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SPECIATION AND CONTAMINATION ASSESSMENT OF METALS IN THE SEDIMENTS FROM THE LANZHOU SECTION OF THE YELLOW RIVER, CHINA

Heavy metals such as Cu, Fe, Mn, Ni, Zn, Cd, Cr and Pb in surface sediments from the Lanzhou Section of the Yellow River were investigated to analyze chemical speciation by a sequential extraction and to evaluate their pollution level. The metal contents in the sediments were found to be in the range of (mg/kg) Cu 15.52–57.50, Fe 19 600.33–48 350.00, Mn 493.50–698.93, Ni 9.34–53.20, Zn 64.86–168.57, Cd 1.09–4.25, Cr 70.00–139.33, Pb 5.66–19.13. The arrangement of metal contents from higher to lower was: Fe > Mn > Cr > Zn > Ni > Cu > Pb > Cd. Fe, Mn and Cu and could have the same source according to their correlations. The quantity of immobile speciation (residual) was observed to be higher when compared with mobile speciation (acid soluble, reducible, and oxidizable) of Fe, Cu, Cd and Cr. The highly enrichment factors of Ni and Cr created a high environmental risk. The order of contamination level for heavy metals in sediment was Cr > Cd > Pb > Cu > Mn > Ni > Fe > Zn on the basis of performance of the geoaccumulation index, enrichment factor and pollution load index.

1. INTRODUCTION

Metals are natural constituents in nature and their deposition in aquatic environment can cause toxicity to aquatic biota. Metals are regarded as serious pollutants of aquatic ecosystems because of their persistence in the environment, toxicity, and ability to be incorporated into food chains [1]. These could be incorporated into marine ecosystems as the results of human activities, creating anomalously high concentrations in coastal sediments where industrial development was intense [2].

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Heavy metals are present in waters in both dissolved and solid forms, and play a role in many biogeochemical cycles. These metals rapidly and efficiently bind with the sediment via adsorption onto surface particles, precipitation, and incorporation into biogenic material. Many metals could also be incorporated into aquatic ecosystems as the result of intense industrial development along the river. Metals such as Ni, Cd, Mn, Zn and other were usually used in baseline and contamination studies in aquatic systems regarding their relationships with anthropogenic activities [3, 4]. Because of their persistence in the environment, biogeochemical recycling, and ecological risks, heavy metals have been of particular concern worldwide [5].

It was accepted that total heavy metal content itself is not a good measure of bioavailability and not a very useful tool to determine the potential risks from soil and sediment contamination. The environment impact of heavy metal contaminants strongly depends on the metal speciation, mobility, and bioavailability [6–9]. Sequential extraction method, based on the process known as fractionation where a sequential series of selective extractants with an increasing extractant power was employed to selectively dissolve or solubilize the different solid phase forms or mineralogical fractions, had 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. [10], and many modified procedures including the those recommended by EU Community, Bureau of Reference (BCR), were developed with the different sequences of reagents or the modified operational conditions [11–16].

Lanzhou is one of the larger cities of China and a hub of industrial activity. The coastal zone of the Yellow River in Lanzhou Reach was extended up to 103 km that was exposed to heavy pollution load of both domestic and industrial origins. This reach covered a range of 85 km long, including industrial area, domestic inhabitation area, and landscape area [17]. This work examined the distribution of Cu, Fe, Mn, Ni, Zn, Cd, Cr, and Pb concentrations in the surface sediments of the coast of the Lanzhou Section of the Yellow River, China. The contamination degree, potential mobility and biological effects of metals in sediments using a five-step (exchangeable, carbonate, Fe--Mn oxides, organic matter, and residual) sequential extraction procedure were examined. The metals speciation in the sediment collected from the Lanzhou Section of the Yellow River was analyzed. Potential risks of the metals to the environment were assessed using the geoaccumulation index (I_{geo}), enrichment factor (EF) and pollution load index (PLI).

