

# Source identification and spatial distribution of heavy metals in tobacco-growing soils in Shandong province of China with multivariate and geostatistical analysis

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**Abstract** Samples of surface soil from tobacco (*Nicotiana tabacum* L.) fields were analysed for heavy metals and showed the following concentrations (mean of 246 samples, mg/kg): As, 5.10; Cd, 0.11; Cr, 49.49; Cu, 14.72; Hg, 0.08; Ni, 19.28; Pb, 20.20 and Zn, 30.76. The values of the index of geoaccumulation ( $I_{geo}$ ) and of the enrichment factor indicated modest enrichment with As, Cd, Cr, Hg, Ni or Pb. Principal component analysis and cluster analysis correctly allocated each investigated element to its source, whether anthropogenic or natural. The results were consistent with estimated inputs of heavy metals from fertilizers, irrigation water and atmospheric deposition. The variation in the concentrations of As, Cd, Cu, Pb and Zn in the soil was mainly due to long-term agricultural practises, and that of Cr and Ni was mainly due to the soil parent material, whereas the source of Hg was industrial activity, which ultimately led to atmospheric deposition. Atmospheric deposition was the main exogenous source of heavy metals, and fertilizers also played an important role in the accumulation of these elements in soil. Identifying the

sources of heavy metals in agricultural soils can serve as a basis for appropriate action to control and reduce the addition of heavy metals to cultivated soils.

**Keywords** Pollution assessment · Agricultural soils · Principal component analysis · Cluster analysis · Geographic information system

## Introduction

Soils polluted with heavy metals are found in many parts of the world, especially in the developing countries such as China. This kind of pollution not only degrades the soil, the atmosphere, the water bodies and the food crops but also threatens the health and well-being of animals and people through the food chain (Nabulo et al. 2010; Dung et al. 2013).

The sources and distribution of heavy metals in soil vary substantially with land use (industrial, urban and agricultural) (Wang et al. 2013; Li et al. 2014). The distribution of heavy metals in agricultural soils was extensively investigated in China during the last decade because of the emerging problems of contamination of soil that accompanies rapid industrialization and urbanization. China's agricultural soils have been generally enriched with Cd, Hg and Pb (Huang and Jin 2008): Cd and Hg in Guangdong province and the Huanghuai plain (Cai et al. 2012; Zhou et al. 2014), Hg and Pb in the arid regions in Gansu province (Li et al. 2008) and Hg in the Yangtze River Delta in Jiangsu province, especially the paddy soils (Hang et al. 2009). Horticultural soils have also been analysed for heavy metals (Cai et al. 2010; Xue et al. 2013; Wang et al. 2015). The main external sources of heavy metals in agricultural soils are irrigation water, the petrochemical industry, atmospheric deposition and agrochemicals and manures used in excess, whereas those in industrial and urban

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soils are industrial operations, vehicle exhaust, mining and smelting (Luo et al. 2009; Cheng et al. 2014; Li et al. 2014).

Tobacco (*Nicotiana tabacum* L.) is widely cultivated in China and many other countries and has also been used as a model plant in many studies because of its greater tolerance to environmental stress and wide distribution. The tobacco plant accumulates Cd preferentially over other metals and could be considered a hyperaccumulator (Liu et al. 2016). The heavy metal content of tobacco leaves is variable and depends on the conditions under which the crop is grown and mostly on the composition and properties of the soil (Zaprjanova et al. 2010); however, little information is available about the sources and distribution of heavy metals in soils on which tobacco is grown.

Shandong is one of the most rapidly developing provinces in eastern China and is also a traditional farming region in which tobacco is grown extensively. Therefore, geostatistical analysis was used in the present study to study the accumulation of eight heavy metals, namely arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn), from the large number of soil surveys that have been carried out in the tobacco-growing areas of Shandong. Multivariate statistical methods combined with a geographic information system (GIS) were also used for identifying the sources and distribution of these metals in the study area. The input of these elements from fertilizers, irrigation water and atmospheric deposition was also calculated. The results of this study will provide baseline information to assess the quality of soil, especially its suitability for tobacco, in northern China and to adopt appropriate measures to reduce the addition of heavy metals to these soils.

## Materials and methods

### Study area

Shandong lies along the north-eastern coast of China and is the country's oldest producer of flue-cured tobacco. The tobacco-growing region largely consists of the hilly areas in the central and southern parts of the province. The area experiences a warm temperate monsoon humid/subhumid climate, and the annual means of the major weather parameters are as follows: temperature, 12.1–13.4 °C; rainfall, 595–950 mm; frost-free period, 182–266 days and duration of sunshine, 2257–2560 h.

### Sample collection and preparation

A total of 246 soil samples were collected in 2012 from the tobacco-growing region of Shandong (Fig. 1). The samples were collected from the top, tilled layer (0–20 cm). Each site was sampled at 5–10 points, and these subsamples were

pooled, from which about 1.5 kg of soil was removed using a stainless steel spade and stored in self-sealing polythene bags. The geographical coordinates of all sampling locations were recorded using a global positioning system. The soil samples were air-dried and ground fine enough with an agate mortar to pass through a 100-mesh (0.15 mm) sieve for determination of heavy metals. The fertilizers used in Shandong's tobacco-growing areas were bought by the Department of Tobacco Management in Shandong to obtain a representative sample; thus, five types of fertilizers from 12 factories were collected from the study area in 2012. A total of 27 samples of irrigation water (from ponds, rivers, reservoirs and groundwater sources) were also collected from the same region for the determination of heavy metals. Each water sample was collected directly into 500-mL pre-washed plastic bottles.

### Analysis of soil samples

After digesting in a mixture of HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HF (5:2:2, v/v), the samples of soils and fertilizers were analysed for the eight heavy metals mentioned earlier using inductively coupled plasma mass spectroscopy (ICP-MS, X Series 2, ThermoFisher Scientific, Waltham, MA, USA). The samples of irrigation water were centrifuged at 3000×g for 5 min, and the supernatant was filtered using a 0.45-μm microporous membrane filter. The concentration of eight elements in each filtrate was also analysed with ICP-MS.

