

## Contamination of Polycyclic Aromatic Hydrocarbons Bound to PM<sub>10</sub>/PM<sub>2.5</sub> in Xiamen, China

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### Abstract

PM<sub>10</sub> (particulate matter which passes through a size selective impactor inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter) and PM<sub>2.5</sub> were collected at four sites (A: Xiaoping, B: Huli, C: Hongwen, D: Gulang Island) from December 20, 2004 to December 29, 2004 in Xiamen. 16 Priority polycyclic aromatic hydrocarbons (PAHs) in PM<sub>10</sub>/PM<sub>2.5</sub> were quantified by using a gas chromatograph/mass spectrometer (GC/MS). EC and OC of PM<sub>10</sub> were analyzed by Thermal/Optical Carbon Analyzer (DRI Model 2001). Concentration, spatial distributions of PAHs and EC/OC were studied and their main sources were identified by diagnostic ratios, correlation analysis and EC/OC analysis. Among the different sampling sites, concentrations of Σ16PAHs were 5.20-28.07 ng/m<sup>3</sup> in PM<sub>10</sub> and 3.04-11.32 ng/m<sup>3</sup> in PM<sub>2.5</sub>. Concentration of OC were 9.83-15.6 µg/m<sup>3</sup> and 1.41-4.73 µg/m<sup>3</sup> for EC associated to PM<sub>10</sub>. The main sources identified were traffic emissions and industry emission/coal combustion.

**Keywords:** PAHs; EC/OC; Source identification; Xiamen.

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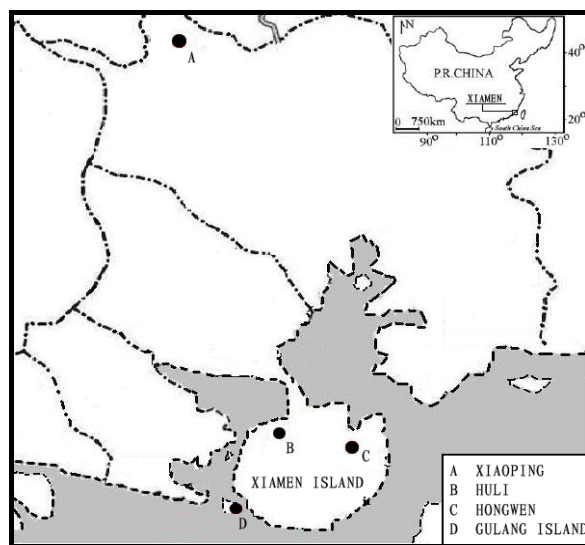
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## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the air which are well-known to be toxic, carcinogenic and mutagenic (Ames *et al.*, 1975; MØller *et al.*, 1982). PAHs bound to PM<sub>10</sub> are considered to be a great threat to the health of human beings because they could be brought into the body through breathing (Spurny, 1996). Many studies indicate that fine particles (PM<sub>2.5</sub>) have greater impact on human health than coarse particles (Schwartz, 1994). Numerous studies were focused on the concentrations and sources of PAHs bound to PM<sub>10</sub>/PM<sub>2.5</sub> in the urban air (Gao *et al.*, 1993; Qi *et al.*, 2000; Guo *et al.*, 2003; Peng *et al.*, 2003; Pan *et al.*, 2003; Guo *et al.*, 2004; Dallarosa *et al.*, 2005; Ding *et al.*, 2007) and found it was important to study the abundance, distribution and potential sources of PAHs associated to PM<sub>10</sub>/PM<sub>2.5</sub> so that the diverse effects caused by particulate matter could be efficiently controlled.

Xiamen is located along the southeastern shore of China at E117°53'-118°27', N24°25'-24°55', as shown in Fig.1. It has a population of about 1.4 million people living in a terrene-area of 1565.09 km<sup>2</sup> and a sea-area of 344 km<sup>2</sup>. It includes Xiamen Island, Gulang Island, Tongan, Jimei, Haicang, Xinglin and many other small islands, amongst which Xiamen Island has an area of 132.5 km<sup>2</sup> and a 234 km coastline. Xiamen has been a famous “garden city” due to its clear sky and beautiful environment, but nowadays its air quality decreased from “excellent” to “good”, with the main pollutants being PM<sub>10</sub>. Other studies (Karar and Gupta, 2006; Valavanidis *et al.*, 2006) showed that the highest concentrations of PAHs in particulate phase always occurred in winter. In this study, we aimed to carry out the wintertime study of concentrations, distribution patterns and main sources of PAHs bound to PM<sub>10</sub>/PM<sub>2.5</sub> in Xiamen.



