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Polycyclic aromatic hydrocarbons in soils of an industrial area of China: multivariate analyses and geostatistics

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Tianjin Bin Hai New Area (BHNA) is the third largest economic zone in China. This is an older industrial area that has been developing rapidly but with many historic sources of contamination. The concentrations of 16 individual polycyclic aromatic hydrocarbons (PAHs) listed for priority control by the US EPA were quantified in 105 surface soil samples by the use of gas chromatography mass spectrometry (GC/MS). Multivariate statistical methods were used to characterise the mixtures and make comparisons in the patterns among areas. Concentrations varied among areas, ranging from moderate to relatively high. The coefficients of determination between concentrations of individual PAHs and total concentration of PAH (\sum PAH) increased with the number of rings. The first three factors from the principal component analysis (PCA) explained 81.6% of the total variation, while ten higher molecular weight (HMW) PAHs' loadings for factor 1 accounted for 51.0%. Based on the patterns of relative loading proportions of individual PAHs calculated by PCA, the primary sources were coal combustion, traffic emissions including gasoline, diesel oil, and the burning of natural gas. The spatial distribution of concentrations of fluorene had a poor spatial autocorrelation in the study area. The sites with the greatest potential risk due to exposure to PAHs were mainly distributed around the chemical industry parks.

Keywords: PAHs; pollution sources; principal component analysis; kriging; soil contamination

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) can be toxic, mutagenic, and carcinogenic to humans [1,2] and are therefore of concern. Exposure of humans to PAHs from soil is generally greater than from either air or water [3], and concentrations of PAHs in soil have been increasing for the last 100–150 years, especially in urban areas [4].

Geostatistics can be applied to describe the distributions of pollutant residues in soils and by interpolating estimate concentrations in un-sampled areas [5]. The technique has been developed

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for use by the mining industry, and subsequently extended to applications in other disciplines, including geomorphology, geology, hydrology and geography [6–8]. Since surveys of soil can be limited by cost and time, small-scale surveys are often implemented. Geostatistical methods can be used to examine contaminated areas to develop the most cost-effective remediation [9]. Concentrations of PAHs in surface soils of the Guanting Reservoir have been studied previously at a medium spatial scale [10]. However, to make decisions about potential risk, policies about agricultural practices, and potential remedial actions, a larger scale survey and assessment was needed.

Principal component analysis (PCA) is useful in determining likely sources of PAHs [11,12]. PCA is one of the simplest and oldest eigenvalue-based ordination methods. Data from an experimental system with similar characteristics lie close together, while those with dissimilar characteristics are plotted far apart [13]. PCA is often used in data reduction to identify a small number of environmental factors or combinations of factors that explain most of the variance observed in a much larger number of variables to infer sources [14]. In general, each principle component (PC) is associated with a source that was characterised by a representative or ‘marker’ PAH. Large loading factors for fluoranthene, pyrene, and especially benzo[ghi]perylene have been suggested as indicators of gasoline-powered vehicles as a source [15,16], while a large proportion of anthracene, phenanthrene, benzo[a]pyrene, benzo[ghi]perylene, and chrysene has been suggested for steel industry emissions [17].

In order to determine the potential risk of PAHs in industrial soils of the Tianjin Bin Hai New Area (BHNA), concentrations of 16 indicator PAHs were determined in 105 samples of surface soils. These included: naphthalene (Nap); acenaphthylene (Acy); acenaphthene (Ace); fluorene (Flu); phenanthrene (Phe); anthracene (An); fluoranthene (Flu); pyrene (Pyr); benz[a]anthracene (Baa); chrysene (Chr); benzo[b]fluoranthene (BbF); benzo[k]fluoranthene (BkF); benzo[a]pyrene (BaP); indeno[1,2,3-cd]pyrene (InP); dibenz[a,h]anthracene (Dba); and benzo[g,h,i] perylene (BgP).

The primary objectives of this study were to: (1) quantify PAHs in surface soil of the BHNA; (2) determine the spatial distribution of PAHs in surface soil of the BHNA on a relatively large scale and develop a map of the concentrations; (3) identify the source of PAHs in the BHNA and factors that influence the distribution of PAHs in the BHNA; and (4) conduct an assessment of the risk posed by PAHs to humans.

2. Materials and methods

2.1. Description of the study area

The BHNA (38°40′–39°00′ N and 117°20′–118°00′ E) is located in northern China, approximately 100 km northeast of Beijing. The total area of the BHNA is approximately 2270 km², in three administrative districts: Tanggu, Hangu, and Dagang. The BHNA is an older chemical industry area and has a long history of pollution from multiple sources. For example, the Tianjin Soda Plant, established in 1917, is well known as the cradle of the Chinese caustic soda industry and the basis of the modern chemical industry in China. The Tianjin Chemical Plant is a large-scale Chlor-alkali enterprise founded in 1938. During the period of 1994 to 2005, when the GDP of the BHNA was increasing at a rate of 20.6% per year, the BHNA was made the third national economic zone. Many industries rely on coal for energy, and are thus the major anthropogenic sources of PAHs. Also, there has been a significant increase in the number of cars over the past decade, especially in the Tanggu District, and this, together with the coal that is used to heat houses in winter, are potential sources of PAHs in the area.

