

Potential sources of and ecological risks from heavy metals in agricultural soils, Daye City, China

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Abstract Concentrations of eight heavy metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn)) were measured in 92 topsoil samples collected from agricultural areas in Daye City to (1) assess the distribution of these heavy metals, (2) discriminate natural and anthropic contributions, and (3) identify possible sources of pollution. Mean concentrations of As, Cd, Cu, and Zn in the investigated soils were 23.8, 1.41, 105, and 159 mg kg⁻¹, respectively. These values were higher, in some cases by several orders of magnitude, than their corresponding background values. Estimated ecological risks, based on contamination factors and potential ecological risk indexes, were mostly low, but were considerable for As and Cd. A range of basic and multivariate statistical analyses (Pearson's correlation analysis, hierarchical cluster analysis, and principal component analysis) clearly revealed two distinct metal groups, comprising As/Cd/Cu/Zn and Cr/Ni/Hg/Pb, whose concentrations were closely associated with the distribution and pollution characteristics of industries in and around the city. Results demonstrated that As/Cd/Cu/Zn were indicators of anthropic pollution, while Cr/Hg/Ni/Pb were from parent materials.

Maps of pollutant distribution compiled for the entire arable area further indicated that non-ferrous metal smelting and mining is the main source of diffuse pollution, and also showed the contribution of point source pollution to metal concentrations in agricultural topsoil. Results of this study will be useful for planning, risk assessment, and decision making by environmental managers in this region.

Keywords Ecological risk · Heavy metals · Daye City · Principal component analysis · Source

Introduction

There are numerous potential harmful sources of environmental contamination, including heavy metals. Soil environmental quality assessments can support development of relevant guidelines for proper land use and soil contamination (UNEP 2008; Suresh et al. 2012). The spatial variability of soil heavy metals can strongly influence these assessments; however, the characterization of heavy metals at most sites is often hindered by multiple sources of pollution, natural processes and anthropogenic activities (Rodríguez-Martin et al. 2006).

Heavy metal inputs to agricultural soils deserve considerable attention worldwide owing to their ability to directly harm the environment by compromising soil ecological function and polluting groundwater. They may also indirectly endanger living organisms, through bio-accumulation and inclusion in the food chain, and inevitably damage human health if ingested (Türkdoğan et al. 2003; Lu et al. 2012). Many surveys of heavy metals in agricultural soils have therefore been carried out in China in recent decades, including in the Northern Plain (Khan et al. 2008; Li et al. 2009), the Pearl River Delta (Wong et al. 2002), the Yangtze River Basin (Huang et al. 2007; Chen et al. 2008), and in south China (Cui et al. 2005). These surveys have

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shown that approximately 10 % of agricultural soils in China are suffering from heavy metal pollution, due mainly to point-source pollution. Large quantities of heavy metals are introduced to these soils from a variety of sources including wastewater irrigation, industrial production, fertilizer and pesticide abuse, and fossil fuel combustion. Understanding the spatial distribution of heavy metals in agricultural topsoil is critical for environmental management and the safety of agricultural produce.

Geostatistics provides us with a set of statistical tools for investigating and mapping soils that have hazardous levels of heavy metals (Facchinelli et al. 2001). Recent studies have attempted to apply geographic information system (GIS) mapping techniques in conjunction with multivariate analyses, in order to identify pollution sources and to establish the relative contributions of natural and anthropogenic sources to the heavy metal contents of agricultural topsoil (Facchinelli et al. 2001; Micó et al. 2006). An extensive dataset has been compiled from analysis of agricultural soils in China, either from single cities or from urban agglomerations within a county, including some studies from Hubei Province. To date however, there have been few studies on the concentrations and possible sources of heavy metals in Daye City.

Daye City is situated in one of China's largest crop producing areas. As well as being a major agricultural area, it has also experienced accelerated industrialization and rapid economic development in recent years. Previous studies have shown that the Daye Lake, a main source of irrigation water for agriculture in the region, is becoming increasingly polluted with heavy metals, such as As, Cd, and Zn, and organic contaminants, such as polycyclic aromatic hydrocarbons. Agricultural soils from Luoqiao Town, a sub-region of Daye City, are similarly polluted (Fig. 1). These observations suggest that concentrations of heavy metals may be high in soils around Daye City.

In this study, concentration data for eight heavy metals (Cu, Zn, Cr, Ni, Pb, Cd, Hg, and As) in agricultural topsoil from Daye City was investigated using statistics, geostatistics and GIS techniques, in order to map the heavy metal distribution in agricultural topsoil in the area, and to allow us to establish the contributions from (1) natural and anthropic sources and (2) point and nonpoint sources of contamination. This study will provide valuable information about environmental soil condition that will be useful for regional soil quality management.

