

Distributional characteristics and sources of elements in soil from typical area of Pearl River Delta economic zone, Guangdong Province, China

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Received: 12 March 2014/Revised: 21 May 2014/Accepted: 5 June 2014/Published online: 27 March 2015
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Abstract Dongguan City, located in the Pearl River Delta economic zone of China, is famous for its rapid developing township-enterprises in the past 30 years. A total of 759 composite soil samples, including 606 surface soil samples and 153 deep soil samples, have been collected in the city. These samples have been analyzed for 13 elements (Al, As, Cu, Cd, Co, Cr, Fe, Hg, Mn, Ni, Pb, Si, and Zn) and other parameters (pH values and organic matter) to evaluate the influence of anthropic activities on the soil environmental quality and to identify the spatial distribution of heavy metals and their possible sources. The results indicate that the average concentrations of heavy metals in soil were significantly lower than the threshold of the second grade of the Soil Environment Quality Standard in China (GB15618-1995) and the soil environmental quality in this area is comparatively good. But in comparison with local soil geochemical baseline values, As, Cd, Cu, Hg, Pb, and Zn have accumulated remarkably. Specifically, the average concentrations of As, Cd, Cu, and Hg in the small part samples of the west plain and central areas are higher than the national second-grade quality standard, indicating some level of contamination. Multivariate and geostatistical methods have been applied to differentiate the influences of natural processes and human activities on the concentration of heavy metals in surface soils in the study area. Cluster and factor analyses result in the grouping of Al, As, Cr, Cu, Fe, Ni, and Si into factor

F1; Co, Mn, Pb, and Zn into F2; and Cd and Hg into F3. The spatial pattern of the three factors may be well demonstrated by geostatistical analysis. It is shown that the first factor could be considered as a natural source controlled by parent material. The second factor could be referred to as “industrial and traffic pollution sources”. The source of the third factor is mainly controlled by long-term anthropic activities, including agricultural activities, fossil fuel consumption, and atmospheric deposition.

Keywords Heavy metals · Distributional characteristics · Source · Multivariate statistics · Geostatistics · Typical intensive area of township-enterprises · Pearl River Delta economic zone

1 Introduction

In the last three decades, the sustained and rapid socio-economic development of the Pearl River Delta (PRD) region was gained at the cost of resources and environment. Soil polluted by heavy metals is one of the main environmental problems in the PRD economic zone (Gao and Guo 2003; Xie 2003; Zhou et al. 2004; Zhu et al. 2005). It directly threatens the stability of regional ecosystem and food safety, and has profound influences on economic sustainability, especially for sustainable agriculture and human health (Chen et al. 1997; Zhu et al. 2005). The natural concentration of heavy metals in soil depends primarily on the geological parent material compositions (De Temmerman et al. 2003). However, normal agricultural practices generally cause an enrichment of some elements (Mantovi et al. 2003). Mining and other human activities, including the combustion of fossil fuels and waste incineration, have significantly increased the emission of heavy

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metals into the atmosphere. The natural input of several trace elements into soils due to pedogenesis has been exceeded by human input (Facchinelli et al. 2001). Whether from natural or anthropogenic sources, heavy metals might have a negative effect on the quality of agricultural products and result in the transfer of trace metals to the human diet (Baranowska et al. 2005; Zheng et al. 2007).

In order to provide a scientific basis for socio-economic development and planning to improve the ecological environment in this region, the People's Government of Guangdong Province and the China Geological Survey (CGS) signed an agreement of "Agro-geological survey and eco-geochemical assessment in Pearl River Delta Economic Zone of Guangdong Province" in January 2006. Dongguan City, a typical intensive area of township-enterprises in the PRD economic zone, was taken as the study area in this paper. The main sources of heavy metals in the soil were analyzed through a combination of multivariate statistics and geostatistics.

Dongguan city (22°39'N–23°09'N, 113°31'E–114°15'E) is famous for its rapid industrialization in the past 30 years. It is the most intensive area of township-enterprises in the PRD economic zone. It is situated within the northeastern PRD and in the south of Guangdong Province, China, and only has a total area of 2465 km² (5.9 % of PRD), with a population over eight million (32 % of PRD). This city connects with Guangzhou City in the north, and Shenzhen City and Hong Kong in the south. The dominant agricultural products include rice, vegetables, banana, litchi, longan, pineapple, and aquatic products.

Since the reform and open policy in China, industry has increased dramatically at 22 % annually. Gradually, export-oriented industries have expanded, including household electrical appliances, communication equipment, textile and clothing, electronics, building materials, medicine, hardware, and the plastic chemical industry. Dongguan has become an important industry base of international manufacturing. According to statistics, the number of industrial enterprises in Dongguan reached 16,000 in 2005. In Humen (a town in Dongguan) alone, there are more than 100 enterprises, including an electroplating factory, a paper mill, a rinsing facility, and other heavy-polluting enterprises. Since the inception of the industrial growth, agro-environmental problems have emerged and agricultural production has been strongly affected. Large amounts of pollutants, including heavy metals, have been transported continuously into agricultural soils either directly or indirectly. With the dual influence of natural and anthropic input, the sources of trace elements become more complex.

The objectives of this study are (i) to investigate the concentrations of heavy metals, including As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the soil of a typical township-

enterprise intensively developed area in the PRD economic zone, (ii) to characterize spatial distribution of heavy metals in soil, and (iii) to identify their possible sources in surface soils by a combination of multivariate statistics and geostatistics.

