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Kriging and PAH Pollution Assessment in the Topsoil of Tianjin Area

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Polycyclic Aromatic Hydrocarbons (PAHs) have been identified as important pollutants in the environment and can cause significant environmental and human health risks (Menzie et al. 1992). In the last 100 years, the occurrence of PAHs in soil, especially in urban areas, has increased significantly (Jones et al. 1989). The assessment of soil polluted by PAHs is essential to determine the feasibility of utilizing polluted land for multi-purposes. Extensive research has been carried out in a number of countries for PAHs in the environment (Trapido 1999; Wania and Mackay 1996; Wilcke et al. 1999). In China, however, most studies have only focused on a limited number of compounds, especially benzo[a]pyrene, and were usually carried out in small areas (He et al. 1995; Liu 1984; Song et al. 1995).

It is well known that the contents of most PAH compounds are unevenly distributed in topsoil due to a couple of reasons. Under these circumstances a simple pollution assessment based on limited sampling data is insufficient. Thus spatial interpolation techniques are necessary when the objective is to map and assess the distribution of PAHs.

A number of interpolation methods, including trend surface analysis, have been used for mapping pollution in unsampled parts of a polluted area. Although these methods may seem appropriate for many applications, they may give biased interpolation as they neither provide any estimate of the error of interpolation, nor do they attempt to minimize that error, as were pointed out earlier by Burgess and Webster (1980).

Kriging analysis was first used in the estimation of ore reserves in mining and has been used extensively since then in many other fields (Burgess and Webster 1980). Based on the theory of regionalized variable developed mainly by Matheron (1963) and Krige (1966), kriging analysis can provide theoretically optimal estimates without bias and with minimal and known variance.

Located in the eastern part of the North China Plain, about 150 km east of Beijing, Tianjin is one of the largest industrial cities in China. In recent years, with the rapid development of the economy, soil pollution is becoming more and more serious. In this paper, kriging analysis was applied to predict the concentration and distribution in unsampled areas for sixteen prior PAH compounds (Keith and Telliard 1979) in surface soil in the Tianjin area. Based on the interpolation results, assessment of pollution level was made.

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MATERIALS AND METHODS

Tianjin City contains one main urban area, four sub-urban areas (Dong Li, Jin Nan, Xi Qing and Bei Chen), and five counties (Ji, Bao Di, Ning He, Jing Hai and Wu Qing). Figure 1 presents the administrative map of Tianjin City. A total of 188 topsoil samples (0-10cm) were collected in Tianjin area in April, 2001. The sampling locations are shown in Figure 2.

Samples were air dried at room temperature and ground in an agate mortar sufficiently to pass through a 70- mesh sieve. The samples were then stored at 4°C before use. Extractions of PAHs were carried out using accelerated solvent extraction (ASE) method. The extracts were analyzed for the 16 PAHs using an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer and a 7683 autosampler (Agilent Technology). The sample extraction and analysis were carried out using a procedure (including quality control) developed by Tao and Cui (2002). TOC, pH value and clay particle (<0.001mm) were also determined in this study. All reagents were of analytical grade or better. All glassware was cleaned in an ultrasonic cleaner.

The sixteen PAH compounds determined are: naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (Baa), chrysene (Chr), benzo[b]fluoranthene (Bbf), benzo[k]fluoranthene (Bkf), benzo[a]pyrene (Bap), ideno[1,2,3-cd]pyrene (Ilp), dibenz[a,h]anthracene (Daa), and benzo[ghi]perylene (Bgp).

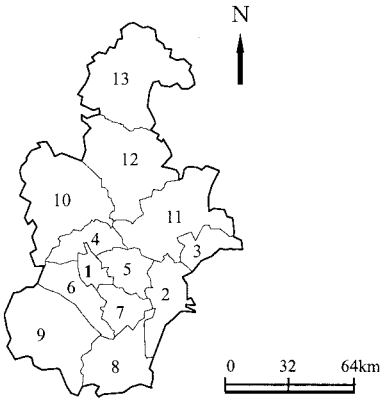
It was found that TOC, pH value and most PAH compounds followed logarithmic normal distribution. Logarithmic transformation was thus carried out for these variables.

