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Study on polycyclic aromatic hydrocarbons (PAHs) contents and sources in the surface soil of Huizhou City, South China, based on multivariate statistics analysis

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Abstract Studies of polycyclic aromatic hydrocarbons (PAHs) in the surface soil were conducted in Huizhou City, which is located in the Pearl River Delta, South China. Sixteen PAHs in 42 soil samples were detected. The results showed that 4 components of PAHs were detectable in all soil samples, and other 12 components were also detectable to some extent. The total PAHs contents range from 35.40 to 534.5 μg/kg with the mean value of 123.09 μg/kg. Soil in Huizhou was slightly polluted by PAHs according to Maliszewska-Kordybach's study. It can be confirmed that the increase of PAHs contents in the surface soil of Huizhou City is closely connected to human activities. Multivariate analysis was also made in this study. Principal component analysis was used to constrain their origins, and 3 principal components (PCs) were extracted. The results showed that coal combustion and oil spilling made the major contributions to PAHs. Cluster analysis was made and 16 priority PAHs were classified as 4 sorts, and the result revealed the differences in environmental behavior, chemical properties and sources of PAHs.

Key words polycyclic aromatic hydrocarbon; surface soil; Huizhou City; source

1 Introduction

In the last 30 years, rapid industrialization and urbanization have led to fast economic growth in the Pearl River Delta (PRD), which thus has become one of the most important industrial and commercial regions in China, but meanwhile large amounts of pollutants have also released into the environments, which has adversely affected environmental quality in the PRD (Ma Jin et al., 2004; Cai Quanying et al., 2007; Tan Jihua et al., 2005). Huizhou City is located in the PRD, which covers an area of 1120 km^2, and accounts for 25% of the total PRD economic area.

Persistent organic pollutants (POPs) are one of the most important types of environmental pollutants, which have become an environmental issue for a long time (Fu Jiamo et al., 2003; Li Chunlei et al., 2007; Luo Xiaojun et al., 2004; Zhang Gan et al., 2006). Polycyclic aromatic hydrocarbons (PAHs) are a typical type of persistent organic polliutants (POPs) widespread in the environment, and have been widely concerned with respect to their persistent, toxic, mutagenic and carcinogenic characteristics (Honda et al., 2007; Thomas et al., 2004; Vane et al., 2007). Sixteen compounds of PAHs have been identified as priority pollutants by U.S. Environmental Protection Agency (US EPA).

Soil, an important environmental material, is a major source and sink of many pollutants (Wild and Jones, 1995; Yi Yang et al., 2008), including heavy metals, polycyclic aromatic hydrocarbons (PAHs), qolychlorinated biphenyls (PCBs), and so on (Qiu Yaowen et al., 2006). It is found that PAHs absorbed by human beings from soil are higher than from air and water (Menzie et al., 1992). Some law-abiding guidelines on soil quality have been set to protect human health in developed countries, but this issue is often neglected in developing countries. Therefore, in this study, the contents and sources of PAHs in the soil in Huizhou City are taken into consideration.

2 Materials and methods

2.1 Site description

Huizhou City can be geographically divided into five parts: Longmen County, Boluo County, Huicheng District, Huiyang District and Huidong County.

2.2 Sampling and sample preparation

The sampling sites were selected according to industrial distributions, soil types and irrigation water types. Forty-two composite soil samples were collected from surface soil (0–20 cm) in Huizhou City (Fig. 1). All soil samples were put into glass jars immediately, then transported to the laboratory and stored in refrigerators at 4℃. Before analysis, all soil samples were air-dried at room temperature of 25℃, and then sieved with 2-mm mesh.

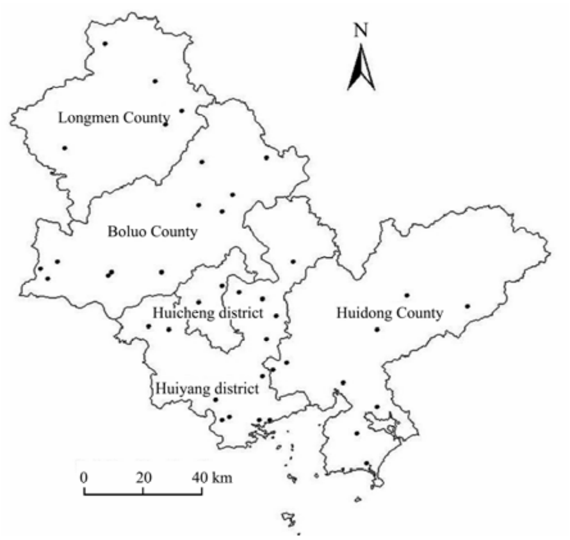

Fig. 1. Sketch map showing the sampling sites in Huizhou City.