**Fig. 1.** Map of Xiamen with sampling sites shown as large dots.

## METHODS

### *Sample collection*

Sampling of PM<sub>10</sub> and PM<sub>2.5</sub> were carried out at several sites (A, B, C, D) during December 21-29, 2004 in Xiamen, Fujian province, P.R. China (Fig. 1). The sampling sites were selected to present the different functional areas: Site A: Xiaoping (N 24°51.218', E118°2.689', 900 m elevation), acted as the control site located in a forest garden to the north of Xiamen island. There is no major pollution source around 25 km area except diesel engine vehicles were used to build the road. Site B: Huli (N24°30.51', E118°6.139', 8 m elevation), as industry/traffic area. The sampling site was located on the roof of an official building, about 100 m away from a road carrying heavy traffic (1300/h, 2800/h) and surrounded by a series of industries, such as tobacco production plant, aluminium plant, building material production, etc. Site C: Hongwen (N24°28.623, E118°8.703, 15 m elevation). The sampling site was located on the roof of a middle school building which is in the center of a residential area, with no other high buildings or industry nearby. Site D: Gulang Island (N24°26.787, E118°3.819, 10 m elevation). The island is separated from Xiamen Island with a 5 min boat ride which is famous for tourism. There is no industry or traffic except for battery driven vehicles on the island. The sampling site was on the roof of a school building, about 500 m from the entrance to the island.

Daily sampling at the four sites began almost simultaneously at 10:00 a.m., with a 23 h duration. PM<sub>10</sub> samplers (100 L/min, Qingdao Laoshan Mechanical Corp., China) with Ø 90 mm glass fiber filters (GFFs, Whatman Corp. USA) and PM<sub>2.5</sub> sampler (MiliVol Airmetrics, USA, 5 L/min) with Ø 47 mm glass fiber filters (GFFs, Whatman Corp. USA) were used to collect aerosols. The samples deposited on the filters were analyzed for 16 priority PAHs, and EC/OC for PM<sub>10</sub>. Due to the limitation of the available PM<sub>2.5</sub> sampler, only two PM<sub>2.5</sub> samples at each site were gotten. So the following discussion was more focused on PM<sub>10</sub>.

### *Sample analysis*

The glass fiber filters were pre-baked at 450 °C for 4 h to lower their carbon blanks. GFF samples were spiked with deuterated PAHs standards (naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, acenaphthene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub>) prior to sample extraction. The filter was extracted with 20 mL aliquots of dichloromethane in the dark overnight, and then ultrasonically extracted for 30min at room temperature, twice. The total extract was concentrated to a volume of 1 mL by vacuum-condensing equipment. The cleanup and fractionation of the extract was done using a self-packed silica gel-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> column, a 5 mL acetone-rinsed burette containing 3 mL firmly packed deactivated silica gel (72-230 mesh, Sigma) in the bottom, a layer of 2 mL firmly packed deactivated Al<sub>2</sub>O<sub>3</sub>, and then 1 cm Na<sub>2</sub>SO<sub>4</sub> on the top. Ten milliliters hexane was added to condition the column. The concentrated extract was then applied to the column with an additional

3 mL hexane for complete transfer. n-Hexane was used to elute the n-alkanes fraction (5 mL, F1), benzene: n-hexane (v/v, 1:1) was used to elute the aromatic fraction (10 mL, F2). The volume of each fraction was concentrated to near dryness by vacuum-condensing equipment, and then fixed to 100  $\mu$ L. The PAHs in F2 fractions were analyzed by GC-MSD (HP 6890 GC-HP 5973 MSD) in Selected Ions Mode (SIM). The GC was equipped with a HP-5 MS capillary column (30 m  $\times$  0.25 mm i.d., film thickness 0.25  $\mu$ m), with helium as carrier gas. The oven temperature program was as follows: hold at 60°C for 2 min, increased to 120°C at a rate of 4°C/min, then increased to 300°C at a rate of 3°C/min and a final hold at 300°C for 10 min. The injector and detector temperature were 250°C and 280°C. 1  $\mu$ L sample was injected in a splitless model. The mass scanning ranged between 50 and 500 m/z.

16 PAHs were quantified in SIM mode according to their elution orders as followed: naphthalene (Nap, m/z = 128), acenaphthylene (Ace, m/z = 152), acenaphthene (Acen, m/z = 154), fluorene (Flu, m/z = 166), phenanthrene (Phen, m/z = 178), anthracene (An, m/z = 178), fluoranthene (Fluo, m/z = 202), pyrene (Pyr, m/z = 202), benzo(a)anthracene (BaA, m/z = 228), chrysene (Chry, m/z = 228), benzo(b)fluoranthene (BbF, m/z = 252), benzo(k)fluoranthene (BkF, m/z = 252), benzo(a)pyrene (BaP, m/z = 252), indeno(1,2,3,-cd)pyrene (Indeo, m/z = 276), dibenzo(a,h)anthracene (DiBa, m/z = 278), benzo(ghi)perylene (BgP, m/z = 276).

EC/OC were analyzed by National Environmental Analysis Center using Thermal/Optical Carbon Analyzer (DRI Model 2001) with the method detection limits (MDL) of 0.82  $\mu$ g C/cm<sup>2</sup> for OC and 0.19  $\mu$ g C/cm<sup>2</sup> for EC.

### **Quality control**

The analytical method was based on the USEPA Method TO-13 (US EPA, 1999). Field blanks, filter blanks and solvent blanks were analyzed by the same procedure as the samples and ensured that there were no significant background interferences with only trace amount of PAHs being detected out (ND-5.13 ng). When compared with the amount (160.94-748.88 ng) in the real samples, the concentration in blank samples could be neglected.

