



## Occurrence and sources of polycyclic aromatic hydrocarbons and *n*-alkanes in PM<sub>2.5</sub> in the roadside environment of a major city in China

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### ABSTRACT

Thirty six PM<sub>2.5</sub> samples were collected at a roadside site of the heaviest traffic road in Qingdao, a coastal mega city in North China, from March 2004 to January 2005 to perform a detailed characterization of 16 priority polycyclic aromatic hydrocarbons (PAHs) proposed by the USEPA and *n*-alkanes. For PAHs, the significant increase in winter was observed with average PAH level of 32.3, 11.5, 48.9 and 263 ng m<sup>-3</sup> for spring, summer, autumn and winter, respectively. The average concentrations of *n*-alkane in PM<sub>2.5</sub> at ground level were 232, 121, 309 and 369 ng m<sup>-3</sup> in spring, summer, autumn, and winter, respectively. The pyrogenic PAHs were mainly from the coal burning, and the liquid fossil fuel combustion was their second contribution even at the roadside of a busy street with heavy traffic in Qingdao. Petroleum residues were the dominant source for the *n*-alkanes. Principal component analysis results indicated that all the measured PAHs but naphthalene and those C<sub>17</sub>–C<sub>26</sub> *n*-alkanes could be attributed to the fossil fuel burning while long-chain *n*-alkanes (C<sub>27</sub>–C<sub>35</sub>) were mainly derived from higher plant waxes. Good correlations between PAHs and *n*-alkanes in summer, autumn and winter suggested that they were mainly from local sources. The poor correlation of *n*-alkanes and PAHs in spring could be mainly due to the shift from the space heating season to non-heating season during the sampling period. This work indicated that the roadside environment in Qingdao was more deteriorated compared with non-roadside environment in other mega cities in China.

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### 1. Introduction

It has been clearly shown that the concentrations of particles with the aerodynamic diameter less than 2.5 μm (PM<sub>2.5</sub>) positively correlate with mortality [1,2]. Carbonaceous aerosol is a major constituent in PM<sub>2.5</sub> in urban areas in China, which is a mixture of hundreds of organic compounds and elemental carbon [3,4]. Some organic compounds, for example, polycyclic aromatic hydrocarbons (PAHs), are listed as priority pollutants since they have been proved to be carcinogenic and mutagenic [5]. Compared to the U.S. [6,7] and Europe [8], atmospheric PAHs in cities in China are much higher especially in winter due to the coal and biomass burning [9–12]. Xu et al. [13] reported that the emission of 16 priority PAHs proposed by the USEPA (16 PAHs) reached 23,300 tons in 2003 in China, largely due to the increasing usage of

coal and petroleum for energy demand to meet the rapid economic growth.

PAHs in atmosphere are primarily the product of low- and high-temperature combustion processes [14]. *n*-Alkanes in aerosols are emitted by anthropogenic and natural sources [15]. PAHs and *n*-alkanes contain useful markers for source identification of fine particles [16,17] and some particle-phase PAHs and *n*-alkanes have been successfully applied in a chemical mass balance model for PM<sub>2.5</sub> source apportionment in the United States [6,18], and China [4].

Qingdao is a coastal mega city situated in the southern tip of the Shandong Peninsula in North China with an urban population of 2.35 millions (Fig. 1). The composition of ions [19] and deposition of metals in aerosols in Qingdao [20] have been reported. The seasonal variation of solvent extractable organic compounds in total suspended particulates (TSP) [9], and elemental and organic compositions of PM<sub>2.5</sub> in the severe Asian dust episodes in Qingdao [21] in non-roadside site have also been studied. However, there is no information on the PAHs and *n*-alkanes in PM<sub>2.5</sub> in the roadside environment of Qingdao. Actually, even in China, these chemical data in the roadside environment is still very limited. Furthermore,

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Fig. 1. Sampling site.

the source of PAHs in Qingdao's atmosphere remains unidentified. In this study, 36  $PM_{2.5}$  samples at a roadside site next to the heaviest traffic road in Qingdao from March 2004 to January 2005 were collected to understand the abundance, seasonal variation and possible origin of particle-associated PAHs and *n*-alkanes at a ground level. These data can provide important information for the health communities to assess the potential health impact of fine particles in China.

