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Source and hazard identification of heavy metals in soils of Changsha based on TIN model and direct exposure method

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Abstract: A total of 153 soil samples were collected from Changsha City, China, to analyze the contents of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn. A combination of sampling data, multivariate statistical method, geostatistical analysis, direct exposure method and triangulated irregular network (TIN) model was successfully employed to discriminate sources, simulate spatial distributions and evaluate children's health risks of heavy metals in soils. The results show that not all sites in Changsha city may be suitable for living without remediation. About 9.0% of the study area provided a hazard index (HI)>1.0, and 1.9% had an HI>2.0. Most high HIs were located in the southern and western areas. The element of arsenic and the pathway of soil ingestion were the largest contribution to potential health risks for children. This study indicates that we should attach great importance to the direct soil heavy metals exposure for children's health.

Key words: soil; heavy metal; geostatistics; health risk; triangulated irregular network (TIN) model; geographic information system (GIS)

1 Introduction

China is the world's most populous country and its economy is growing at the fastest rate of any major nation. However, its environmental problems are among the most severe of any major country, and are mostly getting worse[1]. In recent years, heavy metal (HM) pollutions in soil have become an important environmental issue in China because of their non-biodegradable nature and long biological half-live for elimination from the body[2]. Excessive accumulation of HMs in soils may pose serious health risks to humans and may exert adverse impacts on the ecosystem itself[3−4].

Heavy metal pollutants in soils can enter the human body and pose heath risks through two pathways: 1) soil-food-human body (indirect exposure); and 2) soil-human body (direct exposure). The major public health concern of soil HM exposure for the general population is accumulation over a lifetime and possible renal dysfunction and bone disease through food chain ingestion [5]. Therefore, the indirect soil exposure, including HMs through rice, wheat, vegetable, fruit and other foods, has been given more attention worldwide than the direct soil exposure[6−9]. However, recent studies have shown that the direct soil exposure, including soil ingestion, dermal adsorption and inhalation exposure, is also an important pathway by humans intake HMs and is particularly important for children[10]. Children's behavior can expose them to more toxic effects of soil HMs. For example, young children prefer to play close to the ground and come into contact with polluted soil outdoors and with contaminated dust on surfaces and carpets indoors. Moreover, the developing structure and function of organs for children may result in higher inhalation rates per unit of body mass than adults[11]. Research has shown that long-term health and development issues can arise from intrauterine and early childhood exposures to HMs, which are often undetectable early on and manifest later in life[12−13].

Estimating the source and spatial distribution of pollutants is crucial to quantifying the level of environmental risks[14]. However, due to the high costs and time constraints, the accuracy of the direct analysis

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of *in situ* data in field investigation is often dubious and the observations contain considerable uncertainty[15]. Geostatistical methods provide spatial interpolation and assess uncertainties at unsampled locations, which offer an opportunity to improve the accuracy of estimating spatial distribution of pollutants in a cost-effective manner[16−17]. Previous literature has focused on the identification of sources and human health risk assessment in HM contaminated soils[18−19], but rarely applied the geostatistical simulations. Moreover, previous literature always used the geostatistical methods to draw a 2D map for HM spatial distribution[19−20]. Triangulated irregular network (TIN) model is a popular three-dimensional (3D) model for representing surface models in geographic information system (GIS) because it has a simple data structure and can easily be rendered using common graphics hardware[21]. Hence, combining the geostatistical methods with TIN model may be a better approach to represent the spatial distribution patterns and potential human impacts of HMs in soils. Furthermore, previous researches on HMs mostly focused on one pollutant in isolation[22]. However, humans would actually be exposed to a mixture of heavy metals in real environments, which needs to be further studied.

Hunan province is regarded as the heartland of Chinese nonferrous mining and is under severe HM pollution stress[23−25]. Changsha City, the capital of Hunan province, is a modern industrial city surrounded by agricultural areas. Some potential HM contamination has accumulated in soils on a large scale because of industrial activities in Changsha, which may greatly exceed accepted standards and may thus pose a severe threat to human health. Moreover, Changsha City is under severe H_2SO_4-type acid rain pollution[26], which may greatly increase the mobility of HMs and cause groundwater contamination. Thus, it is very necessary to identify the potential pollution sources and to quantify the health risks of soil HMs in Changsha city.

Therefore, this study set out to determine spatial patterns in the total concentration of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) at the field-scale and to identify their possible sources using multivariate analysis and geostatistical methods. Then, their health risks in soils were estimated by the direct exposure method. Finally, the spatial distribution and human health risks of the mixture of heavy metals were simulated by a TIN model.

