Distributions and sources of *n*-alkanes in PM$_{2.5}$ at urban, industrial and coastal sites in Tianjin, China

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Abstract

Aliphatic hydrocarbons (*n*-alkanes) associated with fine particulate matter were determined in the ambient air of urban, industrial and coastal areas in Tianjin, China, where intensive coal burning for industrial and domestic purpose takes place. *n*-Alkane homologues from C12 to C35 were quantifiable in all samples with C20–C31 being the most abundant species. Average concentrations of the total *n*-alkanes were 148.7, 250.1 and 842.0 ng/m^3 in July, April and January, respectively. Seasonal variations were mainly attributed to ambient temperature changes and coal combustion for residential heating. Among the three studied areas, the highest levels of *n*-alkanes were observed in the industrial complex in winter and spring, but in summer the coastal alkane concentration moved up to the highest. A mono-modal distribution for *n*-alkanes was observed in spring and summer with odd carbon number predominance and a maximum centered at C27–C31, suggesting the release of plant wax into the atmosphere. The bimodal distribution with maxima at C22 and C26 observed in winter indicated a substantial influence of fossil fuel sources. All the CPIs (CPI1, CPI2, CPI3) values, varying between 0.64 and 1.97, indicated the influence of anthropogenic emissions on fine organic aerosols. The estimated contributions of plant wax to total *n*-alkanes were on average of 12.9%, 19.1% and 26.1% for winter, spring and summer, respectively.

Key words: PM$_{2.5}$; *n*-alkanes; distribution pattern; CPIs; plant wax

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Introduction

Organic aerosols, being composed of a complex mixture of hundreds of compounds including many mutagenic or carcinogenic species, have received an increasing attention due to their adverse impacts on human health, terrestrial and aquatic ecosystems, atmospheric chemistry and climate change (Jacobson et al., 2000; Turpin et al., 2000). However, only a small fraction (< 20%) of the organic compounds has been identified at molecular level (Jacobson et al., 2000), and some of them have been successfully used as molecular tracers in source apportionment of atmospheric particulate pollution (Schauer et al., 1996; Cass, 1998; Zheng et al., 2002). Normal alkanes (*n*-alkanes) are an important class of organic compounds in ambient aerosols, and their homologue distribution may indicate different pollution sources (He et al., 2006). Alkane compounds such as hopanes and steranes are regarded as the most valuable tracers of motor vehicles after lead has been removed from the gasoline pool (Cass, 1998; Schauer et al., 2002). Alkanes also have negative impact on human health. For example, the *n*-alkanes with more than

16 carbon number can damnify skin, and even engender skin cancer (Cheng et al., 1999). Anthropogenic sources of *n*-alkanes include fossil fuel combustion, petroleum residues and biomass burning. Biogenic emissions include particles shed from leaf epicuticular wax and from direct suspension of pollen, fungi, bacteria and algae (Brown et al., 2002). Plant wax alkanes are useful in identifying long-range transported aerosols because of their stability and nonvolatility (Fang et al., 1999).

Tianjin is a typical metropolis of China, with a population of approximately 10 million and an area of 11,919 km^2. It is located on the north of China, about 120 km southeast of Beijing, at the lower reaches of Haihe River and adjacent to the Bohai Sea. As an important industrial center in northern China, Tianjin has an integrated industrial structure including electronics, automobile, petrochemical, metallurgy, bio-pharmacy and new energy. Annual consumption of coal and petroleum in Tianjin are about 27.2 million and 12.3 million tons, respectively (Tianjin Statistics Bureau, 2006). Beijing-Tianjin Region, with a high level of industrialization and urbanization, is one of the most developed regions in China, and also in face of serious regional air pollution. Fine particular matter

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(PM$_{2.5}$) and its induced poor visibility are of great concern to scientists and policy makers. However, prior studies of PM in Tianjin mostly focused on the total suspended particulate (TSP) or respirable particulate (PM$_{10}$), and few were related to PM$_{2.5}$, even fewer about the organic composition of PM$_{2.5}$.

