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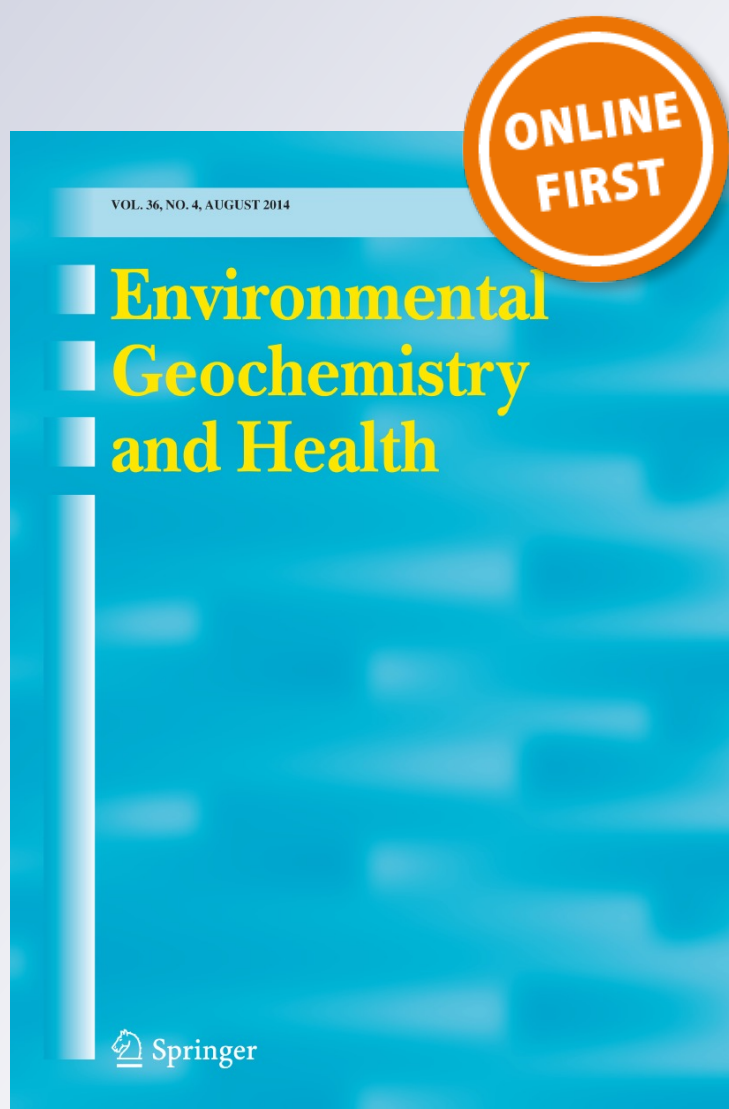
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Seasonal variation and source apportionment of organic tracers in PM₁₀ in Chengdu, China

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Abstract Organic compound tracers including *n*-alkanes, triterpane, sterane, polycyclic aromatic hydrocarbons (PAHs) and dicarboxylic acids of airborne particulate matter (PM₁₀) were characterized for samples collected at five sites from July 2010 to March 2011 using GC/MS. Spatial and temporal variations of these organic tracers in PM₁₀ were studied, and their sources were then identified respectively. Average daily concentrations of PM₁₀ varied in different seasons with the trend of PM₁₀ in winter (0.133 mg/m³) > autumn (0.120 mg/m³) > spring (0.103 mg/m³) > summer (0.098 mg/m³). Daily concentrations of *n*-alkanes (C₁₁–C₃₆) ranged from 12.11 to 163.58 ng/m³ with a mean of 61.99 ng/m³. The *C*_{max} and CPI index of *n*-alkanes indicated that vehicle emissions were the major source in winter, while the contributions of high plant wax emissions became significant in other seasons. It was discovered that the main sources of triterpenoid and steranes were gasoline and diesel engine emissions. Concentrations of ∑15PAHs in PM₁₀ also varied (12.25–58.56 ng/m³) in different seasons, and chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and fluoranthene were the dominant components. In the four seasons, the

concentration of ∑15PAHs was relatively higher at the northern site because of traffic congestion. The main source of airborne PAHs was traffic emissions and coal combustion. Average daily concentrations of dicarboxylic acids (C₄–C₁₀) in PM₁₀ ranged from 12.11 to 163.58 ng/m³, of which azeleic acid was the major compound (0.49–52.04 ng/m³, average 14.93 ng/m³), followed by succinic acid (0.56–19.08 ng/m³, average 6.84 ng/m³). The ratio of C₆/C₉ showed that the major source in winter was biological, while the contributions of emissions from anthropogenic activities were much higher in summer.

