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Application of multivariate spatial analysis in scale-based distribution and source study of PAHs in the topsoil: an example from Tianjin, China

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Abstract Polycyclic aromatic hydrocarbons (PAHs) in soil originate from various sources under different spatial scales. Coregionalization analysis is more revealing than univariate geostatistical analysis. Scale-dependent spatial features of variables reflect different sources of spatial variability. In this study, 188 topsoil samples in the Tianjin area were collected. The contents of 16 PAHs and soil background properties were determined for all samples. A multivariate geostatistical approach was used for multi-scale spatial analysis for PAH compounds. Results show that coal combustion was the major source for the spatial distribution patterns of PAHs in the topsoil of the studied area. It worked mainly at the short-range scale (5–10 km). Significant spatial variation patterns were identified. In contrast, no significant spatial distribution trends at the nugget (0–5 km) or long-range scales (10–50 km) were seen. Long-range transport and site contamination of PAHs might not be key contributors in forming the distribution pattern of PAHs in the topsoil of Tianjin area.

Keywords PAHs · Multi-scale spatial distribution · Sources · Tianjin · China

Introduction

As a class of well known carcinogenic compounds originating from incomplete combustion, polycyclic aromatic hydrocarbons (PAHs) are among the most important environmental contaminants in China (Dong et al. 1999). Soil is the primary storage and transfer media for PAHs in the environment. In the last 100 years, the occurrence of PAHs in soil, especially in urban areas, has increased significantly (Jones et al. 1989). Extensive studies have been carried out (Trapido 1999). In China, however, there is a general lack of information concerning sources, fates and effects of PAHs. There is also a lack of comprehensive regional investigation (Fu et al. 2003). Most studies have only focused on a limited number of compounds, and on selected areas (Fu et al. 2003).

In the soil, the concentrations and distributions of PAHs are influenced by source, redistribution and transformation processes. The geostatistical approach has been widely identified as a useful tool in illustrating the spatial patterns of variables (Wang and Tao 1998). In recent years, geostatistics has been applied in studies on the distribution and environmental behavior of PAHs in soils in small areas (Carlon et al. 2001).

Polycyclic aromatic hydrocarbons in soils originate from various sources under different spatial scales. Therefore, the analysis of coregionalization is more revealing than univariate geostatistical analysis. Scale-dependent correlation structure of soil PAH compounds can reflect the different sources of variability (Castrignano et al. 2000). A particular statistical approach is required that combines classical methods with geostatistics to study the regionalized nature of the variables.

Factorial kriging analysis (FKA), developed by Matheron (1982), is well suited for analyzing multivariate spatial data sets. FKA enables the study of spatial distribution and relationships among pollutants and soil parameters at varying spatial scales. The theory

underlying FKA has been described and evaluated in earlier papers (Goovaerts and Webster 1994; Castrignano et al. 2000).

Tianjin is located in northern China adjacent to Beijing (Fig. 1). The city is highly urbanized and industrialized, while a large portion of the surrounding land is used for agriculture. Tianjin contains one main urban district, seven sub-urban districts and five counties. Soil in the area is heavily contaminated by many kinds of pollutants, including PAHs (Wang et al. 2003). A detailed description of the area can be found elsewhere (Li et al. 1991).

The primary objective of this study was to use a multivariate geostatistical approach for a multi-scale spatial analysis for 16 PAH compounds in topsoil of the Tianjin area to identify sources and spatial distribution features at different spatial scales.

Experimental section

Sampling

A total of 188 topsoil samples (0–10 cm) were collected in the Tianjin area in April, 2001. The administrative regions and sampling locations are shown in Fig. 1. At each site, fresh soil samples were collected from five locations in an area of about 10,000 m^2 (at the four corners and the center), and thoroughly mixed to form a composite soil sample.

Soil samples were air dried at room temperature and sufficiently ground in a grinder (Fritsch Pulveristte 2) to pass through a 70-mesh sieve. Fine roots were removed from the sieved samples using a glass bar rubbed on silk. The samples were then stored at −18°C prior to analysis. All soil samples were subjected to PAH measurement. Contents of total organic carbon (TOC) and clay particles (< 0.001 mm) content, as well as pH of the soil samples, were measured.

### Sample extraction, cleanup and analysis

Extraction and cleanup procedures were conducted on each sample (Cui et al. 2002). The soil samples were extracted using accelerated solvent extraction (Dionex ASE 300). Reagent blank controls were analyzed simultaneously for the presence of PAHs with each series of samples. All samples were analyzed in duplicate.

