



An assessment of spatial distribution and source identification of five toxic heavy metals in Nanjing, China

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Abstract

Spatial distributions and concentrations of heavy metals in vegetable plots in Nanjing were analyzed for assessment of environmental contamination status and source identification by GIS. Compared with background reference values, the average concentrations of all tested elements (Cu, Zn, Cd, As and Pb) except Cu exceeded the secondary evaluation standard of soil environmental quality. Coefficients of variation, arranged from large to small, were Cd > As > Zn > Pb > Cu. Semi-variance functions showed that the five elements were closely spatially correlated within the sampling range. The spatial distributions of Cu and Zn, As and Pb were similar to some extent. Multivariate statistical analysis showed that heavy metal contents were positively correlated with soil nutrients. The organic matter content was highly significantly positively correlated with the content of Zn and Cd and significantly positively correlated with As. CEC was highly significantly positively correlated with Cu and significantly positively correlated with Pb. However, pH and heavy metal concentrations were not significantly correlated. Principal components analysis indicated that Pb and Zn had a natural crustal source; Cu was mainly derived from discharged metallurgical waste; Cd and As came from agricultural pollution. Moreover, correlation analysis indicated that the Cd and As may have the same source.

Keywords: Environmental impact, GIS, Heavy metals, Soil contamination



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1. Introduction

Vegetable fields have been at high risk of heavy metal contamination. Especially with rapid economic development and accelerated urbanization, exploitation and utilization of metals has been increasing. This has resulted in large heavy metals discharges into the soil, posing a serious threat to the quality of farmland and cultivated land [1, 2]. According to the National Soil Pollution Investigation Bulletin [3] issued in April 2014, the total above-standard incidence of soil pollution in China reached 16.1%. At present, the cultivated land polluted by Cd, Pb, Cr and other heavy metals in China is nearly 2×10^7 ha. In addition, heavy metal levels near factories and mining areas seriously exceed the standard, thus causing regional pollution [4]. For example, studies have shown that the near soil lead-zinc mines was highly polluted [5, 6]. Soil concentrations of many heavy metals such as Pb, Zn and Cd were tens or even hundreds of times higher than the environmental background, posing a serious threat to the growth of local vegetables and the quality of agricultural products [7].

Nanjing is a typical lead-zinc mining area in Eastern China and has been chronically exploited approximately 60 years [8, 9]. During this period, a series of environmental problems have occurred. As a major lead and zinc mining areas, many environmental and soil scientists have researched heavy metals pollution there. Hu et al. [10] evaluated the potential health risks of heavy metals for greenhouse and corresponding open field production by studying soil and vegetable consumption. Chu et al. [11] researched mining, Qixia temple, and vegetable fields, and quantified heavy metal levels in soil with reference to national soil environmental quality standards. Identification of pollutants' sources is necessary to qualitatively determine the main pollution sources, but also to quantitate the contributions of various sources. Source

1 identification is the top priority for understanding, and key to dealing with, heavy metal pollution.
2 Therefore, it is necessary to strengthen the deep understanding and evaluation of possible
3 ecological risks due to heavy metal pollution. However, studies on the local characteristics and
4 sources of heavy metal pollution have rarely been reported. Soil, as an independent natural body,
5 is time-space continuous and spatially variable [12, 13]. This makes it suitable for application of
6 GIS tools in soil science at both large and small scales [14, 15].

7 This study aimed to determine the relationships between soil properties (pH, soil organic
8 matter, cation exchange capacity) and the concentrations of heavy metals (Cu, Zn, Cd, As, and
9 Zn) in vegetable soils; to analyze and characterize their spatial distributions; to identify the
10 sources of these heavy metals and evaluate their pollution levels in the complex soil environment;
11 and to provide a scientific basis for the selection of vegetable varieties and rational planning of
12 agricultural production.

13

14 **2. Materials and Methods**

15 **2.1. Study Area**

16 The research area is located northwest of Nanjing, Jiangsu Province (32°02' 50" N, 118°45' 42"
17 E). The landforms in the territory are intricate, with scattered distribution of low mountains, hills
18 and plains. The terrain fluctuates greatly; altitude ranges from 10 to 300 meters. The annual
19 average temperature is 15.3°C, the frost-free period is 7 months and the annual precipitation in
20 the whole region is about 1,000 mm.

21 The bedrock consists mainly of gneiss in Nanjing (Fig. S1) and the vegetable fields were
22 reclaimed from landfill on Yangtze River alluvium. The soil type is yellow brown soil [16]. The

1 vegetable fields studied in this experiment are distributed on both sides of a highway. The pH is
2 about 5.0-6.7, and the salt base saturation is 30%-75%. The surface organic matter accumulation
3 is obvious, about 10-20 g/kg. The soil organic matter content decreases with depth, but the clay
4 content increases. Affected by the northern subtropical bioclimatic climate, temperature and
5 rainfall provide favorable conditions for weathering of the parent material, thus forming a
6 viscous core soil layer at depth. It is suitable for planting trees and developing economic forestry,
7 but soil and water conservation are worthy of more attention. Limited by topography, rivers and
8 other factors, the vegetable fields are small and densely distributed. In order to investigate the
9 distributions of soil nutrients and heavy metals, a vegetable field with an area of 0.66 hm² was
10 selected based on factors such as soil texture, vegetation types and land-use patterns.

11

12 **2.2. Sample Collection and Analysis**

13 In August 2018, surface (0-20 cm) samples were collected using a grid method with 25 m
14 spacing; each sample was positioned by GPS. The sampling area, about 6,600 m², was roughly
15 rectangular with a length of 110 meters and a width of 60 meters. A total of 84 points were
16 sampled with a 5 cm diameter soil auger. Three replicates were collected for each point, the soil
17 was mixed and placed in sealed plastic bags and brought back to the laboratory for air-drying.

