Characteristics and accumulation of heavy metals in sediments originated from an electroplating plant

Xiaoshuai Hang [a,b], Huoyan Wang [a,*], Jianmin Zhou [a], Changwen Du [a], Xiaoqin Chen [a]

[a] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, No. 71 Beijing East Road, Nanjing 210008, Jiangsu Province, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

ABSTRACT

Heavy metals in river water and sediments originated from an electroplating plant in Jiangsu Province of China were studied and analyzed for their environmental impact. The results indicated that the wastewater from the plant degraded the quality of the aquatic environment downstream from the plant. In surface water, considerable concentrations of Cu, Ni, Zn, Mn and Cr were present at the sites near the plant. Unsafe levels of Cu were observed at all sites, and unsafe levels of Ni, Zn, and Cr were present at some sites. Significant accumulation of Ni, Cu, Zn and Cr was identified, and heavy metal longitudinal distribution in sediments was similar to that in water. The contents of Ni, Cu and Cr at all sites and Zn at some sites were likely to result in harmful effects on the environment. The risks posed by Ni, Cu, Zn and Cr in water and sediments decreased with increasing downstream distance. Moreover, a modified sequential extraction procedure was employed to determine exchangeable, carbonate-bound, iron–manganese oxide bound, organic matter bound and residual fractions of metals in sediments. The results showed that Ni was distributed in every fraction except for iron–manganese oxide bound, significant Mn exhibited in exchangeable fractions, and high percentage of Cu was in the organic matter and residual fractions. Residual fraction was the dominant fractions for Pb and Zn. According to RACs, Ni and Mn posed a high risk to the environment, Zn exhibited medium to high risk, Cu had low to high risk, and Pb possessed a low to medium risk.

1. Introduction

The acceleration of industrialization in China has been almost inevitably introduced various pollutants into the natural environment [1]. Heavy metals are one of the most common pollutants in aquatic environments from either natural sources, such as geologic weathering, or anthropogenic sources, such as industrial, agricultural, municipal and residential waste products [2–5]. Heavy metals can be transported into aquatic environments in many ways, and once there they degrade the quality of the stream or river. The fate of heavy metals can be either adsorbed into riverine sediments or accumulated in benthic organisms, sometimes at toxic levels [6]. More importantly, heavy metals can enter the food chain through leaching into groundwater or plant absorption (or bioaccumulation). Therefore, they can threaten human health, and sometimes cause chronic health conditions.

Considering that heavy metal levels in water bodies vary with the seasons and other environmental factors, they do not necessarily accurately and consistently reflect the pollution of a river at all times. However, sediments can act as both carrier and sink for contaminants in aquatic environments [6], thus riverine sediments reflect the history of pollution of a river [7]. In the study on the impact of sediments polluted by heavy metals, total metal levels provide limited information [8]. A good comprehension of pollution levels of sediments requires identification of heavy metal fractions, which impact on the availability and mobility of heavy metals. It is also well known that determining the fractions of heavy metals in sediments is indicative for contamination in hydrologic systems than measuring the total concentrations. A sequential extraction procedure proposed by Tessier et al. [9] and Kersten and Forstner [10] provided more information about the mobility, bioavailability and toxicity of metals than the simple measurement of the dissolved concentrations. In order to obtain enough information about the toxicity of heavy metals in aquatic ecosystems, we must not only understand the characteristics of heavy metals in water, but also the geochemical phases of heavy metals in sediments. The sequential extraction procedure allows us to analyze the fractions of heavy metals in sediments.

* Corresponding author. Tel.: +86 25 86881569; fax: +86 25 86881000.
E-mail address: hywang@issas.ac.cn (H. Wang).
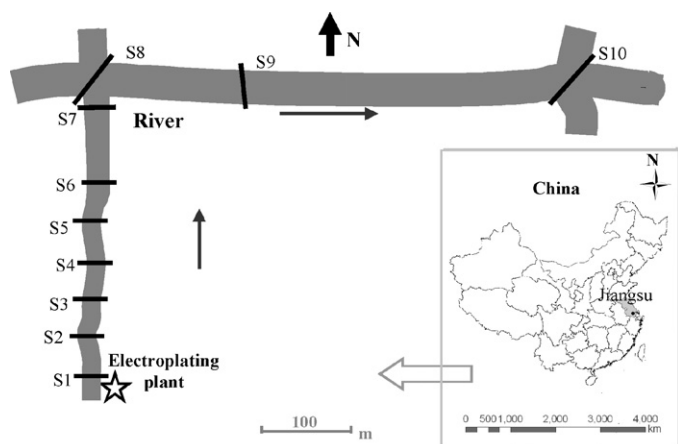
Fig. 1. Distribution of sampling sites in the river (the gray area on the map is Jiangsu Province of eastern China, and the black dot is the study area, located in the south of Jiangsu).

Electroplating industries generate a large volume of wastewater with high concentrations of heavy metals due to metal surface cleaning, rinsing and spent bath bleeding [11–14]. Heavy metals are released into the environment in treated wastewater, which are discharged to surface water systems [15,16], causing a serious environmental concern. Electroplating is a popular industry in the Yangtze River Delta of China. Currently, most of the electroplating wastes in this area are discharged directly into waters without proper treatment. This seriously degraded the quality of the aquatic environment. It is well known that the characteristics of metals in water and sediment adjacent to electroplating plants can provide evidence how the anthropogenic sources impact on the aquatic environment, and aid in assessing the risks associated with wastewater discharge practice. A study that provides insights into metal characteristics and speciation is necessary in order to assess the impact of the wastewater on the surrounding aquatic environment.

The behaviors of heavy metal in water and aquatic ecosystems have been studied extensively [3]. However, a case study on impact of heavy metals in streams and rivers surrounding an electroplating plant can be exemplified for similar situations. In this study, we examine a river that is a major water source with severe pollution from a nearby electroplating factory in the Yangtze River Delta of China. This particular electroplating plant has been in operation for 30 years. However, no systematic study has been conducted previously on the river to assess the distribution of heavy metals in this hydrological system. Our objectives were (1) to identify the impact of wastewater on the distribution of heavy metals in surface water of the river; (2) to examine the characteristics and accumulation of heavy metals in riverine sediments; and (3) to determine the potential cumulative damage to the aquatic ecosystem as a result of wastewater discharge from the factory over a long period of time.