Quantitative analysis of the soil was done by gas chromatography with a mass spectrometer detector. Concentrations were determined for 16 PAHs in all samples. PAHs studied were naphthalene (Nap), acenaphthene (Ane), acenaphthylene (Any), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), fluoranthene (Fla), benz[a]anthracene (Baa), chrysene (Chr), benzo[a]pyrene (Bap), benzo[k]fluoranthene (Bkf), benzo[b]fluoranthene (Bbf), indeno[123cd]pyrene (I1p), benzo[ghi]perylene (Bpe), and dibenz[ah]anthracene (Daa). The analysis was conducted using a Agilent 6890 GC coupled with a Agilent 5973 mass spectrometer and a 7683 autosampler (Agilent Technology). Recovery of individual PAHs ranges from 57.0 to 140.0% with a mean value of 80.4 for the 16 PAHs. TOC content of soil samples was determined using a TOC analyzer (Shimadzu5000-A). Soil clay particle content and pH were also measured.

Data analysis

A distribution test (Ahrens 1954) was applied to the data obtained. TOC, pH value (two samples were eliminated as not significant using Grubb's test at a significant level of 0.05 prior to all statistical analysis) and most PAH compounds followed log-normal distribution. Log-transformation was then carried out for these variables.

Fig. 1 Administrative areas of Tianjin and sampling sites
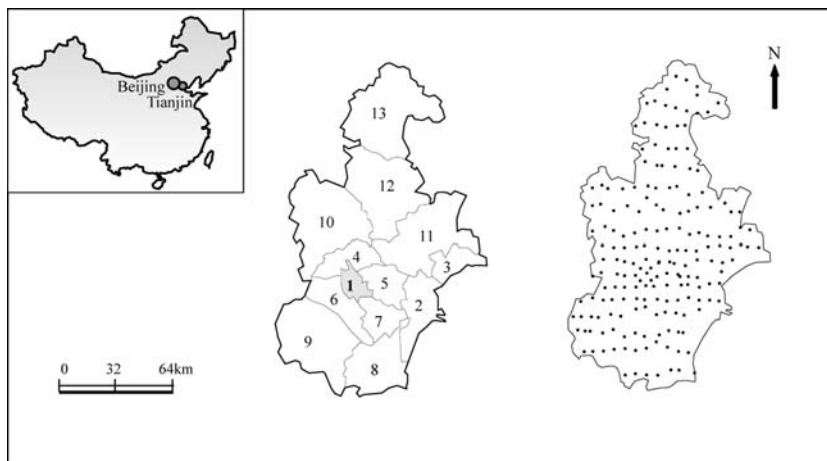
The multivariate statistics were performed using statistical product and service solutions (SPSS) 10.0 and Statistics5.1. The variogram analysis was conducted using Variowin2.2 (Pannatier 1996). FACTOR2D was used to carry out factorial cokriging analysis (Pardo-Iguzquiza and Dowd 2002). Kriging interpolation and contour map generation were made using Surfer7.0 (Golden Software 1999).

For most calculations, Phe, Fla, Pyr and Bap (which represent both low ring and high ring compounds) were selected to illustrate the results of the analysis.

Results and discussion

Coregionalization analysis

The descriptive statistical results of all the parameters are shown elsewhere (Wang et al. 2003). This work showed that coregionalization analysis could be used to separate the different sources of spatial variation (Castrignano et al. 2000). Using the transformed data, experimental simple and cross-variograms were calculated for all PAH compounds, PAH16 (PAH16 is the total concentration of 16 PAH compounds) and soil physico-chemical parameters. Some of the experimental cross-variograms and fitting curves are illustrated in Fig. 2.

Most cross-variograms have similar structures (Fig. 2). Nuggets exist at the origins. From the origin to around 10 km, there were sections with steep rises. From 10 km to around 50 km, the curves become relatively flat. The linear model of coregionalization (LMC) can be used to fit all experimental cross-variograms. The LMC includes three parts. The first structure represents nugget effects, which present measurement errors and variation within the smallest sampling intervals (approximately 5 km). The second structure, on a short-range scale, illustrates the variation within a range of approximately 5–10 km. The third structure, on a long-range scale, represents the variation within a range of approximately 10–50 km.

Structural correlation coefficients and regionalized factors

The linear correlation coefficients between the contents of PAHs and soil physico-chemical parameters could not reveal the real relationships among the variables, since it averages out distinct changes in the correlation structures occurring at different spatial scales (Castrignano et al. 2000). To overcome this problem, the correlation coefficients at three scales were calculated, providing more scale-based information. Table 1 and 2 illustrate some of the correlation coefficients among PAHs and soil physico-chemical parameters at different scales.

Table 1 shows that, at the nugget scale, except for anthracene, all other PAH compounds had significant positive correlation with TOC. No significant correlation between these compounds and soil clay particles and pH values was observed. At the short-range scale (5–10 km), significant positive correlations were seen between soil clay particles and the contents of naphthalene, acenaphthene, anthracene, pyrene, benzo[b]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene; between soil pH value and fluoranthene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[123cd]-pyrene; and also between TOC and naphthalene, acenaphthylene, acenaphthene, benzo[b]fluoranthene, benzo[k]fluoranthene and dibenz[ah]anthracene. At the long-range scale (10–55 km), significant positive correlations were found between soil physico-chemical parameters and almost all PAH compounds.

