Characterization of PM$_{2.5}$ in Guangzhou, China: uses of organic markers for supporting source apportionment

Jingzhi Wang [a,b], Steven Sai Hang Ho [a,c], Shexia Ma [d], Junji Cao [a,b,e,*], Wenting Dai [a,b], Suixin Liu [a,b], Zhenxing Shen [e], Rujin Huang [a,b,f], Gehui Wang [a,b], Yongming Han [a,b]

[a] Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China
[b] State Key Lab of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China
[c] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, United States
[d] South China of Institute of Environmental Sciences, SCIES, Guangzhou, China
[e] Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China
[f] Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland

HIGHLIGHTS

- PM$_{2.5}$, OC, EC and organic biomarkers were quantified in Guangzhou in 2012/2013.
- Vehicle emission, coal combustion and SOC are consistent pollution sources for OC.
- PAHs, alkanes, PAEs, and hopanes were used for the source assessment.

GRAPHICAL ABSTRACT
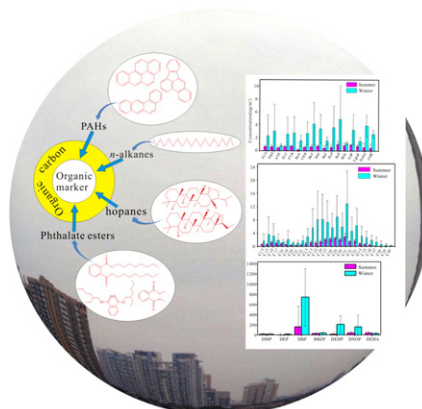
ARTICLE INFO

ABSTRACT

Organic carbon (OC), elemental carbon (EC), and non-polar organic compounds including n-alkanes (n-C$_{14}$-n-C$_{40}$), polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs) and hopanes were quantified in fine particulate (PM$_{2.5}$), which were collected in urban area of Guangzhou, China in winter and summer in 2012/2013. The pollutants levels were well comparable with the data obtained in previous studies in Pearl River Delta (PRD) region but much lower than most northern Chinese megacities. The contribution of EC to PM$_{2.5}$ and OC/EC ratio suggest that the pollution sources were relatively consistent in GZ between the two seasons. Benzo[a]pyrene (BaP) was the most abundant PAHs, which were 4.9 and 1.0 ng/m^3 on average, accounting for 10.7% and 9.1% to the total quantified PAHs in winter and summer, respectively. The total concentrations of PAEs ranged from 289.1 to 2435 ng/m^3 and from 102.4 to 1437 ng/m^3, respectively, in winter and summer. Di-n-butyl phthalate (DBP) was the most dominant PAEs. The ambient levels of PAEs could be partly attributed to the widespread uses of the household products, municipal garbage compressing, sewage, and external painting material on the building. Source apportionment for OC with chemical mass balance (CMB) model demonstrated coal combustion, vehicle emission, cooking, and

* Corresponding author at: Institute of Earth Environment, Chinese Academy of Sciences (CAS), No. 97 Yanxiang Road, Yanta Zone, Xi'an 710061, China.
E-mail address: cao@loess.llqg.ac.cn (J. Cao).

secondary organic compounds (SOC) formation were the four major pollution sources. Both of the indices of *n*-alkanes and diagnostic PAHs ratios support that anthropogenic sources such as vehicle emission and coal combustion were the significant pollution sources with some extents from epicuticular waxes by terrestrial plants. The ratio of hopanes to EC proved the influences from vehicle emission, and displayed a certain degree of the air aging in the Guangzhou ambient air.

1. Introduction

Carbonaceous aerosol, mainly consist of organic carbon (OC) and element carbon (EC), accounted for 20–50% of the $PM_{2.5}$ (particulate matter [PM] with aerodynamic equivalent diameters of Dp < 2.5 μm) mass in Chinese urban atmosphere (Cao et al., 2007). EC is directly emitted from the pollution sources such as the incomplete combustion of fossil fuels. OC can be generated from the direct emission sources or formed as secondary organic carbons (SOC) by photochemical reactions or other reactive ways. Epidemiological studies demonstrated that the carbonaceous materials associated with potential detrimental human health effects, ecosystems, and climate change (Pope and Dockery, 2006; Venkataraman et al., 2002; Oanh et al., 2002; Saxena and Hildemann, 1996). Many organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs) are well-known mutagens or carcinogens (Li et al., 2015; Bui et al., 2016; Marr et al., 2006; Zheng et al., 2000; Takahashi et al., 2006) and a great duel of attentions has been drawn on their ambient levels and potential origins in mega-cities such as Beijing, Shanghai, Guangzhou and Nanjing in China (Lin et al., 2015; Zheng et al., 2011; Feng et al., 2006; Gao et al., 2012a; Wang and Kawamura, 2005).

Guangzhou (GZ), a mega-city in Guangdong province, is located in the center of Pearl River Delta (PRD) region where has been influenced from serious pollutions occasionally. Few researches have been conducted for the characterizations of organic compounds (e.g., Cao et al., 2007; Gao et al., 2015; Gao et al., 2012b). Bi et al. (2005) and Liu et al. (2006) have reported that vehicle emission was the most important local pollution source for PAHs and *n*-alkanes in GZ. This is further supported by Xu et al. (2013) who quantified particulate-phase non-polar organic compounds during the period of 16th Asian Games. In recent years, stricter vehicle emission controls have been established in GZ. Dai et al. (2015) conducted a tunnel study in 2013 and reported that the emission factors for $PM_{2.5}$, OC, EC, and water-soluble inorganic ions (WSII) except chloride ion (Cl^-) and organic compounds, were decreased by 16.0–93.4% compared with the data obtained in 2004 (He et al., 2008). Coal combustion was also significant source for particulate bounded PAHs in wintertime (Gao et al., 2015). Besides, stationed combustion sources (e.g., industries) and kitchen lampblacks contributed to most of the non-volatile organics, while biological source has a minor contribution as well (Liu et al., 2006). In an episode study, Zhang et al. (2015) found that fossil emissions from coal combustion and vehicle exhaust accounted about 75 ± 8% and 35 ± 7%, respectively, for EC and OC during the haze period in January, 2013. Liu et al. (2014) additionally reported that the average contributions of fossil carbon to EC were 71 ± 10% and the local vehicle emission is the main pollution source in the haze samples. Secondary formation also accounted a large fraction of aerosol (Huang et al., 2014). Cui et al. (2015) combined the observation data analysis and chemical transport model simulation to conduct source apportionment of $PM_{2.5}$ in GZ. Stationary source (e.g., industrial and power-generated) was the largest contributor to $PM_{2.5}$ and mobile sector played an important role both in dry and wet seasons, while transport played an important role for $PM_{2.5}$ in dry season. Wang et al. (2016) summarized the variations in $PM_{2.5}$ and its chemical components in the Pearl River Delta Economic Zone (PRDEZ) from 2000 to 2010, showing that motor vehicle had an important impact on the levels of OC and EC. Furthermore, there was a rapid increase for the calculated SOC.

In short, even though many researchers have conducted source characterization in GZ and the PRD region in the past years, comprehensive studies are still needed to investigate on the changes on the compositions of $PM_{2.5}$ and their corresponding pollution sources. This work reports the chemical compositions and seasonal variations of OC, EC and non-polar organic compounds including PAHs, *n*-alkanes, PAEs and hopanes in GZ in 2012 and 2013. Potential pollution sources for OC were identified by means of modeling. Different indices of *n*-alkanes, diagnostic ratios of PAHs, and source markers of hopanes were used to support the source characterization, further compared with the previous studies conducted in GZ.

