The spatial distribution and sources of metals in urban soils of Guangzhou, China

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Abstract
Heavy metals in urban soils are of great environmental concern because of their potential long-term effects on human health. To evaluate soil environmental quality, a total of 426 surface soil samples (0-10cm depth) were collected from different administrative districts of Guangzhou, the largest and developed city in South China. GIS-based geostatistical technique and multivariate statistics were applied to generate metal spatial distribution maps, and to identify metals influenced by anthropogenic activities. Kriging interpolation of spatial data proved to be a powerful tool in identifying the contamination hotspots and possible sources of heavy metals. Hotspot areas of metal contamination were mainly concentrated in the western and southern parts, and closely related to industrial and long-term domestic activities. Principal component analysis (PCA) results suggested the following trends: (i) Fe, Ni and Mn are predominantly derived from natural sources; (ii) As, Cu, Hg, Pb and Zn from anthropogenic sources; and (iii) Cd from both sources.

Key words
Urban geochemistry; Soil survey; Heavy metals; Kriging interpolation map; GIS; Multivariate statistics.

Introduction
In densely populated urban areas, good quality of urban soil is essential to the health of urban inhabitants. Evaluating the environmental impact of contaminants in soils must start with a robust determination of their concentration and spatial distribution. This is especially important in urban areas with soils comprising complex heterogeneous properties and spatial patterns. A number of studies have indicated urban soils are more contaminated than rural soils due to extensive impact from anthropogenic activities. Understanding spatial distribution and sources of metals in surface soils is necessary to implement mitigation strategies to reduce concentrations, minimize human exposure and protect populations at risk. The use of GIS-based geo-statistical techniques to describe the spatial distribution of heavy metals in urban soils has been demonstrated previously (e.g. Davis *et al.* 2009; Lee *et al.* 2006; Zhang 2006). Multivariate analysis (principal component analysis -PCA) provides fingerprints for identifying the origin of soil pollution, and has been widely used to assist the interpretation of environmental data and to distinguish between natural and anthropogenic inputs (Manta 2002). The purposes of this study were: (1) to determine concentrations of metals (As, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn), including variability and spatial distribution patterns by using GIS-based geostatistical techniques in the surface soils in Guangzhou; (2) to undertake a multivariate statistical approach (PCA) for data interpretation to identify possible sources for these metals.

Materials and Methods
Soil sampling and analysis
Guangzhou, the capital city of Guangdong province, is located in South China. More details were described in Lu *et al.* (2007). A total of 426 sampling sites were selected in different areas of Guangzhou, including Tianhe, Yuexiu, Liwan, Baiyun and Haizhu administrative districts (Figure 1). Composite soil samples collected at a depth of 0–10cm were obtained by mixing subsamples from five random points within 2 m^2 in each sampling site.
Bulk soil samples were air dried and hand crushed to pass through a 2-mm nylon sieve. Sub-samples were then ground with an agate grinder to go through a 0.15-mm nylon sieve.
Soil pH values were measured in a 1:2.5 (w/v) ratio of soil to deionised water (w/v). Soil organic matter (SOM) was determined by a wet oxidation method. Soil Cu, Fe, Mn, Ni, Pb and Zn were measured by using flame atomic absorption spectrometry (FAAS)

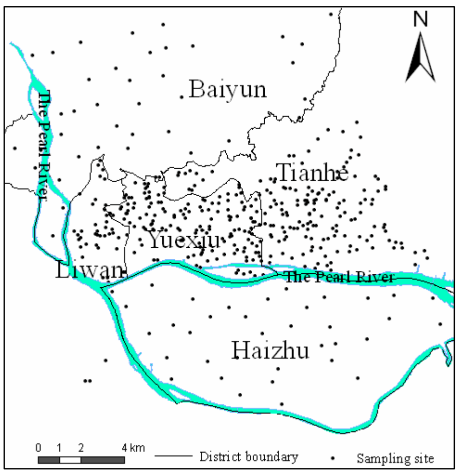

Figure 1. Location map of soil sampling sites in Guangzhou

(Hitachi Z-5300), and Cd by using a graphite furnace AAS (Hitachi Z-5700) after digestion with a mixture of HNO_3, HF and $HClO_4$. Soil As was measured by hydride generation atomic fluorescence spectrometry (HG-AFS 230, Beijing) after digestion with HCl and HNO_3. Soil Hg was measured by cold vapour atomic absorption (F732-V, Shanghai) after digestion with a mixture of H_2SO_4, HNO_3 and $KMnO_4$.