Table 2 gives the correlation coefficients between PAH16 and soil physico-chemical parameters at three scales. At the short-range scale (5–10 km), significant positive correlations were seen between PAH16 and soil clay particles, while at the long-range scale (10–55 km), significant positive correlations were identified between PAH16 and soil pH value and TOC.

The estimation of the structural correlation coefficients indicates that the spatial variation of PAHs in topsoil of Tianjin area has been affected by soil physico-chemical parameters. Highly positive correlations between most PAH compounds and TOC were found in this study, and in other studies (Cousins et al. 1999). PAHs particularly accumulate in organic matter-rich soils because of their persistence and affinity for soil organic matter.

Significant positive correlation between PAH16 and soil pH value at the long-range scale could be explained by the similar distribution patterns. For a big city in the coastal area, soil pH values near the coast were higher than inland soils. Industries and oil fields were also found in coastal districts like Tanggu and Dagang. Although no direct evidence shows that close relations exist between pH value and PAHs, the distribution of pH values and PAHs at the long-range scale presented similar spatial patterns.

To summarize the relationships among the variables at the different spatial scales, and the analysis on separate variables, principal component analysis for 16 PAH compounds were conducted based on the coregionalization matrices. Principal component features under nugget, short and long-range scales, and the factor loadings under different scales are shown in Tables 3 and 4.

At the nugget scale, the first principal component explained nearly 70% of the overall variation. The accumulative variance contribution of the first three principal components exceeded 85%. Most PAH compounds showed high loads on the first principal

Fig. 2 Cross-variograms and fitting curves of PAHs and soil physico-chemical parameters
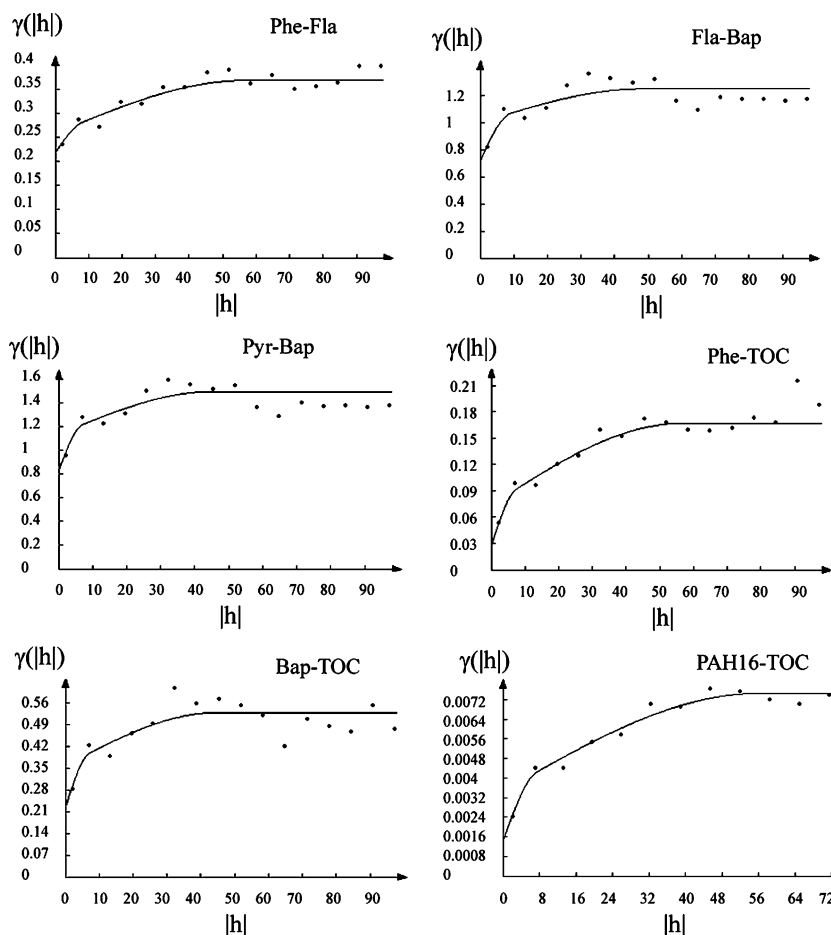
component, while anthracene and naphthalene had high loads on the second principal component. The third principal component represented mainly high ring compounds.