2. MATERIALS AND METHODS

Samples were taken in April 2012 from 12 locations (Table 1). 12 samples were collected from shallow bottom sediments using a grab sampler [18]. A plastic spoon

was used for collecting sediments from grab in order to avoid metal contamination. Immediately after collection, the sediment samples were placed in a 500 cm^3 polyethylene bag and preserved at a low temperature. Samples were transported to the laboratory, freeze dried and ground with a mortar and pestle then passed through a sieve with 1mm opening.

Geological locations of sediment sampling points
at the Lanzhou Section of the Yellow River, China

Station	Location	Latitude	Longitude
GS-02	Dongchuan xiang of Xiguqu	36°06′37″	103°32′52″
GS-03	Anmen cun of Xiguqu	36°06′55″	103°33′52″
GS-04	Xisha Bridge	36°08′23″	103°36′45″
GS-05	Gansu agriculture university	36°05′24″	103°41′23″
GS-06	Gansu provincial party school	36°05′31″	103°43′43″
GS-07	Qilihe Bridge	36°04′50″	103°46′24″
GS-08	Xiaoxihu	36°04′09″	103°47′48″
GS-09	Yantan Bridge	36°04′19″	103°51′20″
GS-10	Donggang yellow bridge	36°03′10″	103°55′40″
GS-11	Dongpingcun of Yuzhong	36°03′27″	103°01′03″
GS-12	Shichuanzhen of Gaolan	36°10′18″	103°00′10″
GS-13	Shichuanzhen entrance of Gaolan	36°08′52″	103°00′14″

The samples were dried at room temperature to a constant weight, then passed through a sieve with 1 mm sieve. The chemical partitioning of metals in sediments was determined by the modified BCR sequential extraction scheme [10, 11, 14].

The enrichment factor (*EF*) was employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites by individual elements in sediments [19]. Iron was chosen as the normalizing element to determe the *EF* values, since in wetlands it was mainly supplied from sediments and is one of the widely used reference elements.

$$ EF = \frac{\left(\dfrac{C_n}{[\text{Fe}]}\right)_{\text{sample}}}{\left(\dfrac{C_n}{[\text{Fe}]}\right)_{\text{background}}} \tag{1} $$

where, C_n (mg/kg) is the concentration of the element n, [Fe] is the concentration of Fe.

The geoaccumulation index (I_{geo}) was used to assess heavy metal accumulation in sediments to measure the degree of metal pollution in aquatic sediment [20]:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \tag{2}$$

where, C_n is the measured concentration of a heavy metal in surface sediments, B_n (mg/kg) is the geochemical background value in average shale of element n, and 1.5 is the background matrix correction due to terrigenous effects.

The pollution load index (*PLI*) for each site was used to evaluate heavy metal contamination [21]:

$$CF_i = \frac{C_i}{C_{0i}} \tag{3}$$

$$PLI = \sqrt[n]{CF_1 CF_2 CF_3 \ldots CF_n} \tag{4}$$

where, n is the number of metals and CF is the contamination factor. C_i is the concentration of metal i in sediments, C_{0i} is the background values for the metal i. The degree of contamination can be determined by the pollution load index.

3. RESULTS AND DISCUSSIONS

Metal contents (mg/kg) ranged over the following intervals: Cu 15.52–57.50, Fe 19 600.33–48 350.00, Mn 493.50–698.93, Ni 9.34–53.20, Zn 64.86–168.57, Cd 1.09–4.25, Cr 70.00–139.33, Pb 5.66–19.13. The mean contents of the metal (mg/kg) were: Cu 25.40, Fe 27532.08, Mn 698.93, Ni 36.26, Zn 96.73, Cd 1209.56, Cr 104.93, Pb 11.56, and arrangement of the metals from higher to lower mean content was: Fe > Mn > Cr > Zn > Ni > Cu > Pb > Cd. These showed that Cr and Cd presented higher levels in the Yellow River sediments, whereas Fe presented the lowest values (Table 2).

