SCIENCE CHINA
Chemistry

• ARTICLES •

May 2010 Vol.53 No.5: 1217–1224
doi: 10.1007/s11426-010-0089-9

Metals in water and surface sediments from Henan reaches of the Yellow River, China

FENG JingLan[1*], WANG GuoLiang[2], SUN JianHui[1], SUN ShengPeng[2] & LIU XiangFu[1]

[1] *Henan Key Laboratory for Environmental Pollution Control; College of Chemistry and Environmental Sciences, Henan Normal University, Xinxiang 453007, China*

[2] *State Key Laboratory of Pollution Control and Resources Reuse; College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China*

Received July 7, 2009; accepted October 10, 2009

The concentrations of Cd, Cr, Cu, Ni, Pb and Zn were determined in the water and surface sediments from the Henan reaches of the Yellow River. Twenty-three sampling sites along the Yellow River and its tributaries were selected. Generally, metal concentrations were found to decrease in sequences of Zn > Cu > Pb > Cr > Ni > Cd in water and Zn > Cr > Pb > Ni > Cu > Cd in sediments. High levels of metal concentration were determined at a few stations of the river and its tributaries, such as Yiluo River, Si River and Qin River. The pollution of the Yellow River by Cd, Cr, Cu, Ni, Pb and Zn can be regarded as much higher compared to the background values, US EPA criteria (1999) and China water quality criteria (2002). For sediments, metal levels except Pb did not significantly exceed the average shale levels and backgrounds in several countries including China. Data analysis manifests that positive correlations were found between Cu, Ni and Zn in water, and Pb, Ni, Zn and Cr in sediments. The Pearson correlation coefficient analysis and Cluster analysis were provided to assess the possible contamination sources. The results indicate a general appearance of serious pollution along the banks of the Yellow River. The wastewaters discharged by the mine plants, smelter plants, power plants, battery plants, tannery plants, etc., and sewage inputs from the cities along the river banks may be the sources of metals.

metals, water, surface sediment, Yellow River

1 Introduction

The Yellow River is the second longest river in China with a length of about 5464 km. From its source at the Yueguzonglie Basin on the north of the Bayankela Mountain in Tibet highlands to the Bohai Sea, it flows through nine provinces in the north of the country (Qinghai, Sichuan, Gansu, Ningxia, Inner Mongolia, Shannxi, Shanxi, Henan, Shandong) with a watershed over 795000 km^2 (including isolated inflow area 42000 km^2). In its drainage basin, especially the Henan reaches, it is the vital water resources for domestic, agricultural and industrial uses.

Unfortunately, rapid population growths, land development along the river basin, urbanization and industrialization have severely reduced the river's water quality [1, 2]. Significantly, large uncontrolled pollutant inputs, including metals from industrial and urban sources, have contributed to increased pollution of the mainstream and tributaries of the Yellow River. Metals such as lead, copper, chromium, cadmium and nickel are serious pollutants of aquatic ecosystems and have attracted considerable attention over the past few decades because of their environmental persistence, toxicity and ability to be incorporated with food chains [3]. Therefore, it is necessary to conduct a comprehensive riverwater quality monitoring program in order to safeguard public health and to protect the valuable fresh water resources. Metal concentrations were investigated in rivers,

*Corresponding author (email: fengjl1123@yahoo.com.cn)

lakes, marine coasts throughout the world, such as Yangtze Estuary [4], Pearl River Estuary [5], Haihe River in China [6], Shing Mun River in Hong Kong, China [7], Almendares River in Cuba [8], Gomit River in India [9], Danube River [10] and Rhine River in Europe [11].

In this study, levels and ecological risk of metals (Cd, Cr, Cu, Ni, Pb and Zn) in water and sediments from the Henan reaches of the Yellow River are systematically conducted. The results provide a comprehensive look at the current pollution status of metals and the potential source of contamination in this basin of Yellow River. These data can form the foundation for water quality protection of the Henan Reaches of the Yellow River.

2 Materials and methods

2.1 Selection of sampling stations and sample collection

The study focused on Henan reaches of the Yellow River, with a length of 177 km, including about five chief tributaries. The drainage area is scattered in many cities, towns and industrial zones. Many industries are related to agriculture, chemistry, pharmaceutical, printing, packing materials, mining, smelting, food and drink processing, building and machinery.

Twenty-three sample stations along Henan reaches of the Yellow River and its tributaries were selected (Figure 1). Surface water and sediment samples were collected from twenty-three sampling sites in November 2005. Surface water samples were collected in polyethylene bottles (washed with detergent, then with deionized water, 2 M nitric acid (Merck), then deionized water again, and finally surface water). Samples were acidified with 10% HNO_3, placed in an ice bath and brought to the laboratory. The samples were filtered through Whatman glass microfibre filters (GF/F, 150 mm) and kept at 5 °C until analysis. Approximately 2 kg sediment samples from a depth of −10 cm from the surface was collected at each of the sampling points using a sediment collector with an acid-washed plastic scoop. Two or more distributed samples (Water samples and sediment samples) were collected in each sampling points according to river width.