## 2. Experimental

### 2.1. Sampling site

The sampling site was located on the rooftop of a one-storey building at the roadside of the middle Hong Kong Road near the Government Hall (GH) of Qingdao (Fig. 1). The sampling height was 3 m above the ground. The middle Hong Kong Road has the heaviest traffic in Qingdao urban area, and is located in a commercial, residential region. On average in the sampling period, there was 4100 vehicles/h during rush hours, while 1700 vehicles/h during non-rush hours. The fleet is dominated by gasoline-powered vehicles, followed by a small number of diesel-powered public buses.

### 2.2. Sampling

$PM_{2.5}$  samples were collected on quartz fiber filters (Whatman QM-A, 90 mm in diameter) using a GIF  $PM_{2.5}$ -2 sampler manufactured by the Beijing Geological Institute [21]. The flow rate was 77 L/min. The sampling time was nominally 48 h starting at 10 a.m. for summer, autumn and winter while for spring it was nominally 24 h in order to capture some Asian Dust episodes.

### 2.3. Organic analysis

$PM_{2.5}$  samples for organic compound analysis were analyzed at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, China. The analytical and QA/QC procedures for PAHs and *n*-alkane followed that described by Bi et al. [17]. Briefly, five deuterated PAHs consisting of naphthalene- $d_8$ , acenaphthene- $d_{10}$ , phenanthrene- $d_{10}$ , chrysene- $d_{12}$  and perlene- $d_{12}$  standards were added prior to extraction. The filter was ultrasonically extracted with three 100-mL aliquots of dichloromethane, each for 15 min at room temperature. The extract was cleaned up by a silica gel chromatographic column and then analyzed by GC-MSD (a HP-5972 mass spectrometer interfaced

**Table 1**  
Concentrations of PAHs and *n*-alkanes, and some important indices of PM<sub>2.5</sub> at Qingdao roadside site.

Date	<i>n</i> -Alkanes yield (ng m <sup>-3</sup> )	PAHs					
		C <sub>max</sub>	Petroleum residues (%)	Yield (ng m <sup>-3</sup> )	BaA/BaA + CHR	FLU/FLU + PYR	INP/INP + BghiP
03-16-04	200	C <sub>22</sub>	89.3	45.8	0.31	0.53	0.50
03-17-04	477	C <sub>22</sub>	91.9	68.3	0.34	0.53	0.49
03-18-04	313	C <sub>21</sub>	94.1	23.1	0.32	0.52	0.52
03-19-04	351	C <sub>22</sub>	93.0	26.3	0.28	0.53	0.47
03-20-04	558	C <sub>23</sub>	90.4	42.3	0.27	0.53	0.50
03-21-04	738	C <sub>22</sub>	92.8	38.0	0.27	0.52	0.47
03-22-04	551	C <sub>23</sub>	90.0	57.1	0.24	0.53	0.50
03-24-04	411	C <sub>22</sub>	90.5	19.8	0.21	0.55	0.46
03-25-04	447	C <sub>22</sub>	90.0	15.3	0.19	0.55	0.47
03-26-04	306	C <sub>23</sub>	90.7	11.4	0.20	0.54	0.46
03-27-04	232	C <sub>23</sub>	91.5	7.7	0.17	0.56	0.50
Average (spring)	417		91.3	32.3	0.25	0.54	0.49
07-26-04	161	C <sub>24</sub>	84.9	2.4	0.30	0.50	0.42
07-28-04	107	C <sub>22</sub>	85.5	2.2	0.21	0.58	0.39
07-30-04	197	C <sub>27</sub>	85.1	23.6	0.40	0.50	0.50
08-01-04	143	C <sub>24</sub>	86.8	14.6	0.32	0.50	0.49
08-03-04	177	C <sub>26</sub>	89.2	10.3	0.30	0.49	0.47
08-05-04	195	C <sub>27</sub>	88.0	31.7	0.44	0.51	0.49
08-07-04	111	C <sub>24</sub>	86.9	3.5	0.22	0.48	0.43
08-09-04	121	C <sub>24</sub>	89.2	3.6	0.27	0.55	0.41
Average (summer)	152		87.0	11.5	0.31	0.51	0.45
10-10-04	236	C <sub>25</sub>	80.0	40.1	0.33	0.52	0.52
10-12-04	189	C <sub>24</sub>	84.6	33.3	0.34	0.52	0.51
10-14-04	377	C <sub>24</sub>	84.7	48.9	0.36	0.52	0.49
10-16-04	344	C <sub>25</sub>	79.6	45.5	0.29	0.52	0.52
10-18-04	453	C <sub>25</sub>	82.7	76.4	0.31	0.50	0.51
10-20-04	365	C <sub>24</sub>	83.3	73.6	0.38	0.51	0.52
10-22-04	227	C <sub>25</sub>	84.3	25.4	0.26	0.52	0.50
10-24-04	194	C <sub>25</sub>	86.8	40.0	0.34	0.50	0.53
10-26-04	398	C <sub>24</sub>	86.6	56.6	0.34	0.51	0.51
Average (autumn)	309		83.6	48.9	0.33	0.51	0.51
01-06-05	177	C <sub>21</sub>	94.3	255	0.33	0.58	0.52
01-08-05	579	C <sub>22</sub>	93.0	150	0.35	0.53	0.50
01-10-05	885	C <sub>22</sub>	92.8	274	0.35	0.54	0.52
01-12-05	1791	C <sub>22</sub>	94.2	588	0.39	0.54	0.52
01-14-05	925	C <sub>22</sub>	92.8	269	0.36	0.54	0.52
01-16-05	954	C <sub>22</sub>	91.4	238	0.32	0.55	0.51
01-18-05	725	C <sub>22</sub>	93.2	251	0.37	0.53	0.52
01-20-05	369	C <sub>22</sub>	91.6	75.3	0.33	0.53	0.51
Average (winter)	801		92.9	263	0.35	0.54	0.51

