

County-scale temporal–spatial distribution and variability tendency of heavy metals in arable soils influenced by policy adjustment during the last decade: a case study of Changxing, China

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Abstract The widespread “pertinacious illness” for environmental management soil contamination by toxic metals has inevitably led to announcement of gradual adjustment for the local government to curb the notorious pollution. An extensive survey was conducted in Changxing County, Zhejiang Province, to investigate the contents of cadmium (Cd), arsenic (As), lead (Pb), and copper (Cu) and characterize the spatial-temporal change pattern to elucidate the current state and performance of policy adjustment. Geostatistic methods were applied in the mapping and characterizing processes to assess the concentrations of heavy metals at unsampled sites. Enrichment factor analysis indicated obvious Cd and As enrichment in the west and northwest of the county. Ordinary kriging interpolation combined with semivariogram revealed that the four heavy metals possessed distinct spatial distribution patterns. However, the distribution patterns for the elevated Cd and Pb concentrations exhibited a similar geographic drift, corresponding primarily to industrial distribution. Compared with the investigation findings in 2003, the results indicated an uptrend of Cd and As and downtrend of Cu, while Pb was a mixture of increase and decrease. However,

strengthened actions aimed at restraining heavy metal contamination are still needed to establish a mechanism to secure residents’ health and livelihood.

Keywords Soil heavy metals · Temporal-spatial distribution · Variability tendency · Anthropogenic inputs · Ordinary kriging · Pollution assessment · Policy adjustment

Introduction

Soil is of vital significance in ecosystem where many intricate interactions take place among air, water, microbes, minerals, and environments (Bloemen et al. 1995). It is not only a medium for plants to grow or a pool to dispose of undesirable materials but also a transmitter of many pollutants to atmosphere, surface water, and groundwater and plant (Chen et al. 1997). Soil contaminated by toxic metals, an exposure routes for surrounding populations, has drawn great attention for potential threats to food safety and detrimental effects on ecosystem (Lu et al. 2012).

Heavy metals are scarcely degradable, but some soil heavy metals are bioavailable. For instance, elevated blood concentrations of Pb in children (Thornton et al. 1990; Mielke et al. 2007) and Cd in adults (Hogervorst et al. 2007) have been recorded. Chronic low-level intake of heavy metals has a negative effect on human health, but no known medical treatment is able to reverse these health effects (Huang et al. 2007).

The spatial variation of soil heavy metals is determined and affected by inputs of either an anthropogenic or geogenic origin, the former governed by human activities and the latter depending largely on the composition of geological parent materials. However, the accumulation of heavy metals in the topsoil is affected by many environmental variables, especially human activities, such as vehicle emissions, industrial

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discharges, waste incineration, and fuel combustion (Hu et al. 2013). The first national census of pollution sources showed that the output of Pb and Cd from industrial sources in Zhejiang Province was up to 40,158.57 and 13,227.71 kg, respectively, in 2007 (Compilation committee of the first China pollution source census 2011). The rapid development of industry and intensive agricultural practices such as excessive usage of agrochemicals encouraged by economic interest has given rise to public concern over the potential accumulation of heavy metals within agricultural soil (Wong et al. 2002). Thus, there is a pressing need to fully understand, characterize, and estimate the current state of soil contamination by heavy metals, which will provide a basis for environmental monitoring, remediation, and policy-making.

China, which has in full gear undergone intensive industrialization and urbanization over the past three decades, is confronted with unprecedented environmental pollution, especially in the fastest developing region like Yangtze River Delta (YRD). Previous studies have observed significant enrichment of heavy metals in the topsoil of the Yangtze River Delta (Zhao et al. 2007, 2010; Yu et al. 2012). Subordinate to YRD, Hangzhou-Jiaxing-Huzhou (HJH) plain is a dominant agricultural area, and considerable parts of the region have been contaminated by heavy metals to different degree.

In this study, we selected Changxing County, Zhejiang Province in HJH as a representative area that is subjected to soil contamination by heavy metals as a result of anthropogenic inputs such as irrational agricultural practices, industrial wastes, and vehicle exhausts. Noticeably, Changxing County is featured with a wide range of industrial-induced activities such as textile industry, building material industry, mining, and manufacturing electronic products.

With the surge of the electric bicycles in China, dating back to the 1970s, lead-acid battery has been in robust development and became one of the pillar industries in Changxing County, accounting for 65 % of all electromobile batteries in China. The fast growth of this industry undoubtedly has been accompanied with soil pollution with heavy metals, especially Pb contamination. However, as the majorities of factories were small scale, geographically dispersed and merely rapid growing in number, the promising industry was subject to comprehensive regulation and management. From 2004, there were 175 lead-acid battery factories and the local government of Changxing formulated and issued a county-wide specific campaign to cast off notoriety of key regulatory targets. The majorities of enterprises had one horse, even no pollution regulation facilities before mediation with an annual emission of lead dust of 8.96 tons, coal consumption of 6009 tons, and smoke dust of 30.8 tons, of ten lead-acid battery enterprises (Technical report of comprehensive remediation of lead-acid battery environment of Changxing

County 2005). In 2009, the volume of lead and cadmium pollutant emission in exhaust gas was 6670.66 and 4.98 kg. The total quantity of solid waste containing heavy metals was 7635.29 tons in 2011 (Comprehensive control planning of heavy metals of Changxing County and Huzhou 2011).

Throughout the policy implementation, enterprises autonomously drew up and carried out regulatory planning and the government officials acted as supervisors and examiners. Besides, realignment and restructuring of enterprises also took place. These actions triggered shutdown of a batch of unqualified lead-acid battery factories, with only 61 factories left. Exhaust gas and waste water had been well treated to reach their standards. Pollutant emissions declined significantly, and solid waste had been effectively disposed. This was the first environmental protection storm in order to realize transformation and upgrade of industries.