2. Material and methods

2.1. Description of the study area

The study sites are located along a river downstream from an electroplating factory, which is located in the south of Jiangsu Province in eastern China (Fig. 1). Surface runoff from agricultural fields and catchments on both sides of the river are the main water sources for the river. The river is a tributary of the Yangtze River, and intercepts many other minor rivers (or streams). The width of the river ranges from 15 to 25 m, and the depth ranges from 3.0 to 5.0 m. Great water fluctuations due to seasonal changes and irrigation practices are observed in the surrounding region. The river is a crucial source of non-potable water, irrigation water, aquatic production water, and also critical to the recharge and discharge of groundwater. In addition, this area is historically famous because of its landscape and its geographical position. The region is also home to a national marsh park. Therefore, the river is considered a protected aquatic system according to national standards of environmental quality for surface water (GB3838-2002) and water quality standards for scenic and recreational areas (GB12941-91) in China.

However, the stream receives industrial discharge and wastewater from the electroplating plant, which contains great quantity of heavy metals as the samples collected in July of 2005 indicated. The pH of the wastewater was 2.32. The concentrations of heavy metals Zn, Mn, Cr, Cu, and Ni in the wastewater were 1.34, 3.77, 28.1, 6.40 and 9.73 mg L^{-1}, respectively, including possible Cr(VI) because Cr(VI) was electroplated in this plant. Neither Pb nor Cd was detected in these samples (our unpublished data).

2.2. Sample collection and preparation

Ten river stations were selected in the study. The sites were chosen according to their downstream distances from the factory (Table 1) as well as whether the sites were located at important river junctions and places where the river changes its course (Fig. 1). Surface water and sediment samples were collected from the sampling sites in the July of 2005. According to climate and hydrology patterns, the sampling period was during the rainy season, but the water of the river was not mobile when the samples were taken. Water samples were collected in acid-washed polyethylene bottles, and kept in a cooler at 4 °C. Samples of about 3 kg of superficial sediment were obtained using an Eckman Dredge grab sampler from site 3 to site 10. A profile sample was also collected from site 10. At each site, three sub-samples of water and sediments were collected, and mixed to ensure that the sample was representative for the site. The pH of all samples was measured in the field using a pH pocket tester (HI98128) made by HANNA with accuracy of 0.01 unit of pH. Sediment samples were transferred to acid-washed and air-sealed plastic bags, placed in a cooler at 4 °C, and transported to the laboratory immediately for further analysis [8].

After transporting to the laboratory, the water samples were filtered through 0.45 μm membrane filter, acidified to pH 2.0 using

Table 1
Distance downstream from the wastewater discharge location and pH values of sampling sites along the river

	Sampling sites									
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Distance downstream (m)	0	50	100	150	200	250	350	400	600	1000
pH										
Surface water	8.11	8.21	8.20	8.00	8.15	7.85	8.08	8.07	8.08	8.03
Superficial sediment	–	–	6.34	5.87	5.90	6.05	5.96	6.86	6.59	6.39

Table 2
Method of metal speciation analysis in sediments

Fractions	Principal extracted component	Reagents and their concentration	Extract conditions	
			pH	$T\,(^{\circ}C)$
F1	Exchangeable	1 M NH$_4$OAc	7.0	25 ± 0.5
F2	Carbonate-bound	1 M NaOAc	5.0	25 ± 0.5
F3	Fe/Mn oxide bound	0.1 M NH$_2$OH·HCl	2.0	25 ± 0.5
F4	Organic matter bound	30% H$_2$O$_2$	2.0	85 ± 5
		1 M NH$_4$OAc	2.0	
F5	Residue	Same process as described for total heavy metals		

nitric acid, and determined dissolved metals. The sediment samples were divided into two parts. One part was analyzed for heavy metal fractions, and the other was air-dried at the ambient temperature, crushed to pass through a 0.149 mm stainless steel sieve, and then analyzed for total heavy metals.

2.3. Sequential extraction procedure

Compared to fresh sediment, none of drying methods (freeze-drying, air-drying, and oven-drying at 105 °C) can completely preserve the original distribution of heavy metals in various geochemical fractions of sediment. This is because atmospheric oxygen can decrease heavy metals in the exchangeable and carbonates fractions, causing corresponding increases in other fractions [8]. Such alteration is directly related to the quantities of metals present in various fractions of the sediment. The effect is much more significant when the quantity is small [8]. In this study, to minimize this effect, a five-step sequential extraction procedure was introduced to determine Cu, Pb, Zn, Ni and Mn fractions for fresh sediments in order to preserve sediment representation for the environment. The fractionation separates heavy metals into exchangeable, carbonate-bound, iron–manganese oxide bound, organic matter bound (or sulfides and organic matter), and residual fractions [9,17] using the sequential extraction procedure as outlined in Table 2 and modified by Yuan et al. [17]. In order to assure the precision and analytical accuracy in analyzing metals of fresh sediment samples, a fresh sediment sample equivalent to 1 g dry sediment was used to analyze five fractions of heavy metals. Moreover, to ensure the comparison of total metals to the residual fraction, the procedure for the residual fraction was same to the method for total metal determination.

2.4. Metal analysis

To determine the contents of total heavy metals, the sediment samples (1 g) were digested with counter-*aqua regia* [18]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Advantage, Thermo Jarell Ash Co., USA) was used to determine Cr, Cu, Ni, Pb, Cd, Zn and Mn in acidified solution [5,19]. Additionally, the concentrations of Cu, Ni, Pb, Zn and Mn in each extract of the sequential extraction procedure were also measured by ICP-AES. The analytical standard solutions (CLMS-2, Multi-Element Solution Standards, SPEX CertiPrep®, Inc.) were matrix-matched to the acidified solution sample as well as each extract of the extraction procedure of sediment. The detection limits of Cr, Cu, Ni, Pb, Cd, Zn and Mn are 1, 1.5, 1, 3, 0.3, 0.2 and 0.1 $\mu g\,L^{-1}$, respectively.