Data analysis and mapping

Basic statistics of the raw data and multivariate analysis (PCA) were performed using Minitab® v.14. The geostatistical analysis was carried out using GS+® v7.0. Based on the fitted semivariogram models, the ordinary Kriging provided by ArcGIS® v9.0 was used to map the spatial distribution of metal concentrations.

Results and Discussions

Descriptive statistical and correlation analysis

A descriptive summary of soil pH, organic matter and metal concentrations in urban soils is provided in Table 1. Acid soils (pH<6.5) accounted for about 28.4% of the soils, neutral (pH 6.5-7.5) and alkaline soils (pH>7.5) accounted for 44.4 and 27.2% respectively. This indicated that the pH for urban soils in Guangzhou has a tendency to be much higher than natural soils, which are dominated by being acidic or strongly acidic (GDSGSO 1993). Soil organic matter varied significantly among urban soils ranging from 2.56 to 199mg/kg.

The distribution of metal concentrations was skewed by a small number of large values. The extent of skewness, shown by difference (expressed as a percentage of median values), was the greatest for Hg (79%) and least for Fe (3%). Similar trends were obtained by examining the ranges of concentration values for each metal. Proportionately (the maximum values as a multiple of the minimum values) Hg (1223) had the largest range, and Fe (10) had the smallest range. The mean concentration of As, Fe and Ni was lower, whereas Cd, Cu, Hg, Mn, Pb and Zn were higher, than soil background values in Guangzhou.

Table 1. Descriptive statistics of soil properties and metal contents in urban soils (n=426).

Parameter	Min	Max	Median	Mean	Std..Dev.	Skewness	Kurtosis	Soil Background Value in Guangzhou
pH	2.55	9.33	7.12	6.86	0.99	-1.23	1.80	-
SOM g/kg	2.56	199	21.8	25.4	18.9	3.58	23.5	-
As mg/kg	1.4	144	14.1	17.4	15.0	4.17	25.9	17.4
Cd mg/kg	0.03	2.41	0.23	0.32	0.29	3.27	15.2	0.083
Cu mg/kg	5.0	417	25.3	35.8	41.4	5.34	37.1	13.6
Fe g/kg	6.1	61.8	27.0	27.9	7.87	0.56	0.61	29.0
Hg mg/kg	0.01	12.2	0.34	0.61	1.00	5.53	47.2	0.157
Mn mg/kg	21.2	1286	185	218	136	2.18	10.4	158.6
Ni mg/kg	2.5	77.6	16.2	18.7	10.3	2.03	6.92	22.03
Pb mg/kg	18.5	4903	63.8	87.6	238	19.5	395	42.88
Zn mg/kg	10.1	1795	78.8	107	116	8.18	108	58.1

Table 2. Pearson correlation coefficients among metals in urban soils and soil properties (n=426).

	SOM	pH	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Zn
SOM	1	-0.083	0.327**	0.427**	0.456**	0.081	0.354**	0.182**	0.371**	0.154**	0.398**
pH		1	-0.154**	0.032	-0.004	-0.058	-0.051	0.085	-0.013	0.012	0.064
As			1	0.237**	0.143**	0.203**	0.190**	0.107*	0.286**	0.061	0.134**
Cd				1	0.530**	0.258**	0.192**	0.401**	0.607**	0.256**	0.603**
Cu					1	0.156**	0.218**	0.233**	0.471**	0.321**	0.616**
Fe						1	0.009	0.315**	0.499**	0.260**	0.223**
Hg							1	0.074	0.173**	0.064	0.160**
Mn								1	0.485**	0.236**	0.348**
Ni									1	0.117*	0.344**
Pb										1	0.763**
Zn											1

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).

Pearson correlation coefficients among metals and soil properties were listed in Table 2. Soil As concentration was negatively correlated with pH, implying that as pH increases, arsenic mobility increases. Therefore, arsenic would have a short residence time in these soils and tend to move downwards as pH increases. Concentrations of all analyzed metals except for Fe were positively correlated with soil organic matter, suggesting an important retention of metals by soil organic matter or metal input to the soil through various organic matter materials. Cd, Cu, Pb and Zn were closely related ($P<0.01$), and Pb showed poorer correlations with As and Hg, which might suggest their common or different origins.