to a HP-5890 II gas chromatography). Hexamethylbenzene was added as internal standard before injection. The GC was equipped with a HP-5 capillary column (25 m × 0.32 mm i.d., film thickness 0.25 μm) with ultra pure helium as carrier gas. The GC operating conditions were: held at 80 °C for 5 min, ramped to 290 °C at 4 °C min<sup>-1</sup> and held for 30 min. The sample was injected splitless with the injector temperature at 290 °C. The MSD was operated with the electron impact (EI) mode at 70 eV using selected-ion-monitoring (SIM).

Target compounds were identified by comparison of retention time and mass spectra with those of authentic standards. Compounds including 16 PAHs in a mixture and 6 *n*-alkanes (C<sub>16</sub>, C<sub>19</sub>, C<sub>24</sub>, C<sub>28</sub>, C<sub>30</sub> and C<sub>32</sub>) were used for quantification. The recovery control of *n*-alkanes was based on deuterated PAHs including phenanthrene-d<sub>10</sub> and chrysene-d<sub>12</sub>, assuming that they have matched molecular weight and chemical properties. The mean recovery for all 36 samples was 67.5 ± 10.5% for naphthalene-d<sub>8</sub>, 76.1 ± 11.9% for acenaphthene-d<sub>10</sub>, 90.4 ± 8.5% for phenanthrene-d<sub>10</sub>, 92.3 ± 7.3% for chrysene-d<sub>12</sub> and 90.5 ± 7.4% for perylene-d<sub>12</sub>. Procedural blanks, standard-spiked blanks, and duplicate samples were analyzed for each set of 10 samples for quality assurance and control. The major contaminants observed were primarily phthalate esters and trace of *n*-alkanes ranging from C<sub>18</sub> to C<sub>26</sub>. PAHs were not detected in the procedural blanks.

### 3. Results and discussion

#### 3.1. PAHs (polycyclic aromatic hydrocarbons)

Sixteen PAHs were measured in this study including naphthalene (NAP), acenaphthylene (AC), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLUO), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (INP), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BghiP). The seasonal average of 16 PAH concentration varied greatly (11.5 ng m<sup>-3</sup> in summer, 32.3 ng m<sup>-3</sup> in spring, 48.9 ng m<sup>-3</sup> in autumn, and 263 ng m<sup>-3</sup> in winter, respectively) (Table 1). The concentration of PAHs was 23-fold higher in winter than in summer. Coal is the main energy source in North China especially in winter when the need of energy especially for space heating is significant [10,22]. Some studies showed that the changes in fuel structure, emission strength (both stationary and mobile) and meteorological conditions (e.g., fewer daylight hours, reduced ambient temperatures and photochemical activity) contributed to higher PAH levels during the winter [5,9,14,23].

