.

One gram of dried sediment sample was placed in a 250 mL pyrex flask. A total of 9 mL of concentrated HNO_3 and 3 mL of concentrated $HClO_4$ were added to the flask and the flask was then placed on a heating plate for digestion. A small amount of nitric acid was added intermittently to digest the sediment completely until the supernatant became clear and a brownish-colored fume was no longer generated. After the sample became nearly

Table 1 Some physicochemical properties of sediments

Location	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16
Sand, %	93.4	88.6	86.3	70.8	85.2	91.8	87	84	82.8	83.8	83.4	70	79	83.1	82.2	85.4
Silt, %	4.4	9	8.5	22.4	9.4	5.4	9.2	13.2	12.4	12	10.2	22.4	15.6	13.5	12.8	12.4
Clay, %	2.2	2.4	5.2	6.8	5.4	2.8	3.8	2.8	4.8	4.2	6.4	7.6	5.4	3.4	5	2.2
f_{oc}, %	0.08	0.13	0.22	0.54	0.16	0.21	0.15	0.16	0.34	0.17	0.43	0.57	0.31	0.36	0.38	0.2

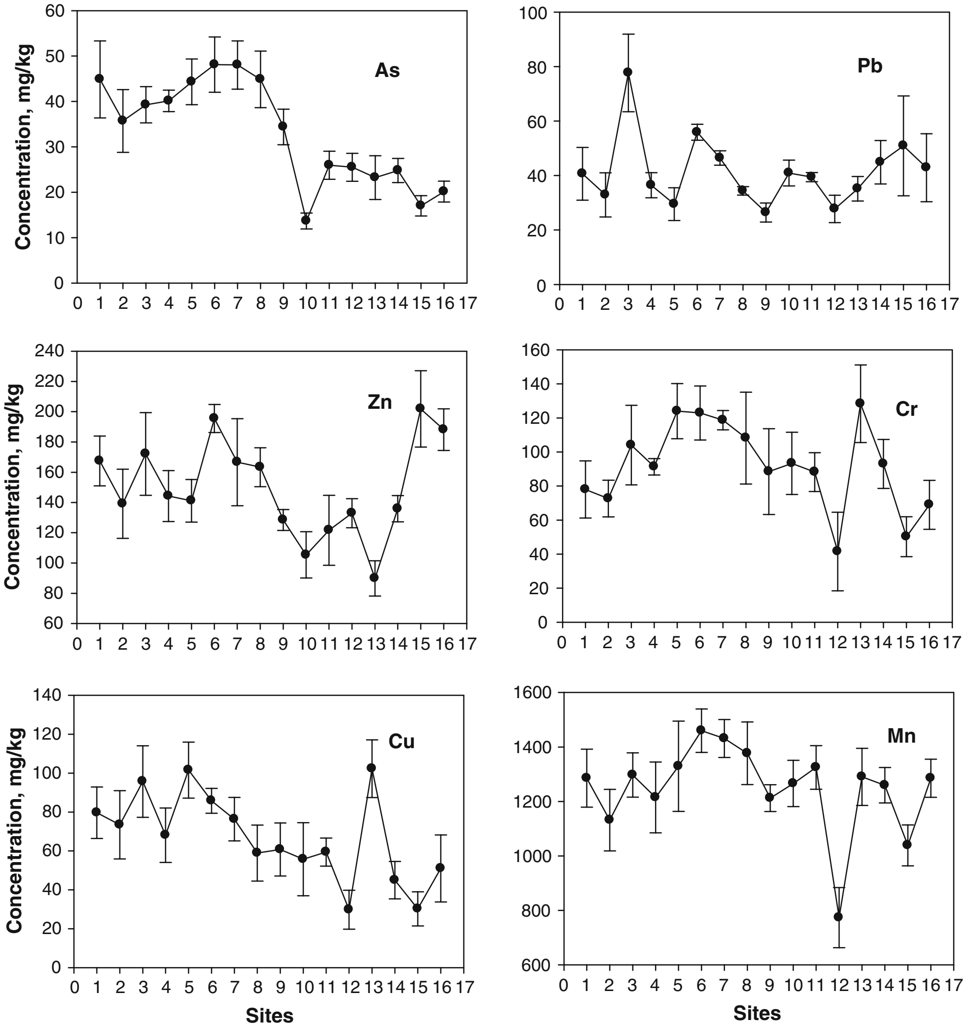
dried, it was taken up in 1% HNO_3, and the solution was filtered through a 0.45 μm membrane filter and ready for analysis.