2. Materials and methods

2.1. Sampling

The sampling site was located at the atmosphere monitoring station of South China Institute of Environmental Sciences, which is in an urban area of GZ city. A high-volume air sampler (Airmetrics, Oregon, USA) was used to collect daily $PM_{2.5}$ samples on quartz-fiber filters (20.3 cm × 25.4 cm, GE Healthcare., Little Chalfont, Buckinghamshire, U.K.) at a flow rate of 1.05 m³/min. One twenty-four hour integrated sample (from 9:00 am to the next day 9:00 am) was collected in each week from 10th May 2012 to 30th May 2013. Field blank was also collected every month which was used to correct for any positive artifacts such as organic absorption. A total of 24 samples were obtained in summer (June to August 2012) and winter (December 2012 to February 2013), respectively. Meteorological parameters, including temperature, relative humidity (RH) and wind speed, were obtained in the website of National Climatic Data Center (NCDC) (ftp://ftp.ncdc.noaa.gov/pub/data/gsod/) (Table S1). The records of boundary layer heights were obtained from the website of European Centre for Medium-Range Weather Forecasts (ECMRWF) (http://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/). All of the samples were wrapped in solvent-washed aluminum foil and stored in a freezer at −20 °C until analysis to prevent any loss of volatiles.

2.2. Mass and carbonaceous aerosol analyses

Our previous studies have detailed the mass and carbonaceous aerosol analysis (Wang et al., 2015a; Cao et al., 2005). In brief, prior to the sampling, blank quartz filters were pre-baked in a furnace at 800 °C for 4 h in order to remove any contaminants, and then stored in freezer at <4 °C. For mass determinations, the filters were weighed before and after the samples were loaded. They were equilibrated in a chamber, which maintained at a constant temperature of 20–23 °C and RH of 40 ± 5% for at least of 24 h. Then the filters were weighted with a Sartorius ME 5-F electronic microbalance (±1 μg sensitivity; Sartorius, Göttingen, Germany). The variances were ≤15 μg and ≤20 μg, respectively, for the pre- and post- sampling weighing. The $PM_{2.5}$ mass on the field blanks were below ≤63 μg and ≤40 μg for summer and winter, respectively.

Carbonaceous aerosol components, OC and EC, were quantified using a Desert Research Institute (DRI) Model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA). The IMPROVE_A thermal/optical reflectance (TOR) protocol was used for the analyses (Chow et al., 2007a). Total OC was defined as the sum of four OC fractions (OC1-OC4) plus

OP, whereas total EC was defined as the sum of three EC sections (EC1-EC3) minus OP.

2.3. Organic speciation

In-injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS) was applied to quantify of the non-polar organic compounds including PAHs, n-alkanes, PAEs and hopanes in the PM$_{2.5}$ filter samples. This approach acts as an alternative method of traditional solvent extraction followed by GC/MS analysis (Wang et al., 2015a). The detail analytical procedures have been reported in our previous publications (Wang et al., 2015a; Ho and Yu, 2004; Chow et al., 2007b; Ho et al., 2008, 2011). An Agilent 7890A GC/5975C MS system (Agilent Technology, Inc., Santa Clara, CA, USA) were used which operated in electron impact (EI) ionization mode. In brief, aliquots of the sample filter (0.1–0.526 cm^2, subjected to the loading) was cut into small pieces and transferred into a TD tube. The sample-loaded tube was placed into the GC injection port at 50 °C. The injection port temperature was then raised to 275 °C for desorption in a splitless mode while the GC oven temperature was kept at 30 °C. Separation of organic compounds was performed with a HP-5MS (30 m × 0.250 mm i.d., 0.25 μm film thickness, Agilent Technologies, Inc.) capillary column. The constant flow rate of carrier gas helium (UHP grade, 99.999% purity) was 1.2 mL/min. The MSD was scanned from 50 to 550 amu. The EI voltage was 70 eV and selected ion mode was applied for the quantification. Identification was achieved by characteristic ion and comparing the retention times of the chromatographic peaks with those of standards. Only trace amounts of volatile n-alkanes (i.e., n-C$_{<17}$) but no targeted PAHs, PAEs, and hopanes were found in the field blanks.

2.4. Quality assurance and control (QA/QC)

The QA/QC procedures used in this study were as the same as those have been previously presented by Cao et al. (2003, 2011) and Ho et al. (2006, 2011). In brief, the aerosol sampler was checked and calibrated regularly during the sampling periods, and the field blank filters were collected to correct for backgrounds. For the OC/EC analysis, the instrument was calibrated with known quantities of methane daily. Replicate analyses were done for each group of ten samples. Blank filters were also analyzed and the sample results were corrected for the average of the blank concentrations, which were 1.72 and 0.09 μg/m^3 for OC and EC, respectively. The detection limits for EC and OC were <1.0 μg/m^3. The relative deviation of replicate analyses was <5% for TC (total carbon), and <10% for OC and EC.

PAHs, n-alkanes (n-C$_{14}$-n-C$_{40}$), PAEs and hopanes were quantified using the TD-GC/MS instrumentation. Chrysene-d$_{12}$ (C$_{18}$D$_{12}$) (98%, Sigma-Aldrich, Bellefonte, PA, USA) was added as internal standard (IS) for the PAH and PAEs and n-tetracosane-d$_{50}$ (n-C$_{24}$D$_{50}$) (98%, Aldrich, Milwaukee, WI, USA) for the n-alkanes and hopanes. A five-point calibration over a concentration range of 0.5–5.0 ng for each of the target compounds from a standard mixture (Sigma-Aldrich, Bellefonte, PA, USA) was established, and the correlation coefficients (R^2) for linear regressions of the calibration curves were >0.99. For each ten samples, one replicate analysis was done; the relative standard deviation of these replicates was <15%. The limits of detection (LOD) for the targeted organic species are listed in Table S2. All data were corrected for the average value of the blanks.

3. Results and discussion

3.1. PM$_{2.5}$ mass and concentrations of OC and EC

The PM$_{2.5}$ masses and concentrations of OC and EC in GZ are summarized in Table 1. The PM$_{2.5}$ masses were in a range of 33.3 to 334.3 μg/m^3 and 21.4 to 163.0 μg/m^3, respectively, in winter and summer. The values

were lower than those measured in northern urban cities such as Beijing, Tianjin, Taiyuan and Xi'an, where are often known as heavy polluted areas in China (Cao et al., 2007; Zhou et al., 2012; Tao et al., 2009). The average concentrations of OC and EC were 12.8 ± 8.7 and 2.1 ± 1.2 μg/m^3, respectively, in winter, and 7.6 ± 2.9 and 1.7 ± 0.5 μg/m^3, respectively, in summer. The statistics showed that there were no obvious differences on OC and EC between winter and summer (P > 0.05). Our OC and EC values were, again, >50% lower than those average levels in the northern cities including Shanghai (28.6 and 8.3 μg/m^3), Beijing (25.9 and 6.1 μg/m^3), and Xi'an (61.9 and 12.3 μg/m^3) (Cao et al., 2005; Cao et al., 2007; Zhou et al., 2012). The finding was consistent with the study conducted by Huang et al. (2014). Besides, the averages were well comparable with the data measured (11.1 and 3.9 μg/m^3 for OC and EC, respectively) in Shenzhen and Dongguan (10.4 and 2.68 μg/m^3 for OC and EC, respectively), another southern city in PRD region (Hagler et al., 2006; Wang et al., 2015b). In comparison with other international urban cities, the OC and EC levels in GZ were higher than in Veneto region in Italy (5.5 and 1.31 μg/m^3, respectively) (Khan et al., 2016), but lower than in Delhi, India (33.8 and 4.0 μg/m^3, respectively in daytime), and Santiago, Chile (5.6–22, 4.3 μg/m^3 respectively) (Tiwari et al., 2015; Villalobos et al., 2015).