The year 2010 witnessed the second storm, with survival of 30 lead-acid battery factories, some of which were allowed to reopen when their situations were rectified. Besides regulation of lead-acid battery industries, other industries associated with heavy metals, such as cement factories, construction material factories, and smeltery, had also been subject to environmental regulation, and some of them were restructured or closed.

A series of policies enacted during the last one decade were bound to affect the spatial distribution and concentrations of heavy metals. Based on former researches in this area (Shi et al. 2007; Liu et al. 2006), at an interval of one decade, our research focuses on comparison of temporal-spatial distribution and variation tendency of soil heavy metals to estimate the current state in Changxing County.

Geostatistics is based on the theory of a regionalized variable (Matheron 1963) using the technique of semivariogram to measure the spatial variability of a regionalized variable. Geostatistics provides a set of statistical tools for incorporating spatial and temporal coordinates of observations in data processing, which has proved useful in characterizing and mapping spatial variability and soil attributes at unsampled sites (Goovaerts 1999). It has been popularly used in characteristics and evaluation of soil pollution by heavy metals (Facchinelli et al. 2001; Lee et al. 2006; Romic and Romic 2003).

With little research recorded on spatial-temporal comparison of soil heavy metal influenced by policy adjustment, the present study was conducted to research the spatial distribution and variation tendency of soil heavy metals at an interval of one decade. The objectives of this paper aimed to: (i) analyze regional concentrations of four heavy metals (Cd, As, Pb, and Cu), (ii) roughly explore the origins of the four heavy metals using EF method, and (iii) map the spatial distribution and one decade variation tendency of the four heavy metals to examine the performance of the policy adjustment.

Materials and methods

Study area

Changxing County, subordinated to Huzhou City, is situated in the northwest of Zhejiang Province in the southeast of China. It borders Taihu Lake in the east and neighbors Anji County in the southwest. It is located in the areas of 119° 33'–120° 06' E, 30° 43'–31° 11' N including 16 administrative districts, covering an area of 1428 km² with a total population of approximately 640,000. The county has a subtropical monsoon climate characterized by hot and humid summer and generally cold and dry winter, with the mean annual temperature and precipitation of 15.6 °C and 1309 mm, respectively. The topography is featured with hill in the east and south and plain in the middle and, overall, higher in the west and lower in the east. The soils at the sampling sites are typical paddy soils derived from fluvial and lacustrine sediments (Agricultural and geological environment investigation and natural resources assessment report of Changxing County, Zhejiang Province 2005).

Soil sampling and chemical analyses

A total of 118 surface soil samples (0–20 cm) were collected from the cultivated cropland (paddy soils) across the selected investigation zone in 2013 (Fig. 1). At each sampling site, five sub-samples were obtained using a wooden shovel and mixed to one composite sample (about 1 kg dry weight). The collected samples were stored in polyethylene bags for transport and storage. The coordinates of the sampling location were recorded by global positioning system (GPS).

The collected soil samples were taken into the laboratory to be air-dried, and coarse gravels and debris were removed. The air-dried samples were sieved through a 2-mm sieve. Portions of the soil samples were then ground with a ceramic pestle and mortar to pass through a 0.15-mm sieve, then stored in plastic bags prior to chemical analysis. The pH of the air-dried soil (<2 mm) was determined in a 1:2.5 soil/water suspension using a pH meter with a glass electrode, previously calibrated with buffer solutions. The soil samples were digested in duplicate with the mixture of HF, HNO₃, and HClO₄. The digestion solution was analyzed by inductively coupled plasma emission spectrometer (iCAP6300, Thermo Fisher Scientific) for Cu by absorption fluorescence spectrometry (AFS) for As and by graphite furnace atomic absorption spectrophotometer (AA800, Perkin Elmer) for Cd and Pb. Standard reference material, GSS-10 obtained from the Institute of Geophysical and Geochemical Exploration, Department of Geology and Minerals of the People's Republic of China, was analyzed as a quality assurance and quality control procedures. The measured values of standard reference materials are 98.9 to 102.5 % the official values. The

accuracy of the analyses was verified, and the quality control gave good precision (SD <5 %).

Geostatistics analysis

The main application of Geostatistics to soil science has been estimation, prediction, and mapping of soil properties at unsampled sites (Goovaerts 1999). Geostatistic techniques, such as kriging interpolation, integrate spatial or temporal features of real data into statistical estimation. Kriging estimates are calculated as weighted sums of the adjacent sampled concentrations. Semivariogram, $\gamma(h)$, is computed as half the average squared difference between the components of data pairs (Wang 1999; Goovaerts 1999; Wang et al. 2012a, b):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \tag{1}$$

where $\gamma(h)$ is the semivariance value at distance interval h , $N(h)$ is the number of sample pairs within the distance h , $Z(x_i)$ is the value of Z at location x_i , and $Z(x_i + h)$ is the value of Z at a location separated from x_i by distance h .

Variograms provide a means of quantifying the commonly observed relationship, either spatially or temporally, between the values of the samples and the samples' proximity, which establish the degree and range of spatial continuity and dependence for soil properties. The experimental variogram is calculated for several lag distances. It is fitted with theoretical models such as exponential, spherical, and Gaussian models.

