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ORIGINAL ARTICLE

Heavy metal contamination of Yellow River alluvial sediments, northwest China

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Abstract This study concerns the distribution and potential sources of elevated heavy metal concentrations (Cr, Ni, Pb, Zn) in alluvial sediments of the Yellow River close to an industrial area in northwest China. Sediment samples were collected from 25 locations and analyzed for common ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-), total salts, and heavy metals (Cr, Ni, Pb, Zn). Concentrations of Cr, Ni, Pb, and Zn were found to exceed background values observed at up-gradient sites and in surrounding non-industrialized areas. The surficial sediments can be classified as "slightly polluted" and seem to present a low, albeit significant potential ecological risk in the center of the study area where elevated Cr, Ni, Pb, and Zn appear to be associated with the presence of several industrial plants and a wastewater drainage ditch. Correlation and multivariate analyses confirm that the heavy metal pollution is anthropogenic in origin. Urgent action is required at both administrative and technical levels to avoid further degradation of the sediments by industrial waste. Necessary measures include the establishment of soil, sediment and water monitoring programs, a strengthening of compliance standards and greater enforcement of regulations.

Keywords Heavy metal contamination · Risk assessment · Sediment pollution · Contamination index · Multivariate statistics · Potential ecological risk

Introduction

Heavy metal pollution of the natural environment has become a global issue due to rapid urbanization and industrialization (Velea et al. 2009; Benhaddya and Hadjel 2013) together with associated mining and agriculture (Wang et al. 2010; Çolak 2012; Tang et al. 2013). Wastewater discharge and atmospheric deposition related to industrial, traffic, and household emissions are important pathways for this pollution (Schulin et al. 2007). Heavy metals are toxic to living organisms when they exceed certain thresholds (Gao and Chen 2012; Raju et al. 2012) and are a particular threat to aquatic ecosystems. Unlike organic pollutants, heavy metals do not biodegrade and can persist in the soil for very long periods (Klimek 2012). For example, Boudissa et al. (2006) reported an extremely high Mn content in soil and water near an abandoned Mn alloy plant in Montreal (Canada), even though it has been closed for more than 10 years.

The Zhongning Shikong industrial of western Ningxia, northwest China (Fig. 1) has developed rapidly during the past decade. Metallurgical, chemical, and coal deep processing plants located in the area produce dust and wastewater containing heavy metals and these, in turn, threaten to contaminate local soils including shallow floodplain sediments of the neighboring Yellow River. An investigation of the potential impacts was carried out

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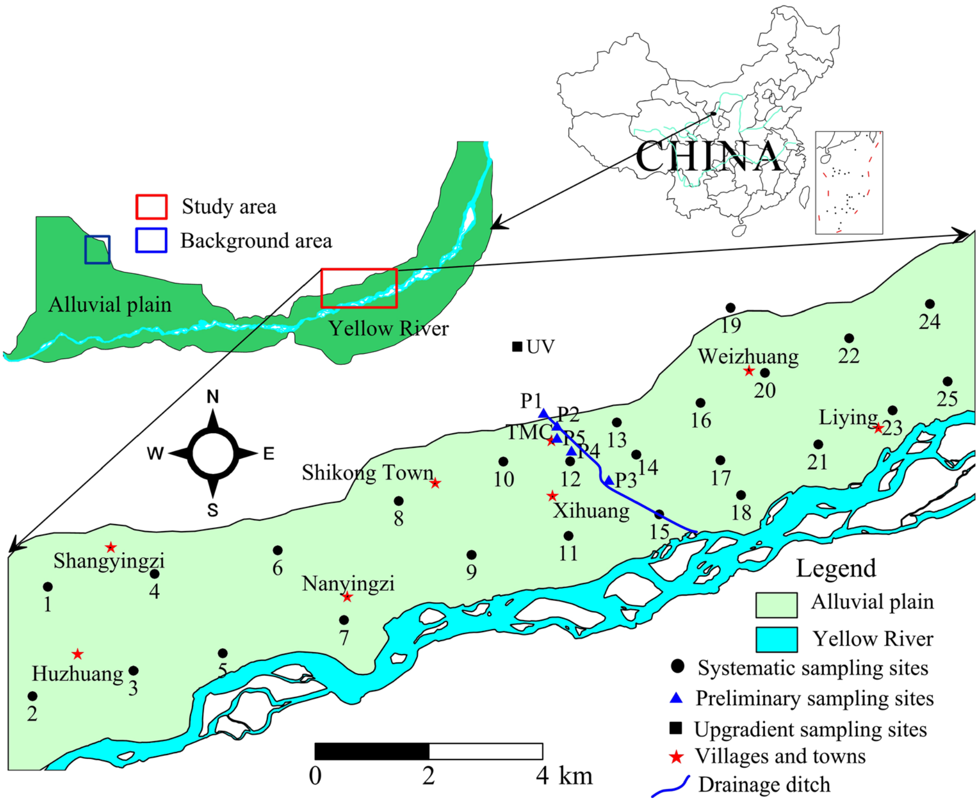

Fig. 1 Study area and sampling sites

beginning with a preliminary study of flood-plain sediments lying in close proximity to the Ningxia Tianyuan Manganese Company (TMC). TMC is the largest manganese electrolytic manufacturer in the world and considered to be one of the most significant pollution-generating industries in the region (Li et al. 2014a, b) and one of the largest polluters in the industrialized area. During a preliminary "scoping" study, five samples were collected and analyzed for a suite of metals. The results revealed significantly elevated concentrations of Cr, Pb, Ni, Zn and Mn and prompted a more detailed investigation of these metals over a much larger area. Since no enrichment was found for Cu, Hg and Cd, these metals were excluded in the follow-up study. Study findings related to manganese pollution of the flood-plain deposits were published recently by Li et al. (2014a). In the current paper, attention is turned toward the four remaining metals (Cr, Pb, Ni, and Zn).

Cr and Pb are amongst the more toxic heavy metals. Human overexposure to Pb may cause both acute and chronic effects to various physiological systems and organs. Most notably, it can affect cardiovascular, neurological, and osteopathic health, especially in children (Egwu and Agbenin 2013). In comparison, the toxicity of chromium depends heavily on its valence state. Chromium (III) is relatively benign and considered by many to be one of the several trace elements that are "essential" for good human nutrition and health. Chromium (VI), on the other hand, is acutely toxic, a known carcinogen and can be readily mobilized in aqueous systems as an oxyanion (CrO_4^{2-}) (Das et al. 2013). In trace amounts, Zn and Ni are also considered to be "essential elements" in the human diet; they are also important for the healthy growth of plants. In excess, both elements can be toxic to humans and plants (Machender et al. 2013), although plants tend to be less tolerant to excesses than humans. $Ni(CO)_4$ is the most toxic form of Ni to humans, and can cause fatal damage to the respiratory system. However, it rarely occurs in nature.