Keywords PM₁₀ · Alkanes · PAHs · Dicarboxylic acid · Source

Introduction

A molecular marker is an important means to study organic geochemistry. With the help of molecular markers, we can not only determine the sources of the organic matter, but also gain insight into organic matter cycling, migration, degradation and the diagenetic evolution process. In recent years, PM₁₀ has attracted great public attention, especially in China, because of its harmful environmental effects and health threat. The sources, composition, size distributions, deposition process and health effects of particulates in big cities have been widely studied (Yassaa

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et al. 2001; Duan et al. 2005; Lima et al. 2005; Mazquiarán and Pinedo 2007; Park et al. 2007; Ding et al. 2007; Rampazzo et al. 2008; Delgado-Saborit et al. 2011; Masiol et al. 2012; Ringuet et al. 2012; Yu and Yu 2012). However, the study of PM₁₀ in Chengdu, which is a typical inland basin city in southwestern China, is unprecedented so far. In order to better understand the pollution level, characteristics and sources of the organic pollutants bound to PM₁₀ in the Chengdu atmosphere, PM₁₀ samples were collected at five sites from July 2010 to March 2011 in Chengdu City, and their organic molecular markers (*n*-alkanes, terpanes, steranes, PAHs and dicarboxylic acids) were analyzed using QP 2010 GC plus -MS. The sources were analyzed with diagnostic ratio, silhouette and molecular marker methods. The knowledge gained from the study will provide the scientific basis for the development of risk assessments for exposure to these pollutants in Chengdu City and the crafting of control strategies to reduce their emissions.

Experimental methods

Sampling program

Chengdu is a typical inland basin city in southwestern China, between longitude 102°54'–104°53', latitude 30°05'–31°26'. Annual average temperature is 15.6–16.9 °C, and average relative humidity is 74 %. The prevailing wind direction in Chengdu is from the north to south, and the annual average wind speed is only 1.2 m/s. The city is divided into the southeast, northeast, northwest and southwest regions by Shudu Avenue and Renmin Road. Sampling site selection was designed to cover all orientations of the urban area in Chengdu (Table 1; Fig. 1). The eastern sampling site was on the roof of a building at Chengdu University, which is close to the railway tracks, Shanghai-Chengdu Highway and Kim Green Expressway. The southern sampling site was on the roof of a teaching building at Sichuan University, away from densely populated areas such as the student canteen and dormitories. It is next to Wangjiang Park and the Moat. The western site was on the roof of a research building surrounded by a plant-covered area and away from the main streets. The northern sampling site was on the roof of a teaching building of Southwest Jiaotong University, near the region's major railway

Table 1 Sampling site information

Sites	Position	Longitude	Latitude
1	East	104°08'28"	30°40'40"
2	South	104°04'29"	30°38'07"
3	West	104°02'05"	30°40'54"
4	North	104°03'02"	30°42'34"
5	Middle	104°03'56"	30°38'39"

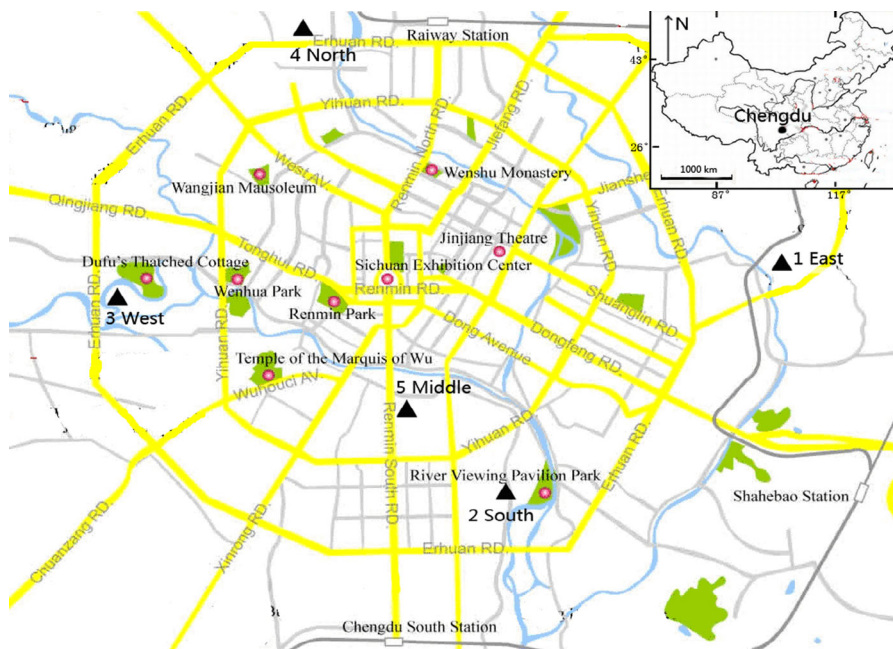
transportation hub and Lotus Pond Wholesale Trade Center. The sampling site during the summer in the center of the city was adjacent to South Renmin Road, surrounded by residential areas. The sampling was performed in spring (March–May), summer (June–August), fall (August–November) and winter (December–February) in 2010 and 2011. Samples were collected for 5–7 consecutive days in every season, except for 3 days in summer because of the unexpected rain. Sampling projects were carried out simultaneously at all five sites in every season.

The meteorological parameters during sample collection are shown in Table 2. PM₁₀ was collected onto precombusted (450 °C for 4 h) glass fiber filters (20–25 cm) with a flow rate of 1.05 m³/min (Tianhong Intelligent Instrument Plant, Wuhan Province, China). The samples deposited on the filters were analyzed for PM₁₀ concentrations, saturated hydrocarbons, dicarboxylic acids and 15 priority PAHs (with the exception of naphthalene).