In our study, the variogram analysis was conducted using Variowin2.2 (Pannatier 1996). Spherical models were used to fit all experimental variograms, except clay particles, for which a linear model was applied. Results of variogram analysis were developed and reported elsewhere (Zheng et al. 2002). Two-dimensional ordinary block kriging was applied in the interpolation process. The kriging analysis and interpolation were conducted using Surfer 7 (Golden Software 1999).

RESULTS AND DISCUSSION

Statistical analysis for all the variables (TPAH is the total concentrations of sixteen PAH compounds) is shown in Table 1. The contour maps of the contents of sixteen PAH compounds and total PAHs were made according to the kriging interpolation. The contour map of total PAHs appears as Figure 3. From Figure 3, we can see that high concentrations are found in the main urban area and the five sub-urban areas. Relatively low concentrations are found in other counties far from urban areas.

PAHs have been identified as important pollutants in the environment, and could cause significant environmental risk (Menzie et al. 1992). They are byproducts of



1: The Main Urban Area, 2: Tang Gu District, 3: Han Gu District, 4: Bei Chen District, 5: Dong Li District, 6: Xi Qing District, 7: Jin Nan District, 8: Da Gang District, 9: Jing Hai County, 10: Wu Qing County, 11: Ning He County, 12: Bao Di County, 13: Ji County

Figure 1. Map of Tianjin Area

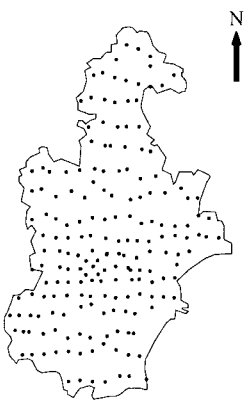


Figure 2. Sampling sites in Tianjin Area

the incomplete combustion or pyrolysis of organic materials, residential heating, incineration, internal combustion engines, and industrial activities (International Agency for Research on Cancer 1983). In Tianjin City, the main urban area and sub-urban areas are the major populated and industrial areas in Tianjin City with high consumption of industrial and domestic fuels. Vehicle emission from these areas is also significant.

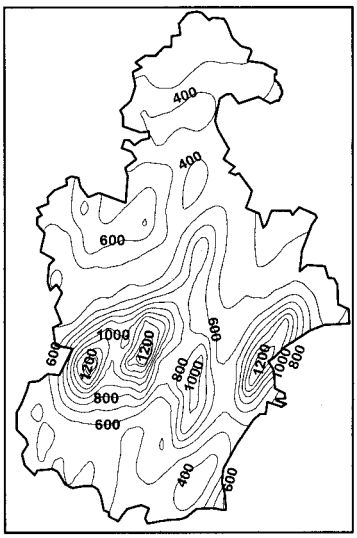


Figure 3. Map of kriging interpolation for the overall PAHs content (μ g/kg)

Table 1. Statistical results of PAHs concentrations and properties in topsoil (μ g/kg).

Variable	Mean	SD	Median	CV(%)	Skewness	Kurtosis
Nap	274.6	275.8	197	100.6%	3.1	11.6
Any	9.3	6.9	7	74.2%	3.5	17.1
Ane	4.5	6.5	2	143.6%	3.2	11.8
Fle	9.0	9.8	6	109.2%	2.6	6.7
Phe	84.2	112.6	41	133.8%	2.8	8.7
Ant	22.9	25.5	20	111.7%	4.0	24.5
Fla	75.4	129.7	27	172.3%	3.4	14.0
Pyr	52.9	91.9	18	174.0%	3.5	14.2
Baa	17.7	34.6	5	195.5%	3.7	15.9
Chr	35.1	51.6	17	147.3%	3.4	13.2
Bbf	54.1	39.0	40	72.2%	3.0	9.8
Bkf	49.3	33.7	37	68.4%	3.1	10.4
Bap	45.9	26.8	39	58.4%	2.7	10.8
Ilp	35.9	29.4	41	82.0%	1.4	4.4
Daa	18.2	24.0	Nd	132.0%	1.4	2.0
Bgp	30.5	33.5	38	110.1%	1.6	4.2
TPAH	818.2	796.2	538	97.4%	2.7	8.5

Nd: not detected

The spatial distributions of other PAH compounds are similar to that for total PAHs, but present some differences among the compounds. Table 2 summarizes the features of spatial distributions of PAH compounds. Those PAHs with similar molecular weights and number of rings show similar spatial patterns.

Table 2. Spatial distribution features of PAH compounds.