In this study, observation campaigns were conducted in urban, industrial and coastal areas of Tianjin during various seasons, for characterizing the concentration and distribution of *n*-alkanes associated with PM$_{2.5}$, and their seasonal/spatial variations. The relative importance of biogenic and petrolic sources was also evaluated based on the *n*-alkane distribution, carbon preference index (CPI), and plant wax index (waxC$_n$).

1 Experimental

1.1 Sampling program

Three types of sampling sites were chosen to represent the different types of Tianjin areas. An urban site (117°10′E, 39°06′N) is located in the downtown areas, which is a commercial-residential site and also influenced by heavy traffic. An industrial site (117°30′E, 39°12′N) is situated in the industrial complex of Dongli District, and there are hundreds of medium- or small-size factories including chemical and metallurgy factories, automotive fitting manufacturing, power plant, etc. in this area. A coastal site (117°41′E, 38°59′N) is located in an open area of Tanggu District, about 50 km southeast of downtown and adjacent to the Tianjin Harbor. Details of the sampling sites were given in our previous study (Li et al., 2009).

Under influence of the continental monsoon weather, Tianjin has distinct seasons with dry and windy spring, hot and humid summer, and cold and hazy winter. Three field campaigns were conducted simultaneously at the three locations during winter (January), spring (April) and summer (July) in 2007, to represent the seasonal meteorological conditions and the emission status. Meteorological conditions in the three campaigns are summarized in Table 1.

The 24-hr PM$_{2.5}$ aerosols were collected on preheated (800°C, 3 hr) quartz membrane filters (Φ90 mm, Pall Life Sciences, USA) using medium-volume impact samplers (TH-150AII, Wuhan Tianhong Intelligence Instrumentation Facility, China) operating at a flow rate of 100 L/min. Sampling was conducted every three days in each of three months, and a total of 90 PM$_{2.5}$ samples were obtained with 30 samples for each site. Field blank filters were collected with the same procedure as ambient samples but without air flow. The exposed filters were packed with aluminum foils and stored in a refrigerator at about −18°C until extraction. All filters were extracted within two weeks after sampling.

1.2 Aliphatic hydrocarbon analysis

To achieve adequate aerosol loadings for detailed organic speciation by gas chromatography-mass spectrometry (GC/MS), two daily samples with similar air mass pathways were grouped together. A total of 45 composite samples were obtained: 5 samples for each site and season.

The sample handling and extraction procedures were described elsewhere (Hu et al., 2007). In brief, each composite sample was cut into pieces, and extracted ultrasonically with 3 × 40 mL dichloromethane for 20 min every time. The extracts were filtered, combined, then rotary evaporated to a volume of about 5 mL, and finally condensed to exactly 1 mL under a gentle nitrogen stream. The concentrated solution were transferred into ampoule bottles and stored in refrigerator until GC/MS analysis.

For aliphatic hydrocarbons determination, an Aglient 5975 GC/MS (USA) was used with a fused-silica DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.2 mL/min. A 1-μL volume was injected in splitless mode at 290°C. The temperature program of the oven was started at 70°C (held for 5 min) and increased at a rate of 20°C/min to 280°C (held for 10 min). The mass spectrometry was operated in the electronic impact (EI) mode with an ion source temperature of 230°C and the electron impact energy was set at 70 eV. Chromatographic peaks of samples were identified by the retention indices and the mass spectra database (NIST98). The authentic standards ASTM D5442 (Supelco, AcuuStandard, Inc., USA) were adopted to confirm the identification and quantify *n*-alkanes.

1.3 Quality assurance

Field blanks were used to determine any background contamination. Trace amount of alkanes, with no carbon number predominance, were found in the field blanks. The background contaminants were low and would not interfere the quantification, therefore, the results were not corrected for field blanks. Method blanks (solvent) were analyzed, and none of the target compounds was found. Known volume of standard solutions was spiked onto blank quartz filters to determine the recoveries in the whole experimental process. The spiked recoveries ranged from 70% to 110%. Data analyzed in the article were not corrected for recoveries.