18 The soil pH was measured by electrode with a ratio of 1:2.5 between soil and distilled water; soil
19 organic matter (SOM) was determined by wet oxidation at 180°C with a mixture of potassium
20 dichromate and sulfuric acid; cation exchange capacity (CEC) was determined using a 1.0
21 mol·L⁻¹ ammonium acetate solution. Heavy metals were measured by inductively coupled
22 plasma mass spectrometry (ICP-MS); precision and recovery were tested by spiking reference

1 samples (GSS-1) [17]. By comparison, the recovery of samples was between 86.7- 92.6 and
2 satisfied analytical standards.

3

4 **2.3. Analysis Method**

5 2.3.1. Data statistics

6 SPSS 22.0 and Excel were used for classical statistical analyses. The Kolmogorov-Smirnov (K-S)
7 test [18] assessed whether data were normally distributed. GS + 9.0 was used to analyze semi-
8 variance and evaluate the spatial continuity of soil variables; Kriging was completed in ArcGIS
9 9.3 using the parameter model. Correspondence between soil properties and heavy metals was
10 analyzed by correlation analysis, and the source of pollution was analyzed by principal
11 components analysis.

12

13 2.3.2. Semi-variance function

14 Semi-variance function is an important tool in geostatistics to explore soil variability. It can be
15 used to represent the spatial variation structure or spatial continuity of random variables. For
16 random function $Z(x)$ with second order stationarity, the semi-variance ($\gamma(h)$) can be expressed
17 using the covariance S^2 of $Z(x)$ and spatial covariance $C(h)$ as: $\gamma(h) = S^2 - C(h)$, where $\gamma(h)$
18 represents the $Z(x)$ in the spatial relevant, which is equal to mathematical expectation of square
19 of difference value of measured value of interval samples. In general, the semi-variance function
20 increases with the separation distance of samples, finally becoming constant at some distance.
21 The commonly used variation functions include spherical, base station, exponential, and

1 Gaussian models. In this study, according to the multiple fittings of the data, the exponential and
2 spherical models were selected:

3 Spherical model :
$$y(h) = \begin{cases} C_0 + C_1 \left[1.5 \frac{h}{A_0} - 0.5 \left(\frac{h}{A_0} \right)^3 \right], & 0 \ll h \ll A_0 \\ C_0 + C_1, & h > A_0 \end{cases} \quad (1)$$

4 Exponential model:
$$y(h) = C_0 + C_1 \left(1 - e^{-\frac{h}{A_0}} \right) \quad A_0 \neq 0 \quad (2)$$

5 where h is separation distance, (m); C_0 is the nugget value representing the amount of random
6 variation; C_1 is the sill, representing structural variance of variable space variation; and A_0 is the
7 range, (m). The nugget coefficient is the ratio of the nugget to the sill, which is the value of the
8 function as semi-variance tends to 0, representing random variation caused by measurement
9 errors or variations in soil properties.

10

11 2.3.3. The rate of heavy metals exceeding

12 Referring to soil quality standards, the heavy metal concentration of each sample is compared
13 with the standard values for the first, second and third levels. The exceeding rate for each level is
14 the ratio of the number of samples exceeding the standard to the total number of samples.

15

16 2.3.4. The method of Cluster analysis

17 Cluster analysis [19] refers to a process of grouping a collection of physical or abstract objects
18 into multiple classes composed of similar objects. In essence, the whole process establishes a
19 classification tree. In the establishment process, a threshold can be set on the second part such
20 that when the distance between the last two classes is greater than this threshold, iteration can be
21 terminated. By taking the distance between two samples to get an average value, the overall

1 characteristics of the data are optimized. The shorter the distance between two sets, the greater
2 the similarity. The two most recent classes are then grouped together and the similarity between
3 the newly generated classes and the old classes is recalculated. Iteration continues until all the
4 sample points are in the same category.

5

6 2.3.5. Single factor pollution index

7 The single factor index method refers to evaluation of a single pollutant in the soil. Because it is
8 simple to calculate and can be used to evaluate each pollutant, it has become a relatively
9 common evaluation method at home and abroad [20]. It is calculated as:

$$10 \quad P_i = C_i / S_i \quad (3)$$

11 where P_i is the pollution index; C_i (mg/kg) is the measured concentration of heavy metal in the
12 soil; and S_i is the evaluation standard for that heavy metal. In this experiment, the secondary
13 level standard of soil environmental quality (Table S1) [21] was used as the evaluation standard.
14 If $P_i \leq 1$, the sample is not contaminated; samples with $P_i > 1$ are contaminated, and the greater
15 the value, the more serious the pollution.

16

17 2.3.6. The Nemerow integrated pollution index

18 The Nemerow index method is used to calculate both single-factor and comprehensive pollution
19 indices of soil, and is one of the commonly used methods for comprehensive pollution
20 assessment at home and abroad [22, 23]. The formula can be expressed as:

$$21 \quad P = \sqrt{P_{\text{imax}}^2 + P_{\text{iavg}}^2} \quad (4)$$

1 where P is the comprehensive pollution index of the monitoring points; P_{imax} is the largest single
2 pollution index; P_{iavg} is the average single pollution index. Soil quality is classified according to
3 P value. The Nemerow comprehensive pollution index was used to determine the pollution level
4 [24]; details are listed in Table S2.

5

6 2.3.7. Coefficient of Variation (CV)

7 The CV is used to compare two groups of data having different measurement scales, or different
8 data dimensions; CV can eliminate the influence of measurement scale and dimension to make
9 an objective comparison. Its calculation formula is [25]:

$$10 \quad CV = SD/MN \quad (5)$$

11 where SD is the standard deviation, and MN is the mean concentration of soil heavy metal.