In this study, the average Zn concentrations in sediments from the Lanzhou Section of the Yellow River was 0.4 times the soil trace element background. The means of Cd and Cr concentrations were and 2.9 times the soil trace element background, which imply that the Yellow River sediments had been polluted by Cd and Cr (Table 2).

Some elemental pairs between Cu and Fe, Cu and Mn, Mn and Fe, Cu and Cd, showed highly significantly positive correlation at 99% confidence level. It suggested that elements Mn, Fe and Cu could have a common origin such as industrial effluents. However a relatively weaker correlation was found between the elemental pairs between Pb and Cu, Fe and Pb, Mn and Pb, the results demonstrated that Pb was mainly of natural origin due to weathering and erosion (Table 3).

Table 2

Heavy metal contents in sediments collected from 12 sites
of the Lanzhou Section of the Yellow River [mg/kg]

Station	Cu	Fe	Mn	Ni	Zn	Cd	Cr	Pb
GS-02	16.31	23673.33	611.90	9.34	64.86	3.90	80.61	5.66
GS-03	57.50	48350.00	1260.00	34.08	113.27	2.95	138.90	14.03
GS-04	29.04	24993.33	626.47	46.70	82.88	2.30	76.99	11.06
GS-05	29.42	31076.67	727.13	50.40	168.57	4.25	125.53	9.64
GS-06	20.10	27993.33	733.43	22.94	74.36	1.09	92.19	5.53
GS-07	17.50	22180.00	493.50	41.03	75.24	1.12	92.71	19.13
GS-08	22.07	20954.67	504.21	36.86	68.96	3.36	70.00	17.19
GS-09	21.92	21316.67	535.17	30.58	67.56	2.08	74.52	12.32
GS-10	29.43	35596.67	913.53	45.39	137.93	1.38	139.33	15.67
GS-11	16.28	19600.33	517.27	36.52	66.42	1.13	105.33	6.46
GS-12	29.76	34923.33	891.20	28.11	154.40	1.30	137.00	8.58
GS-13	15.52	19726.67	573.3	53.2	86.26	1.27	126.07	13.45
Maximum	57.50	48350.00	1260.00	53.20	168.57	4.25	139.33	19.13
Minimum	15.52	19600.33	493.50	9.34	64.86	1.09	70.00	5.66
Mean	25.40	27532.08	698.93	36.26	96.73	2.18	104.93	11.56
Standard deviation	11.57	8642.08	227.31	12.46	37.27	1.16	27.08	4.53
Background value	29.74	35805.00	744.10	39.05	251.31	1.09	36.01	8.35

Table 3

Correlations for the heavy metals in surface sediments
collected from 12 sites of the Lanzhou Section of the Yellow Rriver

Metal	Cu	Fe	Mn	Ni	Zn	Cd	Cr
Fe	0.915[b]						
Mn	0.896[b]	0.985[b]					
Ni	0.096	–0.033	–0.053				
Zn	0.493	0.651	0.597	0.344			
Cd	0.269	0.153	0.090	–0.141	0.167		
Cr	0.506	0.687	0.716[b]	0.338	0.778[b]	–0.182	
Pb	0.183	0.048	0.009	0.530	0.013	0.072	0.037

[a]$P < 0.05$.
[b]$P < 0.01$.
[c]$P < 0.001$.