Sample analysis

Glass filter papers were kept in a desiccator for 24 h before and after the sample collection. The PM₁₀ samples were weighted. A half of the filter paper, spiked with deuterated PAHs standards (naphthalene-d₈, acenaphthene-d₁₀, acenaphthene-d₁₀, chrysene-d₁₂, perylene-d₁₂) prior to sample extraction, was cut into pieces and immersed in 20 ml of dichloromethane in the dark overnight, then ultrasonicated for 30 min three times. The solvent extracts were concentrated by vacuum-condensing equipment (Buchi Syncore Q-101), filtered through a self-packed silica-alumina column (v/v, 3:2) with Na₂SO₄ on the top. The saturated hydrocarbon fractions were eluted with *n*-hexane (10 ml), and the aromatic fraction was eluted with benzene: *n*-hexane (v/v, 1:1) (10 ml). The eluted extracts were concentrated to 300 µl by vacuum-condensing equipment.

Fig. 1 Map of the sampling sites



The saturated hydrocarbons and PAHs were analyzed by GC-MS with a HP-5 MS capillary column (30 m \times 0.25 mm \times 0.25 μ m). The oven temperature program was as follows: hold at 50 $^{\circ}$ C for 1 min, increase to 140 $^{\circ}$ C at a rate of 8 $^{\circ}$ C min $^{-1}$, then increase to 300 $^{\circ}$ C at a rate of 5 $^{\circ}$ C min $^{-1}$ (10 $^{\circ}$ C/min for F3) with a final hold at 300 $^{\circ}$ C for 15 min. The injector and detector temperatures were 280 and 280 $^{\circ}$ C. The 1- μ l sample was injected in a splitless model. The mass scanning ranged between 50 and 500 m/z. Fifteen PAHs were quantified including acenaphthylene (Ace), acenaphthene (Acen), fluorene (Flu), phenanthrene (Phen), anthracene (An), fluoranthene (Fluo), pyrene (Py), benzo(a) anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (Indeo), dibenz(a,h)anthracene (DiBa) and benzo(ghi)perylene (BgP).

To study dicarboxylic acids, a quarter of the filter paper was cut into pieces and immersed in 20 ml of methanol in the dark overnight, then ultrasonicated for 30 min three times. The solvent extract was concentrated to 100 μ l by vacuum-condensing equipment. The extract was treated with 0.3 ml 14 % $\text{BF}_3/\text{CH}_3\text{OH}$ at 80 $^{\circ}$ C for 30 min to convert dicarboxylic acids to their methyl esters. The reaction products were extracted with 5 ml *n*-hexane after adding 3 ml deionized water and 0.3 ml acetonitrile. The *n*-hexane

layer was further washed with 3 ml deionized water and concentrated to 300 μ l by vacuum-condensing equipment.

Quality control

The analytical method was rigorously quality controlled. Recovery experiments, standard curve and blank experiments were used for quality control. The blank experiments showed the whole process of the analysis was not polluted and the standard curves of three types of components were good. Table 3 shows the recoveries of PAHs, and Table 4 shows the parameters of dicarboxylic acids determined by GC/MS. The recovery experiment showed that the recoveries of all three types of components were between 71.9 and 114.7 % and standard deviation was 2.91 and 11.91 %, in line with the requirements of the US EPA method.

Results and discussion

PM₁₀ concentrations and distributions

Table 5 shows the PM₁₀ concentrations in Chengdu and their seasonal variation. In spring, summer, autumn and winter, the concentration ranges of PM₁₀

Table 2 Meteorological parameters during sample collection

Date	Season	Temp _{avg} (°C)	Temperature (°C)	RH (%)	Atm (hPa)	Wind velocity (m/s)	Wind direction
10 July 2010	Summer	26.1	21.1 to 30.9	75	942.6	1.0	W
11 July 2010		24.4	19.7 to 29.1	80	941.7	2.8	NE
12 July 2010		26.8	22.0 to 31.6	64	942.1	1.1	N
1 November 2010	Autumn	13.6	11.3 to 15.5	87	958.4	1.0	w
2 November 2010		13.6	11.7 to 15.5	89	964.1	0.9	W
3 November 2010		11.9	8.7 to 15.0	92	963.9	0.4	NE
4 November 2010		14.1	8.8 to 19.3	80	960.5	0.5	N
5 November 2010		15.4	10.9 to 19.1	61	955.3	1.1	NE
6 November 2010		16.0	13 to 18.9	70	953.5	2.3	NE
10 January 2011	Winter	2.9	1.0 to 4.8	80	963.2	0.6	N
11 January 2011		3.3	−0.7 to 7.2	57	959.5	3.1	SE
12 January 2011		2.4	−3.9 to 7.9	68	952.0	2.8	NE
13 January 2011		2.7	−2.3 to 7.7	39	954.8	1.9	NE
14 January 2011		3.1	0.5 to 8.1	65	957.6	1.8	S
15 January 2011		2.9	0.3 to 6.2	60	957.8	2.2	S
14 March 2011	Spring	9.5	7.1 to 11.9	80	967.1	3.4	S
15 March 2011		10.4	7.9 to 14.2	87	965.5	4.0	S
16 March 2011		9.1	4.0 to 14.2	70	969.0	3.5	N
17 March 2011		10.2	5.5 to 16.3	89	959.3	1.2	N
18 March 2011		10.5	6.9 to 17.2	76	964.3	1.5	S
19 March 2011		10.9	7.1 to 17.1	75	962.7	1.8	S
20 March 2011		11.1	7.0 to 17.2	70	960.5	1.1	S