These 16 PAHs can be classified into 3 groups, including 2 + 3-ring (NAP, AC, ACE, FLU, PHE and ANT), 4-ring (FLUO, PYR, BaA and

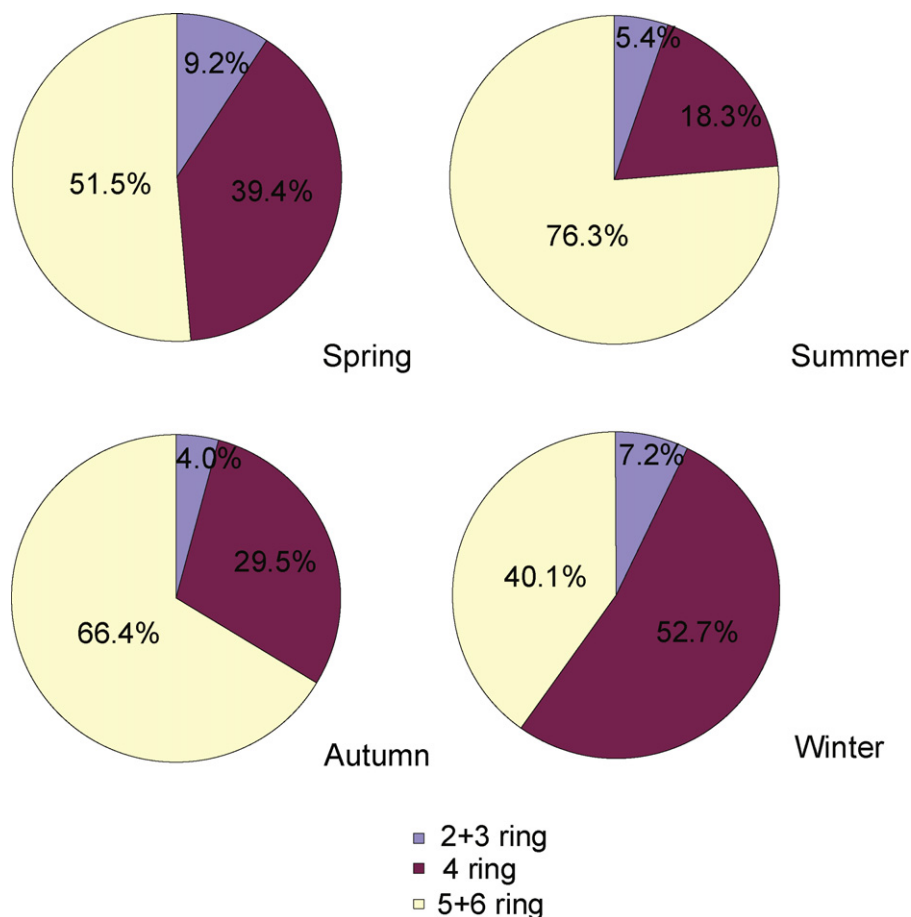


Fig. 2. Relative concentrations of 2 + 3-, 4- and 5 + 6-ring groups in 16 PAHs at different seasons at Qingdao roadside site.

CHR), and 5 + 6-ring (BbF, BkF, BaP, INP, DBA and BghiP) PAHs. The relatively importance of 3-group PAHs in four seasons in Qingdao roadside site is shown in Fig. 2. The 2 + 3-ring PAHs were only a small part in 16 PAHs (less than 10%) because they are primarily in gas phase even in winter owing to their high volatility [14]. Therefore, 4-ring and 5 + 6-ring PAHs dominated in the 16 PAHs. The relative concentration of 4-ring PAHs was the largest in winter (53%) and the smallest in summer (18%) while it was just opposite for 5 + 6-ring PAHs (accounted for 76% of 16 PAHs in summer and 40% in winter). Summer in Qingdao is hot and humid with the ambient temperature of 25–33 °C during the sampling period and the prevailing wind was from southeast bringing in clean oceanic air, while winter is cold and dry (–6 to 4 °C during sampling period) with northerly as the dominant wind (<http://www.qingdao.gov.cn>). Autumn and spring are two transitional seasons in Qingdao. Temperature affects the gas/particle partitioning of 4-ring PAHs in the atmosphere because they are semi-volatile, leading to a strong seasonal variation of relative concentrations for 4-ring PAHs in Qingdao. The 5 + 6-ring PAHs are mainly in particle phase both in summer and winter. Thus, the temperature effect could be the main cause for the seasonal variation of the relative concentrations of 16 PAHs in Qingdao roadside PM<sub>2.5</sub>, especially for 4-ring PAHs.