At the short-range scale, the variance contribution of the first principal component make up less than 50% of the total, much lower than the contribution of the first principal components at the nugget and long-range scales. Most high ring compounds had high loads on the first principal component. The second principal component contained mainly low ring compounds. This means that, unlike the nugget scale, at the short-range scale, high ring compounds and low ring compounds were characterized by two different structures. The contribution of combustion source dominated the spatial processes at this scale.

Table 1 Correlation coefficients among PAH compounds and soil physico-chemical parameters at different scales

	PAHs	Clay	pH	TOC	Clay	pH	TOC
Nugget effect	Phe	0.000	−0.016	0.512			+ +
	Fla	0.000	−0.036	0.253			+ +
	Pyr	0.000	−0.016	0.597			+ +
	Bap	0.000	0.000	0.648			+ +
Short-scale	Phe	0.005	−0.021	0.051			
	Fla	−0.010	0.328	0.068		+ +	
	Pyr	0.190	−0.063	−0.022	+		
	Bap	0.410	0.123	0.078	+ +		
Long-scale	Phe	0.355	0.594	0.894	+ +	+ +	+ +
	Fla	0.320	0.414	0.345	+ +	+ +	+ +
	Pyr	0.172	0.511	0.809	+	+ +	+ +
	Bap	0.493	0.217	0.498	+ +	+ +	+ +

Note: +/− positive/negative correlation at 95% confidence level; + +/−− positive/negative correlation at 99% confidence level

Table 2 Correlation coefficients for PAH16 and soil physico-chemical parameters at different scales

Spatial scale	PAH16	Clay	pH	TOC
Nugget				
Total	1.000	−0.001	−0.002	0.677
Clay		1.000	0.120	0.001
pH			1.000	−0.002
TOC	+ +			1.000
Short-scale (spherical model, 10 km)				
Total	1.000	0.178	−0.078	0.018
Clay	+	1.000	−0.989	0.110
pH		−−	1.000	−0.001
TOC				1.000
Long-scale (spherical model, 55 km)				
Total	1.000	0.118	0.993	0.895
Clay		1.000	−0.003	0.549
pH	+ +		1.000	0.834
TOC	+ +	+ +	+ +	1.000

Note: +/− positive/negative correlation at 95% confidence level; + +/– positive/negative correlation at 99% confidence level

For the long-range scale, the first principal component made nearly 65% of the variance contribution, and the accumulative variance contribution of the first three principal components were nearly 85%. Most low ring compounds at this scale showed high loads on the first principal component. The second principal component contained mainly high ring PAHs.

The differences of the spatial structures of the low and high ring PAH compounds in the scale-based principal component analysis could be attributed to the differences of sources and physico-chemical and biological characteristics of these PAH compounds.

Cokriging analysis for PAHs, soil properties and regionalized factors

Multi-variable geostatistics can be used to estimate the spatial distribution of variables at different spatial scales, and thus is a very helpful tool for understanding the sources and distribution of pollutants.

Before the spatial interpolation was performed, analysis on the precision of interpolation for ordinary kriging and cokriging was made for all PAH compounds. Figure 3 presents the estimation errors for benzo[a]pyrene. Cokriging has higher estimation precision than the ordinary kriging analysis (Fig. 3).

Ordinary kriging analysis for the study area was made elsewhere (Wang et al. 2003). Results showed that the high concentrations of PAH16 were found in both urban and suburban districts. Relatively low concentrations were found in counties far from urban areas. The spatial distributions of individual PAH compounds were similar to the PAH16, but presented some differences among the compounds. Compounds with similar molecular weights and number of rings showed similar spatial patterns.

The spatial structural analysis showed that the cross-variograms for PAHs fell into three spatial structures: nuggets (around 0–5 km), short scale (around 5–10 km) and long-range scale (around 10–50 km). Spatial estimations for individual compounds and PAH16 were made at these spatial scales. Factorial kriging was

Table 3 Principal component features of PAH compounds for each spatial scale

	PC	Eigen value	Variance contribution (%)	Accumulative variance contribution (%)
Nugget scale	PC1	11.15	69.67	69.67
	PC2	1.53	9.54	79.21
	PC3	1.05	6.57	85.78
Short-range scale	PC1	7.76	48.52	48.52
	PC2	2.30	14.35	62.87
	PC3	1.70	10.65	73.52
Long-range scale	PC1	10.20	63.73	63.73
	PC2	1.76	10.99	74.72
	PC3	1.56	9.76	84.48