2.3 Analysis of PAHs

Sixteen priority PAHs were detected from soil samples and they were abbreviated as Nap (naphthalene), Acy (acenaphthylene), Ace (acenaphthene), Daa (dibenzo[a,h]anthracene), Fle (fluorene), Phe (phenanthrene), Ant (anthracene), Fla (fluoranthene), Pyr (pyrene), Baa (benzo[a]anthracene), Chr (chrysene), Bbf (benzo[b]fluoranthene), Bkf (benzo[k]fluoranthene), Bap (benzo[a]pyrene), I1p (indeno[1,2,3-cd] pyrene) and Bgp (benzo[g,h,i]perylene).

Extraction of PAHs from soil samples was performed according to the US EPA Standard Method 3540C (US EPA, 1996a). Samples were spiked with the surrogate standards and Soxhlet extracted with methylene chloride (200 mL) for 48 hours. Activated Cu (2 g) was added for desulfurization. The extract was concentrated and solvent-exchanged to hexane, and then reduced to nearly 1 mL by high pure nitrogen flow. The extract was let to pass through a gel glass column with alumina:silica=1:2 for cleaning-up and fractionation. The fraction was collected by a 70 mL of solution (methylene chloride:hexane=30:70). The fractions were concentrated to 0.4 mL. Then, the samples were added with internal standards and the analyzed by GC-MS.

The analysis methods were developed from method 8270C (US EPA, 1996b). The analysis was carried out in a Hewlett-Packard (HP) 5890II GC system equipped with a 5973 mass selective detector (MSD) and a 30 m×250 μm×0.25 μm DB-5 capillary column with helium as the carrier gas at the flow rate of 1.2 mL/min. Column temperature was programmed from 70 to 200℃ at 3℃/min and then from 200 to 285℃ at 5℃/min, and held at 285℃ for 12 minutes. The temperature of the injection port and the ion source were maintained at 300 and 230℃, respectively. One μL of the prepared sample was injected by means of an auto-injector. Identification of PAHs was conducted by comparing the relative retention time of samples with that of internal standards. Only the peaks located within the proper range (2%) of retention time were integrated for qualification and quantification, and further qualification was performed in selective ion monitoring (SIM) mode using three different ion masses. Quantitations were performed by using external standards of a mixture of PAHs purchased from Chem Service Inc. The final amount of corresponding PAHs was acquired by calculating the relative signal ratio of PAHs in the samples to that in the internal standards.

The detection limit was defined as three times the standard deviation from the mean blank, and the concentrations below the detection limit were reported as not-detected (ND) (US EPA, 2000).

2.4 Quality control

Laboratory analytical blank and certified reference material (CRM) were added in every two batches (18 samples) of Soxhlet extraction to assess the recoveries and procedural performance.

3 Results and discussion

3.1 PAHs contents in the soil of Huizhou City

Listed in Table 1 is a summary of 16 priority PAHs in the surface soil of Huizhou City, and listed in Table 2 are the standards of soil PAHs pollution made by Maliszewska-Kordybach (1996).

As is seen in Table 1, Nap, Fla, Pyr and Baa were detected in all soil samples, and Acy, Fle, Phe, Bbf and Chr were detected in the soil samples with the ratios of 95.24%, 97.62%, 97.62%, 97.62%, and 90.48%, respectively. Daa has the lowest detectable ratio (38.10%). According to Maliszewska-Kordybach's standards, total PAHs contents of 33 soil samples are lower than 200 μg/kg, which are in coincidence with our result (78.57%); and PAHs contents in 9 soil samples range from 200 to 600 μg/kg, indicating that the soil has been lightly polluted by PAHs.