Table 1 Meteorological conditions collected in the three field campaigns

Sampling period	Temperature (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind direction	Number of sample
1–30, Jan 2007	−7.0~2.4 (−2.6)	27–88 (50)	0.5–5.3 (1.8)	NW-N-SW	30
1–30, Apr 2007	9.5–16.2 (12.3)	21–77 (43)	1.2–3.6 (2.5)	E-NW-SE	30
1–30, Jul 2007	24.4–30.6 (27.3)	51–80 (67)	1.3–2.7 (2.0)	S-SE	30

Data are expressed as ranges of daily variation with averages in parentheses.

Table 2 Summary of total alkane concentrations in PM$_{2.5}$ from Tianjin (unit: ng/m^3)

Location	April 2007	July 2007	January 2008
Urban	251.0 (204.9–345.6)	107.2 (62.2–182.1)	875.4 (556.5–1117.2)
Industrial	314.5 (184.3–567.5)	136.3 (83.0–225.9)	1069.9 (582.9–1522.3)
Coastal	198.0 (123.8–252.5)	200.6 (121.1–386.4)	581.9 (122.9–1464.5)
All sites average	250.1 (123.8–567.5)	148.7 (62.2–386.4)	842.0 (122.9–1522.3)

Data are expressed as mean values with ranges in parenthses.

2 Results and discussion

2.1 Seasonal and spatial variations of alkane concentrations

n-Alkane homologues from C12 to C35 were detected in PM$_{2.5}$ from Tianjin. Total alkane concentrations (Table 2), defined as sum of the 24 *n*-alkane compounds, show a clear seasonal pattern with much higher concentrations in winter than in spring and summer. This seasonal pattern is also observed in other Chinese cities (Bi et al., 2003; Zhou et al., 2004; Feng et al., 2006; Wang et al., 2006). The three sites averages of total alkanes were 148.7, 250.1 and 842.0 ng/m^3 in July, April and January, with the range of 62.2–386.4, 123.8–567.5, and 122.9–1522.3 ng/m^3, respectively. Ambient temperature changes should be the major cause of the seasonal variation, because the gas/particle partitioning of *n*-alkanes is temperature dependent due to its semi-volatile property. According to the study on phase distribution of atmospheric alkanes (Tong et al., 1995), about 80% of the total alkanes were in the vapor phase during summer, while most of them were present in the particulate phase during winter. High wintertime concentrations were also related to the greatly increased local emissions from coal combustion heating. The lower concentrations in summer were attributable to the absence of seasonal sources (i.e., residential heating), higher percentage in vapor phase and favorable atmospheric dispersion. The alkane concentrations in this study are within the range of reported data for urban and industrial areas in China (Bi et al., 2003; Feng et al., 2006; Wang et al., 2006) and Chile (Tsapakis et al., 2002), but much higher than those measured in Houston, USA (Fraser et al., 2002), Norway (Cecinato et al., 2000) and western Greece (Kalaitzoglou et al., 2004).

From the concentration profiles of individual alkanes (Fig. 1) averaged for each sampling period, it can be seen that the alkane homologous (C12–C35) detected in the fine aerosols from Tianjin had its most abundances in the middle section (C20–C31) that accounted for about 66% (in Jul) and 83% (in Apr and Jan) of the total alkanes. The concentration profiles of *n*-alkanes are characterized by no odd/even predominance in the range of C12–C26 and odd carbon number predominance with peaks center at C27–C31 in the range of C26–C35, which are indicative of mixed petrolic and biogenic signatures (Rogge et al., 1993, 1996). As Fig. 1 displays, the alkanes with middle molecular weight had much stronger seasonal variations compared with their neighboring homologous with lower and higher molecular weight, implying that they were influenced by seasonal meteorology and source emissions most. The most pronounced seasonal difference came from presence of a broad peak in the range of C19–C25 in the winter samples, indicating that these alkanes are primarily fossil fuel derived.