Metals in the sediments were bound to various geochemical speciation. The major mechanisms oftheir accumulation led to the existence of four basic categories: acid soluble, reducible phase (bound to iron and manganese hydroxides), oxidizable phase (bound to organic matter and sulphides), and residual. These categories displayed different behavior with respect to remobilization under changing environmental conditions such as temperature, pH, redox potential, salinity, distribution of particle size and hydrodynamic conditions.
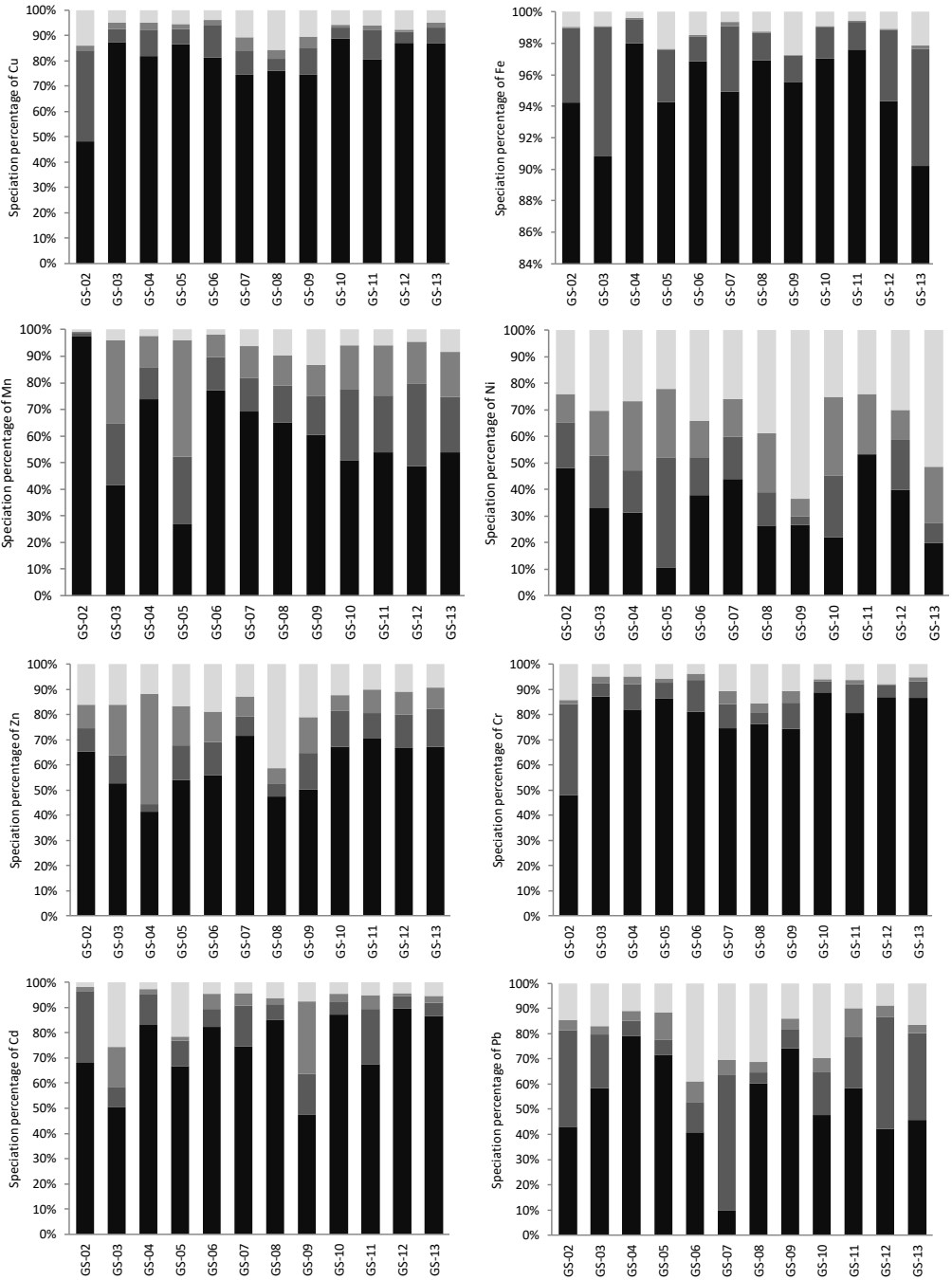
Fig. 1. Distribution of metals in acid soluble, reducible, oxidizable and residual
phases in sediments from 12 sites of Lanzhou Section of the Yellow River

The metal forms present, therefore, gave an indication of sediment reactivity, which in turn assessed the risk associated with the presence of these metals in the sediments. For evaluating the mode of binding of metals in the sediments, sequential extraction studies have been conducted. The results of BCR procedure adopted for geochemical distribution of metals in the sediments were discussed in the following paragraphs and depicted (Fig. 1).