2.5. Validation of sequential extraction method

The metal concentrations of all blanks of each different extraction step in this process were below the analytical detection limit. This study established the identity between the sum of five metal fractions and the total metal to assure the precision in analyzing metal speciation in fresh sediment, because there is no standard reference material for the accuracy of the analysis of fresh sediment. The sum of five fractions extracted using the sequential extraction method was compared with the total metal concentrations extracted using a counter-*aqua regia* digestion procedure (Table 3). The percentage range of recovery was between 82 and 119. Although the sum slightly deviated from the certified value, the extraction efficiency was found to be acceptable, giving the accuracy and reproducibility of the results of sediment fraction extraction using the sequential extraction method.

Table 3
Comparison of metal concentrations (mg kg^{-1}) extracted using the sequential extraction protocol and total concentration in superficial sediments

	Ni			Cu			Mn			Pb			Zn			Cr	Cd
	Sum	Total	Rec[a]	Sum	Total	Rec[a]	Sum	Total	Rec[a]	Sum	Total	Rec[a]	Sum	Total	Rec[a]	Total	Total
Site																	
S3	3186	2846	112	10,920	9797	111	426	451	94	112	106	106	1643	1483	111	9671	1.92
S4	1833	1698	108	8,109	7416	109	312	338	92	85.5	79.0	108	1228	1146	107	5857	1.44
S5	1648	1795	92	5,519	5404	102	437	497	88	28.3	24.9	114	788	762	103	5160	2.33
S6	1733	1643	105	5,181	4989	104	435	475	92	50.3	46.3	109	780	745	105	3398	1.62
S7	719	657	109	3,167	2753	115	465	546	85	36.7	35.1	105	578	502	115	1415	1.89
S8	1750	1703	103	3,738	3851	97	721	782	92	18.6	17.2	108	611	618	99	1518	1.74
S9	408	416	98	778	781	100	549	523	105	24.0	20.1	119	434	427	102	460	1.94
S10	206	251	82	389	440	88	595	625	95	25.2	21.6	117	465	391	119	345	2.17
Consensus-based sediment quality guidelines for metals in freshwater ecosystems																	
PEC[b]		48.6			149			Nv[c]			128			459		111	4.98
TEC[d]		22.7			31.6			Nv[c]			35.8			121		43.4	0.99

[a] Rec = $(C_{F1} + C_{F2} + C_{F3} + C_{F4} + C_{F5})/C_{Total}$, given in percentage (%).

[b] Probable Effect Concentration.

[c] No value.

[d] Threshold Effect Concentration.

Table 4
Freshwater quality criteria for heavy metals ($mg L^{-1}$)

	Ni	Cu	Zn	Cr(VI)
CMC[a], acute	0.470	0.013	0.120	0.016
CCC[b], chronic	0.052	0.009	0.120	0.011

[a] Criterion maximum concentration.
[b] Criterion continuous concentration.

All acids used in this study were of a guaranteed grade. Other reagents were analytical grade. De-ionized water used in each step of the experiment was obtained from a Millipore machine ($18.3 M\Omega cm$ resistivity). All glassware and plastic vessels used for the experiments were first soaked in a solution of nitric acid for 24 h and rinsed with de-ionized water.

In this research, three replicates were performed for all of the samples, including both water and sediment samples. Moreover, analyses were carried out on reagent blanks, a stream sediment reference material (GBW-07310) in an attempt to assure precision and analytical accuracy in analyzing total heavy metals in the sediment samples. All data presented in this study were arithmetic means.

3. Results and discussion

3.1. Water and sediment pH of the river

The pH was measured in surface water and superficial sediment samples of the river downstream from the electroplating plant. The pH values are listed for each site (by downstream distance from the plant) in Table 1. Slightly alkaline character (pH values ranging from 7.85 to 8.21 and average at 8.00) was observed in water samples. There is no significant difference among the 10 sampling sites. The pH of river water in alkaline range was probably caused by quick dilution of abundant river water, suggesting that the wastewater discharge from the plant had very little effect on the pH of river surface water during the rainy season. In contrast to the water sample, the sediment samples showed a slightly acidic character with pH values ranging from 5.87 to 6.86. The physical and chemical properties of sediments may be responsible for their pH. In addition, the pH of sediments should not be significantly impacted within a short time even during rainy season, because riverine sediment is relatively stable.

3.2. Metals in water

The distribution of heavy metals in the surface water is shown in Fig. 2, except for Pb and Cd because we were unable to separate these two metals. The order of heavy metal concentrations in water is Ni > Cu > Mn > Cr > Zn. Among all the sampling sites, the river water heavy metal concentrations (except Pb and Cd) of site 1 were the highest, and the concentrations of Cu and Ni for site 1
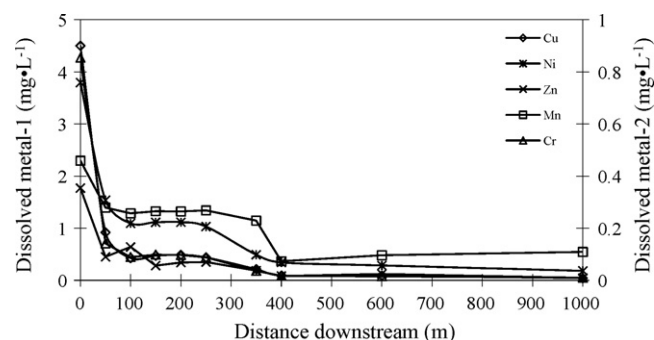
Fig. 2. Distribution of dissolved metals along the river (dissolved metal-1: Cu and Ni; dissolved metal-2: Zn, Mn and Cr).

were 4.50 and 3.80 $mg L^{-1}$. These concentrations were significantly higher than those of other sites, and there was a dramatic decrease from site 1 to site 2. The changes from site 2 to site 6 were no significant. However, there was reduction of metal concentrations from site 6 to site 8. From site 8 to site 10, the concentrations did not change evidently. The distributions of Zn, Mn, and Cr also exhibited the similar changes from site 1 to site 10, and their concentrations at site 1 were 0.354, 0.459 and 0.854 $mg L^{-1}$, respectively.