The primary purpose of the study was to determine the distribution of the heavy metal contamination, assess its environmental threat and establish its origin. Local industry was suspected to be the source, and potential pathways for transport included: (1) direct adsorption from flowing water by surficial sediments, (2) contamination by irrigation water that had been contaminated by heavy metals and (3) contamination by airborne dusts containing heavy metals (Ningxia Institute of Environmental Monitoring 2011). There was concern that heavy metals adsorbed onto shallow surface sediments could eventually leach into deeper sediments and local aquifers, thus posing a potential long-term threat to human health and the aquatic ecosystem. An important secondary purpose of the study was to provide data needed to persuade local authorities of the need to implement a wide range of administrative and technical measures that would avoid further degradation of the sediments by industrial waste. Such measures could include the establishment of soil, sediment and water monitoring programs, a strengthening of compliance standards and greater enforcement of regulations. Prior to this work, there had been no attempt to systematically monitor heavy metal pollution of sediment in this region.

Materials and methods

Study area

The Zhongning Shikong industrial area is located in western Ningxia (latitude 37°30′24.91″–37°37′38.81″N and longitude 105°34′36.47″–105°46′13.09″E) and covers 54 km^2 (Fig. 1). The study site forms part of the Yellow River alluvial basin, an area known locally as the Weining Plain. The Weining Plain sediments accumulated in a Cenozoic fault basin, approximately 1,000 km^2 in area. The sediments are Quaternary in age and comprise weakly consolidated sands and gravels that range up to 100 m or so in thickness. The upper part of the sequence is primarily fine sand, while the lower part is largely gravel and coarse sand. Such materials are porous and highly permeable, and form excellent aquifers that can yield large volumes of groundwater for drinking and industrial purposes. An unfortunate consequence of their high permeability and shallow disposition is that aquifers of the Weining Plain tend to be highly vulnerable to contamination from surface and near-surface pollutant sources.

As shown in Fig. 1, the Ningxia TMC lies at the center of the Zhongning Shikong study area. A drainage ditch runs southeastwards through the industrial area, passing TMC on its route to the Yellow River, the largest river in the area and an important source of irrigation water for the agricultural fields that surround the industrial lands. The drainage ditch conveys wastewater that is released from several industrial plants, often in violation of local environmental protection regulations.

Sample collection and analysis

For the preliminary "scoping" study, five samples were collected close to the drainage ditch that extends toward the Yellow River in close proximity to the TMC plant. Sites are indicated as P1–P5 on Fig. 1. Four other sediment samples were collected in a relatively pristine area to the west (Fig. 1) where soil type was considered to be similar to that of the study area. This allowed mean background values to be obtained for each of the heavy metals and thereby serve as a control.

Table 1 Results of the preliminary investigation (mg/kg)

Sample no.	Cu	Zn	Cd	Ni	Hg	Cr	Pb
1	1.48	49.5	0.0127	27.5	0.0120	66.1	21.9
2	1.25	38.2	0.0112	24.8	0.0157	66.9	13.9
3	1.88	37.4	0.0130	23.8	0.053	89.5	19.6
4	2.39	72.0	0.037	26.3	0.005	71.6	15.8
5	1.6	68.2	0.0203	27.8	0.074	77.8	17.7
Background values	10.5	35.5	0.042	20.0	0.1	49.1	10.3

Samples were prepared for heavy metal analysis using methods prescribed by the State Environmental Protection Administration (2004) and Fan (2011). For the analysis of Pb, Zn, Cd, Cu and Ni, air-dried and sieved sediments were digested with a $HCl–HNO_3–HF–HClO_4$ solution (Fu et al. 2013); for Cr analysis, the prepared sediments were digested with a solution of $HNO_3–HClO_4–HF$ (Yang et al. 2011; Udayakumar et al. 2014). To analyze for Hg, the sediments were first digested using $HNO_3–HCl$ so that Hg contained in the sediments could be extracted in the form of Hg^{2+}. Subsequently KBH_4 was used to reduce Hg^{2+} to Hg.

Following heavy metal extraction, the resulting solutions were analyzed by ICP (ICAP6300) for Cu, Cr, Ni, Pb and Zn. Cd was analyzed using AAS (ZEEnit 700) and Hg was analyzed using AFS (AFS-920). ICP enables detection limits of 0.05, 0.05, 0.05, 0.2 and 0.02 mg/kg, for Cu, Cr, Ni, Pb and Zn, respectively. Methods for the analysis of Cd and Hg provided detection limits of 0.0083 and 0.005 mg/kg, respectively. QA/QC was performed by including standard reference material obtained from the Center for Certified Reference Materials of China in the analytical procedures. Recoveries were found to range from 92 to 106 % for Cr, 95–103 % for Ni, 97–108 % for Zn, and 96–109 % for Pb. By introducing duplicates in the analytical procedure for QA/QC (Ningxia Institute of Environmental Monitoring 2011), the overall measurement errors for Cr, Ni, Pb, and Zn were reduced to 3.5, 0.3, 0.9, and 0.1 %, respectively. Results of the preliminary investigation are shown in Table 1. Because the contents of Cu, Hg and Cd were found to be well below their background values, these metals were excluded from the second phase of the study.

In the second phase of the investigation, 25 sampling sites were evenly distributed throughout the study area (Fig. 1) using technical guidelines established for environmental monitoring of the soil by the State Environmental Protection Administration (2004). In July 2012, these sites were systematically sampled to a maximum depth of 5 cm using a soil collection shovel, and site location coordinates were precisely recorded using a GPS device. At each site, three to five subsamples were taken and mixed to obtain a bulk sample with an average mass of 1 kg. These were stored in clean cloth bags, labeled and transported to the laboratory of the Ningxia Institute of Environmental Monitoring for sample processing and chemical analysis.

