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A seasonal study of polycyclic aromatic hydrocarbons in $PM_{2.5}$ and $PM_{2.5-10}$ in five typical cities of Liaoning Province, China

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ABSTRACT

Fourteen polycyclic aromatic hydrocarbons (PAHs) in $PM_{2.5}$ and $PM_{2.5-10}$ samples collected in five cities (Shenyang, Anshan, Jinzhou, Fushun and Dalian), Liaoning Province, China in 2004 and 2005 were analyzed by using a HPLC equipped with fluorescence and UV detectors. Results showed total PAHs concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ were in the range of 75.32–1900.89 ng m^{-3} and 16.74–303.24 ng m^{-3}, respectively. 90% of the total PAHs were in $PM_{2.5}$. PAHs in $PM_{2.5}$ had a winter to summer ratio varying from 6.5 to 125.8 while PAHs in $PM_{2.5-10}$ had a ratio ranging from 1.7 to 37.6. Total PAHs concentrations were most abundant at residential/commercial sites and were fewest at an industrial site for both $PM_{2.5}$ and $PM_{2.5-10}$. Urban background sites showed unexpected higher PAHs concentrations. Total BaP equivalent concentration (BaPeq) for $PM_{2.5}$ ranged from 7.80 to 88.42 ng m^{-3} in different function zones. Similarities of PAHs profiles between sampling sites and between fine and coarse fractions were compared by coefficient of divergence which indicated that remarkable differences in PAHs compositions existed. Principal component analysis (PCA) associated with diagnostic ratios revealed coal combustion and vehicle emission were the major sources for $PM_{2.5}$ and $PM_{2.5-10}$ associated PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been widely accepted as a class of ubiquitous and mutagenic environmental pollutants and attracted much attention in previous studies on air pollution recently [1,2]. PAHs are products of incomplete combustion and pyrolysis of fossil fuels such as petroleum and coal and other organic materials from natural and anthropogenic sources [3–13] including fossil fuels combustion [14], vehicle exhaust [15,16], open-fire straw burning [16,17], cigarette smoking [17], wood combustion [18], industrial production [19], including waste incineration [6], metal production [20], coke production [20], iron production [5,17], airplane production [17], etc. Results of previous studies had shown that the main sources of PAHs in urban area were traffic exhaust (diesel or gasoline) and certain industrial processes [20,21]. Zhang and Tao [17] pointed out that in China, the major emission sources for atmospheric PAHs were biofuel, coke production, domestic coal, traffic oil, open straw burning, petrol refinery and consumer products which contributed 66.4%, 14.4%, 10.7%, 2.0%, 2.0%, 1.0% and 0.9%, respectively. Tian et al. [22] concluded that in heating period, the main pollution sources were coal-fired boiler emission (56%), residential coal combustion (33%) and traffic emissions (11%). As for non-heating period, the main sources were gasoline engine emission, traffic tunnel emission and coal-fired power plant, and the overall source contributions of traffic emission (gasoline engine in traffic tunnel) was 79% and of coal-fired power plant was 21% in Dalian, China.

An important property-particle size determined the PAHs size distribution, and furthermore, the inhalable and respirable PAHs fractions [3]. In general, average fine particulate PAHs concentrations were all higher than coarse particulate PAHs concentrations [23–25]. Schnelle-Kreis et al. [26] found that in most cases the amount of PAHs associated with coarse particles was less than 10% of the total. Baek et al. [27] reported that 95% of particulate PAHs sampled in London were in particles with diameter less than 3.3 μm.

Temporal variation of PAHs has been investigated in some studies and most results showed higher PAHs concentrations in winter than in summer [4,20,21,24,28,29]. Although several studies have been conducted to compare PAHs between urban sites and suburban sites [4,24,25,30], only a few measurements were conducted to compare the difference in different function zones in urban areas [31–32].