2.2. Soil sampling

One hundred and five samples of surface soils were collected. Sampling locations were evenly distributed across the area, except for some samples that were selected to be adjacent to specific chemical industries. Each sample was a composite of subsamples taken from the top 20 cm of five sites (at the centre and four corners of a grid [7 * 7 km²]). The composite was homogenised and a subsample was collected with the use of a stainless steel shovel and then transferred to brown envelopes. The samples were placed on ice in a cooler and returned to the laboratory. Grass and other sundries were removed from the surface of each sample location before the sample was collected. Throughout the survey, a global positioning system (GPS) was used to locate the sampling locations (Figure 1). Site descriptions including land use type and major environmental features were recorded at the time of sampling.

2.3. Analytical methods

Soils were dried at room temperature, sieved through a 100 mesh sieve, and then stored in glass bottles prior to analysis. PAHs were extracted by Soxhlet apparatus, and concentrations of the 16 PAHs listed for priority control by USEPA were quantified by use of an Agilent 6890 GC equipped with a 5973 mass selective detector (MSD) operated in the selected ion monitoring mode (SIM). The methods used for sample extraction and analysis have been described in detail elsewhere [10,18]. Quantification was made using a five-point calibration curve for individual components. Detection limits were 1.7–4.9 ng g⁻¹ dry weight (dw). Laboratory quality control procedures included analyses of method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, and sample duplicates. Instrument stability and response were monitored by use of NIST standard solutions. Instruments were calibrated daily and the relative percent differences between the five-point calibration and the daily calibrations

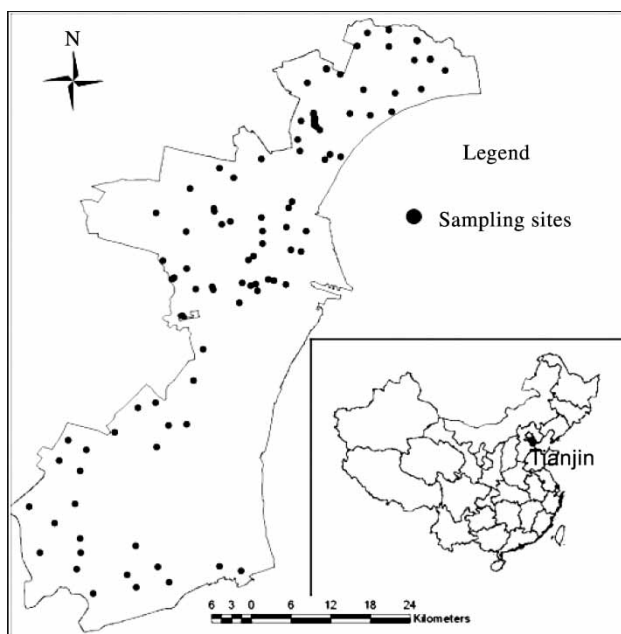


Figure 1. Map of regional site and sampling sites.

were <20% for all of the target analyses. Recoveries of surrogate standards for individual PAHs were between $58.7 \pm 7.4\%$ and $96.3 \pm 5.8\%$.

2.4. *Multivariate and geostatistical methods*

Frequency distributions of concentrations of PAHs were investigated by calculating skewness and kurtosis coefficients. PCA was used to compare patterns of relative concentrations of PAHs. Samples were grouped by use of varimax rotation and the retention of PC having eigenvalues >1. Variables with similar characteristics were grouped into factors. The first and second PC factors often explained more than 70% of the variance. Thus, the first two factors were used to determine possible emission sources. Variography and kriging were used to represent the horizontal distribution of PAH concentrations [19]. Spatial correlation analysis was performed by GS plus software (Ver. 9.0), while kriging and spatial distribution maps of pollutants were generated by the use of GIS software Version 9.0 for Windows.

2.5. *Soil characteristics analysis*

Total organic carbon (TOC) and total nitrogen (N) were analysed using a Universal CHNOS Elemental Analyzer (Elementar Vario EL III, Germany) [20], soil pH was measured using a soil:water ratio of 1:2.5 by a potentiometric glass electrode [21].

3. Results and discussion

3.1. *Preliminary data description*

While total concentrations of PAHs (\sum PAHs) could be calculated for all of the soil samples, not all individual PAHs were quantifiable in all of the samples. Acy was not detected in any samples, and Ace was quantifiable in only 9.62% of samples. The other 14 PAHs were quantifiable in 77.9–99% of the composite samples, except for Pyr and Chr, which were quantifiable in all samples.

