

Gas-particulate distribution of polycyclic aromatic hydrocarbons (PAHs) in Chengdu, China

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Research of gas-particle phase distribution characteristic and source profile distribution characteristics of atmospheric polycyclic aromatic hydrocarbons (PAHs) can help control atmospheric PAHs pollution. Typical southwestern city of Chengdu is selected as study area for long-term continuous sampling monitoring, to analyze change of atmospheric concentrations of PAHs levels, source profile distribution characteristic and gas - particle distribution pattern. The results show that Σ PAHs concentration in study area is between 95.57-930.62ng m⁻³, PAHs concentration decreases with increasing temperature, which concerns increased amount of coal, biomass fuel combustion in low temperature seasons; atmospheric gas phase PAHs concentration is higher than that in particle phase, gas - particle distribution ratio (G / P) is between 1.4 and 7.5, gas - particle distribution ratio (G / P) shows relatively good positive linear correlation with temperature ($r = 0.61$, $p < 0.01$); Nap, Acy, etc. 2-4 ring of low ring PAHs exist mainly in gas form, and BbF, BaP and other 5,6 ring PAHs are mainly adsorbed in atmospheric particulate matters.

Keywords: PAHs, Atmosphere, Source Profile, Gas-Particle Distribution, G/P.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the most widely distributed persistent organic pollutants (POPs) in the atmosphere with greatest harm, which has "three-induced" effect of "mutagenesis, carcinogenesis and teratogenesis". Among 129 kinds of priority control pollutants published by United States Environmental Protection Agency (USEPA), PAHs account for 16 kinds (USEPA, 2002). PAHs exist in two forms of gas / particle in the atmosphere. Small molecular weight PAHs mainly exist in gas form while high molecular weight PAHs mainly in the form of particulate. When the atmospheric conditions change, the two can be transformed into each other.

Overseas research on atmospheric PAHs began in the early 1980s, with relatively comprehensive study of PAHs concentration level and pollution characteristics in air of different cities. Domestic report on atmospheric PAHs pollution shows an upward trend in recent years, but mainly concentrated in PAHs concentration changes in atmospheric particles in the coastal city of Beijing - Tianjin area. Moreover, sampling coverage time is relatively short, lacking of long-term continuous sampling and monitoring.

In this study, typical southwestern city of Chengdu is selected as the study area for long-term continuous sampling and monitoring, concentration

change of atmospheric PAHs levels, source profile distribution characteristics and gas - particle distribution pattern are analyzed, which is of important significance for transformation and conversion processes of PAHs in the environment, population exposure, environmental pollution control.

MATERIALS AND METHODS

Sample collection and analysis

Chengdu Plain is located in the western Sichuan Plain, with an average elevation of 540 meters and surrounded by hills and mountains with relatively high elevation. This particular terrain condition will certainly affect relocation diffusion of atmospheric pollutants, showing unique pollution feature. In this paper, the study area is located in the Chengdu Plain heartland (east longitude 102 ° 54 ' - 104 ° 53' and north latitude 30 ° 05 ' - 31 ° 26'). In this study, the sampling site is located within a university campus in Chengdu east area, with sampling height at 15m. The sampling ran from August 2008 to July 2009, once a week, with a total of 98 samples collected (49 gas phase samples, 49 particle phase samples).

Collected gas and particle phase samples underwent separate sample preparation, with Soxhlet extraction to extract target substance. GC-MS (Agilent GC6890 / 5973 MSD) was used for analysis and determination of 16 kinds of USEPA priority control PAHs.

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Gas-particle distribution coefficient K_p

Gas-solid distribution relationship of PAHs in gas phase and particle phase is described with distribution coefficient K_p ($m^3 \mu g^{-1}$), and K_p is calculated according to the following formula:

$$K_p = \frac{F/C_{TSP}}{A} \quad (1)$$

In the formula: F is PAHs volume concentration in particle phase ($ng\ m^{-3}$)

A is PAHs volume concentration in gas phase ($ng\ m^{-3}$)

C_{TSP} is atmospheric concentration of total suspended particles ($\mu g\ m^{-3}$)