The quantifications were performed using the internal standard method. The recovery test was performed by spiking known amounts of a mixture of PAHs onto the GFFs and then the spiked filter was treated the same way as mentioned above. Method detection limit (MDL) was calculated taking into account 3 times the ratio of the heights obtained for noise. Recovery efficiency of PAHs ranged from 60.1% to 119.8%. Method detection limits were between  $1.5 \times 10^{-3}$  ng/m<sup>3</sup> (BkF) and  $11.4 \times 10^{-3}$  ng/m<sup>3</sup> (Nap), as shown in Table 1.

**Table 1.** The PAHs recovery ratio (RR) and method detection limits (MDL).

Compounds	RR (%)	MDL ( $\times 10^{-3}$ ng/m <sup>3</sup> )
Nap	109.4	11.40
Ace	83.5	5.86
Acen	87.7	6.61
Flu	83.6	5.08
Phen	111.3	2.56
An	93.4	3.08
Fluo	60.1	1.75
Pyr	61.0	1.65
BaA	111.1	2.03
Chry	108.5	1.60
BbF	94.3	1.81
BkF	98.7	1.51
BaP	110.2	2.46
Indeo	118.8	2.83
DiBa	119.8	3.00
BgP	105.5	2.02

## RESULTS AND DISCUSSION

### *Comment on meteorology and PAHs concentrations*

The meteorological conditions and air pollution index during the sampling periods were shown in Table 2. Temperature was about 8-20°C, wind speed was almost higher than 2 m/s and relative humidity was high (71%-92%) which were the typical subtropical climate. The relationship between different PAHs bound to PM<sub>10</sub> and meteorology parameters were analyzed by SPSS packages (Table 3). ΣPAHs have inverse correlation with relative humidity (-0.538) and weak correlations with temperature ( $r = 0.34$ ) or wind speed ( $r = 0.42$ ) ( $p < 0.05$ ). But PM<sub>10</sub> has significant correlation with temperature with  $r = 0.74$  ( $p < 0.05$ ) while inverse correlation with wind speed ( $r = -0.005$ ) and RH ( $r = -0.20$ ). Thus is consistent with results observed by Karar and Gupta (2006) in Kolkata, India and Mantis *et al.* (2005) in the Greater area of Athens, Greece. When relative humidity increases, the fine particulates have more chances to aggregate together and grow bigger, the concentration of PM<sub>10</sub> decreased and also of ΣPAHs bound to PM<sub>10</sub>.

**Table 2.** Meteorological conditions during the sampling duration.

Date	Temp. range (°C)	Average Temp. (°C)	Wind direction	Wind speed (m/s)	Relative humidity (%)
2004-12-20	12-21	16.0	NE35°	3.0	79.2
2004-12-21	14-22	16.6	NNE18°	3.4	77.0
2004-12-22	13-23	17.1	E100°	1.5	84.2
2004-12-23	13-22	16.0	ESE107°	2.0	91.7
2004-12-24	11-20	14.7	ESE103°	2.2	83.2
2004-12-25	12-19	15.0	ESE106°	2.5	81.5
2004-12-26	12-19	15.3	ESE105°	2.2	85.7
2004-12-27	13-19	14.9	WNW288°	2.4	90.5
2004-12-28	12-17	11.6	NE35°	2.1	88.0
2004-12-29	8-14	9.7	NNE18°	4.5	71.0

**Table 3.** Correlation coefficient of meteorological conditions and  $\Sigma$ PAHs in PM<sub>10</sub>.

	$\Sigma$ PAHs	PM <sub>10</sub>	Temp	Wind	RH
$\Sigma$ PAHs	1				
PM <sub>10</sub>	0.810**	1			
Temp	0.337	0.735*	1		
Wind	0.422	-0.005	-0.598	1	
RH	-0.538	-0.204	0.404	-0.826**	1

\* Correlation is significant at the 0.05 level (2-tailed); \*\* Correlation is significant at the 0.01 level (2-tailed).

Conc. = concentration, Temp. = temperature, RH = relative humidity.

In Xiamen, 16 PAHs were detected out in all samples except that Ace was below the detection limit (Table 4). In PM<sub>10</sub>, the concentration range of individual PAHs was from ND-13.31 ng/m<sup>3</sup> and 5.20-28.07 ng/m<sup>3</sup> for  $\Sigma$ 16PAHs. The highest concentration of  $\Sigma$ 16PAHs almost occurred in the first sampling day (Dec. 20) at different sites. From the second sampling day, the variation of total concentrations was not much suggesting the stable pollution level under similar meteorology conditions. Among PAHs, Phen (2.16-13.31 ng/m<sup>3</sup>), Flu (0.21-7.04 ng/m<sup>3</sup>), Pyr (0.53-2.44 ng/m<sup>3</sup>) and Chry (0.40-1.75 ng/m<sup>3</sup>) were main species. They are all lower and medium molecular weight (MW  $\leq$  228) PAHs. In PM<sub>2.5</sub>, the concentration range of  $\Sigma$ 16PAHs was 3.04-11.32 ng/m<sup>3</sup>. Among PAHs, the main species not only include low and middle molecular weight PAHs such as Phen (0.92-1.78 ng/m<sup>3</sup>), Pyr (0.38-1.97 ng/m<sup>3</sup>) and Chry (0.51-1.60 ng/m<sup>3</sup>), etc., but also some higher molecular weight (MW  $\geq$  252) PAHs such as BaP (0.16-1.34 ng/m<sup>3</sup>), Indeo (0.18-1.30

ng/m<sup>3</sup>) and BgP (0.22-1.52 ng/m<sup>3</sup>). These results suggest the higher molecular weight PAHs were more easily bound to fine particulates.