Ratios of PAHs with similar molecular weights have been used as indices for source identification [24,25]. BaA/(BaA + CHR) < 0.2, has been suggested for petrogenic sources, and for pyrogenic sources, this ratio would be >0.35 [24]. BaA/(BaA + CHR) ratios in this study were 0.17–0.44 with average values of 0.25 in spring, 0.31 in summer, 0.33 in autumn and 0.35 in winter, respectively. These ratios were close to 0.35, suggesting that pyrogenic source was the dominant source of PAHs at the roadside environment.

It is indicated that PAHs from petrogenic source has FLUO/(FLUO + PYR) ratio of <0.4, and 0.4–0.5 for liquid fossil fuel (automotive and crude oil) combustion while >0.5 is characteristics of coal, grass or wood combustion [24]. INP/(INP + BghiP) ratio <0.2 is possibly petrogenic, and liquid fossil fuel (automotive and crude oil) combustion would yield a ratio of 0.2–0.5, while a ratio >0.5 is due to coal, grass and wood combustion [24,26]. Average FLUO/(FLUO + PYR) values in our study were 0.54 in spring, 0.51 in summer, 0.51 in autumn and 0.54 in winter, respectively; and the INP/(INP + BghiP) values were 0.49 in spring, 0.45 in summer, 0.51 in autumn and 0.51 in winter, respectively. FLUO/(FLUO + PYR) ratio suggested that the pyrogenic PAHs in Qingdao PM<sub>2.5</sub> were mainly from the coal combustion or grass and wood combustion. Since there was no grass and wood combustion for energy in Qingdao urban areas, coal combustion was most likely the major source, even at the roadside environment. INP/(INP + BghiP) ratio suggested that the pyrogenic PAHs in Qingdao PM<sub>2.5</sub> were mainly from the coal combustion, while the liquid fossil fuel combustion should be a second contribution, especially in summer. It should be noted that both ratios exhibited the lowest values in summer, indicating that the influence of coal combustion was more important in colder seasons. Our work is in agreement with a previous report on the atmospheric deposition samples in urban area of Tianjin, another coastal mega city in North China, where the vehicle emissions contributed relatively more PAHs during non-heating season [22]. Motor vehicles are usually considered to be a significant source of PAHs [14,27], however, this work indicated that coal burning was the major source of PAHs even at the roadside of a busy street with heavy traffic. This could be attributed to a combination of the following causes. Firstly, the middle Hong Kong Road is dom-

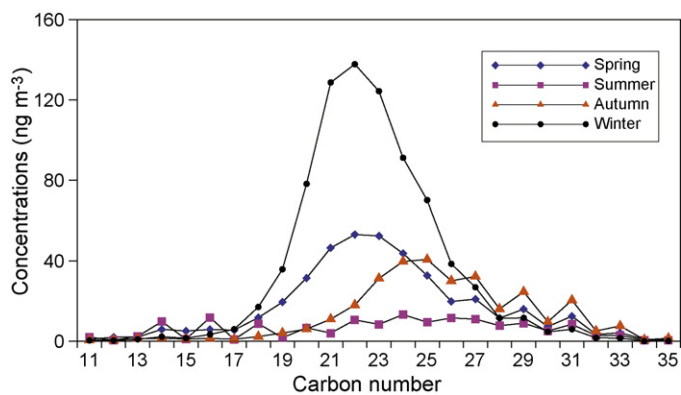


Fig. 3. Distribution diagrams of seasonal average concentrations of *n*-alkanes in  $PM_{2.5}$  at Qingdao roadside site.

inated by gasoline-powered small and light-duty vehicles. There is no permission for heavy-duty diesel trucks through this avenue from 6 a.m. to 11 p.m. It was reported that concentrations of PAHs in the heavy-duty track tunnel were higher than those in the light-duty vehicle tunnel even though the latter tunnel had two times more traffic than the former owing to the more contribution to PAHs from diesel engines [14,27]; thus, the contribution to PAHs from light-duty vehicles was relatively small. Secondly, coal is still the most important energy source in the Northern China including Qingdao. The impact is so huge that it is inevitable that coal still contributed significantly to PAHs in the ambient atmosphere in Qingdao, even at the roadside environment.