Good correlations between PM$_{2.5}$ mass and OC, EC were showed during the sampling periods (Fig. S1) though higher PM$_{2.5}$ masses and concentrations of OC and EC were observed in winter. However, the average contributions of EC to PM$_{2.5}$ were very close between the two seasons (0.33 and 0.40 in winter and summer, respectively). EC is less prone to gas-phase chemical reactions in the atmosphere and often used as an anthropogenic source emissions tracer. In addition, the correlations between OC and EC were 0.87 and 0.85, respectively, in winter and summer. Therefore, even though more pollutants were produced from anthropogenic and biological sources in the wintertime, both of the contribution and ratio suggest that the classes of pollution sources were often consistent in GZ between the two seasons. The meteorological conditions such as temperature (T), RH (H), boundary layer height (MLH) and horizontal wind speed (U) were displayed in Table S1. It is inspected that ventilation coefficient (VC) were the main factors in this study. The VC is calculated by:

$$VC = MLH \times U.$$

VC is used as a direct measure to characterize the degree of transport/dispersion of the pollutants taking place within convective boundary layer. The higher values of VC indicate effective dispersion (Kompalli et al., 2014). The correlation coefficient between the PM$_{2.5}$ concentrations, OC, EC and VC were R^2 = 0.48, 0.41, and 0.39, respectively (Fig. S2).

Fig. 1 shows the average compositions of each carbon fraction to total carbon (TC) in the OC/EC analysis. OP was the highest contributor, followed by OC2, OC3 and EC1. Chow and Watson reported that those individual carbon fractions can be appointed to specific pollution sources (Chow et al., 2004; Watson et al., 1994). The major emission sources for OC and EC in China include coal combustion (mostly residential), motor vehicle, and biomass burning (Streets et al., 2001; Cao et al., 2003). High loading of OP and EC1 generally reflect to gasoline-fueled motor vehicle emission (Chow et al., 2004). OC2, OC3, and EC1 can represent the mixed pollution sources from residential cooking, coal-combustion, vehicle emission and SOC (Cao et al., 2004). The high OP suggested that gasoline-fueled vehicle emission was the most dominant local source in GZ, where was much less influenced by the residential coal combustion than northern China due to warmer climate. No obvious seasonal variation was observed on the carbon fractioning as well, representing that the consistency of classes of carbon pollution sources.

3.2. Concentrations of PAHs and n-alkanes

A total of 17 PAHs and 27 n-alkanes (n-C$_{14}$-n-C$_{40}$) were quantified in this study (Table 1). Their concentrations and abbreviations were

Table 1
Summary of $PM_{2.5}$ mass, concentrations of OC, EC and non-polar organic species in Guangzhou.

Species	Unit	Winter		Summer	
		Mean ± SD	Range	Mean ± SD	Range
$PM_{2.5}$ mass	$\mu g/m^3$	108.3 ± 94.2	33.3–334.3	55.1 ± 43.3	21.4–163.0
OC	$\mu g/m^3$	12.8 ± 8.7	4.9–33.2	7.6 ± 2.9	4.0–12.2
EC	$\mu g/m^3$	2.1 ± 1.2	1.7–2.6	1.7 ± 0.5	1.2–2.7
PAHs	ng/m^3				
Fluorene (FLO)		2.25 ± 3.25	0.30–8.67	0.63 ± 0.18	0.45–0.95
Phenanthrene (PHE)		3.00 ± 4.2	0.40–10.7	0.58 ± 0.36	0.27–1.47
Anthracene (ANT)		0.79 ± 0.26	0.54–1.38	0.46 ± 0.10	0.41–0.71
Fluoranthene (FLU)		2.60 ± 2.51	1.09–9.11	0.66 ± 0.15	0.55–1.05
Pyrene (PYR)		2.73 ± 2.50	1.10–9.00	0.68 ± 0.16	0.56–1.08
Benz[a]anthracene (BaA)		1.56 ± 0.82	0.78–3.24	0.12 ± 0.24	0.008–0.76
Chrysene (CHR)		2.66 ± 1.76	1.05–6.23	0.57 ± 0.11	0.49–0.85
Benzo[b]fluoranthene (BbF)		4.16 ± 3.29	1.28–10.15	0.63 ± 0.25	0.46–1.29
Benzo[k]fluoranthene (BkF)		3.41 ± 2.21	1.30–7.71	0.73 ± 0.17	0.62–1.17
Benzo[a]fluoranthene (BaF)		1.51 ± 0.60	0.87–2.52	0.49 ± 0.30	LOD–0.93
Benzo[e]pyrene (BeP)		3.62 ± 3.28	1.22–10.4	0.51 ± 0.41	LOD–1.07
Benzo[a]pyrene (BaP)		4.86 ± 5.14	1.18–17.6	0.95 ± 0.55	0.56–2.25
Perylene (PER)		1.15 ± 0.26	0.85–1.60	0.80 ± 0.52	0.60–2.15
Indeno[1,2,3-cd]pyrene (IcdP)		3.24 ± 2.36	1.11–8.13	0.92 ± 0.11	0.81–1.17
Dibenzo[a,h]anthracene (DahA)		3.88 ± 1.67	2.17–6.86	0.54 ± 0.67	0.20–2.31
Benzo[ghi] perylene (BghiP)		1.47 ± 0.60	0.90–2.49	0.74 ± 0.29	LOD–1.00
Coronene (COR)		2.60 ± 0.61	1.96–3.83	0.41 ± 0.63	0.14–2.09
$\sum$ PAHs[a]		45.5 ± 29.7	18.6–105.8	10.4 ± 3.9	7.0–19.9
n-alkanes	ng/m^3				
Tetradecane (C_{14})		1.72 ± 2.23	0.32–5.75	0.64 ± 0.10	0.42–0.77
Pentadecane (C_{15})		3.52 ± 5.67	0.32–14.0	0.61 ± 0.18	0.40–0.99
Hexadecane (C_{16})		3.02 ± 4.12	0.53–11.6	1.14 ± 0.52	0.71–2.44
Heptadecane (C_{17})		1.89 ± 1.97	0.44–5.74	1.03 ± 0.61	0.55–2.57
Octadecane (C_{18})		1.21 ± 0.99	0.30–3.28	0.69 ± 0.36	0.36–1.62
Nonadecane (C_{19})		2.00 ± 2.96	0.16–9.72	0.64 ± 0.77	0.07–2.57
Icosane (C_{20})		0.91 ± 0.59	0.22–2.23	0.30 ± 0.17	0.13–0.67
Heneicosane (C_{21})		1.03 ± 0.87	0.12–2.94	0.27 ± 0.12	0.10–0.45
Docosane (C_{22})		1.68 ± 1.34	0.21–4.83	0.42 ± 0.09	0.30–0.57
Tricosane (C_{23})		2.89 ± 2.50	0.87–9.00	0.75 ± 0.37	0.30–1.62
Tetracosane (C_{24})		5.64 ± 5.95	1.54–20.8	1.13 ± 0.54	0.49–2.08
Pentacosane (C_{25})		8.10 ± 8.82	2.37–30.5	1.03 ± 0.29	0.67–1.64
Hexacosane (C_{26})		8.16 ± 7.69	1.54–26.2	1.47 ± 0.46	1.03–2.56
Heptacosane (C_{27})		7.38 ± 6.60	1.79–23.8	2.04 ± 0.35	1.61–2.70
Octacosane (C_{28})		5.59 ± 4.20	1.07–15.3	2.18 ± 0.49	1.58–2.94
Nonacosane (C_{29})		8.82 ± 6.26	2.06–23.2	2.49 ± 0.49	1.75–3.40
Triacontane (C_{30})		5.73 ± 4.23	0.48–14.8	1.96 ± 0.59	1.33–2.91
Hentriacotane (C_{31})		12.8 ± 10.1	1.84–32.9	2.89 ± 1.00	1.91–4.79
Dotriacontane (C_{32})		4.60 ± 4.31	0.45–13.3	1.34 ± 0.30	0.88–1.72
Tritriactotane (C_{33})		6.28 ± 5.28	0.79–16.0	1.60 ± 0.53	1.00–2.52
Tetratriactoane (C_{34})		3.13 ± 3.00	LOD–9.94	0.70 ± 0.30	0.37–1.24
Pentatriacontane (C_{35})		2.60 ± 1.89	LOD–6.44	0.60 ± 0.24	0.30–1.08
Hexatriacontane (C_{36})		1.74 ± 1.54	LOD–4.68	0.29 ± 0.23	LOD–0.69
Heptatriacontane (C_{37})		1.29 ± 1.39	LOD–3.12	0.02 ± 0.061	LOD–0.19
Octatriacontane (C_{38})		0.60 ± 1.10	LOD–3.17	NA	NA
Nonatriacontane (C_{39})		0.30 ± 0.61	LOD–1.64	NA	NA
Tetracontane (C_{40})		0.08 ± 0.25	LOD–0.74	NA	NA
$\sum$ n-alkanes[a]		102.7 ± 73.8	25.4–267.1	26.2 ± 6.9	19.4–42.2
PAEs	ng/m^3				
Dimethyl phthalate(DMP)		23.8 ± 17.1	LOD–41.7	18.5 ± 17.6	LOD–36.2
Diethyl phthalate(DEP)		13.0 ± 18.3	LOD–40.0	8.60 ± 17.1	LOD–39.7
Di-n-butyl phthalate(DBP)		408 ± 237	125–811	162 ± 405	18.5–1242
Benzyl butyl phthalate(BBZP)		39.5 ± 15.4	28.9–72.4	32.6 ± 14.6	26.3–71.6
Bis(2-ethylhexyl)phthalate(DEHP)		148 ± 142	LOD–373	21.6 ± 20.8	LOD–46.2
Di-n-octyl phthalate(DNOP)		202 ± 268	LOD–791	42.3 ± 20.8	32.2–97.5
Bis(2-ethylhexyl)adipate(DEHA)		32.4 ± 20.5	LOD–69.2	37.4 ± 28.8	22.4–109
$\sum$ PAEs[a]		1218.5 ± 653.6	289.1–2434.8	323.2 ± 420.2	102.4–1436.9
Hopanes	ng/m^3				
$17\alpha(H)$-21β(H)-hopane		0.59 ± 0.47	0.26–1.42	0.85 ± 0.25	0.48–1.14
$17\alpha(H)$-21β(H)-30-norhopane		0.33 ± 0.24	0.14–0.81	0.49 ± 0.13	0.32–0.63
$17\alpha(H)$-22,29,30-trisnohopane		0.28 ± 0.17	LOD–0.47	0.32 ± 0.11	LOD–0.43
$\sum$ hopanes[a]		1.2 ± 0.9	0.40–2.71	1.65 ± 0.49	1.2–2.15

