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Pattern of polycyclic aromatic hydrocarbons (PAHs) pollution in communication air of Hangzhou, China

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Abstract: Nine PAHs were surveyed in communication air of Hangzhou. The results indicated that the PAHs pollution is very serious and the total sum of 9 PAHs, on the average are 3.39 - 13.82 $\mu g/m^3$. The PAHs signatures for all streets are similar to each other. Multivariate statistical techniques were used to investigate source apportionment for PAHs. A factor analysis/multiple regression model was successfully applied to the study. The most important three PAHs sources in communication air are diesel emission, gasoline engine emission, coal-burning accounting for 61.1 ± 6.4%, 19.9 ± 8.3%, 10.8 ± 10.8% of total PAHs, respectively. The relationship for three source tracers and total PAHs is: [PAHs] = 1.471(±0.155)[Phen] + 2.538 (±2.522)[1-Mepy] + 2.254 (±0.943)[Chry] + 1.022 (±1.767).

Keywords: PAHs; air; source apportionment; city communication

1 Introduction

Polycyclic aromatic hydrocarbons(PAHs) contain two or more aromatic rings which fused together in different possible arrangements, thus numerous PAHs, their isomers, and their derivatives are theoretically possible. Because many of them and their analogs are strongly potent carcinogens and/or mutagens, the source, occurrence and fate of PAHs in the environment have been studied with great interest. They are usually generated during anthropogenic combustion processes, such as fossil fuel combustion(Rogge, 1993) or in natural processes, such as forest fires or volcanic eruptions. But the contribution of each source to PAHs in environment differs much from each other. Certainly with different PAHs emission factors the contribution of vehicles to PAHs in communication air differ much too. So only we find out the significant sources can we control PAHs pollution effectively. In this way source apportionment is of great importance.

PAHs pollution is a serious public health problem in most metropolitan areas around the world, and rapidly growing vehicle fleets with poor emission and maintenance standards are a significant contributor to PAHs pollution in developing countries. Congested traffic influences PAHs emission and high building, obstacles to ventilation result in high PAHs concentrations. Additionally, we spend so much time on roads everyday going to work, going home, having a walk and so on. Thus PAHs pollution in city communication air are of particular concern. In 1998, PAHs pollution in communication air of Hangzhou was surveyed with relationships between PAHs concentration and distribution in air with traffic intensity, wind velocity, temperature and concentrations of NOx, SO_2 and TSP evaluated. The results indicated that PAHs pollution in street air was very serious and the total sum of nine PAHs, on the average were 3.39 - 13.82 $\mu g/m^3$, among which benzo[a]pyrene changed between 0.08 $\mu g/m^3$ and 0.34 $\mu g/m^3$ much higher than results of other countries (Nielsen, 1996). We also found that the correlation between the concentration variation of PAHs and NOx in the air was significant, but as for the SO_2 the correlation was weak, which showed that vehicle emissions were the main source of PAHs. In Hangzhou gasoline and diesel oil are the two most popular kinds of fuels used to start vehicles. This paper is aimed to estimate the contribution of each kind of vehicles to total PAHs. Thus we can obtain a good understanding of PAHs exposure and control PAHs pollution effectively.

Two basic types of receptor models may be applied to yield quantitative source apportionment-chemical mass balance (CMB) and multivariate techniques (Gordon, 1988; Hopke, 1985). Chemical mass balance models require a priori knowledge of the source signatures for a given area. Since these are not available for

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Hangzhou, and, additionally many kinds of PAHs are active which always take part in chemical reactions once discharged, multivariate techniques must be employed to apportion each source, which does not require the explicit source measurement of priori knowledge of the emission characteristics of the sources. Multivariate techniques include regression of principal components, common factor analysis/multiple linear regression (FA/MR) and target transformation factor analysis (TTFA) (Gordon, 1988; Lioy, 1985; Morandi, 1987; Pratsinis, 1988; Zelenka, 1994).

In this paper, we analyzed PAHs data collected in 1998 with factor analysis/multiple linear regression (FA/MR). We used factor analysis (FA) to relate the different PAHs to the sources and then apportioned the sources using multiple regression (MR). This work was performed using SAS software.