RESULTS AND DISCUSSION

PAHs pollution characteristics

Atmospheric 16-PAHs concentration in gas - particle phase in the study area is shown in Table 1. In gas phase, 16-PAHs annual average concentration is $217.09 \pm 117.09\ ng\ m^{-3}$, the highest concentration of $634.98\ ng\ m^{-3}$ appeared on December 15, 2008, while the lowest concentration of 79.98 appeared on April 4, 2009, with mean concentration about 10 times[1] of PAHs concentration ($26.0\ ng\ m^{-3}$) in atmospheric gas phase of central district of Athens, capital of Greece, which is lower than Chicago ($144\text{-}853\ ng\ m^{-3}$) [2]. In comparison with studies of domestic cities, PAHs concentration in atmospheric gas phase is lower than the of the Beijing ($492\ ng\ m^{-3}$) [3], higher than cities like Harbin ($46.47\text{-}132.41\ ng.m^{-3}$) [4]. The

annual average concentration of 16-PAHs in atmospheric particle phase is $82.16 \pm 53.31\ ng\ m^{-3}$, the highest concentration of $295.63\ ng\ m^{-3}$ appeared on December 15, 2008, while the lowest concentration of $15.75\ ng\ m^{-3}$ appeared on August 29, 2008. PAH monomer with highest concentration in gas phase is 3-ring phenanthrene ($187.87\ ng\ m^{-3}$), followed by fluorene ($122.01\ ng\ m^{-3}$). the highest content in particle phase appears in high ring 5 ring PAH benzo (b) fluoranthene ($47.87\ ng\ m^{-3}$), followed by 4-ring chrysene ($44.06\ ng\ m^{-3}$). in this study, average concentration of benzo (a) pyrene (BaP) is $7.68\ ng\ m^{-3}$, which is lower than China's atmosphere standard value of $10\ ng\ m^{-3}$ EPA 1996, with particle concentration higher than that of gas phase.

Figure 1 shows concentration and temperature variation characteristic of PAHs in atmospheric gas phase and particle phase within a year of sampling period. During the sampling period, atmospheric PAHs concentration in gas phase, particle phase of the study area shows a similar variation, with higher PAHs concentration in winter and spring with lower temperature and lower PAHs concentration in summer and autumn with higher temperature. Peak value appeared in December, January, February with low temperature, with gradual concentration decrease with temperature rise. Atmospheric PAHs concentration peak appeared on December 15, 2008. Atmospheric PAHs concentration variation characteristic in the study area is similar to that in northern China city of Harbin [5]. Studies suggest that this is associated with increased biomass burning capacity in winter and spring.

Table1. PAHs concentration ($ng\ m^{-3}$) statistics in atmospheric gas - particle phase in Chengdu

PAHs	Gas			Particular		
	Max	Min	Average	Max	Min	Average
Naphthalene(Nap)	32.00	0.85	7.15	0.57	0.12	0.25
Acenaphthylene(Acy)	116.69	0.12	13.79	0.44	0.03	0.10
Acenaphthene(Ace)	24.14	0.09	4.26	0.12	-	0.03
Fluorene(Flu)	122.01	2.09	28.90	0.70	0.05	0.17
Phenanthrene(Phe)	187.87	0.50	92.06	9.01	0.56	2.27
Anthracene(Ant)	35.00	1.21	7.55	1.16	0.06	0.26
Fluoranthene(Flua)	79.04	11.73	36.47	42.54	0.93	6.98
Pyrene(Pyr)	49.13	6.08	22.04	38.70	0.80	6.02
Benzo(a)anthracene(BaA)	4.78	0.16	1.29	29.16	0.63	6.11
Chrysene(Chr)	9.30	0.45	2.96	44.06	1.20	10.50
Benzo(b)Fluoranthene(BbF)	1.89	0.03	0.31	47.87	2.58	14.33
Benzo(k)Fluoranthene(BkF)	0.93	0.03	0.19	22.15	1.75	7.85
Benzo(a)Pyrene(BaP)	0.34	0.01	0.06	26.53	1.37	7.68
Indeno(123-c,d)Pyrene(IcdP)	0.23	-	0.02	23.42	2.20	7.71
Dibenzo(ah)anthracene(DahA)	0.05	-	-	7.53	0.47	1.95
Benzo(g,h,i)Perylene(BghiP)	0.29	-	0.03	26.91	2.61	8.90
Σ16PAHs	$217.09 \pm 117.09\ ng\ m^{-3}$			$82.16 \pm 53.31\ ng\ m^{-3}$		