2 Materials and methods

2.1 Characteristics of the study area

The southeast of Dongguan is in low mountains and hilly regions. The northwest tilts over the low hill, platform, and valley plain. The west and south of the study area are low-lying river delta river network areas and marine plain areas. River networks are dense in this area, and it is influenced by the river flood tide because it is situated in an estuary zone. Dongguan belongs to the subtropical monsoon climate—mild and wet with plentiful rainfall. The mean annual temperature is 21.82 °C.

Dongguan City has seven soil types in total, in which the latosolic red soil and paddy soil are the most common types and account for 51.43 % and 45.20 %, respectively, of the total land area. The latosolic red soil is mainly distributed in the hilly and tableland areas, with the parent material mainly of granite and sandy shale. The paddy soils are mainly distributed in the plain area, with the parent materials being mainly diluvial deposits, river alluvium, delta alluvial deposits, and littoral sediments. The rocky soil and seashore saline soil account for 2.56 %, while other soil types account for less than 1 %. The soil textures are mainly clay loam and loam, and secondarily clay and sand.

According to land use surveys in 2008, farm land covers 1780.4 km², which accounts for 72.23 % of total land in the study area. Cultivated land, garden plots, and forest land account for 30.96 %, 35.87 %, and 32.17 % respectively; construction accounts for 20.18 % of total land area; and unused land accounts for 7.59 %.

Dongguan can be divided into four areas based on geomorphological characteristics. The north environmental protection area (I) is so-called due to the strict control of various polluting industries in order to protect the water source since 1991. The area is located in the eastern part of the upriver east river, and covers 213.0 km². It acts as the main water source for the east river, Shenzhen, as well as for the Dongguan canals. The west plain area (II) has abundant water and high density of town-owned enterprises, and consists of 11 towns with an area of 549.7 km². Area soils are predominantly derived from deposits from the east river, and many resource-consuming enterprises were developed at the early stage of China's reform and open policy due to convenient traffic and abundant rivers passing by. The central area (III) consists of eight towns

with an area of 693.5 km². Parent materials of area (III) soils are modern sediments from the east river, granite, and red sandstone. The southeast hilly area (IV) consists of nine towns with an area of 1018.6 km², where the water source is short and the parent materials are mainly granite and sandstone.

2.2 Soil sampling and chemical analysis

Surface and deep soils were separately collected in the study area according to two-layer grid sampling (CGS 2011). Surface soils were collected at a sampling density of one sample/km². All samples were from 0 to 20 cm in depth. Four surface soil samples from adjacent grids were combined into one sample for chemical analysis. Samples from the deep soil at 150–200 cm depth were collected at a sampling density of one sample/4 km². Four deep soil samples from adjacent grids of land area were combined into one sample for chemical analysis. A total of 2424 surface soil samples and 612 deep soil samples have been collected, with 606 composite surface soil samples and 153 composite deep soil samples prepared for analysis (Fig. 1).

Soil samples were prepared according to the standard procedure in the guidebook for multi-purpose regional geochemical survey (DD2005-01). The soil samples were air dried at room temperature. Impurities, such as stones and tree leaves, were removed. Coarse soil particles (>0.84 mm) were crumbled by wooden hammer, and the samples were sieved by a nylon screen to <0.84 mm after being dried; 100 g samples <0.84 mm were further processed with an agate mortar to <0.074 mm for analysis. The test was conducted by the analytical center of the Institute of Geophysical and Geochemical Exploration (IGGE).

Table 1 presents the analytical methods and corresponding detection limits. Standard reference materials (SMR) and duplicate samples were used to control analytical quality. Four SMRs of the GSS series (including GSS1, GSS2, GSS3, GSS8, GSS10, and GSS13), produced by IGGE in China, were inserted blindly into each of the 50 soil samples and were analyzed simultaneously with the samples. The logarithmic difference ($\Delta \lg C_{SRM}$) between the analytical value and the standard value of each determination was then calculated to monitor the accuracy of the sample analyses. Analyses were considered acceptable if the $\Delta \lg C_{SRM}$ was <0.12 for samples with concentration within three times the detection limit and <0.10 for samples with concentrations over three times the detection limit. Duplicate samples, equaling 5 % of the total number of samples, were inserted randomly to evaluate the precision of the analyses. The percentage of relative deviation (RD) was calculated. Analyses were considered acceptable if the RD was $-40 \% \leq RD \leq 40 \%$. The logarithmic

difference of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Al₂O₃, Fe₂O₃, SiO₂, and C_{org} in the GSS series ranged from 0.000 to 0.086. The qualification rate of accuracy obtained from logarithmic difference is 100 %. The precision of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Al₂O₃, Fe₂O₃, SiO₂, and C_{org} obtained from replicate analysis varied from -33.94% to 36.81% (Table 2). The results indicate that the test quality accorded with the standard of multi-purpose regional geochemical survey and the analytical data are reliable (CGS 2006).