The variations of Cu, Ni, Zn, Mn and Cr within the water flow were similar, and the order of heavy metal concentrations in the surface water was nearly the same as that of the wastewater, implying that these metals might be originated from the electroplating plant. In addition, concentrations of the metals of a water sample collected from the upstream of the plant discharge point were 0.040 $mg L^{-1}$ for Cu, 0.181 $mg L^{-1}$ for Ni, 0.009 $mg L^{-1}$ for Zn, 0.109 $mg L^{-1}$ for Mn, and 0.010 $mg L^{-1}$ for Cr. These concentrations were approximately equal to the concentrations of site 10. This indicated that there was no other artificial source near the river and the major source of the contamination was probably the plant wastewater in upper regions of the river. Therefore, we can conclude that the contamination of heavy metals in the river could be attributed to the wastewater discharge from the plant. This can be supported by the fact that the concentrations of heavy metals were the highest in site 1 that was the closest to the discharge site, as we would expect. Subsequently, the concentrations of heavy metals were dispersed by river water or absorbed by sediments [20], as the alkaline pH of river water facilitate the formation of heavy metal precipitation. Therefore, the levels of heavy metals decreased dramatically from site 1 to site 2. There was no significant change from site 2 to site 6, because the narrow river way in this stretch of the river probably elevated the water flow velocity. Thereafter, the river was broadened, resulting in a decrease of heavy metal concentrations from site 6 to site 8. Finally, the levels of heavy metals from site 8 to site 10 were lower, and stayed approximately the same for these sites. Generally, it is clear that the contribution of wastewater from the plant directly determined the distribution of heavy metals in the river, along with the volume of water in the river at any given site.

Table 5
Correlation coefficients obtained from the chemical data of total heavy metals in superficial sediments ($N = 8$, bold values higher than $r > 0.700$)

	Ni	Cu	Mn	Pb	Zn	Cr	Cd
Ni	1.000						
Cu	**0.945****	1.000					
Mn	−0.295	−0.542	1.000				
Pb	**0.714***	**0.868****	−0.674	1.000			
Zn	**0.889****	**0.971****	−0.585	**0.940****	1.000		
Cr	**0.899****	**0.965****	−0.605	**0.882****	**0.971****	1.000	
Cd	−0.229	−0.331	0.278	−0.408	−0.324	−0.132	1.000

* Significant at the 0.05 probability level ($P < 0.05$).
** Significant at the 0.01 probability level ($P < 0.01$).

Table 6
Least-square (r^2) values for regression analysis of metal concentrations in superficial sediments and downstream distance ($N = 8$, bold values are the best least-square, all five bold values are significant at 99% probability level)

Metal	Linear	Logarithmic	Polynomial (second order)	Power	Exponential
Ni	0.666	0.803	0.783	0.815	**0.834**
Cu	0.734	0.940	**0.943**	0.901	0.930
Pb	0.387	0.661	**0.726**	0.668	0.429
Zn	0.557	0.836	0.859	**0.919**	0.699
Cr	0.586	0.869	0.918	**0.963**	0.866

According to the criteria of National Recommended Water Quality Criteria in America [21], the freshwater quality has two classifications (Table 4): criterion maximum concentration (CMC) and criterion continuous concentration (CCC), which signify the acute and chronic freshwater quality criteria for aquatic life. In this study, Cr in surface water was believed to be mainly Cr(VI) because wastewater containing Cr(VI) was discharged from the plant. Furthermore, Cr(VI) is very soluble in wide range of pH, and it is much more toxic to organisms than Cr(III) [16]. A risk assessment based on surface water samples from the river showed that Cu concentration at all the sampling sites was above the acute freshwater quality criterion for aquatic life, and Ni and Cr were above the chronic freshwater quality criteria at all the sampling sites except for Cr at site 10. The concentrations of Ni and Cr exceeded the acute freshwater quality criteria from site 1 to site 7 and from site 1 to site 8, respectively. Only two sites possessed Zn concentration above the acute or chronic freshwater quality criterion. The results indicated that heavy metals in the river course (from 0 to 1000 m downstream from the plant) were at potential risk, and the risk decreased with the downstream distance.

3.3. Metals in sediments

3.3.1. Total metal contents in sediments

The total contents of heavy metals in the superficial sediment samples were generally high (Table 3). The total levels of metals in the superficial sediment samples from the river followed the order: Cu > Cr > Ni > Zn > Mn > Pb > Cd. Statistical analysis showed a clear association among Ni, Cu, Pb, Zn, and Cr in the superficial sediment samples (Table 5). The distribution of total heavy metals in sediments showed that high concentrations of Ni, Cu, Pb, Zn and Cr at site 3 gradually decreased towards site 10, where the lowest level was found. This trend was consistent for the distribution of dissolved heavy metals in water except for Pb, which was below the detection limit. According to some reports [22–24], it is only meaningful to fit mathematical functions to the simplest of geomorphic situations with respect to the downstream metal dispersal in river systems. Only the equations for downstream reduction of Ni, Cu, Pb, Zn and Cr concentrations were considered here, because concentrations of total Mn and Cd did not decrease with downstream distance. The patterns of Mn and Cd distribution will be discussed separately. Five separate regressions were applied to Ni, Cu, Pb, Zn and Cr distribution, and the least-square values were calculated (Table 6). The results showed that all regressions were significant at 95% probability level except linear regression of Pb, illustrating that the accumulation of Ni, Cu, Pb, Zn and Cr significantly decreased downstream from the plant. Interestingly, an exponential regression best described the Ni distribution, and a second-order polynomial function produced the best fit for Cu and Pb values, while a power function best fitted with Zn and Cr. They were at 99% probability level (Table 6). The difference among the best-fit regressions of the five heavy metals indicated their dissimilarity in concentration decline. It is probably caused by the discrepancy precipitation of heavy metals and their subsequent deposition in the streambed.