For each sample, pH, total salts (TS), major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and HCO_3^-), and heavy metals (Cr, Ni, Pb, Zn) were determined using standard analytical procedures (State Environmental Protection Administration 2004). The sediment samples were air-dried, crushed gently to break the aggregates, and sieved through a 0.25 mm mesh to remove extraneous materials such as vegetation, leaves, and roots. Samples for heavy metals were prepared and analyzed using the same techniques adopted for the preliminary investigation. For pH, total salts and major ion analysis, the samples were mixed with deionized water at a ratio of 1:5 (w/w = sediment to water) and shaken for 60 min. After filtering to remove suspended sediment, the eluent was analyzed for pH with a glass electrode and subjected to EDTA titration to determine concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Na^+ and K^+ were determined by flame photometer, and HCO_3^- and Cl^- were measured using routine titrimetric methods.

Pollution assessment

To assess the degree of heavy metal pollution, the contamination index (C_f^i) and pollution load index (PLI) were determined for each sediment sample. C_f^i indicates the degree of pollution for each heavy metal, while PLI provides the degree of heavy metal pollution for the site as a function of all the heavy metals present (Sadhu et al. 2012). The indices are calculated according to the equations:

$$C_f^i = \frac{C_i}{S_i} \tag{1}$$

$$\mathrm{PLI} = (C_f^1 \times C_f^2 \times \cdots \times C_f^n)^{1/n} \tag{2}$$

where C_i is the measured content of heavy metal i, S_i represents the local background value of heavy metal i, and n is the total number of heavy metals analyzed. Pollution levels are defined as: $C_f^i < 1$ = no anthropogenic pollution, $1 < C_f{}^i < 3$ = slight pollution, $3 < C_f^i < 5$ = moderate pollution, and $C_f^i > 5$ = serious pollution (Lu et al. 2009). PLI <1 denotes a pristine site and PLI >1 indicates a deterioration of site quality (Seshan et al. 2010).

Heavy metal contamination due to anthropogenic activity was also assessed by means of the enrichment factor (EF) which according to Li et al. (2014a) is expressed as:

$$\mathrm{EF} = \frac{(C_i/C_{\mathrm{ref}})_{\mathrm{sample}}}{(S_i/C_{\mathrm{ref}})_{\mathrm{background}}} \tag{3}$$

Table 2 Levels of the potential ecological risk of heavy metals

E_f^i	Pollution levels	RI	Pollution levels
$E_f^i < 40$	Low	RI <150	Low
$40 \leq E_f^i < 80$	Moderate	$150 \leq$ RI < 300	Moderate
$80 \leq E_f^i < 160$	Considerable	$300 \leq$ RI < 600	High
$160 \leq E_f^i < 320$	High	RI ≥ 600	Very high
$E_f^i \geq 320$	Very high		

where C_{ref} is the concentration of a reference element for normalization purposes. C_i and S_i are defined above. Usually, Al or Fe is selected as the reference element due to their normally low variability of occurrence. In the present study, Fe was selected. According to Shah et al. (2012), EF <1 indicates no enrichment; $1 < \mathrm{EF} < 3$, minor enrichment; $3 < \mathrm{EF} < 5$, moderate enrichment; $5 < \mathrm{EF} < 20$, significant enrichment; $20 < \mathrm{EF} < 40$, very high enrichment; and EF >40, extremely high enrichment.

Ecological risk due to heavy metal pollution was assessed using the potential ecological risk index method proposed by Hakanson (1980). Ecological risk assessment provides an evaluation of the likelihood that adverse ecological effects will occur as a result of exposure to one or more stressors (USEPA 1998). According to Zhang and Liu (2010), potential ecological risk is calculated by the equations:

$$E_f^i = \sum_{i=1}^{n} (T_f^i \times C_f^i) \tag{4}$$

$$\mathrm{RI} = \sum_{i=1}^{n} E_f^i \tag{5}$$

where E_f^i is the potential ecological risk factor due to heavy metal i and RI is the potential ecological risk index that reflects the integrated influence of multiple heavy metals on the surrounding environment. C_f^i is the contamination index of heavy metal i which is calculated according to Eq. 1, and T_f^i is the response coefficient for toxicity of heavy metal i. According to Hakanson (1980) and Xu et al. (2008), the response coefficients for the heavy metals of concern are as follows: Cr = 2, Pb = 5, Ni = 5, and Zn = 1. The criteria for defining the level of potential ecological risk are shown in Table 2 (Guo et al. 2010; Yu et al. 2012).

Sediment quality guidelines

Sediment quality guidelines (SQGs) provide a means of assessing soil toxicity, i.e., the potential threat of contaminated sediment to aquatic life (Hübner et al. 2009). They have been developed for many jurisdictions worldwide

(Burton 2002; Ghani et al. 2013) but do not exist in China for freshwater ecosystems. For the purposes of the study a consensus-based approach proposed by MacDonald et al. (2000) was adopted. This approach involves two thresholds: a threshold effect level (TEL) that defines the contaminant concentration below which adverse effects on sediment-dwelling organisms are not expected to occur, and a probable effect level (PEL) that represents the concentration above which adverse effects to sediment-dwelling organisms are likely to be observed.

Kriging interpolation

Kriging is an optimal interpolation technique based on geostatistics that is universally applied to predict parameter values at locations that have not been sampled or measured. The technique was used in the study to generate maps showing the regional extent of the heavy metal pollution and to indicate potential contaminant sources. The basic form of the kriging estimator (Bohling 2005) is given by:

$$Z^*(\mathbf{u}) - m(\mathbf{u}) = \sum_{\alpha=1}^{n(\mathbf{u})} \lambda_\alpha [Z(\mathbf{u}_\alpha) - m(\mathbf{u}_\alpha)] \qquad (6)$$

where $\mathbf{u}$ and $\mathbf{u}_\alpha$ are location vectors for the estimation point and one of the neighboring data points, indexed by α, respectively; $n(\mathbf{u})$ is the number of data points in the local neighborhood used for estimation of $Z^*(\mathbf{u})$; $m(\mathbf{u})$ and $m(\mathbf{u}_\alpha)$ are expected values of $Z(\mathbf{u})$ and $Z(\mathbf{u}_\alpha)$, respectively; and λ_α is the weight assigned to the datum $Z(\mathbf{u}_\alpha)$ for estimation at location $\mathbf{u}$. The datum at a different estimation location will receive a different weight. For the purposes of the study, the “ordinary” variant of kriging was used. This variant assumes that the mean is not constant over the entire domain. This is a standard assumption unless there is a good scientific justification to estimate a mean (Li et al. 2014a). This approach has been widely used by researchers and a detailed description of the method is provided by Baye et al. (2013).