Concentrations of PAHs are presented as box and whisker plots with the bottom and top of the box representing the 25th and 75th centiles, respectively (Figure 2). The band near the middle of the box represents the median or 50th centile, while the whiskers represent the minimum and maximum concentration. The greatest concentration of \sum PAHs in all samples was $48,700 \text{ ng g}^{-1} \text{ dw}$ in soils from Tianjin Port. This value is near the maximum concentration \sum PAHs reported in the literature, which is $40,692 \text{ ng g}^{-1} \text{ dw}$ in sediment from the port of New Orleans [22]. Concentrations of \sum PAHs in the other 104 topsoil composites ranged from $68.7\text{--}5990 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$ with an average of $814 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$. This range of concentrations is greater than that in some other developed regions of China, such as the Shantou economic development zone ($317 \text{ ng } \sum\text{PAHs/g dw}$) [23] and Hong Kong ($443 \text{ ng } \sum\text{PAHs/g dw}$) [24], but less than those in Beijing urban soils ($1637 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$) [25], Dalian surface soils ($1738 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$) [21], France surface soils ($2510 \text{ ng g}^{-1} \text{ dw}$) [26], and a suburban district in the USA ($527\text{--}3753 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$) [22]. Based on the soil quality standard proposed by [27], only 7.7% of the soil samples would be classified as unpolluted ($<200 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$), 46.2% slightly polluted ($200\text{--}600 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$), 23.1% moderately polluted ($600\text{--}1000 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$), and 23.1% severely polluted by PAHs ($>1000 \text{ ng } \sum\text{PAHs g}^{-1} \text{ dw}$).

Concentrations of individual components varied considerably among locations and among PAHs. The greatest mean concentration of an individual component was observed for Nap

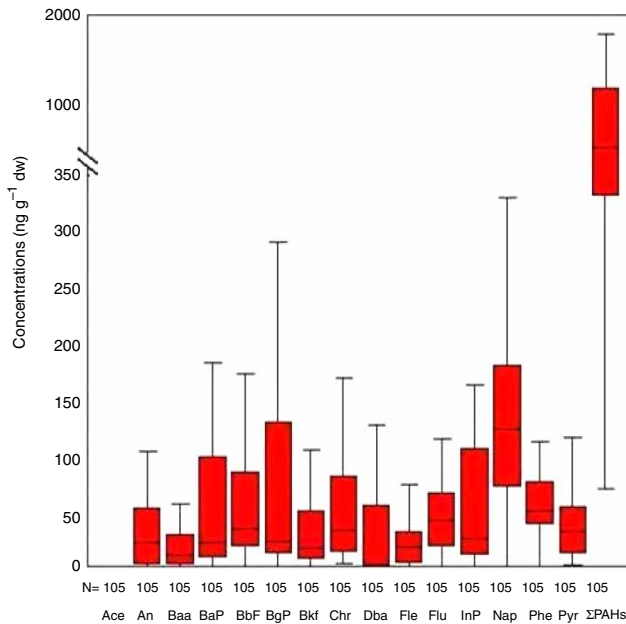


Figure 2. Box-plot chart of concentrations of PAHs in surface soils of BHNA.

(152 ng g⁻¹ dw), while the least was observed for Acy (not detected) and Ace (2.1 ng g⁻¹ dw), with concentrations for the other PAHs ranging from 20.7 to 73.8 ng g⁻¹ dw.

3.2. Correlation coefficients between the PAHs

Relationships between concentrations of individual PAHs were investigated using the nonparametric, Spearman correlation analysis for the non-normal distribution data indicated by skewness and kurtosis coefficients. According to the values of Spearman correlation coefficients (R), typical components were selected to reflect the overall PAHs contamination level, and check whether there was a good correlation between components. Most of the individual PAHs showed a significant correlation with other PAHs as well as the \sum PAHs (Table 1). This result suggested that PAH originated from similar sources [24]. There was a significant positive correlation between all high molecular weight (HMW) PAHs (4–6 rings) with \sum PAHs, and the correlation coefficients increased along with the increase in number of rings in PAHs. Since the correlation coefficient between BaP and \sum PAHs was 0.8, the content of BaP can be used as an indicator to reflect the entire pollution extent, which was confirmed in other studies [28]. On the other hand, lesser molecular weight (LMW) PAHs (2–3 rings) such as Fle and An did not show any correlation with HMW PAHs (4–5 rings). This observation can be attributed to the regional characteristic of PAHs sources and the greater volatility of lesser-ring PAH. It can also be speculated that the principal sources of PAHs in soil in these areas were from remote sites by medium or long range atmospheric deposition. Burning of human bodies in crematoria, combustion of fuels in power plants and incineration of wastes are all known sources of PAHs [29].

The rate of degradation of PAHs depends upon several environmental factors, including, temperature, soil type and pH, redox potential, moisture and organic carbon content [30]. These parameters affect both the current concentration in the soil system as well as possible adsorption onto various soil components. In order to estimate the behaviour of PAHs in the BHNA soil system, correlations between several soil geochemical factors and soil PAH-concentrations were

Table 1. Correlations among 15 polycyclic aromatic hydrocarbons as well as between the \sum PAHs.