2.3 Statistical methods

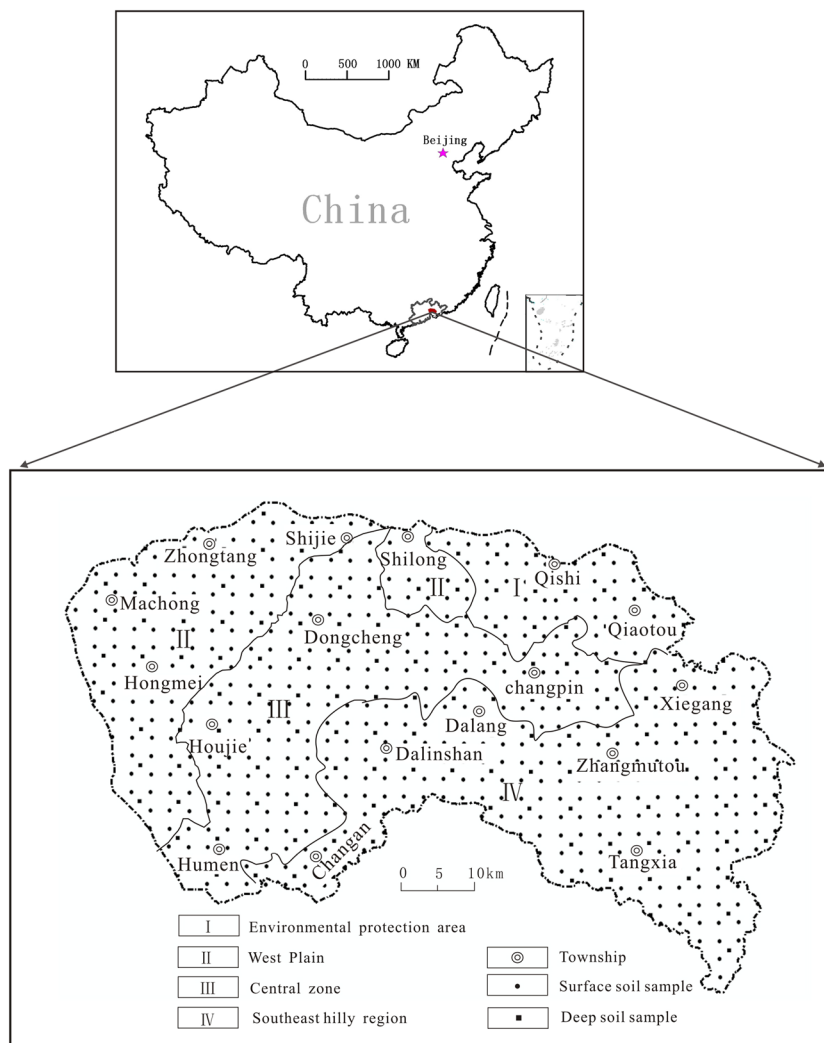
Factor analysis (FA) is applied in this study. FA is a useful statistical tool that can extract latent information from multidimensional data and group the measured elements into fewer groups (Gallego et al. 2002; Liu et al. 2003). Geostatistical analysis is also applied in this study: the technique of a variogram (or semi-variogram) is used to measure the spatial variability of a regionalized variable, and provides the input parameters for the spatial interpolation of kriging (Webster and Oliver 2001; Cai et al. 2008). Ordinary kriging is chosen to create spatial distribution maps of the results of FA.

3 Results

The element concentrations and soil properties of surface soils in Dongguan City are listed in Table 3. The mean value of soil pH was 5.81 (3.91–8.25). The element concentrations range over several orders of magnitude with larger variations. The coefficients of variation (CV) of all heavy metals except Pb (43.93 %) were more than 50 %, and the CV of Hg was the largest (118.18 %). On a large scale, the mean concentrations of heavy metals were significantly lower than the threshold of the second grade of the Soil Environment Quality Standard in China (GB15618 1995).

The mean concentrations of Cd, Cu, Hg, Zn, and SiO₂ in surface soils were significantly higher than in deep soils (Tables 3, 4). The mean concentrations of Mn and Pb in surface soils were similar to those in the deep soil. The mean concentrations of As, Co, Cr, Ni, Al₂O₃, and Fe₂O₃ were significantly lower in surface soils than in deep soils. In this study, the statistics of each element concentration in deep soil were regarded as the soil geochemical baseline value (CGS 2006, 2011). If the element concentration in deep soil obeyed normal distribution or logarithmic normal distribution, the arithmetic mean value or geometric mean value was regarded as the geochemical baseline value. When the element concentration in deep soil did not obey normal or logarithmic normal distribution, the abnormality

Fig. 1 Location of study area and sample sites



higher than mean add three times standard deviation (SD) or lower than mean add three times SD were eliminated repeatedly. If the data that had been eliminated obeyed normal distribution or logarithmic normal distribution, the arithmetic mean value or geometric mean value of the data was regarded as the geochemical baseline value. Otherwise, the mode was regarded as the geochemical baseline value. The geochemical baseline value of each element is listed in Table 3. The mean concentrations of Cr and Ni in surface soil were lower than or close to the soil geochemical baseline values of Dongguan City (Table 3), and the mean concentrations of others in surface soil were higher than the corresponding geochemical baseline value. Results show that Cr and Ni were affected by natural effects; strong leaching action leaves deeper soils enriched in these elements. Other elements affected by human activities are significantly enriched in surface soil. Furthermore, the concentrations of As, Cd, Cu, and Hg of a few samples were significantly higher than the second grade,

with maximums up to 120.3, 128.2, 2.14, and 0.89 mg/kg, respectively.