A sizeable fractions (40.0–64.0%, mean 53.7%, 41.6–71.5%, mean 59.9%) of Cu and Zn were present in the residual form and the rest was more or less evenly distributed in all the three non-residual forms, reducible (Cu, 11.5–24.1%, mean 17.5%, Zn, 2.8–15.1%, mean 10.8%), acid soluble (Cu, 3.8–7.8%, mean 5.7%, Zn, 6.0–43.9%, mean 13.5%) and oxidizable (Cu, 16.8–33.5%, mean 23.9%, Zn, 10.0–41.2%, mean 16.5%). The contents of Fe and Cr in various fractions followed the order, residual (Fe, 64.9–98.2%, mean 92.4%, Cr, 48.1–86.9%, mean 78.0%), acid soluble (Fe, 0.05–0.27%, mean 0.09%, Cr, 0.78–5.20%, mean 2.5%), oxidizable (Fe, 0.4–2.1%, mean 1.2%, Cr, 3.8–15.7%, mean 8.1%) and reducible (Fe, 1.5–8.2%, mean 3.56%, Cr, 4.5–35.9%, mean 10.1%). In the case of Mg and Pb, the residual fractions (Mg, 41.6–97.3%, mean 58.9%, Pb, 48.1–86.9%, mean 78%) were the most dominant followed by acid soluble (Mg, 0.7–43.9%, 16.6.%, Pb, 0.78–5.20%, mean 2.5%), reducible (Mg, 1.5–30.9%, mean 17.9%, Pb, 4.5–35.9%, mean 10.1%) and oxidizable (Mg, 0.5–13.3%, mean 5.6%, Pb, 3.8–15.7%, mean 8.1%). The Cd and Ni content in various fractions followed the order, residual (Cd, 50.1–89.7%, mean 72.6%, Ni, 10.5–53.2%, mean 35.2%), acid soluble (Cd, 1.0–28.9%, mean 6.4%, Ni, 6.0–29.5%, mean 18.4%), oxidisable (Cd, 1.7–25.6%, mean 7.8%, Ni, 22.0–51.3%, mean 33.1%) and reducible (Cd, 5.1–28.5%, mean 11.8%, Ni, 0.0–41.6%, mean 15.7%).

The metals in acid soluble, reducible and oxidizable fractions were most likely to mobilize from the sediments if oxygen or the geochemical conditions change in the surface water [22] and hence are more available for the food chain [23]. On the other hand metals present in the residual fraction were strongly bound to the crystal lattice of minerals and consequently had a low mobility. Therefore, if the sum of all the three non-residual fractions was taken as total available metal against the residual phase it was observed that in the studied lake system more than half of every metal was in remobilisable phases and could be made available to biota with the change in the environmental conditions. The data thus indicated towards the serious pollution level of the present lake system, which was being used for both drinking and agriculture.

The enrichment factor was an effective method for distinguishing between natural and anthropogenic sources of pollutions, and it has been widely used since it was first proposed. According to judgment standard of contamination degree by the enrichment factor [19], it could be classified into the following levels: (1) $EF \leq 1.5$: no enrichment, (2) $1.5 < EF \leq 3$: minor enrichment, (3) $3 < EF \leq 5$: moderate enrichment, (4) $5 < EF \leq 10$: moderate severe enrichment, (5) $10 < EF \leq 25$: severe enrichment, (6) $25 < EF \leq 50$: very severe enrichment, (7) $EF > 50$: extremely severe enrichment. Based on these EF values,