12

13 3. Results and Discussion

14 3.1. Descriptive Statistical Analysis

15 In accordance with national soil nutrient rating standards [26], soil nutrients are rated into six
16 levels, namely, level 1 (very rich, SOM > 40 g/kg, only SOM is described), level 2 (rich, SOM is
17 30~40 g/kg), level 3 (medium, SOM is 20~30 g/kg), level 4 (deficient, SOM is 10~20 g/kg),
18 level 5 (very deficient, SOM is 6~10 g/kg) and level 6 (extremely deficient, SOM is 0~5 g/kg).
19 As shown in Table S3, soil pH ranged from 4.71 to 7.93; soil organic matter ranged from 13.72
20 mg/kg to 26.97 mg/kg and CEC from 10.46 mg/kg to 20.47 mg/kg, which were at the deficient
21 and middle levels, respectively. Referring to the secondary evaluation standard of soil
22 environmental quality, except for Cu being within the background range, the levels of Zn, Cd, As

1 and Pb far exceed the background value, reaching 1.85, 5.38, 4.96 and 2.26 times the background
2 value, respectively.

3 The CV indicates the degree of dispersion between samples and also indirectly reflects
4 the spatial variation of soil indicators. Generally speaking, $CV < 0.1$ shows weak variation, $0.1 <$
5 $CV < 1$ is moderate variation, and $CV > 1$ is strong variation. From Table S3, the coefficients of
6 variation of soil pH, SOM, CEC, Cu, Zn, Cd, As and Pb were between 0.08 and 0.34, among
7 which the coefficient of variation of Cu was the lowest (0.08), followed by Pb. Cd had the
8 highest coefficient of variation (0.34), followed by As. Although Pb and Cu showed weak
9 variation, the other indicators showed moderate variation. The CVs of soil indicators followed
10 the descending order: $Cd > As > Zn > CEC > SOM > pH > Pb > Cu$. Geostatistical analysis
11 requires that data conform to an approximately normal distribution to minimize experimental
12 error [27]. One-sample K-S tests at significance level $\alpha = 0.05$ showed that the data all
13 conformed to the normal distribution.

14 The vegetable field selected for this experiment was a typical mining landscape unit with
15 low-lying terrain, densely dissected by rivers and ditches, and greatly disturbed by human
16 activities. Classical statistical analysis showed that the soil pH in the study area was slightly
17 acidic or alkaline, and levels of SOM and CEC were relatively low and moderately variable. One
18 possible reason is that human activities can decrease soil nutrients [28]. In addition, the effects of
19 topography and surface runoff also reduced accumulation of soil nutrients [29].

20 Some heavy metal standards in these soils were seriously exceeded, although
21 concentrations varied greatly. The most over-standard elements were Cd and As, while Cu was
22 below the nominal pollution threshold. Cu and Pb were slightly variable within the sampling

1 range, and may be regionalized pollutants, which may be related to farmers' fertilization
2 practices.

3

4 **3.2. Characteristics of Soil Properties and Semi-Variance Function**

5 Measured soil parameters were fitted using the geostatistical analysis software GS+ 9.0, and
6 semi-variance functions (Fig. 1) and structural parameters (Table 1) were obtained [30]. The
7 Nugget value (C_0) is the corresponding value of the function at the origin, reflecting the random
8 variation within the system; the Sill ($C_0 + C$) represents the total variation within the system; the
9 Range (A_0) is the maximum spatial correlation distance, which reflects the physical extent of
10 spatial autocorrelation of the variables. The ratio of Nugget to Sill ($C_0/C_0 + C$) is called the
11 Nugget effect, which reflects the spatial dependence of soil properties and indicates the degree of
12 spatial correlation of system variables. When the ratio is less than 25%, the spatial correlation
13 between variables is strong. Between 25% and 75% indicates moderate spatial correlation. When
14 the ratio is more than 75%, the spatial correlation between variables is weak [31, 32].

15 From Table 1 and Fig. 1, soil indicators in the study area had strong semi-variance
16 structure, and the function well fitted the variation of each index within the sampling range. The
17 results showed As had moderate spatial correlation; the other indicators showed strong spatial
18 correlation. The Nugget of each index followed the descending order: As > Cu > SOM > Cd >
19 pH > Zn > CEC > Pb. Considering range of variation, Zn had the largest range (146.7 m) and
20 better spatial continuity. The correlation range of each indicator was 45.3 ~ 146.7 m, which was
21 larger than the sampling scale (10 m). The results showed that all soil indicators presented
22 evident spatial correlation at the sampling scale of 10 m, and the sampling scale met the

1 requirements of spatial variation analysis. That is, soil properties (pH, SOM, CEC) and five
2 heavy metals (Cu, Zn, Cd, As, Pb) presented their own characteristic distribution in area,
3 direction and shape to some extent by their own value or content.