### Assessment of heavy metal pollution

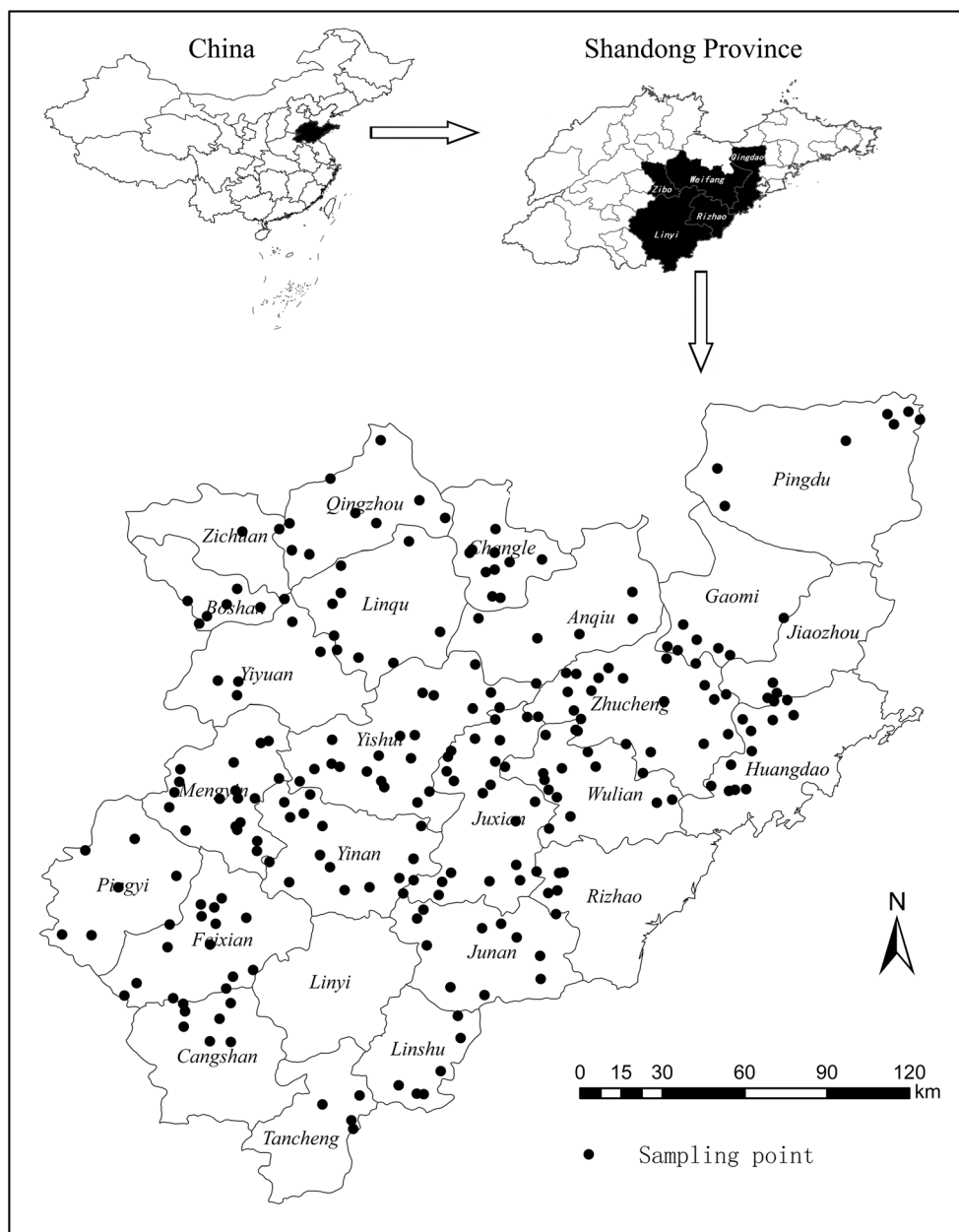
#### *Index of geoaccumulation*

The index of geoaccumulation ( $I_{geo}$ ), originally developed by Müller (1969), makes it possible to assess the extent of contamination by comparing the current and pre-industrial concentrations of a given substance and is computed using the following equation:

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i} \quad (1)$$

where  $C_i$  is the measured content of element  $i$  in soil,  $B_i$  is the geochemical background value of element  $i$  in the earth's crust and 1.5 is a constant. The background concentration of a substance is its concentration at a point distant from a source—a point at which the concentration of the substance can no longer be attributed with certainty to a given source. In the present study, the background values of the elements for the soils of Shandong were obtained from the China National Environmental Monitoring Centre, which was responsible for the first nationwide investigation of soil pollution in China in the 1980s (CNEMC 1990).

**Fig. 1** Study area and sampling sites for soils of the tobacco-growing region of Shandong province, China



Based on the value of the index, the sites were categorized into seven classes:  $I_{geo}$  less than 0, uncontaminated; 0 to less than 1, uncontaminated to moderately contaminated; 1 to less than 2, moderately contaminated; 2 to less than 3, moderately to heavily contaminated; 3 to less than 4, heavily contaminated; 4 to less than 5, heavily to extremely contaminated and more than 5, extremely contaminated.

#### Enrichment factor

The enrichment factor (EF) is based on the standardization of a tested element against a reference element, the value of

which is relatively stable in the environment. The enrichment factor was calculated using a modification of the equation developed by Buat-Menard and Chesselet (1979) and Loska et al. (1997):

$$EF = \frac{C_i / C_r}{B_i / B_r} \quad (2)$$

where  $C_i$  is the measured content of element  $i$  in the soil sample,  $C_r$  is the content of the reference element in the soil sample,  $B_i$  is the background content of element  $i$  in the study

area and  $B_r$  is the background content of the reference element in the study area.

Five categories of the extent of enrichment were defined based on the value of the EF (Sutherland 2000): EF less than 2, deficient to minimal enrichment; 2 to less than 5, moderate enrichment; 5 to less than 20, significant enrichment; 20 to less than 40, very high enrichment and greater than 40, extremely high enrichment.

