

Spatial distribution and source identification of heavy metals in soils under different land uses in a sewage irrigation region, northwest China

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Abstract

Purpose Heavy metal pollution is of major concern due to its potential threat to ecosystem safety and human health. To give a valuable insight into the status of heavy metal pollution in a sewage irrigation region in northwest China, this paper thoroughly studied the spatial distribution and possible source of heavy metals in soils under different land uses.

Materials and methods Soil samples were collected from arable lands (maize field, orchard, and paddy field) and nonarable lands (village and barren hill) from a sewage irrigation region, northwest China. The concentrations of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in the soils, together with soil pH, soil organic matter (SOM), and soil particle size distribution, were detected. GIS-based approach was employed to construct the spatial distribution maps of heavy metals, and multivariate analysis was used to identify their possible source.

Results and discussion Although elevated concentrations of Zn, Pb, and Cu are detected, Cd is the priority pollutant in the soils. Land use, location, and SOM are crucial factors affecting metal distribution in the soils. Metal concentrations in different land uses arrange in the order of orchard > paddy field/maize field > village > barren hill. The area within the basin of Dongdagou stream presents the most pollution,

whereas the northeast side far from the stream is the least. Irrigation water both from Dongdagou stream and the Yellow River are deemed as primary sources of Cd, Zn, Pb, and Cu. Besides, agrichemical application particularly contributes to metal accumulation in orchard soils, and Cd and Zn partially derive from atmospheric deposition. Nickel and Mn predominately originate from the soils.

Conclusions When studying metal pollution in soils, land use should be taken into account because of its important roles in determining metal concentrations. In the study area, arable lands are more likely to be polluted by Cd, Zn, Pb, and Cu than nonarable lands via sewage irrigation; moreover, agrichemical application and atmospheric deposition also should be held responsible for metal accumulation in the soils.

Keywords Heavy metal · Land use · Soil · Source identification · Spatial distribution

1 Introduction

With the rapid development of China, plenty of hazardous materials have been introduced into agro-ecosystem, among which heavy metals are of great concern due to their nondegradation and biotoxicity. Heavy metals in soils not only reduce the yield and quality of crops but also threaten the safety of ecosystem and human health (Raghunath et al. 1999). A recent official survey reported that heavy metals are thought to pose the greatest risks to food safety than other pollutants in China (Lu et al. 2015). Arable lands in China are mostly influenced by Cd, Pb, Cu, and Zn (Wei and Yang 2010), and Cd particularly presents serious pollution (Niu et al. 2013). Although many efforts have been made to prevent their hazards, it is reported that heavy metals continue posing

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risks to the public (Li et al. 2014), especially in the areas severely affected by metal mining (Liu et al. 2014a).

Baiyin city is a famous base of nonferrous metal mining and smelting in the middle of Gansu province, northwest China. Previous reports showed that arable lands here had been polluted by Cd, Cu, Pb and Zn (Nan and Zhao 2000; Li et al. 2006; Si et al. 2011). In May 2015, the Ministries of Finance and Environment Protection planned to provide special support for the comprehensive prevention and control of heavy metal pollution in 30 cities nationwide, among which Baiyin city took the first place. The study area, a major sewage irrigation region in Baiyin city, can be divided into arable lands (maize field, paddy field, and orchard) and nonarable lands (village and barren hill). Land use's change directly reflects the change of human activity (Pielke 2005), which further determines heavy metal levels in soils (Zhao et al. 2012). Accordingly, the roles of land use should be taken into account when assessing heavy metal pollution in soils. However, little is known about the status of heavy metal pollution in soils under different land uses in the study area.

GIS-based approach and multivariate analysis are increasingly used to interpret geochemical data (Facchinelli et al. 2001). GIS-based approach aids in quantifying the spatial distribution of heavy metals and constructing their distribution maps (Niu et al. 2013), and multivariate analysis provides a sound measure for source identification (Micó et al. 2006). They are proved to be very effective methods which have been successfully used in studying metal pollution in dusts (Han et al. 2006), arable lands (Bhuiyan et al. 2010), sediments (Varol 2011), and urban lands (Xia et al. 2011), etc.

The primary objective of this study is to shed light on the spatial distribution and possible source of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in soils of the sewage irrigation region, northwest China. We (1) detected their concentrations in soils under different land uses, (2) delineated their spatial distribution maps, and (3) identify their possible source. Results of this study will give a comprehensive understanding of metal pollution in the soils and provide significant guidance for local pollution prevention and control.

2 Materials and methods

2.1 Study area

The study area (36° 25'~36° 28' N, 104° 21'~104° 27' E) (Fig. 1) is located in the vicinity of Baiyin city. It is an important agricultural district because most cereals for the city dwellers are produced here. It belongs to arid and semi-arid area with an annual average precipitation of 220 mm. The Yellow River flows by the area from the southwest to

the northeast. Dongdagou stream, one local drainage ditch as marked yellow in Fig. 1, originates in local industrial district and drains into the Yellow River. Arable lands within the basin of Dongdagou stream had once been irrigated with sewage from the stream for a long period. Then, irrigation water has been changed into the relatively pollution-slight ones from the Yellow River. Along the Yellow River, the water pump used for irrigation was installed roughly 100 m after the estuary of Dongdagou stream. Nowadays, the Yellow River becomes increasingly polluted, and irrigation water from the Yellow River contains many hazardous pollutants, such as heavy metals (Li et al. 2006; Si et al. 2011).

