Source Identification of Polycyclic Aromatic Hydrocarbons in Atmosphere Particulate of Qingdao, China

Yinhai LANG[1,2], Fangfang CHENG[1,2]

[1]*College of Environmental Science and Engineering, Ocean University of China, Qingdao, China, 266100*

[2]*Key Laboratory of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao, China, 266100*

Email: yhlang@ouc.edu.cn

Abstract: Identification and quantification of 16 priority Polycyclic Aromatic Hydrocarbons (PAHs) collected from 4 atmosphere particulate samples in December 2008 to January 2009 were determined by gas chromatography (GC). The source of the PAHs in atmosphere particulate was estimated by chemical mass balance model and improved source apportionment technique. Dust was the major PAHs source in Qingdao, accounting for 60.69% of the total PAHs emissions, followed by coal dust (20.50%), soil dust wind (11.47%), and vehicle exhaust (7.34 %).

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Source apportionment; CMB; Improved source apportionment

1 Introduction

PAHs as one of the air most complex and most damaging pollutants has drawn serious pollutions especially in the urban areas. PAHs are introduced into the environment mainly via anthropogenic inputs and biological conversion of biogenic precursors. Anthropogenic input was regarded as the main source for the elevated concentration of PAHs in the environmental matrix including combustion of fuels, power generation and heat generation from fossil fuels, wood burning, and incineration of industrial and domestic wastes, automobile exhaust, and road runoff/street dust [1]**.** And PAHs are formed mainly via two mechanisms: incomplete combustion of fossil fuels and discharge of petroleum-related materials [2]. Other sources all have inter-relationship with the two mechanisms. After entering the environment, more are accumulated in atmosphere particulate [3].

There is an increasing concern about the hazardous effects of PAHs on humans and other living organisms. PAHs have been identified to be one of the major toxic air pollutants in Chinese urban air. Source apportionment is an effective method for air quality assessment. Numerous studies have been carried out to understand the air pollution source, chemical mass balance (CMB) modeling has been widely used as a tool in source apportionment of atmospheric PAHs in urban areas of china, such as Urumqi, Shenzhen [4-5]. But there are some problems of CMB model, aim to solve the shortcomings CMB model exits, Feng put forward the improved source apportionment technique to solve the difficult problems[6]. The improved source apportionment technique has been applied in the source apportionment of TSP and PM_{10} in Jinan successfully [7].

Qingdao is a developed industrial coastal city in china, which is temperate monsoon and significant maritime climate. The concentrations of PAHs have evident seasonal distribution in Qingdao [8]. The study is attempted to calculate the source contributions of PAHs in atmosphere by CMB model and improved source apportionment technique [9-11].

This work was supported by National Natural Science Foundation of China (No. 40706039).

2. Materials and methods

2.1 Sampling

In order to investigate the pollution of PAHs in environmental function zone, the particulate matter monitoring and sampling program in Qingdao city was carried out from December 2008 to January 2009 in winter. A total 4 sampling sites were selected to measure and determine the PAHs concentrations in the ambient air in Qingdao. These sites were located in the north, east, west, and center of bustling urban district of Qingdao city , representing industrial zone (R1: 36°8'N, 120°21'E), commercial traffic residential areas (R2: 36°7'N, 120°21'E), coastal settlements (R3: 36°3'N, 120°24'E) and cultural scenic area(R4: 36°4'N, 120°20'E) respectively. After completing sample collection, recorded the flow. Filters were wrapped the glass fiber filters with aluminum foil, put it back into desiccators, and then carry them to laboratory until analyses were performed.

2.2 Analytical procedure

The glass fiber filters were cut into pieces with stainless steel scissors, and then put into the 100 ml stoppered curettes, add in 30 ml hexane/dichloromethane（1:1, V/V）and 1 g activated copper granules, standing for 20

min after ultrasound at 40℃, shift the supernatant to rotary evaporator bottle. The concentrate was transferred into a chromatography with inner diameter of 10 mm, then eluted by 50 ml dichloromethane/hexane（3:7, V/V）controlling the flow at 2 ml/min, the final volume was concentrated to 0.5 ml under a gentle N_2 stream , at the last, constant volume to 1 ml.