The change in concentration is due to the release of these metals from the pollution resource. Because the sampling sites are downstream from the electroplating plant, the wastes from the plant are discharged directly into the river, contaminating the superficial sediments [25]. Despite the high metal pollution levels, sediments generally possess high ability to adsorb metals released from pollution sources [20]. Moreover, the correlation coefficients of total heavy metals suggest that discharged wastewater from the plant not only enhances the concentrations of heavy metals, but also influences the topography of the river. The order of heavy metals in the sediment is dissimilar to the order in water, indicating the distinct difference in the balance of different heavy metals in aquatic and sedimentary systems. Overall, total metals in the sediment samples decreased with increasing distance from the plant except for Mn and Cd. The distribution of Zn, Cr, Cu and Ni in the sediment samples corresponded to the distribution of dissolved metals in water. However, Ni, Cu, Zn and Cr in site 8 were higher than the surrounding sites. This may be caused by the depth of the river at this site, because the water at this site is much deeper than the depth at upstream sites. The difference in depths might result in the migration of polluted sediment from upstream to this site.

These results demonstrate the spatial differences between the intensity of contamination of riverine sediments and the role of different elements in the contamination. Background values of total heavy metals in the studied riverine sediment were obtained from

Table 7
Total heavy metals in superficial sediments and their background values (mg kg^{-1})

Element	Mean ± standard deviation ($N = 8$)	Maximum	Minimum	Reference values[a]/% of sites exceeding reference values	Background values[b]/% of sites exceeding background values
Ni	1376 ± 871	2846	251	40/100	55/100
Cu	4429 ± 3193	9797	440	35/100	41/100
Mn	530 ± 131	782	338	NB[c]	408/87.5
Pb	43.8 ± 32	106	17.2	35/50	16/100
Zn	759 ± 379	1483	391	100/100	156/100
Cr	3478 ± 3249	9671	345	90/100	74/100
Cd	1.88 ± 0.29	2.33	1.44	0.20/100	1.6/87.5

[a] Reference values (i.e. reference background values) are from the Environmental Quality Standard for Soils of China (GB15618-1995).

[b] Background values of studied riverine sediments.

[c] NB indicates that there was no reference background value in the Environmental Quality Standard for Soils of China (GB15618-1995).
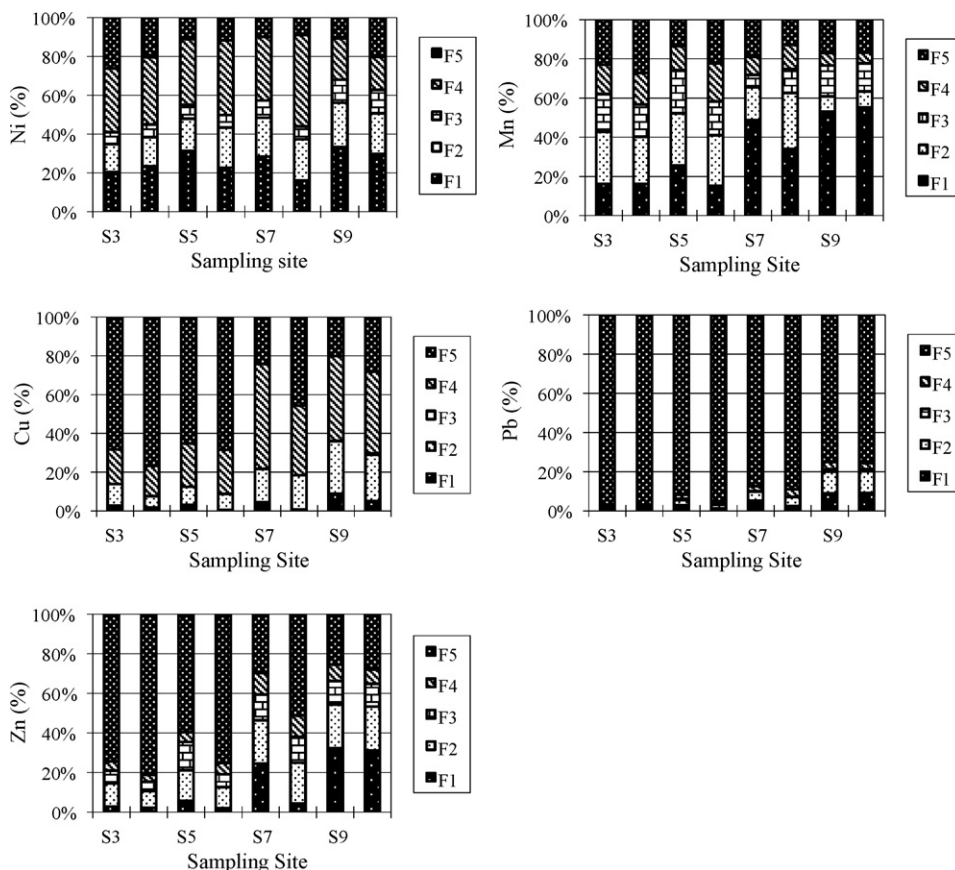
Fig. 3. Metal distribution in the superficial sediments along the river according to the sequential extraction procedure (F1: exchangeable; F2: carbonate-bound; F3: iron–manganese oxide bound; F4: organic matter bound; F5: residue).

a profile at site 10, since we have no previous value from this particular river to which we can compare our results. To ascertain an estimation of the background metal values, the sediment sample was taken at depths of 40–50 cm at site 10. Moreover, in the absence of Chinese guidelines for acceptable heavy metals in sediments, we utilize reference background values from the Environmental Quality Standards for Soils in China (GB15618-1995) as a benchmark for contamination (Table 7). There is no reference background value listed for Mn in that standard. The concentrations of Ni, Cu, Zn and Cd in the sample collected at site 10 for background value exceeded the reference background values by 37.5, 17.1, 56.0 and 700%, respectively (Table 7). In contrast, the estimated values of Pb and Cr represented only 45.7 and 82.2% of the reference background values. The concentrations of these metals could be the result of geological influence. The background values of Cu, Zn and Pb were similar to the reference values for heavy metals in the river sediments in Queensland, Australia [26], but the value of Cd was higher than the one for Queensland (Table 7). In our analysis, Ni, Cu, Zn and Cr substantially exceeded the background values at all sites, and Mn and Pb were also excessive at almost all the sites, especially at the sites near the plant. The concentration of Cd was generally equivalent to background value. These results indicated that accumulation of Ni, Cu, Zn and Cr was significant, and the accumulation of Mn and Pb was also noticeable.