**Table 4.** Concentrations and ratios of PAHs in PM<sub>10</sub> and PM<sub>2.5</sub> at different sampling sites (ng/m<sup>3</sup>).

Conc.	PM <sub>10</sub>				PM <sub>2.5</sub>			
	A	B	C	D	A	B	C	D
Nap	0.01 ± 0.02	0.01 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	0.01	0.03	0.06	0.05
Ace	ND	ND	ND	ND	ND	ND	ND	ND
Acen	0.07 ± 0.02	0.23 ± 0.13	0.10 ± 0.04	0.11 ± 0.07	ND	ND	ND	ND
Flu	0.39 ± 0.16	1.53 ± 2.07	0.56 ± 0.30	1.17 ± 1.91	0.12	0.15	0.14	0.14
Phen	3.40 ± 1.63	8.24 ± 2.50	3.31 ± 1.61	5.07 ± 1.85	1.16	1.39	0.92	1.78
An	0.20 ± 0.11	0.22 ± 0.12	0.22 ± 0.12	0.28 ± 0.12	ND	0.11	0.11	0.11
Fluo	0.31 ± 0.06	0.63 ± 0.21	0.31 ± 0.12	0.54 ± 0.14	0.13	0.4	0.22	0.45
Pyr	0.79 ± 0.17	1.75 ± 0.46	0.99 ± 0.39	1.49 ± 0.41	0.38	1.97	0.96	1.45
BaA	0.10 ± 0.06	0.34 ± 0.12	0.29 ± 0.13	0.26 ± 0.17	0.58	1.6	0.89	0.51
Chry	0.54 ± 0.13	0.81 ± 0.43	0.64 ± 0.17	0.57 ± 0.15	ND	ND	ND	ND
BbF	0.13 ± 0.03	0.20 ± 0.09	0.25 ± 0.06	0.22 ± 0.10	0.1	0.65	0.25	0.15
BkF	0.14 ± 0.05	0.25 ± 0.10	0.29 ± 0.08	0.26 ± 0.17	ND	0.81	0.31	0.17
BaP	0.24 ± 0.07	0.51 ± 0.24	0.48 ± 0.18	0.45 ± 0.32	0.16	1.34	0.46	0.22
Indeo	0.28 ± 0.06	0.51 ± 0.19	0.50 ± 0.13	0.45 ± 0.23	0.18	1.3	0.57	0.26
DiBa	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	ND	0.05	0.03	ND
BgP	0.26 ± 0.06	0.45 ± 0.19	0.46 ± 0.11	0.41 ± 0.17	0.22	1.52	0.62	0.3
ΣPAHs	6.81 ± 1.97	16.09 ± 5.10	8.34 ± 2.42	11.20 ± 4.11	3.04	11.3	5.54	5.59
Fluo/Pyr	0.39 ± 0.02	0.36 ± 0.03	0.32 ± 0.05	0.36 ± 0.04	0.35	0.2	0.23	0.31
BaA/Chry	0.18 ± 0.08	0.50 ± 0.22	0.44 ± 0.14	0.43 ± 0.18	-	-	-	-
Pyr/BaP	3.51 ± 1.12	4.17 ± 2.35	2.16 ± 0.74	4.17 ± 1.80	2.3	1.48	2.11	6.5

ND = not detected. SD = standard deviation.

Compared with other cities in China, concentration of ΣPAHs associated to PM<sub>10</sub> in Xiamen was significantly lower than those in inland cities, such as Beijing (116.0 ng/m<sup>3</sup> for annual average concentration) (Zhou *et al.*, 2005) and Shanghai (245.52 ng/m<sup>3</sup> for winter) (Guo *et al.*, 2004), but in the similar level as the southern coastal cities including Guangzhou (55.49 ng/m<sup>3</sup> for winter and spring), Hongkong (14.88 ng/m<sup>3</sup> for winter and spring) and Macao (41.70 ng/m<sup>3</sup> for winter and spring) (Qi *et al.*, 2000), etc. One of the most obvious reasons for this is that central or residential heating in winter is a major pollution source in the northern inland cities (Beijing, etc.) while southern cities do not have this pollution source. Compared with overseas

cities, concentration of  $\Sigma$ PAHs in Xiamen was lower than that in New Delhi (Sharma *et al.*, 2003), but in the same level of that in some coastal cities, such as Naples (Caricchia *et al.*, 1999), Athens (Mantis *et al.*, 2005) and Santiago (Romero, 2002), etc.