[a] $\sum$PAHs is sum of fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi] perylene, dibenzo[a,h]anthracene, and coronene. $\sum$ n-alkanes are sum of alkanes, which carbon atoms were from C_{14} to C_{41}. $\sum$ PAEs is sum of dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl)phthalate, di-n-octyl phthalate, and bis(2-ethylhexyl)adipate. $\sum$ hopanes is sum of $17\alpha(H)$-21β(H)-hopane, $17\alpha(H)$-21β(H)-30-norhopane and $17\alpha(H)$-22,29,30-trisnohopane.

showed in Table 1. In winter, the total concentrations of PAHs ($\sum$ PAHs) and n-alkanes ($\sum$ n-alkanes) were in a range of 18.6 to 105.8 and 25.4 to 267.1 ng/m^3, respectively, which were much higher than those in summer, ranging from 7.0 to 19.9 and 19.4 to 42.2 ng/m^3, respectively ($P < 0.05$). Such seasonal differences are consistent with the typical findings in the urban atmospheres, where influenced by a higher amount of
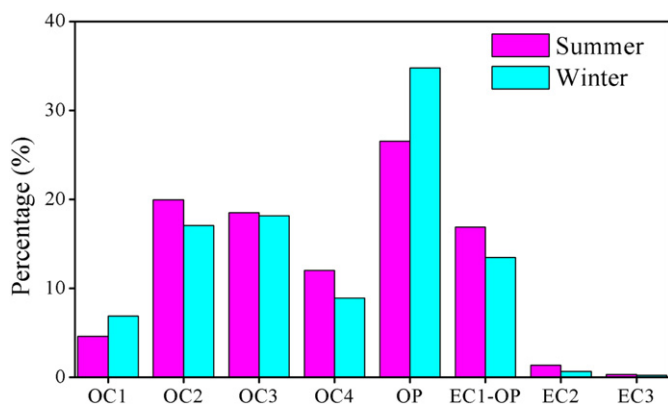
Fig. 1. Average percentage of carbon fractions in $PM_{2.5}$ in Guangzhou.

pollution sources in wintertime (Panther et al., 1999; Guo et al., 2003a). Meteorological conditions (such as lower boundary layer height and lower horizontal wind speed) are usually controlling factors for more pollutants accumulated in the winter.

Benzo[a]pyrene (BaP) was the most abundant PAHs, which were 4.9 and 1.0 ng/m^3 on average, accounting for 10.7% and 9.1% to the total quantified PAHs in winter and summer, respectively. It is usually used as the marker for the carcinogenic risk assessment. The level in most of the GZ samples was higher than the air quality guideline set by World Health Organization (WHO) (1.0 ng/m^3), suggesting the potential risk in this area.

Most organic speciation works often focused on the 16 priority PAHs and n-alkanes with number of carbons ranged from 10 to 35 (n-C_{10}–n-C_{35}) in China. Compared with other studies conducted in GZ, our values were close to the levels in the urban area (Feng et al., 2006) but slightly higher than those in the colleges or high schools (Gao et al., 2012a) (Table 2). In further, both were also comparable with the average values measured in different locations in PRD region (Guo et al., 2003a; Zheng et al., 2011). Similar to the findings for OC and EC, the total concentrations of PAHs and n-alkanes were much lower than those quantified in other heavy-polluted northern Chinese cities (Duan et al., 2010; Liu et al., 2008; Feng et al., 2006; Li et al., 2010a; Guo et al., 2009; Kong et al., 2010). The highest level of n-alkane reached to 1685 ng/m^3 in

Beijing during the Spring Festival (Yao et al., 2009) which was at least one magnitude higher than our levels. The concentrations in this study were also comparable with those megacities located in the central part of China such as Shanghai and Nanjing (Cao et al., 2013; Feng et al., 2006; Wang and Kawamura, 2005), but higher than the background areas such in Lulang of Tibet, Mount Taishan and Sanya (Chen et al., 2014; Li et al., 2010b; Wang et al., 2015a).