1.1 Factor analysis

Factor analysis attempts to reduce the number of dimensions in a multivariate data set while preserving most of the variance in the original data. The original variables are transformed into new sets of variables, or factors, in such a way that the first factor accounts for most of the variability in the data. The successive factors account for decreasing amounts of the residual variance. The factors are formed by linear combinations of the original variables and are orthogonal to each other. In a receptor modeling approach, each factor may be considered to be one source. Each original data point(referred to as an object) in fewer dimensions as a function of the factors and is a point in the new data space. Its coordinates are called factor score. For n-dimensional measurements of y objects, the Xth factor scores of the Yth object, Z_{XY} is expressed as follows (Smyers, 1984):

$$Z_{XY} = \sum_{j=1}^{n} a_{xj} v_{jy},$$

where a_{xj} is the loading of the Jth variable on the Xth component for the Yth observation and v_{jy} is the Jth variable of the Yth observation. The loadings a_{xj} are a measure of the correlation of the corresponding variable along the particular factor. That is, they measure the contribution of the original variable to the factor Z_{XY}.

1.2 Multiple regression

The multiple regression model is represented by the simple formula:

$$Y = \sum_{i=1}^{p} m_i x_i + b,$$

where Y is the dependent variable concentration, m_i is the modeled regression coefficient, x_i is the concentration of the unique tracer, p is the number of sources identified by factor analysis (Morandi, 1987). If a tracer is not unique then its concentration must be reduced by the amount accounted for by other factors. This is performed by applying the following formula:

$$x_i = \sum_{i=1}^{p'-1} m_i' n_i + b,$$

where x_i is the measured concentration of the non-unique tracer, p' is the number of factors that contribute to x_i, m_i' is the modiled regression coefficients, and n_i is the concentration of the unique tracers of the factors that difference between the actual concentration of the non-unique tracer and that which is accounted for by the other factors:

$$b' = x_i + \sum_{i=1}^{p'-1} m_i' n_i,$$

where b' is no longer the modeled constant from the multiple regression, but the value calculated for each sample. The modified tracer, b', is then used in the multiple regression.

2 Experimental

The sampling and analysis of PAHs in communication air were described elsewhere (Zhu, 1997; 2000). Except sampling point 1, which was in a campus with clear air the other three sites all located in city communication with congested traffic and heavily polluted air. PAHs air samples were got with low noise small samplers at a flow rate of 1.0 L/min for three hours: 7:00 am—10:00 am, 11:00 am—14:00 pm, 15:00 pm—18:00 pm. Before and after the sampling programs, the flow rates were measured and all the derivations of the rates were less than 1%. The sampler was equipped with a 25 mm glass-fiber filter (GF, Whatman, England) and XAD-2 (2.5g) to collect particle and gas phase PAHs, respectively. All sampling program lasted for three days.

3 Results and discussion

3.1 Signature for PAHs

The PAHs concentrations were evaluated in summer season. It was indicated that mean PAHs concentrations of four sampling points ranged from 3.39 $\mu g/m^3$ to 13.82 $\mu g/m^3$. Fig. 1 shows the average concentration distributions for 9 PAHs in sampling point 1, 2, 3 and 4. It was obvious that PAHs of point 2,3, 4 had a well similar distribution because environment there was alike crowded with large quantities of vehicles and bad ventilation. With the same main source the distribution of PAHs of point 2, 3 and 4 were similar to that of PAHs in a tunnel which had been studied before(Zhu, 1999). But PAHs in a tunnel air originated only from vehicle emission while PAHs of point 2, 3 and 4 had many sources(such as distant transmission). At the same time, without sunlight in a tunnel PAHs were not active enough to take part in many reactions. But things were different in sampling points with strong sunlight and other PAHs sources. Thus their distributions differed a little with many similarities. Point 1 is in campus with clear air. PAHs attributed greatly to distant transmission thus had a low concentration. It was clear that PAHs with high molecular weight are the main part, about 90% of the total PAHs, among which phenanthrene had a predominant position accounting for about 40% of 9 PAHs. The results agreed to Halsall's findings (Halsall, 1994).