2 Materials and methods

2.1 Sampling and laboratory analyses

Changsha City has a total area of 11 819.5 km^2 and is located in the eastern part of Hunan province (111°53′–114°15′E, 27°51′–28°40′N) (Fig.1). About 6.1×10^6 people inhabit Changsha city and the annual population growth rate is 1.08% and 44.63% of the population live in urban areas. Changsha City has a subtropical monsoon climate with an annual rainfall of 1 483.6 mm and most rainfall occurs between April to July.

The surface soil samples (0−20 cm) were collected using a global positioning system (GPS) to identify its locations (Fig.1). Because of the vast area in Changsha city, the sampling density was one sample per 5 to 10 km^2. The moisture soil samples were air-dried and sieved (<0.15 mm) to determine the content of HMs including As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn. Then, soil samples (0.5 g) were digested with a mixture of HNO_3 (5 mL) and H_2O_2 (2 mL) at about 180 °C for about 20 min in a closed-Tefon vessel in a microwave oven to avoid losses of some metals via volatilization. The total contents of Cd, Cu, Ni and Pb in the digested solution were measured by inductively coupled plasma-mass spectrometry (ICP-MS). Cr, Zn and Mn were analyzed

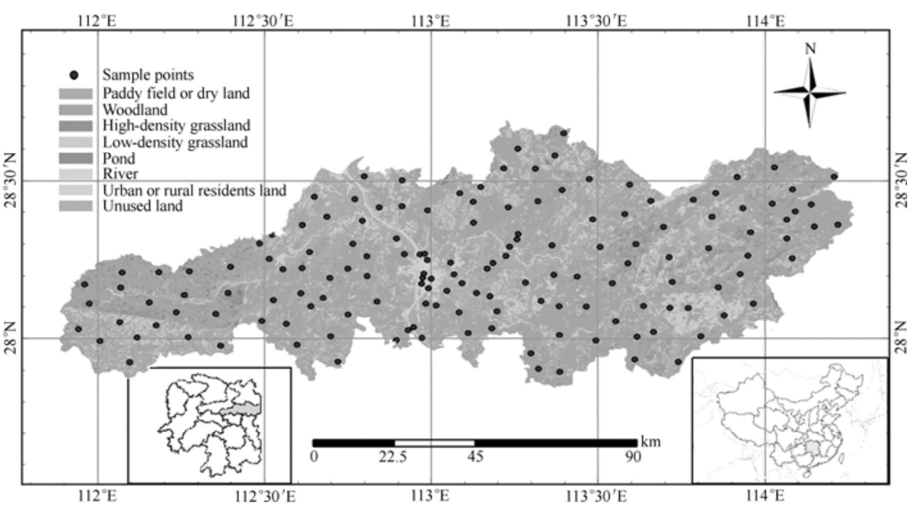

Fig.1 Location and distribution of sampling points

by inductively coupled plasma-optical emission spectrometry (ICP-OES). In addition, the contents of As and Hg were determined by atomic fluorescence spectrophotometry (AFS). All samples were analyzed in three replicates. The quality control of analytical accuracy was performed by reagent blanks and reference soils. Standard reference materials for soil (GBW 07401) obtained from the China National Center for Standard Reference Materials were digested along with the samples and used for the quality assurance control program.

2.2 Statistical methods

2.2.1 Principal component analysis

Principal component analysis (PCA) is a useful multivariate statistical method in environmental studies[27]. In this study, the PCA was used to extract latent information from multidimensional data, to gain the observed correlation matrix, to classify the measured elements into fewer groups, to facilitate the interpretation of the results, and to define natural or anthropogenic origin. The PCA was processed with SPSS (version 16.0).

2.2.2 Geostatistical analysis

Kriging has been widely applied in environment science because of its unbiased character and its advantage in geostatistical techniques relative to other methods (such as the inverse distance weighted method, IDW)[28]. Among the numerous kriging techniques, ordinary kriging and log-normal kriging are widely used and can effectively interpolate values at unsampled locations[2]. For this reason, both of the kriging methods were chosen to detect the spatial structure of HMs and to provide unbiased prediction in the study area. Moreover, contour lines were created by kriging for the TIN model. The geostatistical analysis and maps were produced with ArcGIS (version 9.2). Detailed algorithms of geostatistical theory and kriging can be found in many textbooks and monographs[16, 29].