	Nap	Ace	Fle	Phe	An	Flu	Pyr	Baa	Chr	BbF	Bkf	BaP	InP	DbA	BgP	\sum PAHs	pH	N	TOC	
Nap	1																			
Ace	0.440**	1																		
Fle	0.378**	0.370**	1																	
Phe	0.357**	0.321**	0.525**	1																
An	-0.07	-0.065	0.250*	0.365**	1															
Flu	0.489**	0.392**	0.099	0.533**	-0.045	1														
Pyr	0.426**	0.350**	-0.01	0.479**	-0.031	0.972**	1													
Baa	0.181	0.359**	0.417**	0.413**	0.383**	0.335**	0.291**	1												
Chr	0.317**	0.221*	-0.139	0.360**	-0.083	0.895**	0.910**	0.259**	1											
BbF	0.333**	0.336**	0.186	0.359**	0.125	0.669**	0.668**	0.444**	0.597**	1										
Bkf	0.282**	0.159	-0.102	0.410**	0.04	0.818**	0.836**	0.174	0.849**	0.588**	1									
BaP	0.345**	0.241*	-0.065	0.309**	-0.01	0.799**	0.817**	0.337**	0.826**	0.653**	0.730**	1								
InP	0.274**	0.215*	-0.071	0.309**	0.044	0.789**	0.805**	0.316**	0.816**	0.682**	0.746**	0.839**	1							
DbA	0.175	0.127	-0.129	0.299**	0.112	0.686**	0.718**	0.295**	0.743**	0.444**	0.670**	0.776**	0.786**	1						
BgP	0.327**	0.247*	0.02	0.353**	-0.023	0.729**	0.709**	0.238*	0.688**	0.554**	0.655**	0.769**	0.784**	0.607**	1					
\sum PAHs	0.586**	0.316**	0.153	0.559**	0.106	0.895**	0.881**	0.314**	0.838**	0.664**	0.822**	0.806**	0.817**	0.718**	0.779**	1				
pH	0.279**	0.222*	0.086	0.04	-0.084	-0.01	-0.016	0.046	-0.04	-0.084	-0.041	0.021	-0.037	-0.011	0.015	0.066	1			
N	0.343**	0.249*	0.118	0.332**	0.094	0.454**	0.420**	0.365**	0.338**	0.429**	0.415**	0.436**	0.329**	0.326**	0.417**	0.423**	0.172	1		
TOC	0.440**	0.397**	0.132	0.515**	0.135	0.664**	0.655**	0.401**	0.544**	0.553**	0.543**	0.589**	0.519**	0.505**	0.537**	0.638**	0.062	0.826**	1	

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

calculated (Table 1). The results of these calculations indicated a significant correlation between PAHs and soil organic factors ($p < 0.01$), and the method of linear regression analysis showed that the related correlation coefficient reached 0.847, while there was a poor correlation between the concentration of PAHs and pH. Because degradation of PAHs in soil is complicated, this finding suggests that the use of the soil geochemical factors alone is insufficient to assess the soils ability to absorb the PAHs.

3.3. Principal component analysis (PCA)

PAHs could be grouped as a function of their degradation behaviour, and their probable sources determined. When the principal components were ranked by their eigenvalues, most of the variation (>80%) was explained by the first three factors (PC 1, 2 and 3), and the corresponding eigenvectors are given in Table 2. The values of the first three principal components after rotation for the maximum variance are also given. The first three factors were chosen based on their eigenvalues, which were all greater than 1.0.

Sources of PAHs have been discussed in a range of reviews [31–33]. Due to the general lack of characteristic parameters of PAHs in soil, those in air were used as a first approximation to infer sources of the PAHs observed in soils [1,24,33]. The ratio of LMW to HMW PAHs, as well as the presence of specific indicators, was used to discriminate the petroleum/combustion sources of PAHs. This was possible because the types of PAH emitted by each source have been characterised, and a range of signatures have been catalogued. Briefly, HMW PAHs are mainly

Table 2. Total variance explained and component matrices.

Component	Total variance explained								
	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of		Total	% of		Total	% of	
		Variance	Cumulative %		Variance	Cumulative %		Variance	Cumulative %
1	9.17	61.14	61.14	9.17	61.14	61.14	7.65	50.97	50.97
2	2.01	13.41	74.55	2.01	13.41	74.55	2.52	16.82	67.79
3	1.06	7.06	81.60	1.06	7.06	81.60	2.07	13.81	81.60

Variables	Component matrices					
	Component matrix			Rotated component matrix		
	F1	F2	F3	F1	F2	F3
Nap	0.29	0.80	-0.16	0.12	0.15	0.84
Ace	0.11	0.82	-0.28	0.00	-0.03	0.87
Fle	0.45	0.57	0.55	0.06	0.79	0.44
Phe	0.89	0.09	0.32	0.66	0.68	0.12
An	0.62	-0.23	0.50	0.43	0.65	-0.28
Flu	0.89	0.21	-0.18	0.82	0.26	0.37
Pyr	0.97	0.06	-0.02	0.86	0.40	0.20
Baa	0.89	-0.12	0.12	0.78	0.46	-0.02
Chr	0.95	-0.07	-0.09	0.90	0.30	0.09
BbF	0.92	0.13	-0.02	0.80	0.39	0.26
Bkf	0.95	-0.13	0.12	0.83	0.48	-0.03
BaP	0.92	-0.12	-0.29	0.96	0.11	0.10
InP	0.91	-0.15	-0.26	0.94	0.12	0.06
DbA	0.68	-0.41	-0.30	0.82	-0.06	-0.21
BgP	0.64	-0.11	0.00	0.59	0.25	-0.01

Note: Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalisation. Rotation converged in 5 iterations.