Table 4 Factor loadings for PAH compounds at different scales

PAHs	Nugget scale			Short-range scale			Long-range scale		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Nap	0.53	0.67	0.20	0.04	0.88	−0.02	0.94	0.25	0.03
Any	0.88	0.07	0.10	0.22	0.72	0.33	0.48	0.25	−0.09
Ane	0.62	0.46	0.46	0.15	0.93	0.02	0.86	0.39	0.24
Fle	0.71	0.53	0.32	0.24	0.84	0.11	0.88	0.31	0.14
Phe	0.74	0.08	0.42	0.51	0.54	0.55	0.86	0.40	0.17
Ant	−0.06	0.98	0.08	0.03	0.02	−0.95	−0.04	−0.15	0.94
Fla	0.74	0.28	0.60	0.94	0.14	0.06	0.87	0.45	0.12
Pyr	0.77	0.27	0.61	0.93	0.15	0.06	0.84	0.46	0.10
Baa	0.62	0.19	0.69	0.88	0.16	0.03	0.73	0.64	0.14
Chr	0.67	0.23	0.60	0.92	0.15	−0.01	0.65	0.64	0.15
Bbf	0.64	0.13	0.59	0.13	−0.04	0.06	0.55	0.51	0.13
Bkf	0.68	0.41	0.42	0.64	0.20	0.01	0.32	0.57	0.70
Bap	0.69	0.00	0.45	0.67	0.38	0.55	0.07	0.89	−0.33
I1p	0.61	−0.01	0.75	0.08	−0.01	0.25	0.85	−0.29	−0.21
Daa	0.22	0.10	0.91	0.64	0.62	0.10	0.31	0.86	0.18
Bpe	0.22	0.28	0.90	0.64	0.10	−0.02	0.52	0.70	0.05

applied to carry out spatial interpolations. Contour maps were generated. Some results are presented in Fig. 4.

For most PAH compounds at the nugget scale, small areas of high or low concentration were found separately within the overall sampling area. Measurement errors and variation within the smallest sampling intervals were the major contributors to the distribution patterns. Significantly different spatial distribution patterns were identified for PAH compounds at the short-range scale. For acenaphthylene, fluorene, phenanthrene, pyrene and dibenz[ah]anthracene, one high value center at the boundary areas of Beichen, Xiqing and the urban district was found. A low value center was seen in Wuqing and Baodi counties. For pyrene, benz[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene and chrysene, the highest values appeared in the Xiqing district. The low content areas are distributed mainly in southern and northern part of the study area. At the long-range scale, no significant high or low content areas were identified,

and the distribution patterns for most compounds were similar to each other.

Significantly different spatial distribution patterns existed for particular PAH compounds at different spatial scales. Taking benzo[a]pyrene as an example, the high concentration areas at the nugget, short and long-range scales were significantly different. The sources and driving forces for transport at different spatial scales must be different. Some pollution sources, such as industrial wastewater discharge, might contribute only to small areas. Other sources, especially from combustion, might cause long distance effects. These contributions from different sources overlapped and formed the existing spatial distribution patterns of PAH compounds in the soil.

For PAH16 (Fig. 4), no clear spatial distribution patterns were identified at any scale. This is attributed partly to the differences of behaviors of low ring and high ring PAH compounds. Therefore, FKA for principal components obtained from PCA for PAH16 was conducted. Results showed that the variance contributions of the first three principal components were 67.39, 8.63 and 5.95%, respectively. The cumulative variance contribution of the first three principal components was 81.96%. High ring PAH components had high loadings on the first principal component, while low ring PAH components had high loadings on the second principal component. Anthracene had high loading on the third one.

Contour maps of principal components for PAH16 are presented in Fig. 5. Spatial distribution patterns varied significantly among different principal components. For the first principal component, which represented mainly the high ring compounds of PAHs, the high concentration areas were distributed mainly in Xiqing district and urban district. The low concentration areas were concentrated in Wuqing County, Jinghai
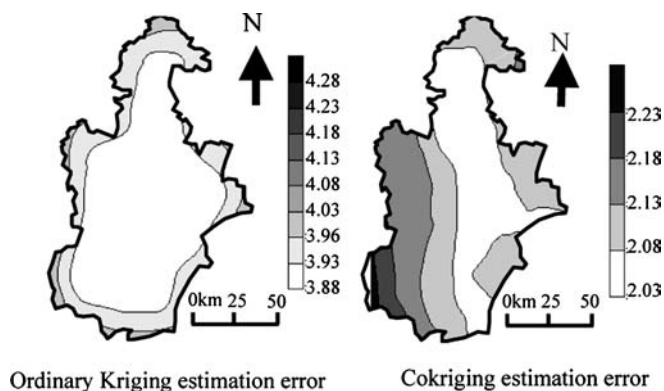
Fig. 3 Estimation errors of ordinary kriging and cokriging for benzo[a]pyrene