Multivariate analysis

Multivariate techniques such as principal components analysis (PCA) and cluster analysis (CA) are popular methods of solving multiple-parameter problems (Kim et al. 2010; Tang 2010; Wu et al. 2013b) and were adopted for the study. Analyses were performed using the statistical package SPSS 13.0 for Windows® (SPSS Inc. 2004) and invoked an R-mode hierarchical clustering analysis (HCA) approach based on the farthest neighbor method and squared Euclidean distance. Tang (2010) and Wu et al. (2013b) provide a thorough description of these methods.

Study results and discussion

Heavy metal concentrations and distributions

Sample analyses and statistical data (maxima, minima, means and standard deviations) for all the physicochemical variables determined during the study are shown in Table 3. For comparative purposes, the table includes sediment quality guideline levels (TEL and PEL) as adopted by Esen et al. (2010). Also shown in the table is the analysis of a soil sample (UV) collected nearly 2 km northwest of TMC in one of very few study area locales that were thought to be negligibly affected by anthropogenic pollution. Reassuringly, values of Cr, Ni, Pb, and Zn obtained for this site compare very closely to the heavy metal background concentrations obtained from samples collected in the more remote area to the west (Fig. 1; Table 1).

Of the heavy metals examined, Zn shows the highest concentrations, ranging from 49.4 to 129.0 mg/kg with a mean value of 81.8 mg/kg. All of the samples exhibit Zn concentrations well in excess of the background value (35.5 mg/kg) and confirm significant anthropogenic contamination by Zn. Cr also displays significant anthropogenic contamination. Cr is the second most common heavy metal in the study area and ranges in concentration from 53.2 to 82.6 mg/kg (mean 63.7 mg/kg). All 25 samples display Cr levels in excess of the background value of 49.1 mg/L. Levels of Ni and Pb are much lower than those of Zn and Cr and range from 22.2 to 37.0 mg/kg and from 8.5 to 25.1 mg/kg, respectively. Nevertheless, all 25 samples display Ni levels in excess of the background value of 20.0 mg/L, and 23 of the 25 samples show Pb levels that exceed the background value of 10.3 mg/kg.

The highest concentrations of Cr, Ni, Pb, and Zn were found at sites 12, 14 and 18 (Table 1) which are located close to the TMC and drainage ditch, a region where many metallurgical and chemical plants are concentrated. This finding is re-affirmed by Fig. 2 which shows the spatial distribution maps of Cr, Ni, Pb, and Zn that were generated using kriging. All four metals show the highest concentrations toward the center of the study area near the TMC and drainage ditch, an association that was similarly made for the elevated presence of Mn by Li et al. (2014a). More difficult to understand is how the discharge of wastewater can cause anthropogenic pollution of the entire study area, in some cases affecting sediments nearly 10 km from the TMC and drainage ditch. An explanation lies in the work of the Ningxia Institute of Environmental Monitoring (2011) which has reported higher total suspended particle (TSP) levels in air downwind of the industrialized areas (0.38 mg/m^3) than upwind (0.21 mg/m^3). This suggests

Table 3 Sediment concentrations and statistical analysis for study area samples

Sample no.	pH	TS	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cr	Ni	Pb	Zn
Unit	–	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	8.22	740	230	30	360	80	40	20	100	63.5	29.3	12.9	80.6
2	7.67	700	220	60	260	60	20	10	140	62.7	29.4	12.5	76.1
3	7.57	1,930	200	170	1,060	180	120	10	240	57.5	22.2	9.7	67.2
4	8.14	700	230	30	300	20	70	10	120	60.8	28.7	11.6	66.0
5	7.41	1,260	140	60	730	150	80	40	80	60.0	28.0	10.9	69.1
6	7.82	550	220	20	180	40	10	10	80	57.4	28.4	11.0	70.6
7	8.11	1,470	210	170	650	80	70	10	260	61.0	27.6	11.4	69.3
8	7.55	680	200	50	270	60	30	20	60	69.0	31.1	14.8	96.2
9	7.12	6,000	150	500	4,640	1,180	380	240	90	57.5	25.1	10.6	85.6
10	8.23	540	230	20	250	60	20	20	60	64.9	30.3	15.0	83.9
11	7.66	1,750	260	200	850	160	70	20	290	67.5	31.8	13.4	85.9
12	7.64	540	210	30	200	60	30	10	80	78.8	37.0	22.1	113.0
13	7.61	2,450	210	260	1,320	270	120	20	360	63.1	30.4	14.3	75.0
14	7.75	460	200	20	180	50	20	20	60	63.1	28.1	22.7	129.0
15	8.00	680	260	20	210	30	30	100	70	64.2	30.7	13.9	86.1
16	7.56	540	240	20	250	60	30	10	60	60.7	29.8	12.7	71.6
17	7.63	670	220	30	260	60	20	10	90	63.3	28.7	13.1	74.2
18	7.45	1,240	170	90	560	140	40	40	130	82.6	36.4	25.1	112.0
19	8.29	620	430	30	130	20	20	20	50	55.1	23.2	8.5	49.4
20	8.12	650	240	30	240	70	20	30	120	72.1	33.9	14.0	86.8
21	7.66	10,400	160	1,620	7,660	2,180	620	500	1,250	53.2	24.2	10.9	62.6
22	7.55	1,110	170	70	480	100	40	80	110	62.5	29.6	13.5	80.0
23	7.41	1,730	200	140	800	260	70	20	140	62.4	29.6	13.3	82.2
24	7.02	2,400	170	200	1,500	380	120	120	220	63.4	29.6	12.4	85.2
25	7.04	8,500	200	1,270	5,660	1,160	530	200	1,880	65.0	31.2	18.6	87.3
Max	8.29	10,400	430	1,620	7,660	2,180	620	500	1,880	82.6	37.0	25.1	129.0
Min	7.02	460	140	20	130	20	10	10	50	53.2	22.2	8.5	49.4
Mean	7.69	1,930	210	210	1,160	280	100	60	250	63.7	29.4	14.0	81.8
SD	0.36	2,550	50	390	1,910	500	160	110	420	6.6	3.5	4.1	17.1
UV	–	–	–	–	–	–	–	–	–	46.9	24.8	13.9	38.2
TEL	–	–	–	–	–	–	–	–	–	52.3	15.9	30.2	124
PEL	–	–	–	–	–	–	–	–	–	160	42.8	112	271

UV up-gradient background value, *SD* standard deviation, *TEL* threshold effect level, *PEL* probable effect level (soil quality effect levels extracted from Esen et al. 2010)

that atmospheric fallout of production dusts containing heavy metals is also contaminating the surficial sediments.