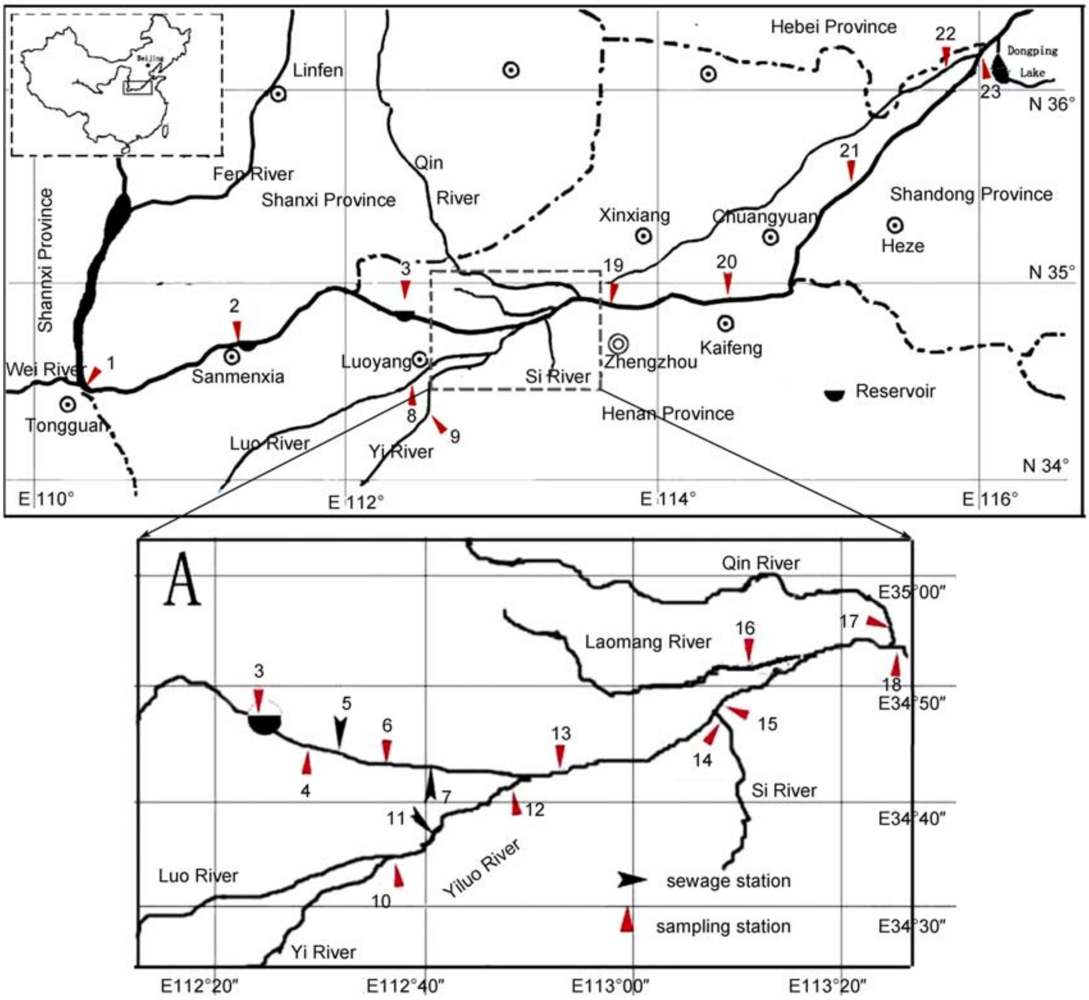

Figure 1 Sampling locations along the Henan reaches of the Yellow River.

2.2 Sample pre-treatment and analysis

The digestion method employed for metals in water is similar to that described by the reference [12]. The sediment samples were transferred into acid washed plastic containers and freeze-dried for 72 h, then passed through a 150 μm nylon sieve so as to remove any large debris and were thoroughly homogenized using a pestle and mortar. Samples for the determination of total metal levels were digested using $HF/HNO_3/HClO_4$ (2:1:2, *V*/*V*) mixture at 200 °C. The residue was transferred to a clean 25 mL volumetric flask and deionized water was added to make up to the volume.

The concentrations of Cd, Cr, Cu, Ni, Pb and Zn were determined using an atomic absorption spectrometer (Z-5000 AAS, HITACHI, Japan). Flame AAS was applied to detect the metals of Zn, Cu and Pb, while graphite furnace AAS was used to measure Cd, Cr, and Ni. The quality controls for the strong acid and digestion method included reagent blanks, duplicate samples, and stream sediment conference materials (GBW07306-GBW073010, 1986). The QA/QC results showed no signs of contamination in all the analysis. The recoveries for metals in the reference materials were around 95%–105%.