Fig. 4 Distribution of PAH compounds in topsoil of Tianjin at different scales (the data in this figure represents the content levels, not the exact concentration)
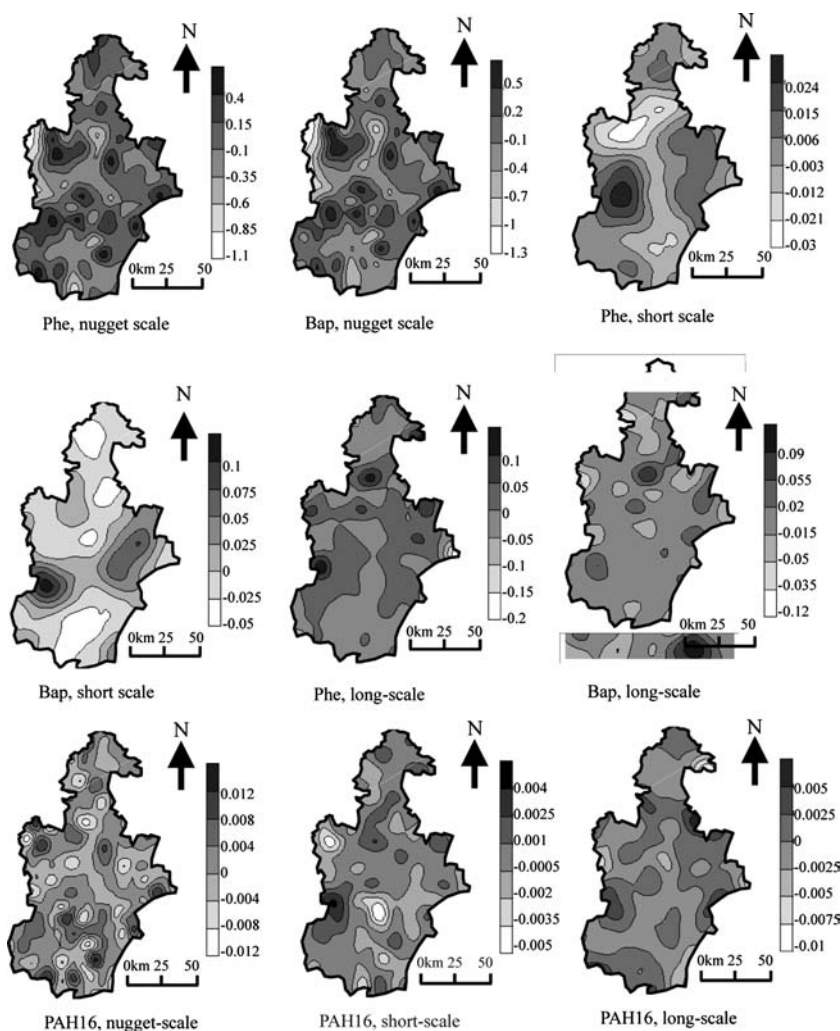
County, Baodi County, and Ji County. From the urban district to the surrounding counties, the concentration decreased gradually. For the second principal component, representing mainly the low ring components of PAHs, the high concentration areas were distributed mainly in the urban district and the surrounding areas, as well as in the Tanggu district, decreased toward the south and north. The third principal component presented only anthracene. More studies are needed to ascertain the sources and spatial processes of anthracene distribution in this area.

Sources of PAH contamination

The identification of sources is essential for understanding PAH distribution in soil, carrying out pollution risk assessment, and taking mitigation measures. Studies have shown that ratios of PAH compounds can be used to trace the sources of PAHs (Soclo et al. 2000). Soclo et al. (2000)

used phenanthrene/anthracene, fluoranthene/pyrene, chrysene/benz[a]anthracene and low ring compounds/high ring compounds to identify the sources of PAH pollutants in marine sediment. Trapido (1999) used 3–4 ring compounds/5–6 ring compounds in making a comparison of pollution characteristics of different areas. In the present study, two ratios (low ring/high ring, phenanthrene/anthracene) were calculated. Low ring compounds included phenanthrene, anthracene, pyrene and fluoranthene. High ring compounds were benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene, indeno[123cd]pyrene and benzo[ghi]perylene. Experimental variograms for these ratios after log-transformation were calculated and presented in Fig. 6. A spherical model was applied to fit the experimental variograms. Variograms were presented in three parts: nuggets, short scale with ranges around 10 km and long scale with ranges around 60 km.