### 3.2. *n*-Alkanes

The average concentrations of *n*-alkane in  $PM_{2.5}$  at the roadside environment in Qingdao were 232, 121, 309 and 369  $ng\ m^{-3}$  in spring, summer, autumn, and winter, respectively. *n*-Alkane occurrence level in winter was 3-fold increase compared to summer. Distributions of *n*-alkanes in different seasons are shown in Fig. 3.

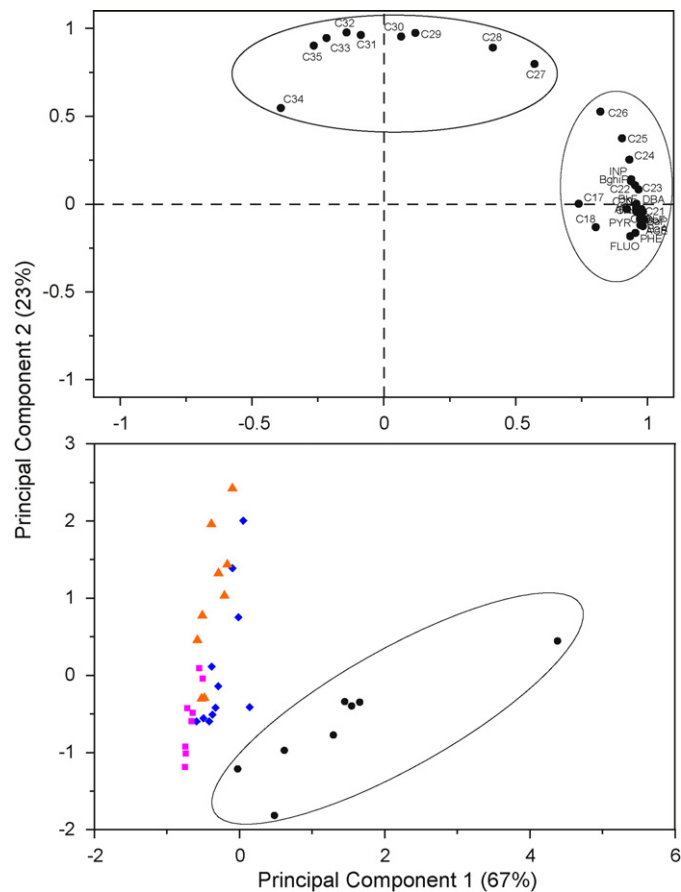


Fig. 5. Principal component analysis for PAHs and *n*-alkanes of Qingdao roadside  $PM_{2.5}$  samples.