Table 3 Recovery and standard deviation of PAHs

Species	m/z	Correlation factor	Recovery (%)
Ace	152	0.982	75.22 ± 11.37
Acen	154	0.996	75.02 ± 7.04
Flu	166	0.968	83.35 ± 9.93
Phen	168	0.968	92.72 ± 8.15
An	178	0.982	89.76 ± 11.78
Fluo	202	0.969	86.19 ± 2.91
Py	202	0.997	104.35 ± 6.16
BaA	228	0.964	75.67 ± 4.33
Chry	228	0.999	114.73 ± 4.60
BbF	252	0.981	82.71 ± 11.91
BkF	252	0.992	89.23 ± 10.12
BaP	252	0.992	82.68 ± 8.73
Indeo	276	0.992	86.04 ± 3.99
DiBa	278	0.978	107.25 ± 3.78
BgP	276	0.974	95.00 ± 7.44

Table 4 Parameters of dicarboxylic acids by GC/MS

Species	m/z	R ²	Recovery acids (%)
C5	59,100,129,55,87	0.990	83.4
C6	59,114,111,101,143,55	0.993	89.8
C7	115,74,83,157,125	0.998	82.5
C8	129,74,69,138,97,171	0.996	85.3
C9	152,111,55,74,185,143	0.944	71.9

Table 5 The concentrations of PM₁₀ in Chengdu (mg/m³)

	East	South	West	North	Central	Average
Spring	0.103	0.085	0.091	0.108	0.127	0.103
Summer	0.106	0.095	0.086	0.104	0.102	0.098
Autumn	0.126	0.106	0.107	0.146	0.116	0.120
Winter	0.143	0.120	0.117	0.119	0.166	0.133

were 0.085–0.127 mg/m³ (average 0.103 mg/m³), 0.086–0.106 mg/m³ (average 0.098 mg/m³), 0.106–0.146 mg/m³ (average 0.120 mg/m³) and 0.119–0.166 mg/m³ (average 0.133 mg/m³), respectively. So the PM₁₀ concentration decreased in the order of: winter > autumn > spring > summer, with the highest concentration of PM₁₀ (0.133 mg/m³) occurring in winter and the lowest (0.098 mg/m³) in summer. Compared to the National Ambient Air Quality Standards (GB3095-2012), the average concentrations of PM₁₀ in every season in Chengdu City were below the daily average of PM₁₀ 0.15 mg/m³ for grade 2. These observations can be attributed to two factors: (1) in summer, the strong wind could better mix, diffuse and transport the PM₁₀ in the atmosphere; (2) the washing out effect of particulates during rainy days in summer could significantly decrease the PM₁₀ concentration.

Spatial distribution of PM₁₀ at five sampling sites representing the east, west, central, south and north area of Chengdu City showed that the highest PM₁₀ concentration appeared in the central area in the spring and winter, while in the northern area in autumn and in the eastern area in summer. These differences might be related to the differences in anthropogenic sources. In the central area of the city, because of the heavy traffic, frequent human activities and urban heat island effect, the pollutants were not easily spread, leading to the highest PM₁₀ concentrations in winter and spring. In the northern area, the biggest train station and busy bus station, large commercial centers such as the Lotus Pond commercial area and serious traffic jams may lead to the highest concentration of PM₁₀ in autumn. In summer, the concentrations of PM₁₀ in the eastern area were almost the same as in the central and northern areas, indicating that the dilution and dispersion of air pollutants in the summer were quite good. Therefore, we concluded that the dominant factors for seasonal differences in the PM₁₀ levels were mainly associated with two factors: meteorological conditions and anthropogenic emissions.

n-Alkanes

Concentrations and distribution patterns of *n*-alkanes (C11–C36) in PM₁₀ in different seasons were also studied. Homologs (C18–C36) of *n*-alkanes were detected in all samples with different concentration levels and molecular compositions (Table 6). The annual

Table 6 Distribution of *n*-alkanes in PM₁₀ in different seasons (ng/m³)

<i>n</i> -Alkanes	Spring	Summer	Autumn	Winter
C11	0.55	1.43	11.93	7.65
C12	0.97	0.64	4.50	3.67
C13	0.67	0.22	1.61	2.86
C14	0.52	0.27	0.44	0.77
C15	0.52	0.11	0.60	0.58
C16	0.54	0.22	0.43	0.59
C17	0.58	0.07	0.43	0.91
C18	0.78	0.17	0.25	0.95
C19	0.81	0.05	1.08	1.41
C20	1.04	0.16	2.37	1.62
C21	1.21	0.14	4.13	2.68
C22	0.77	0.34	4.60	3.61
C23	1.70	0.64	38.02	5.29
C24	2.24	1.36	15.11	5.52
C25	2.36	2.55	2.64	4.86
C26	2.72	3.09	4.26	5.46
C27	2.08	3.81	1.90	4.11
C28	2.44	3.34	3.89	4.92
C29	1.53	5.92	1.29	3.28
C30	2.48	2.16	1.80	3.53
C31	0.87	4.18	1.81	2.31
C32	2.32	1.32	1.34	3.47
C33	0.66	1.35	1.04	1.30
C34	0.65	0.63	0.74	1.20
C35	0.29	0.52	0.11	0.37
C36	0.30	0.26	0.19	0.34
ΣC11–C36	31.58	36.22	106.82	73.25