Studies elsewhere (Trapido 1999; Soclo et al. 2000) showed that when low ring/high ring >1, a petroleum

Fig. 5 Contour maps of PCs of PAH16 for topsoil in Tianjin (the data in this figure represents the content levels, not the exact concentration)
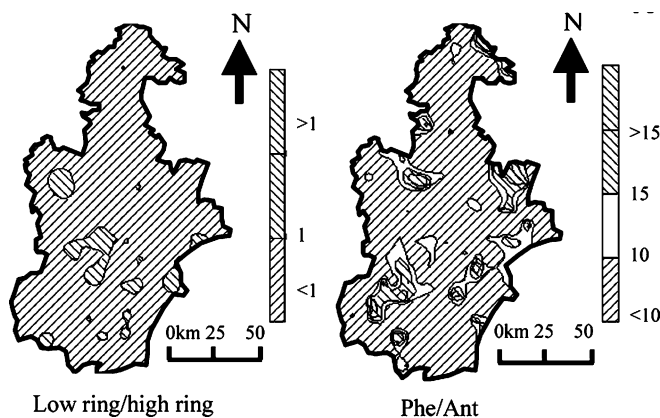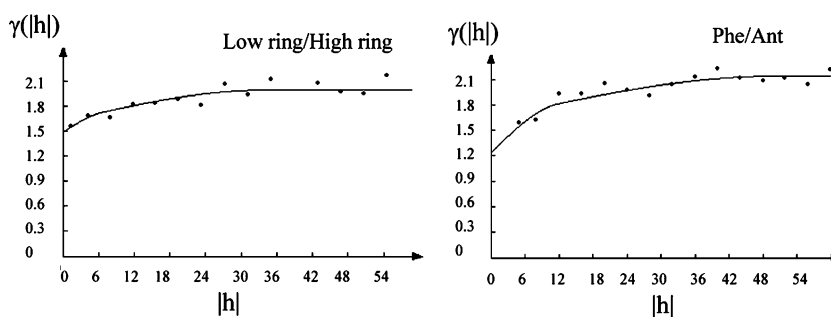

First PC   Second PC   Third PC
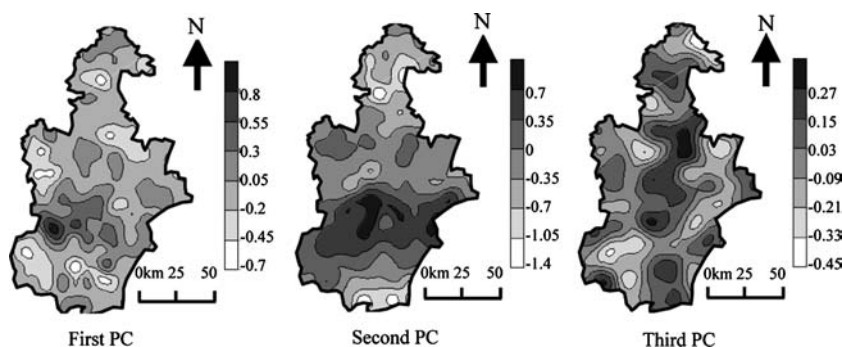
source is indicated. If low ring/high ring < 1, a combustion source is indicated. Phenanthrene/anthracene > 15 represents a petroleum source, while phenanthrene/anthracene < 10 indicates a combustion source. Based on the spatial structural analysis, kriging interpolations for these ratios were performed. Contour maps are presented in Fig. 7.

Studies have shown that combustion of coal was the major contributor of PAH accumulation in topsoil of the study area (Wang et al. 2003). Figure 7 supports this conclusion. The scale-dependent variogram and cokriging analysis indicates that a combustion source played a key role, especially at the short-range scale.

As one of the major industrialized cities in China, Tianjin consumes a large amount of coal. Statistics from the Tianjin Environmental Protection Bureau (TEPB) demonstrate that (TEPB 2001) the energy consumption in Tianjin was dominated by coal (Fig. 8). The regional distribution of energy consumption in Tianjin city showed that (TEPB 2001) in the year of 2000, Dongli District, Ji County, Dagang District, Xiqing District, Heding District (part of the urban district) and Tanggu District consumed 78.7% of the total coal used by the city.

Contributions from other sources may also influence results. There is a large oil field and with refineries near the urban district and coastal areas, which contribute to the accumulation of PAHs from scattered petroleum sources (Fig. 7). Road transportation in the urban areas of Tianjin is quite heavy, and may also play an important role in PAH accumulation from urban runoff.

Low ring/high ring   Phe/Ant

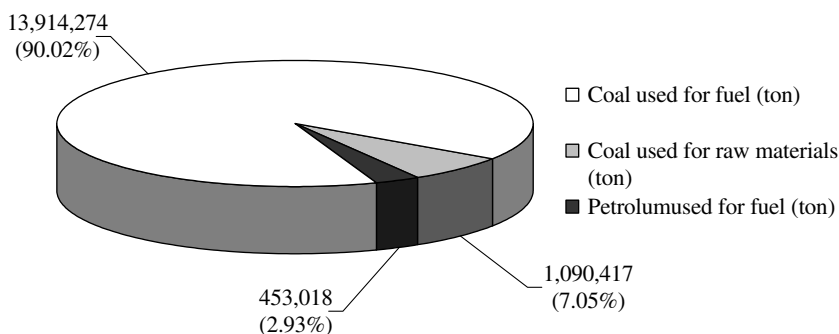**Fig. 7** Spatial distribution of ratios of PAH compounds in the topsoil of Tianjin area

Domestic and industrial wastewater has been used for agricultural irrigation in Tianjin for quite a long time. Wastewater irrigated agricultural lands are located in scattered areas outside of the urban areas. Studies have shown that untreated wastewater irrigation may add contamination of PAHs (Wang et al. 2004).