The pollution level of *n*-alkanes also varied among different locations, as a result of the influences of local factors at various types of sampling sites. Total alkane concentrations ranked in the order of industrial > urban > coastal in April and January, which is proportional to the source density and emission intensity at each site. Intensive coal burning and industrial process emissions lead to an severe air pollution in the industrial complex, which is of great concern to people living in the region. At the same time, the lower coastal concentrations correspond to less traffic and fewer factories around this location. However, in the summer campaign, alkane concentrations at the coastal site moved up to the highest (i.e., averages of 107.2, 136.3 and 200.6 ng/m^3 for the urban, industrial and coastal site, respectively), the same order was also found in PM$_{2.5}$ mass. This phenomenon can be attributed to the strong sea-land wind circulation during summer months, which can cause the accumulation of inland and marine pollutants in the coastal region. Further investigation of the coastal pollution is needed.

2.2 *n*-Alkane distribution

The distribution of *n*-alkanes, expressed as the relative abundance of homologues of differing molecular weight in total alkanes, provides some insight into the likely sources that contribute to ambient aerosols. Typically, plant epicuticular waxes, introduced into air by wind and abrasive processes, consist mainly of high molecular weight aliphatic compounds (> C27) with odd-even carbon number predominance and maxima (C_{max}) centered at C27–C31 (Rogge et al., 1993, Simoneit, 1999). While alkanes from fossil fuel related sources comprise mainly of lower carbon number compounds with C_{max} centered at C22–C25, and show no carbon predominance (Rogge
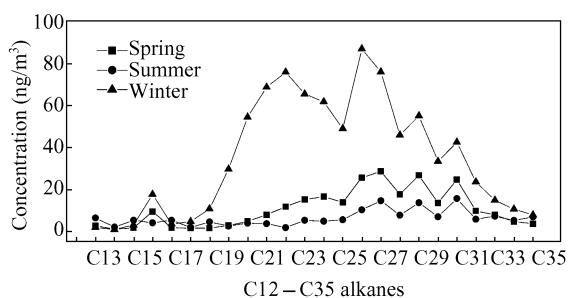

Fig. 1 Distribution diagrams of individual alkane concentrations during various seasons. Concentration values are averages of the three sites.

et al., 1996). For an ambient sample, the distribution of n-alkane is determined by the typology of sampling site and particularly by the relative impact of biogenic and anthropogenic sources (Kalaitzoglou et al., 2004).

Four typical distribution patterns for n-alkanes associated with $PM_{2.5}$ were found in this study, as shown in Fig. 2. Mono-modal distributions were observed in spring and summer, with carbon maxima centered at C27–C31 and preferential presence of odd-carbon numbered homologues. The predominance of biogenic hydrocarbons (C27, C29, C31) suggested more plant wax release into the atmosphere in spring and summer. Carbon maxima at C27 and C29 were also reported for fine particle emissions from open burning of various vegetal foliage (Hays et al., 2002). A bimodal distribution was observed at all sites in winter with a first C_{max} at C22 being representative of fossil fuel emissions, and a second at C26. The C_{max} ranges in winter were indicative of a substantial influence of anthropogenic sources on ambient organic aerosol. The C19–C25 homologues, typical components of fossil fuel residues, constituted approximately 50% (3-sites average) of total alkanes in winter, while the corresponding percentages in spring and summer were 37% and 25%, respectively. The seasonal differences in alkane composition can also be seen in the relative abundances of low molecular weight alkanes between summer and other seasons. The n-alkanes

less than C20, mainly originated from oceanic low plankton such as bacteria and algae (Zhou et al., 2004), was over 10% higher in July (25.1%) than those in April (10.8%) and January (14.9%). In addition, this range of alkanes was characterized by even carbon number predominance, suggesting an input of microbial components to organic aerosols in summer. There existed a distinct peak at C15 in the low carbon number homologues for the spring and winter $PM_{2.5}$ samples (Fig. 2), reflecting another type of contributing source. Considering the meteorology and pollution situations in spring and winter, C15 might be from long-range transport or soil microorganisms blown into the air by wind erosion. Despite the significant seasonal variations, the differences in alkane distribution patterns among the locations were minor, suggesting the contribution from common major sources in different areas of the city. The C_{max} of C27 was observed at all 3 sites in spring, while in summer, C_{max} of C31 was found for the coastal site, and C27 for the urban and industrial sites.