Concentration of BaP is an indicator for the control of  $\Sigma$ PAHs in the atmosphere. Its acceptable concentration limit is 10 ng/m<sup>3</sup> based on the Chinese standard (GB3095-1996). The concentrations of BaP in PM<sub>10</sub> and PM<sub>2.5</sub> were in the range 0.10-1.34 ng/m<sup>3</sup> meaning that the PAHs pollution was not serious in Xiamen.

For better quantification of whole carcinogenicity from whole PAH fraction, "BEQ" (Benzo[a]pyrene Equivalence) was introduced as an index and calculated by the following formula using the toxic equivalency factors (TEFs) of the individual PAHs (Robert *et al.*, 1999) and their concentrations:

$$\text{BEQ} = \text{BaP} \times 1 + \text{BaA} \times 0.12 + \text{An} \times 0.002 + \text{Phen} \times 0.028 + \text{Fluo} \times 0.033 + \text{BbF} \times 0.15 + \text{Pyr} \times 0.046 + \text{Chry} \times 0.25. \quad (1)$$

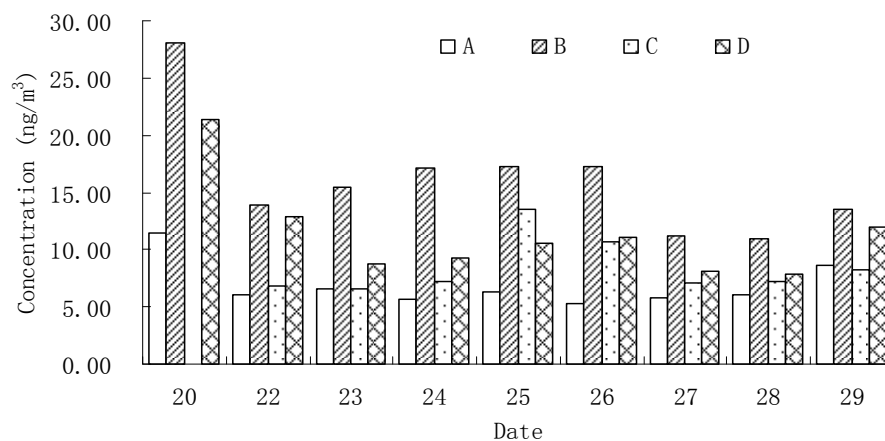
The BEQ index was 0.85 and 0.92 for PAHs in PM<sub>10</sub> and PM<sub>2.5</sub> in Xiamen which was much lower than that of Shanghai (15.77) (Guo *et al.*, 2004), but in the same level of that in some Japanese cities (1.91) (Takeshi *et al.*, 2004).

Relationship of concentration of  $\Sigma$ PAHs and concentration of PM<sub>10</sub> was analyzed by SPSS (Table 3). Results showed that there were significant correlation ( $r = 0.71$ ,  $p < 0.01$ ,  $n = 35$ ) between the concentration of  $\Sigma$ PAHs and PM<sub>10</sub>. These results suggested that sources of PM<sub>10</sub> and PAHs in the air were similar, and the control of PM<sub>10</sub> was an effective way to decrease the PAHs pollution level in the air as well.

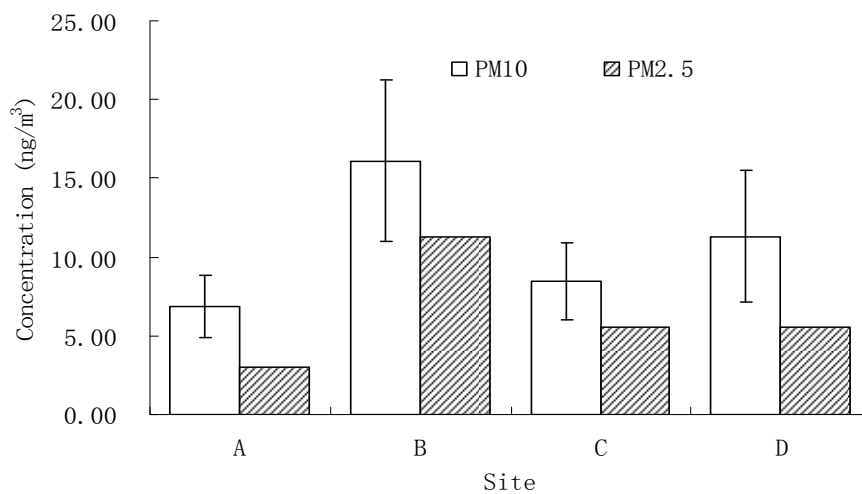
#### ***Distribution of PAHs bound to PM<sub>10</sub>/PM<sub>2.5</sub>***