The chemical forms of heavy metals in the sediments were divided into the following fractions: (1) Fraction I-exchangeable. The sample was extracted with 0.5 M $MgCl_2$ at pH 7.0 at a solid to solution ratio of 1:8, with continuous agitation for 1 h at room temperature; (2) Fraction II-bound to carbonates. The residue from (1) was extracted with 1 M NaOAc (adjusted to pH 5.0 with HOAc) at a solid to solution ratio of 1:8. Continuous agitation was maintained for 5 h at room temperature; (3) Fraction III-bound to iron and manganese oxides. The residue from (2) was extracted with 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 h at 96°C; (4) Fraction IV-bound to organic matter/sulfide. The residue from (3) was extracted with 30% H_2O_2 (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 h at 85°C, and then extracted with 3.2 M NH_4OAc in 20% (v/v) HNO_3 with continuous agitation for 30 min; (5) Fraction V-residual fraction. The residue from (4) was digested with concentrated HNO_3 and $HClO_4$ at 90–190°C for 18 h.

All glassware used in this study was previously soaked in 15% HNO_3 (v/v) and rinsed with de-ionized water. Concentrations of heavy metals were determined with an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Intrepid II XSP, Thermo Electron Corporation, USA). The limits of detection (LODs) of target heavy metals were as follows: As, 2 μg/L; Pb, 2 μg/L; Zn, 4 μg/L; Cr, 6 μg/L; Cu, 2 μg/L; Mn, 4 μg/L. All samples were treated in triplicate, and data shown below were average values of the triplicates.

In order to evaluate the precision and recovery of the extraction procedure, a stream sediment reference material (GBW07310) was used following the course of sequential extraction. Results showed that the sequential extraction procedure is repeatable and reliable, with recoveries for all heavy metals ranging from 92.8 to 108.5%.

Fig. 2 Spatial distributions of heavy metal concentrations in surface sediments



Results and Discussion

The distribution of particle size and organic carbon content in the sediments are given in Table 1. The surface sediment samples consist of more than 70% sand content in the studied reach. The organic carbon contents of sediments ranged between 0.08% and 0.57%, representing a typical torrential river environment.

The concentrations of examined metals (As, Pb, Zn, Cr, Cu, and Mn) in the surface sediments of the river are presented in Fig. 2. In this reach, metal concentrations remain almost constant. Higher levels of As occurred in the upstream section of the river from Site 1 to Site 9, and from Site 10 to Site 16 its levels decreased. For other metals, sediment concentrations varied at different sites. For example, concentrations of Cr, Cu and Mn in the sediment of Site 12 reached the lowest, and got higher at Site 13. The highest concentration of Pb occurred at Site 3, and at Site 15 Zn reached its highest sediment concentration in this reach. The spatial variations of metal levels in the sediments were related to the pollution discharging points along Yellow River in this reach. Xu et al. (2006, 2007) reported the spatial distributions of PAHs and nonylphenol in sediments and water samples in this reach, and found that wastewater discharged into the river was the dominant pollution sources. Many factories discharge the wastewater consisting of organic pollutants and heavy metals directly into the river, and the composition of wastewater vary significantly, which is one of the reasons for spatial variation of metal levels in the surface sediments.

The concentration data of metals in the sediments were subjected to the simple linear regression analysis to examine the possible correlation among different metals. Correlation coefficients among different metals are shown in Table 2. Correlation coefficients were found to be higher than 0.6 for Cu–Cr and Mn–Cr, between 0.1 and 0.38 for Zn–As, Zn–Pb, Cu–As, and Mn–Cu, and less than 0.1 for other combinations. High correlation coefficient between different metals means their common sources, mutual dependence and identical behavior during transport. The absence of strong correlation among other metals suggests that the concentrations of these metals are not controlled by a single factor, but a combination of geochemical support phases and their mixed associations (Jain et al. 2005). The results in this study indicate that most examined metals don't have common sources, that is, they may originate from various sources, and their behavior during the transport may be varied. The close inter-element relationship of Cu–Cr and Mn–Cr suggests a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments.