The exponential function is:

$$\gamma(h) = 0h = 0 \tag{2}$$

$$\gamma(h) = C_0 + C \left(1 - e^{-\frac{h}{a}}\right) h > 0 \tag{3}$$

The spherical function is:

$$\gamma(h) = C_0 + C \left[\frac{3h}{2a} - \frac{1}{2} \left(\frac{h}{a}\right)^3 \right] 0 < h \leq a \tag{4}$$

$$\gamma(h) = C_0 + Ch > a \tag{5}$$

The Gaussian function is:

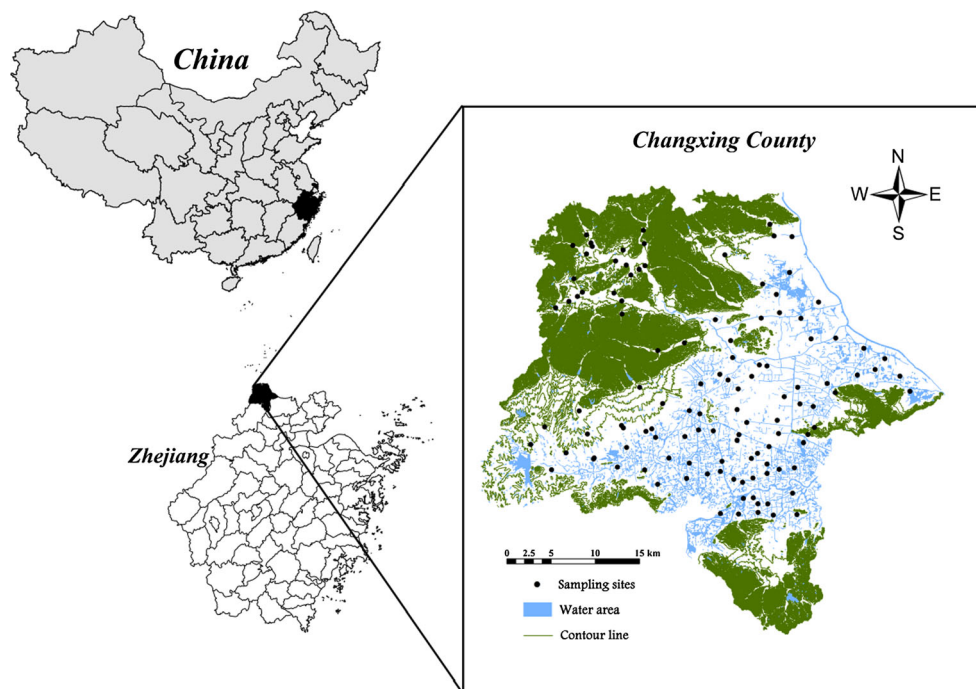
$$\gamma(h) = 0h = 0 \tag{6}$$

$$\gamma(h) = C_0 + C \left(1 - e^{-\frac{h^2}{a^2}}\right) h > 0 \tag{7}$$

where C_0 is the nugget variance ($h=0$), representing the experimental error and field variation within the minimum sampling spacing.

Typically, the semivariance increases with increasing lag distance to approach or attain a maximum value or sill $C_0 + C$ equivalent to the population variance. C is the structural

Fig. 1 Study area and sampling sites



variance, and a is the spatial range across which the data exhibit spatial correlation.

Enrichment factors

Enrichment factor (EF) was widely employed to speculate on the origins of metallic elements in the atmosphere, seawater, and progressively extended to soils and other environmental media (Reimann and de Caritat 2005; Wang et al. 2012a, b). The formula to calculate EF can be generalized from Zoller et al. (1974) as:

$$EF = \frac{\frac{[E]_{\text{sample}}}{[X]_{\text{sample}}}}{\frac{[E]_{\text{background}}}{[X]_{\text{background}}}} \quad (8)$$

where EF is the element under consideration, the square brackets indicate concentration (mg/kg), and X is the chosen reference element, often taken to be aluminum (Al), lithium (Li), or iron (Fe). In this study, Al is used as the reference element. EF values less than 5.0 are not regarded significance because such small enrichment may derive from differences of compositions of geological parent materials. Four contamination categories are recognized on the basis of EF: $EF < 2$ represents deficiency to minimal enrichment, $EF = 2-5$ moderate enrichment, $EF = 5-20$ significant enrichment, $EF = 20-40$ high enrichment, and $EF > 40$ extremely high enrichment (Li and Feng 2012).

Results and discussion

Heavy metal concentrations in the study area

Descriptive statistical results of pH and four heavy metals concentrations (Cu, Pb, As, and Cd) in the investigated agricultural topsoil, as well as background and guide values of China, are listed in Table 1. The soil pH ranged from 4.22 to 8.20, with an average of 5.72, suggesting the sampled arable soil in Changxing County was acidic. Mobility and retention of heavy metals were strongly affected by soil pH.

As shown in Table 1, there was a distinct variation in the contents of heavy metals and the means of Cd, Pb, Cu, and As were 0.23, 28.58, 17.14, and 11.28 mg kg⁻¹, respectively. Cd concentrations ranged from 0.06 to 1.03 mg kg⁻¹ while As concentrations ranged from 4.88 to 43.54 mg kg⁻¹. The maximums of Cd and As were 6.4 and 5.4 times those of their corresponding background values. Although the mean concentration of Pb was 28.58 mg kg⁻¹, comparable to their background values, it was found that in 23.73 % of the samples, Pb concentrations were higher than its mean background value. In 68.64, 8.47, and 83.05 % of the samples, the measured Cd, Cu, and As concentrations exceeded their respective background values. Besides, 16.95 and 3.39 % Cd and As concentrations were higher than the China Environmental Quality Standards for soils (CEPA 1995). However, both Cu and Pb concentrations were less than the China Environmental Quality Standards for soils. It was apparent that Cd and As were subject to contamination in this area.