*Pollution indexes and Nemerow integrated pollution index*

To assess the degree of contamination with heavy metals, a pollution index (PI) for each metal and a Nemerow integrated pollution index (NIPI) of all the eight elements were calculated for each sampling site. The formula for calculating the PI was as follows:

$$PI = \frac{C_i}{S_i} \tag{3}$$

where  $C_i$  is the measured content of element  $i$  in the soil sample and  $S_i$  is the maximum permissible limit of element  $i$ .

The integrated index for each sampling site was defined as follows (Nemerow 1974):

$$NIPI = \sqrt{\frac{PI_{max}^2 + PI_{ave}^2}{2}} \tag{4}$$

where  $PI_{max}$  is the maximum value of PI for each heavy metal and  $PI_{ave}$  is the average value of PI for each heavy metal. Based on the PI and NIPI, five categories of pollution were defined: less than 0.7, no pollution; 0.7 to less than 1, the warning threshold; 1 to less than 2, low; 2 to less than 3, moderate and greater than 3, severe.

**Statistical analysis**

Spatial and statistical analyses were performed using ArcGIS 10.0 (ESRI, Redlands, CA, USA) and SPSS 19.0 (IBM, Armonk, NY, USA). Basic statistical parameters were established for the raw data, and the Kolmogorov–Smirnov test (K–S test) was used for normality assessment of the data. A  $p$  value higher than 0.05 meant that the data set conformed to the normal distribution. Pearson correlation analysis was used for determining the relationships between the heavy metals in the sediment. Principal component analysis (PCA) and cluster analysis (CA) were employed to identify associations among and common sources of the metals. Graphs were created with ArcGIS or SPSS and modified using Photoshop CS2 (Adobe, San Jose, CA, USA).

**Results and discussion**

**Concentrations of heavy metals in soil**

The descriptive statistics of the concentrations of heavy metals in the sampled soils is given in Table 1 together with the background concentrations for Shandong and the maximum permissible limits for each heavy metal as defined in the Environmental Quality Standard for Soils in China (GB 15618-1995) (SEPAC 1995). The mean values (mg/kg) were as follows: As, 5.10; Cd, 0.11; Cr, 49.49; Cu, 14.72; Hg, 0.08; Ni, 19.28; Pb, 20.20 and Zn, 30.76. The coefficients of variation (CVs) were high for As, Cr, Hg and Pb, reflecting their large geochemical variability in the sampled soils. The comparatively high variability of Hg and Pb indicated the heterogeneity of the sources of the two metals. Application of the K–S test showed that concentrations of all the metals followed the normal distribution. The skewness, which is a measure of the degree of asymmetry of a distribution in relation to the normal distribution, also confirmed the above observation. Moreover, kurtosis values of As, Cr, Hg, Ni and Pb were very high because the majority of the samples were clustered around relatively low values.

The topsoil in the tobacco-growing region of Shandong may have been enriched with some metals such as Cd and Hg because their average concentrations were higher than their background values—by as much as 1.31 times for Cd and 2.16 times for Hg—whereas the mean concentrations of the rest of the heavy metals were far lower than their local background values, because the sampling sites were located in a farming belt where contamination from vehicular traffic and industrial units was far less serious than that in urban areas.

The mean concentrations in soil of all the eight elements in the tobacco-growing region of Shandong were lower than their mean concentrations for the country as a whole, as recorded in the first national soil pollution survey from 2005 to 2013 (Chen et al. 2015). The mean concentrations of all except Hg were also lower than those reported for agricultural soils of Yucheng (Jia et al. 2010), Wulian (Lv et al. 2014) and Ju counties in Shandong (Lv et al. 2015), and those of all except Cr and Pb were lower than those in the horticultural soils in Shandong. The results were mainly due to the significant differences in farming practises under different land use categories (Liu et al. 2011).

**Pollution assessment of heavy metals**

*Index of geoaccumulation*

The values of  $I_{geo}$  for all the eight elements are shown in Fig. 2. The background values used in calculating the  $I_{geo}$  values for each of the eight elements are also listed in Table 1. According to the defined  $I_{geo}$  classes, more than

**Table 1** Descriptive statistics of heavy metal concentrations in soils from the tobacco-growing region of Shandong province ( $n = 246$ )

	Concentration (mg/kg)						CV (%)	Kurtosis	Skewness	K-S
	Mean	Median	Min.	Max	Background <sup>a</sup>	Standard <sup>b</sup>				
pH	6.12	5.72	4.33	8.62	7.7		20.42	-1.09	0.57	2.46**
OC	0.93	0.87	0.17	2.43	1.16		41.94	1.49	1	1.69**
As	5.1	4	0	30.69	9.3	30/25/20	96.27	11.46	2.94	2.35**
Cd	0.11	0.09	0.01	0.39	0.084	0.3/0.3/0.6	54.55	4.29	1.66	2.20**
Cr	49.49	42.62	4.38	446.6	66	150/200/250	81.90	43.19	5.3	2.44**
Cu	14.72	13.41	3	52.07	20	50/100/100	55.43	3.17	1.47	5.43**
Hg	0.08	0.02	0	2.14	0.037	0.3/0.5/1.0	237.50	57.88	6.64	4.58**
Ni	19.28	17.03	2.72	129.61	22.8	40/50/60	74.64	19.25	3.51	1.73**
Pb	20.2	16.23	4.3	327.08	24.2	300/300/300	115.64	123.84	9.95	2.28**
Zn	30.76	26.84	5.34	140.46	70.7	200/250/300	62.32	7.1	2.06	1.93**
V	57.45	54.29	10.32	149.18	81.9		45.66	1.16	0.94	1.42*

<sup>a</sup> Data from the first national soil pollution investigation of China in the 1980s (CNEMC (China National Environmental Monitoring Centre) 1990)

<sup>b</sup> Based on the guidelines in the Environmental Quality Standard for Soils in China (GB 15618-1995) and the permissible limits for soils with pH less than 6.5, 6.5–7.5 and more than 7.5