average concentrations of *n*-alkanes ranged from 31.58 to 106.52 ng/m³, and the seasonal variation trend was: autumn (75.86–112.2 ng m⁻³, average 106.52 ng m⁻³) > winter (44.18–163.58 ng m⁻³, average 73.25 ng m⁻³) > summer (12.11–87.06 ng m⁻³, average 36.22 ng m⁻³) > spring (15.22–94.56 ng m⁻³, average 31.58 ng m⁻³). The concentrations in autumn were about three times higher than those in spring. The total *n*-alkane concentrations were lower than those in Beijing City (201.7–2,715.6 ng/m³) and Guangzhou City (52.1–238.28 ng/m³), but were similar to those in Wuhan City (22.9–96.1 ng m⁻³), Shenzhen (23.9–106.0 ng/m³) and Algiers (14.3–92.3 ng/m³) (Bi et al. 2004; Zhou et al. 2009; Huang et al. 2012).

The *n*-alkane distribution in samples is shown in Table 6. The determination of C_{max} for *n*-alkanes

gives a strong indication of either an anthropogenic pollution source or natural biological input, since a smaller C_{max} suggests input mainly from the combustion of fossil fuels. In addition, the carbon preference index (CPI^*), which is the ratio of the sum of even carbon number n -alkanes and the sum of odd carbon number n -alkanes, was also used as an indicator. Generally, the CPI of the anthropogenic n -alkanes is close to 1. In contrast, n -alkanes originating from epicuticular waxes of terrestrial plants exhibit a high value of CPI ($CPI \gg 1$). In winter, the n -alkane distribution showed a bimodal distribution with two peaks at C11 and C24, $CPI = 1.04$, while in the spring, summer and autumn, it presented a unimodal distribution with a peak at C26, C29 and C23, $CPI = 1.32, 1.50$ and 1.29 , respectively. Hauser and Pattison (1972) reported that n -alkanes of $<C_{19}$ were mainly in petrol and diesel fuel, but C24 was mainly in petrol and diesel exhaust. Therefore, the distribution of n -alkanes in PM_{10} in Chengdu suggested anthropogenic sources, including fossil fuel combustion and diesel exhaust, as the main source, and some contribution of plant wax. In spring and summer, the contribution of n -alkanes originating from plant wax ($>C_{25}$) increased, which is consistent with the fact that in spring and summer the plant growth is much more luxuriant.

In order to compare the spatial variations of n -alkane distribution in PM_{10} in Chengdu, two seasons (winter and summer) were selected, and the results are shown in Fig. 2. The highest concentrations of n -alkanes appeared at the northern sampling site in both winter (110.35 ng/m^3) and summer (45.44 ng/m^3); these were about two times as high as at the western

site. This could be explained by the fact that this region has a larger flow of people, busy transportation and serious traffic congestion, which was reflected by its $CPI = 1.24$. In contrast, the western sampling site was close to the residential area with better plant coverage and far away from the main traffic artery, so the concentration of n -alkanes was the lowest among all sites, only 56.09 ng/m^3 in winter and 25.48 ng/m^3 in summer. The concentration of n -alkanes at the central site was as high as 39.32 ng/m^3 in summer, with $CPI = 1.23$, also suggesting that the pollutants are primarily emitted from anthropogenic sources such as vehicle exhaust.

Steroid and terpane compounds

Steroid and terpane compounds are abundant in coal and crude oils and could be used as molecular markers. In the early diagenetic stage, they are primarily dominated by the biological R configuration. Then the R configuration is slowly transformed into a 22S and 22R epimeric mixture, which reaches the equilibrium state, with the ratio of $S/(S + R)$ being about 0.6. A series of parameters including $Ts/(Ts + Tm)$, C_{31} rose hopane $22S/(22S + 22R)$, $\alpha\alpha C_{29}$ sterane $20S/(20S + 20R)$ and C_{29} sterane $\beta\beta/(\alpha\alpha + \beta\beta)$ could be used to determine the oil input and non-oil input.

In all PM_{10} samples, C27–C29 steranes, rear-ranged steranes, progesterone sterane and terpenoids were detected. Sterane compounds are primarily characterized by anti-L-type distribution: $\alpha\alpha\alpha 20RC_{29}$ steranes $> \alpha\alpha\alpha 20RC_{28}$ steranes $> \alpha\alpha\alpha 20RC_{27}$ steranes. This distribution pattern was similar to that in coal burning, suggesting a greater contribution of coal-burning sources than vehicle exhaust emissions. Some typical molecular marker parameters of PM_{10} were calculated and are shown in Table 7. The organic matter maturity index ratio of sterane $20S/(20S + 20R)$ was 0.32–0.46 (average 0.39), which is consistent with that in crude oil compounds, indicating that sterane compounds were mainly from mineral oil and its derivatives. The ratio of C31 hopane $22S/(22S + 22R)$ had reached the equilibrium point, with an average value of 0.51, suggesting that major compositions of steranes and terpenoids were from the residue of incomplete combustion of fossil fuels.