5 **3.3. Spatial Distribution of Soil Properties and Heavy Metals**

6 As shown in Fig. 2, spatial distributions of soil properties and heavy metals differed in area,
7 direction and shape. pH showed a relatively concentrated patchy distribution, with most values
8 between 6.29 and 7.37. Organic matter showed a scattered patchy distribution, the areas with
9 higher content were distributed around the study area, and the sub-marginal content was
10 generally lower than inside. Generally speaking, the distribution of organic matter was uneven
11 under natural condition. Vegetable farmers in this area spread farm manure along ditches over
12 long periods; this may have caused the scattered patchy SOM distribution. The overall
13 distribution characteristics of CEC were “concave” type (low in the center and higher east and
14 west). It is usually seen that CEC increases with increasing values of pH and SOM. In this study,
15 CEC trends were similar to pH while different from SOM. Therefore, pH and SOM influenced
16 distribution of CEC. Spatial distributions of Cu and Zn were similar, with higher values in the
17 eastern part of the study area, and the lowest contents on both sides. The higher eastern values
18 were due to a copper-zinc deposit nearby. Cu and Zn concentrations were roughly decreased
19 with distance from eastern. The Cd concentration was mostly between 2.40 and 3.29 mg/kg, and
20 gradually increased from the southwest to the northeast. Spatial distributions of As and Pb were
21 similar, but highly fragmented, with no obvious regularity.

22

1 **3.4. Correlation Analysis**

2 Table 2 shows the correlations between pH, SOM, CEC and the content of heavy metals. Among
3 these, pH and heavy metals were not significantly correlated; soil organic matter was
4 significantly positively correlated with Zn and Cd, and positively correlated with As; CEC was
5 significantly positively correlated with Cu, and positively correlated with Pb. For heavy metals,
6 apart from Cd having no correlation with Zn or Cd, other pairs of elements all had highly
7 significant positive correlation, which proved the complexity of pollution among elements. The
8 results also showed that, within a range, the concentrations and availability of heavy metals
9 decreased with the increase of pH, suggesting that soil pH could be improved by amendments
10 such as lime and biochar [33]. Concentrations of Zn and Cd increased with the increase of
11 organic matter, indicating that the organic matter had a great influence on the bioavailability of
12 heavy metals [34, 35]. In addition, the concentration of Cu increased with the increase of CEC,
13 and decreased with the increase of pH. This phenomenon may be closely related to soil texture
14 and field fertilization.

16 **3.5. Standard-Exceeding Concentrations of Elements and Assessment of Heavy Metal** 17 **Pollution**

18 Referring to national standards [21], the degree of heavy metal pollution is divided into three
19 grades (Table S4). As shown in Fig. 3, the safety of Cu in vegetable soil was 100%, reflecting a
20 nominally low or zero degree of Cu pollution. The other four elements met various levels of
21 pollution. The concentrations of Cd and As at each sampling point exceeded the national third-
22 level standards. On the other hand, the secondary over-standard rate of Zn and Pb reached 70.24%

1 and 96.43%, respectively, indicating that heavy metal pollution in these vegetable plots was
2 prevalent and the data dispersion was small.

3 As mentioned above, these five elements were taken as pollution evaluation indicators.
4 The degree of heavy metal pollution was evaluated according to the single factor pollution index
5 and the Nemerow comprehensive pollution index (Table 3).

6 From Table 3, the single factor pollution index of Cu was less than 1, which is a safe
7 level. However, pollution indices of Pb, As, Zn, Cd were greater than 1. The degree of pollution
8 in these vegetable fields was ranked as $Cd > As > Pb > Zn$. The degree of Cd pollution was the
9 worst, with Nemerow comprehensive index (P) reaching 11.55, while the Nemerow index of As
10 reached 9.19.

11 The migration rates of heavy metals depend on soil texture; the “stickier” the soil, the
12 slower they move. Soil texture is the consequence of multiple formative factors, including parent
13 material, climate, landform, even biology and development time. Abundant rainfall aggravates
14 soil stickiness in the study area; the more abundant the rainfall, the stickier the soil, resulting in a
15 relatively heavy texture. Heavy metals migrate slowly in this soil and accumulate in the stickier
16 layers. In addition, lead and zinc mining in the nearby Qixia area have also increased the risk of
17 contamination by Cd and As. Based on the results of pollution assessment, it is suggested that in
18 addition to reducing pesticide spraying and fertilizer application, farmers can transfer heavy
19 metals from the soil layer to the ground by plowing. In addition, hyperaccumulative plants such
20 as *Viola baoshanica* (accumulates Cd) and Centipede (accumulates As) can be planted on
21 vegetable garden soils to absorb and fix heavy metals.

22

1 **3.6. Principal Component Analysis (PCA)**

2 Table 4 shows the variance contribution rate and cumulative contribution rate of each component.
3 It can be seen that only the eigenvalue of the first principal component was greater than 1 [36,
4 37]. However, the second principal component eigenvalue was also greater than 1 after rotation
5 of the matrix. Therefore, SPSS extracted the first two principal components, accounting for
6 83.78% of the total variance, which demonstrated that the extracted two common factors had a
7 strong explanatory power for soil variables.

8 As shown in Table 4, the first principal component (PC1) explained 46.82% of the total
9 variance and loads heavily on Cu (0.919), Zn (0.770), and Pb (0.868). According to the statistical
10 analysis and local actual situation, Pb and Zn were derived from crustal magmatic rocks and
11 regolith, and gradually formed deposits accumulated on the surface due to continuous excavation
12 and mining, so the presence of these two elements can be attributed to natural sources. Cu mainly
13 came from wastewater discharged from nearby metallurgical plants and introduced into nearby
14 fields through a mixed sewage outlet. Therefore, the PC1 reflected the impact of industrial
15 pollution and mine emissions on vegetable fields.

16 The contribution rate of the second principal component (PC2) was 36.96%, loading
17 heavily on Cd and As with values 0.918 and 0.828, respectively. Sampling sites in this
18 experiment were in agricultural tillage fields and it can be judged that Cd and As, originating
19 from agricultural pollution, were mainly affected by human activities including fertilizer and
20 pesticide application. On the other hand, Pearson analysis showed a very significant correlation
21 (0.670**) between the two elements, indicating that there may be compound pollution of the two

1 elements. The correlation analysis results further showed the complexity of the pollution of the
2 two elements.