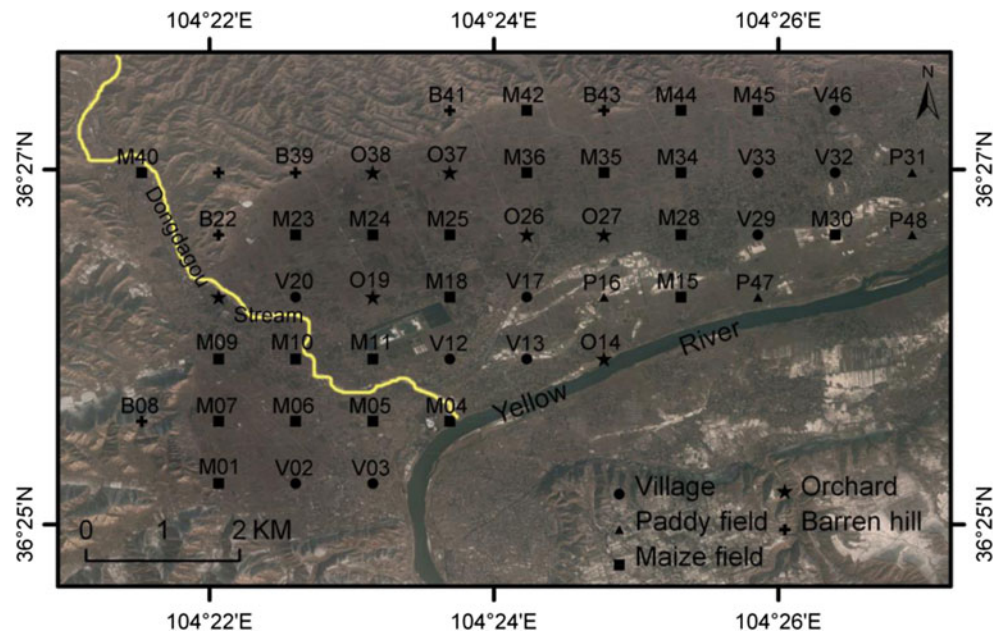
2.2 Sampling and analysis

In December 2013, 48 sampling sites were selected with a portable GPS. At each site, five surface soil samples (0–20 cm depth) were collected with a stainless spatula in a range of 50 m × 50 m, and then mixed thoroughly for a composite one. In total, 48 composite soil samples were collected, consisting of 22 samples from maize field (M), 4 from paddy field (P), 7 from orchard (O), 10 from village (V), and 5 from barren hill (B), respectively (Fig. 1). They were placed in sealed polyethylene bags and transported to the laboratory immediately.

In lab, the soil samples were air-dried, ground, and sieved. The value of soil pH was measured by a pH electrode (PB-10, Sartorius, Germany) in a 1:2.5 w/v soil-liquid suspension, and the content of soil organic matter (SOM) was determined by the method of potassium dichromate oxidation (Lu 1999). Soil particle size distribution was measured by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK) to determine the clay, silt, and sand percentages. Statistic results of soil properties (pH, SOM, clay, silt, and sand) are shown in Table 1. As shown, the study area has alkalescence soils with low SOM content.

To determine the concentrations of Cd, Cr, Cu, Mn, Ni, Pb, and Zn, 0.3000 g soil sample (fine particles < 149 μm) was accurately weighed into a 50-ml teflon crucible. It was initially digested with 5-ml concentrated HCl, and then digested with a mixture acid system of “HNO₃-HF-HClO₄” (5, 4, and 2 ml for each). Finally, the digestion solution was diluted with deionized water to a constant volume of 25 ml and measured by flame atomic absorption spectrometry (FAAS, ZENit700P, Analytik Jena, Germany) at the Instrument Analysis Research Center of Lanzhou University. Triplicates and blank samples were conducted at the same time. Quality assurance was checked with the reference material of Soil GBW 07402 (GSS-2). Results showed that the relative standard deviation (%RSD) was less than 5 %, and the recovery percentages were within ±10 %, both of which satisfied the requirements well.

Fig. 1 Map of the study area and sampling sites



2.3 Pollution assessment

The single factor pollution index (P_i) and the Nemerow synthetic pollution index (P_N) were employed to assess the pollution degree of these heavy metals investigated. Briefly, the higher the indexes are, the more the pollution is. They are calculated as follows:

$$P_i = \frac{C_i}{S_i} \tag{1}$$

$$P_N = \sqrt{\frac{P_{max}^2 + P_{ave}^2}{2}} \tag{2}$$

where C_i is the measured metal concentration; S_i is the permissible maximum concentration (MC) in the Grade II national standards (GB 15618–1995) (Table 1); P_{max} is the maximum value of P_i at a given site, and P_{ave} is the arithmetic average of P_i at the same site. Soil quality criteria are as follows: $P_i \leq 0.7$, safe; $0.7 < P_i \leq 1.0$,