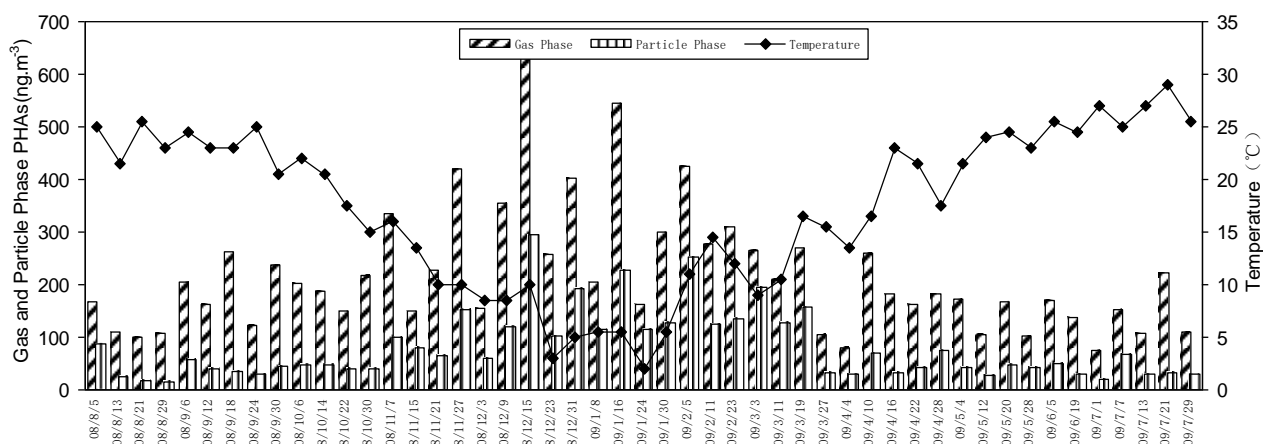


Fig. 1. Atmospheric PAHs gas - particle concentration distribution in Chengdu and temperature change map.

PAHs gas-particle distribution characteristics

PAHs gas-particle source profile distribution characteristic. In view of concentration distribution of atmospheric PAHs in the two phases (Figure 2), PAHs monomer with the highest content in gas phase is 3-ring Phe, whose contribution rate in gas phase reaches 42.5%, followed by: Flua (16.8%)>

Flu (13.3%)> Pyr (10.1%)> Acy (6.3%)> Ant (3.5%)> Nap (3.3%). What contributes most in particle phase is 5-ring benzo [b] BbF. Ranking of PAHs contribution rate in particle phase is respectively: BbF (17.9%)> Chr (12.8%)> BghiP (11.0%)> BkF (9.7%)> BaP (9.6%)> IcdP (9.5%)> Flua (8.4%)> BaA (7.6%)> Pyr (7.3%).