A comparison of the levels of Cr, Ni, Pb, and Zn at Zhongning Shikong with those reported in the literature shows that heavy metal concentrations in the study area are lower than those recorded in industrial areas in most other regions and countries of Asia and Europe (Table 4). This is because the Zhongning Shikong industrial area is a newly developed industrial area and most industrial plants have been producing heavy metal-laced effluent for only a few years. The case studies listed in Table 4 illustrate what could materialize in Zhongning without early, proactive intervention. For example, Yangzhou, a mature city located in the Yangtze River watershed of eastern China, reports levels of Cr, Pb, and Zn (Zhou et al. 2008) that are at least double than those observed in the study area. Significantly elevated levels of Cr, Ni, Pb, and Zn are also observed in central Taiwan (Cheng et al. 2013) where industrial wastewater has been discharged directly onto farmland and spread by irrigation channels. Substantial efforts were made to remediate the Taiwanese sediments between 2003 and 2008, but despite considerable financial investment, only moderate improvements were achieved and heavy metal contamination remained unacceptably high in 2010. One of the most serious documented examples of heavy metal pollution is in the Saronikos Gulf, Greece

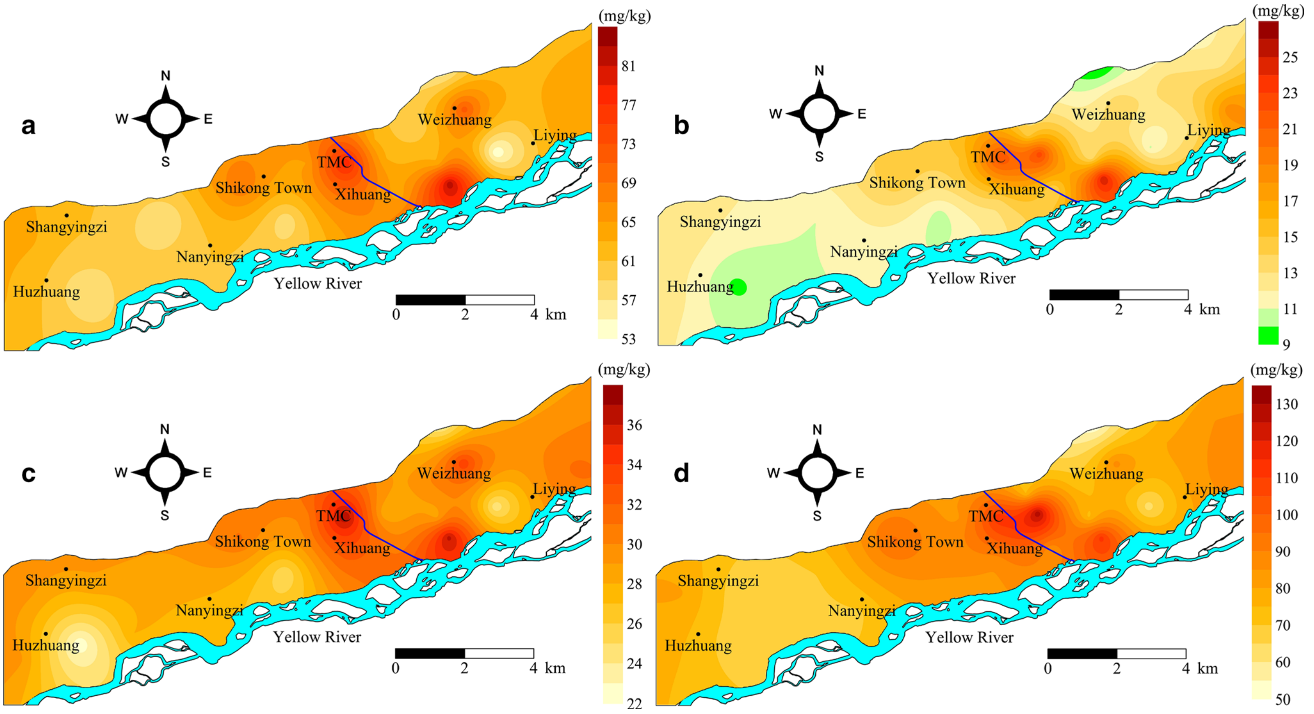

Fig. 2 Distribution of heavy metals: **a** Cr, **b** Pb, **c** Ni and **d** Zn

Table 4 Comparison of heavy metal concentrations between Zhongning and other parts of the world

Locations	Unit	Levels of heavy metals				References
		Cr	Ni	Pb	Zn	
Zhongning	mg/kg	53.2–62.6	22.2–37.0	8.5–25.1	49.4–129.0	Present study
Yangzhong, China	mg/kg	68.70–139.52	–	23.94–67.21	66.09–1,457	Zhou et al. (2008)
Central Taiwan	mg/kg	24.0–14,561	12.0–1,358	12.5–306	94.5–62,300	Cheng et al. (2013)
		22.2–16,100	19.3–57,500	13.8–2,500	76–63,400	Cheng et al. (2013)
Dumai, Indonesia	mg/kg	–	7.26–19.97	14.63–84.90	31.49–87.11	Amin et al. (2009)
Hindon River, India	mg/kg	17.48–33.70	13.90–57.66	27.56–313.57	22.50–288.29	Chabukdhara and Nema (2012)
River Cauvery, India	mg/kg	0–145.2	1.3–108.0	0.1–33.9	11.5–211.0	Raju et al. (2012)
Izmit Bay, Turkey	mg/kg	57.9–116	38.4–70.7	23.8–178	500–1,190	Pekey (2006)
Gulf of Gemlik, Turkey	mg/kg	71–181	35–165	0.1–67	88–185	Ünlü et al. (2008)
Kapulukaya Dam Lake, Turkey	mg/kg	98–1,116	24.7–127.1	8.6–34	14.8–124.2	Kankılıç et al. (2013)
Saronikos Gulf, Greece	mg/kg	264–860	–	521–1,263	409–6,725	Galanopoulou et al. (2009)
Nemrut Bay, Aegean Sea	mg/kg	35.7–98.8	18.1–63.4	22.3–89.4	75–271	Esen et al. (2010)

(Galanopoulou et al. 2009). The gulf is surrounded by a heavily industrialized area and prior to 1994 accepted untreated waste from the greater Athens area via the central sewer outfall (Galanopoulou et al. 2009). Although the central sewer outfall has now been replaced by a new waste treatment plant and disposal system, the heavy metal contents in the surficial sediments remain very high (Table 3) and have proved very difficult to remediate. Neighbouring Turkey also reports serious heavy metal pollution problems, as does India. Only Dumai, Indonesia (Amin et al. 2009) seems to report heavy metal contamination (by Ni and Zn) that is less serious than that observed in Zhongning, but again it may be simply a matter of time before serious degradation occurs.