Table 1 Statistic results of soil properties ($n=3$) and the reference values of metal concentrations

Land use		pH	SOM (g kg ⁻¹)	Clay (%)	Silt (%)	Sand (%)		BC ^a (mg kg ⁻¹)	MC ^a (mg kg ⁻¹)
M	Mean ± SD	8.31 ± 0.25 a	15.28 ± 4.72 ab	7.56 ± 1.59 a	66.81 ± 9.88 a	25.63 ± 11.11 a	Cd	0.116	0.60
	Range	7.66–8.59	8.04–25.99	3.61–10.59	32.39–79.68	12.55–63.99			
O	Mean ± SD	8.26 ± 0.14 a	19.06 ± 6.36 cb	7.09 ± 0.67 ab	62.72 ± 9.22 a	30.18 ± 9.59 a	Cr	70.2	250
	Range	8.06–8.43	10.49–27.83	6.18–7.82	51.35–74.91	17.27–41.80			
P	Mean ± SD	8.27 ± 0.09 ab	21.29 ± 1.97 c	7.91 ± 0.66 ab	72.01 ± 4.79 a	20.08 ± 4.75 a	Cu	24.1	100
	Range	8.15–8.38	19.60–23.50	7.52–8.68	67.65–77.13	15.33–24.83			
V	Mean ± SD	7.94 ± 0.13 c	13.41 ± 3.49 a	6.45 ± 1.30 ab	63.80 ± 5.77 a	29.75 ± 6.85 a	Ni	35.2	60
	Range	7.72–8.08	8.48–18.56	4.94–8.52	54.18–70.17	21.72–40.17			
B	Mean ± SD	8.25 ± 0.39 ab	5.59 ± 1.31 d	9.64 ± 4.65 b	63.66 ± 9.97 a	26.71 ± 12.00 a	Pb	18.8	350
	Range	7.94–8.82	3.75–6.72	6.39–18.79	44.13–72.17	16.25–49.48			
Total	Mean ± SD	8.22 ± 0.26	14.93 ± 5.80	7.59 ± 2.23	65.66 ± 8.82	26.76 ± 9.98	Zn	68.5	300
	Range	7.66–8.82	3.75–27.83	3.61–18.79	32.39–79.68	12.55–63.99			
							Mn	653	1800 ^b

Different small letters (a, b, c, and d) within each column represent significant differences among land uses ($p < 0.05$)

M maize field, O orchard, P paddy field, V village, B barren hill

^a BC: the background value of heavy metal concentration in soils of Gansu province; MC: the permissible maximum value of heavy metal concentration in the Grade II national standards (GB 15618–1995)

^b MC for Cr in paddy soil and Cu in orchard soil are 350 and 200 mg kg⁻¹, respectively (Zhong et al. 2011); for Mn, the threshold value of 1800 mg kg⁻¹ is used (Liu et al. 2014b)

alarm; $1.0 < P_i \leq 2.0$, slightly polluted; $2.0 < P_i \leq 3.0$, moderately polluted; and $3.0 < P_i$, seriously polluted (Zhang et al. 2013). In this study, it is defined that the soils are unpolluted, when $P_i \leq 1.0$. The classification of P_N is the same as P_i .

2.4 Statistical analysis

Statistical analysis was made with SPSS statistical software package (version 16.0 for Windows, SPSS Inc.). One-way ANOVA followed by LSD test was conducted to compare the differences. Pearson correlation matrix was employed to determine the interrelationships between heavy metals and soil properties. Principal component analysis (PCA) was used to identify possible source, and the rotation method was adopted with varimax with Kaiser Normalization. Hierarchical cluster analysis (HCA) was used to identify different geochemical clusters according to the furthest neighbor method, and the squared Euclidean distance was applied to measure the distance between clusters. GIS-based approach with kriging interpolation method was operated to delineate the spatial distribution maps of heavy metals.

3 Results

3.1 Spatial distribution of heavy metals

Spatial distribution of Cd, Zn, Pb, Cu, Mn, Ni, and Cr in soils is shown in Fig. 2. As shown, the area within the basin of Dongdagou stream is more seriously polluted by heavy metals, except for Cr, while the southwest and northeast sides of the study area show relatively lower metal concentrations. Cadmium displays the similar distribution pattern to Zn. Both of them present the highest element concentrations in the soils around site O19 which is located in the orchard near Dongdagou stream, and their concentrations decrease gradually with the distance away from the site. Although the concentrations of Pb and Cu in soils change little throughout the whole region, their levels in the area within the basin of Dongdagou stream are visibly higher than those outside. Nickel and Mn display a similar distribution pattern to each other, and both the northwest and east sides show higher concentrations. For Cr, it varies distinctively from others, which shows higher level in the middle area.