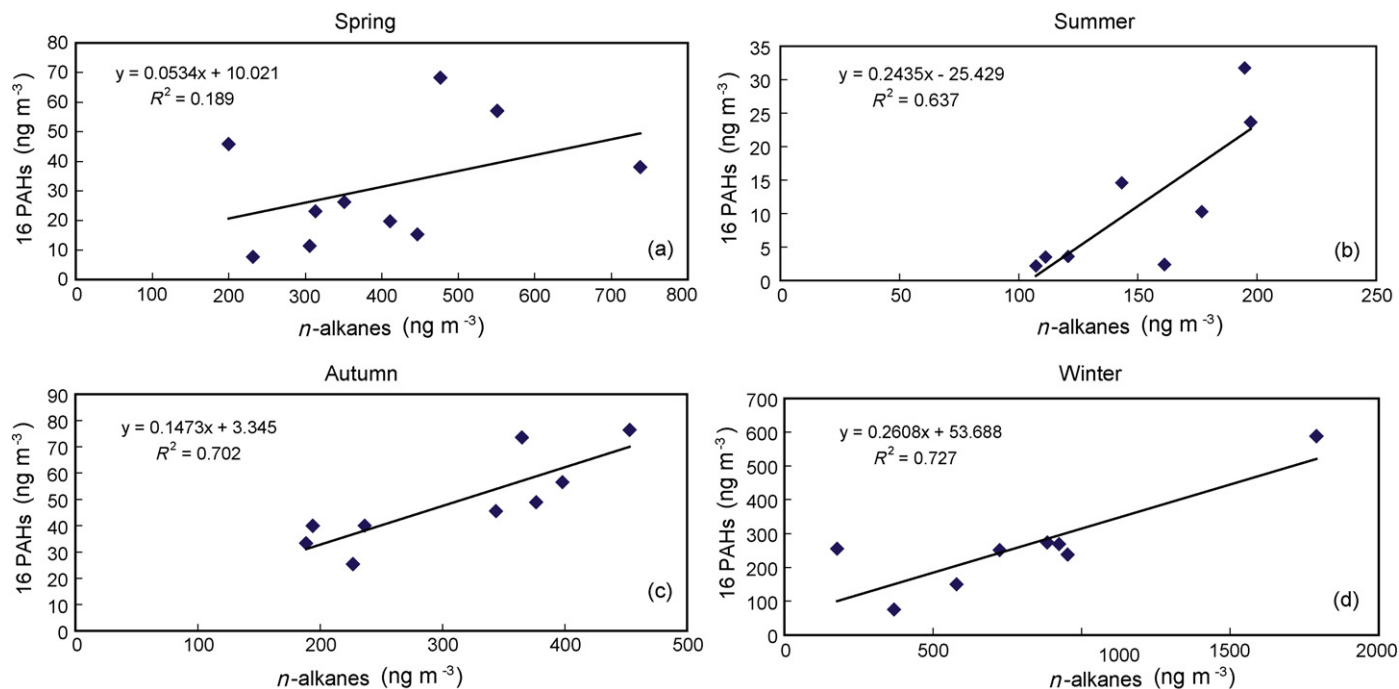


Fig. 4. Correlations between PAHs and *n*-alkanes in spring (a), summer (b), autumn (c) and winter (d).



**Table 2**Comparison of occurrence levels of PAHs and *n*-alkanes in aerosols in some mega cities in China (units: ng m<sup>-3</sup>).

Site	Alkanes				PAHs				References
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	
Qingdao PM <sub>2.5</sub> , urban, roadside	417	152	309	801	32	12	49	263	This work
Qingdao TSP, urban, non-roadside	180	53	90	408	37	34	28	177	[9]
Beijing PM <sub>2.5</sub> , urban, non-roadside	52	39	183	477	17	8	59	229	[12]
Shanghai PM <sub>2.5</sub> , urban, non-roadside	nd	22.5	nd	149	nd	7	nd	52	[11]
Guangzhou, PM <sub>2.5</sub> , urban, non-roadside	nd	46	nd	150	nd	13	nd	63	[11]

nd: No data.

The carbon number maximum ( $C_{\max}$ ) in summer was from  $C_{22}$  to  $C_{27}$ , with most of the samples at  $C_{23}$  to  $C_{27}$ . It was  $C_{21}$  or  $C_{22}$  in winter,  $C_{22}$  or  $C_{23}$  in spring and  $C_{24}$  or  $C_{25}$  in autumn. It can be clearly seen that  $C_{\max}$  seemed to shift to lower carbon number in winter. This could be due to the temperature effect of gas/particle partitioning [10,28]. Assuming that the emission strength was constant over the whole year, semi-volatile organic compounds could partition differently in summer and winter. Lighter *n*-alkanes were relatively enriched in particle phase in winter. Besides the shift towards particulate phase due to temperature effect, the dry weather with few precipitations and less atmospheric mixing in winter in Qingdao could lead to an accumulation for *n*-alkanes and PAHs in the atmosphere.

The *n*-alkanes can be divided into two source categories: higher plant wax and petroleum residues. The plant wax derived alkanes can be calculated from the following equation according to Simoneit et al. [16].

$$\text{Wax } C_n = C_n - \left[ \frac{(C_{n+1} + C_{n-1})}{2} \right] \quad (1)$$

Based on Eq. (1), the petroleum residue contributions in Qingdao PM<sub>2.5</sub> ranged from 80% to 94% with average contributions of 91% for spring, 87% for summer, 84% for autumn, and 93% for winter, respectively, indicating that petroleum residues was absolutely the dominant source of *n*-alkanes in Qingdao roadside PM<sub>2.5</sub>.