Conclusion

The understanding of spatial distribution patterns of pollutants is essential for pollution risk assessment and remediation. The spatial distribution patterns of principal components at different scales could be used to

Fig. 6 Experimental variograms and fitting curves of the ratios of PAH compounds

Fig. 8 Energy consumptions in different industrial sectors in 2000 in Tianjin City

13,914,274 (90.02%)

☐ Coal used for fuel (ton)

☐ Coal used for raw materials (ton)

■ Petrolumused for fuel (ton)

1,090,417 (7.05%)

453,018 (2.93%)

reflect the spatial processes of specific PAH groups, and could also help to identify the pollution sources of PAHs in the topsoil. Coal combustion was the major source for the spatial distribution patterns of PAHs in the topsoil of the studied area. It worked mainly at the short-range scale (5–10 km). Significant spatial variation patterns were identified. In contrast, no significant spatial distribution trends at the nugget (0–5 km) or long-range scales (10–50 km) were seen. Long-range transport and site contamination of PAHs might not be key contributors in forming the distribution pattern of PAHs in the topsoil of Tianjin area.

References

Ahrens LH (1954) The lognormal distribution of the elements (a fundamental law of geochemistry and its subsidiary). Geochim Cosmochim Acta 5:49–73

Carlon C, Critto A, Marcomini A (2001) Risk based characterization of contaminated industrial site using multivariate and geostatistical tools. Environ Pollut 111:417–427

Castrignano A, Giugliarini L, Risaliti R, Martinelli N (2000) Study of spatial relationships among some soil physico-chemical properties of a field in central Italy using multivariate geostatistics. Geoderma 97:39–60

Cousins IT, Gevao B, Jones KC (1999) Measuring and modeling the vertical distribution of semi-volatile organic compounds in soils: I. PCB and PAH soil core data. Chemosphere 39:2507–2518

Cui YH, Zhu XM, Guo LQ, Gong ZM, Tao S (2002) Extraction cleanup and measurement of PAHs in wastewater irrigated agricultural soils from Tianjin. Environ Chem 21:392–396

Dong RB, Xu DF, Liu LD (1999) Behavior of PAHs in the environment. Environ Dev 14:10–11

Fu JM, Mai BX, Sheng GY, Zhang G, Wang XM, Peng PA, Xiao XM, Ran R, Cheng FZ, Peng XZ, Wang ZS, Tang UW (2003) Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52:1411–1422

Golden Software (1999) Surfer 7.0 user's guide. Golden, Colorado

Goovaerts P, Webster R (1994) Scale-dependent correlation between topsoil copper and cobalt concentrations in Scotland. Eur J Soil Sci 45:79–95

Jones KC, Stratford JA, Waterhouse KS (1989) Organic contaminants in Welsh soils: polycyclic aromatic hydrocarbons. Environ Sci Technol 23:540–550

Li HC, Liu LC, Wei SZ, Zhang CT (1991) Atlas of land resources of Tianjin. Tianjin People's Press, Tianjin

Matheron G (1982) Pour une analyse krigeante des donnees regionalisees. Report N-732. Centre de Geostatistique, Fontainebleau

Pannatier Y (1996) VARIOWIN: software for spatial data analysis in 2D. Springer, Berlin Heidelberg New York

Pardo-Iguzquiza E, Dowd PA (2002) FACTOR2D: a computer program for factorial cokriging. Comput Geosci 28:857–875

Soclo HH, Garrigues PH, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar Pollut B 40:387–396

TEPB (Tianjin Environmental Protection Bureau) (2001) Environmental quality statement 1996–2000. Tianjin Environmental Protection Bureau, Tianjin

Trapido M (1999) Polycyclic aromatic hydrocarbons in Estonian soil: contamination and profiles. Environ Pollut 105:67–74

Wang XJ, Chen J, Zhang ZH, Piao XY, Hu JD, Tao S (2004) Distribution and sources of polycyclic aromatic hydrocarbons in soil profiles of Tianjin area, China. Bull Environ Contam Toxicol 73:739–748

Wang XJ, Tao S (1998) Spatial structures and relations of heavy metal content in wastewater irrigated agricultural soil of Beijing's eastern farming regions. J Environ Sci Health B 61:261–268

Wang XJ, Zheng Y, Liu RM, Li BG, Cao J, Tao S (2003) Kriging and PAHs pollution assessment in the topsoil of Tianjin area. Bull Environ Contam Toxicol 71:189–195