3.2 Heavy metals in soils under different land uses

A statistical summary of the mean concentrations of heavy metals are shown in Table 2. In the study area, land

use has a remarkable effect on heavy metal concentrations in soils. Heavy metal concentrations in soils roughly arrange in the following order: orchard > paddy field/maize field > village > barren hill. The mean concentration of Cd in each land use ranges from 1.27 to 2.51 mg kg⁻¹, being 10.95–21.64 times greater than its background concentration (BC) in soils of Gansu province. It is even 2.12 to 4.18 times more than the permissible maximum concentration (MC) in GB 15618–1995. Similar situation can also be observed for Zn which ranges from 75.92 to 139.7 mg kg⁻¹ and outnumbers the BC by 1.11–2.04 times; however, it is much less than the corresponding MC. Only in orchard soils, the mean concentrations of Pb and Cu (34.85 and 35.79 mg kg⁻¹, respectively) are slightly but significantly higher than their respective BCs. As for Cr, Mn, and Ni, their concentrations are no more than the BCs. All in all, although Zn, Pb, and Cu show elevated concentrations in the soils, only Cd pollution is notable in the study area.

3.3 Pollution assessment

To further assess the pollution degree of these heavy metals, pollution indexes of P_i and P_N are employed. Descriptive statistics of P_i for single heavy metal are listed in Table 3. As shown, the P_i for Cd has the greatest variability coefficient of 53.14 %, followed by Pb (50.33 %), Zn (29.66 %), Cu (26.29 %), Mn (19.28 %), Cr (18.35 %), and Ni (16.03 %). The P_i for Cd ranges from 0 to 6.29 with a mean value of 2.84, suggesting a moderate pollution. Except for Cd, other metals have quite low values of P_i (less than 1.0). Thus, Cd is perceived as the priority pollutant in the sewage irrigation region. Based on P_N , the vast majority of the study area presents a certain degree of pollution (Fig. 3), while only few sites in the northeast side such as site M44 and M45 have not yet been polluted ($P_i \leq 1.0$). The most heavily polluted area is found in the basin of Dongdagou stream, including site M11, M18, O19, V20, M24, and O37 ($P_N > 3.0$), which agrees well with the spatial distribution of Cd.

3.4 Interrelationships between heavy metals and soil properties

The results of Pearson correlation coefficient are presented in Table 4. As shown, Cu has significant positive correlations with other heavy metals ($p < 0.01$), and the same situations are also found in Zn and Pb. Cadmium is significantly correlated with Cr ($r = 0.309$, $p < 0.05$), while Mn is highly correlated with Ni ($r = 0.928$, $p < 0.01$). However, neither Cd nor Cr is correlated with Mn and Ni. No obvious correlations are found between soil pH and heavy