Materials and methods

Study area

The research area included 426 km² of agricultural land (spread across a total area of approximately 1,156 km²) in Daye City (29° 40' N, 114° 31' E–30° 15' N, 115° 20' E), comprising the regions of Baoan (BA), Chengui (CG), Dajipu (DJ), Haidiqiao (HD), Jinhu (JH), Jinniu (JN), Jinshandian

(JS), Luoqiao (LJ), Liurenba (LR), Lingxiang (LX), Mingshan (MS), and Yinzu (YZ) (Fig. 1). It is an important farming belt, with a population of approximately 874,000. The region has a sub-tropical monsoon climate; the annual average temperature is 16.9 °C, and the average annual precipitation is 1,386 mm. From a geomorphologic perspective, the Mufu Mountains are in the southern part of the study area, while the Daye Lake is in the northern part. Agriculture is dominated by corn and vegetable cultivation.

Sample collection

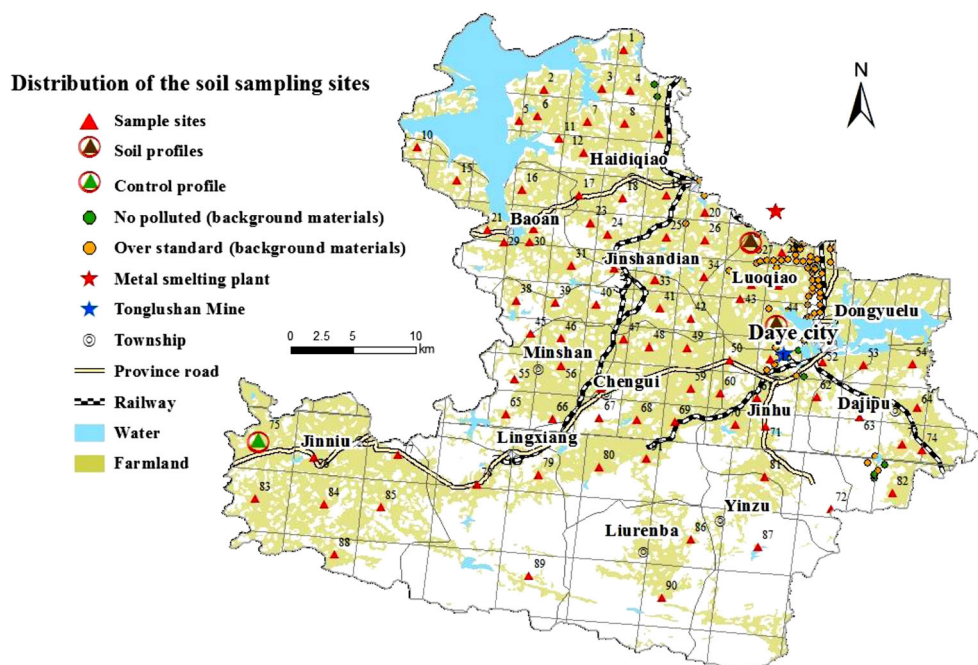
The basic sampling grid was a square mesh. As far as possible, and taking into consideration the limitations of potential difficult sampling conditions, sampling points were selected at intervals of 1 km×1 km using 1:25,000 topographic maps. This resulted in 92 geo-referenced sampling points (Fig. 1), at which topsoil samples (0–20 cm in depth) were collected in April 2012. Five random subsamples were collected from each sampling site (approximately 20 m×20 m) and were mixed into one composite sample. Samples, weighing approximately 500–1,000 g after stones, coarse plant roots and residues were removed, were put into clean polyethylene bags and transported to the laboratory. The central point of each sampling site was recorded with a global positioning system (Garmin eTrexH). Site descriptions were recorded at the time of sampling, so that the sample information could be placed in the context of land use and major environmental features.

Sample analysis

Soil samples were air-dried and sieved to separate the <2.00 mm fraction from coarser material. They were then homogenized and stored in polyethylene bags at room temperature prior to analysis. Soil subsamples were digested with aqua regia solution, based on the United States Environmental Protection Agency Method 3051A (United States Environmental Protection Agency USEPA 1998) with minor modifications. Briefly, approximately 0.200 g of soil sample was digested with a 15-mL mixture of HNO₃, HCl, and HClO₄ (1:3:1, v/v/v). The digestion process was carried out in closed polytetrafluoroethylene vessels in a microwave digester (Perkin Elmer Multiwave 6MF 100 (1,000 W), USA) with automatic pressure and temperature regulation. Heavy metal concentrations of As, Cd, Cr, Hg, Ni, Pb, and Zn in soil digestions were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500c, USA).

Soil pH was measured in a soil-to-water suspension (1:5, v/v) using a pH meter (PHS-3C, Hino Technology).