Spatial distribution pattern of metals

Since the probability distributions of the As, Cd, Cu, Hg, Pb, and Zn concentration data were heavily skewed (Table 1), the Box-Cox transformation was used to make the data more normal and less skewness prior to geostatistical analyses, and all metals mentioned above passed the normality at the level of 0.05. Experimental semivariograms suggested that the theoretical Gaussian model was in reasonable agreement with the data for soil As, Cu, Pb and Zn, whereas Hg and Cd data were best fitted to the Spherical and Exponential model respectively. The ordinary Kriging interpolation was used to generate the filled contour maps (Figure 2). Similar spatial distribution of Cu, Zn, Cd, and Pb were found in the geochemical maps, and As and Hg showed similarity. This provided a spatial refinement and reconfirmation of the results in the statistical analysis, in which strong associations were found among Cu, Zn Pb and Cd, and between As and Hg (Table 2). The contour maps displayed several critical concentration 'hotspots' for each of the metals investigated. In general, the higher concentrations of metals (hotspots) were located in Liwan, Yuexiu and Haizhu districts.

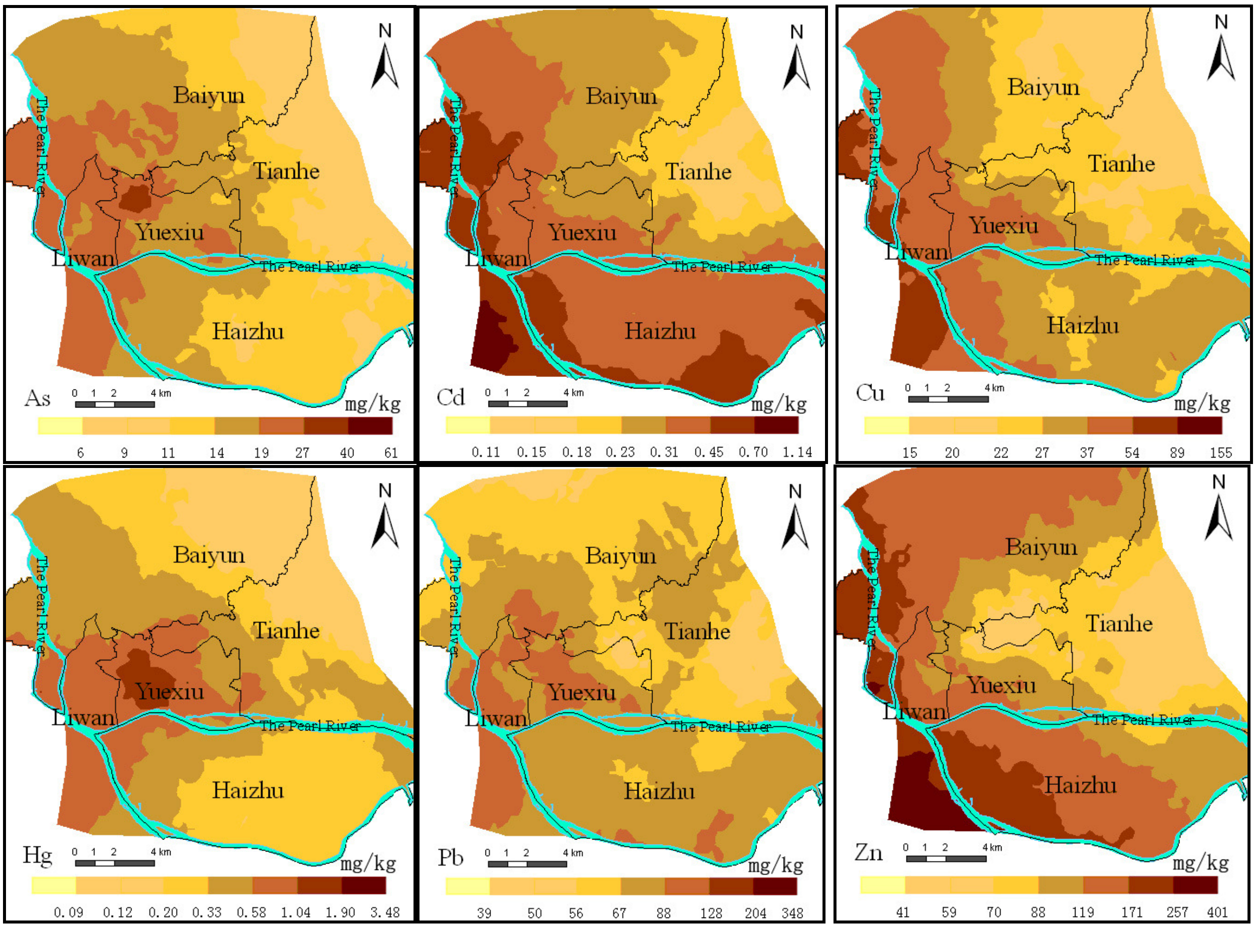

Figure 2. Distribution maps of As, Cd, Cu, Hg, Pb, and Zn concentrations in urban soils.

Metal distribution was closely related with industrial activities and city history. For example, several factories were located in the Liwan district such as a power plant, cement factory, casting factory and smelting plant. Similarly, in the Haizhu district a chemical plant, battery factory and toy factory existed. Waste emission from factories has led to elevated metal (Cu, Cd, Pb and Zn) concentration in soils. In the Yuexiu district, the old city centre has more than a 2000-year history of domestic activities such as coal burning, which has resulted in As and Hg accumulations in soils. Furthermore, some urban parks were formerly a rubbish dumping site for both municipal and industrial wastes. The data presented here established a baseline for future monitoring and management of these metals in urban soils.

Principal components analysis (PCA)