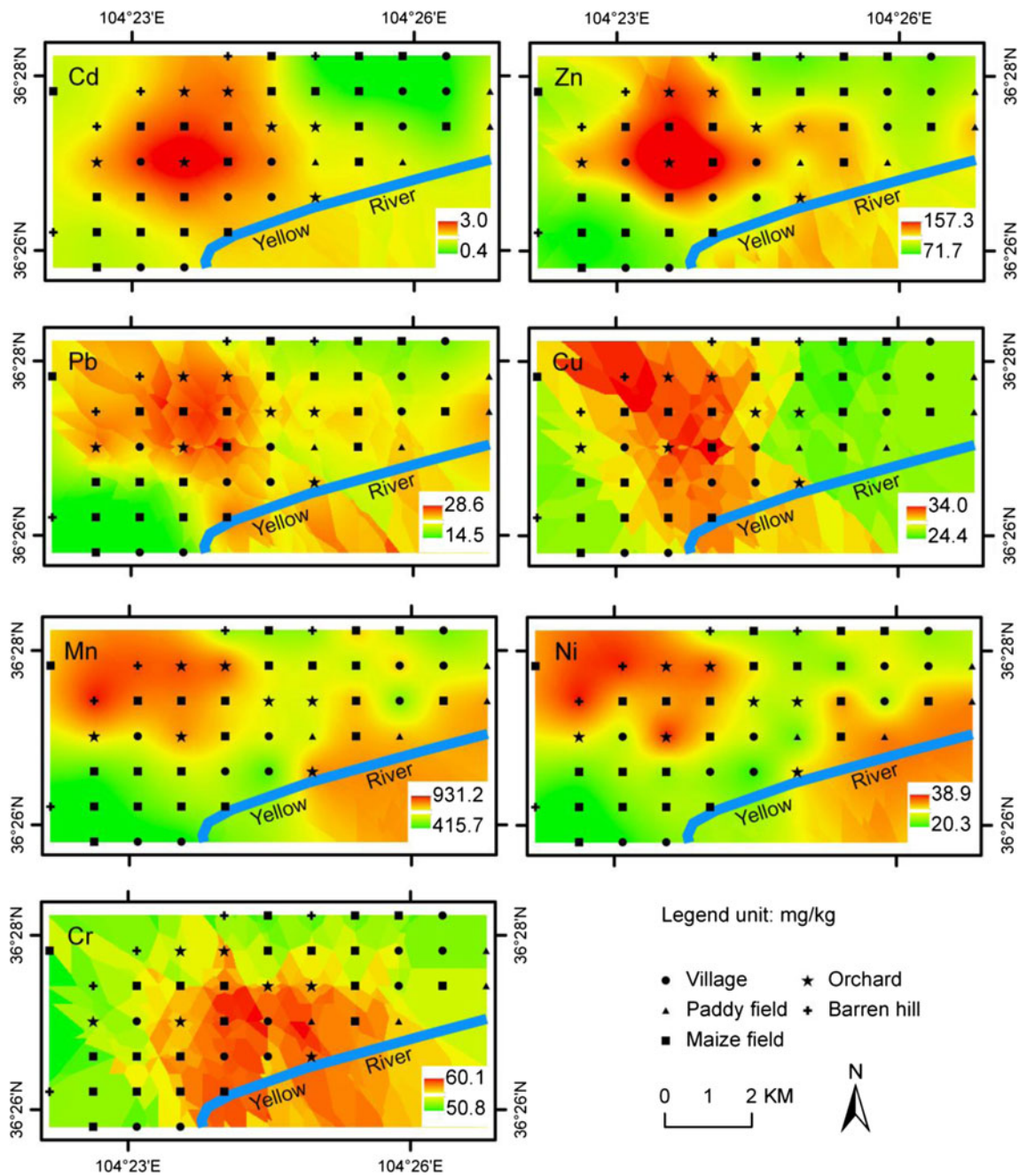


Fig. 2 Spatial distribution maps of heavy metal concentrations in soils of the study area

metals ($p > 0.05$). SOM shows positive correlations with Cr, Cu, Pb, Zn ($p < 0.01$), Mn, and Ni ($p < 0.05$); nevertheless, no correlation is found between SOM and Cd ($r = 0.121, p > 0.05$). Both clay and silt exhibit positive correlation with Mn and Ni ($r > 0.487, p < 0.01$), and sand exhibits negative correlations ($p < 0.01$), whereas none of them show significant correlations with other heavy metals ($p < 0.05$).

3.5 Multivariate analysis

3.5.1 Principal component analysis

Principal component analysis (PCA) was performed to aid in identifying the possible source of these heavy metals. According to PCA, these heavy metals can be reduced to two components (initial eigenvalue > 1.0) which account for

Table 2 The mean concentrations of heavy metals in soils under different land uses (mg kg⁻¹)

	M (22)	O (7)	P (4)	V (10)	B (5)
Cd	1.59±0.91 a	2.51±0.67 b	1.90±0.52 ab	1.54±0.99 a	1.27±0.79 a
Zn	96.25±25.38 a	139.7±31.63 b	99.75±20.22 a	94.83±26.37 a	75.92±8.25 a
Cu	26.92±6.95 a	35.79±10.36 b	26.23±5.75 a	24.55±4.74 a	22.95±3.04 a
Pb	22.59±10.21 a	34.85±12.13 b	25.94±7.43 abc	15.09±6.64 cd	13.00±4.13 d
Cr	53.36±8.18 a	61.36±11.17 b	51.62±3.48 ab	54.89±5.25 ab	48.17±9.08 a
Mn	664.0±118.9 a	787.7±83.82 b	728.8±65.53 ab	601.6±109.6 a	684.1±213.2 ab
Ni	29.14±4.24 a	33.48±4.20 b	31.15±5.17 ab	27.03±2.92 a	30.67±7.60 ab

Figures in parentheses represent the number of soil samples in each land use; different small letters (a, b, c, and d) within each row represent significant differences among land uses ($p < 0.05$)

M maize field, O orchard, P paddy field, V village, B barren hill

about 74 % of the total variation (Table 5). All heavy metals can be well represented in these two components (Table 6). As shown in the rotated component matrix, PC1, accounting for 40.42 % of the total variance, is strongly and positively related to Zn, Cd, Cu, Pb, and Cr, while PC2, sharing 33.66 % of the total variance, shows highly positive factor loadings (more than 0.94) on Mn and Ni. In addition, Zn, Pb, and Cu are also partially represented in PC2. Since Cd and Zn in soils under all five land uses as well as Pb and Cu in orchard soils exceed their respective BCs, PC1 can be better explained as an anthropogenic component, while PC2 is a natural one. This indicates that Zn, Cd, Cu, Pb, and Cr may mainly stem from anthropogenic inputs, while Mn and Ni are predominately controlled by the parent materials of the soils.

3.5.2 Hierarchical cluster analysis

Clustering method was used to apportion identical geochemical group of sampling sites. According to HCA, all sampling sites can be divided into six major clusters (Fig. 4). Cluster I, consisting of eight sites, shows the second lowest concentration for Cd and the lowest for other metals (Table 7). Most sites in this cluster such as site M01, V02, V03, M07, B08, and M09 are located in the southwest side of the study area. Cluster II shares comparable levels of Cd, Cu, and Cr to cluster I. Some sites in cluster II (e.g., sites M05, M06, and M10) are close to those in cluster I, and the rest are located in the

northeast side far from Dongdagou stream. No significant differences for Cd, Zn, Cu, Pb, and Cr can be observed between cluster II and cluster III. This may be explained by the fact that sampling sites in these two clusters are geographically close and thereby suffered from the same degree of anthropogenic activities.