PAHs	Areas with high PAH contents
Nap, Any, Ane	The main urban area, Xi Qing, and the border area of Tang Gu and Han Gu
Fle, Phe	High content areas: the main urban area, Dong Li and the border area of Tang Gu and Han Gu. Relatively high contents can also be found in Bao Di
Ant	High content areas distributed separately in the whole sampling area
Fla, Pyr, Baa, Chr	The main urban area, the border area of Tang Gu and Han Gu
Bbf, Bkf, Bap	Highest contents were found in Xi Qing. Other high content areas can be seen in the main urban area, the sub-urban areas, and seaside areas
Ilp, Daa	Highest contents were found in the main urban area. They also distributed separately in many other areas.
Bgp	Xi Qing

The assessment of soil contaminated with PAHs is very important for identifying pollution sources and taking remediation actions. There is no unified standard and method for environmental quality assessment of soils in China, especially for PAHs. In this study, a pollution assessment standard shown in column A of Table 3 (Annokkee 1990) was applied to evaluate the pollution situation of ten PAH compounds in the topsoil in Tianjin area. This standard was designed to allow the soil to be used for multiple purposes (Annokkee 1990).

Table 3. Environmental standards for soil PAHs (Annokkee 1990).

PAHs	Standard (mg/kg)		
	A	B	C
Nap	0.015	5	50
Phe	0.05	10	100
Ant	0.05	10	100
Fla	0.015	10	100
Chr	0.02	5	50
Baa	0.02	5	50
Bap	0.025	1	10
Bkf	0.025	5	50
Bgp	0.02	10	100
Ilp	0.025	5	50

A: Used for multiple purposes; B: Relatively high treatment requirement; C: Relatively low treatment requirement

Based on the kriging interpolation of the PAH compounds, an assessment of soil pollution was carried out. It can be seen that topsoil in Tianjin area is polluted to a greater or lesser degree by PAH compounds, especially those areas near the industrial and urban areas. Results shown that the contents of naphthalene and fluoranthene exceed the standard for the whole study area. In contrast, anthracene and ideno[1,2,3-cd]pyrene meet the standard for the whole sampling area. For the other six PAH compounds, the results of assessment are illustrated in Figure 4. All the assessment results are presented in Table 4.

Table 4. Assessment for PAHs pollution of topsoil in Tianjin Area.

PAHs	Areas with heavy pollution	Percentage area exceeding the standard	Largest times exceeding the standard
Nap	Xi Qing	100%	>30
Phe	The Main Urban Area	32%	>3
Ant	-	0%	None
Fla	The Main Urban Area, Xi Qing	100%	>7
Chr	Xi Qing	36%	>3
Baa	Xi Qing	3%	>1
Bap	Xi Qing	93%	>3
Bkf	Xi Qing	97%	>6
Bgp	Xi Qing	3%	>2
Ilp	-	0%	None

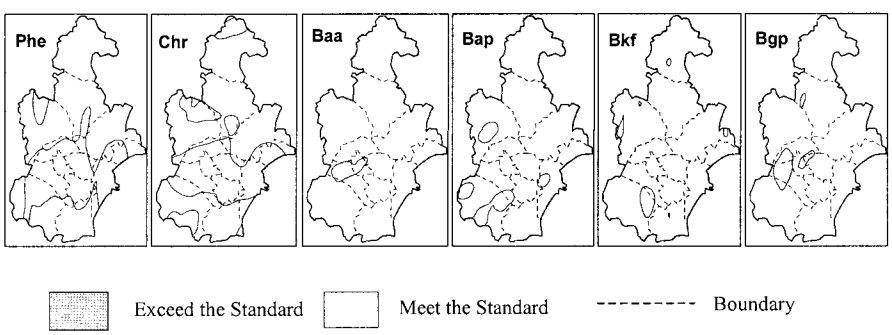


Figure 4. Map of polluted area

Results also show that naphthalene exceeds the standard more than any of the other PAHs and has the largest spatial impact. Fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene were the next, and anthracene and ideno[1,2,3-cd]pyrene the lowest. The highest concentrations of most PAH compounds are found in the main urban area and Xiqing District. Relatively low concentrations are found in other areas, especially in the five counties, where the population density is low and economy is relatively backward.

It can be expected that rapid economic development in the area may increase the

level of pollution. Thus, strict regulations need to be adopted, and more detailed assessment should be carried out before new land use planning and soil treatment measures are taken.

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