3

4 **3.7. Cluster Analysis of Five Soil Heavy Metals**

5 As can be seen in Fig. 4, within the range of 10-15, the five heavy metal elements can be roughly
6 divided into three categories: Cd, As and Cu fall into the first category; Cu and Zn fall into the
7 second category; Pb belongs to the third category. Meanwhile, in the first category, Cd and As
8 were more closely related. When the distance was less than 1, Cd and As grouped together,
9 reflecting that the differences between Cd and As in soil were small, and pollution by them may
10 be homologous. At the same time, the average soil concentrations of Cd and As exceeded the
11 secondary evaluation standard for soil environmental quality (GB 15618-1995). The results of
12 cluster analysis were in agreement with those of principal component analysis, providing a basis
13 for further analysis and exploration of the sources of heavy metal pollution.

14

15 **4. Conclusions**

16 The concentrations and sources of the heavy metals Cu, Zn, Cd, As and Pb in vegetable soil
17 samples were studied. Results showed that this field soil was threatened by four of the heavy
18 metals (excluding Cu); Zn, Cd, As and Pb were contaminants, to varying degrees. Cd and As, the
19 most serious pollutants, were 5.38 and 4.96 times the background values, respectively. Farmers'
20 fertilization practices played a major role in the variation of soil nutrients in these vegetable
21 fields. Chemical fertilizers (such as phosphates) and pesticides resulted in accumulation of Cd
22 and As.

1 We tested the correlation between soil properties and heavy metal concentrations and
2 found that the five heavy metals were closely correlated with soil properties. Zn, Cd and As
3 increased with increasing soil organic matter; Cu and Pb increased with soil CEC. However,
4 there was no direct evidence that pH values and heavy metals were correlated. Geostatistical
5 analysis indicated that the soil indicators had measurable spatial variation at the field scale.
6 Multivariate analysis suggested that the heavy metals could be grouped according to their
7 sources: natural and anthropogenic. Pb and Zn mainly originated from a natural source. Cu came
8 from metallurgical waste discharge. As and Pb originated mainly from agricultural pollution.

9

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15

16 **Author Contributions**

17 S.H. (Ph.D. student) conducted the experiment and finished this manuscript. X.C.(Professor)
18 designed the whole experiment and provided laboratory equipment. F.J. (Ph.D. student)
19 Participated in the whole experiment. W.L. (Master student) and X.W. (Master student) finished
20 determination of samples data.

21

22

1 **References**

- 2 1. Cai L, Xu Z, Ren M, Guo Q, Hu X, Hu G. Source identification of eight hazardous heavy
3 metals in agricultural soils of huizhou, guangdong province, China. *Ecotoxicol. Environ. Saf.*
4 2012;78:2-9.
- 5 2. Hu Y, Liu X, Bai J, Shih K, Zeng EY, Cheng H. Assessing heavy metal pollution in the
6 surface soils of a region that had undergone three decades of intense industrialization and
7 urbanization. *Environ. Sci. Pollut. Res. Int.* 2013;20:6150-6159.
- 8 3. Chen NY, Zhen YJ, He XF, Li XF, Zhang XX. Analysis of the report on the national general
9 survey of soil contamination. *J. Agro-Environ. Sci.* 2017;36(09):1689-1692 (in Chinese).
- 10 4. Cai LM, Xu ZC, Qi JY, Feng ZZ, Xiang TS. Assessment of exposure to heavy metals and
11 health risks among residents near Tonglushan mine in Hubei, China. *Chemosphere*
12 2015;127:127-135.
- 13 5. Cui Y, Du X. Soil heavy-metal speciation and wheat phytotoxicity in the vicinity of an
14 abandoned lead–zinc mine in shangyu city, eastern China. *Environ. Earth. Sci.* 2011;62:257-264.
- 15 6. Zhan HY, Jiang YF, Yuan J, Hu XF, Nartey OD, Wang BL. Trace metal pollution in soil and
16 wild plants from lead–zinc smelting areas in huixian county, northwest china. *J. Geochem.*
17 *Explor.* 2014;147:182-188.
- 18 7. Kennou B, Meray ME, Romane A. Assessment of heavy metal availability (Pb, Cu, Cr, Cd, Zn)
19 and speciation in contaminated soils and sediment of discharge by sequential extraction. *Environ.*
20 *Earth Sci.* 2015;74:5849-5858.

- 1 8. Ding Z, Wang Q, Hu X. Fractionation of zn and pb in bulk soil and size fractions of water-
2 stable micro-aggregates of lead/zinc tailing soil under simulated acid rain. *Procedia Environ. Sci.*
3 2011;10:325-330.
- 4 9. Ma Z, Li T, Qu C, Bi J, Huang L. Evaluation and source identification of trace element
5 contamination of soils in the qixia lead-zinc mining area, Jiangsu, China. *Soil Sediment Contam.*
6 2014;14:1703-1712.
- 7 10. Hu W, Chen Y, Huang B, Niedermann S. Health risk assessment of heavy metals in soils and
8 vegetables from a typical greenhouse vegetable production system in China. *Hum. Ecolo. Risk*
9 *Assess.* 2014;20(5):1264-1280.
- 10 11. Chu BB, Luo LQ. Evaluation of heavy metal pollution in soils from Nanjing Qixiashang
11 lead-zinc mines. *Rock Miner. Anal.* 2010;29:5-846 (in Chinese).
- 12 12. Stark CHE, Condron LM, Stewart A, Di HJ, O'Callaghan M. Small-scale spatial variability
13 of selected soil biological properties. *Soil Biol. Biochem.* 2004;36:601-608.
- 14 13. Conant RT, Paustian K. Spatial variability of soil organic carbon in grasslands: implications
15 for detecting change at different scales. *Environ. Pollut.* 2002;116:S127-135.
- 16 14. Chen FS, Zeng DH, Xing HE. Small-scale spatial variability of soil nutrients and vegetation
17 properties in semi-arid northern China. *Pedosphere* 2006;16:778-787.
- 18 15. Zhu H, Chen X, Zhang Y. Temporal and spatial variability of nitrogen in rice-wheat rotation
19 in field scale. *Environ. Earth Sci.* 2013;68:585-590.
- 20 16. Ma YJ, Yuan CL. Agricultural ecosystem construction and development in Nanjing suburb.
21 *Resour. Environ. Yangtze Basin.* 1997;6(1):45-51 (in Chinese).

