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ORIGINAL ARTICLE

Changes of spatial distributions in copper and lead in Shenzhen surface soil over a 20-year period

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Abstract Fifty-two surface soil samples from agricultural, forest, and grassland sites were collected from the Shenzhen municipal area for determination of copper and lead levels. The spatial dependence of the measured results was quantified using semivariogram modeling, and structural changes in copper and lead in Shenzhen surface soil were analyzed during the past 20 years from the late 1980s to 2009. The resulting semivariogram direction of copper was from northwest to southwest, while that of lead was from east to northwest.

Keywords Structural change · Surface soil · Shenzhen

Introduction

Soil acts as a substrate for plants, which form the primary level of the terrestrial food chain. Many trace metals in soil are essential to plants at low levels but toxic above certain limits. In the 1980s, Tao (1990, 1995a, b, 1998) studied the background levels of copper and lead in Shenzhen surface soil followed by a number of other studies (Liao et al. 1999; Zheng and Lin 1996a, 1996b). In recent years, Shenzhen has undergone rapid development and urbanization, leading to the accumulation of heavy metals in different areas. Furthermore, previous studies (Lin et al. 2004; Lu et al. 2009; Ning et al. 2007; Shi et al. 2006; Shi et al. 2007; Tang et al. 2007) focused primarily on agricultural lands, reservoir areas, and mangroves. Thus a new system of soil research is needed as structural changes of copper and lead in the surface soil of Shenzhen over the past 20 years have not been investigated.

Spatial autocorrelation is the correlation among values of a single variable across a two-dimensional surface that are locationally referenced or tied together by an underlying spatial structure. Like many other geochemical parameters, trace metal contents in soil are typically regionalized variables (Rivoirard 1987). The values of such variables are usually position dependent. A number of mathematical methods are available for analysis of this kind of data, of which autocorrelation calculation, trend surface fitting, moving average smoothing, geometric interpolation, and geostatistical analysis are most often used (Tao 1995a).

One of the most important purposes of applying spatial analysis to environmental geochemical data is to interpolate values between sampling locations based on a discrete data set and to create a grid of predicted estimates for mapping purposes (Tao 1995a). This paper focuses solely on the structural changes of copper and lead in Shenzhen soil over the last 20 years.

Materials and methods

Research background

The Shenzhen region, located along the central coastal area of southern Guangdong Province, is the passageway from mainland China to Hong Kong (Fig. 1) and has a total land

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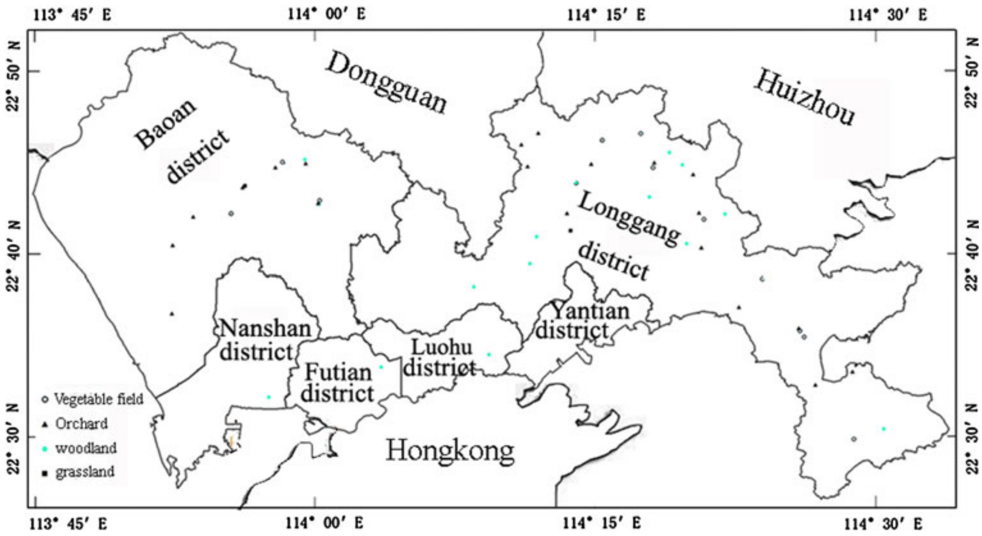
Fig. 1 Sampling map