2.3 Data analysis

This study employed Pearson correlation analysis of Cd, Cr, Cu, Ni, Pb and Zn to examine the relationships between the concentrations of metals in water and sediments. Hierarchical cluster analysis (HCA) was applied to determine sample stations which had similar or different contamination patterns [13]. All statistical treatments mentioned in this paper were performed using Origin Pro. 6.0 software and SPSS 12.0 statistical calculation program.

3 Results and discussion

3.1 Metals in water

Table 1 shows the levels of metals in water from Henan reaches of the Yellow River. It is generated by comparing measured concentration of metals with world average background levels [14] and water quality standards currently effective in USA and China [15, 16], and the results are obtained from the literature [9, 17–19]. In China the water bodies are divided into five classes according to the utilization purposes and protection objectives: Class I is mainly applicable to the water from sources, and the national nature reserves. Class II is mainly applicable to first class of protected areas for centralized sources of drinking water, the protected areas for rare fishes, and the spawning fields of fishes and shrimps. Class III is mainly applicable to second class of protected areas for centralized sources of drinking water, protected areas for the common fishes and swimming areas. Class IV is mainly applicable to the water areas for industrial use and entertainment which are not directly touched by human bodies. Class V is mainly applicable to the water bodies for agricultural use and landscape requirement. When the metal level in this study is compared with Water Quality Criteria, it is noted that the concentration ranges of Cu and Pb are over that of Class V, while other metals of Cr and Cd are higher than that of Class I and Zn is

Table 1 Metal concentration in water from the Henan reaches of Yellow River and other study areas and water quality criteria (10^{-3} mg L^{-1})

		Pb	Cu	Cr	Cd	Ni	Zn	Ref.
World average background		0.2	1.00		0.02	0.3	10	[14]
US EPA criteria								[15]
CMC		65	13	16	4.3	470	120	
CCC		2.5	9	11	2.2	52	120	
China water quality criteria								[16]
Class I		10	10	10	1		50	
Class II		10	1000	50	5		1000	
Class III		50	1000	50	5		1000	
Class IV		50	1000	50	5		2000	
Class V		100	1000	100	10		2000	
Gomti River, Turkey		10–39	*n.d.	1.3–5.7	n.d.	10–17	11–32	[9]
Guadiamar River, Spain		13.1–98.7	13–39.9		n.d. ~286.7		86.7–1000.8	[17]
Selenga River Delta, Russia		1–54	15–54	11–44			14–464	[18]
Lake District, West Poland		2–143	7–198	2.6–7.0	0.1–4.9	n.d.~55	86–751	[19]
Yellow River, China,	MD±SD	75.14 ± 48.56	553.99 ± 657.80	26.24 ± 10.75	0.80 ± 0.52	15.34 ± 8.58	639.01 ± 365.28	this study
Mainstream	Min-Max	5.34–164.92	7.98–2192.25	11.83–46.48	n.d.~1.74	4.80–28.30	317.17–1385.32	

*: n.d. = not detected

higher than that of Class II. The mean value of concentrations except Pb is just a little higher than that of Class I. Several element concentrations are observed to be much greater than those in the Standards. For example, the measured concentration of Pb is higher than that given for Class IV, and the measured concentrations of Cu and Zn are also greater than that given for Class II. When compared to the background values, our results show that the concentrations of metals are much higher and the Yellow River has been contaminated by some of them. When compared with the priority toxic pollutants, such as Cd, Cr, Cu, Pb and Zn (listed in US EPA, 1999, for water quality criteria), concentrations of Pb, Cu, Cr and Zn are observed to be greater than the criteria maximum concentration (CMC) values of US EPA water quality criteria (Table 1). However, the concentrations of Cd and Ni are lower than criteria continuous concentration (CCC) values. Most of the metal concentrations are much higher than those in other river and lake water collected from Gomti River, Turkey, Guadiamar River, Spain, Selenga River Delta, Russia, and Lake district, West Poland. The similar metal levels of Pd are present in Lake District, West Poland and the Yellow River, while metal levels of Cr in the water of Selenga river delta, Russia and the Yellow River are almost the same. All of the results indicate that the Yellow River water is polluted to some extent by some kinds of metals, especially Pb, Cd and Ni, which may be caused by some discharge sources of metals, such as chemical fertilizers containing Ni and Pb in agricultural and industrial wastewater including Pb, Cr, Cu, Ni, etc.