The PAHs levels were lower in GZ than few worldwide developing areas such as Mumbai (India) and Zonguldak (Turkey) (Abba et al., 2012; Akyüz and Cabuk, 2009); however, were still higher than those measured in the developed cities including São Paulo (Brazil), Tuscany (Italy), Hamilton (Canada), Hiroshima (Japan), and many United States regions and cities (i.e., Atlanta, Southern California, and Chapel Hill) (Bourotte et al., 2005; Martellini et al., 2012; Zheng et al., 2009; Eiguren-Fernandez et al., 2004; Pleil et al., 2004; Tham et al., 2008; Anastasopoulos et al., 2012). GZ is one of the earliest developed cities in China. The comparison represents that the proper environmental controls and policies are still required to improve the air quality to this urban area.

3.3. Concentrations of phthalate esters

PAEs are one of the most abundant and ubiquitous organic compounds in the environments. They were widely used in numerous consumer products, such as household and industry products (Myridakis et al., 2015). As a class of endocrine disruptors, PAEs may cause adverse health effects. Previous studies have showed that dietary intake was the main source of exposure to DEHP but it has been being focused in indoor exposure already (Song et al., 2015; Guo and Kannan, 2011). However PAEs are still rarely reported in the ambient monitoring. Six PAEs (dimethylphthalate, DMP; diethyl phthalate, DEP; di-n-butyl phthalate, DBP; butyl benzyl phthalate, BBZP; bis(2-ethylhexyl)phthalate, DEHP; di-n-octyl phthalate, DNOP) and one plasticizer of di-2-ethylhexyl adipate (DEHA) were detected and quantified in the GZ samples. The total concentrations of PAEs ranged from 289.1 to 2435 ng/m^3 and from 102.4 to 1437 ng/m^3, respectively, in winter and summer. Similar PAEs levels were reported in $PM_{2.5}$ and PM_{10} in Tianjin, but these were lower than the data obtained in the indoor environments (Song et al., 2015; Kong et al., 2013; Zhang et al., 2014). Indoor PAEs can be directly emitted from many kinds of household products. However, the sources for outdoor PAEs are not well defined and their levels can be greatly

Table 2
Comparison of the PAHs concentrations with previous studies in Guangzhou.

PAHs	This study		Bi et al. (2002)		Li et al. (2006)	Yang et al. (2010)		Gao et al. (2012a)	
	Winter $PM_{2.5}$	Summer $PM_{2.5}$	April PM_{10}	July PM_{10}	Annual $PM_{2.5}$	Annual TSP^c	Annual TSP^d	Winter $PM_{2.5}$	Winter $PM_{2.5}$
	Urban	Urban	Urban(traffic)	Urban	Urban(Park)	Urban	Suburban	Urban[c]	Rural (School)[c]
FLO	0.30–8.67	0.45–0.95	0.13–0.27	0.05–0.30	0.2 ± 0.1	0.1 ± 0.1	0.09 ± 0.07	0.04	0.03
PHE	0.40–10.7	0.27–1.47	0.79–1.85	0.13–0.39	1.6 ± 0.9	1.1 ± 1.4	0.8 ± 0.9	0.15	0.12
ANT	0.54–1.38	0.41–0.71	0.08–0.29	0.02–0.06	0.2 ± 0.1	0.1 ± 0.1	0.09 ± 0.09	0.08	0.07
FLU	1.09–9.11	0.55–1.05	0.56–1.80	0.06–0.51	1.5 ± 1.4	1.7 ± 2.3	1.2 ± 1.4	0.47	0.73
PYR	1.10–9.00	0.56–1.08	0.70–2.30	0.07–0.63	1.6 ± 1.6	1.6 ± 2.1	1.2 ± 1.3	0.43	0.63
BaA	0.78–3.24	0.008–0.76	0.99–3.81	0.05–0.50	1.4 ± 1.3	0.8 ± 1.1	0.6 ± 0.8	0.71	0.46
CHR	1.05–6.23	0.49–0.85	NA^a	NA	2.7 ± 2.3	1.6 ± 1.9	1.2 ± 1.4	1.11	1.17
BbF	1.28–10.15	0.46–1.29	2.76–7.39[b]	0.32–1.38	2.6 ± 2.1	4.2 ± 3.7	4.0 ± 3.3	1.99	2.08
BkF	1.30–7.71	0.62–1.17	-	-	2.7 ± 2.3	1.0 ± 0.9	1.0 ± 0.8	1.38	1.69
BaF	0.87–2.52	LOD-0.93	0.17–0.82	0.02–0.14	NA	NA	NA	NA	
BeP	1.22–10.4	LOD-1.07	5.88–13.69	0.67–3.18	NA	NA	NA	1.81	1.82
BaP	1.18–17.6	0.56–2.25	3.74–15.38	0.52–2.81	2.3 ± 2.1	1.6 ± 2.0	1.4 ± 1.5	1.16	1.14
PER	0.85–1.60	0.60–2.15	0.73–2.08	0.08–0.51	NA	NA	NA	NA	
IcdP	1.11–8.13	0.81–1.17	6.50–18.95	1.06–4.74	2.7 ± 1.9	2.5 ± 2.1	2.5 ± 1.9	3.12	2.26
DahA	2.17–6.86	0.20–2.31	3.22–10.61	0.53–2.65	0.3 ± 0.4	0.3 ± 0.3	0.3 ± 0.2	0.37	0.21
BghiP	0.90–2.49	LOD-1.00	11.84–29.43	1.53–8.35	3.1 ± 2.2	2.6 ± 2.3	2.5 ± 1.8	1.94	1.59
COR	1.96–3.83	0.14–2.09	1.68–9.28	0.22–1.69	NA	NA	NA	0.64	0.54

[a] NA: not available.
[b] Represents as BbF + BkF.
[c] Only mean values were provided.

affected by equilibrium partition in gas and particle phases. Fig. 2 demonstrates the seasonal distributions and compositions of the PAEs. In winter, DBP was the most dominant which accounted for 61% of the total quantified PAEs, followed by DEHP. Similar distribution pattern was observed on the studies conducted in Tianjin and Norway (Zhang et al., 2014; Rakkestad et al., 2007). DEHP is mainly used mainly as a plasticizer for polyvinyl chloride (PVC) which contains in ca. 80% of the phthalates products in China (Meng et al., 2014). DBP is also one of the most widely used phthalates globally. A rapid growth of their consumptions has been showed (Gao and Wen, 2016). Compared with DEHP, DBP has a longer half-life in the atmosphere and has higher vapor pressure (7.3×10^{-5} VS 9.8×10^{-8}) (Salgueiro-González et al., 2015). Municipal garbage compressing and sewage, involving a high quantity of plastic household products, is one of the potential sources for urban phthalates (Meng et al., 2014).

High concentrations of DBP, DEHP, and DNOP were reported in the Bulgarian homes as well (Kolarik et al., 2008). The outdoor levels could be partly attributed to the widespread uses of the household products due to the air exchanges (Zhang et al., 2014; Weschler, 1980). In summer, DBP was also predominant, accounting for 50% of the total quantified PAEs. External painting material on the building is a potential source for the outdoor PAEs (Guidotti et al., 1998). Due to their potential impacts on human health and abundant in particle, further researches on their sources identification are required.

3.4. Source characterization

OC fractions are critical which can be used to source apportionment. Based on the source profiles shown in the literatures (Sheesley et al., 2003; He et al., 2008; Zhang et al., 2008; Yu and Yu, 2011), Chemical mass balance (CMB) 8.2 model was used to analyze the contributions of OC sources. The results demonstrated that coal combustion, vehicle emission, cooking, and SOC formation were the four major pollution sources in GZ (Fig. 3). Dissimilar with the findings in most northern Chinese cities, there was no significant increase of contribution from coal combustion in winter as coal is not necessary to be used as fuel for residential warming. Biomass burning was appointed as a less significant contributor (<10%) compared with other pollution sources, its influences was still greater in winter.