The results of PCA for metal contents indicated that the "eigenvalues" of the three extracted components are greater than one, both before and after the matrix rotation. As a consequence, metals could be grouped into a three-component model, which accounted for about 66% of all data variation. Spatial representation of the three rotated components is shown in Figure 3. The first principal component (PC1), explains 26.03% of the total variation, which exhibited a high positive factor loading on Cu, Zn, Pb and Cd. The second principal component (PC2) explains 23.39% of the total variation, and exhibited a high positive factor loading on Ni, Fe Mn and Cd. The third principal component (PC3) shows a high positive factor loading on Hg and As. For the first and third group metals, they illustrated an obvious accumulation according to their soil background values (Table 1), and previous investigations indicated they were strongly related to the impact of urbanization and industrialization. They probably mainly originated from anthropogenic origins, including industrial, road traffic and domestic emission.
The second group consisted of Fe, Ni, and Mn whose concentrations were dominated by the mineralogy of soil parent material. This may be explained by the mean Fe and Ni concentrations measured in these soils, which did not exceed soil background values and Fe had a normal distribution with skewness of 0.61 (Table 1). Similar results can be found in other studies (Lee *et al.* 2006; Zhang 2006).
Cd had a high loading for both PC1 and PC2, which indicates that it possibly has both natural and anthropogenic sources.

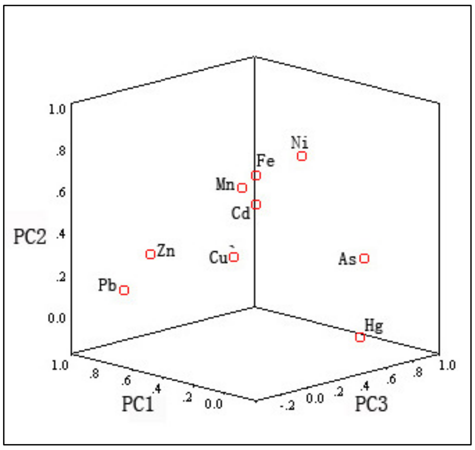

Figure 3. Principal component analysis loading plot for the three rotated components.

Conclusion

The urban soils in Guangzhou showed a wide range in metal concentrations. Additional information from the data set was extracted by GIS-based geostatistics and PCA. The spatial distribution maps of As, Cd, Cu, Hg, Pb, and Zn concentrations, which was generated using Kriging interpolation, displayed several hotspots of heavy metal pollution in Liwan, Yuexiu and Haizhu administrative districts. PCA suggested that Fe, Ni and Mn are predominantly derived from natural sources; As, Cu, Hg, Pb and Zn from anthropogenic sources; and Cd from both sources.

Furthermore, this work also highlights the need for: (i) further studies in assessing both the human and ecosystem risks associated with urban contaminated soils, (ii) establishing Chinese soil guideline values for urban environments, and (iii) undertaking remediation measures for contaminated urban soils.

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