Fig. 1 Locations of sampling sites from 12 subareas in Daye City, China



Quality control and quality assurance

All samples were analyzed at the State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences. Ultra-pure grade acids were used for digestion and other reagents were of analytical grade. All glass- and plasticware used was soaked overnight in a HNO_3 solution (10 %, v/v) and then rinsed thoroughly with deionized water before use. The quality control procedure to verify the accuracy of the digestion procedure consisted of reagent blanks, duplicate samples and several referenced soils (GBW07405, National Standard Detection Research Center, Beijing, China). Detection limits for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 1, 30, 5, 2, 2, 2, 2, and 2 ng/g, respectively. Analytical precision was determined by the 20 % analysis (in duplicate) of randomly chosen samples and reference samples, with a variation coefficient for all investigated elements of <8 %. Recoveries were as follows: As (88–99 %), Cd (92–101 %), Cr (96–100 %), Cu (89–102 %), Hg (90–115 %), Ni (90–95 %), Pb (95–105 %), and Zn (99–110 %); these are within the acceptable ranges of the USEPA Method 3051A (1998).

Statistical analysis

Data were expressed on a basis of dry weight. SPSS 17.0 was used for descriptive statistics and multivariate analysis. Geostatistical analyses and probability calculations were carried out with VarioWin 2.2. Maps of the spatial distribution of the eight metals were produced using ArcGIS 8.3 using kriging interpolation.

Summary statistics were used to evaluate the data distribution. Frequency distributions of the metals were examined using

histograms, background normality tests and calculations of skewness (to measure the asymmetry of the observations). Concentrations of geochemical variables, especially trace elements, are generally low in the environment. Anomalies from both natural processes and anthropogenic activities lead to high concentrations in data sets, resulting in positively skewed probability distributions. The data were log-transformed before further statistical analysis so that they approximately conformed to the normal distribution and to reduce the influence of extreme high values.

Pearson's correlation analysis was used to determine the relationships between the different heavy metals. The relationships between concentrations of the investigated heavy metals and selected soil properties (pH) were also examined. The raw data were standardized using the Z score (with a mean of 0 and a standard deviation of 1) to render the data dimensionless and to allow easy comparison of variables (Facchinelli et al. 2001; Lee et al. 2006).

GIS was used to display the sampling locations and the heavy metal concentrations in topsoil. The results of factor analysis were mapped by kriging interpolation, using a grid-based graphics program in ArcGIS (Lee et al. 2006).

Results and discussion

Descriptive statistics and normality tests

Table 1 presents descriptive statistics of heavy metals in soils. All the metals data passed the Kolmogorov–Smirnov normality test ($K-S p < 0.05$), and raw data for all heavy metals

Table 1 Descriptive statistics parameters of heavy metals in soils from Daye City ($n=92$, mg/kg)

| Items | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|--------------------------------|---------|---------|-------|---------|---------|-------|---------|---------|
| Min | 8.80 | 0.60 | 22.0 | 15.6 | 0.03 | 10.4 | 21.0 | 39.9 |
| Max | 117 | 4.60 | 182 | 1,480 | 0.45 | 54.4 | 459 | 4,150 |
| Median | 18.7 | 1.30 | 58.1 | 45.0 | 0.07 | 24.7 | 32.8 | 89.4 |
| Mean | 23.8 | 1.41 | 60.7 | 105 | 0.09 | 25.8 | 43.7 | 159 |
| S.D. | 17.8 | 0.58 | 22.9 | 211 | 0.06 | 8.64 | 48.6 | 425 |
| C.V. | 74.8 | 41.1 | 37.7 | 201 | 66.7 | 33.5 | 111 | 267 |
| Skewness | 3.13 | 2.28 | 1.90 | 5.04 | 3.02 | 0.97 | 7.21 | 9.29 |
| Kurtosis | 11.5 | 9.51 | 8.00 | 27.1 | 14.4 | 1.29 | 59.9 | 88.1 |
| K-S p | < 0.001 | < 0.001 | 0.001 | < 0.001 | < 0.001 | 0.002 | < 0.001 | < 0.001 |
| K-S p (Box-Cox) | 0.20 | 0.20 | 0.07 | 0.04 | < 0.001 | 0.20 | 0.20 | 0.02 |
| Background values ^a | 10.0 | 0.50 | 147 | 37.5 | 0.243 | 61.3 | 46.4 | 114 |
| Background values ^b | 12.3 | 0.172 | 30.7 | 30.7 | 0.08 | 86.0 | 26.7 | 83.6 |
| Threshold values ^c | 40.0 | 0.30 | 150 | 50 | 0.30 | 40.0 | 250 | 200 |

Min minimum value; Max maximum value; S.D. standard deviation; K-S p Kolmogorov–Smirnov test; C.V. coefficient of variation (%)

^a Soil background values for heavy metals in Daye City

^b Soil background values for heavy metals in Hubei Province

^c Chinese Environmental Quality Standard for Soils (II Grade: pH<6.5; GB15618—1995) (National Environmental Protection Administration of China 1995)

showed an abnormal distribution. Data for zinc were most highly skewed, and had a skewness value of 9.29. Regardless of skewness, the mean and the median were similar for most metals, with median values generally lower than the mean. Data were transformed so that they conformed to a normal distribution before further geostatistical and multivariate analysis. Results showed that, after the Box-Cox transformation, Cd, Pb, Ni, As, and Cr approximately followed a normal distribution ($K-S p < 0.05$), but other variables, such as Zn, Hg, and Cu, did not (Table 1).