2.3 TIN model

The TIN data structure was based on two basic elements: points and a series of edges. The points have *x*, *y* and *z* values, and the *z* values represente health risk values in this study. The edges are used to join the points to form triangles. This triangular mosaic forms a continuous faceted surface, much like a jewel. In addition, TIN's triangulation method satisfies the Delaunay criterion[30]. The first phase of generating a TIN was to extract the skeleton of contour lines (isolines) from the result of previous geostatistical analysis. Then, possible points on the contour lines were identified by a local geometric operator. Subsequently, these points were linked into new contour lines and automatically connected in a Delaunay triangulation. Finally, compared with the original dense grid, additional support points were added to the resulting model at the points of worst fit, which was used to ensure that the maximum discrepancy between the TIN model and the original model was within a pre-specified tolerance[21, 30].

In this study, a TIN model was established using contours created by geostatistical analysis to better assess HM health risks. The TIN model was established with the extension module of 3D Analyst in ArcGIS (version 9.2).

2.4 Health risk assessment and direct exposure method

Health risks for the local population derived from the exposure to HM pollutants were evaluated after understanding the main sources of HMs. Three pathways were considered to estimate the direct exposure to soil metals: 1) incidental ingestion of soil; 2) inhalation of particulates emitted from soil; and 3) dermal contact with soil. The potential health risk of individual soil HM is characterized using a hazard quotient (HQ), which is the ratio of the chronic daily intake (CDI, mg/(kg·d)) to the reference dose (RfD, mg/(kg·d)). The HQ was calculated using the following equation in the three selected exposure pathways[31].

$$\begin{aligned}\mathrm{HQ}&=\frac{\mathrm{CDI_{dermal}}+\mathrm{CDI_{inhalation}}+\mathrm{CDI_{ingestion}}}{\mathrm{RfD}}\\&=(\mathrm{CS}\times\mathrm{CF}\times\mathrm{SA}\times\mathrm{AF}\times\mathrm{ABS}+\mathrm{DPM}\times\mathrm{MPM}\times\\&\quad\mathrm{IR}\times\mathrm{ET}+\mathrm{CS}\times\mathrm{Isp}\times\mathrm{CF})\times\frac{\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}\times\mathrm{RfD}}\end{aligned} \tag{1}$$

where CS is metal content in soil (mg/kg), which is the analysis result of geostatistical analysis; DPM is the concentration of particulate matter that is respirable in the air (For time spent outdoors, DPM is assumed to be 0.104 mg/m^3, which is the annual mean concentration for Changsha City[32]. When indoors, DPM=0.445×0.104 mg/m^3 because 44.5% of indoor dust is considered to be derived from outdoor soil[33]); MPM is the HM concentration on airborne particulate matter (assumed equal to CS where dust is derived from the soil[8]. The reference dose (RfD) is an estimate of a daily exposure to the human population. RfDs based on 3×10^{-4}, 1×10^{-3}, 1.5, 4×10^{-2}, 3×10^{-4}, 1.4×10^{-1} , 2×10^{-2}, 0.035 and 0.3 mg/(kg·d) for As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn, respectively. The RfDs were obtained from Integrated Risk Information System[34], with the exception of lead, in which we used the formula RfD=PTWI/7, where PTWI is provisional tolerable weekly intake (mg/(kg·week))[35−36]. Detailed information of the parameters in Eq.(1) is provided in Table 1.

The overall potential risk posed by a mixture of HMs is assessed by the summed HQs calculated for each

Table 1 Direct soil exposure parameters

Parameter	Value	Reference
Body mass (BW)/kg	15	[31]
Exposure duration (ED)/a	6	[31]
Averaging time (AT)/d	2 190	[31]
Exposure frequency (EF)/($d \cdot a^{-1}$)	350	[31]
Conversion factor (CF)/($kg \cdot mg^{-1}$)	10^{-6}	[31]
Exposed skin surface area (SA)/cm^2	2 800	[31]
Soil-to-skin adherence factor (AF)/($mg \cdot cm^{-2}$)	0.2	[31]
Inhalation rate (IR)/($m^3 \cdot d^{-1}$)	10.9	[31]
Dermal absorption factor (ABS, unitless) of arsenic	3.2%	[31]
Dermal absorption factor (ABS, unitless) of other metals	1.0%	[31]
Exposure time (ET) indoor/($h \cdot d^{-1}$)	16	[31]
Exposure time (ET) outdoor/($h \cdot d^{-1}$)	8	[31]
Respirable particulate matter concentration indoor (D_{PM})/($kg \cdot m^{-3}$)	0.463×10^{-7}	[33]
Respirable particulate matter concentration outdoor (D_{PM})/($kg \cdot m^{-3}$)	0.104×10^{-6}	[33]
Ingestion rate of soil particle (I_{sp})/($mg \cdot d^{-1}$)	100	[31]