There are 13 sites in cluster IV which presents the second highest metal concentrations. Sampling sites in this cluster mainly belong to the arable lands within the basin of Dongdagou stream. Cluster V including site M18, O19, O21, and O37 shows the highest metal concentrations compare to other clusters (Fig. 4). The only site in cluster VI (site M04) is the nearest one to the estuary of Dongdagou stream. Although no comparison can be conducted between cluster VI and other clusters, it seems that site M04 shows higher metal concentrations, especially for Cu and Pb. Except for site V17 and V20, the rest of these sites in cluster IV, V, and VI were located in arable lands which were either within the basin of Dongdagou stream (e.g., sites M11, M18, O19, O21, M24, and O37) or along the Yellow River behind the estuary of Dongdagou stream (e.g., sites O14, M15, P47, and P48).

4 Discussion

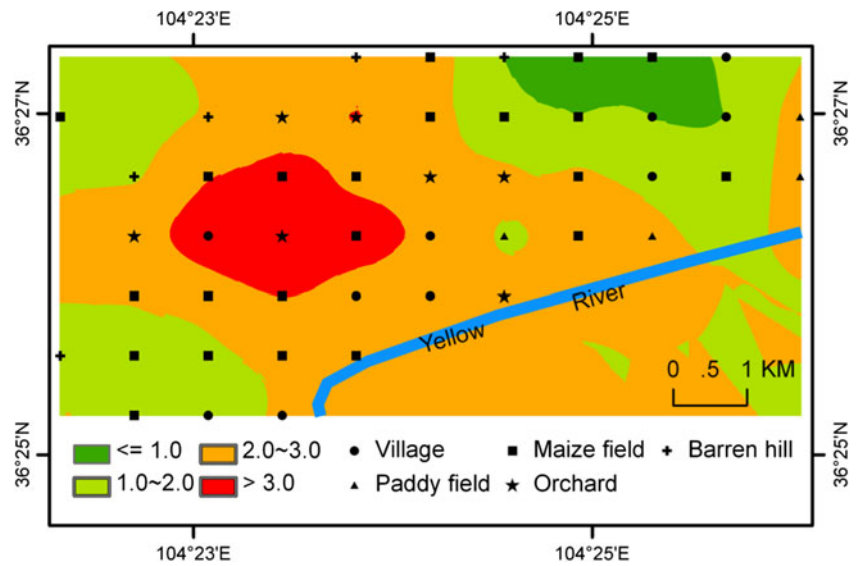
Both external and internal factors have important effects on heavy metal pollution in soils. On the one hand, external factors, mainly anthropogenic activities such as mining, smelting, cultivation, and transportation, may drastically increase heavy metal content in soils. On the other hand, heavy metals will be greatly affected by soil properties (internal factors) via many geochemical processes (e.g., sorption-desorption, dissolution-precipitation, oxidoreduction, and coordination-chelation). In this study, spatial distribution of heavy metals in soils under different land uses seems to be mainly influenced by factors of land use, location, and selected soil properties.

Table 3 Descriptive statistics of P_i for single heavy metal in soils of the study area ($n = 48$)

P_i	Cd	Zn	Cu	Pb	Cr	Mn	Ni
Mean	2.84	0.33	0.25	0.06	0.21	0.38	0.49
SD	1.51	0.10	0.06	0.03	0.04	0.07	0.08
Min	0.00	0.22	0.12	0.01	0.13	0.23	0.34
Max	6.29	0.65	0.54	0.16	0.34	0.52	0.65
CV (%)	53.14	29.66	26.29	50.33	18.35	19.28	16.03

CV coefficient of variation

Fig. 3 Assessment map of soil quality based on the P_N



4.1 Effects of land use on heavy metals

Land use can affect the levels of pollutants in soils (Zhao et al. 2012), among which arable lands are likely to accumulate more heavy metals compared to nonarable lands (Niu et al. 2013). Rodríguez et al. (2009) found that arable lands in the surrounding of a Spanish mining tail showed higher concentrations of Cd, Pb, Zn, and Cu in soils than nearby pasture lands (Rodríguez et al. 2009). Bai et al. (2010) concluded that the contents of Cr, Ni, Cu, As, Cd, and Zn in soils of a foodstuff base in northeast China arranged in the order of greenhouse field, uncovered vegetable field, maize field, and forest field (Bai et al. 2010). In this study, the soils of orchard show the highest metal concentrations, followed by paddy field and maize field, while relatively lower metal levels are detected in barren hill for Cd, Cu, Pb, Zn, and Cr, and village for Mn and Ni. Significant differences for metal concentrations in soils between arable lands

and nonarable lands indicates that land use affects metal distribution mainly through distinctive agricultural activities, and the pollution level increases with cultivation intensity.

In a previous report, elevated concentrations of Cd, Cu, Pb, and Zn in irrigation water from the Yellow River had been detected, and arable lands irrigated with those water after being treated with constructed wetland showed a downtrend of metal contents in soils (Si et al. 2011). Thus, irrigation using water from the Yellow River is an important source for heavy metal pollution in the Yellow River irrigation region (Kong et al. 2014). For crop growth, paddy field usually has a huge demand for water than orchard or maize field, and thus, it should display the highest metal levels in soils. However, in this study, heavy metal concentrations in paddy field are not greater than those in orchard/maize field, which indicates that there must be some other reasons to explain the pollution.