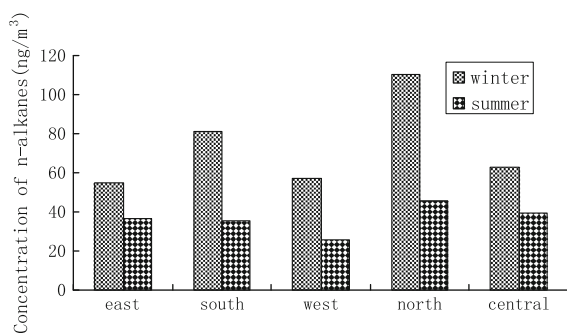


Fig. 2 Spatial distributions of n -alkanes in PM_{10} in winter and summer

Table 7 Some molecular marker parameters of samples

Sites	Ts/(Ts + Tm)	C ₃₁ rose hopanes 22S/(22S + 22R)	$\alpha\alpha\alpha$ C ₂₉ sterane 20S/(20S + 20R)	C ₂₉ sterane $\beta\beta$ / ($\alpha\alpha$ + $\beta\beta$)
East	0.34	0.57	0.46	0.48
South	0.43	0.53	0.32	0.36
West	0.51	0.55	0.38	0.35
North	0.45	0.54	0.34	0.41
Central	0.37	0.59	0.43	0.43

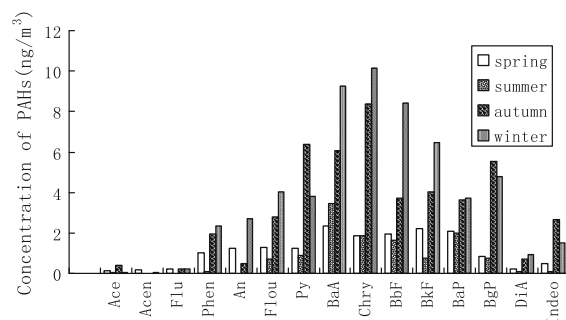
Hopanes

Hopanes are primarily derived from bacteria and produced by diagenesis in sediments over geological time. They are ample in coal and crude oils and become enriched in lubricant oil fractions. The distribution of 17 α , 21 β (H)—hopane compounds could differentiate vehicle emission from coal-fired sources (Yassaa et al. 2001). Pentacyclic terpanes of C27–C32 $\alpha\beta$ type hopane compounds were detected in all samples. Molecular compositions of hopanes in the all PM₁₀ samples are characterized by one peak at 17 α , 21 β (H)-C30 hopane, which is consistent with the oil import source, suggesting that the contributions of incomplete combustion of oil in automobile emissions to hopanes are pronounced. Their dominations are different from those of the urban aerosol and mountaintop samples in eastern Asia (Wang et al. 2009).

The ratios of Ts/(Ts + Tm) for all sampling sites were about 0.34–0.51 (average 0.42). The ratio of 22S/(22S + 22R) was about 0.5, meaning that the content of 22S was very close to that of 22R isomers. These distribution characteristics of hopanes were similar to those in coal and oil, indicating anthropogenic sources were the primary sources.

PAHs

Polycyclic aromatic hydrocarbons (PAHs) have received much attention because of their potential toxic, carcinogenic and mutagenic effects. Significant seasonal variations of $\sum 15$ PAHs concentrations in PM₁₀ were observed in Chengdu (Fig. 3). The average concentration of $\sum 15$ PAHs presented the trend of winter (58.56 ng/m³) > autumn (46.74 ng/m³) > spring (17.45 ng/m³) > summer (12.52 ng/m³), which was consistent with the results of the studies conducted in Guangzhou (Bi et al. 2004), Wuhan (Zhou et al. 2009) and Shenzhen (Huang et al. 2012). The reason

**Fig. 3** Seasonal variation of the distribution of PAHs in PM₁₀

for the lowest concentration in summer is that because the temperature is higher, the photochemical reactions in the atmosphere take place more easily, and this could lead to greater degradation of PAHs. Furthermore, with increasing temperature, as the PAH concentration ratio of the gas/particle phase indicates, more PAHs are distributed in the gas phase and fewer are left to be detected in the particle phase. The concentration of PAHs in spring was lower than in autumn and winter. This was the result of better diffusion and dilution of pollutants in spring due to the abundant rain and high humidity in spring. In autumn and winter, the dry weather, less precipitation and stability of the atmosphere were the adverse conditions for the diffusion and dilution of pollutants. In these two seasons, more energy was used, leading to more pollutant emissions and an increase in the PAH concentrations. Compared with other cities at home and abroad, the concentration of PAHs in Chengdu City was comparable to those in Hong Kong (Zheng and Fang 2000), Greece (Mantis et al. 2005) and Mexico City (Thornhill et al. 2008), and much higher than that in Los Angeles (Eiguren-Fernandez et al. 2004).