HM, which is expressed as a hazard index (HI):

$$HI = HQ_1 + HQ_2 \cdots + HQ_n \quad (2)$$

3 Results and discussion

3.1 Heavy metals in soil

The mean concentrations of all metals were higher than their background values at Changsha City (Table 2). Although the mean concentrations of Cu and Zn were higher than their local background values, the differences between their concentrations and the background contents were slight. Moreover, Cu and Zn displayed low coefficients of variation (CVs) and fairly homogeneous distributions across the study area, suggesting that there was a major natural source of Cu and Zn in Changsha City. The average concentrations of Cd, Ni, Pb, Hg, Cr, Mn and As were higher than the background values and had high CVs, indicating that anthropogenic inputs are the main sources of these HMs in this area. Moreover, the maximum concentrations of Hg, Cd, As and Ni in the soils exceeded the critical level of the Secondary Environmental Quality Standards for Soil in China by 1.2, 2.4, 3.2 and 6.8 times, and they were 4.1, 10.4, 6.4 and 9.6 times higher, respectively, than local background values at the control site. Thus, these metals require intensive monitoring and essential measures to prevent further enrichment.

3.2 Data transformation

The normality of all HMs was checked before PCA and spatial analyses were conducted. Values of skewness and kurtosis, and the significance level of the One-Sample Kolmogorov-Smirnov Test for normality (K-S_p) are shown in Table 3. It was found that only Cu, Zn, Cr and Hg were in accordance with normal distribution using K-S_p (>0.05) before data transformation, whereas other variables were all positively skewed. To make the data more normal, a logarithmic transformation was used [38]. Table 3 shows that a logarithmic transformation can produce smaller skewness and kurtosis values for all HMs except for Cu and Zn. Thus, in the following steps, a logarithmic transformation was applied to all HMs except for Cu and Zn.

3.3 Principal component analysis

PCA was applied to the transformed data matrices and the results are presented in Table 4. As indicated in the results of the rotated component matrix for data in Table 4, three factors were extracted, and Ni, Cr, As and Mn were strongly associated with the first factor (F_1) with similarly high values. Elements such as Pb, Cd and Hg are associated with the second factor (F_2), while the third factor (F_3) was mostly associated with Cu and Zn.

Table 2 Descriptive statistics for HM concentrations ($mg \cdot kg^{-1}$) in soil

Statistical item	Cu	Pb	Zn	Cd	Ni	Cr	Hg	As	Mn
Mean	27.56	36.5	94.6	0.11	34.4	74.21	0.113	18.98	477
Median	27.00	28.5	95.0	0.067	27.5	69.00	0.100	15.65	270
Minimum	14.00	14.0	31.9	0.006	8.0	20.00	0.003	5.28	23
Maximum	42.60	234.0	170.0	0.73	270.0	228.00	0.367	96.48	1 700
Skewness	0.32	5.22	0.17	2.93	5.28	2.19	1.415	3.79	2.21
Kurtosis	0.08	34.51	0.02	11.95	28.51	5.61	2.57	17.57	5.75
CV/%	23.58	77.75	30.47	81.48	91.33	57.45	61.61	74.92	68.56
Background value *	25	30	94	0.07	28	68	0.09	15	459

* Data from the report of the key scientific research project of the sixth plans[37].

Table 3 Skewness, kurtosis, and significance level of Kolmogorov-Smirnov's test for normality (K-Sp) of raw data (RD) and log-transformed data (LD) of soil heavy metal concentrations

Parameter		Cu	Pb	Zn	Cd	Ni	Cr	Hg	As	Mn
RD	Skewness	0.32	5.22	0.17	2.93	5.28	2.19	1.42	3.79	2.21
	Kurtosis	0.08	34.52	0.02	11.95	28.54	5.60	2.57	17.57	5.75
	$K\text{-}S_p$	0.267	0.003	0.930	0.003	0.000	0.067	0.085	0.003	0.023
LD	Skewness	−0.44	1.41	−0.83	0.05	1.49	0.44	−1.74	0.77	−0.15
	Kurtosis	0.50	4.08	0.93	0.03	6.48	0.68	6.35	2.06	0.54
	$K\text{-}S_p$	0.103	0.361	0.458	0.698	0.025	0.779	0.292	0.690	0.843