- 1 17. Cloquet C, Rouxel O, Carignan J, Libourel G. Natural cadmium isotopic variations in eight
2 geological reference materials (nist srm 2711, bcr 176, gss-1, gxr-1, gxr-2, gsd-12, nod-p-1, nod-
3 a-1) and anthropogenic samples, measured by mc-icp-ms. *Rock Miner. Anal.* 2010;29:95-106.
- 4 18. Ming DX. Field Experiments and Statistical Analysis. 3rd ed. Science Press; 2013. p.187-190.
- 5 19. Ciaramella A, Coccozza S, Iorio F, et al. Interactive data analysis and clustering of genomic
6 data. *Neural Networks.* 2008;21(2-3):368-378.
- 7 20. Dong H, Shi X, Wu D. Particle-size distribution characteristics and pollution of heavy metals
8 in the surface sediments of Kuitun River in Xinjiang, China. *Environ. Earth Sci.* 2016;75:104.
- 9 21. NEPA China. Environmental quality standard for soils. [Internet]. Available from:
10 http://www.mee.gov.cn/ywgz/fgbz/bz/bzwb/trhj/199603/t19960301_82028.shtml22.
- 11 22. Zhao B, Wang G. Preliminary investigation and assessment of farmland soils
12 contaminated by heavy metal around baiyin city. *Environ. Sci. Technol.* 2010;30:79-84.
- 13 23. Wang LF, Bai YX, Gai SN. Single-factor and nemerow multi-factor index to assess heavy
14 metals contamination in soils on railway side of harbin-suifenhe railway in northeastern china. *J.*
15 *Appl. Biomater. Biomech.* 2011;71-78:3033-3036.
- 16 24. Deng MJ, Luo Y. Evaluation on heavy metal pollution of soil in pollution-free agricultural
17 product bases in Guangxi. *Asian J. Agric. Res.* 2014;06(7):63-65.
- 18 25. Hair C, Mills DJ, McIntyre R, Southgate P. Optimising methods for community-based sea
19 cucumber ranching: Experimental releases of cultured juvenile *Holothuria scabra* into seagrass
20 meadows in Papua New Guinea. *Aquac. Rep.* 2016;3:198-208.
- 21 26. Lv ZZ, Liu GM, Yang JS, Zhang MM. Spatial variability and distribution pattern of soil
22 nutrients in bohai coastal area. *Acta Pedol. Sin.* 2014;51:944-952 (in Chinese).

- 1 27. Chen LJ, and Feng Q. Geostatistical analysis of temporal and spatial variations in;
2 groundwater levels and quality in the Minqin oasis, Northwest China. *Environ. Earth Sci.*
3 2013;70:1367-1378.
- 4 28. Li QQ, Yue TX, Wang CQ, Zhang WJ. Yu Y, Li B. Spatially distributed modeling of soil
5 organic matter across china: an application of artificial neural network approach. *Catena.*
6 2013;104:210-218.
- 7 29. Mckee LJ, Eyre BD, Hossain S, Pepperell PR. Influence of climate, geology and humans on
8 spatial and temporal nutrient geochemistry in the subtropical richmond river catchment,
9 Australia. *Mar. Freshwater Res.* 2001;52:235-248.
- 10 30. Panosso AR, Marques J, Pereira GT, Scala NL. Spatial and temporal variability of soil CO₂
11 emission in a sugarcane area under green and slash-and-burn managements. *Soil Tillage Res.*
12 2009;105:275-282.
- 13 31. Zhou HH, Chen YN, Li WH. Soil properties and their spatial pattern in an oasis on the lower
14 reaches of the tarim river, northwest china. *Agric. Water Manage.* 2010;97:1915-1922.
- 15 32. Chen C, Chen DL, Lam SK. Simulation of nitrous oxide emission and mineralized nitrogen
16 under different straw retention conditions using a denitrification–decomposition model. *Clean*
17 *Soil Air Water.* 2015;43:577-583
- 18 33. Peng X, Ye LL, Wang CH, Zhou H, Sun B. Temperature-and duration-dependent rice straw-
19 derived biochar: characteristics and its effects on soil properties of an ultisol in southern China.
20 *Soil Tillage Res.* 2011;112:159-166.

- 1 34. Samuel WA, Lee YY, Anthony WB. The influence of organic matter content of
2 contaminated soils on the leaching rate of heavy metals. *Environ. Prog. Sust. Energy*.
3 2010;19:53-58.
- 4 35. Ingelmo F, Molina MJ, Soriano MD, Gallardo A, Lapeña L. Influence of organic matter
5 transformations on the bioavailability of heavy metals in a sludge based compost. *J. Environ.*
6 *Manage.* 2012;95:S104-S10.
- 7 36. Bhuiyan MAH, Islam MA, Dampare SB, Parvez L, Suzuki S. Evaluation of hazardous metal
8 pollution in irrigation and drinking water systems in the vicinity of a coalmine area of
9 northwestern bangladesh. *J. Hazard. Mater.* 2010;179:1065-1077.
- 10 37. Huang LM, Deng CB, Huang N, Huang XJ. Multivariate statistical approach to identify
11 heavy metal sources in agricultural soil around an abandoned pb–zn mine in Guangxi Zhuang
12 autonomous region, China. *Environ. Earth Sci.* 2013;68:1331-1348.