area of 1948.69 km^2. According to soil horizontal zonality, the main soil types are yellow soil, red soil, and lateritic red soil. Furthermore, Shenzhen was once a rural area, so other soil types also include lactose, paddy soil, seashore sand soil, and saline soil. Vegetation covers 50–80% of the land area. From the 1880s to the 1910s, local industry shifted from traditional agriculture to modern industry, leading to increased pollution of air, water, and soil.

Sampling

A total of 52 surface soil (0–10 cm) samples were collected in March 2009 from agricultural fields, orchards, woodland, and grasslands in Shenzhen on an 8 × 8 km grid. Five blocks of intact soil in an area of approximately 100 m^2 were collected for one sample; the blocks were mixed together and part of the sample was then chosen using the quartation method. Figure 1 presents a map of the sampling locations. All the samples were ground after air drying, passed through 10 mesh and 20 mesh screens, and reserved. Some samples chosen by quartation were analyzed for heavy metal quality and chemical configuration, ground again by carnelian mortar, and passed through a 100 mesh screen.

Soil analysis

Concentrations of copper, lead, zinc, cadmium, chromium, and nickel were measured at the Institute of Soil Science, Chinese Academy of Sciences. All six of these heavy metals except cadmium were digested with HF–HNO$_3$–HClO$_4$ and measured with an atomic absorption spectrophotometer. The concentration of cadmium was digested with HF–HNO$_3$–HClO$_4$ and measured with a graphite furnace atomic absorption spectrophotometer (Varian SpectrAA220FS). To ensure data accuracy, national soil criterion material (GSS series) was used as an inner label during the measurement process.

Methods

The software package GS+ Geostatistics for the Environmental Sciences was used to analyze the semivariance of copper and lead.

Results and discussion

Overall changes in copper and lead contents over 20 years

In the late of 1980s, Tao (1998) collected 83 surface soil samples in Shenzhen area and measured its content of copper and lead with flameless atomic absorption photospectrometry. Geostatistical techniques were applied to analyze the spatial variations of the factor scores of the first two principal components. The experimental variograms of the factor scores were calculated and fitted with theoretical models both isotropically and anisotropically (in four directions).

Table 1 shows the overall changes in copper and lead contents from the late 1980s to 2009. It shows that the minimum, mean, maximum, and percentile contents of copper and lead increased in varying degrees in Shenzhen soil. The coefficient of variance (CV) can exhibit variations in space. The CV of copper and lead were 59 and 55, respectively, in 2009 and 99 and 72, respectively, in the late 1980s. Both copper and lead had lower variance coefficients in 2009 than in the late 1980s, which indicates that the spatial deviations of copper and lead have

Table 1 Descriptive statistics for copper and lead contents in Shenzhen soil

Heavy metal	Copper[a]	Copper[b]	Lead[a]	Lead[b]
CV	59	99	55	72
Skewness	1.4	2.37	1.86	2.37
Kurtosis	2.69	6.62	5.9	10.37
Mean[c]	21.64	10.8	60.66	38.9
Minimum[c]	5.04	2.1	16.38	3.4
5th Percentile[c]	6.74	2.6	21.94	8.2
10th Percentile[c]	8.00	2.8	26.11	11.3
25th Percentile[c]	12.44	3.9	37.79	20.7
50th Percentile[c]	18.41	6.9	51.58	33.6
75th Percentile[c]	29.44	13.6	76.55	52.6
90th Percentile[c]	34.91	25.2	96.81	67.3
95th Percentile[c]	45.82	38.4	111.9	92.1
Maximum	67.79	61.5	206.3	193

[a] Element contents in 2009

[b] Background contents in the late 1980s

[c] Values are in mg kg^{-1}

decreased due to inhomogeneous pollution source distribution. The spatial distribution of pollution sources can be identified by the semivariance of the samples, as shown in subsections Change of spatial structure of elemental contents over 20 years and Change of directional variograms of elemental contents over 20 years.