Table 4 Component matrix and rotated component matrix for heavy metal contents

Element	Component matrix			Rotated component matrix		
	F_1	F_2	F_3	F_1	F_2	F_3
Cu	0.378	−0.249	0.708	0.182	−0.146	0.807
Pb	0.002	0.638	0.111	−0.225	0.604	0.062
Zn	0.358	0.373	0.574	0.021	0.444	0.632
Cd	0.401	0.618	−0.215	0.244	0.719	−0.116
Ni	0.903	−0.198	−0.267	0.956	0.097	0.051
Cr	0.752	−0.427	0.161	0.749	−0.182	0.423
Hg	0.653	0.513	−0.049	0.447	0.690	0.128
As	0.829	−0.182	−0.346	0.911	0.092	−0.048
Mn	0.755	0.035	0.069	0.643	0.262	0.305

3.3.1 Ni, Cr, As and Mn

The first factor (F_1) was mainly associated with Ni, Cr, As and Mn, which can be considered to be an anthropogenic component. These four elements all displayed a high association with the first factor. According to the earlier discussions, the mean concentrations of Ni and As exceeded their local background values and were moderately enriched in surface soil. The major types of industry in Changsha city are mining, machinery, metallurgy, chemical and production of building materials, some of which have backward technology and serious pollution, particularly the non-ferrous mining industry. There are almost 1 000 mining, 200 metal smelting, 700 chemical material and chemical products industries, 340 printeries and 200 paper mills in the study area. It was found that most of the above industries were related to F_1. For example, printery and alloy melting factories often cause Mn and Cr contamination. Additionally, coal mining activities contribute greatly to Mn, Ni, Cr and As pollution in the soils of Changsha city.

3.3.2 Pb, Cd and Hg

The second factor (F_2) included Pb, Cd and Hg. Their CVs were high, suggesting that these factors could be a second anthropogenic component. Moreover, there were some samples with very high Cd and Hg contents whose sources could have been attributed to adjacent industry production. The non-ferrous metal mining, mineral processing and smelting along the Xiangjiang River mainly deal with the ore of lead sulfide, accompanied by Cd, Hg and other metal elements, which caused some soil population and health problems according to previous studies[7, 39−40]. Therefore, the enrichment of F_2 in soils is likely due to anthropogenic causes.

3.3.3 Cu and Zn

The third factor (F_3) mainly included Cu and Zn. In contrast with F_1 and F_2, F_3 can be defined as a natural component because it was found that the mean concentrations of these two elements were very close to the local background values and that their CVs were also very low, suggesting that a natural factor controlled their distribution.

3.4 Geostatistical analysis

3.4.1 Spatial structure analysis of heavy metals

Soil heavy metals are regionalized variables as they are distributed in geographical space. They have spatial structures with spatial autocorrelation. In this study, geostatistics were used to analyze the spatial structure and visualization for interpretation of the results. The parameters of the semivariogram for each HM are summarized in Table 5.

The parameters of nugget variance, sill and range have often been ignored in other similar studies. These parameters cannot only be used to characterize the heterogeneity of the environment but can also help to identify their sources [2]. The term 'nugget' in geostatistics can describe the apparent discontinuity near the origin and can represent field variation within the

Table 5 Best-fitted semivariogram models and parameters of soil heavy metals

Element	Model	Nugget	Partial sill	Sill	Range/m
As	Spherical	0.016	0.250	0.265	7 136
Cd	Exponential	0.645	0.237	0.882	26 497
Cr	Exponential	0.087	0.193	0.280	16 576
Cu	Spherical	0.018	0.056	0.075	32 062
Hg	Exponential	0.139	0.608	0.747	5 436
Mn	Spherical	0.360	0.344	0.704	28 281
Ni	Exponential	0.132	0.138	0.270	11 532
Pb	Exponential	0.052	0.113	0.165	14 654
Zn	Exponential	0.028	0.048	0.076	34 931

minimum sampling spacing[41]. From Table 5, the nugget variances of Cd, Cr, Hg, Mn, Ni and Pb were higher than those of Cu and Zn, suggesting a greater variation for Cd, Cr, Hg, Mn, Ni and Pb at a small-scale. However, the element As revealed a relatively low nugget variance like Cu and Zn, which could be due to the applications of pesticides and phosphate fertilizers in farm land. Furthermore, the sill of As was larger than that of Cu or Zn but was close to that of Cr or Ni (Table 5). The sill indicates the maximum structural variability; thus, a larger sill indicates a higher degree of spatial variance. Therefore, it can be concluded that the spatial variance of As was similar to that of Cr or Ni at a large-scale, and it was similar to that of Cu or Zn at a small-scale, suggesting that both industry and farming could be the source of As in top soil in Changsha city. Although the nugget variance can reflect some information about the spatial variance of environmental variables, this parameter could not be as sensitive or robust as the range value[2]. When comparing the range of nine elements, Cu and Zn are found to have a longer effective range (32 062 m and 34 931 m, respectively) than other HMs, indicating that Cu and Zn have a better spatial structure and less variation caused by extrinsic factors. This is consistent with the earlier discussion of the PCA (Table 4).