The Kolmogorov-Smirnov test ($p > 0.05$) indicated that among all the analyzed elements, only Cu concentrations were

Table 1 Descriptive statistics of heavy metal concentrations (mg kg⁻¹) and pH in arable topsoils in Changxing County

| Soil property | Mean | Median | Minimum | Maximum | SD | CV (%) | Kurtosis | Skewness | K-S test | Number | Background of Changxing ^a | Guide Value ^b |
|---------------|-------|--------|---------|---------|------|--------|----------|----------|----------|--------|--------------------------------------|--------------------------|
| pH | 5.72 | 5.55 | 4.22 | 8.20 | 0.86 | 0.15 | 0.36 | 0.85 | 0.20 | 118 | – | – |
| Cd | 0.23 | 0.21 | 0.06 | 1.03 | 0.13 | 0.57 | 12.43 | 2.55 | 0.192 | 118 | 0.16 | 0.3 |
| Pb | 28.58 | 27.70 | 10.07 | 67.14 | 8.47 | 0.30 | 5.94 | 1.72 | 0.156 | 118 | 32 | 250 |
| Cu | 17.14 | 16.92 | 7.39 | 31.94 | 4.35 | 0.25 | 1.86 | 0.82 | 0.122 | 118 | 23 | 50 |
| As | 11.28 | 10.15 | 4.88 | 43.54 | 6.07 | 0.54 | 16.55 | 3.82 | 0.001 | 118 | 8 | 30 |

SD standard deviation, CV coefficient of variation

^aZhejiang Province geological survey agency, The Background of Soil Environment in Changxing county, Zhejiang Province 2005

^bChinese Environmental Quality Standard for Soils State Environmental Protection Administration of China, 1995

normally distributed, as can be inferred by the low values of kurtosis and skewness. The distributions of Cd, Pb, and As concentrations were all positively skewed, indicating strong heterogeneities of their spatial distributions.

Since occurrence of exceptional values can result in data discontinuity and violate the geostatistical theory, the concentration values out of the range of $A \pm 3S$ were treated as the exceptional values and they were replaced with the maximum or minimum values within $A \pm 3S$ in the data set (Liu et al. 2004, 2006). Cd and Pb concentrations showed a normal distribution after the data transformation while As concentrations had a normal distribution after being logarithmically transformed. The ordinary kriging interpolation was based on the transformed data.

The coefficients of variation (CV) for the four heavy metals ranged from 0.25 to 0.57. These relatively high CVs indicated that heavy metals had wide concentration ranges and was an indication of the presence of anthropogenic inputs (Han et al. 2006; Manta et al. 2002). The coefficients of variation for Cd and As (0.57 and 0.54) were higher than the other metals, which further revealed that anthropogenic inputs of Cd and As were considerably high.

Enrichment factor

Enrichment factors (EFs) are prevalently employed to support the hypothesis that a particular suite of heavy metal elements is of anthropogenic origin and to quantify human interference (Reimann and de Caritat 2005). EFs were calculated for the four heavy metals relative to Al and shown in Fig. 2. The ranges of EFs for Cd, Pb, Cu, and As were 0.43–7.17, 0.34–3.50, 0.51–2.33, and 1.02–9.87, respectively, with their respective averages of 2.33, 1.45, 1.19, and 2.31. On the other hand, the maximums of EFs for Cd and As were greater than 3. The higher and several anomalous EFs indicated that Cd and As were significantly enriched in this area by human intervenes. With regard to Cu and Pb, their average EFs were less than 2, showing absence to minimal enrichment. The mean EFs decreased in the order of As>Cd>Pb>Cu,

corresponding to a decreasing order of their contamination levels. In short, it was obvious that Cd and As were enriched in the presence of anthropogenic inputs with their wide-range concentration values. It seemed that, therefore, EF can be used as an effective tool to differentiate natural origin from anthropogenic sources (Lu et al. 2009a, b).

Experimental semivariograms and their parameters

The best fitted semivariogram models of the measured heavy metals and their corresponding model parameters were listed in Table 2. Figure 3 presented these models as solid lines, with the experimental values plotted as points. The Nug/Sill ratio can be regarded as a criterion to classify the spatial dependence of a soil attribute. If the ratio is less than 0.25, the variable has strong spatial dependence; 0.25–0.75, the variable has moderate spatial dependence; and greater than 0.75, the variable shows only weak spatial dependence (Chien et al. 1997; Chang et al. 1998).

The spatial variability of soil attributes can be affected by intrinsic and extrinsic factors, the former being geological composition, such as parent material and the latter anthropogenic inputs as a result of industrial process and agricultural

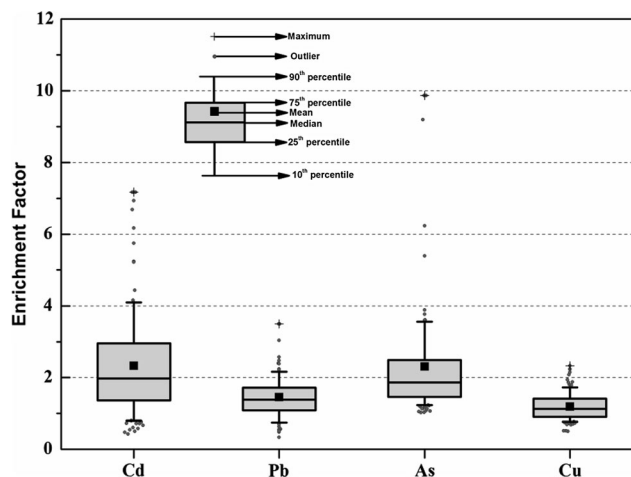


Fig. 2 Box-and-whisker plots of the four heavy metals' EFs

Table 2 Best fitted semivariogram models of heavy metals and corresponding parameters

| Soil heavy metal | Model | C_0 | $C+C_0$ | $C_0/C+C_0$ | Range (km) | R^2 |
|------------------|-------------|--------|---------|-------------|------------|-------|
| Cd | Spherical | 0.006 | 0.015 | 0.41 | 29.59 | 0.89 |
| Pb | Exponential | 31.700 | 63.410 | 0.50 | 11.88 | 0.45 |
| Cu | Gaussian | 9.530 | 22.590 | 0.42 | 20.82 | 0.92 |
| As | Gaussian | 0.0363 | 0.1376 | 0.26 | 14.19 | 0.93 |

C_0 nugget variance, C structural variance, $C+C_0$ sill variance

practices. Generally, strong spatial dependence can be ascribed to intrinsic factors, while weak spatial dependence is ascribed to extrinsic factors (Cambardella et al. 1994). It was observed that Cd was well fitted for spherical model, Pb for exponential model, and Cu and As for Gaussian model. The Nug/Sill ratio ranged from 0.26 to 0.50. Presumably, it was derived from human-induced activities, which weakened its original spatial dependence.