The distribution of high/low copper and lead contents in Shenzhen surface soil can be determined using sample skewness and kurtosis values. The skewness values of copper and lead were 1.4 and 1.86, respectively, in 2009, showing a decrease of more than 1 compared to the late 1980s when both had skewness values of 2.37. The kurtosis values of copper and lead were 2.69 and 5.9, respectively, in 2009, also showing a decrease of more than 1 compared to values of 6.62 and 10.37 in the late 1980s. When both skewness and kurtosis values are less than 1, the sample distribution is considered to be a normal distribution. A comparison of the results of skewness and kurtosis in Table 1 shows that samples collected in 2009 were nearer to a normal distribution, i.e., more areas of surface soil in the Shenzhen were polluted and had increased copper and lead contents. Detailed structure information is also presented in subsections Change of spatial structure of elemental contents over 20 years and Change of directional variograms of elemental contents over 20 years.

Change of spatial structure of elemental contents over 20 years

The detailed spatial structure of the elemental contents was examined using variogram analysis with GS+ software. Changes in semivariance of elements according to distance can show the degree of human activity in an area. When human activities are minimal and natural processes are dominant, the line of semivariance shows a rise with increasing distance and then shifts to a flat line arriving on some constant value, which means that the semivariance model is spherical or exponential. Figures 2 and 3 show that the lead distribution was more influenced by human activity than was the copper distribution in 2009, and that human activity influenced lead distribution in Shenzhen surface soil over the 20 years. Nugget (Co) refers to the error caused by experience or small dimension (Yang et al. 2010) and the sill (Co + C) refers to the total variance of structure variance and random variance (Luo et al. 2009). The degree of influence by human activity can be indicated by Co/(Co + C). As Co/(Co + C) becomes smaller, the degree of influence becomes larger. Generally as Co/(Co + C) is smaller than 0.5, human activity has a strong influence to the distribution of heavy metal in soil. When Co/(Co + C) is between of 0.5 and 0.75, human activity has middle influence to the distribution of heavy metal in soil. And when Co/(Co + C) is greater than 0.75, human activity has weak influence to the distribution of heavy metal in soil. Table 2 shows that Co/(Co + C) in 2009 was smaller than 0.5, indicating that human activity has had a strong influence on lead, much stronger than on copper.

Effective range is also an important parameter. Autocorrelation exists in an effective range (Luo et al. 2009). Table 2 shows that the effective ranges of copper were 800 and 10,500 m in 2009 and in the late 1980s, respectively. Copper autocorrelation was obviously stronger in the late 1980s than in 2009. Combining Table 2 and Fig. 3, we find that no autocorrelation exists. Although an effective range exists in Table 2, R^2 has decreased to 0.049. These results show that autocorrelations have decreased over 20 years.

The following analysis shows that human activities have had an influence on almost all surface soil through atmospheric precipitation and agricultural irrigation, with lead influenced more than copper over the 20 studied years.

Change of directional variograms of elemental contents over 20 years

Like many other regionalized variables, two element contents of soil may vary in quite different ways and in different directions. As a consequence, variograms are often two-dimensional functions. To assess possible anisotropy, all variograms were recomputed in all directions with GS+ Geostatistics for the Environmental Sciences software. The directional variograms of copper and lead in the late 1980s and 2009 are illustrated in Figs. 4 and 5, respectively. The results for the late 1980s are shown on the left and those for 2009 on the right in Figs. 4 and 5.