3.2 Metals in sediments

Metal levels in sediments from Henan reaches of the Yellow River and other rivers of China, US, India, etc. and average shale values are presented in Table 2, including background value of soil in China and background levels of metals in US and Canada, in order to evaluate metal contamination of sediments. A comparison of metal concentrations in the sediment with the average shale levels is generally taken as a quick and practical method of tracing metal enrichment. Soil background of China has a similar metal element levels with US background and Canadian background except that Cd is much lower than that of Canadian background, which indicates that the characteristics of soil about the metal level do not differ too much. However, the average shale has about two or three times higher metal levels of Cu, Cr, Ni and Zn, while Pb presents the similar level. When the metal levels in the Yellow River are compared with the average shale level, the mean metal values for Pb and Cd are on the high side and Cu, Cr, Ni and Zn are on the lower side. Compared with soil background levels of metals in China, the concentrations of metals determined are lower than the background except Pb and Zn. The elements of Pb, Cr and Zn exceed the Canadian background and US background levels, and the other elements are well within the guidelines of US and Canadian backgrounds except Cd. The higher concentrations of each metal element are found from the sediment of the Yangtze River in a comparison of those from the sediment of the Yellow River, and the concentrations of Cu, Pb and Zn in the sediment from the Mississippi River are higher than those from the Yellow River, with a little lower level of Pb and Cr. When it comes to the levels of metal in the sediment from Gediz River, Turkey, the results show that metal contamination is much more serious than that in the Yellow River, for the concentrations of metals detected are several to ten of times over those from the Yellow River. For Guadaira River, the concentrations of Cu, Cd and Ni in the sediment are

Table 2 Metal concentration in sediment samples from the Henan reaches of the Yellow River and other study areas and background concentration levels (mg kg^{-1})

		Pb	Cu	Cr	Cd	Ni	Zn	Ref.
Average shale levels		20	45	90	0.3	68	95	[20]
China soil background levels		23.5	20.7	57.3	0.079	24.9	68	[21]
US background levels		23	20	51		25	88	[22]
Canadian background levels		23	25	31	1.1	31	65	[22]
Gediz Rvier , Turkey		128	140	200		106	160	[23]
Cuadaira River, Spain		20	25	38	3	37	51	[24]
Mississippi River, US		27.41	21.31	71.62	0.175		144	[25]
Danube River and Tributaries, Turkey		14.70	26.90	26.50	<1.10	17.50	78	[10]
Gomti River, India		40.33	5.00	8.15	2.42	15.17	41.67	[9]
Yangtze River, China	Min-max	21.00–65.00	26.00–68.00	59.00–117.00	0.30–3.40	27.00–57.00	71.00–187.00	[26]
Mainstream	MD±SD	45.18 ± 13.30	51.64 ± 12.54	87.82 ± 15.68	1.53 ± 1.00	40.91 ± 8.73	140.27 ± 36.45	
Yellow River, China	Min-max	17.42–55.13	10.95–34.87	30.89–102.72	0.07–1.41	14.37–59.14	51.06–133.77	this study
Mainstream	MD±SD	32.24 ± 10.85	17.54 ± 7.47	52.44 ± 18.30	0.48 ± 0.36	24.71 ± 11.75	74.77 ± 25.65	

higher than those in the Yellow River, which differ from the higher levels of Cu, Cd and Zn for the Danube River and Tributaries, Turkey and the higher levels of Pb and Cd for Gomti River, India, which may be caused by the varied and complicated distribution of agriculture, industry and so on. Generally, all the metals in the sediment from Henan reaches of the Yellow River are revealed to be in a little lower level, but the relatively higher concentrations of Pb, Cr and Ni are detected compared with those of other rivers from different regions, except Yangtze River, China and Gediz River, Turkey. There are logical reasons: First, the Yellow River has the highest sand percentage of river water in the world and the amount of sand from Loess Plateau in the west of China could be settled down and decreased the metal level in the sediment. Second, during recent scores of years a variety of industries have developed and increased fast, especially in Luoyang District along the Yellow River and its tributary, Liluo River, such as mine plants, smelter plants, electronics plants, battery plants, and tannery plants. The wastewater of these industries is discharged to the Yellow River directly or indirectly without remediation to enrich the metal levels of Pb, Cr and Ni in the sediments from Henan reaches of the Yellow River.

3.3 Spatial distribution of metals in water and sediments

The concentrations of metals from each sample station in water and sediments are shown in Figure 2. Generally, metal concentrations in the water and sediments decreased in sequences of Zn > Cu >> Pb > Cr > Ni > Cd and Zn > Cr > Pb > Ni > Cu > Cd, respectively. Avila-Pérez and Balcázar [27] investigated metal concentrations in the bottom sediments of a Mexican reservoir and reported the sequence to be Zn > Cr > Cu > Ni > Pb > Cd. The concentrations of Pb, Cu and Zn observed in water were much higher than those in the sediments (Figure 2(a)), while the concentration of Cr in water showed a different behavior and was lower than that in sediments (Figure 2(b)). The concentrations of Ni and Cd in sediments and water varied very much in all sampling stations (Figure 2(b)).