Table 4 Pearson correlation coefficient for heavy metals and selected soil properties

	pH	SOM	Clay	Silt	Sand	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Cd	-0.011	0.121	0.009	0.066	-0.060	1						
Cr	-0.073	0.390**	-0.074	0.158	-0.123	0.309*	1					
Cu	-0.089	0.510**	-0.002	0.077	-0.068	0.489**	0.387**	1				
Mn	0.027	0.343*	0.543**	0.487**	-0.552**	0.250	0.201	0.433**	1			
Ni	0.043	0.316*	0.562**	0.528**	-0.593**	0.274	0.277	0.477**	0.928**	1		
Pb	0.106	0.577**	-0.018	0.034	-0.026	0.427**	0.404**	0.780**	0.507**	0.493**	1	
Zn	-0.084	0.458**	0.012	0.120	-0.109	0.696**	0.520**	0.638**	0.609**	0.578**	0.672**	1

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

Table 5 Total variance explained by principal component analysis of heavy metals

Component	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	4.027	57.532	57.532	2.829	40.417	40.417
2	1.158	16.540	74.072	2.356	33.655	74.072
3	0.712	10.172	84.244			
4	0.645	9.214	93.457			
5	0.241	3.442	96.900			
6	0.162	2.320	99.219			
7	0.055	0.781	100.00			

4.2 Effects of location on heavy metals

The locations of sampling sites related to Dongdagou stream seem to have an important effect on heavy metals in soils. Dongdagou stream accepts domestic wastewater and industrial sewage (Nan and Zhao 2000). According to the results of HCA, all sites can be classified into two groups: the low concentration group (including those sites in clusters I, II, and III) and the high concentration group (including those sites in clusters IV, V, and VI). As discussed above, sampling sites in the low concentration group are collected from the southwest and northeast sides of the study area. They are located either at the upstream of the Yellow River or at the area far from the stream. Comparatively, sampling sites in the high concentration group were located either within the basin of Dongdagou stream or along the Yellow River behind the estuary of Dongdagou stream. Thus, we speculate that there is a cause-and-effect relationship between heavy metals in soils and Dongdagou stream.

The hypothesis is verified by the fact that arable lands within the basin of Dongdagou stream had once been irrigated with sewage from the stream for years. Moreover, the fact that heavy metal concentrations in the sediments of Dongdagou stream shows extremely high levels of Cd, Zn, Cu, and Pb (Fig. S1, [Electronic Supplementary Material](#)) further strengthens this conclusion. Although the accurate position of sewage-irrigated lands cannot be figured out, it seems that

the area including site M11, M18, O19, O21, and M24 are the possible sewage-irrigated soils. Given the hazards of heavy metals, irrigation water from Dongdagou stream has been replaced by relatively pollution-slight one from the Yellow River; however, Cd pollution is still considerable.

4.3 Effects of soil properties on heavy metals

Adsorption and retention of heavy metals in soils are affected by several factors (Micó et al. 2006). In this study, selected soil properties (i.e., pH, SOM, clay, silt, and sand) are taken into account. Despite of its low content (Table 1), SOM which has strong complexing capacity for metallic pollutants shows significantly positive correlations with all these heavy metals, except for Cd (Table 4). This is in accordance with the previous reports that SOM has an important role in controlling the sorption of heavy metals by soils (Bhuiyan et al. 2010). The study area has alkalescence soils, where the mobility of heavy metals is considered to be low. Even so, no significant correlations are detected between pH and heavy metals. This agrees with the findings of Micó et al. (2006) who stated that it may be due to the narrow range of pH (7.66–8.82 in this region). Clay and silt only show significantly positive correlations with Mn and Ni, whereas sand shows negative correlations with them. Besides, no correlations can be found between soil particle size and other heavy metals. This further proves that Mn

Table 6 Component matrices for heavy metals

Heavy metal	Component matrix		Heavy metal	Rotated component matrix	
	1	2		1	2
Zn	0.896	0.157	Zn	0.785	0.459
Pb	0.824	0.123	Cd	0.781	0.070
Cu	0.806	0.198	Cu	0.743	0.370
Ni	0.774	−0.576	Pb	0.708	0.439
Mn	0.760	−0.616	Cr	0.684	0.049
Cd	0.641	0.451	Mn	0.182	0.962
Cr	0.554	0.404	Ni	0.218	0.940