Organic markers were used to evidence the source characterization for OC. Similar seasonal and bimodal distributions were observed for n-alkanes homologs (Fig. 2). The concentrations of higher carbon number (n-C_{24}-n-C_{33}) accounted for 69.1% on average of the total quantified n-alkanes. Few important indices were efficient tools to identify the potential source for n-alkanes. Such as the carbon maximum number (C_{max}; the n-alkane exhibiting the highest concentration among the homologs) is generally used to distinguish biogenic from anthropogenic sources (Simoneit, 1999; Simoneit and Mazurek, 1982). The carbon preference index (CPI; the relative quantities of odd/even carbon
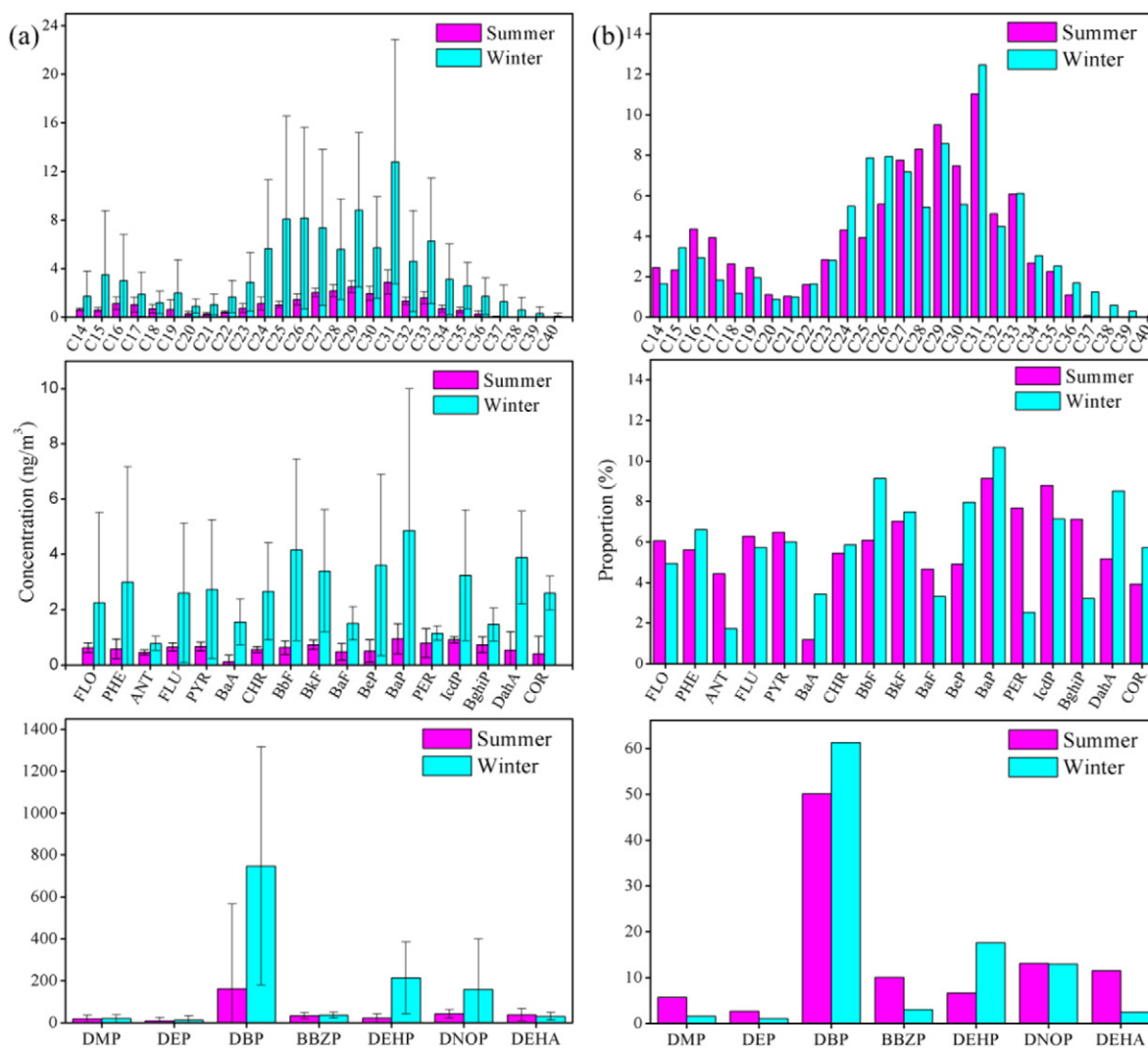

Fig. 2. Distribution (a) and composition (b)of n-alkanes, PAHs and PAEs inPM$_{2.5}$ in Guangzhou.
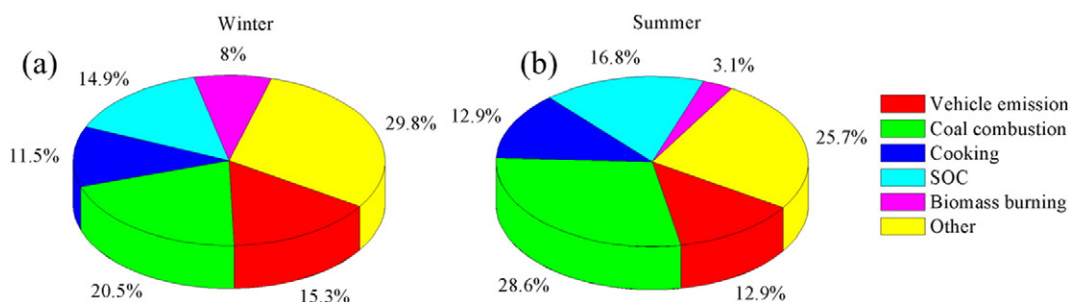
Fig. 3. Sources contributions of OC in PM$_{2.5}$ in Guangzhou.

number n-alkanes) has been also used for the same purpose. The n-alkanes that originate from vascular plants waxes typically exhibit high values for the CPI (CPI >> 1), that is inductive of a strong odd over even carbon number preference. In comparison, the CPI values for vehicle emissions and other anthropogenic sources, in contrast, are close to unity (CPI ≈ 1) (Kavouras et al., 1999).

In addition, the contribution of wax n-alkanes (% wax C_n) can be used to evaluate the contributions of biogenic versus anthropogenic sources. Higher % wax C_n values indicate greater contributions from biogenic sources (Bi et al., 2003; Wang and Kawamura, 2005). And the odd to even predominance (OEP) ratio was used to supporting the existence of odd to even predominance. Our previous paper demonstrated the calculation equations for those indices (Wang et al., 2015a).

Table 3 summarizes these indices calculated for the GZ sample sets. The C_{max} was n-C_{31} in most of the samples, followed by n-C_{29} in both of summer and winter. Higher C_{max} values (i.e., n-$C_{>26}$) can be ascribed to the shedding of epicuticular waxes by terrestrial plants while lower C_{max} values are linked to anthropogenic sources. The results reflect that besides vehicular emission, epicuticular wax is also an important contributor to the n-alkanes in GZ. It is also worth noting that odd-to-even carbon number (2.0 and 1.6 in winter and summer, respectively) was predominance at OEP$_{31}$, further supporting that plant wax contributed to the organic fraction.