2.3 Carbon preference index

Carbon preference index (CPI), defined as concentration ratio of odd to even carbon number n-alkanes, has been widely used to evaluate biogenic and anthropogenic contributions to organic aerosol (Simoneit et al., 1999; Bi et al., 2003; Kalaitzoglou et al., 2004; Wu et al., 2005; Feng et al.,
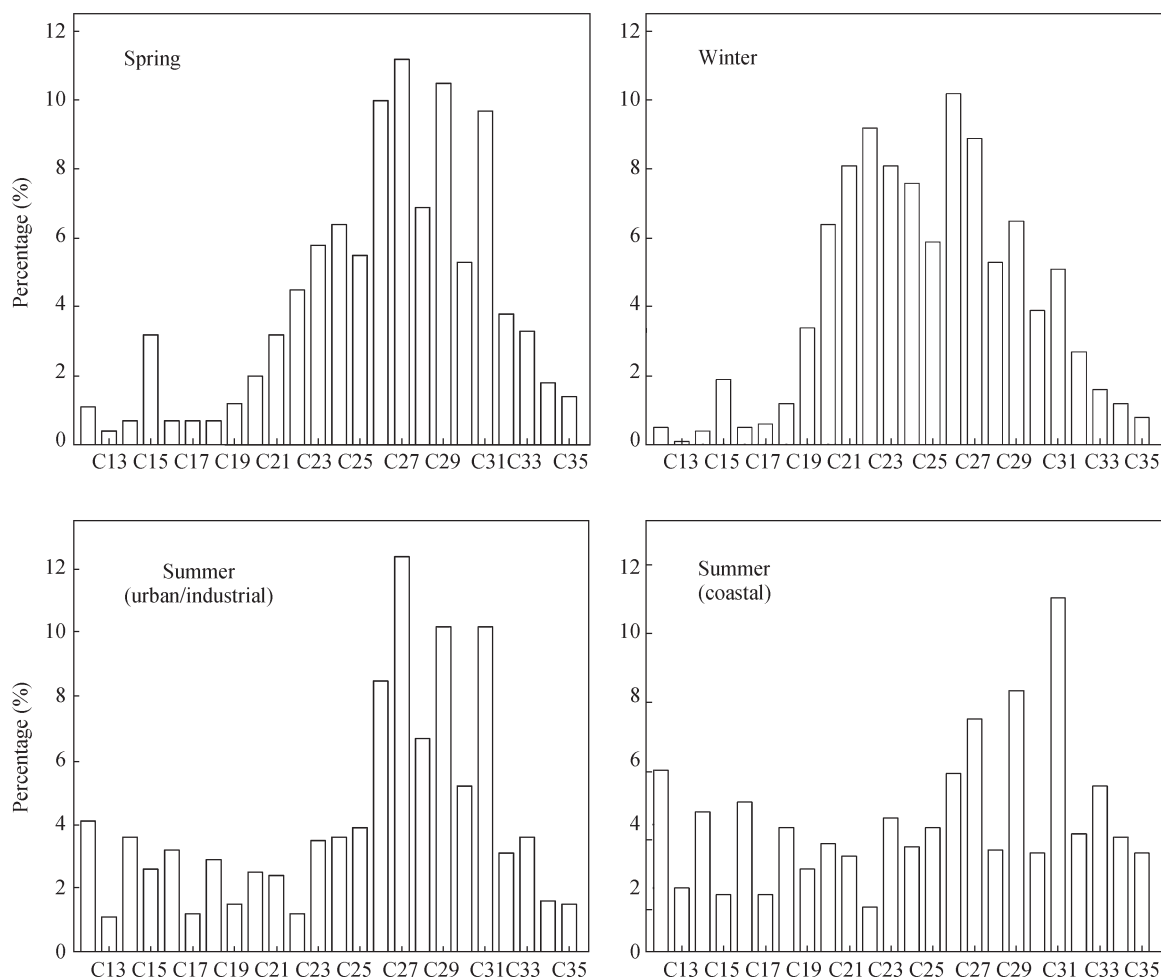

Fig. 2 Typical distribution patterns for n-alkanes associated with $PM_{2.5}$ in Tianjin. Similar patterns were found at all sites in spring and winter, and the relative abundances of individual n-alkanes in the plots are 3-sites averages.