Polycyclic aromatic hydrocarbon compounds with different ring sizes present different environmental

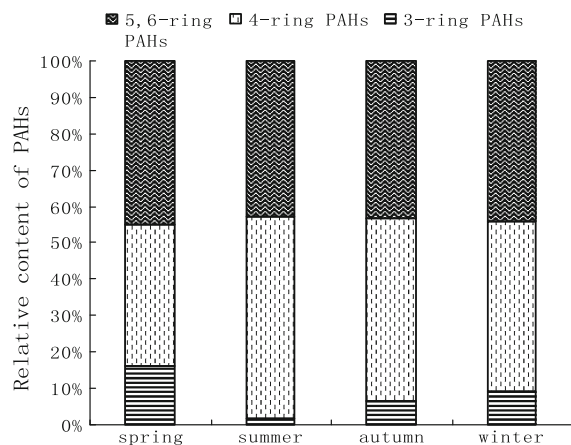


Fig. 4 Distribution of PAHs with various ring sizes

effects. Four-ring PAHs are a type of semivolatile organic compound, existing in both gaseous and particulate phases, and five- and six-ring PAHs present mainly in particle phase, and they can be removed more easily in the process of atmospheric transport. As Fig. 4 shows, the relative contributions of PAHs with different ring sizes in PM_{10} were different in each season. While the contribution ratios of five- and six-ring PAHs are relatively steady, covering about 40 % of $\sum 15PAHs$, the contribution of three-ring PAHs varied most significantly throughout the year and especially noticeably was reduced to 1.7 % in summer. This could be explained by the fact that these low-molecular-weight volatiles could very easily change from the particle phase to gas phase under the conditions of high temperature and strong solar radiation in summer. On the contrary, in winter, the temperature is relatively low and solar radiation relatively weak, so the loss from photodegradation is reduced, and the low ring PAHs are more likely to load on the particle phase, leading to a higher concentration. The contributions of four-ring PAHs were relatively large in both winter (46.6 %) and summer (55.51 %).

The ratio of $Phen/(Phen + An)$ is commonly used to distinguish PAH different sources. For PAHs from crude oil, the ratio of $Phen/(Phen + An)$ is normally higher than 0.7 (Sicre et al. 1987), and values of 0.50, 0.65 and 0.76 indicate gasoline, diesel and coal-fired emission sources (Kahalili et al. 1995). As seen in Table 8, the ratios of $Phen/(Phen + An)$ were 0.45, 0.88, 0.79 and 0.46 in spring, summer, autumn and winter, respectively, indicating that the contribution of gasoline was the primary source in spring and winter,

Table 8 Characteristic ratios of PAHs in PM_{10} in Chengdu

Characteristic ratios	Spring	Summer	Autumn	Winter
Phen/(Phen + An)	0.45	0.88	0.79	0.46
Flou/(Flou + Py)	0.50	0.44	0.31	0.51
BaA/(BaA + Chr)	0.56	0.64	0.42	0.48
BaP/BgP	2.46	2.69	0.65	0.77
Indeo/(Indeo + Bghip)	0.37	0.12	0.33	0.24

and crude oil and coal were the primary sources in summer and autumn, respectively.

Likewise, if the ratio of $Flou/(Flou + Py)$ is less than 0.4, oil emissions are the main source. If the ratio is between 0.4 and 0.5, this suggests liquid fossil fuel (motor fuel and crude oil) combustion emissions as the main sources. As seen in Table 8, the ratio of $Flou/(Flou + Py)$ was 0.50, 0.44, 0.31 and 0.51 in spring, summer, autumn and winter, respectively. This result showed that in all seasons, the contribution of vehicle emissions was pronounced. A ratio of $BaA/(BaA + Chry)$ between 0.38 and 0.64 suggests diesel engine exhaust emissions as the pollution source. In Chengdu, the value of this ratio was between 0.42 and 0.64, clearly indicating the presence of this source. Greenberg et al. (1981) used the ratio of BaP/BgP as a supplementary indicator to distinguish between fuel oil and coal-based pollution sources. A ratio between 0.3 and 0.44 suggests traffic pollution as the source, and a ratio between 0.9 and 6.6 indicates a coal-burning source. In this study, the ratio was 0.65 in autumn and 0.77 in winter, reflecting mixed pollution from traffic and coal burning.

A ratio of $Indeo/(Indeo + Bghip)$ less than 0.20 indicates an oil source, a ratio between 0.20 and 0.50 indicates a liquid fossil fuel combustion source, and a ratio of more than 0.5 indicates a coal- or wood-burning source (Grimmer et al. 1983; Park et al. 2002; Huang et al. 2012). In this study, the ratio of $Indeo/(Indeo + Bghip)$ was 0.12 in summer, showing that oil sources made a significant contribution in summer. The ratio was between 0.24 and 0.37 in spring, autumn and winter, indicating the contribution of liquid fossil fuel combustion.

From the ratios of these compounds, PAHs in PM_{10} in Chengdu were dominantly contributed by mixed traffic and coal-burning pollutions. Motor vehicle exhaust was an important source as well.

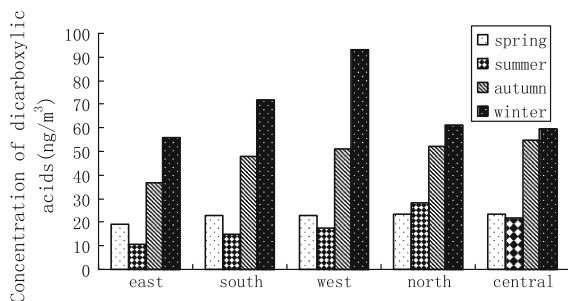


Fig. 5 The seasonal variation of dicarboxylic acids in PM₁₀ in Chengdu

Dicarboxylic acids

Dicarboxylic acids have many important properties, such as an excellent moisture absorption capability, and their presence is associated with the formation of secondary organic aerosols and the formation of cloud condensation nuclei (CCN), which could affect the regional and global climate.