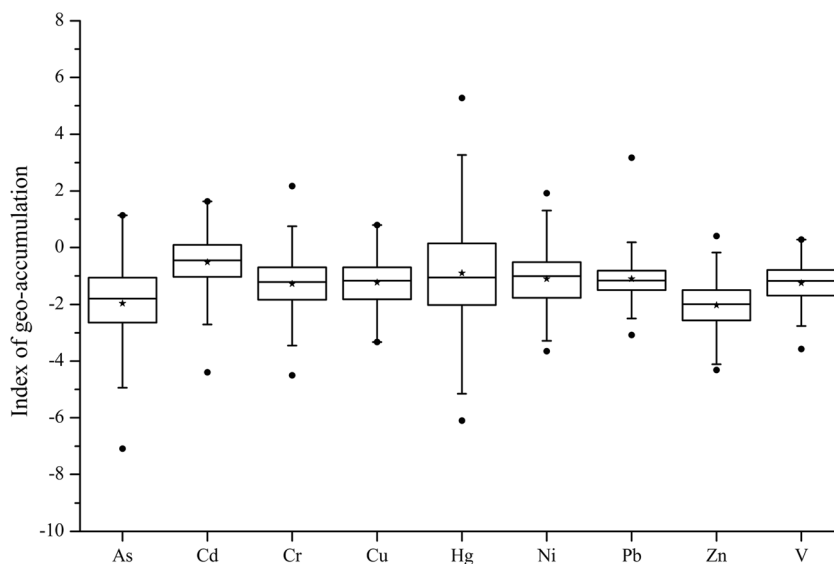
\* $p < 0.05$ , \*\* $p < 0.01$

90% of the soil samples belonged to the uncontaminated category with respect to As, Cr, Cu, Ni, Pb and Zn (Table 2). In the case of Cd, about 71.5% of the samples were in the uncontaminated category and about 26.0% in the next category, namely uncontaminated to moderately contaminated, whereas in the case of Hg, the corresponding figures were 71.5 and 14.0%. At one sampling location, the soils were extremely contaminated with Hg, probably because of some point sources of pollution in the form of some industrial plants nearby.

#### Enrichment factor

The values of EF for the eight elements are shown in Table 3. The reference element used in calculating the EFs is usually a conservative element that originates mainly from the soil's parent material and probably little affected by anthropogenic activity. The most commonly used reference elements are scandium (Sc), manganese (Mn), titanium (Ti), aluminium (Al), vanadium (V) and iron (Fe) (Schiff and Weisberg 1999). In the present study, V was selected as the reference

**Fig. 2** Indexes of geoaccumulation of heavy metals in soils of the tobacco-growing region of Shandong province. Circles at the top and bottom of box plots correspond to the maximum and minimum values, respectively. The pentagram in the box plot is the average value. Horizontal lines at the top, middle and bottom of the box plot correspond to 75% percentile, median and 25% percentile, respectively ( $n = 246$ )





**Table 2** Percentages of class distribution for pollution assessment of heavy metals in soils from the tobacco-growing region of Shandong province using geoaccumulation index ( $I_{geo}$ ) and enrichment factor index (EF) ( $n = 246$ )

Class	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
$I_{geo}$								
Uncontaminated	95.9%	71.5%	94.7%	94.7%	71.5%	93.1%	93.5%	99.2%
Uncontaminated to moderately contaminated	2.1%	26.0%	4.1%	5.3%	14.0%	4.9%	4.9%	0.8%
Moderately contaminated	2.1%	2.4%	0.8%	0.0%	6.1%	2.0%	1.2%	0.0%
Moderately to heavily contaminated	0.0%	0.0%	0.4%	0.0%	4.8%	0.0%	0.0%	0.0%
Heavily contaminated	0.0%	0.0%	0.0%	0.0%	2.6%	0.0%	0.4%	0.0%
Heavily to extremely contaminated	0.0%	0.0%	0.0%	0.0%	0.4%	0.0%	0.0%	0.0%
Extremely contaminated	0.0%	0.0%	0.0%	0.0%	0.4%	0.0%	0.0%	0.0%
Enrichment factor								
Deficient to minimal enrichment	95.9%	61.0%	94.7%	97.6%	71.1%	94.3%	90.2%	98.4%
Moderate enrichment	3.3%	37.4%	4.5%	2.4%	16.7%	4.9%	6.5%	1.6%
Significant enrichment	0.8%	1.6%	0.8%	0.0%	9.3%	0.8%	3.3%	0.0%
Very high enrichment	0.0%	0.0%	0.0%	0.0%	2.0%	0.0%	0.0%	0.0%
Extremely high enrichment	0.0%	0.0%	0.0%	0.0%	0.8%	0.0%	0.0%	0.0%

element for the following reasons: (1) its natural concentration tends to be uniform, (2) its lowest variability ensures that it is less vulnerable to anthropogenic changes (Table 1) and (3) its geochemistry is similar to that of many trace metals. Some authors have successfully used V to get geochemical normalization of heavy metals (Wu et al. 2015). The values of EF also suggested that the proportions of samples in the deficient to minimal-enriched category with respect to As, Cr, Cu, Ni, Pb or Zn were more than 90% (Table 2). Compared to the background values, 37.4% of the samples were moderately enriched with Cd and 1.6% of those were significantly enriched. The corresponding figures for Hg were 16.7 and 9.3%. In addition, the EF values of Zn in majority of the soils (88.2% of the samples) were less than 1, indicating depletion rather than enrichment of Zn; therefore, most of these soils in Shandong need Zn.

*Pollution indexes and Nemerow integrated pollution index*

The extent of pollution was evaluated using the PI for the eight heavy metals based on the guidelines given in the soil

environment quality standards of China (GB 15168-1995) (SEPAC 1995): None of the samples were polluted with Cu or Zn; as to the other metals, 98.4% were uncontaminated with As and 98.4% were uncontaminated with Cd, the corresponding values for the rest being as follows: Cr, 98.8%; Hg, 95.5%; Ni, 97.2% and Pb, 99.6% (Table 3).

As to the NIPI, the values ranged from 0.05 to 3.03 and the mean value was 0.37. Overall, 89.4% of the soils showed no pollution with heavy metals; 6.1% were near the threshold; 4.1% showed low levels of pollution, and 0.4% (only one site) showed moderate levels of pollution.