### 3.3. Seasonal correlations between *n*-alkanes and PAHs

Seasonal correlations between PAHs and *n*-alkanes are shown in Fig. 4. It showed that PAHs had good correlations with *n*-alkanes in summer ( $R^2 = 0.638$ ,  $n = 8$ ), autumn ( $R^2 = 0.702$ ,  $n = 9$ ) and winter ( $R^2 = 0.727$ ,  $n = 8$ ). Significant correlations between these two classes suggested that PAHs and *n*-alkanes were mainly from local sources, namely vehicular emissions and coal burning. However, in spring, this correlation was rather poor ( $R^2 = 0.189$ ,  $n = 11$ ). The end of the space heating season in Qingdao and the northern China starts around March 16–20 every year. As a consequence, the emission of PAHs from coal burning decreased dramatically since then, while there was almost no transformation for the emission of *n*-alkanes during this period since the dominating *n*-alkanes at roadside environment in Qingdao were from petroleum residues. This could lead to a poor correlation between *n*-alkanes and PAHs in Qingdao PM<sub>2.5</sub> samples in spring. Another possible cause was the Asian dust effect which is known to have significant impact on the air quality in spring in North China [21], however, this explanation could not be confirmed since there was no obvious occurrence of Asian dust during our sampling period. Based on above discussion, the lowest correlation between *n*-alkanes and PAHs could be mainly attributed to the change of emission sources in spring.

### 3.4. Source apportionment using principal component analysis

Principal component analysis (PCA) using SPSS 13.0 for Windows (SPSS Inc., Chicago, IL) was performed on the selected datasets

containing 15 PAHs and *n*-alkanes ( $C_{17}$ – $C_{35}$ ). The measured *n*-alkanes of  $C_{11}$ – $C_{16}$  and NAP were not included in the PCA as they are mainly in gas phase and showed low concentrations in this work. The two major principal components for loadings (variables) and scores (samples) are shown in Fig. 5. According to PCA results, two principal components (PC1 and PC2) were identified, which were responsible for 90% of the total variance. PC1 accounting for 67% of the data variance had a high positive loading of the combination variables of 15 PAHs and  $C_{17}$ – $C_{26}$  *n*-alkanes, and could be attributed to the fossil fuel burning contribution mainly from the vehicle emission and coal burning. PC2 representing 23% of the total variance was characterized by a high positive loading of the long-chain *n*-alkanes ( $C_{27}$ – $C_{35}$ ), corresponding to the biogenic source derived from higher plant waxes.

The samples in winter were obviously characterized by a higher score of PC1, suggesting a higher contribution from fossil fuel combustion sources due to the space heating in North China. The *n*-alkanes in  $C_{17}$ – $C_{26}$  range are semi-volatile, therefore, the higher loading of these *n*-alkanes for the winter samples in PC1 could be partly attributed to the temperature effect as discussed above. The most samples in autumn were identified by the higher values of PC2 because of the relatively higher loading of long-chain *n*-alkanes ( $>C_{27}$ ). The contribution of biogenic source was larger in the autumn samples due to the mechanical abrasion of higher plant waxes, vegetation debris and soil erosion [9].

### 3.5. Comparison of PAHs and *n*-alkanes between Qingdao and other mega cities in China

Comparing with Beijing, Shanghai and Guangzhou (urban, non-roadside sites), the concentrations of PAHs and *n*-alkanes at the Qingdao roadside site were much higher both in summer and winter (Table 2). This indicated that the roadside environment in Qingdao was more polluted compared with non-roadside sites in other mega cities in China although the previous reports indicated that the PAHs occurrence levels in Beijing were higher than those in Qingdao at non-roadside sites [10]. Unlike the US, the majority of the population in the urban of China is exposed to the roadside air pollutant emissions due to the active activities including walking on the side track and shopping, etc. Epidemiology studies have shown the increase of mortality with the increase of fine particulate matter concentrations [1]. Therefore, the detailed chemical measurements of air pollutants at their roadside environment should be very important for the mega cities in China.

## 4. Conclusions

There was a strong seasonal variation for the concentrations and compositions of PAHs and *n*-alkanes in the roadside environment in Qingdao. The pyrogenic PAHs in Qingdao roadside PM<sub>2.5</sub> samples were mainly from the coal combustion and the liquid fossil fuel combustion from gasoline-powered vehicle could be a second contributor. The petroleum residues were the dominant contribution for the *n*-alkanes. The seasonal variation of the composition

of 16 PAHs in Qingdao roadside environment was mainly due to the temperature effect. The long-chain *n*-alkanes were mainly from higher plant waxes while *n*-alkanes in range of C<sub>17</sub>–C<sub>26</sub> and almost all measured PAHs could be dominantly derived from the fossil fuel burning. As the first study to characterize particle-associated PAHs and *n*-alkanes at the roadside environment in Qingdao, these data are particularly useful for future assessment of health impact of fine particulate matter in Qingdao, or even in China.

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