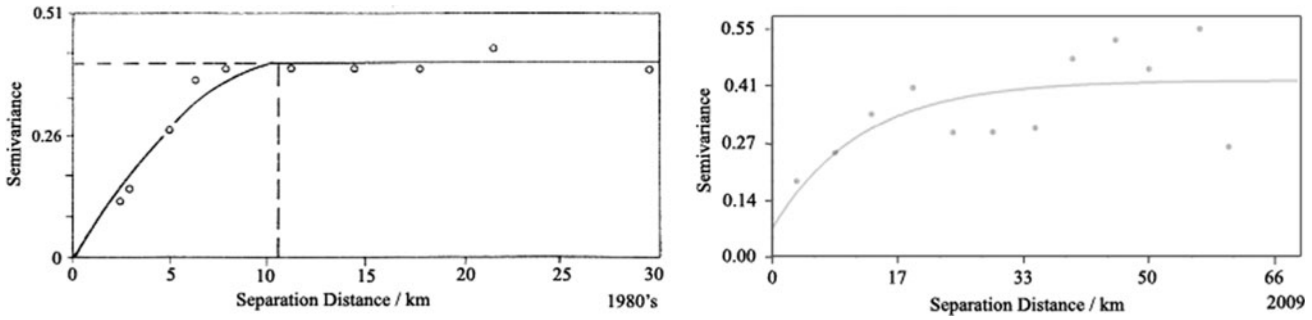


Fig. 2 Change of copper semivariance over 20 years

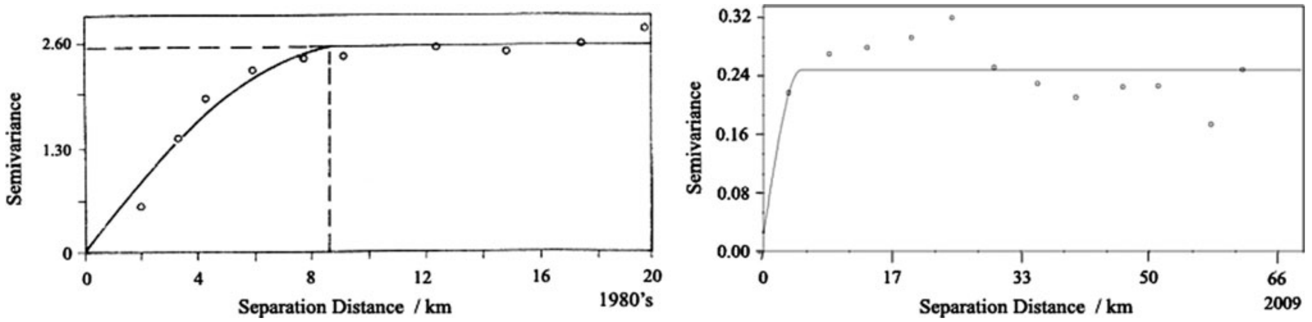


Fig. 3 Change of lead semivariance over 20 years

Table 2 Change of theoretical semivariogram model parameters of copper and lead over 20 years

Elements	model	Nugget Co	Sill Co + C	Effective range/m	Co/(Co + C)	R^2	RSS
Copper[a]	Exponential	0.069	0.424	800	0.163	0.420	0.0871
Copper[b]	Spherical	0	0.408	10,500	–	–	–
Lead[a]	Spherical	0.023	0.246	800	0.092	0.049	0.0167
Lead[b]	Spherical	0	2.535	8,700	–	–	–