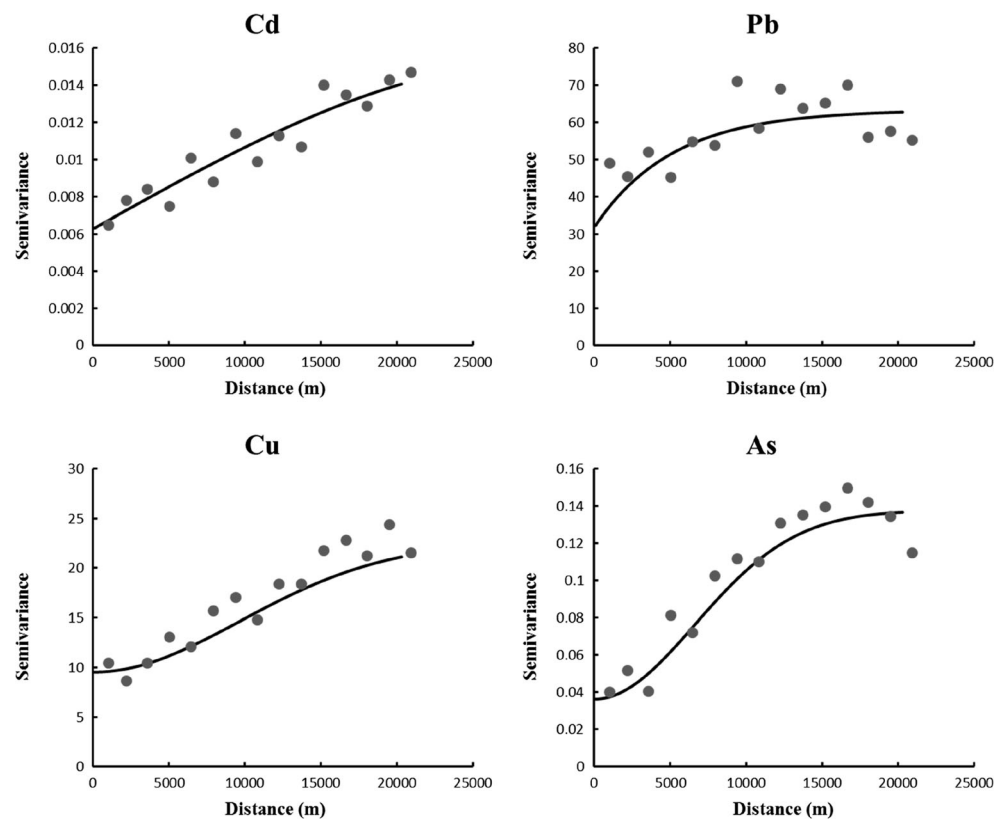
The distance ranged from 11.88 km for Pb to 29.59 km for Cd, and the range of influence is considered as the distance beyond which observations are not spatially dependent (Gallardo 2003; Sun et al. 2003). The experimental semivariograms for concentrations of the four heavy metals indicated that spatial correlations were present at local scales (approximately 20 km). However, the decrease of the ranges of the semivariogram was ascribed to the influence of anthropogenic inputs. Agricultural practices, which were limited to a short-range effect, such as the application of fertilizers and

pesticides, can noticeably increase the soil metals load in agricultural soils.

Geological distributions of the industrial enterprises

Changxing County, Zhejiang Province, located in the Yangtze River Delta Region, boasts geological and strategic advantages. The traditional industries with high proportions in Changxing County have been growing both in scale and speed, and they are of paramount significance for accelerating economic growth, promoting urban development and offering job opportunities. However, the quickening pace of industry has necessarily deteriorated the environmental quality due to the pollutant discharge containing toxic heavy metals through atmospheric deposition. Industrial pollution has been a principal factor affecting the distribution pattern of heavy metals.

Geological distributions of the industrial enterprises in Changxing County were presented in Fig. 4. There were five

Fig. 3 Experimental semivariograms (dots) and the best fitted models (lines) of the four soil heavy metals