4 Discussion

4.1 Distributional characteristics and sources of elements in surface soils

Ranges, means, and SD of elements for each district were calculated and are listed in Table 5. The average concentration of Pb in the west plain and central areas was higher than the local geochemical baseline value and followed the order: west plain > central > southeast hill > north environmental protection area. The average concentration of Cd in the west plain area was the highest among all the districts. The highest average concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were all in the west plain area, while the lowest ones were in the north environmental

Table 1 Analysis method and detection limits for samples

Element	Analysis method	Method detection limit
As	HG-AFS	1
Cd	ICP-MS	0.02
Co	ICP-MS	1
Cr	XRF	5
Cu	XRF	1
Hg	CV-AFS	0.0005
Mn	XRF	10
Ni	XRF	2
Pb	XRF	2
Zn	XRF	2
Al ₂ O ₃	XRF	0.05
TFe ₂ O ₃	XRF	0.05
SiO ₂	XRF	0.1
C _{org}	Oxidative pyrolysis—potentiometry	0.1
pH	Potentiometry	0.10

The unit for the content of Al₂O₃, TFe₂O₃, SiO₂, and C_{org} is %; pH is dimensionless; other measurement units are mg/kg

protection area and southeast hilly area. In general, each element in the soil existed at a concentration based on its natural conditions. The results show that the sample sites with elements over the soil geochemical baseline values were concentrated in the west and central areas (Cd, Cu, Hg, Ni, Pb, Zn), and appeared least in the north environmental protection area. The results indicate that soil environmental quality in the area is comparatively good, but some sites in the west plain and central area might be slightly contaminated.

4.2 Source of elements in surface soils

Generally, heavy metal pollution is complicated. Inter-element relationships can provide useful information on trace element sources and pathways (Manta et al. 2002). To obtain valuable information, the partial correlation coefficients are calculated between 13 elements and their related soil properties (pH, organic matter). The correlation analyses show that As, Cr, and Ni are significantly as well as positively correlated at the 0.01 significance level, which may suggest a common origin. Cd has a significant correlation with Hg, Ni, Zn, and organic matter, but little significant correlation with Cu.

The results of FA for trace element concentrations are presented in Table 6. Three factors are extracted from the available data set, and account for over 75 % of all the data variation. Al, As, Cr, Cu, Fe, Ni, and Si are strongly associated with the first factor (F1). The second factor (F2) includes Co, Mn, Pb, and Zn. The third factor (F3) mostly condenses the information of Cd, Cu, Hg, and Zn; it is

worth noting that Cu and Zn are also partially represented in F1 and F2, respectively.

F1 can be considered to be a lithogenic component, as the variability of the elements seems to be controlled by the parent material. The parent material factor explains 33.06 % of the total variance and it is the most important component. This result suggests that the distributions of As, Cr, Cu, and Ni have a lithogenic control. On the other hand, relatively lower loading factors of As, Cr, Cu, and Ni in the anthropogenic components (F2 and F3), suggest other effects (e.g., agricultural practices or industrial contamination) on the status of these elements in the soil.

F2 includes Co, Pb, and Zn and can be considered to be an anthropogenic component. According to earlier discussion, the mean concentration of Pb has exceeded the local geochemical baseline value and is moderately enriched in the topsoil. This indicates an anthropic input. Common sources of Pb in soils are manure, sewage sludge, lead-arsenate pesticides, vehicle exhaust, and industrial fumes. Coal burning is also acknowledged to be a source of lead pollution. Although Pb derived from car exhausts does not extend appreciably beyond 30 m from the road (Facchinelli et al. 2001), lead aerosols, industrial fumes, and coal burning exhausts can be carried over longer distances (Kober et al. 1999; Facchinelli et al. 2001).

F3 includes Hg and Cd concentrations, which can be a distinguishing anthropogenic component. It is well known that a lot of chemical fertilizers, manures, and sludge are used in the vegetable fields to increase vegetable outputs (Liu et al. 2004). Phosphate fertilizers are an important source of heavy metals, especially Cd, Cu, and Zn, which

Table 2 Parameters for quality assurance and quality control for soil sample analysis

n	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	C _{org}
Al ₂ C _{SRM}														
GSS1	8	Min	0.0	0.00	0.0	0.00	0	0.0	0.00	0.0	0.01	0.01	0.01	0.00
		Max	0.0	0.06	0.0	0.01	0	0.0	0.01	0.0	0.02	0.01	0.01	0.02
		Mean	0.0	0.02	0.0	0.01	0	0.0	0.01	0.0	0.01	0.01	0.01	0.01
GSS2	8	Min	0.0	0.01	0.0	0.00	0	0.0	0.00	0.0	0.01	0.01	0.00	0.00
		Max	0.0	0.09	0.0	0.03	0	0.0	0.03	0.0	0.02	0.01	0.00	0.01
		Mean	0.0	0.05	0.0	0.02	0	0.0	0.01	0.0	0.01	0.01	0.00	0.01
GSS3	8	Min	0.0	0.01	0.0	0.00	0	0.0	0.02	0.0	0.00	0.01	0.01	0.00
		Max	0.1	0.03	0.0	0.03	0	0.0	0.06	0.0	0.00	0.02	0.02	0.01
		Mean	0.0	0.02	0.0	0.02	0	0.0	0.04	0.0	0.00	0.01	0.01	0.00
GSS8	8	Min	0.0	0.00	0.0	0.00	0	0.0	0.01	0.0	0.01	0.00	0.01	0.02
		Max	0.1	0.03	0.0	0.03	0	0.0	0.03	0.0	0.01	0.01	0.01	0.04
		Mean	0.0	0.02	0.0	0.02	0	0.0	0.02	0.0	0.01	0.00	0.01	0.03
GSS10	8	Min	0.0	0.05	0.0	0.01	0	0.0	0.05	0.0	0.01	0.01	0.00	0.00
		Max	0.0	0.07	0.0	0.05	0	0.0	0.09	0.0	0.01	0.01	0.01	0.02
		Mean	0.0	0.06	0.0	0.04	0	0.0	0.07	0.0	0.01	0.01	0.00	0.01
GSS13	8	Min	0.0	0.01	0.0	0.00	0	0.0	0.00	0.0	0.00	0.01	0.00	0.00
		Max	0.0	0.07	0.0	0.07	0	0.0	0.07	0.0	0.01	0.01	0.00	0.02
		Mean	0.0	0.04	0.0	0.03	0	0.0	0.03	0.0	0.01	0.01	0.00	0.01
RD (%)														
31	Min	-9.24	-33.94	-10.86	-13.20	-8.61	-24.01	-6.21	-7.49	-9.34	-18.74	-5.27	-7.07	-8.22
	Max	17.96	20.39	9.53	28.19	18.92	9.14	13.58	14.58	12.21	6.57	5.38	6.61	18.76
	Mean	2.20	-6.68	0.14	0.93	0.92	-2.70	1.01	2.88	-0.52	-2.97	-0.19	0.39	3.34