[a] Element contents in 2009

[b] Background contents in the late 1980s

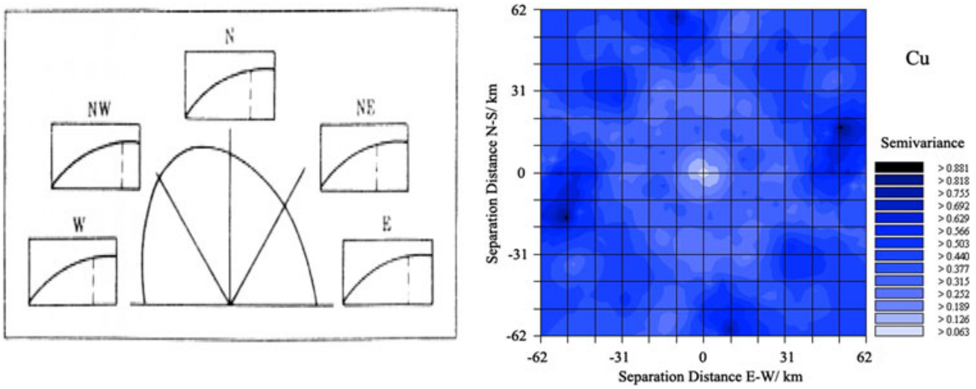


Fig. 4 Change of geometric anisotropy of copper over 20 years

Figure 4 shows that in the late 1980s, the high-content areas of copper were mainly centralized in the north and northwest directions, while in 2009, the high-content areas of copper were mainly centralized in the northeast direction, excluding the north and northwest directions. Comparing the late 1980s with 2009, the copper content in the

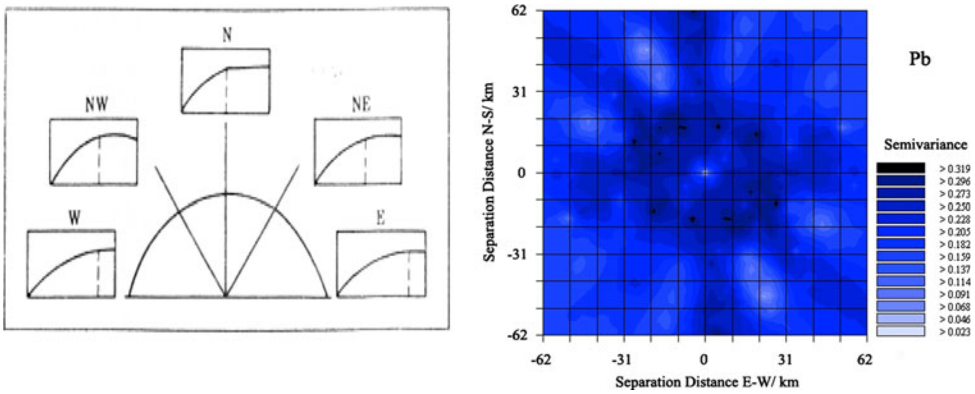


Fig. 5 Change of geometric anisotropy of lead over 20 years

northeast area perhaps changed greatly, from the lowest to the highest level. Of course, minor result errors perhaps exist in different time scale using different software, although the theory and method of software used in 1980s and 2009 are identical. In other words, larger copper accumulation occurred in the Longgang district than in other areas during the 20-year period.

Figure 5 shows that in the late 1980s, there was no obvious direction to the high lead content areas. In 2009, the high lead content areas were centralized more in the northwest direction than in the northeast direction. Comparing the late 1980s with 2009, the lead content changed most in the northwest over 20 years. In other words, lead accumulated more in the Baoan district than in the Longgang district. Lead content also increased outside the old Shenzhen special administrative region during the 20-year period.

In recent years, the Longgang and Baoan districts outside the old Shenzhen special administrative region have industrialized rapidly and many factories have been established. The high copper content in the Longgang district indicates soil environmental problems in areas of development outside the old special administrative region. The source of lead pollution was mainly vehicle traffic before the leaded-gasoline restriction policy was instituted in 1999. These results highlight the influence of traffic on soil lead contents, which have accumulated over 20 years. It is worth emphasizing that high lead content in surface soil may also exist inside the old special region but no relevant information appears in past or current research reports.

Conclusion

According to the results of this study, we conclude that autocorrelation of lead does not exist as compared to 20 years ago, as human activity has changed the state of its spatial distribution. Although slight autocorrelation of copper exists compared with 20 years ago, the autocorrelation has decreased greatly. Human activity has changed the soil environment in the Shenzhen area.

In the late 1980s, there was no obvious directional pattern for lead content in the surface soil of Shenzhen, but over 20 years lead accumulation appeared significantly in the northwest and northeast regions, with more serious accumulation in the northwest. In the same period, obvious accumulation of copper appears to have occurred in the northeast direction. Further research is needed to investigate the significant copper changes in recent years in the Longgang district, located in northeast Shenzhen.

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