Among different function areas, there were some difference existed in the concentration and distribution patterns of PAHs in PM<sub>10</sub>/PM<sub>2.5</sub> (Fig. 2-Fig. 5, Table 4). The concentration ranges and standard deviation of  $\Sigma$ 16PAHs bound to PM<sub>10</sub> at different sampling sites were as follows: B: 11.0-28.1 ng/m<sup>3</sup> ( $16.1 \pm 5.1$  ng/m<sup>3</sup>) > D: 7.8-21.1 ng/m<sup>3</sup> ( $11.2 \pm 4.1$  ng/m<sup>3</sup>) > C: 6.6-13.5 ng/m<sup>3</sup> ( $8.4 \pm 2.5$  ng/m<sup>3</sup>) > A: 5.2-11.5 ng/m<sup>3</sup> ( $6.9 \pm 2.0$  ng/m<sup>3</sup>), respectively. The concentration of  $\Sigma$ 16PAHs bound to PM<sub>2.5</sub> showed the same patterns: B (11.32 ng/m<sup>3</sup>) > D (5.59 ng/m<sup>3</sup>) > C (5.54 ng/m<sup>3</sup>) > A (3.04 ng/m<sup>3</sup>).

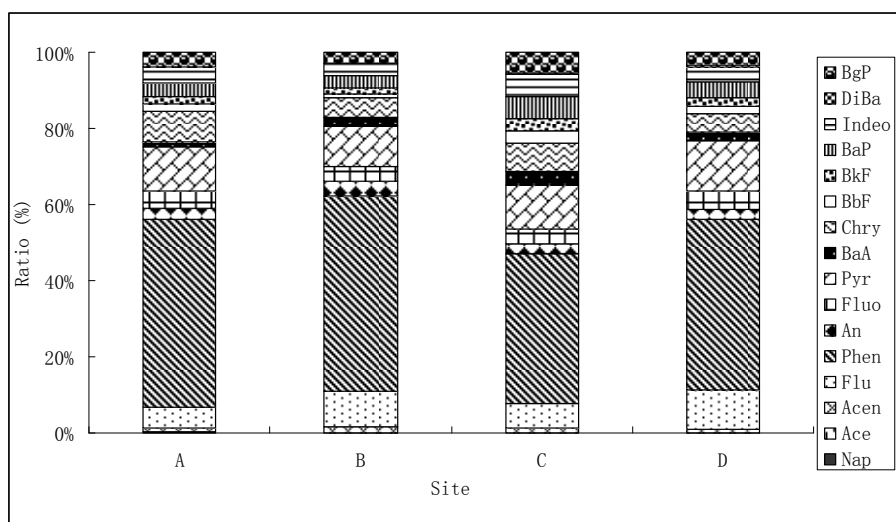




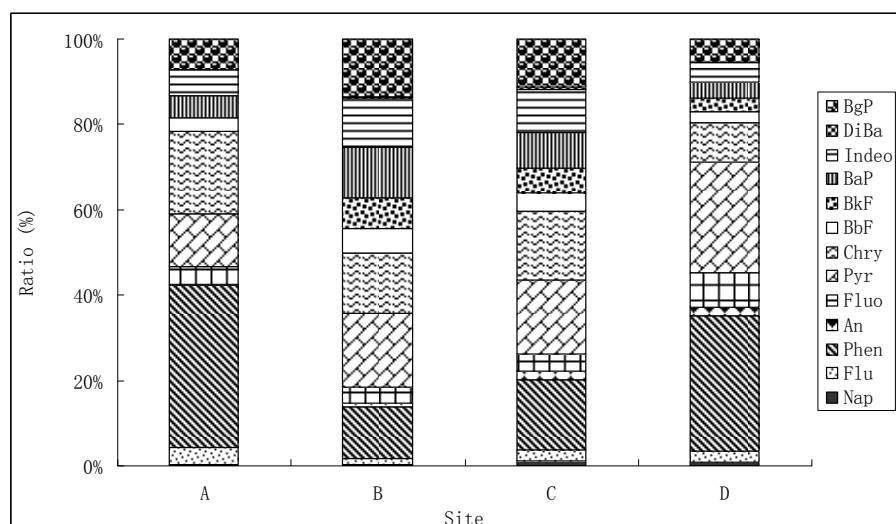
**Fig. 2.** Concentrations of Σ16PAHs in PM<sub>10</sub> at four sites of Xiamen.



**Fig. 3.** Average concentration of Σ16PAHs bound to PM<sub>10</sub>/PM<sub>2.5</sub> at four sites of Xiamen.



**Fig. 4.** Distribution of PAHs in PM<sub>10</sub> at different sites.



**Fig. 5.** Distribution of PAHs in PM<sub>2.5</sub> at different sites.

In PM<sub>10</sub> and PM<sub>2.5</sub>, the highest concentration of Σ16PAHs always occurred at site B (industry/traffic area) which was quite related to its environmental conditions. Site B was 100 m away from the main line carrying heavy traffic (1300/h, 2800/h) and also surrounded by a series of industries, such as tobacco production plant, aluminium smelting plant, etc. Large amount of industry and traffic emissions made the concentration of PAHs highest at this site. Among PAHs, Flu and Phen covered much more of total PAHs at this site than at other sites in PM<sub>10</sub>. This was consistent with the fact that this area was a dense traffic area with more contribution of heavy-duty vehicles emissions (Marr *et al.*, 1999; Rogge *et al.*, 1993). In PM<sub>2.5</sub>, BaP, Indo and BgP covered more of Σ16PAHs at site B than at other sites meaning that there is more