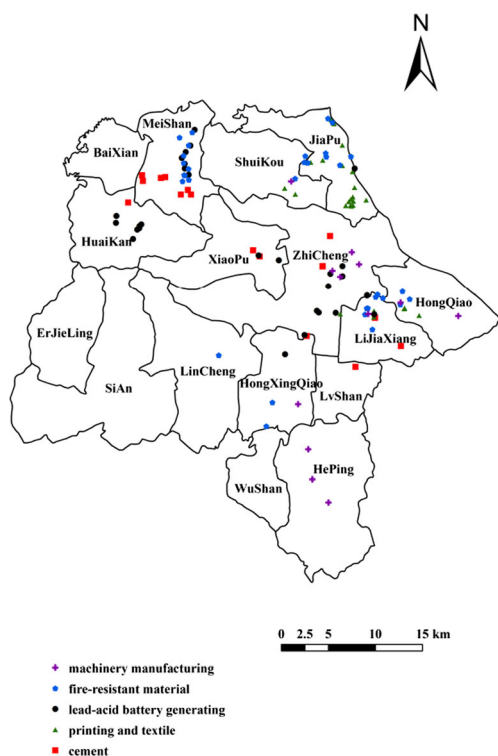


Fig. 4 Geological distributions of the industrial enterprises

major industries, including machinery manufacturing, fire-resistant material, lead-acid battery generating, textile, and cement industries. As was depicted in Fig. 4, the lead-acid battery generating industries, which featured high pollutant discharge of Cd and Pb mainly distributed in Huaikan, Meishan, Zhicheng, and Lijiexiang. In Jiapu lied some textile industries. In the process of printing and dyeing, textile dyes and additives might contain Cr and Cu, and improper disposal would result in Cu and Cr contamination. Fire-resistant industries were specialty, primarily located in Meishan, Jiapu, Lijiexiang, and Hongqiao. As traditional industries, cement industries enjoyed rapid development and distributed in Meishan, Zhicheng, Xiaopu, and Lijiexiang. Due to the usage of local materials in the process of cement manufacturing, heavy metal contamination might occur, especially Cd and Pb pollution. A relatively few machinery manufacturing industries were found in Zhicheng and Hongqiao, with Cu involvement. It was indicated in Fig. 4 that Meishan, along with Lijiexiang and Zhicheng, was an area of various industries, where concentrations of heavy metals were much higher.

Spatial distribution

Filled contour maps of the regional distribution pattern for Cd, Pb, Cu, and As by ordinary kriging were shown in Fig. 5. Compared with the sampling area (Fig. 1), the interpolated

area was smaller since four towns (Erjieling, Sian, Wushan, and Heping) were excluded. The four towns were dense forestry areas with scarce agricultural land and underdeveloped industry. The maps in Fig. 5 showed that most of the measured concentration values were within their guide values. Slightly higher levels of all toxic metals were found in the northwest and southeast of the county.

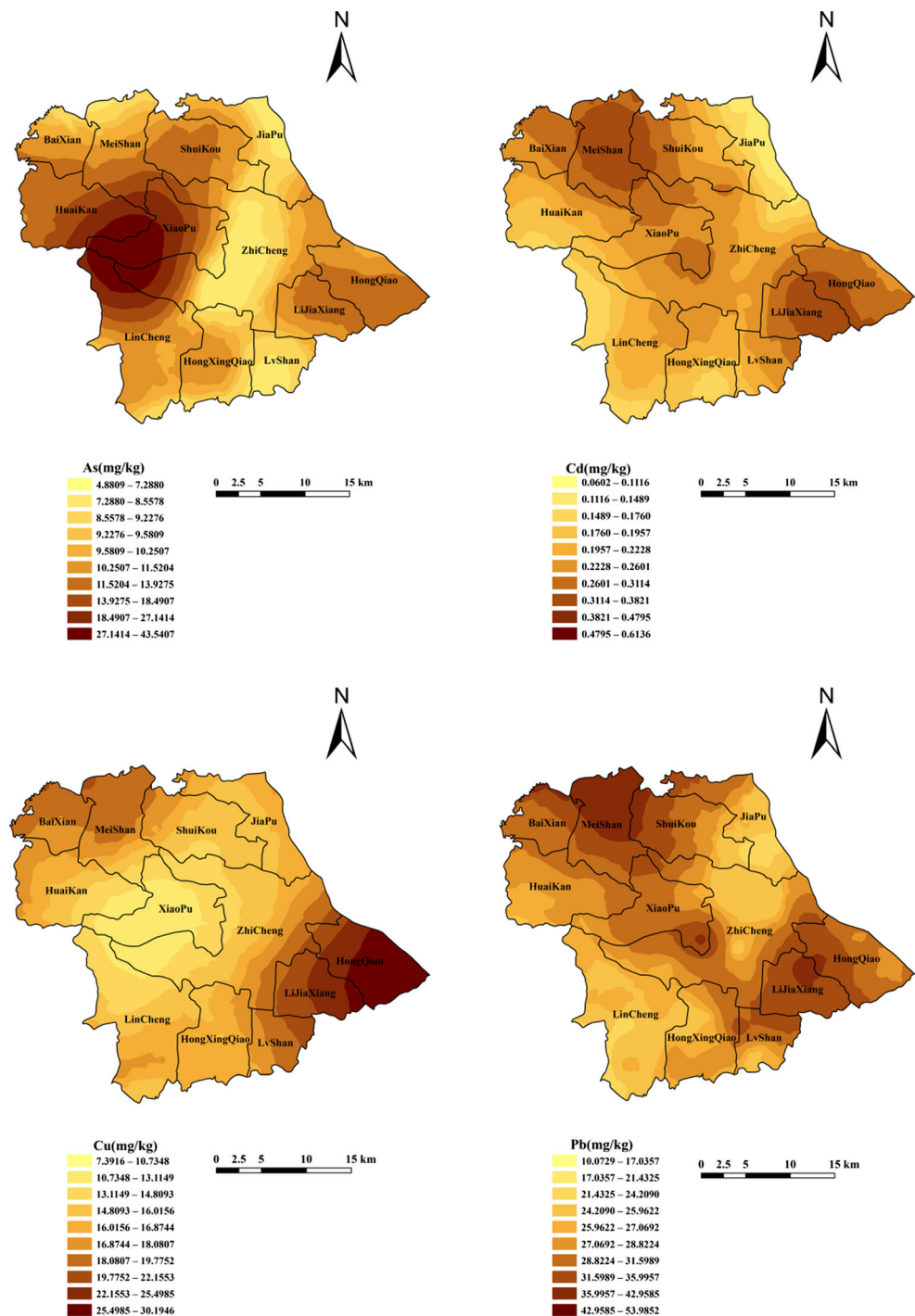
Spatial distribution patterns for Cd and Pb were remarkably similar. Elevated concentrations for both Cd and Pb were found in towns of Meishan, Lijiexiang, and Hongqiao. Some of the significantly higher concentrations of the heavy metals were close to industries, such as mining, generating stations, and metal-working factories. More noticeably, some chemical plants, especially cement plants and lead-acid battery plants that were responsible for the elevated higher Cd and Pb concentrations, were intensively distributed in the towns of Meishan, Xiaopu, Lijiexiang, and Lvshan.