The accumulation of heavy metals in sediments can be a secondary source of water pollution once environmental condition is changed [27,28]. Therefore, an assessment of heavy metal contamination in sediments is an indispensable tool to assess the risk of an aquatic environment. Numerical Sediment Quality Guidelines (SQGs) have been used by many scientists to identify contaminants

of concern in aquatic ecosystems and to rank areas of concern on a regional or national basis [29,30]. Two SQGs for metals in freshwater ecosystems were developed from the published SQGs, including a Threshold Effect Concentration (TEC) and a Probable Effect Concentration (PEC). If the metals in sediments are below the TEC, harmful effects are unlikely to be observed. If the metals are above the PEC, harmful effects are likely to be observed [30]. MacDonald et al. [30] noted in his studies that most of the TECs provide an accurate basis for predicting the absence of sediment toxicity, and most of the PECs provide an accurate basis for predicting sediment toxicity. The consensus-based SQGs are listed in Table 3, and they can provide a reliable basis for assessing sediment quality conditions in freshwater ecosystems [30]. The concentrations of Ni, Cu, Pb, Zn, Cr and Cd in all of our sediment samples are higher than
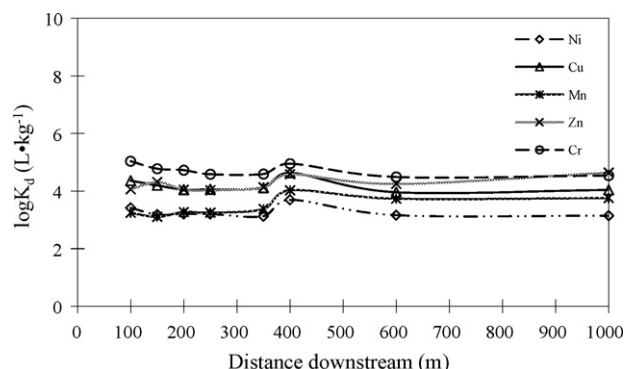

Fig. 4. Distribution coefficients ($\log K_d$) of metals with distance downstream.

proposed TECs, except for Pb, in four of the sites far from the plant. The concentrations of Ni, Cu and Cr exceeded PECs in all samples, while Zn from site 3 to site 8 was above PEC. The peak values at site 3 for Ni, Cu, Cr and Zn were 57.6, 64.8, 86.1 and 2.1, all higher than PECs. However, Pb and Cd were below their PECs. These results indicated that Ni, Cu and Cr in the riverway from 0 to 1000 m downstream of plant discharge were likely to result in harmful effects in the fluvial ecosystem. In some sites, Zn was also likely to result in harmful effects, whereas Pb and Cd were in potential risk. It is evident that riverine sediment was polluted with heavy metals, and the pollution decreased with the downstream distance. This conclusion was the same as the conclusion obtained for the river water samples.

3.3.2. Metal fractions in sediments

The patterns of metal speciation in the downstream sediments demonstrated several important trends with respect to the availability of metals in the environment [24]. Five fractions (exchangeable, carbonate-bound, iron–manganese oxide bound, organic matter bound and residue) are likely to be affected by various environmental conditions, according to Tessier et al. [9]. In order to provide more information about mobility, bioavailability and toxicity of metals in sediments, the sequential extraction procedure was introduced to determine metal fractions in fresh sediments. The fractions of metals in the superficial sediment downstream from the plant were determined using the sequential extraction procedure (Fig. 3). Metal speciation analysis of the river sediments indicated that Ni in the superficial sediment was distributed in every fraction except for iron–manganese oxide bound. A significant amount was found in the exchangeable fraction (16–33%) and bound to organic matter (17–47%). This is contrary to the results of Taylor and Kesterton [24], because they found that greater than half of the total Ni contamination was preferentially bound to ferromanganese materials under normal or slightly alkaline pH conditions. The discrepancy could be the result of the difference in pH of the sediment. The slightly acidic pH condition found in the downstream (Table 1) in our study might partly explain the low Ni concentration associating with ferromanganese oxides. Manganese was distributed in all five fractions with a significant amount found in the exchangeable fraction (15–55%). This is consistent with results reported by Pertsemli and Voutsa [31]. This indicates that Mn in this weakly sorbed metal fraction is retained on the sediment surface by relatively weak electrostatic interactions and can be released easily by ion-exchange processes and dissociation of Mn carbonate-bound [17,31–34].

Relatively lower proportions of Cu and Pb were found in the exchangeable fractions, and their range was from 0.7 to 8.9% for Cu and from 0.8 to 9.2% for Pb, hinting little threat to the aquatic environment. The distribution patterns of Cu and Pb were consistent with the observations of Šurija and Branica [35] and Yuan et al. [17]. Moreover, considerable fraction of Cu was bound to organic matter (16–54%) coinciding with organic and sulfur compounds, and a dominant fraction was in the residual fraction (20–77%), which was associated mainly with aluminosilicate minerals. Copper can easily form complexes with organic compounds due to its high affinity and stability constant of organic copper complexes [31] in addition to be held in crystal lattices. The majority of Pb was found in the residual fraction (75–97%). Heavy metals held in crystal lattices by primary and secondary minerals are not subject to remobilization under normal conditions [9,36]. Similarly, the dominant proportion of Zn was also found in the residual fraction (25–81%).

In summary, the five fractions of Ni, Cu, Pb and Zn decreased with the distance from the plant except for Cu in iron–manganese oxide bound fraction, Pb in three fractions (exchangeable, carbonate-bound and iron–manganese oxide bound), and Zn in the exchangeable fraction. These distributions are similar to their total concentrations. The distribution Mn in the residual fraction is more stable than in the other four fractions with increasing downstream distance.