the concentrations of heavy metals in the surface sediments increased as follows: Cu (EF = 0.82–1.43, no pollution), Mn (EF = 1.07–1.39, no pollution), Ni (EF = 0.36-2.47, minor pollution in stations GS-04, GS-07, GS-08, GS-11 and GS-13), Zn (EF = 0.43–1.14, no
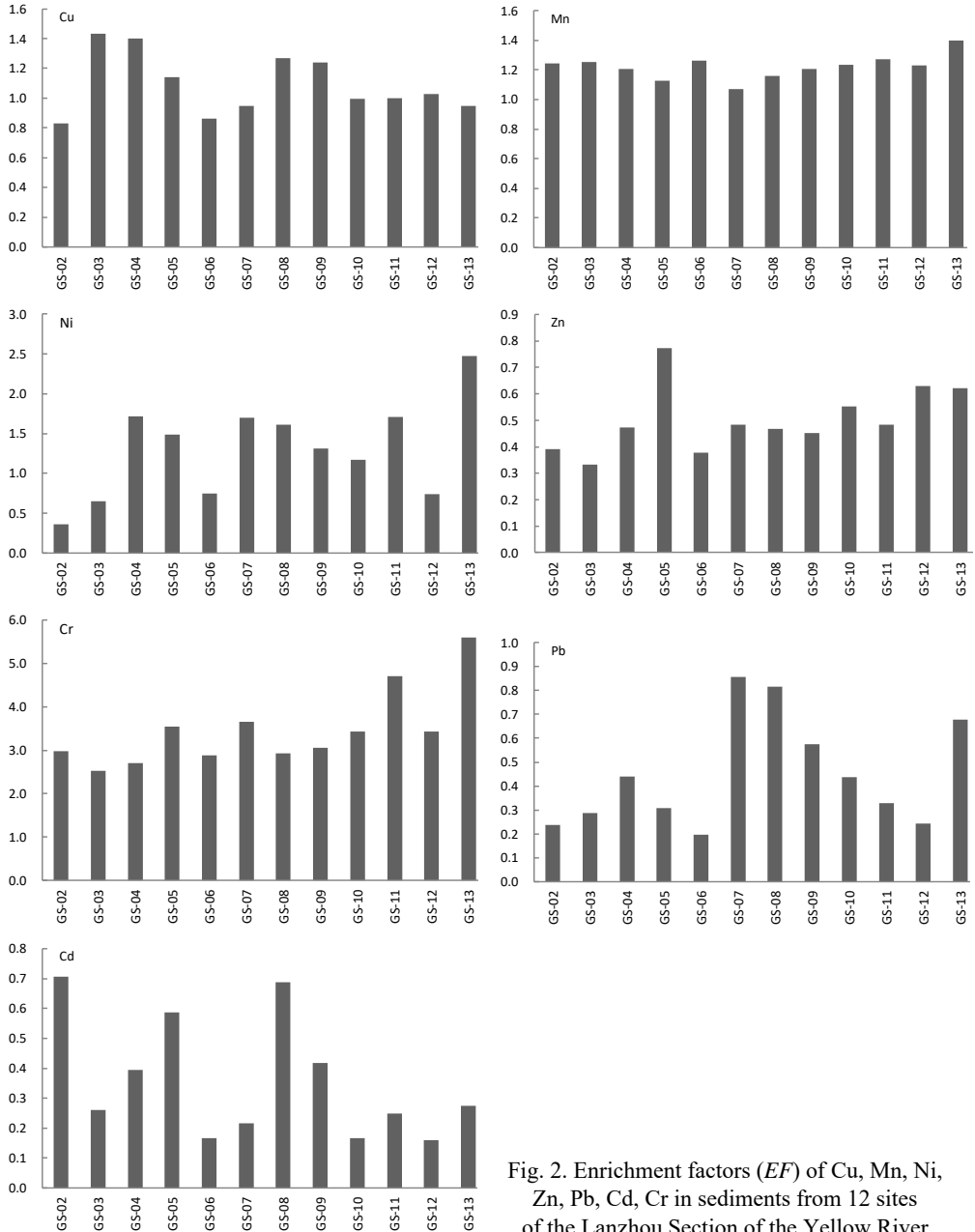