The unit for the content of Al₂O₃, TFe₂O₃, SiO₂, and C_{org} is %; other measurement units are mg/kg

Table 3 Summary statistics for element concentrations (mg/kg) in surface soil (n = 606)

	C _{org}	pH	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂
Mean	0.80	5.81	11.7	0.12	6.5	45	21.7	0.11	279	13.7	42.84	61.9	15.84	4.31	70.53
Geometric mean	0.74	5.72	8.7	0.09	5.3	40	18.6	0.08	243	11.6	38.92	53.9	15.04	4.02	70.06
Min	0.13	3.91	0.7	0.02	1.1	2	2.0	0.003	54	1.7	12.00	11.9	3.93	1.03	45.42
25%	0.58	4.99	5.3	0.07	3.1	32	13.8	0.01	171	7.9	28.01	37.0	12.05	3.09	65.11
Median	0.76	5.57	9.2	0.09	5.6	44	19.1	0.08	239	12.2	40.61	54.8	16.22	4.15	70.25
75%	0.95	6.54	14.9	0.15	9.0	56	26.0	0.13	343	17.8	53.00	76.7	19.34	5.20	76.70
Max	2.15	8.25	120.3	0.89	21.6	360	128.2	2.14	2760	211.6	119.00	345.1	27.74	12.03	90.43
SD	0.30	1.02	10.6	0.09	4.0	23	13.5	0.13	186	10.8	19.26	36.5	4.76	1.61	8.04
CV (%)	37.50	17.56	90.50	75.00	62.30	51.01	62.32	117.86	67.00	78.66	43.93	58.86	29.80	37.50	11.40
Soil geochemical baseline value			9.8	0.05	5.9	51	16.6	0.05	240	14.3	40.15	49.0	18.93	5.17	66.42
Exceeding standard rate (%)			46.20	85.97	N/A	38.94	56.44	74.75	N/A	38.78	50.33	58.09	N/A	N/A	N/A
Threshold of second grade ^a		<6.5	40	0.30	N/A	150	50	0.30	N/A	40	250	200	N/A	N/A	N/A
		6.5–7.5	30	0.30	N/A	200	100	0.50	N/A	50	300	250	N/A	N/A	N/A
		>7.5	25	0.60	N/A	250	100	1.0	N/A	60	350	300	N/A	N/A	N/A
Exceeding standard rate /%			2.31	1.32	N/A	0.17	2.15	2.15	N/A	0.50	0.00	0.83	N/A	N/A	N/A

The unit for the content of C_{org} is %; pH is dimensionless; other measurement units are mg/kg

^a Soil environment quality standards of China (GB15618 1995)

Table 4 Summary statistics for element concentrations (mg/kg) in deep soil (n = 153)

	C _{org}	pH	As	Cd	Co	Cr	Cu	Hg	Ni	Mn	Pb	Zn	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂
Mean	0.46	5.26	18.1	0.09	7.7	52	19.8	0.07	16.3	264	43.51	56.9	19.01	5.20	66.27
Geometric mean	0.40	5.23	10.2	0.07	6.2	48	17.3	0.05	14.5	226	40.31	49.3	18.54	4.97	65.90
Median	0.36	5.19	10.3	0.05	6.1	51	16.8	0.05	14.7	240	41.32	47.0	19.09	5.12	66.52
Min	0.14	3.61	1.0	0.02	2.2	12	3.3	0.02	3.9	60	15.57	15.0	8.52	1.84	50.27
Max	1.43	7.22	838.0	0.58	44.9	122	137.4	0.83	86.1	1077	115.11	271.0	28.87	9.52	84.11
SD	0.28	0.62	67.2	0.08	6.2	19	13.0	0.07	9.3	152	17.45	35.3	4.12	1.49	7.00
CV (%)	60.48	11.86	371.77	90.39	80.20	36.52	65.80	110.82	57.07	57.87	40.10	62.07	21.67	28.68	10.57