The CPI$_1$ for the full range of n-alkanes ranged from 1.1 to 1.7 with an average of 1.3 and from 1.0 to 1.3 with an average of 1.1 in winter and summer, respectively. The variations of CPI$_1$ among the samples can be ascribed by different mixing of pollution origins such as petroleum residues and vascular plant wax. The petrogenic CPI$_2$ and biogenic CPI$_3$ values indicate that organic lipid from leaf epicuticular waxes is the predominant source for the heavier n-alkanes in winter whereas

large contributions from vehicle emission to lighter n-alkanes in both winter and summer. The average of % wax was 17.3% (ranged from 9.3 to 28.7%) and 12.0% (ranged from 8.4 to 16.6%) in winter and summer, respectively. The percentages were comparable with the range of 11.3 to 27.7% (average 18.5%) measured in Qingdao in winter (Guo et al., 2003b). Both of the n-alkane indices suggest that the anthropogenic activities were dominant for the contributions of n-alkanes but with some extent from terrestrial plants.

No obvious seasonal difference was shown on the PAHs distributions (Fig. 2). In winter, benzo[b]fluoranthene (BbF), dibenzo[a,h]anthracene (DahA), benzo[e]pyrene (BeP), and benzo[k]fluoranthene (BkF) had slightly higher compositions to the total quantified PAHs (34%), whereas higher proportions of benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), perylene (PER), benzo[ghi]perylene (BghiP) were found in summer (33%). The high compositions of IcdP and BghiP in both seasons suggest significant contribution from vehicle emission (Smith and Harrison, 1998), and additionally with tracers for gasoline-fueled vehicle emission (i.e., BaP and DahA) (Miguel et al., 1998; Marr et al., 1999). The higher proportion of BkF in winter might represent more influences from coal combustion from regional transport (Ravindra et al., 2008). BeP, BaP and DahA can be originated from the industrial chimney emission in Guangdong province. The co-existences of phenanthrene (PHE) and fluoranthene (FLU) also proved the contributions from the biomass burning. Diagnostic ratios of few atmospheric PAHs have been used to identify potential pollution sources (Cotham and Bidleman, 1995; Lohmann et al., 2000; Yunker et al., 2000) which were calculated and summarized in Table 3. The ratios of anthracene (ANT)/(ANT + PHE) were 0.37 and 0.47 on average in winter and summer, respectively, indicating that the significant contributions from combustion sources such as petroleum and coal. The ratios of BaA/(BaA + chrysene (CHR)) were 0.39 and 0.11, respectively, in winter and summer. The higher values suggested that more wood, grass, and coal burning and diesel combustion activities were influenced in winter while petroleum was the major pollution source in summer. The ratios of IcdP/(IcdP + BghiP) were >0.5 in all of the samples, promising that burning of grass and wood and coal combustion were significant in GZ as well. Higher BaP/BghiP value was obtained in winter than that in summer, revealing more contributions of coal burning in cold season, potentially from regional transportation from northern areas. The ratios of FLU/(FLU + PYR) and BbF/BkF also demonstrated that vehicle emission was the main pollution sources in GZ, especially in summer. Source identification were further performed by computing additional diagnostic ratios, including FLU/PYR, IcdP/BghiP, and BaP/BeP with laboratory generated source in GZ (i.e., rice straw and sugar cane burning, vehicle emission, and bituminite coal combustion) and ambient samples (Fig. 4). In comparison of the ratios of FLU/PYR, the rice straw and sugar cane burning were potential sources in both seasons. IcdP and BghiP are the two organic tracers widely used for the source apportionment. We found that the ratio of IcdP/BghiP in GZ was close to that of the rice straw and sugar cane burning in summer, but more similar with the value of bituminite coal combustion in winter. The ratio of BaP/BeP also sugge.sted the combined influences from the

Table 3
Indices of n-alkanes and diagnostic ratios of PAHs in PM$_{2.5}$ in Guangzhou.

	Winter	Summer
	Average (range)	Average (range)
C_{max}	C_{29} and C_{31}	C_{29} and C_{31}
CPI1(C_{14}–C_{40})[a]	1.3(1.1–1.7)	1.1(1.0–1.3)
CPI2(C_{14}–C_{24})[a]	0.8(0.5–1.3)	0.7(0.6–1.1)
CPI3(C_{25}–C_{40})[a]	1.5(1.2–2.0)	1.1(1.0–1.3)
waxC_n%	17.3% (9.3–28.7%)	12.0% (8.4–16.6%)
OEP$_{31}$[b]	2.0(1.4–3.6)	1.6(1.3–2.0)
ANT/(ANT + PHE)	0.37(0.09–0.58)	0.47(0.32–0.61)
BaA/(BaA + CHR)	0.39(0.29–0.43)	0.11(0.02–0.15)
IcdP/(IcdP + BghiP)	0.65(0.53–0.77)	0.58(0.51–1.0)
Flu/(Flu + PYR)	0.49(0.43–0.52)	0.49(0.48–0.50)
BbF/BkF	1.1(0.89–1.58)	0.84(0.74–1.10)
BaP/BghiP	3.3(1.2–12.6)	1.1(0.75–2.68)

[a] Whole range for n-alkanes: $CPI_1 = \sum (C_{15}$–$C_{39})/\sum (C_{16}$–$C_{40})$, Petrogenic n-alkanes: $CPI_2 = \sum (C_{15}$–$C_{25}) / \sum (C_{14}$–$C_{24})$, Biogenic n-alkanes: $CPI_3 = \sum (C_{25}$–$C_{39}) / \sum (C_{26}$–$C_{40})$.
[b] $OEP_{31} = [(C_n + 6C_{n+2} + C_{n+4}) / (4C_{n+1} + 4C_{n+3})]^{(-1)^{n+1}}$, n = 31.
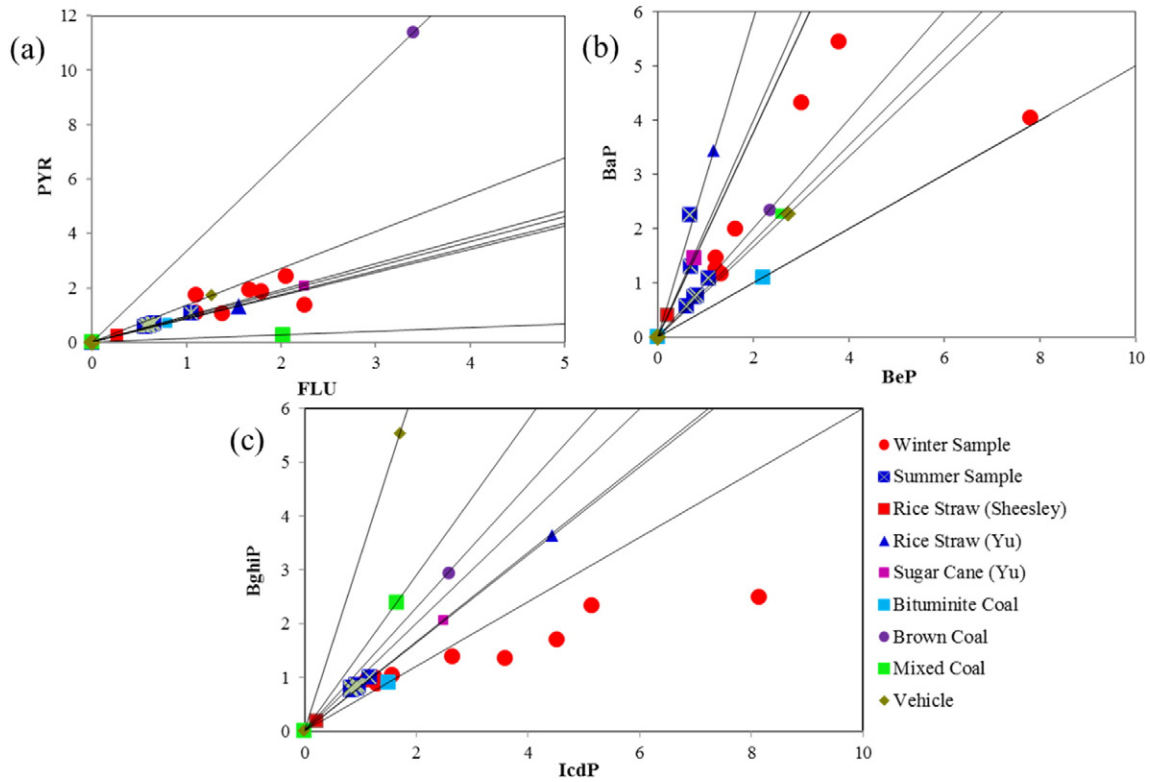
Fig. 4. Scatter diagrams for the ratios of FLU/PYR (a), BaP/BeP (b) and IcdP/BghiP (c) in PM$_{2.5}$ in Guangzhou.