As might be expected, concentrations of each heavy metal spanned a wide range, such that maximum observation values of every heavy metal were five times more than the minimum values. The average concentrations (plus standard deviation (SD)) of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 23.8 ± 17.8 mg/kg, 1.41 ± 0.58 mg/kg, 60.7 ± 22.9 mg/kg, 105 ± 211 mg/kg, 0.09 ± 0.06 mg/kg, 25.8 ± 8.64 mg/kg, 43.7 ± 48.6 mg/kg, and 159 ± 425 mg/kg. The high variability may be the result of sampling across an area of more than 1,000 km² (Fig. 1), showing its inherent spatial heterogeneity (Wong et al. 2007; Yang et al. 2012). Industrial activities, such as mining and its associated heavy metal discharges, in some subareas may be another possible explanation for this variability.

To determine the variability of heavy metals in agricultural topsoil, comparative analysis was first performed. Mean concentrations of As, Cd, Cu, and Zn were higher than the corresponding natural background values (Table 2). The observed concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 98, 100, 1, 59, 2, 0, 22, and 36 %, respectively, above

background values (Wang et al. 1982). Soils in the study area were weakly acidic and had an average pH value of 6.11. The pH of 72.8 % of the soil samples was less than 6.5. Except for Cd and Cu, the average metal values were generally well below the corresponding State Environmental Protection Administration of China (GB15618—1995) threshold values for cultivated areas (Table 1), indicating that the threats to either the environment or human health from soil quality in study area were minimal. However, in 100 % of the soil samples, Cd concentrations were higher than their threshold value of 0.3 mg/kg, while Cu concentrations were higher than their threshold value in 45.7 % of the samples. Moreover, few soil samples showed higher values for other metals. For instance, nearly 10.9 % of the soil samples had As concentrations that were higher than the 40 mg/kg threshold value. These results suggest that soils are polluted with Cu and Cd at most locations, and with As, Pb, and Zn at fewer locations, in the study area. This pollution is probably the result of anthropogenic activities such as fertilizer applications, pesticide use, vehicle exhausts, industrial fumes, and coal burning. These influences are consistent with the high coefficients of variation (C.V.) found in most of the measured heavy metals, which ranged from 33.5 % (Ni) to 267 % (Zn) (Table 1) (Manta et al. 2002; Hani and Pazira 2011). Ni had the lowest C.V. (33.5 %), which suggests little variation in Ni concentrations across Daye City. Zn had a C.V. of 267, the highest of the eight heavy metals, suggesting that concentrations varied most among the soil samples; Zn concentrations were most likely influenced by external factors, such as human activities.

Table 2 Comparison of average concentrations of heavy metals in agricultural soils from some countries/regions (mg/kg)

| Country/region | n | Concentrations | | | | | | | | Reference |
|-----------------------------------|-----|----------------|------|------|------|------|------|------|------|--------------------------|
| | | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn | |
| Outside of China | | | | | | | | | | |
| Zagreb, Croatia | 331 | – | 0.66 | – | 20.8 | – | 49.5 | 25.9 | 77.9 | Romic and Romic 2003 |
| European Mediterranean, Spain | 54 | – | 0.34 | 26.5 | 22.5 | – | 20.9 | 22.8 | 52.8 | Micó, et al. 2006 |
| Dhaka, Bangladesh | 45 | – | 11.4 | 53.7 | 39.1 | – | 58.2 | 49.7 | 115 | Ahmad and Goni 2010 |
| Piedmont, Italy | 50 | – | – | 46.2 | 58.3 | – | 83.2 | 16.1 | 62.7 | Facchinelli, et al. 2001 |
| Leipzig-Halle-Bitterfeld, Germany | 30 | 6.93 | – | 52.4 | 27.9 | 0.35 | 20.9 | 40.0 | 75.0 | Manz, et al. 1999 |
| Southern Tehran, Iran | 106 | – | 0.77 | 67.9 | 36.1 | – | 36.9 | 16.5 | 218 | Hani and Pazira 2011 |
| China | | | | | | | | | | |
| Beijing | 412 | 7.85 | 0.14 | – | 22.4 | 0.07 | – | 20.4 | 69.3 | Lu, et al. 2012 |
| Hong Kong | 31 | – | 0.35 | 21.8 | 6.37 | – | 5.30 | 39.6 | 46.8 | Lee, et al. 2006 |
| Changshu | 155 | 8.60 | 0.17 | 53.4 | 30.5 | 0.56 | – | 44.5 | 90.1 | Hang, et al. 2009 |
| Yangzhong | 76 | 10.2 | 0.30 | 77.2 | 33.9 | 0.20 | 38.5 | 35.7 | 98.1 | Huang, et al. 2007 |
| Gansu | 45 | 8.80 | – | 40.1 | 17.1 | 0.03 | – | 23.3 | – | Li, et al. 2008 |
| Pearl River delta | 38 | – | 0.58 | 71.4 | 33.0 | – | 21.2 | 40.0 | 84.7 | Wong, et al. 2002 |
| Taihang piedmont Plain | 100 | 6.16 | 0.15 | 52.8 | 21.2 | 0.08 | 25.0 | 18.8 | 69.9 | Yang, et al. 2009 |
| Hangzhou | 74 | 6.25 | 0.26 | 62.2 | 36.6 | 0.69 | 20.0 | 46.2 | 116 | Chen, et al. 2008 |
| Huanghuai Plain | 224 | 11.8 | 0.17 | 79.0 | | 0.04 | 35.3 | 25.3 | 73.8 | Zhou et al., 2013 |
| Daye | 92 | 23.8 | 1.41 | 60.7 | 105 | 0.09 | 25.8 | 43.7 | 159 | In this study |