Assessment of heavy metal pollution and potential ecological risks

Heavy metal pollution of the study area was assessed using EF, C_f^i and PLI (Table 5). EFs for Cr, Ni, Pb and Zn are in

Table 5 Results of heavy metal pollution assessment and potential ecological risk

Sample no.	Enrichment factor (EF)				Contamination index (C_f^i)				PLI	E_f^i				RI
	Cr	Ni	Pb	Zn	Cr	Ni	Pb	Zn		Cr	Ni	Pb	Zn	
1	1.17	1.32	1.13	2.05	1.29	1.47	1.25	2.27	1.52	2.59	7.33	6.26	2.27	18.44
2	1.11	1.27	1.05	1.86	1.28	1.47	1.21	2.14	1.49	2.55	7.35	6.07	2.14	18.12
3	0.98	0.93	0.79	1.58	1.17	1.11	0.94	1.89	1.23	2.34	5.55	4.72	1.89	14.51
4	1.09	1.26	0.99	1.63	1.24	1.44	1.13	1.86	1.39	2.48	7.18	5.63	1.86	17.14
5	1.07	1.23	0.93	1.71	1.22	1.40	1.06	1.95	1.37	2.44	7.00	5.29	1.95	16.68
6	0.96	1.17	0.88	1.64	1.17	1.42	1.07	1.99	1.37	2.34	7.10	5.34	1.99	16.77
7	1.01	1.12	0.90	1.59	1.24	1.38	1.11	1.95	1.39	2.48	6.90	5.53	1.95	16.87
8	1.13	1.25	1.15	2.17	1.41	1.56	1.44	2.71	1.71	2.81	7.78	7.18	2.71	20.48
9	0.96	1.03	0.85	1.98	1.17	1.26	1.03	2.41	1.38	2.34	6.28	5.15	2.41	16.17
10	0.86	0.98	0.95	1.54	1.32	1.52	1.46	2.36	1.62	2.64	7.58	7.28	2.36	19.86
11	1.09	1.26	1.03	1.92	1.37	1.59	1.30	2.42	1.62	2.75	7.95	6.50	2.42	19.62
12	1.37	1.58	1.84	2.72	1.60	1.85	2.15	3.18	2.12	3.21	9.25	10.73	3.18	26.37
13	1.29	1.52	1.39	2.11	1.29	1.52	1.39	2.11	1.55	2.57	7.60	6.94	2.11	19.22
14	1.04	1.14	1.79	2.95	1.29	1.41	2.20	3.63	1.95	2.57	7.03	11.02	3.63	24.25
15	1.05	1.23	1.08	1.95	1.31	1.54	1.35	2.43	1.60	2.62	7.68	6.75	2.43	19.46
16	1.02	1.23	1.01	1.66	1.24	1.49	1.23	2.02	1.46	2.47	7.45	6.17	2.02	18.10
17	1.02	1.14	1.01	1.66	1.29	1.44	1.27	2.09	1.49	2.58	7.18	6.36	2.09	18.20
18	1.66	1.79	2.40	3.11	1.68	1.82	2.44	3.15	2.20	3.36	9.10	12.18	3.15	27.80
19	0.96	0.99	0.70	1.19	1.12	1.16	0.82	1.39	1.10	2.24	5.80	4.11	1.39	13.54
20	1.12	1.30	1.04	1.87	1.47	1.70	1.36	2.45	1.70	2.94	8.48	6.80	2.45	20.65
21	0.85	0.95	0.83	1.38	1.08	1.21	1.06	1.76	1.25	2.17	6.05	5.29	1.76	15.27
22	1.05	1.22	1.08	1.85	1.27	1.48	1.31	2.25	1.54	2.55	7.40	6.55	2.25	18.75
23	1.05	1.22	1.06	1.91	1.27	1.48	1.29	2.32	1.54	2.54	7.40	6.46	2.32	18.71
24	1.13	1.30	1.06	2.11	1.29	1.48	1.20	2.40	1.53	2.58	7.40	6.02	2.40	18.40
25	1.08	1.27	1.47	2.00	1.32	1.56	1.81	2.46	1.74	2.65	7.80	9.03	2.46	21.94
Max	1.66	1.79	2.40	3.11	1.68	1.85	2.44	3.63	2.20	3.36	9.25	12.18	3.63	27.80
Min	0.85	0.93	0.70	1.19	1.08	1.11	0.82	1.39	1.10	2.17	5.55	4.11	1.39	13.54
Mean	1.08	1.23	1.14	1.93	1.30	1.47	1.35	2.30	1.55	2.59	7.34	6.77	2.30	19.01
SD	0.16	0.19	0.38	0.45	0.13	0.17	0.40	0.48	0.25	0.27	0.87	1.98	0.48	3.34

the range of 0.85–1.66, 0.93–1.79, 0.70–2.40, and 1.19–3.11, respectively, indicating minor enrichment, or in some cases either "no enrichment" or "moderate enrichment". Higher EF values are observed at sites 12, 13, 14, 16 and 18 (Fig. 1), reiterating the close association between heavy metal contamination of the surface sediments and TMC and the drainage ditch. The contamination index (C_f^i) for Cr ranges between 1.08 and 1.68 and averages 1.30. This indicates "slight pollution" by Cr in all 25 samples. The contamination indices for Ni and Zn also tend to indicate "slight pollution" of the sediments, although Zn appears to be the more serious, approaching or exceeding the criterion for "moderate pollution" in several samples. With regards to Pb, 23 out of the 25 samples indicate "slight pollution" (the contamination index ranging up to 2.44).