produced by combustion, while LMW PAHs are released during petroleum processing [26]. HMWs, such as Flu, Pyr, Chr, BbF, BkF, BaP, InP and BgP, are considered to be derived primarily from combustion [28]. Pyr is one of the primary products of the combustion of fossil fuels, especially coal and kerosene, and other organic materials [31]. Since BaP is not found in petroleum products, it is usually used as an indicator of combustion sources of PAHs, mostly from combustion of coal and vehicle emissions [32]. Baa and Chr are the combustion products of kerosene and natural gas [34]. BbF, BkF, Chr, and BgP are usually formed during incomplete combustion of gasoline [35], while InP has been reported to be a marker for the combustion of kerosene [33]. Ten HMW PAHs (Flu, Pyr, Baa, Chr, BbF, BkF, BaP, InP, DbA and BgP) accounted for the greatest proportion of the loading for PC 1, and explained 51.0% of the total variation among samples, which have been identified as typical tracers of incomplete combustion sources of PAHs. Based on this analysis, it can be concluded that approximately half of the PAHs came from the incomplete combustion of fossil fuels, including coal and natural gas, and the emissions of internal combustion engines. PC 2 accounted for 16.8% of the total variation and was weighted by Fle, Phe and An, LMW PAHs with 3-rings. Fle has been identified as the dominant PAH from the production of coke, and Phe has been used as an indicator of PAHs produced in coke oven sources [35]. As a

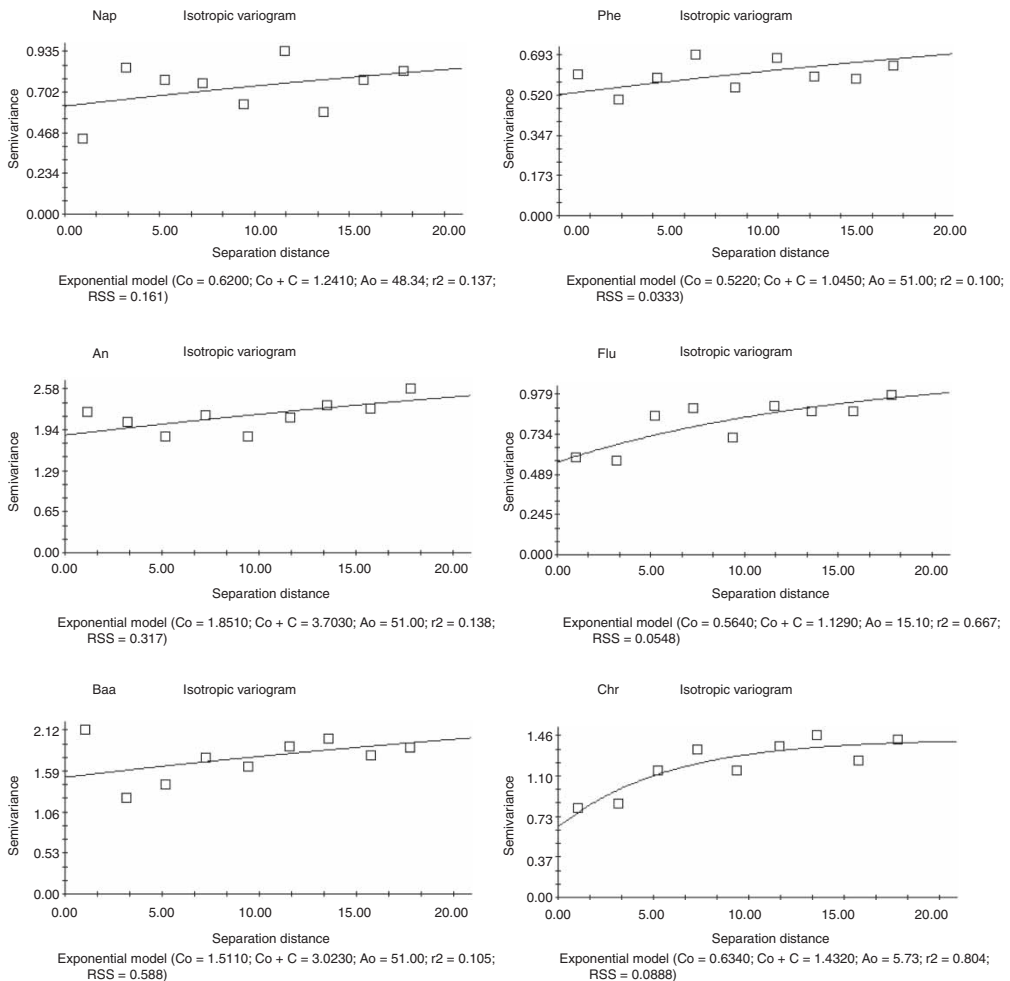


Figure 3. Semi-variograms of Ln-transformed PAH concentrations and the key parameters.