– not available

Mean concentrations of As, Cu, and Zn in soils from Daye City were much higher than the corresponding values found in previous studies both in China and other countries (Table 2). There are few data sets available for As, but comparison shows that the mean concentration of As was high compared with those reported in available studies (Manz, et al. 1999; Hang, et al. 2009). With the exception of the sample from Dhaka (a wastewater irrigated soil area), which had a Cd concentration of 11.4 mg/kg, the mean Cd concentration (1.41 mg/kg) was higher than those found in other studies (Ahmad and Goni 2010). Concentrations of Cr are comparable with the higher concentrations reported in previous studies (Wong et al. 2002; Hani and Pazira 2011). Notably, the mean concentrations of Hg, Ni, and Pb were among the lowest of all metals observed across the study area, although concentrations were very high at a few sites. These findings highlight the fact that concentrations of As, Cd, Cu, and Zn are relatively high in the investigated soils, and that they deserve special attention.

Assessment of potential ecological risk

The potential ecological risk index (RI) is commonly used to give a comprehensive assessment of the harmful effects of all heavy metals in the environment, including soils and sediments (Hakanson 1980). The RI was

calculated using the following equations (Zhu et al. 2008):

$$C_f^i = \frac{C^i}{C_n^i}$$

$$C_{deg} = \sum C_f^i$$

$$E_r^i = T_r^i \times C_f^i$$

$$RI = \sum E_r^i$$

where C_f^i is the contamination factor of the individual i th metal species; C^i is the concentration of the i th metal species in the samples; C_n^i is the pre-industrial concentration of the individual i th metal species, in this study taken as the background values of heavy metals in the Huanghuai Plain, China (China National Environmental Monitoring Centre CNEMC 1990). C_{deg} represents the integrated level of environmental pollution, and is expressed by the sum of C_f^i for all examined metals. There are four pollution levels: $C_{deg} < 5$, low pollution; $5 \leq C_{deg} < 10$, medium pollution; $10 \leq C_{deg} < 20$, high pollution; $C_{deg} \geq 20$, very high pollution (Loska et al. 2004). E_r^i is the monomial potential ecological risk factor of the i th metal species, and T_r^i is the toxic factor for the i th metal species. Following the method of Hakanson (1980), we used the following T_r^i values: Hg, 40; Cd, 30; As, 10; Pb, 5; Ni=Cr, 2; Zn, 1. RI is defined as the sum of E_r^i for all heavy metals,

and can be grouped into four categories—low risk ($RI \leq 50$), moderate risk ($50 < RI \leq 100$), considerable risk ($100 < RI \leq 200$), and high risk ($RI > 200$)—according to the recommended values by Zhu et al. (2008).

The C_f^i values for the measured heavy metals ranged from 0.10 to 39.5, suggesting low levels of contamination for As, Cd, and Cu except in samples which may be considered “clean” (Fig. 2a). C_{deg} ranged from 4.4 to 53.4 and had an average value of 11.5, indicating low contamination for the most soil samples (61 %), even though 30 % of the soil samples had medium contamination. The E_r^i value for Cd was 84.8, and is significantly higher than for the other metals. Results suggest a considerable ecological risk from Cd, but a low potential ecological risk from other metals (Fig. 2b), which is consistent with conclusions of Suresh et al. (2012). The E_r^i difference between Cd and the other metals results from highly toxic factors (Suresh et al. 2012) and the abnormally high concentrations at most sites. In fact, the median and mean values for Cd (1.4 and 1.3 mg/kg, respectively) were generally four times higher than the corresponding threshold values (0.3 mg/kg) (Table 2), indicating that all the Cd concentrations were very high (>0.6 mg/kg). However, Hg had the highest toxicity factor, but 98 % of soil samples had Hg concentrations that were between 0.03 and 0.23 mg/kg. These concentrations were thought to be lower than the background value, indicating a low potential ecological risk. This result suggests that a more careful analysis is necessary for metals, especially with highly toxic factors, when estimating their ecological risks in terms of the backgrounds values.