In particular, benzo[a]pyrene (BaP) had always been selected as an indicator of carcinogenic PAHs [24,32] and some countries and organizations had also set up standards for it. The guided level of

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BaP is 0.25 ng m^{-3} in USA [8], 1.0 ng m^{-3} in European Union [8,21], 0.25 ng m^{-3} in UK [21,24], 1.0 ng m^{-3} in Italy [24], 1.0 ng m^{-3} in WHO [33] and 10 ng m^{-3} in China [34]. While the environmental health risk associated with exposure to atmospheric particulate PAHs has yet not to be assessed for the cities of Liaoning Province.

PAHs are present in both aerosol phases. The PAHs of low molecular weight (2 and 3 aromatic rings) were found preferentially in the gas phase while the ones of larger molecular weight (4–6 aromatic rings) were found adsorbed on the surface of suspended particles [2,3,11,19,20,29,32]. Therefore, it is important to evaluate the amount, distribution and possible sources of PAHs in the atmospheric aerosols since their absorbed amount through breathing depends upon their atmospheric concentration [35].

In Liaoning Province, air quality monitoring networks have been constructed to monitor criteria air pollutants such as SO_2, NO_x, CO, O_3 and PM_{10}. Less attention has been paid on monitoring PAHs that requires more elaborate sampling and analytical protocols. Studies related to PAHs have recently been conducted in some cities such as Shenyang [36] and Dalian [22]. The main objectives of these studies were to detect and quantify the PAHs compounds in PM. However, PAHs partition between $PM_{2.5}$ (particles with aerodynamic diameter less than 2.5 μm, fine fraction) and $PM_{2.5-10}$ (2.5 μm <aerodynamic diameter <10 μm, coarse fraction) is still unknown. It is important to conduct detailed and systematic PAHs profiles for particulate matter for the purpose of effective air pollution control and establishing air quality standards by assessing public exposure to PAHs and their associated health risks [23].

We have performed a four-season $PM_{2.5}$ and $PM_{2.5-10}$ sampling in 2004 and 2005 at 10 sites in five cities which covered different city zones of Liaoning Province. We focused on characteristic, temporal and spatial distribution as well as sources for both fine and coarse particulate PAHs. The main objectives of this study were to: (1) give the PAHs levels of PM in Liaoning Province; (2) identify the seasonal variation of PAHs concentration and distribution pattern associated with fine and coarse fraction; (3) compare the status of PAHs pollution in different city function zones; (4) identify their possible sources. It is expected that the results from this study will provide a baseline reference for a global database as well as for regulatory action to improve air quality in these cities.

2. Experimental

2.1. Sampling area and sites description

Liaoning province is located in the eastern shore of Eurasia, under the control of a continental monsoonal climate within a warm temperate zone. The terrain of the province is complex, including mountain, plain, hill and coast. Annual average temperature is between 5 and 10 °C, decreasing from coastal area to inland. The average yearly rainfall is between 500 and 1000 mm, decreasing from east to west. The precipitation is mainly in summer, accounting for 60–75%. Long cold period, strong wind in the plain area, wet in the east and dry in the west, concentrative precipitation in summer, plenitudinous sunlight and distinct four seasons are the main climate characteristics of the province. As the traditionary heavy-industrial base of China, the major industry system of the province includes metallurgy, mechanics, petrochemical, construction material and so on.

Considering differences in topography, meteorology, industrial structure and air quality, five representative cities including Shenyang (122°25′–123°48′E, 41°11′–43°02′N), Anshan (122°10′–123°13′E, 40°27′–41°34′N), Fushun (123°39′–125°28′E, 41°41′–42°38′N), Jinzhou (120°42′–122°37′E, 40°48′–42°08′N) and Dalian (120°58′–123°31′E, 38°43′–40°10′N) were selected to study the characterization of PM-bound PAHs in Liaoning Province. Locations of these five cities are indicated in Fig. 1.

Table 1
Geometric mean concentrations of PAHs in $PM_{2.5}$ and $PM_{2.5-10}$ at 10 sites in five selected cities during sampling periods (ng m^{-3}).