Chromatographic analysis used GC (Japan Shimadzu Corporation) equipped with FID detector. The qualitative analysis of 16 PAHs took the retention time of the known standard material as reference, and the quantitative analysis determine the contents of 16 PAHs used external standard quantitative method. GC was used with splitless injection mode of sample introduction accomplished by AOC-20i+s (Japan Shimadzu Corporation), and the injection volume was 1 μl. Analytics were separated with a DB5 column (30.0 m × 0.25 mm diameter, 0.25 μm film thickness).The GC temperature program was as follows: initially at 80℃ for 1 min, increased to 255℃ at 15℃/min, and held for 1 min, increased to 265℃ at 1℃/min for 1 min, then increased to 295℃ at 2.5℃/min for 5 min. The inlet temperature was 250℃, detector temperature was 300℃, the flow of hydrogen was 40.0 ml/min and gas was 400.0 ml/min.

2. 3 Quality Control and Assurance

Quality control and assurance for PAHs analysis were based on the precision which is finished by the study of parallel samples. It indicates the random error of analysis and measure system. In the current manuscript, parallel experiments have been used to individual samples of monitoring stations. The precision in this study have been evaluated by relative standard deviation（RSD）of 16 PAHs species, and the RSD is in the range of 3.47% ~ 6.53%.

2.4 CMB model

CMB calculates source contribution estimates using a linear combination of source profiles to describe the ambient concentrations of a set of fitting species of atmospheric particles. The CMB model provides technical methods for decision-making on air pollution control base on mass balance assumptions. The CMB model assumptions[12] are: (1) compositions of source emissions are constant over the period of ambient and source sampling; (2) chemical species do not react with each other (i.e., they add linearly); (3) all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized; (4) the number of sources or source categories is less than or equal to the number of species; (5) the source profiles are linearly independent of each other; and (6) measurement uncertainties are random, uncorrelated, and normally distributed.

The purpose of improved source apportion method is to deal with the collinearity of different emission sources. Improved source apportion method can be used to solve the technical difficulties in ambient air, and the problems in particles shifting from different forms in different ways into the atmosphere. This method is a technology basis for quantitative management.

3 Results and discussion

3.1 Source profile

Source apportionment was conducted using the EPA-CMB Model. The basic idea of CMB model is that the measured chemical pollutants in a sample are the sums of the contributions from several sources. 16 individual polycyclic aromatic hydrocarbons, including naphthalene (NaP), acenaphthylene (APY), acenaphthene (ACP), fluorene (FLU), 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), indeno(1,2,3-cd)pyrene (IND), dibenzo(a,h)anthracene (DbAha) and benzo(ghi)perylene(BghiP), were applied in the CMB model for apportioning primary sources.

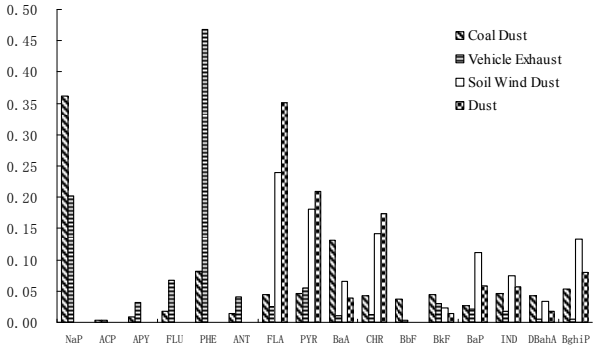

Figure 1. Percent contributions for individual samples

The CMB modeling studies are generally based on literature source reports analyzed by chemical analysis techniques. Ratios of specific PAH compounds were calculated to evaluate the possible sources of PAH in atmosphere particulate. Four sources were considered in the CMB model based on the result of ratio analysis. The four sources were coal dust, vehicle exhaust, soil wind dust, and dust.

Figure 1 suggested the percent contribution of NaP, PHE, FLA, PYR, BaA, BkF and BghiP with the higher contribution. Several PAH compounds were selected as marker compounds for the model. NaP, PHE, FLA and PYR were as the marker of coal dust, vehicle exhaust, soil wind dust and dust, respectively. Because of the number of marker compounds must be greater than the number of sources [1]. And some correlations can be

978-1-935068-16-7 © 2010 SciRes.

found among the compounds, such as FLA and PYR from soil wind dust and dust. So also select BaA, BkF, BghiP for fitting calculation.

3.2 Source apportionment

The improved source apportionment results (showed in Table 1) of PAHs at the four sampling stations are different from each other. The R1 and the R2 are dominated by dust and coal dust, but for the R3 and R4, dust and soil wind dust are important contributions. For the average contribution of the four monitor stations, coal dust and dust were the main components (occupy 81.19%). So the coal dust of R1 and R2 contribute more for the average.