In Figure 2(a), the highest concentrations of Pb, Cu and Zn in water were observed at station 5, because this sample station was close to chemical plants and pollutants including untreated wastewater discharged into the Yellow River. The elements of Pb, Cu and Zn have similar distributions in water and the sampling stations of 8, 10, 12, 13, 16 and 19 were observed with higher levels of them in water and

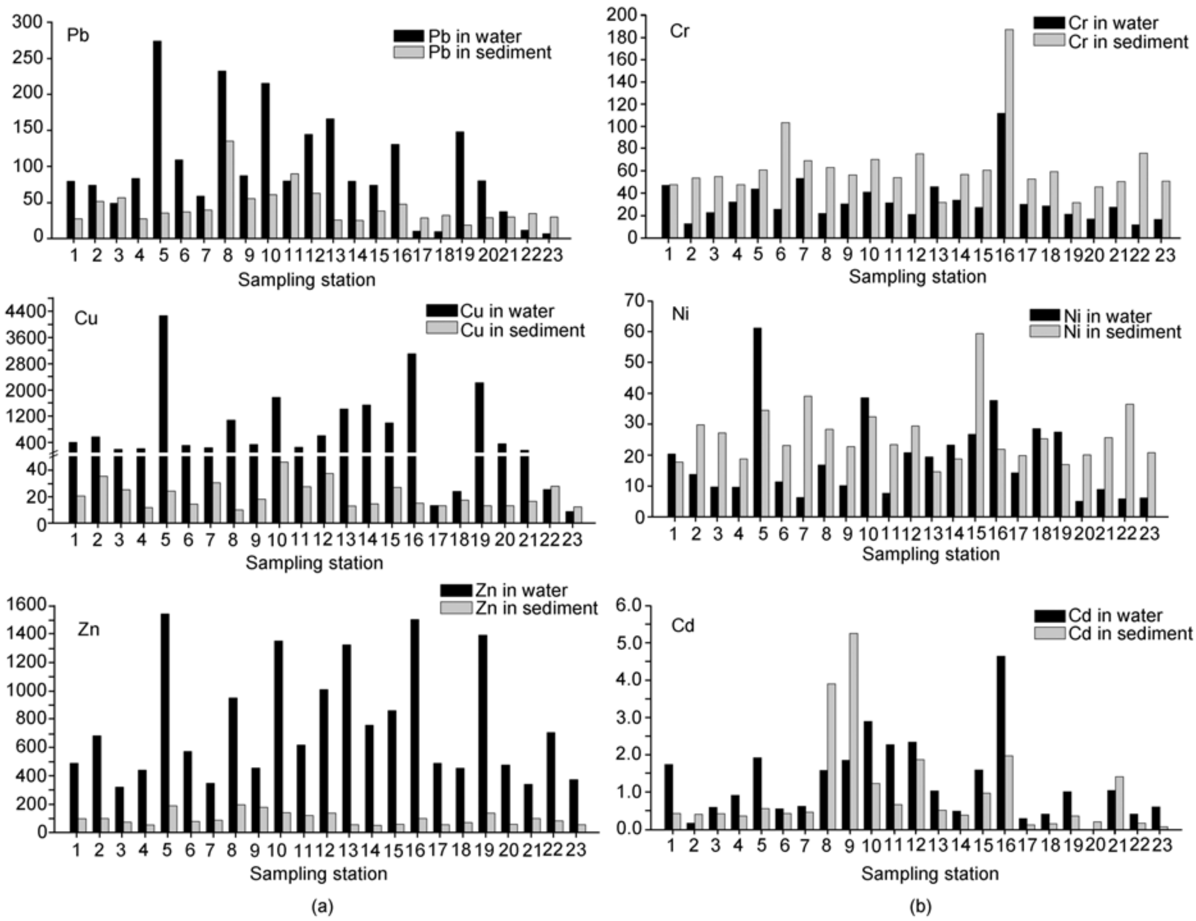

Figure 2 Spatial distribution of metal levels in water and sediments from the Henan reaches of the Yellow River (mg kg^{-1} for sediments and 10^{-3} mg L^{-1} for water). (a) Spatial distribution of Pb, Cu and Zn; (b) spatial distribution of Cr, Ni and Cd.

sediments, possibly because of some effluence from a nearby sewage treatment plant and a waste dumping site. In addition, the agricultural activities around the river may have contributed to the observed high levels of Pb and Cu, because of the use of pesticides, compost and manure.

Figure 2(b) shows that all samples have a consistent distribution of Cr in sediments with the highest concentration in water and sediments at station 16 for Cr. Because of the influence of wastewater and untreated sewage discharged from plants and factories, Ni and Cd in water varied significantly. In the sediment the highest concentrations of Ni and Cd are present at stations 15 and 9, respectively, which indicates that a long-term contamination of Ni and Cd occurred and was enriched. The water and sediment samples collected from stations 2, 3, 21, 22 and 23 showed a lower concentration, for these sample areas are far from industrial areas and with no wastewater discharged.