Table 2 Correlation among different metals in surface sediments

	As	Pb	Zn	Cr	Cu	Mn
As	1.000					
Pb	0.018	1.000				
Zn	0.115	0.279	1.000			
Cr	0.243	0.027	0.034	1.000		
Cu	0.300	0.043	0.019	0.635	1.000	
Mn	0.055	0.099	0.019	0.679	0.376	1.000

Table 3 Average percentage of each fraction in 16 sampling sites

Metal	Percentage of each fraction, %				
	Exchangeable	Carbonates	Fe/Mn oxides	Organic	Residual
As	0.42	1.33	8.72	24.04	65.49
Pb	0	7.52	63.25	10.62	18.61
Zn	0.35	4.91	32.09	13.53	49.12
Cr	0.40	0.55	9.88	3.69	85.48
Cu	0.35	12.22	21.13	10.67	55.63
Mn	0.95	19.32	20.31	4.83	54.59

The concentrations of six heavy metals in surface sediments determined at each sequential extract step reveal five fractions of each metal. The results of average percentage of each fraction in the 16 sampling sites are listed in Table 3. The percent of five fractions for Zn and Cr in the sediments follow the same order as residual > Fe–Mn oxide > organic > carbonate > exchangeable, while those of Cu and Mn follow the order as residual > Fe–Mn oxide > carbonate > organic > exchangeable. The percentage of Pb associated with different fractions is in the order of Fe–Mn oxide > residual > organic > carbonate > exchangeable. All metals are found in all of the five fractions except for Pb, which is not detected in the exchangeable fraction (Table 3). The result that most of Pb was present in the Fe–Mn oxide fraction in this study is in agreement with other studies (Jones and Turki 1997). It has been reported that Pb can form stable complexes with Fe–Mn oxides (Ramos et al. 1994). It is notable that proportions of carbonate fraction for Cu and Mn are relatively high (12.22% and 19.32%, respectively), which imply their high risk due to the unstable character of this fraction. For most of the other metals, they are mainly bound to organic and residual phases. Most As and Cr were retained in less mobile phases (about 90% of the total levels were found in organic and residual fractions), suggesting their lower pollution risks. For Pb, Zn, Cu, and Mn, the first three labile fractions accounted for 70.77, 37.45, 33.7 and 40.58% of the total concentrations, respectively, indicating their potential pollution risks to the aquatic environment.

For organic contaminants in sediments, their levels were significantly correlated with sediment's organic carbon contents (Xu et al. 2007). Heavy metal levels in sediments are reported to be mainly influenced by particle size and composition of sediments (Krumlgalz 1989; Jain et al. 2005). The relationships of total heavy metal concentrations in sediments versus sediment organic carbon content (f_{oc}) or sediment sand contents (sand%), the sum concentrations of first three fractions (exchangeable + carbonate + Fe–Mn oxide) versus f_{oc} or sand% were calculated. Correlation coefficients between the sum of the first three fractions and f_{oc} or sand% were less than 0.10 except for Cu, which were 0.24 and 0.23, respectively. Correlation coefficients between total heavy metals and f_{oc} were between 0.04 and 0.36, while those between total heavy metals and sand% were between 0.10 and 0.39. Results in the present study are quite different from other studies, which reported significant correlations between sediment concentrations and organic matter contents or grain size (Jain and Sharma 2001; Conrad and Chisholm-Brause 2004).

Organic matter can sorb heavy metals from solution and a close relationship between them might be expected in the sediments. Weak correlations of heavy metal concentrations with organic carbon contents in this study may be due to the torrential river environment, with very low organic carbon contents (<0.57%) in the sediments of this reach, indicating that organic content is not a good predictor of the concentration of elements in this study area. The results that metal concentrations and grain size in the sediments are also not associated agree with the result from Taylor (1996), which reported they were apparently unrelated.

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