3.4.2 Spatial distribution of heavy metals

In order to better understand the distribution patterns of the nine heavy elements, kriging interpolation and TIN models were used to produce 3D maps (Fig.2). The 3D spatial distribution maps of Mn, Ni, Cr and As concentrations show similar distributional trends with high concentrations in the southwest and east areas where the traditional industrial zone is located. This result is consistent with that found in the PCA analysis, indicating that the former discussion on F_1 is reasonable.

Pb, Cd and Hg also show similar distributional trends and high concentrations of the HMs are mainly found in central and eastern areas. The result is consistent with that observed in the PCA in which Pb, Cd and Hg were associated with the second component (F_2). The Xiangjiang River watershed is located in the center area of Changsha city and many non-ferrous metal mining, mineral processing and smelters are located in this region. Moreover, the representative industry cities, Zhuzhou and Xiangtan City, are also located in the upstream portion of the Xiangjiang River. Industrial activities could contribute to the source of Pb, Cd and Hg pollution in the central and southern areas of Changsha city. The eastern area of Changsha City has always been rich in lead, iron, borax, green alum and blue vitriol. In addition, the eastern part of the city also has numerous mining enterprises where the acid mine drainage and flotation wastewater containing Cd, Pb, Al and Hg are the main sources of pollution.

In many studies, Pb pollution was primarily related to vehicle sources[42], which were also found in the study area and particularly in the central area. Kriging was further used only in the urban area to better study the relationship between vehicle and Pb distribution for two main reasons: 1) because the smoothing effect of the kriging estimator depends on the local data configuration; and 2) because the inherent smoothing effect tends to overestimate small values and to underestimate large values. Fig.2 also shows that Pb was distributed in the center of the city, mainly in the southern area and along the Xiangjiang River bank, which corresponded well with the spatial distribution of traffic flow. The wider roads along the river and the frequent exchanges of vehicles between both sides of the river lead to a large traffic flow. The southern area had the largest proportion of traffic flow into and out of Changsha city. Therefore, it is reasonable to assume that Pb in the center city comes primarily from vehicles. Furthermore, the distribution map of Pb in the city zone was created only by geostatistical simulation, which was always used by previous studies. By comparing, it was found that the maps created by TIN model not only had better visual effects, but also reflected the characteristics of HM concentration and spatial distribution more clearly.

The spatial distribution of Hg represented a litter difference from that of Pb and Cd in F_2 and showed a non-point source pollution trend. Hg pollution in urban soils has been found to be universal in China because of the use of coal, which usually causes atmospheric deposition[43−44], over a long time period. Therefore, coal consumption and atmospheric deposition may be the other source of Hg.

As shown in Fig.2, the distributional patterns of Cu and Zn were more regular, suggesting that a natural factor plays an important role in controlling their distributions as described in the third component (F_3) of the PCA. The location of high Zn concentration is