Table 5 Average concentrations of elements in surface soil in different areas

	I (n = 58) Mean ± SD	II (n = 106) Mean ± SD	III (n = 228) Mean ± SD	IV (n = 214) Mean ± SD
As (mg/kg)	8.4 ± 3.3	17.6 ± 6.6	9.0 ± 5.3	12.5 ± 15.3
Cd (mg/kg)	0.14 ± 0.15	0.17 ± 0.07	0.11 ± 0.08	0.09 ± 0.06
Co (mg/kg)	4.7 ± 2.5	10.0 ± 2.5	5.7 ± 4.0	5.9 ± 4.0
Cr (mg/kg)	43 ± 10	54 ± 16	45 ± 27	43 ± 23
Cu (mg/kg)	19.3 ± 9.0	28.4 ± 14.1	21.8 ± 14.1	19.0 ± 12.6
Hg (mg/kg)	0.17 ± 0.24	0.16 ± 0.21	0.12 ± 0.08	0.06 ± 0.03
Mn (mg/kg)	237 ± 125	325 ± 119	246 ± 145	295 ± 249
Ni (mg/kg)	12.3 ± 4.0	19.9 ± 6.1	13.5 ± 14.9	11.4 ± 6.8
Pb (mg/kg)	34.28 ± 10.96	53.88 ± 11.06	44.01 ± 20.82	38.44 ± 19.95
Zn (mg/kg)	62.3 ± 38.0	93.3 ± 36.5	57.9 ± 37.4	50.7 ± 24.6
Al ₂ O ₃ (%)	13.66 ± 3.97	18.09 ± 3.23	15.43 ± 4.53	15.54 ± 5.39
Fe ₂ O ₃ (%)	3.47 ± 0.88	5.17 ± 1.26	3.88 ± 1.29	4.53 ± 1.95
SiO ₂ (%)	74.41 ± 5.76	64.64 ± 5.65	71.73 ± 7.18	71.34 ± 9.06
C _{org} (%)	0.74 ± 0.33	0.95 ± 0.33	0.73 ± 0.24	0.81 ± 0.32
pH	6.06 ± 0.92	5.55 ± 1.18	6.13 ± 1.04	5.53 ± 0.80

I north environmental protection area, II west plain area, III central area, IV southeast hill area

Table 6 Component matrix for 13 element concentrations in surface soil (n = 606)

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Cumulative (%)
F1	0.793	0.212	0.411	0.843	0.727	0.073	0.022	0.798	0.197	0.269	0.582	0.803	-0.694	33.06
F2	0.140	0.465	0.764	-0.035	0.157	0.026	-0.861	0.371	0.696	0.766	0.561	0.426	-0.574	60.92
F3	0.166	0.67	0.067	0.28	0.484	0.765	-0.033	0.242	0.185	0.387	-0.343	-0.225	0.238	75.14

Extraction method principal component analysis, Rotation method varimax with Kaiser normalization

enter agricultural soils. Other sources of Cd may include other inorganic fertilizers (e.g., nitrogen or potash), atmospheric deposition or anthropic wastes such as sewage sludge, wastewater, or waste materials. Meanwhile, because the area is an important international manufacturing industry base in China, and connects with Guangzhou and Shenzhen, which are two economically developed cities in China, the industrial fumes and atmospheric deposition may also be important sources of Hg enrichment in soil

(Linak and Wendt 1994; Ikingura et al. 2006; Wang et al. 2003; Mukherjee and Zevenhoven 2006; Mukherjee et al. 2008). Zheng et al. (2011) estimated the total mercury emissions to be 17,244 kg in the PRD region for the year of 2008, and anthropogenic activities were dominant sources. Dongguan is one of the largest regions for mercury emission (Zheng et al. 2011). Therefore, F3 can also be an anthropogenic component due to the isolation of Cd and Hg from lithogenic elements.

Cluster analysis is often coupled with FA to confirm results and provide grouping of variables (Facchinelli et al. 2001). In order to identify distinct sources of heavy metals, cluster analysis was performed on 13 elements. The 13 elements in soils can be classified into three types based on the correlation coefficients by using the furthest neighbor linkage method. Group I is comprised of Al, As, Cr, Fe, Mn, Ni, and Si; Group 2 is comprised of Co, Pb, and Zn; and Group 3 includes Cd and Hg. The elements in each group have similar sources or releasing principles in soils. The results are in good agreement with FA results.

Cu has approximative loading factors in the first and third principal factors, indicating a mixed source from natural and anthropic origins. Cd and Zn have approximative loading factors in the second and third principal factors, indicating a mixed source from two different kinds of anthropogenic inputs. The sources may be associated with Cd-based or Zn-based agrochemicals related to specific agronomic practices.

According to the above discussion, it seems reasonable to conclude that Cd, Hg, Pb, and Zn constitute an anthropogenic component related to specific human activities, whereas the other elements (As, Cr, and Ni) are obviously associated with parent material. In the case of Cu, it displays a combined relationship with both groups and seems to have both natural and anthropic origins.

The attributes of the semivariograms for each factor are summarized in Table 7. Semivariograms show that the first and the second factors are well fitted with the spherical model ($r^2 = 0.852, 0.993$, respectively), whereas the third factor is better fitted to the exponential model ($r^2 = 0.973$). The theoretical model is plotted for each factor obtained.

The nugget/still ratios can be regarded as the criterion to classify the spatial dependence of soil properties (Facchinelli et al. 2001). The nugget/sill ratio for all the three factors is below 50 % (Table 4), which suggests that the spatial heterogeneity of these factors is mainly caused by their spatial correlation. Among these factors, the first factor ($C_0/(C + C_0) = 0.35$) and the second factor ($C_0/(C + C_0) = 0.36$) show a stronger spatial correlation than the third factor ($C_0/(C + C_0) = 0.46$).