3.4 Correlation analysis and hierarchical cluster analysis

Correlation analysis was performed on metals in water and sediments at each station to assess possible co-contamination from the similar sources among the data set. The Pearson correlation coefficients of metals in water and surface sediments are summarized in Tables 3 and 4. Table 3 shows that there are strong associations between Pb and Cu, Cd, Ni and Zn, and between Zn and Cu, Cd, Ni and Cr. Table 4 shows there are weaker associations among metals in sediments, compared with correlations among metals in water. In addition, there are strong associations between Pb and Cr, Zn and Pb, Cu and Ni, Zn and Cr. No remarkable correlation between the elements of Cd and Cu, Ni, Pb, and Cr was observed.

Table 3 Pearson correlation coefficient of metals in water from Henan reaches of the Yellow River

	Pb	Cu	Cd	Cr	Ni	Zn
Pb	1	0.763**	0.506*	0.254	0.670**	0.792**
Cu		1	0.556**	0.533**	0.882**	0.882**
Cd			1	0.723**	0.532**	0.604**
Cr				1	0.452*	0.431*
Ni					1	0.788**
Zn						1

** Correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed).

Table 4 Pearson correlation coefficients of metals in surface sediments from Henan reaches of the Yellow River

	Pb	Cu	Cr	Cd	Ni	Zn
Pb	1	0.204	0.596**	0.148	0.177	0.605**
Cu		1	−0.037	0.059	0.551**	0.240
Cr			1	0.201	0.051	0.680**
Cd				1	0.113	0.070
Ni					1	0.107
Zn						1

** Correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed).

Cluster analysis method has proved useful in solving classification problems [28] where the object is to sort cases or variables into groups or clusters, for example, the degree of association is strong between members of the same cluster and weak between members of different clusters. Hierarchical cluster analysis based on the concentrations of all elements in water presented in Figure 3 and Table 5 indicates that all the stations were classified into five clusters using a criterion value of rescaled distance. There were thirteen stations in cluster A, five stations in cluster B, two stations in clusters C and D separately, and only one in cluster E (Figure 3). Cluster E only included station 5, which markedly differs from the rest due to the highest concentrations of Pb, Cu, Ni and Zn present in the water. The logical reason is that the sample station was located near the Luoyang Petrochemical Company, which was the biggest local chemical plant. Cluster D included stations 1 and 18, which were situated at the mainstream converged with the tributaries of Wei River and Qin River. The low mean concentrations of Pb, Cu and Zn were determined at station 18. Cluster C was unique because of the highest mean concentrations of Pb, Cu, Cd, Cr and Ni. The samples in this cluster were taken from the industrialization districts, in which many smelter plants, electronics plants, battery plants and tannery plants were distributed. Clusters A and B included

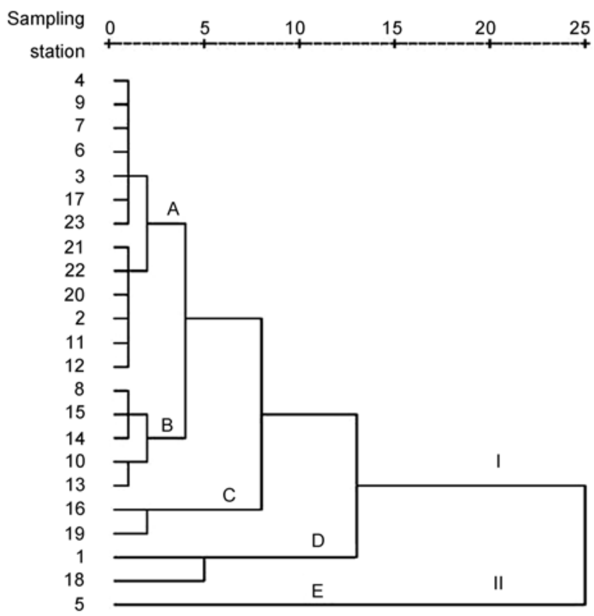

Figure 3 Dendrogram of hierarchical cluster analysis of metal concentrations in water.