The partitions of 9 PAHs between vapor and particulate phase were mostly depended on their own chemical and physical characteristics. Pankow reported that in urban samples the concentrations of vapor PAHs correlate well with their subcooled liquid vapor pressures. The vapor pressures of PAHs strongly correlate with their molecular weights. With the increase of molecular weights the estimated the vapor pressures bring down correspondingly. Fig. 2 shows the partition of each PAHs between vapor and particulate phase. As we can see that about 90% of the total PAHs existed in gas phase.

3.2 Qualitative analysis of sources

Ratios of specific PAHs are characteristic of different sources and usually are used to do qualitative analysis of sources. Common ratios used include phenanthrene to anthracene (Phen/Anthr), benao[a] anthracene to chrysene (BaA/Chry) and benzo[e]pyrene to benzo[a]pyrene(BeP/BaP). The mean values ($\pm$ s.d.) for these ratios in sampling points were presented along with values for several sources in Table 1. Since some kinds of PAHs are active and are apt to take part in many reactions the results may be wrong in a sense. Additionally ratios are different with changes of climate, environment and so on. In a word ratios can only be used to identify sources roughly. From Table 1 we found ratios of sampling points were close to those of gasoline and diesel exhaust.

3.3 Factor analysis

The original study was not designed with factor analysis in mind, thus the number of samples was a little small but statistics believes when the number of samples is large than that of variables it may perform well only with a little unstable result.

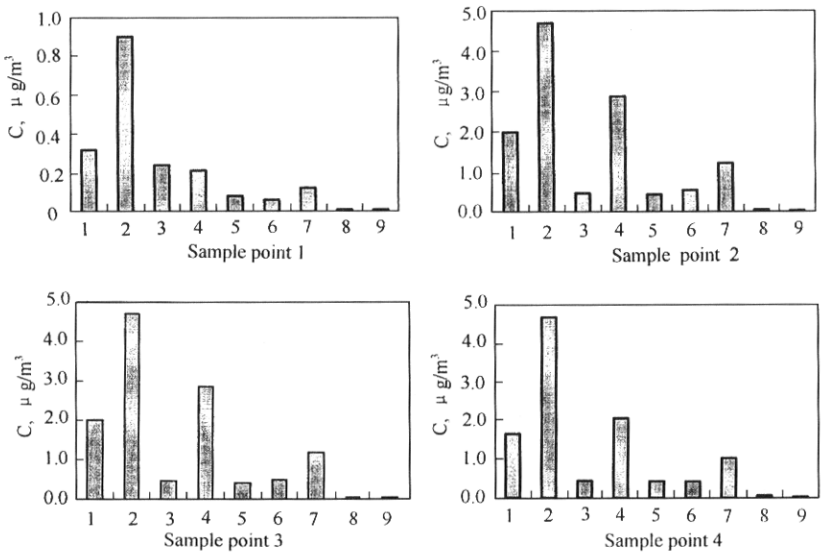

Fig.1 Concentrations of PAHs in air of sample point 1,2,3 and 4
1—9: Fluor, Phen, An, Flur, Py, 1-Mepy, Chry, BeP and BaP

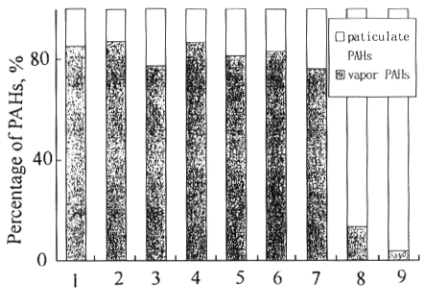

Fig. 2 Distribution of PAHs in vapor and particulate phase
1—9: Fluor, Phen, An, Flur, Py, 1—Mepy, Chry, BeP and BaP