The results of  $I_{geo}$ , EF, PI and NIPI were broadly consistent. Most of the sites were neither enriched nor contaminated with heavy metals; virtually, no site was enriched with Cu and Zn, and only a few were enriched with one or more of the other six elements, especially Cd, Hg and Pb. No obvious contamination with heavy metals was observed in agricultural soils in Yucheng and Wulian counties, although long-term accumulation of Cd, Cu, Hg, Pb and Zn has been reported for these soils (Jia et al. 2010; Lv et al. 2014, 2015): These results are in agreement with those obtained in the present study.

**Table 3** Enrichment factor (EF) and pollution indexes (PIs) of metals in soils from the tobacco-growing region of Shandong province

Measure of pollution	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EF mean	0.80	1.95	1.11	1.06	2.92	1.23	1.38	0.66
EF max	6.27	7.43	15.09	2.60	102.71	12.68	17.55	2.71
EF min	0.00	0.13	0.25	0.42	0.00	0.29	0.21	0.17
PI mean	0.17	0.35	0.20	0.15	0.15	0.39	0.07	0.12
PI max	1.02	1.30	1.79	0.52	4.28	2.59	1.09	0.56
PI min	0.00	0.02	0.02	0.03	0.00	0.05	0.01	0.02

## Source identification of heavy metals

### *Pearson correlation*

The relationships between metals can provide noteworthy information on their sources and pathways. Pearson correlation coefficients were calculated for all possible pairs of the eight elements, and the correlation matrix is shown in Table 4. Most of the heavy metals were positively correlated with each other in terms of their concentration. The correlations between every pair in which As, Cd, Cr, Cu, Ni or Zn was a member were highly significant. These results suggest that most of the eight heavy metals are associated with each other and probably share some common sources. Moreover, no significant correlation was found between Hg and the other metals, indicating a specific source for Hg—probably vehicular traffic and atmospheric deposition (Jia et al. 2010). The significant correlations between heavy metals in horticultural soils were fewer than those in the present study of tobacco soils in Shandong, and the difference may reflect the differences in farming practices between field crops and horticultural crops (Liu et al. 2011).

### *Principal component analysis*

The sources of heavy metals in agricultural soils were identified using PCA. The analysis was performed with Varimax rotation, which facilitates the interpretation of results by minimizing the number of variables with a high loading on each component. The result of the Kaiser–Meyer–Olkin (KMO) test was 0.69, and that of Bartlett's test was very significant ( $p < 0.01$ ), suggesting that the concentrations of heavy metals in soils of the tobacco-growing region of Shandong can be analysed with PCA for reducing the number of factors. The rotated component matrix is shown in Table 5, and that of the three major components is also shown in Fig. 3, in which the associations between these metals are clearly evident. The results indicate that PCA narrowed the initial scope of the data set to three components, which explained 72.08% of the variation in the data. The rotated component matrix demonstrated that the first component (PC1) comprised As, Cd, Cu, Pb and Zn, the second component (PC2) comprised Cr and Ni and the third component (PC3) comprised Hg alone.

The first component of PCA explained 40.64% of the total variance and loaded heavily on As, Cd and Zn and moderately on Cu and Pb. That component could be considered an anthropogenic component related to long-standing farming practices followed in the area, such as the application of phosphatic, organic and nitrogenous fertilizers and of some pesticides and germicides. In the developing countries, however, anthropogenic sources have been increasing with rapid industrialization and urbanization (Wang et al. 2013; Li et al. 2014). Increasing attention is now focused on regions where

industrialization is under way. Although many of the agricultural inputs into soils include metals, only a few are major inputs. One of the main sources of Cd is fertilizers, and the accumulation of Cd in agricultural soils is a result of applying phosphatic fertilizers with high Cd content (Cai et al. 2012). Long-term application of pesticides and fungicides containing As and Cu contributes to the increased accumulation of these heavy metals in soils. Typically, Pb and Zn in agricultural soils are metals reported to have a mix of sources, both lithogenic and anthropogenic (Luo et al. 2009; Sun et al. 2010); nevertheless, the CV of Pb was much greater than that of any other element in the present study, indicating a point source as well for Pb. The soils could be contaminated by mining activities either directly or indirectly through air pollution and atmospheric deposition (Li et al. 2014).

In the present study, the cropping patterns and agricultural activities at different sampling sites have generally been in step with each other over the last few decades. Moreover, fertilizers, pesticides and germicides applied in the study area were generally bought from a central source and applied in similar amounts. In addition, instead of livestock manure, commercial organic fertilizers or cake fertilizer were used, and pesticides that contain As were banned for tobacco in China decades ago. Therefore, samples of commonly used fertilizers and irrigation water were also collected and analysed for heavy metals (Tables A1 and A2 in supplementary materials). The conventional doses ( $\text{kg}/\text{hm}^2$ ) of these fertilizers that are particularly used for tobacco are as follows: tobacco specialty fertilizer, 900; calcium magnesium phosphate, 150; sulphate–potassium magnesium, 225; commercial organic fertilizers, 225 and cake fertilizers, 375. Thus, the input of heavy metals by each fertilizer during the growing season of tobacco was also calculated. The total inputs of heavy metals (Table A1) suggest that the tobacco specialty fertilizer contributed more than half of As, Cd, Cr, Hg, Ni and Pb from fertilizers. In the case of Cu, the cake fertilizers contributed more than 20% of the input as well as calcium magnesium phosphate, whereas in the case of Zn, the corresponding fertilizers were specialty fertilizer, commercial organic fertilizers and cake fertilizers. In addition, the input of Ni from calcium magnesium phosphate and that of Pb from sulphate–potassium magnesium were also more than 20% of the total from all fertilizers. Therefore, in the present study, the tobacco specialty fertilizer and organic fertilizers were the main sources of heavy metals.