Table 1. The double source apportionment results of PAHs in atmospheric aerosol in winter (relative contribution %)

	R1	R2	R3	R4	Average
coal dust	24.61%	24.25%	17.35%	16.95%	20.50%
vehicle exhaust	13.04%	0.00%	9.00%	7.16%	7.34%
soil wind dust	8.78%	22.17%	20.07%	22.32%	11.47%
dust	53.58%	58.66%	61.95%	64.17%	60.69%

For the source apportionment results of four environmental function zones, the dust all with the highest contribution of PAHs during winter months in Qingdao, are roughly 60% of total sources in average. It was interpreted as other three sources have significant corrections with dust and all have contributions for dust to some extent. For R1 station the dust was 53.58%, is lower than the others, the main reason is the factory have adopt some environment protection measures to conform to the government's environmental requirements, water spray dust is an approach used widely. The dust contribution for R2 and R3 are approach to the average, but the R4 was 64.17%, little higher than average, can be interpreted as street cleaning around and other activities.

The contribution value of coal dust accounted for 20.50% of the total variance. It was interpreted as the heating is universal in winter in the north, and the other coal combustion as the main heat energy consumption for heating. Several factories located around the R1, these factories could perform industrial combustion consuming considerable amounts of fuels. For site R2, heating system in winter compare to R3 and R4 were more powerful, so lead to a higher contribution.

The third principal source was soil wind dust, result from the climate of Qingdao is temperate monsoon climate and significant maritime climate, strong northern wind is frequently in winter, which can accelerate the formation of sand. In addition, coastal PAHs and manufacturing process also can affect the result. Since environmental protection measures have been adopted in the factory, So soil wind dust only with 8.78% in R1, much lower than the average contribution. That attribute to a low average contribution 11.47%.

Vehicle exhaust identified with 7.34% and explained by the heavy traffic in the bustling city center. In this case, the PAHs were higher molecular mass parent PAH compounds due to the higher temperature [2].For R1, representing the industrial zone, vehicle exhaust has a higher contribution due to the transportation of raw materials and products to some extent. Vehicle exhaust is rarely in R2, which causes no contribution, which is because vehicles are prohibited in the educational district. The contribution of R3 and R4 was mainly draw up by the traffic around.

In this study, the average of four sample sites representing four environment function area was observed as the general result of Qingdao. The primary PAH sources to Qingdao atmosphere particulate are dust (60.69 %), coal dust (20.50%), soil dust wind (11.47%), and vehicle exhaust (7.34 %).

Though receptor methods have increased the reliability of source apportionment and the improved source apportionment used by CMB model have given a better results, there also limitations of CMB model exits: the chemical reaction among pollutants occurred easily after PAHs are released into the atmosphere, the receptor component of sources will have a greater concentration of errors[13], and the same type of pollution emission profiles of PAHs changed greatly (such as the component spectrum of coal dust have relationships with the model of boiler, the type of coal, combustion temperature, oxygen supply and so on.). However, in order to improve the air quality of Qingdao, the chemical profiles of studies sources could guide various stakeholders including the researcher and policy makers in implementing a suitable pollution abatement policy in the area of concern.

3.3 Diagnostic tools results

The absolute accuracy of each case is also assessed by determining whether the solution is statistically reasonable and if so, whether it is also accurate. Three outcomes are possible. The CMB results are evaluated by using R^2 value, chi^2, and the percent mass. The diagnostic results are showed in Table 2:

Table 2. The diagnostic results for data from different monitoring stations (after fitting)

Index	Standard	R1	R2	R3	R4	Average
R^2	0.8－1.0	0.90	0.96	0.91	0.90	0.91
CHI^2	<4.0	1.16	0.22	0.85	0.89	0.83
%	80%－120%	106.00%	121.60%	107.80%	111.20%	109.90%

The R^2 of PAHs explained by the CMB model ranges from 0.90 to 0.96, with all runs being within the acceptable range of 0.8 − 1.0; the values of CHI^2 with the results statistics of 4 sampling sites showing a good fit to

the data (Chi^2< 4.0); the determination of mass fraction for 3 other sampling sites except site R^2 are within the standard ranges from 80% to 120%. But the average values of the three diagnostic parameters are within the standard. The analysis result is possibly because that the percent contributions from literature in a single season used to source apportionment may show some differences. But the total results are accurate and convincing.