Atmospheric deposition is a dominant source for the heavy metals in the soils. Diffuse Cd sources, notably P-fertilizers and atmospheric deposition, have increased Cd concentrations by about 0.10 to 0.30 mg kg⁻¹ (Alloway 2013). Thus, atmospheric deposition especially from industrial emissions was bound to raise Cd and Pb concentration levels. However, no areas with extreme Pb concentrations were found. Apparently, the distribution pattern of higher concentrations for Cd and Pb responded well to factory geographical locations. The majority of Pb concentrations were far lower than the guide value (250 mg kg⁻¹) but noticeably higher than the background value (32 mg kg⁻¹). Compared with Pb, Cd exhibited a greater pollution risk.

With regard to Cu, the mean and maximum were less than the background value and the spatial distribution for the most parts were controlled by the main geological process. Overall, Cu concentrations descended explicitly from the east to the west of the study area. The highest concentrations were found in Hongqiao. It was probably associated with industrial processes. Cu concentrations ranged from 7.39 to 30.19 mg kg⁻¹, much less than the guide value. Thus, the spatial distribution of Cu was mainly affected by lithogenic processes. However, anthropogenic involvement contributed to portions of exceptionally high values.

The far-ranging interpolated As concentrations were from 4.88 to 43.54 mg kg⁻¹. Elevated As concentrations spread in the western and eastern county, especially the towns of Huaikan, Xiaopu, and Lincheng. The distribution pattern of As concentrations was not well associated with the geologically industrial enterprises. It was speculated that it was originated from agricultural practices such as the usage of As-containing pesticides and herbicides (Matschullat 2000). Large quantities of As were released into the environment, which can be dispersed widely and played a crucial role in the contamination of soils (Nriagu et al. 2007; Pacyna and Pacyna 2001). In addition, during manufacturing of As-

Fig. 5 Filled contour maps of Cd, Pb, Cu, and As produced by ordinary kriging



containing pesticides and herbicides, release of waste and As-laden liquids near the manufacturing areas may also contaminate soils (Mahimairaja et al. 2005).

Changxing County has witnessed decades of prosperity, and many large-scale industrial enterprises sprung up as the result of rapid industrialization and urbanization. However, it was a mixed blessing: behind the splendid phenomenon was a trail of notorious and undesirable side effects, especially

inevitable environmental problems. Heavy metal contamination was an urgent issue, and it required the attention of policy-makers. Remediation of air and water pollution, with restructuring of industrial enterprises was initiated in 2004. In the move to get rid of severe heavy metal pollution, the Changxing County government launched a campaign of “Environmental Protection Storm.” A series of policies involving heavy metals management ensued within one decade.

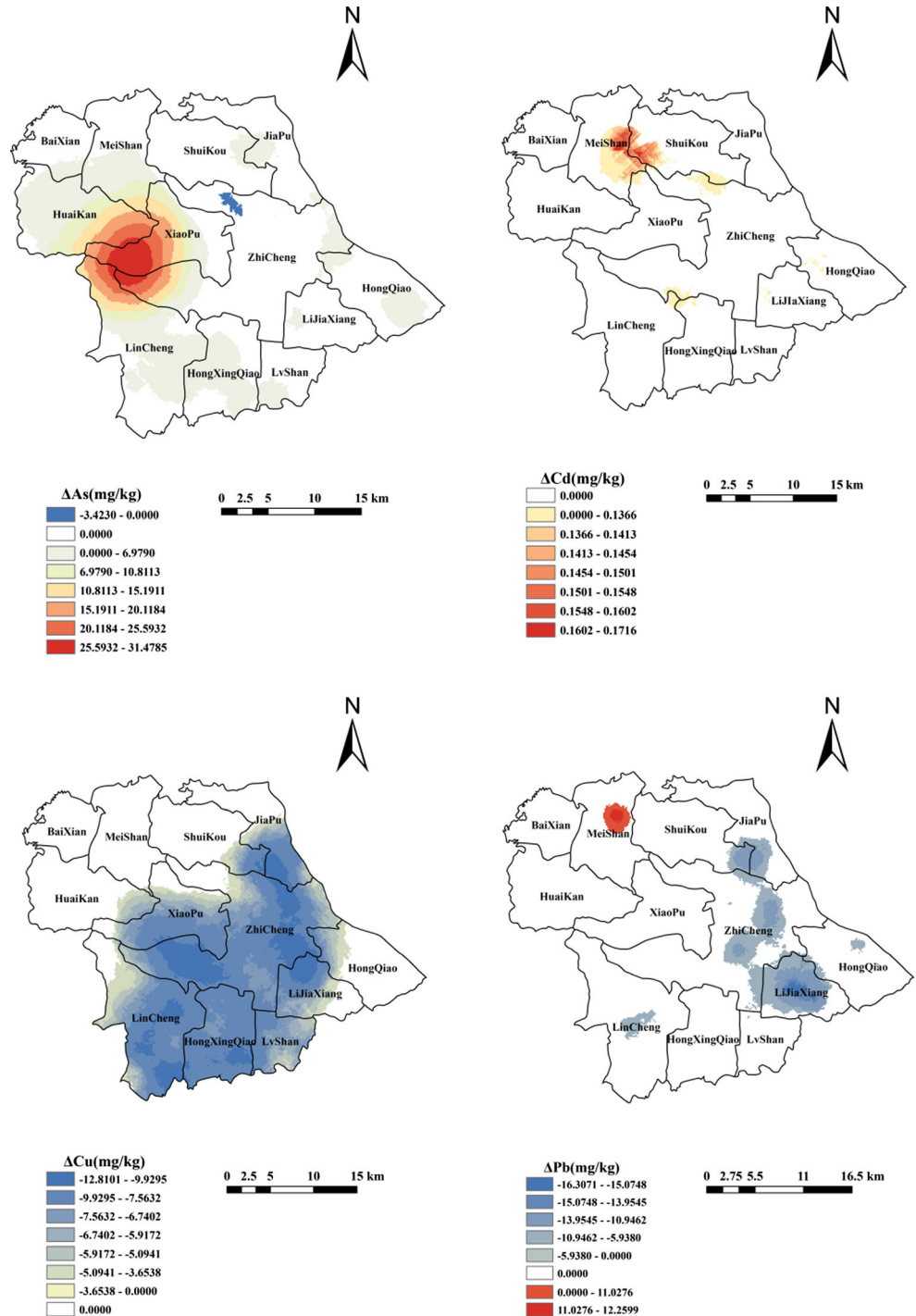
As many small, backward and energy-wasting factories were regulated and then successive transitions took place. In 2012, Changxing County was listed as a demonstration area of heavy metal prevention and control.