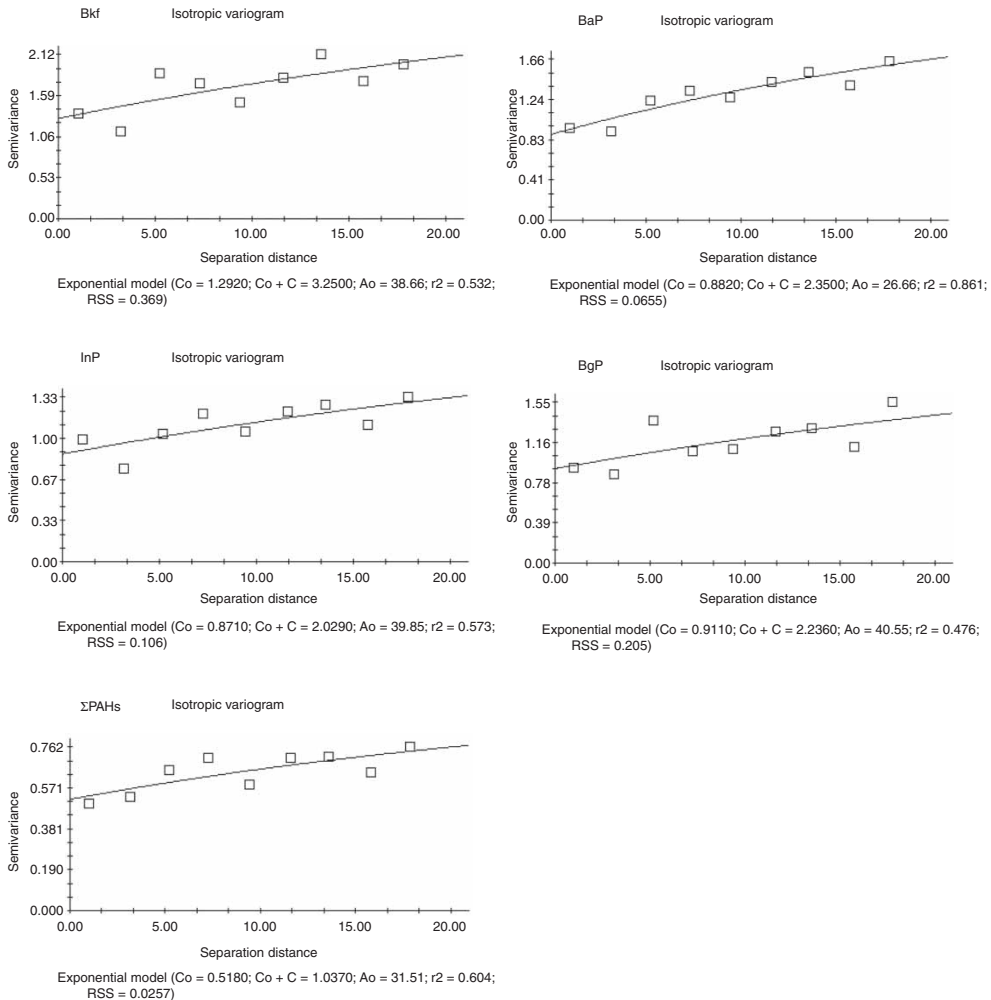


Figure 3. Continued.

result, it was concluded that about 17% of the PAHs came from coke ovens. PC 3 accounted for 13.8% of the total variation and was characterised by Nap and Ace, LMW PAHs with 2–3 rings. We speculate that the contribution of oil leakage and the release of volatile of oil products are likely to be from petroleum processing in the Dagang district [26].

3.4. Spatial variation and distribution analysis of PAHs in BHNA (kriging)

One geostatistical procedure, kriging, was used to impute values for areas that were not sampled from the data that was available [5]. Application of this sort of semi-variance analysis assumes that the data have a normal or approximately normal distribution. Based on concentrations of PAHs measured in this study, the frequency histograms of the log-transformed data produced a general unimodal distribution, suggesting they were approximately normally distributed. The abscissa of an experimental variogram represents the mean of all distances included in a corresponding class, where the maximum distance component equals half of the largest dimension in the area [36]. It has been suggested that it is inadvisable to interpret lags longer than a fifth to

Table 3. Theoretical semi-variogram models for PAHs in the studied area and their corresponding parameters.

Variable	C_0	$C_0 + C$	$C_0/C + C_0$	a (km)	RSS	Model
Nap	0.62	1.24	0.50	48.34	0.16	E
Ace	0.09	1.04	0.09	4.73	1.27	S
Fle	1.21	1.21	1.00	17.79	0.09	L
Phe	0.52	1.05	0.50	51.00	0.03	E
An	1.85	3.87	0.50	51.00	0.32	E
Flu	0.56	1.13	0.50	15.10	0.05	E
Pyr	0.76	2.15	0.35	40.38	0.07	E
Baa	1.51	3.02	0.50	51.00	0.59	E
Chr	0.63	1.43	0.44	5.73	0.09	E
BbF	0.65	1.30	0.50	48.40	0.07	E
Bkf	1.29	3.25	0.40	38.66	0.37	E
BaP	0.88	2.35	0.38	26.66	0.07	E
InP	0.87	2.03	0.43	39.85	0.11	E
DbA	0.01	4.40	0.002	3.46	2.48	S
BgP	0.91	2.24	0.41	40.55	0.21	E
\sum PAHs	0.52	1.04	0.50	31.50	0.03	E

Notes: E, S, and L represent exponential model, spherical model, and linear models, respectively. a (km) means the distance between sampling pairs where the semivariogram reaches maximum. RSS (residual sums of squares) provides an indication of how well the model fits the variogram data: the lower the RSS, the better the model fits.

a third of the transect length, and for reasons of caution only lags up to a fifth of the transect length [37].

Here we have plotted variograms developed from kriging to establish the spatial structure (Figure 3) and determine the potential sources of the measured PAH. The results of the semi-variogram model are presented as solid curves, with the measured values plotted as points and their three key terms – a nugget (C_0), a sill ($C + C_0$), and a range (A) are given (Table 3). There are several terms used to describe the results of such an analysis. Here we give a brief description of each term and how it is used.