contribution from gasoline vehicles (Simicik *et al.*, 1999) at site B. The concentration of PAHs at site D (Gulang Island) was ranked second. Though there was no direct automobile emission or industry emission, the heavy ship traffic to this famous tourist island and the wind bringing with the particulates from the southwest SongYu coal-generating electricity plant and the influence of the heavy road traffic emissions from the thither area could not be neglected. Site A (forest garden area) and site C (residential area) were relatively clean which were in consistent with the fact that there were no heavy traffic or industry nearby. Also plants could effectively clean out PAHs in the atmosphere (Simonich *et al.*, 1994).

Though the concentration of PAHs was quite different, the distribution patterns of PAHs bound to PM<sub>10</sub> in different function areas were quite similar. At all sites, 3-4 ring PAHs including Phen (39.2%-51.2%), Flu (5.7%-10.4%), Pyr (10.9%-11.8%) and Chry (5.0%-7.9%) were the dominant PAHs components bound to PM<sub>10</sub> (Fig. 4). These four PAHs covered 60.8%-81.3% of  $\Sigma$ 16PAHs. These distribution profiles were quite different from many other cities (Papageorgopoulou *et al.*, 1999; Caricchia *et al.*, 1999; Chetwittachan *et al.*, 2002; Pan *et al.*, 2003; Manoli *et al.*, 2004; Christine *et al.*, 2005), but similar with that in Athens, Greece which pointed out the great contribution from traffic emissions (Valavanidis, 2006). In PM<sub>2.5</sub>, some higher molecular weight PAHs such as BaP (5.3-11.8%), Indeo (4.7-11.5%), BgP (5.4-13.4) covered more than that of PM<sub>10</sub>. Among low and middle molecular PAHs, Phen was the dominant component which covered 12.3-38.2% of  $\Sigma$ 16PAHs, Pyr, Chry and Fluo covered 12.5-25.9%, 9.1-19.1% and 3.5-8.1% of  $\Sigma$ 16PAHs, respectively.

**Table 5.** Correlations of standardized concentration of PAHs at different sampling sites.

r	PM <sub>10</sub>				PM <sub>2.5</sub>			
	A	B	C	D	A	B	C	D
A	1.000				1.000			
B	0.994 **	1.000			0.514	1.000		
C	0.993 **	0.986 **	1.000		0.756*	0.945**	1.000	
D	0.990 **	0.995 **	0.990 **	1.000	0.843**	0.597*	0.780*	1.000

\* Correlation is significant at the 0.05 level (2-tailed); \*\* Correlation is significant at the 0.01 level (2-tailed).

SPSS packages were used to detect the correlation of distribution patterns of individual PAHs at different sampling sites. Results showed that there was no significant difference in the distribution of PAHs in different function areas (Table 5). In PM<sub>10</sub>, all the values of correlation coefficient (r) were much higher than 0.9 (P = 0.01) meaning that the sources of PAHs were quite similar at different sampling sites. In PM<sub>2.5</sub>, all the values of r were higher than 0.50, in which values of 0.95, 0.84 and 0.76 were for PAHs at site B and C, A and D, A and C, respectively.

Thus could be explained by the fact that Xiamen was a coastal city with relative simple energy structure and the wind from the sea could better dilute and diffuse the pollutants in the air.

### **Source identification of PAHs in PM<sub>10</sub>/PM<sub>2.5</sub>**

#### *Diagnostic ratio*

PAHs have been used as tracers to distinguish between diverse sources (Venkataraman and Friedlander, 1994; Mandalakis *et al.*, 2002; Guo *et al.*, 2005). Different profiles and distribution patterns of individual PAHs were characteristic of different pollution sources. As a result of numerous studies, Kulkarni and Venkataraman (2000) identified some PAHs as tracers of several sources in the urban atmosphere: Phen, Fluo and Pyr are characteristic of coal combustion; Pyr, Phen, Fluo are derived from incineration processes; BaP and Fluo are tracers for wood combustion; BgP and Indeo for vehicular fuels; and Fluo, Pyr, BbF and BkF for heavy-duty diesel vehicles. The main PAHs sources in the Asian area were traffic exhausts (Acen, Fluo, Flu, Pyr, Chry, BeP) and industrial emissions (BaP, BaA, BeP, Cor) (Chang *et al.*, 2005).