Table 5 Statistics of the clusters in hierarchical cluster analysis (HCA) in water and sediments from the Henan reaches of the Yellow River

Clusters	No. of stations	Pb	Cu	Cd	Cr	Ni	Zn
In water (10^{-3} mg L^{-1})							
A	13	62.67	234.97	0.90	24.77	9.70	520.78
B	5	152.2	1340.88	1.516	33.18	24.73	1042.72
C	2	138.025	2634.79	2.825	65.74	32.38	1440.51
D	2	43.39	203.83	1.075	37.18	24.225	467.16
E	1	272.63	4234.44	1.92	43.07	60.98	1535.32
In sediments (mg kg^{-1})							
A	8	36.97	21.13	0.68	71.05	26.99	103.12
B	7	27.39	15.39	0.42	48.30	23.93	58.03
C	3	50.39	22.62	2.52	77.71	24.85	127.76
D	5	69.70	24.62	1.26	60.81	28.57	116.25

most of the samples in the mainstream of the study areas and showed lower concentrations of Ni, Cd, Cr and Cu.

All the sampling stations were again divided into two sets based on the concentrations of metals in sediments using hierarchical cluster analysis (Figure 4 and Table 5). The first cluster (cluster I) included 15 stations, which was further divided into 2 sub-clusters (A and B). Cluster A mostly included the stations from the mainstream upstream of station 6 and downstream of station 20 where there was no tributary converged into the river. Cluster B included most of the sample stations where three tributaries such as Yiluo river, Si river and Qin river come into the mainstream. The second cluster (cluster II) included 8 stations and had two sub-clusters (clusters C and D). The mean concentrations of Cd, Cr and Zn were higher in cluster C than those in other clusters, with the highest concentration of Cd in station 9. The stations 7, 8, 10 and 11 have the similar contamination because of a power plant and some rural enterprises standing

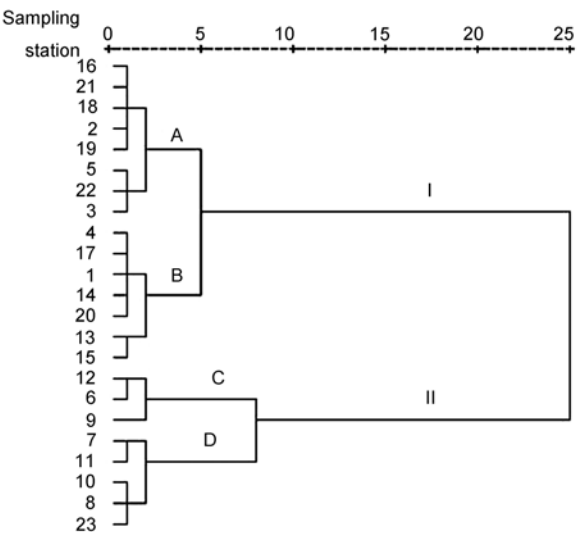

Figure 4 Dendrogram of hierarchical cluster analysis of metal concentrations in sediments.

on the banks of Yiluo River, one of the chief tributaries of the Yellow River in Henan reaches. The toxic metal concentrations of Pb, Cu and Ni are significantly higher than those in other clusters.

4 Conclusions

The purpose of this study is to determine the metal contamination status in water and sediments from Henan reaches of the Yellow River. Generally, metal levels in water and sediments were high and varied widely among sampling stations. This variation may be due to the change in the volume of industrial and sewage waste discharged to river at different sampling stations. In most cases, the average concentrations determined in Yellow River's water were found to be much higher than the world average background and US EPA criteria. According to China water quality criteria, the water quality exceeded class VI limit values of guideline. The mean concentrations of metals in water were higher than those of other rivers such as Guadiamar River, Gomti River, and Selenga River. The metal levels in sediments were slightly higher than backgrounds of China and other countries for most of the cases. Overall, the concentrations of metals in sediments were higher than those of Gomti River and Danube River but lower than those of Gediz River and Guadaira River. In all, water and sediments in the Yellow River have been contaminated by metals. The Pearson correlation analysis and cluster analysis were used to assess the possible contamination sources, and the results show that there is a significant correlation among Cu, Ni and Zn in water, Pb, Ni, Zn and Cr in sediments. The cluster analysis suggests that the wastewater discharged by the mine plants, smelter plants, electronics plants, battery plants, tannery plants, etc., and sewage inputs from the cities along the river banks may be the sources of these elements.

The authors express their great thanks to the Institute of Water Resource Protection of the Yellow River and local environmental protection agencies for their assistance with sample collection and for the support from the Key Scientific and Technological Project in Henan Province (0624440040).