Table 1 Diagnostic PAHs ratios in air of samples and typical sources

	Phen/An	BeP/BaP
Point 1	9.6(6.5)	1.1(0.4)
Point 2	9.4(1.5)	2.8(1.4)
Point 3	9.1(1.0)	2.9(1.6)
Point 4	11.7(3.4)	2.2(1.1)
Vehicles[a]	2.7	
Gasoline exhaust[b]	3.4 - 8	1.1 - 1.3
Firewood fire[c]	3.0	0.44
Coal[c]	3.0	0.84 - 1.6
Diesel[b]	7.6 - 8.8	2 - 2.5
Tunnel	6.6	1.1

Notes: a. Harrison R M, 1996; b. Rogge W F, 1993; c. Gschend P M, 1981

The rotated factors of PAHs air concentrations are presented in Table 2. According to statistics we selected factors with eigenvalues larger than 1. The first three factors accounted for 70% of the variability in the data and separated the PAHs into identifiable source categories.

Factor 1: Accounting for 36% of the total variance, factor 1 was highly loaded on the fluorene, anthracene and benzo[e]pyrene with the largest load on phenanthrene which had predominant position (about 60%) in diesel emissions (Kulkarni, 2000). Diesel emissions mainly produce PAHs with low molecular weight while gasoline emissions mainly produce PAHs with high molecule weight (Westerholm, 1994). Based on above information factor 1 was selected to represent diesel emissions and the tracer used for the multiple linear regression was phenanthrene.

Factor 2: Accounting for 18% of the total variance factor 2 had the same loading pattern with factor 1, only higher loaded on PAHs with four or five aromatic rings and lower loaded on PAHs with three aromatic rings. Factos 2 was assigned to represent gasoline emissions and the tracer was chrysene.

Factor 3: Accounting for 16% of the total variance factor 3 was highly loaded on pyrene, anthracene with the highest load on 1-methypyrene which are predominant in coal combustion signal (Harrison, 1996;

Masclet, 1987; Mastral, 1996). Emissions from coal combustion exhibit relatively amounts of alkyl PAHs than other combustion sources (Lee, 1977; Simo, 1987). Factor 4 was selected to represent coal combustion and the tracer was 1-methypyrene.

3.4 Multiple regression

The results of the multiple regression are shown in Table 3 and indicated the diesel emissions, gasoline emissions and coal combustion accounted for 61.1 ± 6.4%, 19.9 ± 8.3%, 10.8 ± 10.8% of the total PAHs, respectively. The relationship between total PAHs and three source tracers were: [PAHs] = 1.471 (±0.155)[Phen] + 2.538 (±2.522)[1-Mepy] + 2.254 (±0.943)[Chry] + 1.022 (±1.767). Hangzhou is a middle city with not-wide roads crowded with buses running everyday, most of which work with diesel engines. So to the city, PAHs mainly originates from oil-burning. But coal is still playing an important role in factory productive activities and producing PAHs too.

Table 2 Rotated factor loading matrix

	1	2	3
Fluor	0.205	0.751	0.000
Phen	0.840	0.244	0.000
An	0.567	0.422	0.434
Flur	0.474	0.576	-0.362
Py	-0.314	-0.253	0.778
1-Mepy	0.142	0.105	0.840
Chry	-0.104	0.806	0.045
BeP	0.702	0.102	0.056
BaP	-0.863	0.156	0.210
Cumulative, %	36	54	70

Table 3 Tracers of sources and their contributions to PAHs

Type	Tracer	Contribution, %
Diesel exhaust emission	Phen	61.1 ± 6.4
Gasoline exhaust emission	Chry	19.9 ± 8.3
Coal combustion	1-Mepy	10.8 ± 10.8

4 Conclusions

In communication air of Hangzhou the three most significant PAHs sources were diesel exhaust emission, gasoline exhaust emission, coal combustion accounting for 61.1 ± 6.4%, 19.9 ± 8.3%, 10.8 ± 10.8% of the total PAHs, respectively. The relationship between total PAHs and three source tracers was: [PAHs] = 1.471 (±0.155)[Phen] + 2.538 (±2.522)[1-Mepy] + 2.254 (±0.943)[Chry] + 1.022 (±1.767).

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