The nugget value, C_0 , represents the spatially random variance of concentrations of PAHs at zero distance, which were caused by measurement or scale affects. A similar nugget effect structure existed in all components in origin. The sill ($C_0 + C$) is the maximum variance between data pairs and reflects the variations of regionalised variables in the studied space. The value C presents the explainable proportion of the sill. For each individual PAH component, the sill values are quite different from each other (Table 3). The nugget:sill ratio, $C_0/(C_0 + C)$, is commonly used to express short-distance autocorrelation of regionalised variables. If the nugget:sill ratio is less than 25%, then the variable can be considered to have a strong spatial dependence. If this ratio is between 25% and 75%, the spatial dependence will be considered moderate, and if the ratio equals or exceeds 75% then the spatial dependence will be considered weak [38]. Based on this criterion, the Fle content in BHNA ($C_0/(C_0 + C)$ of 99.99% value) had poor spatial autocorrelation on the study area, indicating that the spatial variation of Fle was mainly caused by natural factors which have equivalent effect, while the NSR values of DbA and Ace were 0.2% and 9.3%, respectively, which indicates that they had extremely strong spatial dependence and were dominated by human activities.

DbA is a major component of gasoline engine exhausts [39] and Ace is possibly from petroleum [26]. The Dagang region is a major base for the petroleum chemical industry in China, with many large state-owned enterprises like the China National Petroleum Corporation located there. More than 4.3 million tons of oil are pumped there annually. All of the other individual PAHs exhibited moderate spatial autocorrelation, which were caused by a combination of natural factors and human activities.

Key parameters of semi-variogram models of PAHs were selected as input to ArcGIS and ordinary kriging was used to do the interpolation and develop isopleths maps. Concentrations of PAHs in the BHNA were closely associated with the various industrial activities. Concentrations of PAHs are generally less in rural soils [31,40]. The greatest concentrations of PAHs were observed in the most industrialised district, Tanggu (1150 ng Σ PAH/g dw), followed by Hangu (657.67 ng Σ PAH/g dw) and Dagang (573.34 ng Σ PAH/g dw).

Since there is no unified international standard for soil PAHs, the Dutch Soil Recovery Standard, which states that each individual PAH has different toxicity potencies [41] and lists 10 PAH guidelines (for Nap, Phe, An, Flu, Chr, Baa, BaP, Bkf, BgP, InP), was selected as a reference to which concentrations of PAHs could be compared. A value of 3 mg/kg dw has been established for sludge in China (GB4284-84). Spatial classified distribution maps were then developed for these 10 PAHs separately (Figure 4). The Dutch standards were applied, and the areas where the concentrations were below the standard were set as blank. It meant that, except for the blank realms in this figure, the concentrations of the PAHs in all the other areas were above the permitted