The contents of eight elements in the different sources of irrigation water are listed in Table A2. The climate of the study area was humid/subhumid, and the average rate of conventional irrigation was  $225 \text{ m}^3/\text{hm}^2$ . The contents of each element were not significantly different between the different sources (pond, river, reservoir and groundwater) except As in pond water. The inputs of all the heavy metals except Hg from irrigation water throughout the year were less than 5% of

**Table 4** Pearson’s correlation matrix for the concentrations of heavy metals in soils from the tobacco-growing region of Shandong province

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As	1							
Cd	0.624**	1						
Cr	0.169**	0.184**	1					
Cu	0.476**	0.459**	0.375**	1				
Hg	0.018	0.110	0.017	0.103	1			
Ni	0.240**	0.230**	0.891**	0.545**	0.024	1		
Pb	0.289**	0.284**	0.038	0.136*	0.018	0.056	1	
Zn	0.470**	0.535**	0.276**	0.551**	0.116	0.410**	0.249**	1

\* $p < 0.05$ , \*\* $p < 0.01$

those from fertilizers, whereas the input of Hg from irrigation water was as much as 63.6% of that from fertilizers.

The second component of PCA, comprising Cr and Ni, explained 18.85% of the total variance and showed a heavy loading on Cr and Ni and moderate loading on Cu, as the variability of the elements seemed to be controlled by the parent rocks. This conclusion agreed with that from the study by Wei and Yang (2010), namely that Ni and Cr appeared to be the least contaminating elements in all the cities in China, whereas Cd and Hg showed high values of  $I_{geo}$  for most cities. Thus, Ni and Cr are known to be indicators of the nature’s influence in many reports about China and other countries (Hani and Pazira 2011; Liu et al. 2011; Sun et al. 2013; Lv et al. 2014; Cai et al. 2015).

The soils of the tobacco-growing region of Shandong were identified as calcaric regosols (RGc), calcic luvisols (LVk), eutric regosols (RGe), calcaric cambisols (CMc), gleyic luvisols (LVg), eutric cambisols (CMe), haplic luvisols (LVh) and calcaric fluvisols (FLc) by matching the locations of the sampling sites with the Harmonized World Soil

Database (FAO/IIASA/ISRIC/ISSCAS/JRC 2012). The mean contents of heavy metals in different soil types are shown in Table 6.

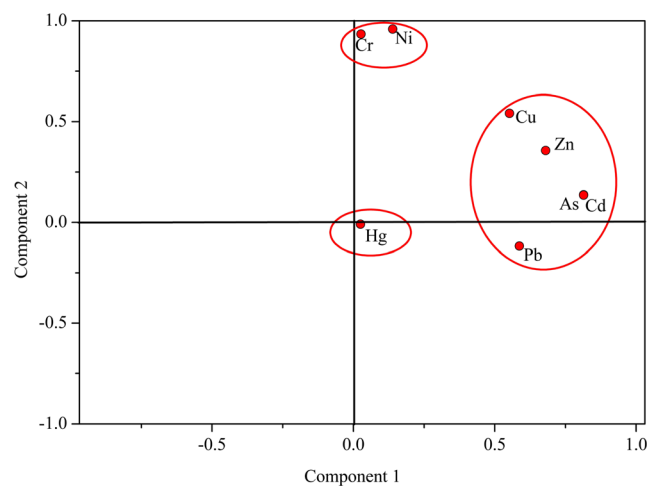
The contents of Cr and Pb did not differ significantly between the eight soil types mentioned above, whereas those of As, Cd, Cu, Hg, Ni and Zn did, at least between some soil types. The mean content of heavy metals in LVh or FLC was higher than that in the other soil types, whereas that in RGc, LVk and RGe was lower. This pattern may reveal the impact of natural, or lithogenic, factors on the distribution of heavy metals in soils. Soil parent material determines the contents of metals initially present in the soil although they may be leached out during weathering. As a result, the type of soil can make a significant difference to the contents of some heavy metals (Hu and Cheng 2013).

The third component of PCA, namely Hg, explained 12.58% of the total variance and could be defined as an anthropogenic component, related to industry and automobile traffic and, in turn, to atmospheric deposition. Shandong is also rich in mineral resources, comprising cobalt, iron, gold, copper, lead, zinc, molybdenum, bauxite, coal, limestone, etc. The soils could be contaminated by

**Table 5** Matrix of principal component analysis for concentrations of heavy metals in soils from the tobacco-growing region of Shandong province

Heavy metal	Rotated component matrix		
	PC1	PC2	PC3
As	<b>0.814</b>	0.137	-0.019
Cd	<b>0.814</b>	0.135	0.129
Cr	0.027	<b>0.934</b>	-0.031
Cu	<b>0.552</b>	0.542	0.161
Hg	0.025	-0.009	<b>0.974</b>
Ni	0.139	<b>0.959</b>	0.001
Pb	<b>0.587</b>	-0.118	-0.149
Zn	<b>0.680</b>	0.357	0.172
Variance explained %	40.64	18.85	12.58
Cumulative variance %	40.64	59.49	72.08

The bold type just suggested that these elements were in the component



**Fig. 3** Loading plots of the two components influencing geochemical variation in soils from the tobacco-growing region of Shandong province



**Table 6** Contents of heavy metals in different types of soils from the tobacco-growing region of Shandong province

Soil	n	pH	OC	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
RGe	24	5.30e	0.78b	3.61c	0.09bc	45.71a	11.93b	0.05b	15.09b	18.22a	23.37b
LVk	40	5.74de	0.79b	3.98bc	0.08c	37.62a	11.46b	0.04b	15.51b	21.21a	29.79ab
RGe	50	5.55de	0.80b	4.08bc	0.08c	49.21a	12.60b	0.11ab	18.26ab	16.32a	27.22ab
CMc	16	6.74ab	1.11a	5.09abc	0.11abc	52.16a	14.20b	0.06ab	20.77ab	17.77a	29.20ab
LVg	18	5.98 cd	0.87b	5.31abc	0.11abc	48.97a	14.64b	0.03b	17.72ab	18.62a	27.21ab
CMe	26	6.42bc	0.94ab	5.25abc	0.12ab	58.61a	15.86ab	0.05ab	21.82ab	17.80a	30.37ab
LVh	38	7.09a	1.15a	6.72ab	0.13a	53.69a	19.62a	0.08ab	22.96ab	27.45a	38.85a
FLc	21	6.75ab	1.14a	7.50a	0.13ab	60.08a	19.21a	0.17a	25.30a	21.05a	38.89a