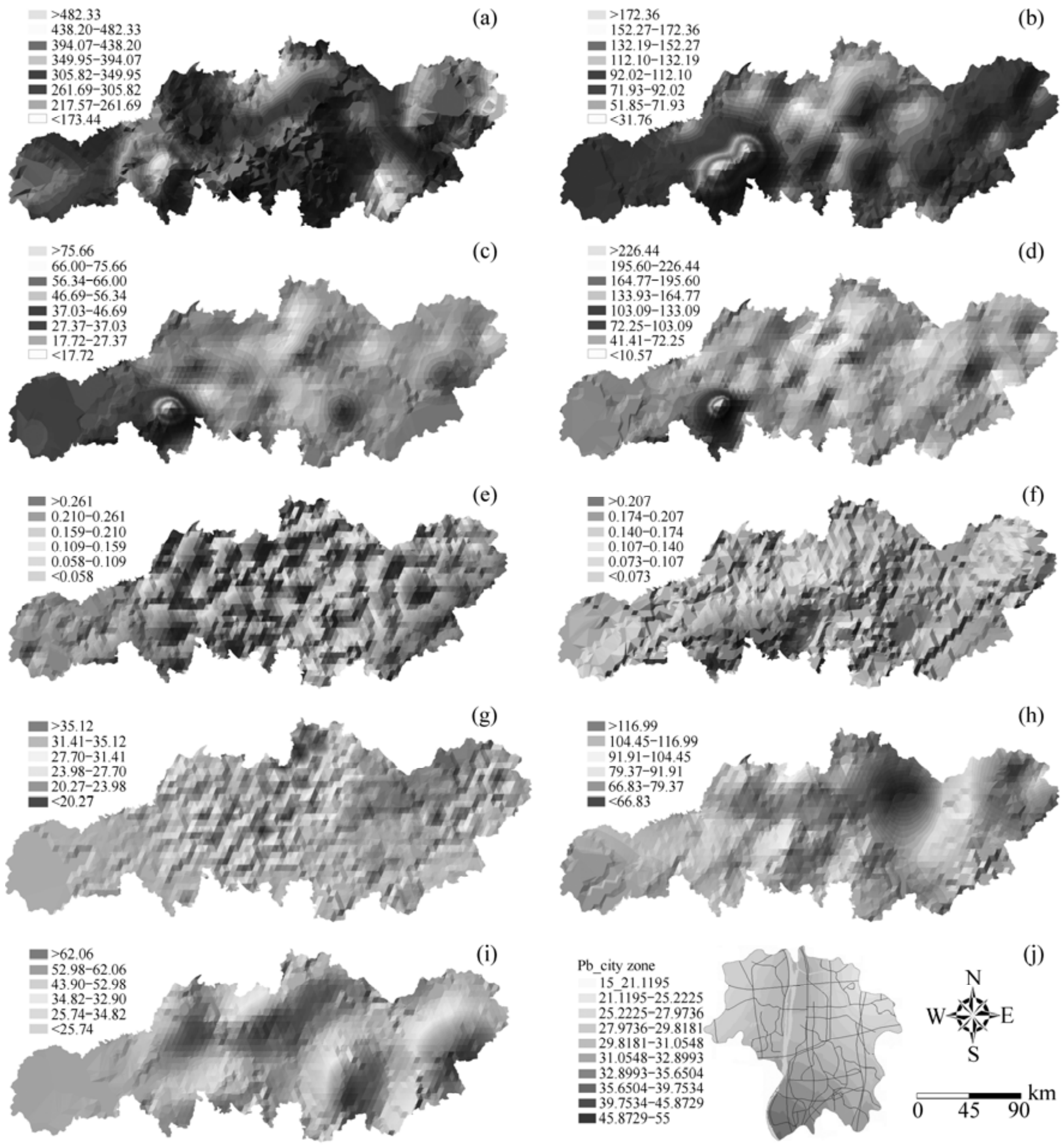

Fig.2 Spatial distribution of soil heavy metals (mg·kg^{-1})

similar to that of Pb, which may be caused by lead-zinc mineral resources in the areas. However, in the whole study area, the mean concentration and CVs of Zn are low, which suggests a major natural source.

Integrating the above model analysis and the HM source hypothesis, As, Cd, Cr, Hg, Ni, Pb and Mn should mainly be controlled by anthropogenic factors, whereas Cu and Zn should be controlled by natural factors.

3.5 Human health risk assessment

After understanding the main sources of HMs in Changsha City, we carried out an evaluation of the risk of direct soil HMs exposure to children (Fig.3). An HI greater than 1.0 suggests that the child may experience adverse health effects during his or her lifetime. Fig.3 shows that about 9.0% of the study area provides an HI>1.0, and 1.9% has an HI>2.0. The average HI is 0.6 and the maximum value reaches 3.0. It was also found that high health risks mainly located in the southern and western locations. Therefore, the direct exposure to soil HMs plays an important role in health risks for children in Changsha city, which should be taken into consideration by some of the decision makers and researchers.

With respect to the pathway of soil HM exposure, it was found that soil ingestion was the main route for children. The risk of soil ingestion was more than five times that of inhalation and dermal absorption. In addition, there was a large discrepancy of hazard quotients (HQ) among different HMs (Fig.4). The HQ of different HMs was in the sequence As>Mn>Ni>Pb>Cu>Hg>Zn>Cd>Cr. Chromium had the lowest HQ value, which may be related to its high RfD, 1.5 mg/(kg·d). However, arsenic was the largest contributor to HI, which may be related to poor pollution control for this metal and its low RfD, 0.000 3 mg/(kg·d). Recent research has shown that long-term health and development issues can arise from intrauterine and early childhood exposures to As[12], thus, legislative policy and advanced technology should be used to prevent arsenic contamination.