Fig. 2. Enrichment factors (EF) of Cu, Mn, Ni, Zn, Pb, Cd, Cr in sediments from 12 sites of the Lanzhou Section of the Yellow River

pollution), Pb (*EF* = 0.19–0.85, no pollution), Cd (*EF* = 0.15–0.71, no pollution), Cr (*EF* = 7.6–13.8, moderately severe pollution in stations GS-03, GS-11 and GS-13, severe pollution in stations GS-02, GS-04, GS-05, GS-06, GS-07, GS-08, GS-09, GS-10, GS-12). Average *EF* of Mn (1.20), Ni (1.29), and Zn (0.99) was close to 1, which could indicate some crustal origin for these metals. The *EF*s for Cr and Cu are particularly high, which could be interpreted as a situation of contamination due to siltation (Fig. 2).

Sediments which can act as secondary source of pollutants are generally taken as a medium for the assessment of the risk posed by the pollutants. There were several sediment quality assessment methodologies used for the said purpose. One of the methods was the risk assessment code (RAC) criteria, which was based on the percentage of metal present in acid soluble speciation [22]. Although the criteria were arbitrary and classical still it was very popular for the risk assessment. According to these criteria, sediment which can release the metal in acid soluble fraction less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing the metal more than 50% of total metal in this fraction is considered to be severely dangerous and could easily enter the food chain. According to this criteria, Cd appeared to pose low to medium risk at most of the sites of the system but high risk at sites GS-06. However, Ni, Cu and Mn pose medium to high risk. But at a few spots Mn crosses the level of very high ecological risk (Fig. 3). Other metals were low risks. A perusal of data further revealed that the sites having one or more metals in the high risk zone generally belong to the Yellow River.
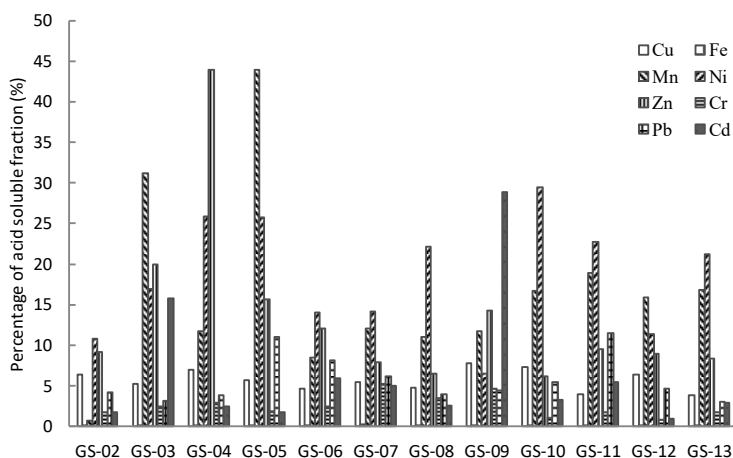

Fig. 3. Acid soluble fraction of heavy metal sediments
from 12 sites of the Lanzhou Section of the Yellow River, China

Metal pollution could be assessed with respect to world surface rock averages [24] or the widely used average shale [25] with reference to the degree of contamination.

The source of pollution was therefore determined through the normalization of geo-accumulation values to the reference element. The degree of pollution in sediments could be assessed by determining the enrichment factor and indices such as the pollution load index and geoaccumulation index [19]. According to the Muller scale [20], the calculated results of I_{geo} indicated that only Cr could be considered as from moderate to strong polluter or strong polluter at some of the study stations ($2 < I_{geo} < 4$). Cu was extremely polluted at Qilihe bridge. All other metals showed unpolluted or moderate polluter situation for other stations. The contamination order on the basis of the mean I_{geo} values was in the following: Cr > Cd > Pb > Cu > Mn > Ni > Fe > Zn (Table 4).