2006). CPI for *n*-alkanes originated from plant wax exhibit high values (6–10), whereas CPI for *n*-alkanes from vehicular emissions and other anthropogenic activities (fossil fuels and biomass combustion) is close to unit (Wu et al., 2005). Urban environments, with large contributions from anthropogenic emissions, generally have CPIs ranging between 1.1 and 2.0, while rural environments with more biogenic influence generally have CPIs above 2.0 (Brown et al., 2002).

Three CPI parameters were adopted in the present study to discriminate between biogenic and anthropogenic influences, and they were CPI1 for the whole range of *n*-alkanes (C12–C35), CPI2 for petrogenic *n*-alkanes (C12–C25) and CPI3 for biogenic-*n*-alkanes (C26–C35). The CPIs values measured in this study, along with CPI determined for various aerosol sources, are shown in Table 3. CPI1 values at the three sites ranged from 1.02 to 1.40 with an average of 1.29, 1.21 and 1.07 in April, July and January, respectively, which were close to the reported values for vehicle exhaust, fly ash, refuse burning, and also in agreement with those in other urban areas around the world (Brown et al., 2002; Kalaitzoglou et al., 2004; Park et al., 2006). CPI2 values were in the range of 0.64–1.38 for all aerosol samples, confirming that *n*-alkanes less than C25 were primarily fossil fuel derived. CPI3 values at all sites ranged from 0.93 to 1.97 with an average of 1.00, 1.30 and 1.72 in January, April and July, respectively, pointing to an increasing input of plant waxes from winter to summer. It can be seen that only CPI1 will lead to an underestimation of biogenic contribution in summer. There was no significant difference in the ratios of CPI1, CPI2 and CPI3 among the locations, suggesting common sources of *n*-alkanes in different areas of the city. All the CPI values indicated a dominant influence of anthropogenic activities (fossil fuel combustion, petroleum and diesel residues) on primary fine organic aerosol in Tianjin and a minor contribution from plant epicuticular wax.

2.4 Contribution of plant wax

Since petroleum-derived *n*-alkanes have CPI near unity, the residual plant wax *n*-alkanes can be separated from petroleum component by subtracting the concentration of next higher and lower even carbon numbered homologues from the average (Simoneit et al., 1991). To determine the relative importance of biogenic and petrogenic sources, the contribution of plant wax was estimated using the following formular:

$$\text{wax}C_n = \sum (C_n - 0.5(C_{n-1} + C_{n+1}))/ \sum C_n \times 100\%$$

where, waxC_n (ng/m^3) is the concentration of plant wax *n*-alkane, negative values are taken as zero. C_n, C_{n-1} and C_{n+1} are the concentrations of *n*-alkanes with neighboring carbon numbers.

The fractions of wax alkanes in the total homologues at various sites and seasons are compared in Fig. 3. In general, the plant wax contribution was the lowest in winter, then increased in spring and reached to the maximum in summer, which was accordant with the seasonal variation of biogenic CPI3. The 3-sites average contribution of wax alkanes was 12.9% in winter, 19.1% in spring and 26.1% in summer, demonstrating that most of the aliphatic compounds in PM$_{2.5}$ were anthropogenic in origin. The differences in the relative abundance of wax alkanes between locations indicated the influence of local factors at various types of sampling sites. The highest biogenic input found at the industrial site in summer was probably related to its close vicinity to agricultural field in the suburban area. However, in winter, the industrial site appeared to carry the greatest imprint of anthropogenic emissions from industrial activities. The contributions of wax alkanes to the total alkanes in PM$_{2.5}$ from this study were higher than those measured in urban sites of Shanghai (8.0%–18.8%, Feng et al., 2006), Guangzhou (1.05%–7.54%, Bi et al., 2003), Korea (9.0%–22.5%, Park et al., 2006), but lower than those in Nanjing (20%–43%, Niu et al., 2005) and western Greece (20.7%–35.9%, Kalaitzoglou et al., 2004).