4 Conclusions

Four possible sources were considered in the CMB model based on analysis, and seven PAH compounds (including NaP, PHE, FLA, PYR, BaA, BkF and BghiP) were selected for fitting calculation. It appears that the improved source apportionment used by CMB model gives good model results: Dust (60.69 %), coal dust (20.50%), soil dust wind (11.47%), and vehicle exhaust (7.34%) are the major PAH sources to Qingdao, respectively. In conjunction with the source apportionment modeling results, these indicators suggest that dust and coal dust were the major source of PAHs in Qingdao throughout the winter months, account for about 81% of the contribution. The analysis results also can be affected by meteorological and environment conditions.

References

[1] Li Kai, Christensen Erik R., Vancamp Ryanp, Moglu Ipekima. PAHs in Dated Sediments of Ashtabula River, Ohio, USA [J] Environmental Science and Technology. 2001, 35: 2896-2902.

[2] Zhang, Z. L., Hong, H. S., Zhou, J. L., Yu G. Phase association of polycyclic hydrocarbons in the Minjiang River estuary, China [J]. Science of the Total Environment. 2004, 323: 71-86.

[3] Yang Xushu, Wang Zhengping, Song Yantao. Discussion on methods of source apportionment of Polycyclic Aromatic Hydrocarbons on airborne particulate [J]. The Administration and Technique of Environmental Monitoring.2002, 14(4): 10-14.

[4] Zhang Ketan, Lv Aihua, Feng Yinchang, Zhu Tan. Analysis on Source of Polyaromatic Hydrocarbon of Inhalable Particulate Matter in Urumqi [J]. Arid Environmental Monitoring.2005, 19(3): 147-150 (Ch).

[5] Liu Guoqing, Tong Yongpeng, Luong J.H.T, Zhang Hong, Sun Huibin. A source study of atmospheric polycyclic aromatic hydrocarbons in Shenzhen, South China [J]. Environmental Monitoring and Assessment.2010, 163(1-4): 599-606.

[6] Feng Yinchang, Bai Zhipeng, Zhu Tan. The principle and application of improved-source-apportionment technique of atmospheric particulate matter [J]. Enviromental Science. 2002, 23: 106-108 (Ch).

[7] Feng Yinchang, Wu Jianhui, Zhu Tan，Bai Zhipeng, Yan Huaizhong, Tan Xiaozhe. Study on source appointment of TSP and PM_{10} in air environment in Jinan [J]. Research of Environmental Sciences. 2004, 17: 1-5 (Ch).

[8] Zhang Tingting. Pollution and source identification of Polycyclic Aromatic Hydrocarbons in atmosphere of Qingdao, China [D]. Ocean University of China.2007 (Ch).

[9] Farah Halek, M. Kianpour-rad, A. Kavousi. Characterization and source apportionment of polycyclic aromatic hydrocarbons in the ambient air (Tehran, Iran) [J]. Environmental Chemistry Letters.2010, 8: 39-44.

[10] Petch Pengchai, Somporn Chantara, Khajornsak Sopajaree, Sunanta Wangkarn, Urai Tengcharoenkul, Mongkon Rayanakorn. Seasonal variation, risk assessment and source estimation of PM_{10} and PM_{10}-bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand [J]. Environmental Monitoring and Assessment. 2009, 154(1-4): 197-218.

[11] Yin Jianxin, Harrison R.M., Chen Qiang, Rutter Andrew, Schauer J. J.. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere [J]. Atmospheric Environment. 2010, 44: 841-851.

[12] Hao Mingtu, Hou Wanguo, Qu Xiaohui, Liu Chunbo. The method amending of improved-source-analysis technique of atmospheric particulate matter[J]. China Environmental Science. 2005, 25(2): 138-141.

[13] USEPA. EPA-CMB 8.2 User's Manual [M]. Research Triangle Park, NC: Office of Air Quality Planning and Standards. 2004. (2000). CMB 8.2 User's manual, Office of Air Quality Planning and Standards: Research Triangle Park, NC.

[14] Wang Shuaijie, Zhu Tan. The research progress of source apportionment of airborne particulate matter [J]. Techniques and Equipment for Environmental Pollution Control. 2002, 3(8): 8-12.

978-1-935068-16-7 © 2010 SciRes.