Table 4

Geoaccumulation index (I_{geo}) and pollution load index (PLI) of heavy metal sediments from 12 sites the Lanzhou Section of the Yellow River, China

Metal	Cu	Fe	Mn	Ni	Zn	Cd	Cr	Pb	PLI
GS-02	−1.68	−1.54	−1.05	−2.64	−1.04	1.35	−1.29	−1.14	0.69
GS-03	0.23	−0.41	0.07	−0.89	−2.14	1.17	1.43	0.17	1.45
GS-04	−0.97	−0.60	−0.50	−0.64	−1.75	0.41	0.90	0.17	1.12
GS-05	−1.14	−1.18	−0.97	−0.41	0.02	1.37	2.90	−0.36	1.52
GS-06	−1.95	−1.56	−1.10	−1.86	−1.51	−0.83	1.80	−1.16	0.73
GS-07	5.12	−0.64	−0.56	0.21	−0.63	−0.83	−0.45	0.61	1.92
GS-08	−0.97	−0.85	−0.90	−0.50	−1.47	1.08	1.79	0.46	1.33
GS-09	−0.77	−1.04	−1.07	−0.84	−1.65	0.40	2.43	−0.01	1.20
GS-10	−0.91	−0.69	−0.34	−0.16	0.17	−0.05	3.07	0.33	1.70
GS-11	2.29	−0.48	−0.33	−0.43	−3.85	−0.19	−0.10	−0.97	1.06
GS-12	−0.48	−0.42	−0.29	−1.08	−3.26	−0.46	3.58	−0.54	1.16
GS-13	−1.79	−1.87	−1.24	−0.11	−0.84	−0.50	3.23	0.11	1.15
Mean	−0.25	−0.94	−0.69	−0.78	−1.50	0.25	1.61	−0.22	

PLI could reflect the extent of heavy metal pollution and the changing extent in time and space [21]. The result of the assessment showed that expect for the unpolluted region of sites GS-02 and GS-06, other sites belong to moderately polluted or strongly polluted. The sequence of pollution level from high to low of different heavy metals was: Cr > Cu > Cd > Pb > Ni > Mn > Fe > Zn. The maximum of *PLI* was at site GS-07, while the minimum is at site GS-02 (Table 4).

4. CONCLUSION

This study pointed to the heavy metals estimation as well as the sediment quality criteria of surface sediments along the Yellow river coast. The average concentrations of heavy metals were in Fe > Mn > Cr > Zn > Ni > Cu > Pb > Cd order. The statistical analysis reflected the insignificant correlations among most determined heavy metals.

The significant correlation among Fe, Mn and Cu indicated that these three metals could have common origin. The absent relation among most heavy metals and different anthropogenic and nature sources may lead to this insignificant. Fe, Cu, Cd and Cr performed less proportion of mobile speciation (acid soluble, reducible, and oxidizable) comparing with immobile speciation (residual) demonstrated their stronger stability and lower environmental risk which could result in negative impact on the aquatic biota of the Yellow River.

The sediment quality was achieved by using the geoaccumulation index, enrichment factor, pollution load index and risk assessment code. The results indicated that Cd, Cr, and Cu caused moderate pollution or strongly pollution along most studied area. Accordingly, except for Cd, Cr, Cu, all studied heavy metals concentrations in the sediments from the Lanzhou Section of the Yellow River resulted in unpolluted or moderately polluted. The high enrichment factors of Ni and Cr created a high environmental risk. Actually, in spite of the rapid recreational and human developments taken place in the Yellow River coast, the Yellow River coast will face to seriously threatened. These results could be used as a contribution to the knowledge and rational management of the river. Additionally, they could serve as a reference database to assess the future impacts of human activities for the Yellow River.

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