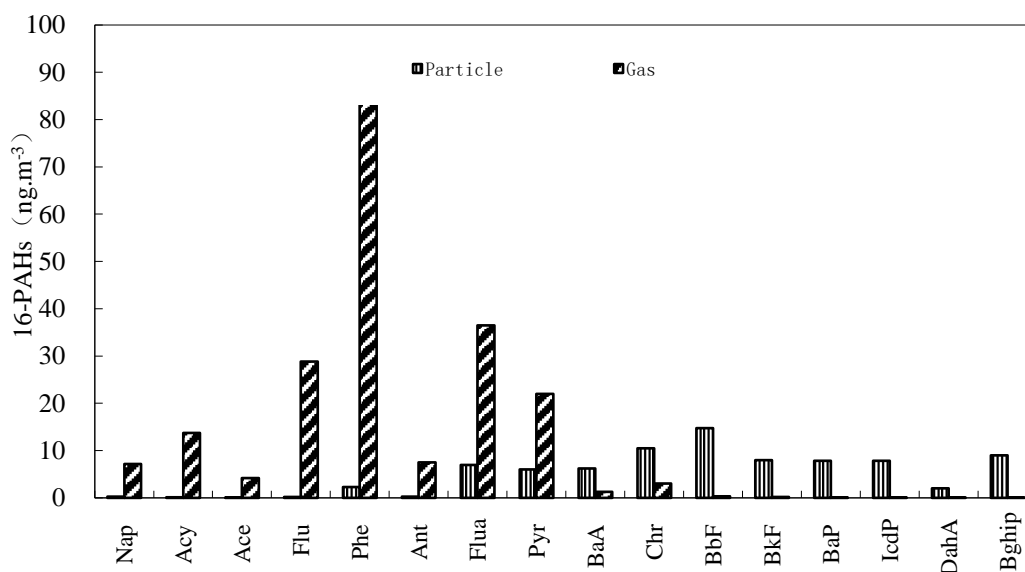


Fig. 2. PAHs source profile distribution characteristic in gas - particle.

Thus, low ring PAHs with low molecular weight mainly exists in gas state. With increase in molecular weight and number of rings, PAHs gradually tends to exist in particle state. In gas phase, contribution rate of 2,3 ring PAHs monomer to concentration is greater than that of high-ring PAHs. However, in particle phase, contribution rate of 5,6 high ring PAHs monomer to concentration is greater than that of low ring, which is opposite to the situation in gas phase. Contribution rate of 4 ring PAHs monomer in two phases is roughly equal, but Flua and Pyr concentration in gas phase is

higher than that in particle phase, which is easier to concentrate in gas phase, while concentration of BaA and Chr in particle phase is higher than that in gas phase, which is more easily absorbed in particulate matters.

PAHs gas - particle ratio (G/P). PAHs in atmospheric environment exists in two forms of gas and particle. Proportion of gas phase PAHs in total atmospheric PAHs is greater than that of particle phase. PAHs concentration distribution ratio (G / P) in gas and particle phase in the study area is between 1.4 and 7.5, with average gas - particle ratio (G / P) at

3.12, which shows relatively good positive correlation with temperature change ($r = 0.61$, $p < 0.01$) (Figure 3). Compared with the findings in different regions at home and abroad, it is higher than Seoul, South Korea in Asian countries 2.3[6],

China Harbin 1.2[5]; lower than Turkey in European region 9.36 [7], Birmingham, UK 5-6 [8], Guangzhou, China 13.2 [9], Nanjing 8.9[10], Shanghai > 10[11]; comparable to Athens, Greece 5.2 [1], western region of circum-Bohai Sea <5 [12].

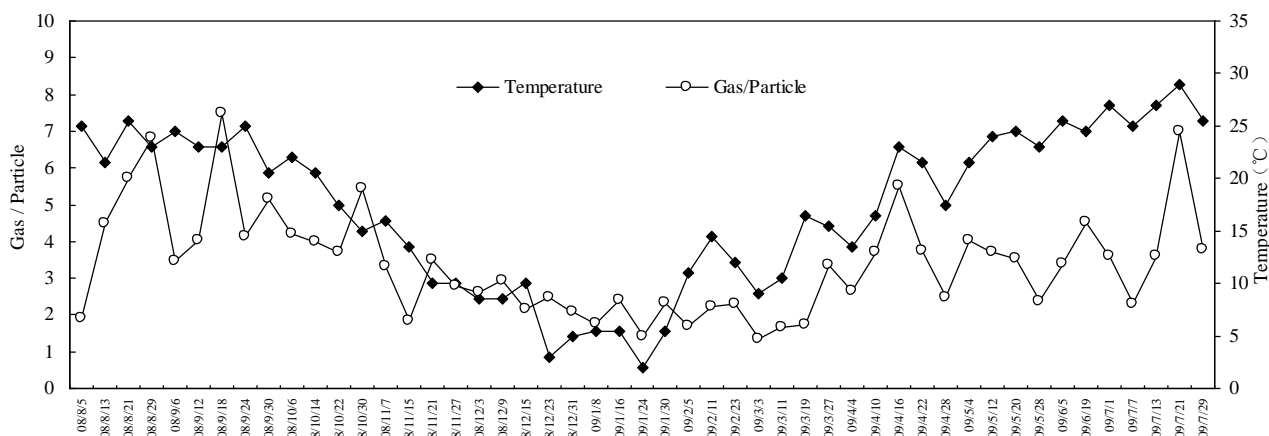


Fig. 3. PAHs gas – particle distribution ratio and temperature change trends.