Overall, the RI value ranged from 59.5 to 519, and had a mean value of 145, suggesting considerable ecological risk from heavy metals in this study area. Based on the classification suggested by Zhu et al. (2008), 12.0 % of the samples in this study were classified as causing a high potential ecological risk, 67.4 % were classified as causing considerable potential ecological risk, and 20.7 % were considered to represent a moderate potential ecological risk. Cd was the highest contributor to the RI value, accounting for between 32.2 and 82.7 % (mean of 58.5 %), followed closely by As, which accounted for between 5.9 % and 47.4 % (mean of

16.5 %) of the RI values. Based on the estimates of the C_f^i , C_{deg} , E_r^i , and RI, it seems reasonable to conclude that the investigated soils had low to medium heavy metal contamination and may represent a considerable ecological risk to ecosystems at least at some of the sampling locations. Areas in the study area where concentrations of Cr, Ni and Zn are less than the threshold values can be regarded as safe for crop growth.

Spatial distribution of metals and factors controlling contamination

ArcGIS is a valuable tool for interpreting spatial variability and environmental monitoring results. Information generated by a semivariogram (nugget, sill, range) was used to calculate sample weighting factors for spatial interpolation by the simple point kriging procedure. This method used the nearest eight sampling points and a maximum searching distance equal to the range distance of the variable. Mapping the conditional probabilities of a soil property is particularly important for management decisions. Such decisions, including delineation of safe or hazardous areas and identification of zones that are suitable for crop growth or that need to be remediated, are generally based on threshold values of soil properties.

Figure 3 shows the spatial distribution patterns of the eight metals, which have been visualized from the semivariograms of all the heavy metals gathered from the study area. Cd and Cu have similar spatial distributions, and semivariograms indicate two significantly polluted zones corresponding with (i) the historical center of the city (a large area in the top right-hand side of the maps) that is influenced by mining activities in the Tonglushan Mine, and (ii) brown areas close to the crossing of a major agriculture axes (a small area in the central part of the maps). Multivariate analysis gave similar results for the spatial distribution of Cd and Cu. There was a significant positive relationship ($p < 0.001$) between Cd and Cu ($r = 0.60$) (Table S1), and HCA and PCA analysis shows that Cd and Cu were roughly clustered into the same group (Fig. 4 and Table S2). Environmental geochemical phenomena, including

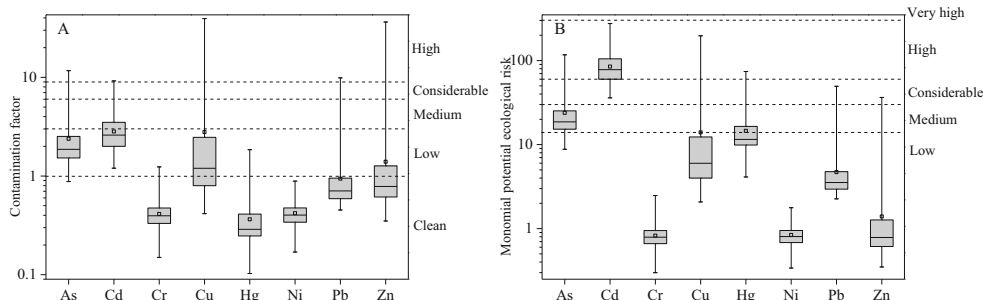


Fig. 2 Boxplot of contamination factors (a) and monomial potential ecological risk factor (b) for heavy metals in agricultural soils from Daye City. Contamination factors: Clean ($C_f^i \leq 1$), Low ($1 < C_f^i \leq 3$), Moderate

($3 < C_f^i \leq 6$), Considerable ($6 < C_f^i \leq 9$), and High ($C_f^i > 9$). Ecological risks: Low ($E_r^i \leq 15$), Moderate ($15 < E_r^i \leq 30$), Considerable ($30 < E_r^i \leq 60$), High ($60 < E_r^i \leq 120$), and Very high ($E_r^i > 120$)