The sum of the concentrations of the nine following combustion PAHs (CPAHs): Fluo, Pyr, BaA, BbF, BkF, BaP, BeP, Indeo and BgP has often been used as a characteristic diagnostic parameter for PAHs produced by stationary combustion sources (Rogge, 1993; Kavouras, 1999; Bi *et al.*, 2002; Manoli *et al.*, 2002; 2004; Sienna, 2005), Rogge *et al.* (1993) determined the value of CPAHs/ $\Sigma$ PAHs ratio for non-catalyst (0.4) and catalyst-equipped (0.5) automobiles and for heavy-duty diesel trucks (0.3). In this study, the value of CPAHs/ $\Sigma$ PAHs in PM<sub>10</sub> was 0.3-0.4 meaning that stationary combustion sources (industry emission) was a contributor for the PAHs pollution in the air. In PM<sub>2.5</sub>, its value was 0.4-0.7 meaning that stationary combustion sources contribute much more than that at PM<sub>10</sub>. Lee *et al.* (1977) suggested value of Fluo/Pyr for coal combustion (1.4) and for wood burning (1.0) and for fuel combustion (<1). Gschwend *et al.* (1981) indicated value of BaA/Chry ratio was 0.93 for wood burning and 0.28-1.2 for gasoline combustion and 0.17-0.36 for coal combustion. In this study, the values of Fluo/Pyr both in PM<sub>10</sub> and PM<sub>2.5</sub> were 0.20-0.39 indicating the fuel combustion source especially traffic emissions source was a great contributor; BaA/Chry in PM<sub>10</sub> was 0.18-0.50 meaning the gasoline and diesel vehicles emission sources. Thus most of the diagnostic ratios in PM<sub>10</sub> and PM<sub>2.5</sub> suggested the significant contribution of gasoline exhaust and diesel exhaust, with some contribution from coal and wood combustion sources.

#### *OC/EC and inorganic analysis*

Carbonaceous particles consist of two major components, elemental carbon (EC) and organic carbon (OC), the sum of them being defined as total carbon (TC). Elemental carbon (EC) was associated with primary emission from fossil fuel combustion and wood burning. Because of its stability in the atmosphere, EC was usually used as the marker for anthropogenic pollution.

Organic carbon (OC) can be emitted directly from the emission sources or produced from atmospheric transformation of organic gases. Secondary OC is formed by condensation of low vapor pressure products during photo-oxidation of hydrocarbons (Seinfeld *et al.*, 1998; Chow *et al.*, 1996).

In this study, OC/EC in PM<sub>10</sub> was analyzed. Concentrations of OC were in the range of 9.83-15.60 µg/m<sup>3</sup> and 1.41-4.73 µg/m<sup>3</sup> for EC in Xiamen (Wang *et al.*, 2006). Among different function areas, the concentrations of OC were as following: B (15.60 µg/m<sup>3</sup>) > D (11.83 µg/m<sup>3</sup>) > C (10.99 µg/m<sup>3</sup>) > A (9.83 µg/m<sup>3</sup>) and the concentrations of EC were: B (4.73 µg/m<sup>3</sup>) > C (3.13 µg/m<sup>3</sup>) > D (2.86 µg/m<sup>3</sup>) > A (1.41 µg/m<sup>3</sup>). Ratios of OC/EC were as following: 6.98 (A) > D (4.13) > C (3.52) > B (3.30). These results meant the secondary organic carbon (SOC) contributed much to the PM<sub>10</sub> of Xiamen with all ratios higher than 3. Its contribution was calculated by the following equation:

$$\text{SOC} = \text{TC} - \text{EC} \times (\text{OC/EC})_{\text{min}} \quad (2)$$

Results showed the secondary OC covered 38.1% in average of the total OC in Xiamen atmosphere. Generally, these results could be explained by the mild meteorology conditions with high temperature and good sunshine even in winter. They were quite suitable for the photochemical reactions to generate the SOC. The differences among sites were quite consistent with the fact that the pollutants at site B were more contributed by the continuous fresh input from traffic emission and industry emission while site A and D were more contributed by the secondary pollution due to the lack of the primary emission sources.

Concentration of  $\Sigma$ PAHs and OC significantly correlated with  $r = 0.59$  ( $p < 0.01$ ) while correlation coefficient between EC and OC was 0.80 ( $p < 0.01$ ). Thus meant EC and OC were from similar sources (Offenberg *et al.*, 2000). In conjunction with the results of the high accumulation level of S, Se, Zn and Br in PM<sub>10</sub> by the elemental and inorganic analysis (Zhuang *et al.*, 2006), the mixing pollution sources of coal combustion/industry emission and serious traffic emissions were identified.

## CONCLUSIONS

Wintertime study of atmospheric concentration of  $\Sigma$ 16PAHs bound to PM<sub>10</sub>/PM<sub>2.5</sub>, EC/OC were carried out during Dec. 21, 2004-Dec. 29, 2004. Concentrations of  $\Sigma$ 16PAHs were 5.20-28.07 ng/m<sup>3</sup> in PM<sub>10</sub> and 3.04-11.32 ng/m<sup>3</sup> in PM<sub>2.5</sub>. Concentration of OC was 9.83-15.6 µg/m<sup>3</sup> and 1.41-4.73 µg/m<sup>3</sup> for EC. The highest concentration of  $\Sigma$ 16PAHs always occurred at site B meant the industry emission and traffic emission were great contributor for PAHs pollution

in Xiamen. Ratio analysis, EC/OC analysis and correlation analysis suggested the main sources of PAHs in PM<sub>10</sub>/PM<sub>2.5</sub> were traffic emissions, industry emission and coal combustion.

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