The characteristics of heavy metals in different fractions offer help in determining their toxicity in an aquatic environment, and can also be used to conduct a risk assessment. Risk Assessment Codes (RACs) provide indication of the possible risk by applying a scale to the percentage of metals found in exchangeable and carbonate-bound (i.e. labile) phases [31]. According to RACs, if these fractions of the sediments are below 1%, there is no significant risk for the aquatic system. With percentages between 1 and 10%, there is a low risk, 11–30% for medium risk, 31–50% for high risk, and above 75% for very high risk [6,31,37]. Significant amounts of Ni (34.9–56.3%), Cu (7.7–35.9%), Mn (40.3–63.6%), Pb (2.3–20.4%) and Zn (10.6–54.6%) were found in the labile phases (Fig. 3). Thus, Ni and Mn posed a high risk to the environment, while Zn also exhibited significant labile fraction and posed a medium to high risk. The risk of Cu was from low to high, and that of Pb posed a low to medium risk.

3.4. The relationship between metals in water and metals in sediments

Some heavy metals in the water and the sediment samples exhibited similar distribution trends. Statistical analysis showed that the correlation coefficients between concentrations of Zn, Cr, Cu, and Ni in water and those in sediment were 0.879 ($P < 0.005$), 0.829 ($P < 0.05$), 0.820 ($P < 0.05$), and 0.780 ($P < 0.05$), respectively. This suggests that the accumulation of Zn, Cr, Cu and Ni in the sediments is related to the corresponding levels in the aquatic environment. This is also an indication that Zn, Cr, Cu and Ni levels in the sediment samples are affected by wastewater from the plant. In other words, these heavy metals serve as indicators for a history of pollution. For example, the undetectable level of Pb in the water suggests no Pb in recent wastewater discharge, and this is also consistent with the negligible levels of Pb in the exchangeable fractions of the sediments. There is no positive correlation between Mn in the surface water and sediment samples, implying that Mn behave differently from other metals. The correlation between Ni in water and the exchangeable fraction in the sediments was 0.906 ($P < 0.005$), but no significant positive correlation was observed for other metals between the dissolved amounts in the water and various fractions in the sediments, indicating lack of equilibrium controls in the systems [6].

The distribution coefficient (K_d) of metals can also express the relationship between metals in the water and sediments. It can be defined as the ratio of the metal concentration in the sediments ($\mu g\,kg^{-1}$) over the dissolved metal concentration in the water ($\mu g\,L^{-1}$) [31]. The logarithmic values of K_d according to downstream distance are shown in Fig. 4. This graph demonstrates that the values of $\log(K_d)$ have a similar trend according to the distance downstream for all five metals. The $\log(K_d)$ values ranged from 3.1 to 5.0 L kg^{-1}. The order of $\log(K_d)$ values is Cr > Zn > Cu > Mn > Ni. Because we were unable to detect Pb and Cd in water, the $\log(K_d)$ values for these metals were the highest values. These results are similar to the results in a study of particulate metal concentrations over dissolved metal concentrations by Nguyen et al. [38]. The value of K_d depends on the nature of the sediment, the geochemical parameters of the water, and the specific characteristics of each metal [31,38,39]. The values obtained are due to the specific characteristics of each metal in a similar environment. For Pb, its high particle reactivity promotes association with particulate matter [38], and the particulate matter eventually deposits in

sediments. On the contrary, low particle reactivity and a stronger potential to form stable complexes allow Ni and Cu to remain in the dissolved phase [38].

4. Conclusions

In order to understand the impact of wastewater from an electroplating plant on the fluvial ecosystem, seven heavy metals (Ni, Cu, Zn, Mn, Cr, Pb and Cd) were analyzed in both surface water and sediment samples of the river downstream from the plant. The results revealed that the fluvial ecosystem downstream from the electroplating plant was contaminated by heavy metals, probably originated from the plant wastewater discharge. Levels of Cu, Ni, Zn, Mn and Cr in the surface water of the river correlate with the distance of the sample site from the electroplating plant. Copper levels in the surface water pose an environmental risk, while Ni, Zn and Cr pose a risk at some of the sampling sites. Their risk decreased with increasing downstream distance.

Significant accumulation was found for heavy metals (Ni, Cu, Zn and Cr) in the sediments. A similar trend to the one observed for the water samples was found in the sediment samples. According to the risk assessment, Ni, Cu and Cr in sediments were likely to result in harmful effects to the fluvial ecosystem, and in some sites, Zn was also likely to result in harmful effects. Lead and Cd were at potential risk. The risk of Ni, Cu, Zn and Cr due to their concentrations in the sediment decreased with increasing downstream distance.

The modified sequential extraction procedure was introduced to determine the five fractions of metals in the superficial sediment samples downstream from the plant. The analysis of the metal speciation indicated that Ni was distributed into every fraction except for iron–manganese oxide bound. Significant percentage of Mn existed in the exchangeable fraction, while considerable percentage of Cu was in the organic matter and residual fractions. The residual fraction was also the dominant fraction for Pb and Zn. Overall, the contents of Ni, Cu, Pb and Zn in five fractions decreased with the distance from the plant. According to RACs, Ni and Mn posed a high risk to the environment, Zn exhibited medium to high risk, Cu was at low to high, and Pb possessed a low to medium risk. In summary, the accumulation of heavy metals in sediments downstream from the electroplating plant suggests that the wastewater discharge have had severe consequence on the fluvial environment.