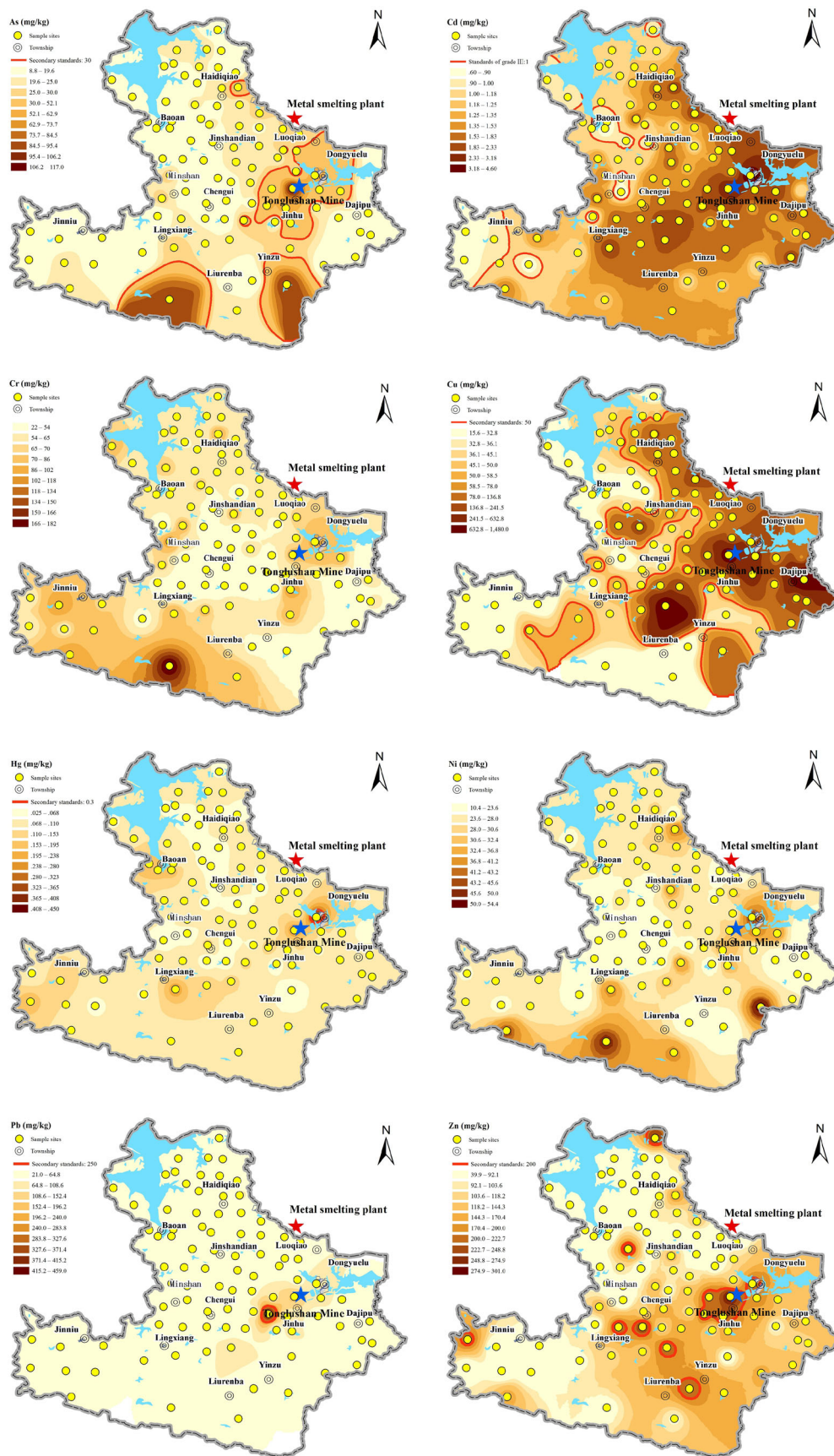


Fig. 3 Spatial distribution maps of the concentrations of eight hazardous heavy metals

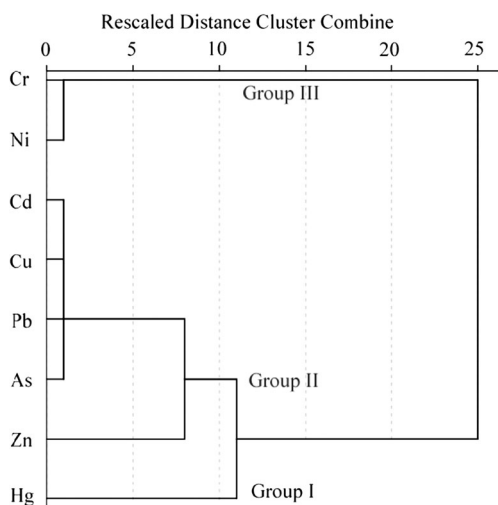


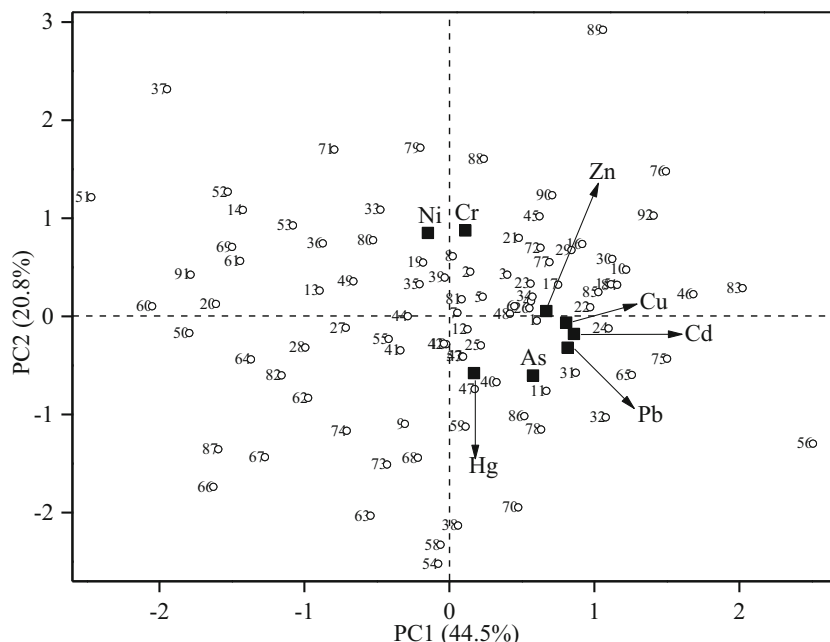
Fig. 4 Hierarchical clustering results (dendrogram) of the heavy metal concentrations in topsoil samples of Daye City