Table 1. Descriptive statistics of PAHs contents in the soil of Huizhou City (μg/kg)

PAH	Max	Min	Mean	S.D.	Detectable ratio (%)
Naphthalene	27.63	1.00	5.10	13.31	100
Acenaphthene	1.90	ND	0.73	2.45	66.67
Acenaphthylene	4.74	ND	1.76	2.37	95.24
Fluorene	4.90	ND	2.28	2.45	97.62
Phenanthrene	7.50	ND	18.63	28.75	97.62
Anthracene	4.31	ND	1.21	0	52.38
Fluoranthene	56.50	3.05	18.53	26.73	100
Pyrene	51.50	2.31	11.11	24.60	100
Chrysene	24.50	ND	6.03	12.25	90.48
Benzo(a)anthracene	62.50	1.93	11.54	30.28	100
Benzo(b)fluoranthene	140.5	ND	22.87	1.52	97.62
Benzo(k)fluoranthene	22.00	ND	2.50	0	52.38
Benzo(a)pyrene	15.00	ND	5.67	20.00	85.71
Indeno(1,2,3-cd)pyrene	50.50	ND	7.98	25.25	78.57
Dibenzo(a,h)anthracene	9.50	ND	1.32	21.5	38.10
Benzo(ghi)perylene	51.00	ND	7.27	25.5	71.43
Total	534.5	35.40	123.09	196.28	100

Note: ND. not detected.

Table 2. Standards of soil PAHs pollution (μg/kg)

Class	Clear	Polluted slightly	Polluted in middle degree	Polluted seriously
∑PAHs	＜200	200–600	600–1000	＞1000

Table 3. Total variance obtained by principal component analysis

Component	Initial eigenvalue			Extraction sum of squared loading		
	Total	Variance (%)	Cumulative (%)	Total	Variance (%)	Cumulative (%)
1	8.061	50.380	50.380	8.061	50.380	50.380
2	3.351	20.946	71.326	3.351	20.946	71.326
3	1.546	9.663	80.989	1.546	9.663	80.989
4	0.952	5.953	86.942			
5	0.733	4.582	91.524			
6	0.606	3.789	95.313			
7	0.259	1.621	96.934			
8	0.175	1.092	98.025			
9	0.100	0.622	98.648			
10	0.086	0.540	99.188			
11	0.046	0.285	99.472			
12	0.030	0.190	99.663			
13	0.025	0.155	99.818			
14	0.018	0.115	99.933			
15	0.007	0.044	99.977			
16	0.004	0.023	100.000			

Note: Extraction method: Principal component analysis.

According to Edwas (1983), the concentrations of endogenic PAHs are within range from 1 to 10 μg/kg, mainly derived from plant decomposation and fire disasters. But the total PAHs contents in this study range from 35.40 to 534.5 μg/kg, and even their lowest content (35.40 μg/kg) is much higher than Edwards's standard. So, it can be seen that PAHs in the soil of Huizhou City mainly comes from human activities.

3.2 Principal component analysis

Principal component analysis (PCA) as a multivariate analytical tool is often used to reduce the original variables, which has been used to identify the major sources of PAHs emissions (Dusan et al., 2004). The contributions of each of the sources could be distinguished by their different physical and chemical properties. Sixteen types of PAHs as active variables and 42 soil samples as subjects were selected to normalize and make PCA by using the SPSS 13.0 software (Table 3).

The PCA calculations for 16 PAHs at 42 sites resulted in three PCs accounting for 80.989% of the total variance of the data. PC1, PC2, and PC3 account for 50.380%, 20.946%, and 9.633% of the data, respectively. PC1 has high concentrations of Baa, Bbf and Inp. PC2 is dominated by Acy and Ant. PC3 is highly loaded with Phe (Table 4).

Table 4. Component matrix of PAHs

		Component		
		PC1	PC2	PC3
1	Nap	0.405	0.742	0.197
2	Acy	-0.226	0.925	-0.022
3	Ace	-0.187	0.595	-0.317
4	Fle	0.387	0.467	0.223
5	Phe	0.816	-0.067	0.520
6	Ant	-0.285	0.807	-0.221
7	Fla	0.877	-0.018	0.406
8	Pyr	0.785	0.139	0.450
9	Chr	0.761	0.534	-0.187
10	Baa	0.920	-0.223	0.026
11	Bbf	0.945	-0.174	-0.156
12	Bkf	-0.100	0.514	0.419
13	Bap	0.854	0.169	-0.438
14	I1p	0.947	0.007	-0.230
15	Daa	0.876	-0.186	-0.372
16	Bgp	0.898	0.063	-0.225

Note: Extraction Method: Principal Component Analysis. 3 components extracted.