Distribution and gas - solid balance of atmospheric PAHs in different particles vary. A lot of 3-4 low ring, volatile PAHs mainly exist in gas form in gas phase, while 5,6 ring hardly volatile PAHs are mainly adsorbed in atmospheric particles[9][13]. PAHs content in small particles is high, but low in larger particles. Studies have shown that PAHs contained in inhalable particle accounts for about 95% of the total amount, while PAHs contained in tiny particles with particle size <1.1 μm account for 60% to 70% of the total [14][15].

PAHs gas - particle distribution characteristic.

In this study, as IcdP, DahA, BghiP and other PAHs were not detected in part of gas phase samples, the

remaining 13 PAHs are selected for fitting analysis. Sampling period is divided into four seasons of spring, summer, autumn and winter, and concentration average of 13 PAHs is substituted to formula (1) for calculation. Distribution coefficient K_p of 13 PAHs components is between 3.34×10^{-5} -2.49. 2,3 ring Nap, Acy, Ace, Flu, Phe, etc. have low boiling point and are volatile, with occurrence ratio in gas phase higher than that in particle phase, and therefore K_p value is minimum. K_p value of Ant, Flua, Pyr, etc. is between 1.08×10^{-4} - 9.17×10^{-4} . 5,6 ring PAHs mostly exist in particle phase, with higher K_p value.

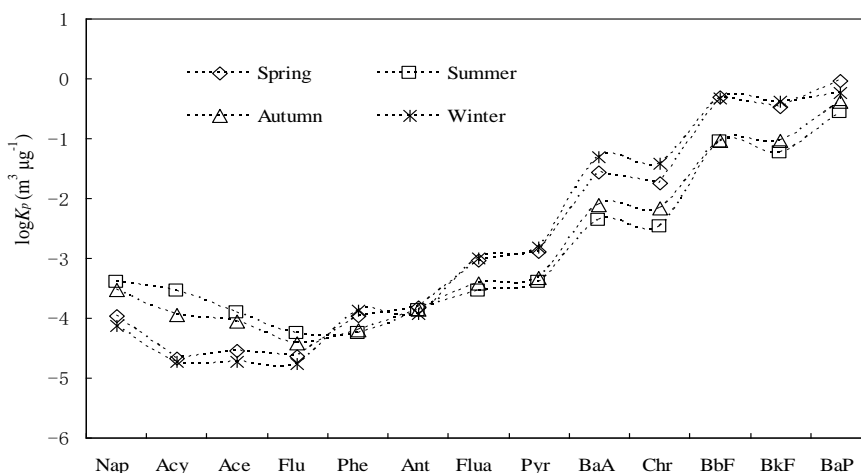


Fig. 4. Seasonal variation diagram of 13-PAHs monomer logKp.

As shown in Figure 4, $\log K_p$ value of 13 kinds of PAHs increases with increase in molecular weight,

components with small molecular weight are volatile, mainly in gas phase. Distribution

coefficient of various substances of PAHs also shows certain seasonal variations, with $\log K_p$ value of lower ring of 2, 3 ring PAHs: summer > autumn > spring > winter; $\log K_p$ value of high ring of 4, 5, 6 ring PAHs shows change law of: winter > spring > autumn > summer. Seasonal variation characteristic of $\log K_p$ value is temperature-related. In high-temperature season, PAHs components are more volatile, especially highly volatile low ring material with small molecular weight [16][17]. Distribution and transformation of PAHs in gas-particle phase has a close relationship with meteorological elements such as temperature, wind direction, etc. When environmental conditions change, gas-solid phase transformation will occur [18].

CONCLUSIONS

In the study area, atmospheric Σ PAHs average concentration in gas - particle phases is respectively $217.09 \pm 117.09 \text{ ng m}^{-3}$ and $82.16 \pm 53.31 \text{ ng m}^{-3}$; PAHs in atmosphere mainly exists in the form of gas (73%), gas - particle distribution ratio (G / P) is between 1.4 and 7.5, gas - particle distribution ratio shows relatively good positive linear correlation with temperature ($r = 0.61$, $p < 0.01$); Nap, Acy, etc. 2-4 ring of low ring volatile PAHs exist mainly in gas form in gas phase, and BbF, BaP and other 5,6 ring hardly volatile PAHs are mainly adsorbed in atmospheric particulate matters.

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