1 Bulletin of Water Resources of the Yellow River for 2007. The Yellow River Conservancy Commission, Zhengzhou, 2007

2 Xia XH, Zhou JS, Yang ZF. Nitrogen contamination in the Yellow River Basin of China. *J Environ Quality*, 2002, 31(3): 917–925

3 Főrstner U, Wittman GTW. Metal Pollution in the Aquatic Environment. Berlin: Springer-Verlag, 1983

4 Gorenc S, Kostaschuk R, Chen Z. Spatial variations in metals on tidal flats in the Yangtze Estuary, China. *Environ Geology*, 2004, 45(8): 1101–1108

5 Li X, Wai OWH, Li YS, Coles BJ, Ramsey MH. Thornton L. Metal distribution in sediment profiles of the Pearl River estuary, South China. *Appl Geochem*, 2000, 15(5): 567–581

6 Huang H, Ou WH, Wang LS. Semivolatile organic compounds, organochlorine pesticides and metals in sediments and risk assessment in Huaihe River of China. *J Environ Sci*, 2006, 18(2): 236–241

7 Sin SN, Chua H, Lo W, Ng LM. Assessment of metal cations in sediments of Shing Mun River, Hong Kong. *Environ Int*, 2001, 26(5-6): 297–301

8 Olivares-Rieumont S, De La Rosa D, Lima L, Graham DW, Alessandro KD, Borroto J, Martínez F, Sánchez J. Assessment of metal levels in Almendares River sediments-Havana City, Cuba. *Water Res*, 2005, 39(16): 3945–3953

9 Singh KP, Mohan D, Singh VK. Malik A. Studies on distribution and fractionation of metals in Gomti river sediments-a tributary of the Ganges, India. *J Hydrology*, 2005, 312(1-4): 14–27

10 Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litheraty P. Analysis and assessment of metal pollution in suspended solids and sediments of the river Danube. *Chemosphere*, 2003, 51(8):633–642

11 Qu WC, Kelderman P. Metal contents in the Delft canal sediments and suspended solids of the River Rhine: multivariate analysis for source tracing. *Chemosphere*, 2001, 45(6-7), 919–925

12 Okonkwo JO, Mothiba M. Physico-chemical characteristics and pollution levels of metals in the rivers in Thohoyandou, South Africa. *J Hydrology*, 2005, 308(1-4): 122–127

13 Miller NJ, Miller JC. Statistic and Chemometrics for Analytical Chemistry, 4th ed. New York: Prentice Hall, 2001

14 Klavins M, Briede A, Rodinov V, Kokorite I, Parele E, Klavina I. Metals in rivers of Latvia. *Sci Total Environ*, 2000, 262(1/2): 175–183

15 State environmental protection administration of China. China environmental quality standards for surface water GB3838-2002, 2002. 2

16 US EPA. National Recommended Water Quality Criteria Correction of Water. 1999, EPA v822-Z-99-001, 25

17 Alonso A, Santos M, Callejón M, Jiménez JC. Speciation as a screening tool for the determination of metal surface water pollution in the Guadiamar river basin. *Chemosphere*, 2004, 56: 561–570

18 Khazheeva ZI, Urbazaeva SD, Bodoev NV, Radnaeva LD, Kalinin YO. Metals in the water and bottom sediments of the Selenga River Delta. *Water Resour*, 2004, 31(1): 69–72

19 Cymerman SA, Kerpers AJ. Concentrations of metals and plant nutrients in water, sediments and aquatic macrophytes of anthropogenic lakes (former open cut brown coal mines) differing in stage of acidification. *Sci Total Environ*, 2001, 281: 87–98

20 Turekian KK, Wedepohl KH, Distribution of elements in some major units of the earth's crust. *Geologic Soc Am Bull*, 1961, 72:175–192

21 Background Value of Soil Element, China. National Environmental Protection Bureau and China Environmental Monitoring Center. Beijing: China Environmental Science Press, 1990

22 Grosbois CA, Horowitz AJ, Smith JJ, Elrick KA. The effect of mining and related activities on the sediment trace element geochemistry of Lake Coeur D'Alene, Idaho, USA. Part III: the Spokane River Basin. *Hydrologic Processes*, 2001, 15(5): 855–875

23 Akcay H, Oguz A, Karapire C. Study of metal pollution and speciation in Buyuk Menderes and Gediz River sediments. *Water Res*, 2003, 37(4): 813–822

24 Enguix GA, Ternero RM, Jiménez Sá JC, Fernández Espinosa AJ; Barragán de la Rosa FJ. Assessment of metals in sediments in a tributary of Guadalquiver River (Spain), metal partitioning and relation between the water and the sediment system. *Water, Air Soil Pollut*, 2000, 121(1-4): 11–29

25 Santschi PH, Presley BJ, Wade TL, Garcia-Romero B, Baskaran M. Historical contamination of PAHs, PCBs, DDTs and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. *Marine Environ Res*, 2001, 52(1): 51–79

26 Yang Z, Wang Y, Shen Z, Niu J, Tang Z. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *J Hazard Mater*, 2009, 166(2-3): 1186–1194

27 Avila-Pérez P, Balcázar M, Zarazúa-Ortega G, Barceló-Quintal I, Díaz-Delgado C. Metal concentrations in water and bottom sediments of a Mexican reservoir. *Sci Total Environ*, 1999, 234(1-3): 185–196

28 Livingstone DJ. Data analysis for chemists: application to QSAR and chemical product design. London: Oxford University Press, 1995