In order to know the distribution patterns of the three factors, kriging interpolation is used to obtain the spatial distribution of the scores on principal components (Figs. 2, 3, 4). The higher scores of the first factor are in the west of the study area (Fig. 2). Compared to the parent materials of the soil, the distribution of the higher scores of F1 shows similar trends to the distribution of alluvial and marine deposits (Fig. 5). The distribution of the lower scores is controlled by the soil derived from acidic eruptive rocks and granite. All of these observations suggest that natural factors play an important role in controlling the distribution

Table 7 Best-fitted semivariogram models of surface soil elements and their parameters (n = 606)

Element	Model	Nugget (C_0)	Still ($C + C_0$)	Nugget/still ($C_0/(C + C_0)$)	Range (A_0) (m)	r^2	RSS
F1	Spherical	0.319	0.909	0.351	11420	0.852	0.043
F2	Spherical	0.430	1.168	0.368	30970	0.993	0.008
F3	Exponential	0.461	1.005	0.459	32610	0.973	0.008

Fig. 2 Spatial distributions of factor 1



Fig. 3 Spatial distributions of factor 2

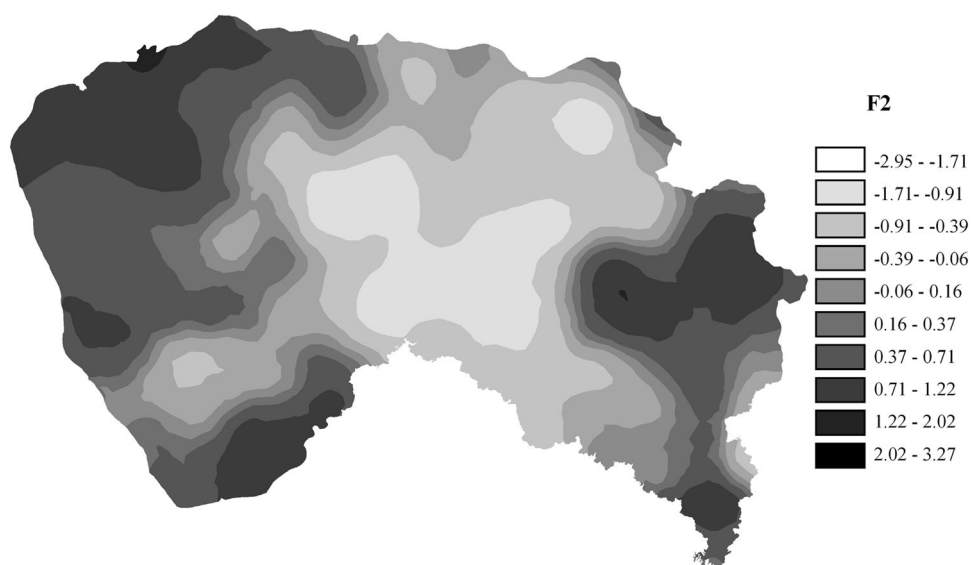
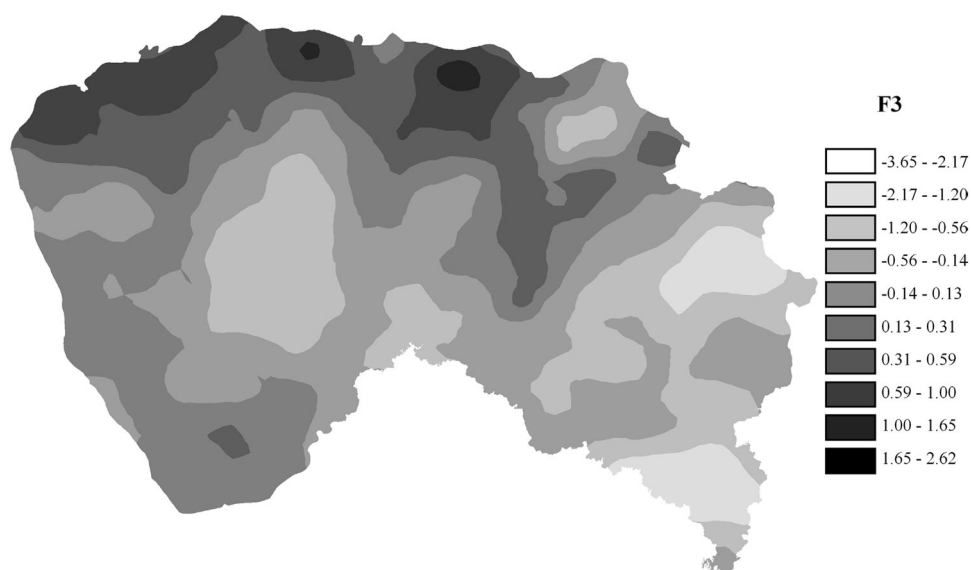