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1 **Table 1.** Theoretical Models and Corresponding Parameters for Semi-variance of Soil Properties
 2 and Heavy Metals

Measured Items	Theoretical Models	Nugget (C_0)	Sill (C_0+C)	Nugget/Sill $C_0/(C_0+C)$	Range (A_0)	RSS	R^2
pH	Spherical	0.1	38.99	0.26	126.8	49.5	0.925
SOM	Spherical	0.41	6.67	6.15	45.3	0.06	0.898
CEC	Exponential	0.01	11.56	0.09	108.6	3.99	0.828
Cu	Gaussian	38	427.1	8.9	106.69	6132	0.922
Zn	Spherical	100	57480	0.2	146.7	4.13×10^7	0.975
Cd	Gaussian	3.7	66.72	5.54	112.76	159	0.925
As	Gaussian	939	3377	27.8	85.91	1.15×10^5	0.947
Pb	Spherical	100	113900	0.08	133.1	5.17×10^8	0.924

3

4 **Table 2.** Correlation Analysis of Soil Properties and Heavy Metals

	Cu	Zn	Cd	As	Pb	pH	SOM	CEC
Cu	1							
Zn	<i>0.698**</i>	1						
Cd	<i>0.305**</i>	0.119	1					
As	<i>0.407**</i>	<i>0.627**</i>	<i>0.670**</i>	1				
Pb	<i>0.736**</i>	<i>0.728**</i>	0.178	<i>0.562**</i>	1			
pH	-0.161	0.025	-0.056	-0.079	-0.090	1		
SOM	0.082	<i>0.231**</i>	<i>0.334**</i>	0.254*	0.075	-	1	
CEC	<i>0.354**</i>	0.097	0.126	0.156	0.249*	-0.187	0.198	1

5 Values in italics are the best correlation coefficients between heavy metals and soil properties

6 *At the 0.05 significance level **At the 0.01 significance level

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8 **Table 3.** Comparison of Average Concentration of Heavy Metals with Background Values

Heavy metal	P_i	P	Pollution levels
Cu	0.59	0.67	Clean
Zn	1.85	2.33	Soil and crops are moderately polluted
Cd	5.39	11.55	Soil and crops are seriously polluted
As	4.96	9.19	Soil and crops are seriously polluted
Pb	2.26	2.59	Soil and crops are moderately polluted

1

2 **Table 4.** Total Variance Explained and Matrix of Principal Components Analysis (significant
3 loading factors are remarked in bold)

Component	Initial eigenvalues			Extraction sums of squared loadings ^a			Rotation sums of squared loading ^b		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	3.272	65.443	65.443	3.272	65.443	65.443	2.343	46.861	46.816
2	0.917	18.335	83.777	0.917	18.335	83.777	1.846	36.916	83.777
3	0.338	6.756	90.533						
4	0.252	5.041	95.574						
5	0.221	4.426	100.000						

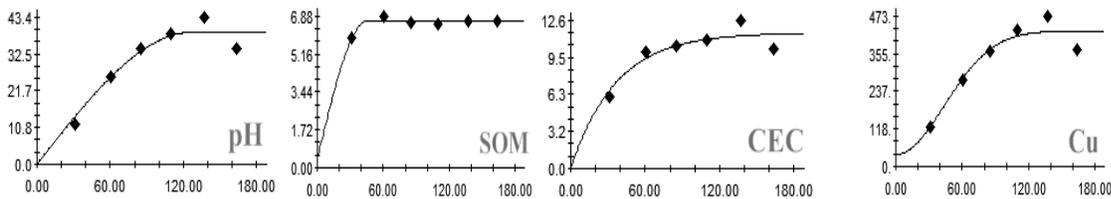
Component matrix			Rotated component matrix		
Element	PC1	PC2	Element	PC1	PC2
Cu	0.788	-0.487	Cu	0.919	0.116
Zn	0.895	-0.117	Zn	0.770	0.471
Cd	0.689	0.624	Cd	0.145	0.918
As	0.803	0.416	As	0.363	0.828
Pb	0.855	-0.323	Pb	0.868	0.286

4 ^a extraction method : the principal components. ^b rotation method: orthogonal rotation with Kaiser
5 standardization.

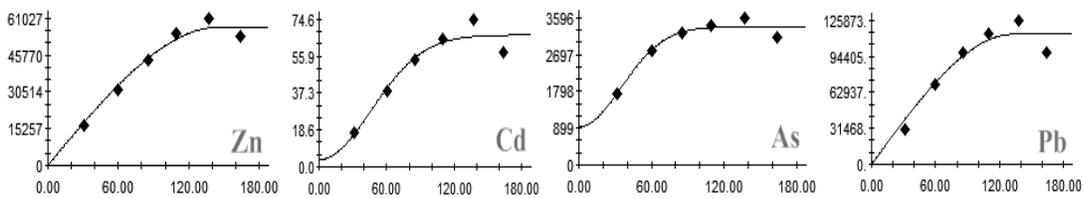
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10 **Fig. 1.** Semi-variance function of soil properties and heavy metals.