heavy metal concentrations in soils, are usually correlated, as a result of physico-chemical features of elements and geochemical processes (Loska and Wiechula 2003; Zhang 2006). The significantly positive correlations among these elements suggest, to some extent, a common source (Al-Khashman and Shawabkeh 2006). To support this hypothesis, canonical correlation analysis showed that soil samples from certain subareas (e.g., JH with minor variation in PC1 axes) had much higher concentrations of Cd and/or Cu than other subareas (Fig. 5 and Table S3), highlighting an obvious input of heavy metals in those subareas. Therefore, the median concentrations and ranges (in brackets) of As, Cd, Cu, Pb, and Zn were 42.6 mg/kg (10.0–1,176 mg/kg), 1.9 mg/kg (1.0–3.4 mg/kg), 99.5 mg/kg (29.2–994 mg/kg), 62.8 mg/kg (25.7–459 mg/kg),

and 168 mg/kg (67.2–301 mg/kg), respectively (Table S3). The spatial distribution of Cd and Cu suggests that non-ferrous metal smelting and mining are key pollutant sources (Chen et al. 1999), as described in the Yearbook of Hubei Province 2012 (Bureau of Statistics of Anhui Province 2012). In other areas, their concentrations are relatively low. However, we must remember that the enhanced levels of Cd and Zn may be attributed to additional point sources, such as irrigation with sewage effluent (Nicholson et al. 2003; Zhang 2006) and the use, and sometimes abuse, of organic manures (Jiang et al. 2010; Hani and Pazira 2011). In the study area, the three main sources of irrigation water (Daye Lake, Baoan Lake, and Sanshan Lake) have received wastewater containing considerable amounts of heavy metals, including Cd and Cu (Wang and Lin 2003; Huang et al. 2004; Li et al. 2006). Heavy metals inevitably accumulate in agricultural soils as a consequence of long-term effluent irrigation, as was reported by Rattan et al. (2005). In addition, organic fertilizers may also contribute significantly to elevated concentrations of these two elements in croplands (Chen et al. 2008; Jiao et al. 2012). The huge quantity of phosphate fertilizers (about 7.48×10^6 tons) used in China annually (National Bureau of Statistics of China NBSC 2006; Luo et al. 2009), introduces considerable amounts of Cd and Cu to soil (Zhang et al. 2005), as reflected by the rather high concentrations of these metals (5.6 and 75.4 mg/kg, respectively).

As and Zn values were generally low, apart from in the southeast of the study area. Concentrations of As and Zn were elevated in three polluted zones including Jinhu, Lingxiang, and Yinzu (Fig. S1), but the correlation coefficient between them was relatively low ($r=0.23$, $p<0.05$, Table S1), most likely attributable to land use. As shown in Table 1, there is no

Fig. 5 Canonical variate analysis (CVA) for heavy metals in agricultural soils from Daye City. The definition of the subareas refers to Fig. 1



risk of Pb or Hg contamination in this study area. High Ni concentrations were distributed in the southern part of the study area (limited to two hot spots). Cr is a dangerous metal; the highest soil Cr concentrations were confined to a small area at the southern edge of the study area. Ni and Cr concentrations varied from north to south, while Zn and As displayed most variability from northeast to southwest. Generally, anthropic inputs of Cr and Ni from fertilizers, limestone and manures were lower than the concentrations already present in the soil. Since the release and transport of heavy metals is complex, the lack of significant correlations between soil properties and heavy metals may be due to either a continuous input of heavy metals or several pollution sources (Chen et al. 2008; Lu et al. 2012; Grant and Sheppard 2008). It may also be due to variations in soil type, fertilizer use, and the cultivation system within the sampling area (Grant and Sheppard 2008; Lu et al. 2012).

Conclusion

In 2011, the State Council of China presented its 12th Five Year Plan on the control and abatement of heavy metals in the environment. The timing of this present study fits well with implementation of the plan. Using soil sampling at a relatively small scale, concentrations of eight heavy metals in arable areas in the study area were estimated. Local anomalies were observed for As, Cd, and Cu, which to a great extent led to verify that high level of heavy metal pollution should be present in the agricultural soils from Daye City. Moreover, multivariate analysis revealed that the main sources of the investigated heavy metals might be linked to anthropic and industrial activities, such as smelting and mining. Results demonstrated that there was spatial variability in the distribution of the eight heavy metals in arable soils in Daye City. Studies such as this one could help validate spatial prediction methods where there are limited measured data. Results from similar studies will be helpful for improving agricultural and forest ecosystems in the region.

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