Acknowledgements

References

[1] J. Ščančar, R. Milačič, M. Horvat, Comparison of various digestion and extraction procedures in analysis of heavy metals in sediments, Water Air Soil Pollut. 118 (2000) 87–99.
[2] U. Förstner, G.T.W. Wittman, Metal Pollution in the Aquatic Environment, Springer, Berlin, 1979.
[3] M. Kļaviņš, A. Briede, V. Rodinov, I. Kokorīte, E. Parele, I. Kļaviņa, Heavy metals in rivers of Latvia, Sci. Total Environ. 262 (2000) 175–183.
[4] E.J. Dawson, M.G. Macklin, Speciation of heavy metals in floodplain and flood sediments: a reconnaissance survey of the Aire Valley, West Yorkshire, Great Britain, Environ. Geochem. Health 20 (1998) 67–76.
[5] A. Demirak, F. Yilmaz, A.L. Tuna, N. Ozdemir, Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey, Chemosphere 63 (2006) 1451–1458.
[6] K.P. Singh, D. Mohan, V.K. Singh, A. Malik, Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India, J. Hydrol. 312 (2005) 14–17.
[7] C.K. Jain, Metal fractionation study on bed sediments of river Yamuna, India, Water Res. 38 (2004) 569–578.
[8] F. Bordas, A.M. Bourg, A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load, Water Air Soil Pollut. 103 (1998) 137–149.
[9] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.
[10] M. Kersten, U. Forstner, Chemical fraction of heavy metals in anoxic estuarine and coastal sediments, Water Sci. Technol. 18 (1986) 121–130.
[11] N.L. Nemerow, A. Dasgupta, Industrial and Hazardous Waste Treatment, Van Nostrand Reinhold, New York, 1991.
[12] A.J.B. Dutra, G.P. Rocha, F.R. Pombo, Copper recovery and cyanide oxidation by electrowinning from a spent copper–cyanide electroplating electrolyte, J. Hazard. Mater. 152 (2008) 648–655.
[13] T. Panayotova, M. Dimova-Todorova, I. Dobrevsky, Purification and reuse of heavy metals containing wastewaters from electroplating plants, Desalination 206 (2007) 135–140.
[14] C.P. Jordão, L.L. Fialho, J.C.L. Neves, P.R. Cecon, E.S. Mendonça, R.L.F. Fontes, Reduction of heavy metal contents in liquid effluents by vermicomposts and the use of the metal-enriched vermicomposts in lettuce cultivation, Bioresour. Technol. 98 (2007) 2800–2813.
[15] S.K. Ouki, R.D. Neufeld, Use of activated carbon for the recovery of chromium from industrial wastewaters, J. Chem. Technol. Biotechnol. 70 (1997) 3–8.
[16] I.S. Chang, B.H. Kim, Effect of sulfate reduction activity on biological treatment of hexavalent chromium [Cr(VI)] contaminated electroplating wastewater under sulfate-rich condition, Chemosphere 68 (2007) 218–226.
[17] C. Yuan, G. Jiang, L. Liang, X. Jin, J. Shi, Sequential extraction of some heavy metals in Haihe River sediments, People's Republic of China, Bull. Environ. Contam. Toxicol. 73 (2004) 59–66.
[18] R. Burt, M.A. Wilson, M.D. Mays, C.W. Lee, Major and trace elements of selected pedons in the USA, J. Environ. Qual. 32 (2003) 2109–2121.
[19] H. Pekey, The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream, Mar. Pollut. Bull. 52 (2006) 1197–1208.
[20] N. Vdović, G. Billon, C. Gabelle, J. Potdevin, Remobilization of metals from slag and polluted sediments (Case Study: The canal of the Deûle River, northern France), Environ. Pollut. 141 (2006) 359–369.
[21] EPA, National Recommended Water Quality Criteria, Office of water, EPA-822-R-02-047, 2006.
[22] J. Lewin, B.E. Davies, P.J. Wolfenden, Interactions between channel change and historic mining sediments, in: K.J. Gregory (Ed.), River Channel Changes, Wiley, Chichester, 1977, pp. 353–367.
[23] J.R. Miller, The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites, J. Geochem. Explor. 58 (1997) 101–118.
[24] M.P. Taylor, R.G.H. Kesterton, Heavy metal contamination of an arid river environment: Gruben River, Namibia, Geomorphology 42 (2002) 311–327.
[25] R. Segura, V. Arancibia, M.C. Zúñiga, P. Pastén, Distribution of copper, zinc, lead and cadmium concentrations in sediments from the Mapocho River in Santiago, Chile, J. Geochem. Explor. 91 (2006) 71–80.
[26] A. Moss, S. Contanzo, Environment technical report, vol. 20, Department of Environment of Queensland Government, ISSN 1037-4671 RE200, February 1998.
[27] W. Chen, S.K. Tan, J.H. Tay, Distribution, fractional composition and release of sediment-bound heavy metals in tropical reservoirs, Water Air Soil Pollut. 92 (1996) 273–287.
[28] K.C. Cheung, B.H.T. Poon, C.Y. Lan, M.H. Wong, Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China, Chemosphere 52 (2003) 1431–1440.
[29] EPA, The incidence and severity of sediment contamination in surface waters of the United States, vol. 1: national sediment quality survey, Office of Science and Technology, EPA-823-R-97-006, 1997.
[30] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Arch. Environ. Contam. Toxicol. 39 (2000) 20–31.
[31] E. Pertsemli, D. Voutsa, Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece, J. Hazard. Mater. 148 (2007) 529–537.
[32] C. Yuan, J. Shi, B. He, J. Liu, L. Liang, G. Jiang, Speciation of heavy metals in marine sediments from the East Chine Sea by ICP-MS with sequential extraction, Environ. Int. 30 (2004) 769–783.
[33] S. Tokalioğlu, S. Kartal, L. Elçi, Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four stage sequential extraction procedure, Anal. Chim. Acta 413 (2000) 33–40.
[34] C. Caplat, H. Texier, D. Barillier, C. Lelievre, Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin, Mar. Pollut. Bull. 50 (2005) 504–511.
[35] B. Šurija, M. Branica, Distribution of Cd, Pb, Cu and Zn in carbonate sediments from the Krka river estuary obtained by sequential extraction, Sci. Total Environ. 170 (1995) 101–118.

[36] K.A. Hudson-Edwards, M.G. Macklin, C.D. Curtis, D.J. Vaughan, Chemical remobilisation of contaminated metals within floodplain sediments in an incising river system: implications for dating and chemostratigraphy, Earth Surf. Proc. Land. 23 (1998) 684–761.

[37] H. Özmen, F. Külahci, A. Çukurovali, M. Doğru, Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake (Elaziğ, Turkey), Chemosphere 55 (2004) 401–408.

[38] H.L. Nguyen, M. Leermakers, M. Elskens, F.D. Ridder, T.H. Doan, W. Baeyens, Correlations, partitioning and bioaccumulation of heavy metals between different compartments of Lake Balaton, Sci. Total Environ. 341 (2005) 211–226.

[39] EPA, Partition coefficients for metals in surface water, soil and waste, Office of Research and Development, EPA-600-R-05-074, 2005.