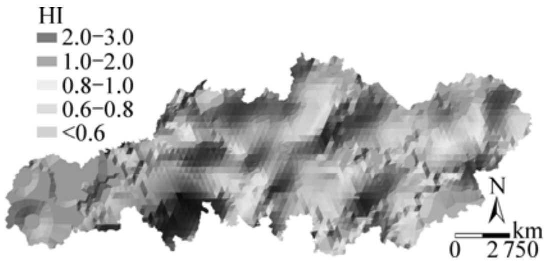

Fig.3 Health risk distribution of heavy metals in soils

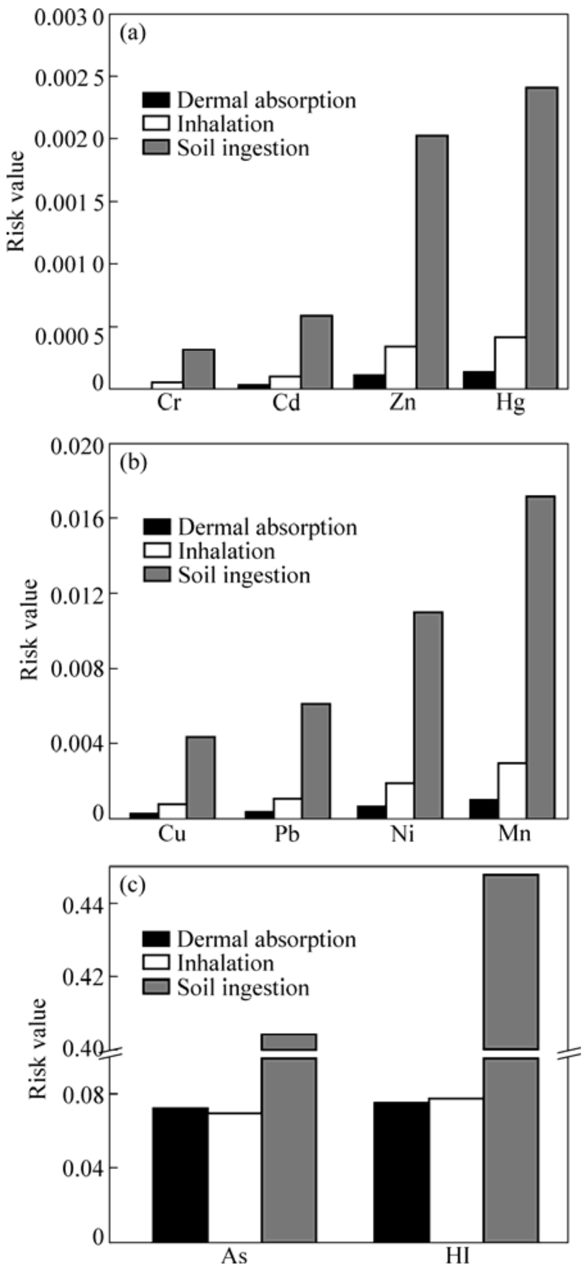

Fig.4 Health risk of heavy metals exposure to children through three different pathways

4 Conclusions

1) This work spatially analyzed the potential health risk for children associated with direct exposure to As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn in soil in Changsha city. The combination of sampling data, multivariate statistical method, geostatistical analysis and TIN model was used to determine heavy metal sources, spatial distributions and health risks in soil. Result showed that not all sites within the study area may be suitable for living without remediation.

2) The concentrations of heavy metals such as As, Cd, Hg and Ni observed in some locations exceeded the critical level of Secondary Environmental Quality Standards for Soil in China. Results also showed that about 9.0% of the study area provided an HI>1.0, and 1.9% had an HI>2.0. Most high HIs were located in the southern and western areas. Arsenic presented a high risk in comparison with other elements and most HI was attributable to soil ingestion. This study indicates that we should attach great importance to the direct soil heavy metal exposure for children's health. Regardless of the HI maps, more detailed investigation would be required when assessing a specific site within the study area, because the sampling data used to construct the health risk maps are of fairly low resolution.

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基于 TIN 模型和直接暴露方法的长沙土壤中重金属来源识别及人类健康风险评价

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摘 要：通过采集 153 个样品分析长沙市土壤中 As、Cd、Cr、Cu、Hg、Mn、Ni、Pb 和 Zn 的含量，利用多元统计、地学统计、直接暴露以及不规则三角网模型(TIN 模型)等方法分析土壤中重金属的来源、空间分布以及对儿童的健康风险。结果表明：长沙地区部分区域需经过污染治理后才适合人类生活；约 9.0%的区域风险值超过了临界值 1.0, 1.9%的区域风险值大于 2.0，其中高风险主要集中在南部和西部地区；元素 As 和口腔摄入途径是儿童的主要健康风险来源；土壤重金属的直接暴露对儿童所产生的健康风险应该受到研究者的重视。

关键词：土壤；重金属；地统计学；健康风险；TIN 模型；地理信息系统

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