According to McCready et al. (2000), 4-, 5-, and 6-ring PAHs are mainly derived from combustion, while 2- and 3-ring PAHs mainly from oil spilling. In this study, Baa, Bbf and I1p are 4-, 4- and 5-ring, respectively, and distributed in PC1. Acy is 2- ring which is contained in PC2. So, it can be deduced that PC1 is indicative of combustion origin and PC2 of oil spilling origin. Phe is an important referent of coal burning, so, PC3 is regarded as one of coal combustion origin.

Recently, some PAHs isomer ratios were used to elucidate the possible sources of PAHs (Budzinski et al., 1997). According to Yunker et al. (2002), the ratio of (Fla+Pyr)$<$0.4 tends to indicate that PAHs are derived from crude oils; the ratio of (Fla+Pyr)$>$0.5 indicates that PAHs are derived from biomaterial burning, and the ratio of 0.4$<$(Fla+Pyr)$<$0.5 indicates that PAHs come from gasoline burning. In this study, (Fla+Pyr)=0.625, so, it can be indicated that PAHs in the soil of Huizhou City are mainly derived from biomaterial burning.

3.3 Cluster analysis

Sixteen types of PAHs as active variables and 42 soil samples as subjects were also selected to make Hierarchical cluster analysis (HCA) with the SPSS 13.0 software, in order to further constrain the sources of PAHs and analyze their characteristics. The result of HCA analysis can be used to verify the result of PCA (Facchinelli et al., 2001).

Sixteen types of PAHs were distinctly classified as 4 clusters for HCA (Fig. 2). Acy, Ant, Ace, Fle, Daa, Bkf, and Nap constitute the first cluster; Chr, Bap, I1p, and Bpe, the second cluster; Phe, Fla, Pyr, and Baa, the third cluster; and Bbf alone, the forth cluster.

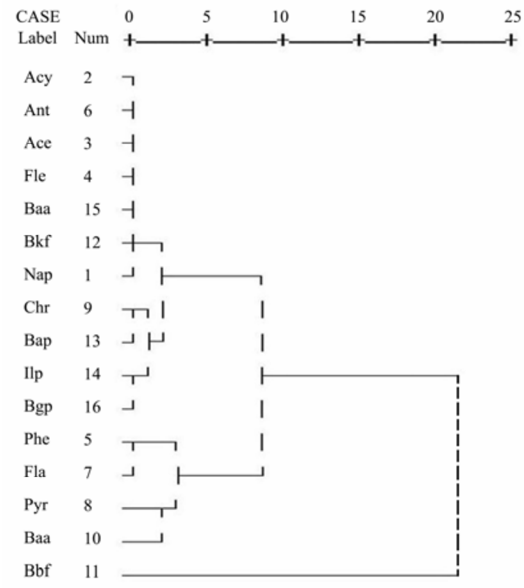

Fig. 2. Clustering tree of PAHs concentrations in soil.

The results showed that PAHs clusters are classified mainly according to the numbers of aromatic rings. The first cluster mainly contains 2- and 3-ring PAHs. The second and third clusters are mainly related to 4- and 5-ring PAHs.

The results revealed the differences in environmental behaviors and physical and chemical properties of PAHs. For example, 2- and 3-ring PAHs can be volatilized from the soil (Kipopoulou et al., 1999), while 4-, 5-, and 6- ring PAHs cannot be. 2- and 3-ring PAHs can be decomposed by microorganisms in the soil, while 4-, 5-, and 6-ring PAHs are more stable and can not be decomposed by microorganisms (Gao Xuesheng et al., 2002).

The results can also provide information about the sources of PAHs. According to Harrison et al. (1996) and Mastral et al. (1996), Phe, Fla and Pyr mainly come from coal combustion.

4 Conclusions

Results of this study showed that 16 priority PAHs are widespread in the surface soil in Huizhou City. The concentrations of PAHs in the soil are closely connected with human activities. Fle and Phe contents are highest in the surface soil, and Ant is lowest. 21.43% of the soil samples are lightly polluted by PAHs. The result of PCA indicates that coal combustion and oil spilling have made the main contributions to PAHs in the soil of Huizhou City. The results of HCA revealed the differences in the environmental behaviors, physical and chemical properties and sources of PAHs.

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