Table 3 CPI values of *n*-alkanes determined in this study and those for various aerosol sources

Location	CPI	April 2007	July 2007	January 2008
Urban	CPI1[a]	1.32	1.03	1.16
	CPI2[b]	1.33	0.64	1.35
	CPI3[c]	1.31	1.45	1.06
Industrial	CPI1	1.23	1.40	1.03
	CPI2	1.12	0.97	1.13
	CPI3	1.32	1.74	0.93
Coastal	CPI1	1.32	1.18	1.02
	CPI2	1.38	0.72	1.03
	CPI3	1.28	1.97	1.02
n-Alkane CPI for various aerosol sources[d]				
Vascular plant wax		6–10		
Natural fire smoke		1.2–1.0		
Atlantic oceanic aerosol		5–10		
Vehicle exhaust		0.93		
Diesel vehicle exhaust		1.02		
Fly ash from power generation		1.1–1.4		
Open biomass burning		2.2		
Refuse burning		1.2		

[a] Whole range for *n*-alkanes: CPI1 = $\sum$C13–C35/$\sum$C12–C34; [b] petrogenic *n*-alkanes: CPI2=$\sum$C13-C25/$\sum$C12-C24; [c] biogenic *n*-alkanes: CPI3 = $\sum$C27–C35/$\sum$C26–C34; [d] CPI refers to CPI1 (Brown et al., 2002; Kalaitzoglou et al., 2004).
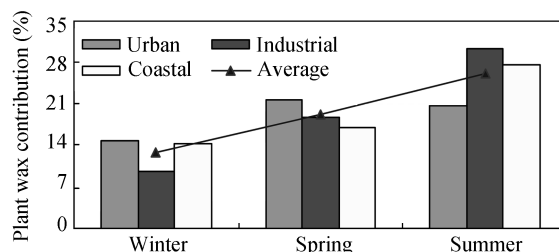

Fig. 3 Contributions of plant wax to total *n*-alkanes in PM$_{2.5}$.

3 Conclusions

Ambient PM$_{2.5}$ samples were simultaneously collected at an urban, an industrial and a coastal site of Tianjin in April 2007, July 2007, and January 2008, and 24 *n*-alkanes

(C12–C35) were identified and quantified by GS-MS to determine the characteristics and sources of fine organic aerosol. Major findings are as follows:

(1) Distinct seasonal variations were found in total alkane concentrations, with averages of 148.7, 250.1 and 842.0 ng/m^3 in July, April and January during 2007–2008, respectively. The obvious seasonal variation came from the significant increase of middle molecular weight species (C20–C31) in winter.

(2) Higher alkane concentrations were observed in the industrial complex in winter and spring, due to intensive coal burning and industrial process emissions. However, in summer, the alkane concentrations at the coastal site were higher than other two sites, possibly due to the strong sea-land wind circulation.

(3) Mono-modal distributions were observed in spring and summer with a maximum centered at C27–C31 and odd carbon number predominance, suggesting plant wax inputs to the atmosphere. The bimodal distribution with maxima at C22 and C26 observed in winter indicated a substantial influence of fossil fuel related sources.

(4) The ranges of CPI1, CPI2 and CPI3 at all sites were 1.02–1.40, 0.64–1.38 and 0.93–1.97, respectively, suggesting that most of the measured alkanes were of anthropogenic in origin. The contributions of plant wax to total n-alkanes during the entire sampling period ranged from 9.6% to 30.2% with the highest contribution in summer and the lowest in winter.

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