PAHs	$PM_{2.5}$										$PM_{2.5-10}$									
	Shenyang		Anshan			Fushun		Jinzhou		Dalian	Shenyang		Anshan			Fushun		Jinzhou		Dalian
	SZ (n = 53)	TYJ (n = 51)	SGS (n = 51)	ASJ (n = 51)	TXZ (n = 45)	SK (n = 53)	ZQ (n = 53)	NS (n = 51)	JZJ (n = 50)	GJZ (n = 50)	SZ (n = 53)	TYJ (n = 51)	SGS (n = 51)	ASJ (n = 51)	TXZ (n = 45)	SK (n = 53)	ZQ (n = 53)	NS (n = 51)	JZJ (n = 50)	GJZ (n = 50)
Nap	3.49	4.81	0.98	1.01	1.00	0.73	1.53	0.65	0.92	1.52	3.57	3.09	0.39	0.23	0.18	2.62	6.33	0.55	0.74	1.04
Ace	4.05	3.56	103.41	133.90	212.72	1.79	2.33	2.53	0.41	1.14	1.52	1.54	4.73	7.41	22.61	3.45	2.94	0.35	1.66	0.85
Phe	69.98	92.68	15.19	14.40	29.84	21.08	74.18	10.73	5.58	7.09	48.46	5.03	3.06	4.41	6.50	15.41	28.4	2.57	2.49	4.43
Ant	1.76	64.07	4.23	5.60	10.24	8.39	10.77	3.50	1.73	0.98	0.51	1.09	0.68	0.71	1.72	2.74	3.41	0.74	0.56	0.62
Flu	20.39	311.77	48.64	67.94	116.60	70.45	560.38	42.53	29.69	12.51	5.16	14.27	6.61	5.32	15.87	17.71	47.43	4.98	4.30	4.38
Pyr	15.23	272.81	51.07	62.28	108.99	52.26	583.67	30.69	14.13	8.10	2.17	10.40	5.39	7.22	15.33	13.43	45.56	2.87	1.55	2.40
BaA	5.90	64.05	21.12	26.50	50.48	17.71	190.23	20.73	10.37	6.06	0.77	2.86	2.65	2.74	6.51	3.43	11.45	1.87	1.10	1.28
Chr	8.13	81.04	22.33	26.71	49.85	23.09	203.78	13.64	5.81	7.63	1.68	3.69	2.38	2.82	6.21	4.85	12.81	1.49	0.61	1.66
BbF	14.21	65.67	25.47	29.79	56.69	23.96	115.17	19.53	10.81	8.92	2.16	4.44	2.61	3.02	6.41	3.62	5.70	1.66	0.96	1.92
BkF	3.55	16.37	19.77	22.22	44.17	6.09	33.61	6.17	3.60	2.88	0.71	1.06	2.71	2.95	5.36	1.38	1.83	0.56	0.24	0.77
BaP	5.93	31.71	20.15	24.09	47.38	10.71	48.44	13.61	6.61	5.39	1.13	2.04	2.50	2.95	6.01	1.98	3.44	1.13	0.77	0.91
DbA	9.14	23.64	42.47	52.48	105.07	12.89	41.82	13.84	10.45	6.65	2.56	1.83	3.28	4.34	10.55	1.92	2.03	1.23	1.07	1.29
BghiP	1.40	4.76	23.94	29.92	60.08	4.42	8.62	2.61	1.59	1.63	0.70	0.72	1.87	2.41	6.28	1.06	0.38	0.42	0.13	0.35
Ind	7.35	16.89	12.43	15.24	29.90	8.98	26.37	10.75	6.16	4.83	1.18	1.66	1.07	1.41	3.20	1.46	1.54	0.91	0.56	1.22
$\sum$PAHs	170.50	1053.83	411.21	512.08	923.01	262.53	1900.89	191.49	107.87	75.32	72.27	53.73	39.92	47.96	112.72	75.07	173.24	21.35	16.74	23.12