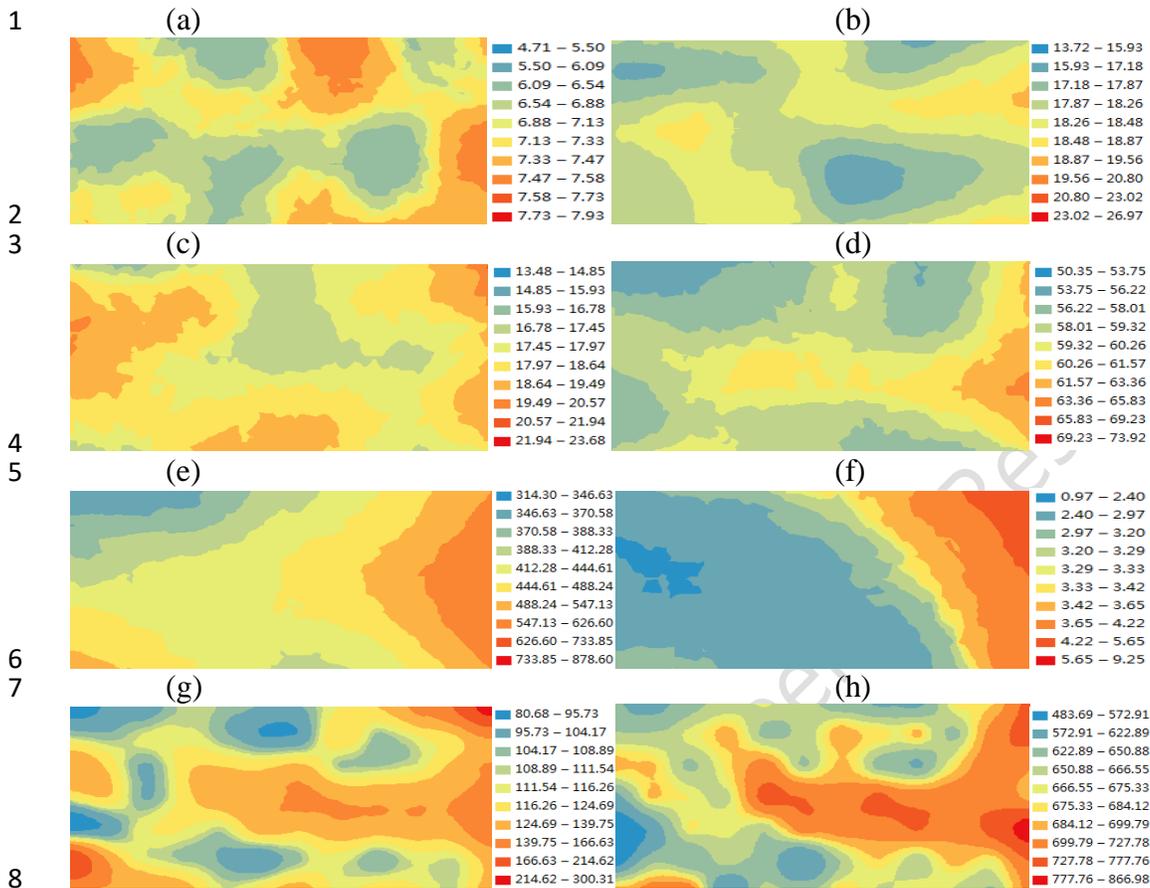


Fig. 2. Spatial distribution pattern of soil nutrients and heavy metals. (a) pH, (b) SOM (mg/kg), (c) CEC (cmol/kg), (d) Cu (mg/kg), (e) Zn (mg/kg), (f) Cd (mg/kg), (g) As (mg/kg) and (h) Pb (mg/kg).

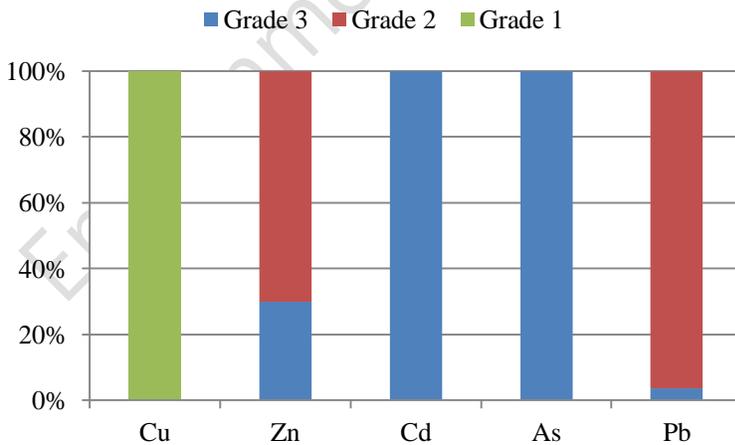
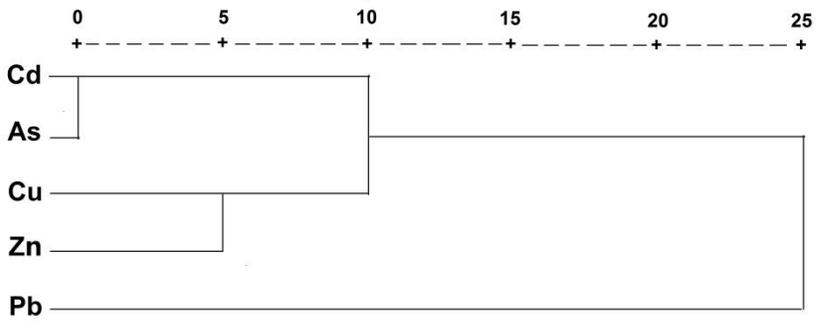


Fig. 3. The over-limit rates of heavy metals compared with national standards.



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 2 **Fig. 4.** Cluster analysis of soil available heavy metals.

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