In this study, the total concentration of dicarboxylic acids (C4–C10) ranged from 12.07 to 107.45 ng/m³. Compared with other cities in China and abroad, the concentration was lower than in Nanjing (Wang et al. 2002) and Finland (Kawamura and Ikushima 1993), and much higher than at the North Pole (Ricard et al. 2002). Azelaic acid (C9) had the highest concentration (0.49–52.0 ng/m³, average 14.93 ng/m³). This distribution was similar to that in Nanjing (Wang et al. 2002) and Finland (Kawamura and Ikushima 1993). The second largest amount was that of succinate (0.56–19.08 ng/m³, average 6.84 ng/m³). Azelaic acid and succinic acid accounted for 36.4 and 16.7 % of the total amount of dicarboxylic acids, respectively.

According to Fig. 5, the concentration of dicarboxylic acids varied in different seasons as follows: winter > autumn > spring > summer. The appearances of high concentrations in winter and low concentrations in summer were also observed in Hong Kong (Ho et al. 2006) and Nanjing (Wang et al. 2002). On the contrary, a high concentration of dicarboxylic acid was observed in autumn and a low concentration in spring in Shenzhen (Huang et al. 2012).

As seen in Table 9, azelaic acid (C9) was the primary component among dicarboxylic acids at every sampling site. A high concentration level of azelaic acid was reported in Chinese cooking source samples (Yu 2000; He et al. 2004; Huang et al. 2012), and its concentration was 5–7 times higher than that of adipic acid. Interestingly, studies of cooking (such as cooking meat) in the USA showed that adipic acid was the primary compound in dicarboxylic acids, and azelaic acid was not detected. This difference is most likely the result of different cooking styles. Wang et al. (2002) analyzed the content of the dicarboxylic acids in PM₁₀ and concluded that in the cooking process, the volatile oxidation of vegetable oils leads to high concentrations of azelaic acid. In Chengdu, the higher temperatures used in the Sichuan cooking process produce more organic matter and also cause the double bond of unsaturated fatty acids to fracture, leading to the production of azelaic acid. Furthermore, the lowest ratio of C6/C9 appeared in winter and the highest in summer. This suggested that in winter the major source of dicarboxylic acids was biological; in summer, anthropogenic activity was the primary source.

Table 9 Spatial distribution characteristics of dicarboxylic acids in PM₁₀ in Chengdu

	East	South	West	North	Central
C4(ng/m ³)	7.82	6.85	10.00	8.26	8.04
C5(ng/m ³)	3.05	2.22	2.31	2.99	3.52
C6(ng/m ³)	3.31	3.16	3.86	3.31	4.99
C7(ng/m ³)	2.57	1.65	3.41	2.31	2.07
C8(ng/m ³)	6.93	6.11	6.75	6.38	6.51
C9(ng/m ³)	15.17	21.88	22.56	17.15	17.18
C10(ng/m ³)	4.62	3.95	4.40	3.38	3.03
C6/C9	0.22	0.14	0.17	0.19	0.29
C9/∑C4–C10	34.90 %	47.75 %	42.34 %	39.18 %	37.89 %

Conclusions

Seasonal variation and source apportionment of organic tracers (*n*-alkanes, triterpane, sterane, PAHs and dicarboxylic acids) in PM₁₀ were studied. The results showed the following:

1. The seasonal trend of the concentration of *n*-alkanes (C₁₁–C₃₆) in PM₁₀ was: autumn > winter > summer > spring, the range was 12.11–163.58 ng/m³, and the average was 61.99 ng/m³. The highest concentration of *n*-alkanes appeared at the northern sampling site in both winter and summer. Judging from the values of CPI, C_{max} and the distribution type of *n*-alkanes, the *n*-alkanes in PM₁₀ in Chengdu were mainly affected by automobile exhaust and incomplete combustion of fossil fuel. The primary sources of hopane, steroid and terpane series compounds were anthropogenic.
2. Significant seasonal variations in PAHs were observed, and the total concentration was between 12.25 and 58.56 ng/m³, in the order of winter > autumn > spring > summer. The highest concentrations of PAHs were observed at the northern sampling and central sampling sites. The main sources of PAHs were automobile emissions and coal combustion.
3. The concentration of dicarboxylic acids (C₄–C₁₀) was between 12.07 and 107.45 ng/m³. Azelaic acid was the primary component, followed by succinate. The ratio of C₆/C₉ indicated that in winter the major source was biological, and the contributions of emissions from anthropogenic activities were much higher in summer.

Overview of organic tracers

We have analyzed and reported on several classes of organic chemicals—*n*-alkanes, triterpane, sterane, PAHs and dicarboxylic acids—and only a range of specific compounds within those classes in airborne particles. They are not only tracers for finding the sources of pollution, but also dangerous organic pollutants in airborne particles that damage the environment and cause health risk. Therefore, continuous monitoring of these chemicals is suggested in an effort to improve the air quality of Chengdu, and it is reasonable to expect that the urban environmental atmospheric chemistry of other organic chemicals in

Chengdu with physical chemical properties similar to *n*-alkanes, triterpane, sterane, PAHs, and dicarboxylic acids in airborne particles will be governed in part in the same manner as for the chemicals we have reported here.

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