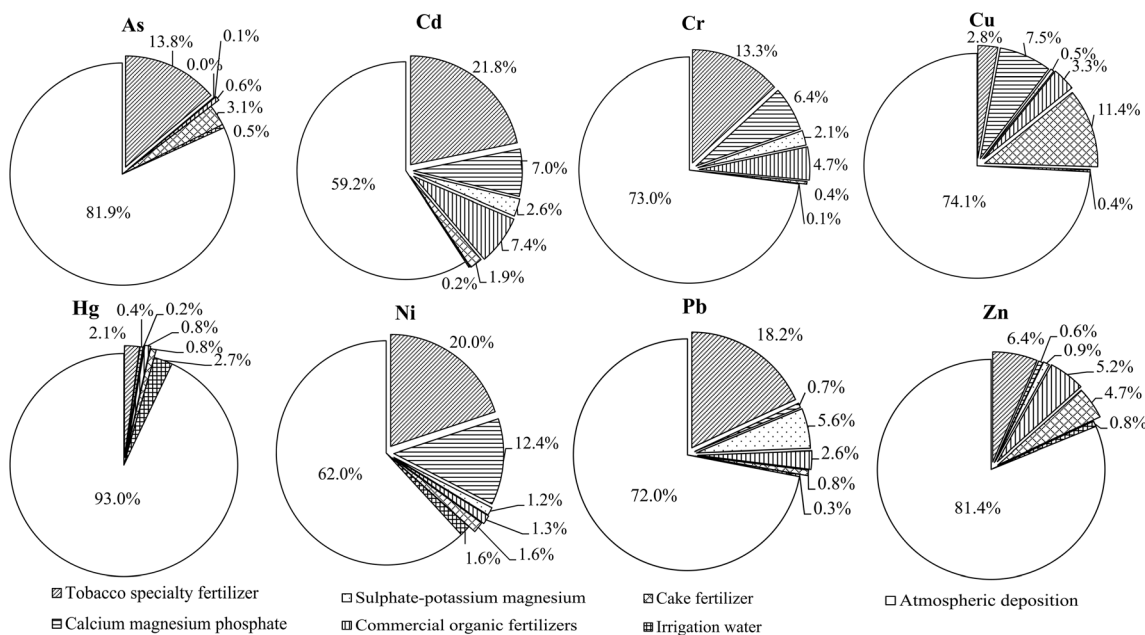
The data in the same column marked with the same letter do not differ significantly at  $p < 0.05$

mining activities directly or indirectly through air pollution and atmospheric deposition. Streets et al. (2005) reported that in China, approximately 38% of Hg came from coal combustion, 45% from smelting of non-ferrous metals and 17% from miscellaneous activities, of which the production of batteries (dry cells), fluorescent lamps and cement formed the largest part.

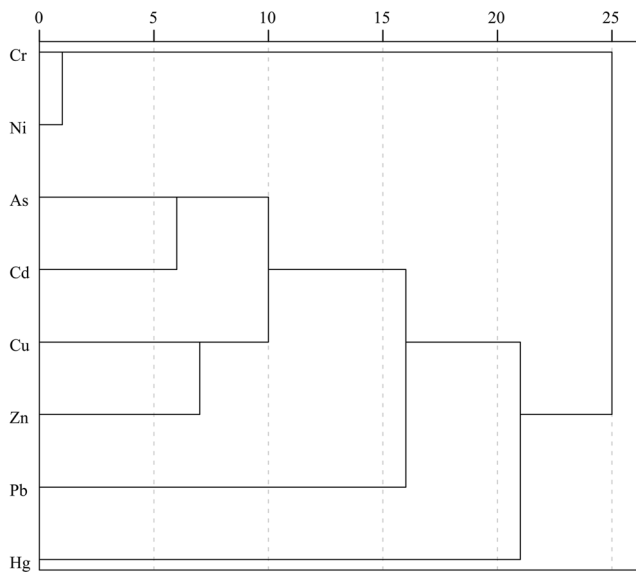
In the present study, the sources of heavy metals in tobacco soils were mainly atmospheric deposition, fertilizers and irrigation water: The relative contribution of different sources of heavy metals is shown in Fig. 4. The data on atmospheric depositions are the mean values for China as a whole (Luo et al. 2009). Overall, atmospheric deposition contributed more than half the total amount of heavy metals from exogenous sources and as much as 93% of Hg, which is why PC3 comprised only Hg. The percentages of As, Cd, Cr, Ni and Pb

from specialty fertilizer, of Cu from cake fertilizers and of Ni from calcium magnesium phosphate were also more than 10%, indicating the importance of these components in the main sources.

The total annual input of heavy metals from atmospheric deposition, fertilizers and irrigation was estimated in absolute quantities and as percentages of the total input (Table A3). The proportions of Cr and Ni from exogenous sources were 0.07 and 0.21%, respectively, and smaller than those of the other elements. This division makes Cr and Ni the least contaminating elements in soil, the variability of which is due to the parent rocks. At the other end was Cd, which, at 2.67%, not only accounted for the highest share in the total inputs from exogenous sources but was also present in largest amount in the topsoil. This finding is consistent with the results reported by Luo et al. (2009), who also found that Cd was present in the



**Fig. 4** Shares (%) of heavy metals in exogenous sources of heavy metals in soils from the tobacco-growing region of Shandong province



**Fig. 5** Dendrogram showing hierarchical cluster analysis for eight heavy metals

largest quantities among the heavy metals in agricultural soils in China, with average annual input rate of 0.004 mg/kg. These results indicate that accumulation of Cd in agricultural soils probably constitutes a safety hazard for agricultural products from China and perhaps from other countries.