Fig. 4 Spatial distributions of factor 3



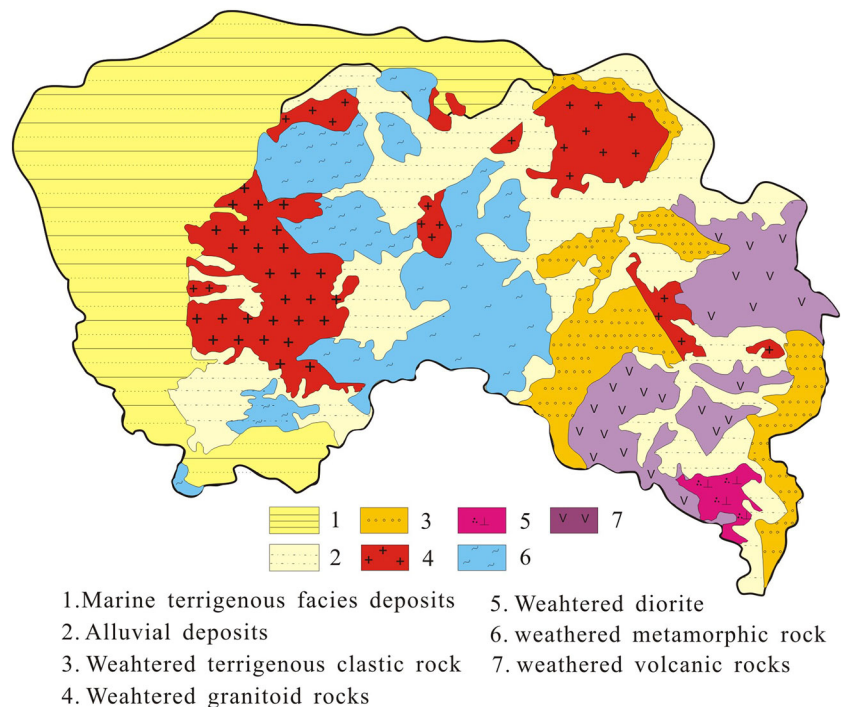
of F1. The result coincides with the analysis of the structure mentioned earlier in this article.

The higher scores of F2 are distributed in the west plain and central areas, especially in Zhongtang, Humeng, and Chashan (three towns in Dongguan) (Fig. 3). Because of the prominent regional advantages, convenient traffic, and abundant water resources, some resource-consuming enterprises have developed rapidly in the west plain area, at the initial stage of the reform period and during the past 30 years. With the increasing development of heavily polluting industries, a great number of heavy metal pollutants have been discharged into the environment, and the area has become the most severely polluted part of Dongguan City.

The spatial distribution of F3 distinctly differs from the other two factors, showing a trend of nonpoint source

pollution (Fig. 4). It is reported that Cd and Hg pollution in urban soil is widespread in China, and usually originates from the application of agrochemicals, sewage irrigation, fossil fuel consumption (especially coal burning), and atmospheric deposition (Nakagawa and Hiromoto 1997; Wang et al. 2003; Kuo et al. 2006). Cd is usually considered as a marking element of agricultural activities, which includes the use of pesticides, chemical fertilizers, and so on (Nicholson et al. 2003; Rodriguez et al. 2006). According to statistics (Bureau of Statistics of Dongguan 2005), there have been two million tons of chemical fertilizers and 35 thousand tons of pesticides used in Dongguan City since 1990. The application rate of pesticides and chemical fertilizers is generally much lower in China. Approximately 70 % of pesticides and fertilizers drain into

Fig. 5 Soil parent materials in study area



the soil, water, and air. Long-term agricultural production activities result in an obvious accumulation of heavy metals such as As, Cd, and Cu in the soils. In addition, coal has been used for many years in China. Many cities have been reported to have Hg pollution problems, especially in South China (Nakagawa and Hiromoto 1997; Wang et al. 2003). Therefore, the source of F3 must mainly be controlled by long-term anthropic activities as a consequence of agricultural activities, fossil fuel consumption, and atmospheric deposition.

The concentrations of heavy metals in soils from different parent materials vary greatly. The mean concentrations of As, Cr, and Ni in soils derived from marine terrigenous facies deposits are 2.79, 2.77, and 2.87 times of those derived from sandstone and shale, respectively. The concentrations of As, Cr, Cu, Hg, Ni, and Zn in surface soils derived from marine terrigenous facies deposits are the highest in all parent materials. The concentrations of Pb in surface soils derived from marine terrigenous facies deposits and granite are higher than concentrations derived from the other parent materials. Moreover, the average concentration of Cd in surface soils derived from granite is the lowest.

5 Conclusions

The results obtained in this study increase one's knowledge of heavy metal concentrations and their possible sources in the soils. The results obtained in this study indicate soil

environmental quality in the area of Dongguan City, China, is comparatively good. On a large scale, the average concentrations of heavy metals were significantly lower than the threshold of the second grade of Soil Environment Quality Standard in China (GB15618 1995), but higher than local soil geochemical baseline values for elements analyzed (the exceptions being Cr and Ni). Isolated areas of the west plain and central areas are slightly contaminated, probably due to different amounts and types of key pollution sources in each area. The concentrations of As, Cd, Cu, and Hg in the samples are higher than the national second grade quality standard, with maximum values up to 120.3, 0.89, 128.2, and 2.14 mg/kg respectively.

A combination of multivariate statistical and geostatistical methods was performed on 13 heavy metals, identifying three principal components to represent the variability of heavy metals in agricultural soils.

As, Cr, Ni, and partial Cu concentrations, dominating the first principal component, represent natural soil parent materials. The higher values of F1 distributed in the west plain area are affected by marine sediment and fluvial deposition; the lower values in the central and southeast hilly areas are mainly controlled by the distribution of weathering materials derived from granites and acidic volcanic rocks. Variability of scores on the second and third principal components (F2 and F3) may mainly be due to the influence of anthropic activities. The higher scores of F2 (Pb) are distributed in the west plain and central areas, especially in Zhongtang, Humen, and Chashan, which are

mainly affected by industry and traffic pollution. Finally, the spatial distribution of F3 (Cd and Hg) shows a trend of nonpoint source pollution, mainly due to long-term anthropic activities, especially fossil fuel consumption, atmospheric deposition, and agricultural activities.

Acknowledgments This work was supported by the China Geological Survey Project (1212010511216) and Environmental Protection Special Foundation of Guangdong Provincial (Guangdong Environment [2014]126). We also would like to thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of the paper.

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