The pollution load analysis reveals PLI indices that range from 1.10 to 2.20 with a mean of 1.55. This confirms that all sites in the study area have undergone sediment quality deterioration caused by heavy metal pollution. The most seriously contaminated sites (represented by higher C_f^i and PLI values in Table 5) are mainly distributed in the middle of the study area where most industrial plants are located.

The potential ecological risks associated with the heavy metals are denoted by values E_f^i and RI in Table 5. Fortunately all 25 sites presently fall into the low risk category (E_f^i values for all four heavy metals are less than 40 and RI is <150). Ni, Pb, and to a lesser extent Cr impose the highest risks to the ecosystem and can be regarded as the greatest threats to organisms in the sediments. For example, the E_f^i for Ni ranges from 5.55 to 9.25 with a mean of 7.34, followed by Pb, which ranges from 4.11 to 12.18 with a mean of 6.77. Zn possesses the lowest potential ecological risk. Because it is an essential element for living organisms when present in trace amounts (Vázquez-Sauceda et al. 2011), it has a relatively small response coefficient for toxicity.

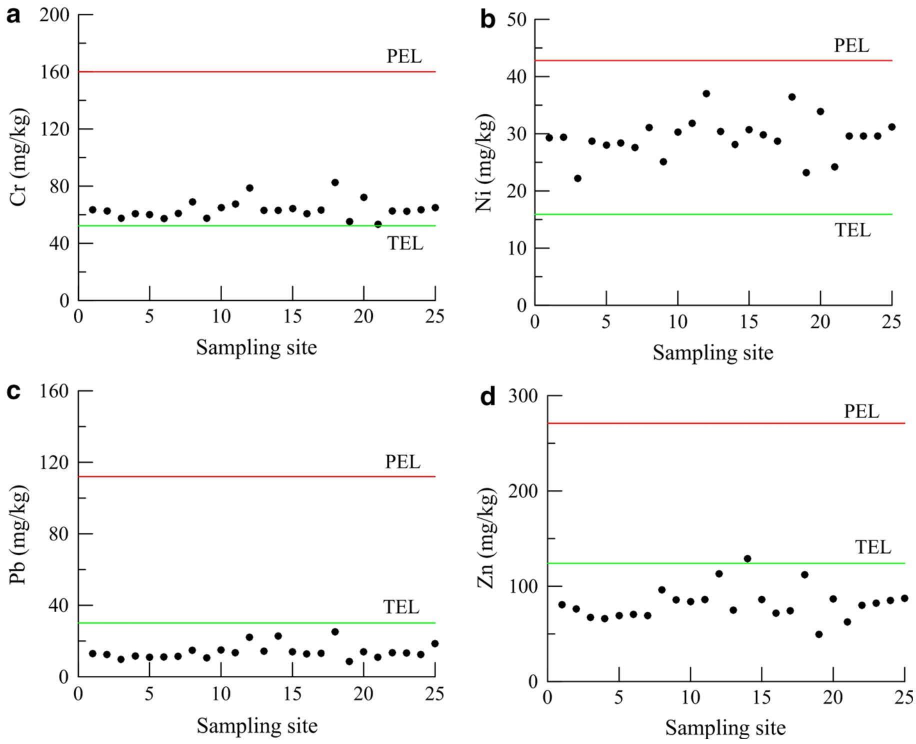

Fig. 3 Comparison of heavy metal concentrations with SQGs: **a** Cr, **b** Ni, **c** Pb, and **d** Zn

In similar studies, Amuno (2013) reported low ecological risk in contaminated soils around the largest mass grave in Rwanda, and Yu et al. (2012) reported a moderate to very high ecological risk in Fujian province, China. In the latter study, Hg and Cd contributed the majority of the risk, followed by Pb. The ecological risks associated with Ni, Zn, and Cr were found to be low.

Figure 3 compares heavy metal concentrations in study area samples with TEL and PEL criteria. In the case of Cr and Ni, concentrations exceed the TEL threshold at all sampling sites but currently remain lower than the PEL. This indicates that adverse effects may be encountered occasionally but the risk of such an occurrence is only slight (Ghani et al. 2013). The concentrations of Pb and Zn are, as expected, well below the TEL (except in the case of Zn at site 14). This suggests that no adverse effects would be anticipated with respect to Pb and Zn under the current circumstances.

Correlation analysis

Correlation analysis has been widely used to analyze chemical data for water and soil (Jamshidi-Zanjani and Saeedi 2013; Li et al. 2011, 2013a, b; Raju et al. 2012; Yu et al. 2012). It is used to test for interdependence of the variables and thereby provide an improved understanding of the dataset. Table 6 shows a matrix of Pearson correlation coefficients that were calculated for the physicochemical variables determined during the study. In the table, bold numbers indicate a correlation that is significant at the 0.05 level, while bold, italicized numbers indicate significance at the 0.01 level.

The correlation matrix shows that Cr is significantly correlated with Ni, Pb, and Zn ($r > 0.7$, $p < 0.01$). This is a firm indication that the metals share a common pollution source (Yu et al. 2012). Similarly, strong positive correlations were found between each pair of cations and anions with the exception of HCO_3^- ($r > 0.6$, $p < 0.01$), indicating they may share the same source or formation process. Meanwhile, pH is positively correlated with HCO_3^- ($r = 0.621$, $p < 0.01$), but negatively correlated with TS, SO_4^{2-}, Ca^{2+} and Mg^{2+} ($r < -0.4$, $p < 0.05$). This probably reflects the role of HCO_3^- in increasing pH and the action of soluble ions such as SO_4^{2-}, Ca^{2+}, and Mg^{2+} in lowering pH. Weak correlations between the heavy metals and the major ions suggest that these chemical groups are independent of each other and controlled by different factors. In all likelihood the major ions are natural in origin (i.e., sediment derived) but in part could be associated with a non-industrial source. Recognizing that the highest levels of heavy metals occur in close proximity to the TMC and drainage ditch, it is reasonable to conclude that elevated heavy metal concentrations in the study area are the product of industrial pollution.