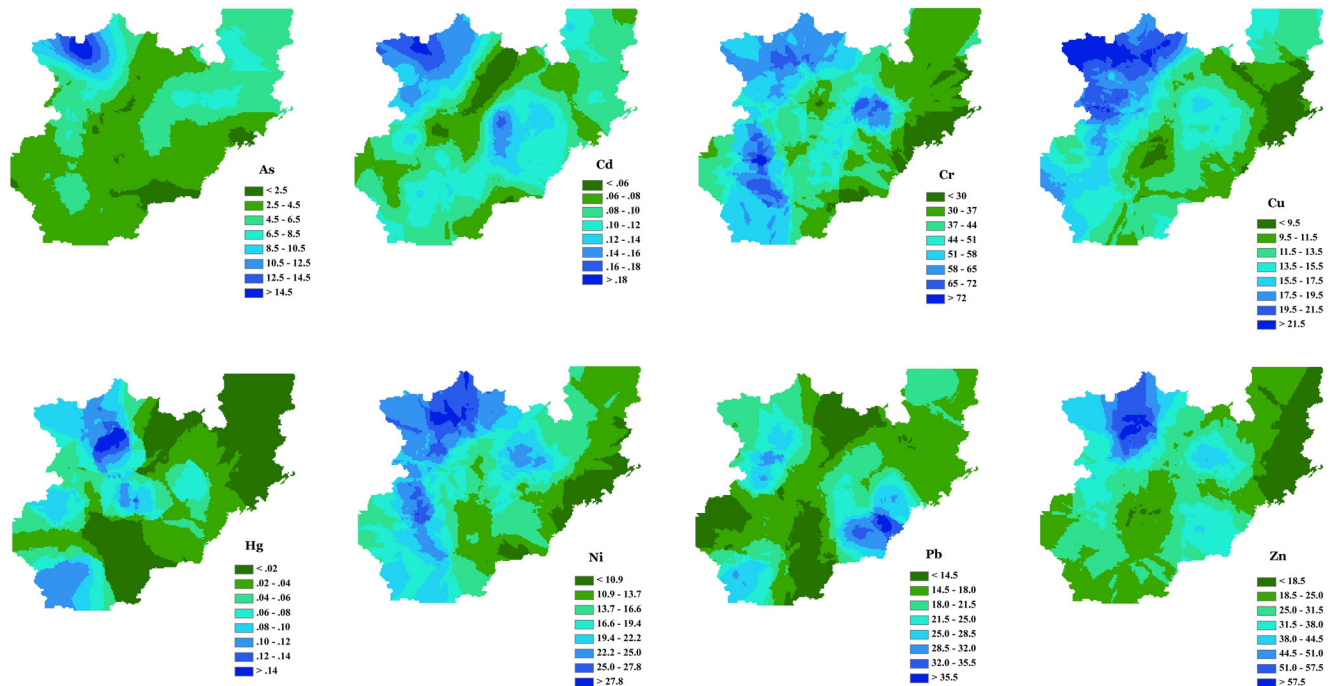
*Cluster analysis*

Cluster analysis is often coupled with PCA to confirm the results and for grouping the variables. Hierarchical CA was

developed following the Ward’s method, and the results are shown in the form of a dendrogram in Fig. 5. The analysis grouped the eight elements into three well-defined groups, reflecting the geochemical complexity of the study area: Cr and Ni in group I, As, Cd, Cu, Pb and Zn in group II and Hg in group III. Therefore, the results of CA closely matched those of PCA, pointing to at least three different sources of heavy metals in tobacco soils of Shandong.

**Spatial distribution of heavy metals**

Geostatistical methods provide an unbiased estimation of variables at locations without sampling. Plotting the spatial distribution of heavy metals in soil is crucial to quantifying the risks from heavy metal pollution at different locations, and spatial interpolation methods such as Kriging estimation have been widely used for revealing the spatial distribution of pollutants. The spatial distribution maps of the investigated elements are shown in Fig. 6 and were used for identifying metal-enriched areas. Eight class intervals were defined for each element based on the range of values in the original data. The spatial patterns of the eight heavy metals were similar, with the highest concentrations in the north-western parts of the study area, indicating the natural influence of parent rocks. Both Cd and Pb accumulated predominantly in the central parts of the eastern side, and the spatial distribution of Cr and Ni showed a clear boundary to the west of the area, with both the metals showing similar geographical patterns. These observations indicate that soil parent materials and pedogenic



**Fig. 6** Spatial distribution maps of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in soils from the tobacco-growing region of Shandong province, China

processes are the major factors that determine the amounts and the distribution of heavy metals in the study area (Sun et al. 2013). The effect of lithogenic factors on the spatial distribution of Cu also matched the results of PCA. High values of Hg were observed in the central, south-western and north-western parts of the study area: Hg is carried in the form of aerosols and industrial fumes over longer distances in the atmosphere, leading to the high contents of Hg in soils downwind of the town and of heavy traffic sites through atmospheric deposition (Lu et al. 2012). Spatial analysis supports the interpretation of the results of multivariate analysis, namely that application of large quantities of agrochemicals during the last 50 years has contributed to the accumulation of the metals in agricultural fields.

## Conclusion

The present study sought to delineate the pattern of accumulation of heavy metals and to identify their sources in soils of the tobacco-growing region of Shandong, a representative farming area of northern China. Although the overall environmental quality of the soils from Shandong province makes them safe enough for producing non-polluted tobacco leaves, As, Cd, Cr, Hg, Ni and Pb have accumulated in these soils at levels slightly higher than the respective background values for each of these metals, and a few samples were found to be moderately contaminated with Cd, Hg or Ni, with Cd being present in the largest amounts.

Both PCA and CA showed that the distribution of As, Cd, Cu, Pb and Zn is probably governed by anthropogenic activities, that of Cr and Ni, by parent rocks and that of Hg, by atmospheric deposition. These analyses were consistent with the estimated amounts of heavy metals added through fertilizers, irrigation water and atmospheric deposition. Atmospheric deposition contributed 93% of the Hg being added to the agricultural soils and was also the main exogenous source of the other seven elements. Local farming practices, particularly application of fertilizers, play an important role in the accumulation of heavy metals in these soils. The specialty fertilizer was an important source of As, Cd, Cr, Ni and Pb, whereas cake fertilizers and calcium magnesium phosphate also added considerable quantities of Cu and Ni, respectively. The spatial distribution of heavy metals was affected by both anthropogenic and natural factors. Appropriate measures, such as reducing the use of agrochemicals, avoiding the discharge of industrial waste and preventing atmospheric deposition on agricultural soils should be undertaken to control the high levels of heavy metals effectively in the agricultural ecosystems.

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