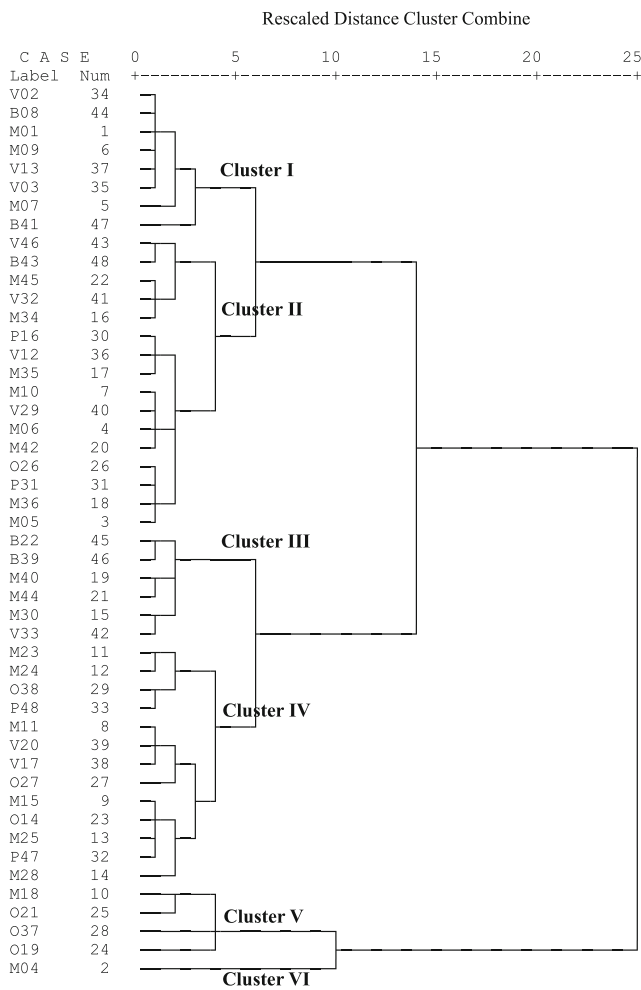


Fig. 4 Tree diagram obtained by clustering of sampling sites

and Ni originate from internal sources of the soils (Micó et al. 2006).

4.4 Source identification

Although elevated levels of Zn, Cu, and Pb are detected in soils, Cd is the priority pollutant in the study area. Sewage

from local factories was fed into arable lands within the basin of Dongdagou stream for years. As discussed above, it is deemed as the primary pollution source. Irrigation using water from the Yellow River is another source of metal pollution, since the water from the Yellow River becomes increasingly polluted (Li et al. 2006; Si et al. 2011). As stated, heavy metals can stem from metal-based pesticide, fungicidal spray (Micó et al. 2006), and phosphate fertilizer (Jiao et al. 2012). The orchard soils show the highest metal concentrations than other arable lands, which may be the result of more frequent agro-chemical application (Ross 1994). Compared to the BCs, the soils of nonarable lands also show a slight but significant elevation of Cd and Zn concentrations. For example, Zn concentrations in soils of village and barren hill exceed the BC by 38.44 % and 10.83 %, respectively. That is to say, source irrelevant to agricultural activities such as atmospheric deposition should be the contributor.

With regard to Mn and Ni, they are classified into the natural component with factor loadings > 0.9 (Table 6), which verifies that they predominately result from the soils, and human activities may have negligible effects on their distribution in the soils. In the study area, Cr is mainly represented in the anthropogenic component (Table 6), which indicates Cr stems from anthropogenic input, but it shows a lower level than the BC. This makes it difficult to give a clear conclusion for Cr’s origin.

5 Conclusions

When studying metal pollution in soils, land use should be taken into account because of its important roles in determining heavy metal distribution. In the sewage irrigation region, Cd is the priority pollutant in the soils. Arable lands, especially orchard, are more likely to be polluted by heavy metals than nonarable lands. Irrigation with sewage once from local drainage ditch (Dongdagou stream) is the first important source of heavy metals, which leads to the fact that the area within the

Table 7 Statistics of heavy metal concentrations in different clusters from HCA (mg kg⁻¹)

	Cluster I (8)	Cluster II (16)	Cluster III (6)	Cluster IV (13)	Cluster V (4)	Cluster VI (1)
Cd	1.60±0.31 a	1.18±0.84 ab	0.87±0.56 b	2.31±0.45 c	3.19±0.53 d	2.25
Zn	71.07±4.24 a	84.63±7.56 b	87.63±8.05 b	124.5±17.05 c	163.0±25.11 d	103.7
Cu	21.17±1.72 a	24.26±3.47 ab	26.32±2.57 bc	28.55±3.80 c	41.96±9.00 d	53.66
Pb	11.52±2.84 a	18.66±5.88 b	18.66±2.61 b	25.04±7.23 c	43.78±8.01 d	57.25
Cr	49.83±9.01 a	54.39±6.00 a	50.32±7.03 a	53.97±6.92 a	68.45±11.08 a	53.66
Mn	474.4±58.73 a	627.0±53.06 b	807.3±78.33 c	768.2±66.66 c	795.2±64.21 c	632.8
Ni	23.15±2.39 a	27.65±1.75 b	34.68±3.48 c	32.32±3.06 c	34.93±3.79 c	27.96

Different small letters (a, b, c, and d) within each row represent significant differences among clusters (*p*<0.05)

basin of Dongdagou stream is more seriously polluted. Additionally, the current irrigation using the Yellow River water is thought to still pose threats to the agro-ecosystem. More agrichemical application contributes to the highest metal concentrations in orchard than in paddy field/maize field. Moreover, in the sewage irrigation region, Cd and Zn partially stem from atmospheric deposition. Further study should focus on the bioavailability of heavy metals in soils to assess their potential transfer from soils to crops.

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