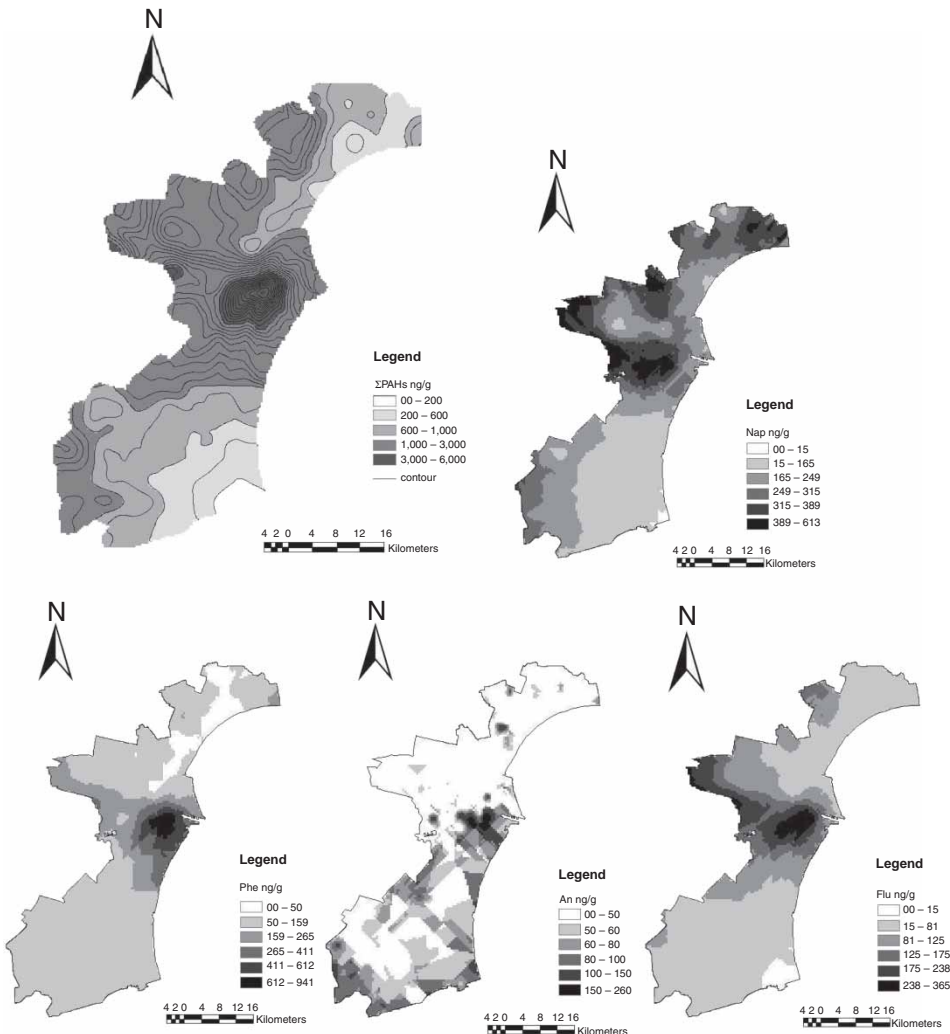


Figure 4. Spatial risk variation of soil PAHs in the study area.

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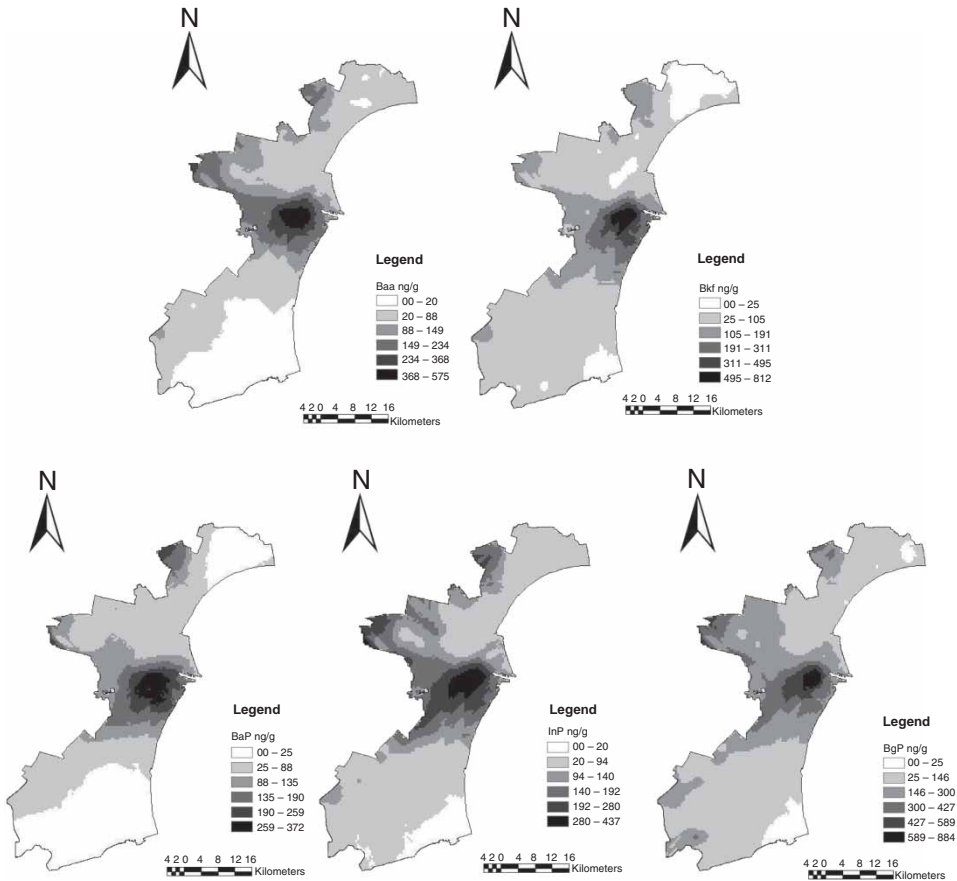


Figure 4. Continued.

values, and the darker the shading the greater the concentration of the PAH exceeds the Dutch guidelines. Nap exceeded the standard the most, with 85.6% of the area exceeding the standard. Flu exceeded the standard as the second greatest proportion of the area (80.8%). An and Baa did not exceed the standard as much, with excesses of 26% and 30.8%, respectively. The other PAHs exceeded the Dutch guidelines by values ranging from 30.8–61.5%.

4. Conclusions

- (1) \sum PAHs were detected in 100% of the surface soil samples in the study area, and the mean concentration of \sum PAHs based on 16 individual PAHs was 814.15 ng \sum PAHs/g dw. Based on the standard proposed by [27], only 7.7% of the soil samples were unpolluted (200 ng \sum PAHs/g dw). The greatest concentrations of PAHs were observed in the more industrialised district of Tanggu, particularly in the vicinity of the chemical industry parks. The greatest risk was due to Nap, which was 1.85 times the Dutch Soil Recovery Standard.
- (2) In the principle component analysis, the first three PCs explained 81.6% of the total rotated variance, while PC 1 accounted for 51% of the total variation. Based on this analysis, the most likely origins of the PAHs were from the combustion of coal, gasoline, diesel oil, and natural gas. Concentrations of individual PAHs were correlated with each other as well as

∑PAHs. However, concentrations of Fle and Ant were not correlated with HMW PAHs, and they had the greatest loadings on PC2, which suggests coke ovens as the source.

- (3) Concentrations of PAHs exhibited moderate spatial autocorrelation, which was the result of combinations of natural factors and human activities.

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