Changes in concentrations of the four heavy metals between 2013 and 2003 were presented in Fig. 6. It was obvious in Fig. 6 that Cd, As, and Pb concentrations increased inordinately. The range of concentration change for Cd during the past 10 years (2003 to 2013) was from 0 to 0.17 mg kg⁻¹,

indicating an increasing trend. Greater Cd concentration increase was found in the towns of ShuiKou and Meishan, a pool of industry, while a slight increase in Cd concentration was sparsely found in the towns of ZhiCheng and HongQiao which were thickly populated residential areas. Nevertheless, it did not show significant changes in most parts of the study area.

Both increase and decrease in Pb concentrations were observed during the past 10 years. The increase was found in

Fig. 6 Changes in concentrations of the four heavy metals between 2003 and 2013



towns of Meishan, reaching the maximum of 12.60 mg kg^{-1} , but the decrease area was much greater. It decreased up to 16.31 mg kg^{-1} . The Cd and Pb decrease was attributed to the shutdown or rebuilding of illegal lead-acid battery plants and cement factories.

After the implementation of environmental regulations, Pb emission via exhaust gases was reduced. In the meantime, soil remediation also took place. Besides, the off-take in harvested or grazed plants, erosion of soil particles by wind or water, leaching down through soil profile in form of solution, and volatilization of gaseous forms of elements also contributed to the decrease of heavy metals in surface soil.

Although not many factories were closed, many of them were relocated to government-designated industry zones, which made the levels of Cd and Pb in the industrial zone somewhat inevitably higher. The increase of As concentration was found mainly in the west of the county, especially the town of Xiaopu where the majority of concentrations were about or below 30 mg kg^{-1} . The wide spread of As concentration increase was related to derive from agricultural practices such as As-containing agrochemical and discharge of industrial pollutants.

Copper concentration decreased in most parts of the county especially the middle and southern county. The decrease for Cu was up to 12.81 mg kg^{-1} . Changxing County is the largest grape-growing zone in Zhejiang province. In the past few decades, many farmer households used Bordeaux mixture, which contained copper sulphate and slaked limes to protect grapes from diseases and pests. The widespread use of it would inevitably increase Cu level in soils (Brun et al. 2001). Besides, the local farmers were also accustomed to fertilize the soils with livestock manures. This organic fertilizer also contained several heavy metals, especially Cu, but now, agricultural practices have changed and farmers hardly use Bordeaux mixture and livestock manure anymore.

The one decade policy had a certain effect as there were no significant change in concentrations of the four heavy metals in the most county and Cu and Pb concentrations decreased significantly. Although Cd and As concentrations increased, the elevated Cd only covered a relatively small areas. The distribution patterns of Cd, Pb, and Cu were well associated with the geologically industrial distributions. Cd contamination in this region has always been a serious issue and As concentrations presumably originated from the usage of As-containing pesticides and herbicides which was not the content of the policy. In the long run, the policy effect would be more obvious. However, ongoing remediation of Cd and As should still be required.

Conclusion

The data obtained demonstrated that heavy metals could be used as powerful geochemical tracers for evaluating

contamination. The result indicated the average concentrations of the heavy metals in the investigated arable topsoils, except for Cd and As, were comparable to those of background soils, with 16.95 % Cd and 3.39 % As exceeding the corresponding guide values. Based on the enrichment factor analysis, except for a few anomalously high EFs, Pb and Cu were interpreted to reflect a natural enrichment by weathering and pedogenesis processes. However, the high EFs of Cd and As were expressions of the influence of anthropogenic pollutant sources. Cd and As posed potential risks of toxicity whereas Cu and Pb were relatively free from contamination.

The present study examined the distinct spatial distribution explored by well-performed ordinary kriging, among which Cd and Pb had a similar geographic drift. Largely, they were affected by industrial sources. In addition to industrial processes for the genesis of high As concentrations such as fuel combustion and metal smelting, they were possibly derived from high usage of As-containing herbicides and pesticides. The tendency of change in concentrations demonstrated that Cd, As, and Pb increased to a different degree in the west and north of the county where plenty of industries were intensively distributed. However, the spread and level of increase of Cd and Pb were not substantial. The varying decreases of Cu and Pb concentrations were mainly observed in the middle and south of the county. The localized one decade effort of rectification and restructuring of backward and unqualified industries contributed to the lower of heavy metal pollution. Nevertheless, the ongoing management of degraded Cd and As should be brought to the forefront.

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