Table 6 Pearson correlation matrix of physicochemical variables

	pH	TS	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cr	Ni	Pb	Zn
pH	1												
TS	**−0.466**	1											
HCO_3^-	***0.621***	−0.348	1										
Cl^-	−0.380	***0.980***	−0.288	1									
SO_4^{2-}	**−0.456**	***0.996***	−0.362	***0.969***	1								
Ca^{2+}	**−0.416**	***0.976***	−0.368	***0.952***	***0.987***	1							
Mg^{2+}	**−0.454**	***0.995***	−0.349	***0.971***	***0.995***	***0.969***	1						
K^+	−0.338	***0.911***	−0.342	***0.893***	***0.930***	***0.962***	***0.902***	1					
Na^+	−0.360	***0.855***	−0.186	***0.910***	***0.818***	***0.749***	***0.850***	***0.662***	1				
Cr	−0.075	−0.309	−0.132	−0.283	−0.324	−0.336	−0.326	−0.331	−0.145	1			
Ni	−0.074	−0.290	−0.148	−0.248	−0.308	−0.320	−0.309	−0.305	−0.081	***0.918***	1		
Pb	−0.188	−0.080	−0.236	−0.039	−0.094	−0.111	−0.090	−0.124	0.090	***0.799***	***0.728***	1	
Zn	−0.250	−0.148	−0.337	−0.154	−0.142	−0.143	−0.153	−0.133	−0.101	***0.719***	***0.640***	***0.891***	1

Bold numbers indicate significance at the 0.05 level, bold and italic numbers indicate significance at the 0.01 level

Multivariate analyses

Cluster analysis of the physicochemical data generated dendrograms (Fig. 4) that revealed three distinct clusters (C1–C3). TS, SO_4^{2-}, Cl^-, Mg^{2+}, Ca^{2+}, K^+, and Na^+ are clustered as C1, while Cr, Ni, Pb and Zn occur in the C2 group. This reaffirms the findings of the correlation analysis that the heavy metals and soluble ions are derived from disparate sources. HCO_3^- and pH form the C3 cluster suggesting that hydrochemical factors influencing HCO_3^- concentrations are somewhat different from those affecting the other soluble ions. It is possible that HCO_3^- and pH may be overtly affected by the chemical composition of the irrigation water, a suggestion that appears to be supported by Wu et al. (2013a) who showed that local irrigation water belongs to the HCO_3^-Ca·Mg·Na water type and has a pH of 8.1 and a concentration of HCO_3^- up to 69 times higher than other major ions.

During principal component analysis, three principal components (PCs) were extracted with eigenvalues higher than 1.0. Together these accounted for 89 % of the total variance (Table 7). PC1 accounted for 55 % of the total variance, showing strong positive loadings (>0.8) for SO_4^{2-}, TS, Mg^{2+}, Ca^{2+}, Cl^-, K^+ and Na^+. This is thought to be a reflection of the parent rock and the sedimentary, lithological origin of these ions. Parent rock and weathering is a major factor influencing sediment chemistry. PC2 explains 26 % of the total variance and shows strong positive loadings (>0.75) for Pb, Zn, Cr, and Ni, representing anthropogenic pollution due to industrial activities. PC3 includes only HCO_3^- and pH with moderate positive loadings (>0.5), explaining 8 % of the total variance. PC3 represents the effects of irrigation water chemistry.

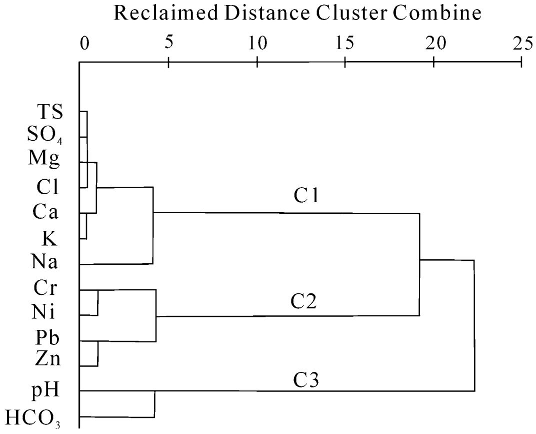

Fig. 4 Dendrogram of indices of sediment samples

Conclusions and recommendations

Surficial sediments of the Yellow River alluvial plain were investigated for potential heavy metal pollution by an adjacent, relatively new, industrial area. Possible sources of elevated Cr, Ni, Pb, and Zn were explored through correlation analysis, hierarchical cluster analysis and principal component analysis. Key findings are as follows:

- Concentrations of Cr, Ni, Pb, and Zn in the surficial sediments of the study area range from 53.2 to 82.6, 22.2 to 37.0, 8.5 to 25.1, and 49.4 to 129.0 mg/kg, respectively. These values are significantly higher than local background concentrations and indicate anthropogenic industrial pollution.
- Heavy metal concentrations are highest around the TMC plant and the adjacent wastewater drainage ditch

Table 7 Total variance associated with each PC and the loading matrix of PCs

	Component		
	PC1	PC2	PC3
SO_4^{2-}	**0.990**	0.086	0.049
TS	**0.989**	0.097	0.073
Mg^{2+}	**0.987**	0.083	0.067
Ca^{2+}	**0.976**	0.066	0.034
Cl-	**0.970**	0.104	0.192
K^+	**0.924**	0.044	0.046
Na^+	**0.826**	0.191	0.320
Pb	−0.179	**0.906**	0.206
Zn	−0.230	**0.868**	−0.035
Cr	−0.418	**0.826**	0.207
Ni	−0.388	**0.795**	0.217
pH	−0.461	−0.451	**0.588**
HCO_3^-	−0.361	−0.501	**0.673**
Total eigenvalues	7.115	3.421	1.087
% of variance	54.731	26.316	8.365
Cumulative %	54.731	81.047	89.412

Bold numbers indicate strong correlations between transformed parameters and PCs

and strongly suggest that wastewater from TMC and nearby industries are a primary source of the pollution.

- The presence of elevated heavy metal concentrations throughout the 54 km^2 study suggests that waste water is not the sole source of the pollution and that airborne emissions may be a secondary contaminant source.
- Statistical analysis confirms that Cr, Ni, Pb, and Zn levels are strongly correlated ($r > 0.7$, $p < 0.01$) and associated with the same industrial pollution source.
- Currently, the adverse effects caused by heavy metal pollution are slight and the potential ecological risks associated with the heavy metal pollution are low. Further degradation of sediment quality can be anticipated, however, as the industrial area develops and emissions increase.

It is recommended that urgent action be taken at both administrative and technical levels to prevent escalation of the problem. Necessary measures include the establishment of soil, sediment and water monitoring programs, a strengthening of compliance standards and greater enforcement of regulations. All stakeholders including the public should be involved. Ultimately the issue can be resolved if polluting enterprises can be persuaded to adopt more effective production and wastewater treatment technologies.

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