sugar cane burning and vehicle emission. Besides, Fig. 5a demonstrates the ratio of BghiP/EC to IcdP/EC of the source and ambient samples. The ambient samples were in line with the rice straw and sugar cane. Based on these diagnostic ratios, we conclude that vehicle emission, biomass burning, and coal combustions were the significant pollution sources in GZ.
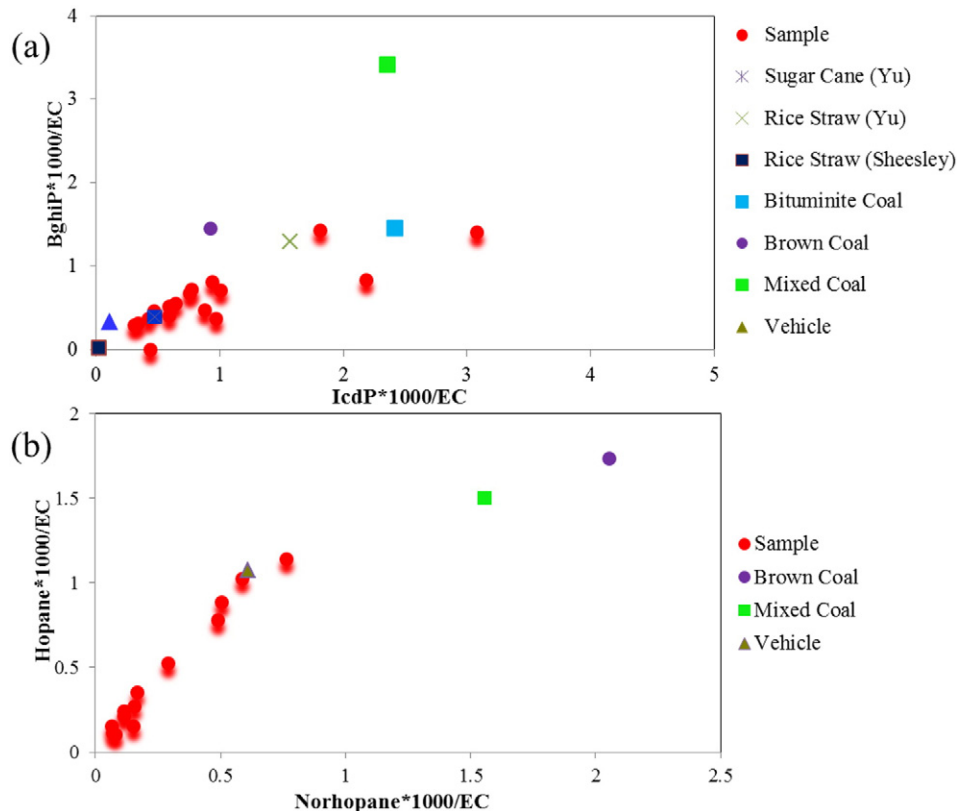

Fig. 5. Ratio-ratio diagrams for BghiP/EC to IcdP/EC (a) and hopane/EC to norhopane/EC (b) in PM$_{2.5}$ in Guangzhou.

Petroleum organic tracers of hopanes including 17α(H)-22,29,30-trisnohopane, 17α(H)-21β(H)-30-norhopane, and 17α(H)-21β(H)-hopane were quantified in this study. Fig. 5b illustrates the ratio of hopane/EC to norhopane/EC in the GZ ambient samples, additional with the spectrum from the source samples. The average ratios were found to be 0.91 and 1.76 ng/µg, respectively, for coal combustion and vehicle emission source-dominated samples collected in Zhujiang tunnel (He et al., 2008). The ambient ratios obviously were higher than that of coal combustion and were more comparable with value of the tunnel samples, promising that both hopane and EC can be originated from vehicle emission. The ΣHopanes/EC in this study was 0.75 ng/µg, compared with 1.14 ng/µg from the fresh vehicle emission dominated samples (He et al., 2008), much lower than the vehicle emission by Dai et al. (2015). The lower values might suggest a certain degree of the air aging in the ambient.

4. Conclusion

Organic tracers are the efficient and supportive tools for source apportionment. Good agreement with the receptor model and the organic indices and diagnostic ratios evidenced that anthropogenic sources such as vehicle emission, biomass burning and coal combustion were the major pollution sources in urban GZ city. Biological sources of organic lipid from leaf epicuticular waxes also contributed to the PM$_{2.5}$. Determination and quantification of more potential source markers are benefit for the source characterizations. Though there were minor differences in the source contribution, but the main pollution sources were consistent between winter and summer. This phenomenon is quite dissimilar with most northern cities in China. Few organics, such as PAHs and PAEs, have strong environmental and health impacts to the urban cities.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.01.138.

References

Abba, E.J., Unnikrishnan, S., Kumar, R., Yeole, B., Chowdhury, Z., 2012. Fine aerosol and PAH carcinogenicity estimation in outdoor environment of Mumbai city, India. inter. J. Environ. Heal. R. 22 (2), 134–149.

Akyüz, M., Cabuk, H., 2009. Meteorological variation of PM$_{2.5}$/PM$_{10}$ concentrations and particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. J. Hazard. Mater. 170, 13–21.

Anastasopoulos, A.T., Wheeler, A.J., Karman, D., Kulka, R.H., 2012. Intraurban concentrations, spatial variability and correlation of ambient polycyclic aromatic hydrocarbons (PAH) and PM$_{2.5}$. Atmos. Environ. 59, 272–283.

Bi, X.H., Sheng, G.Y., Peng, P.A., Zhang, Z.Q., Fu, J.M., 2002. Extractable organic matter in PM$_{10}$ from Liwan district of Guangzhou city, PR China. Sci. Total Environ. 300, 213–228.

Bi, X.H., Sheng, G.Y., Peng, P.A., Chen, Y.J., Zhang, Z.Q., Fu, J.M., 2003. Distribution of particulate- and vapor- phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. Atmos. Environ. 37, 289–298.

Bi, X.H., Sheng, G.Y., Peng, P.A., Chen, Y.J., Fu, J.M., 2005. Size distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhou. Chin. Atmos. Environ. 39, 477–487.

Bourotte, C., Forti, M., Taniguchi, S., Bícego, M.C., Lotufo, P.A., 2005. A wintertime study of PAHs in fine and coarse aerosols in São Paulo city, Brazil. Atmos. Environ. 39, 3799–3811.

Bui, T.T., Giovanoulis, G., Cousins, A.P., Magner, J., Cousins, I.T., De Wit, C.A., 2016. Human exposure, hazard and risk of alternative plasticizers to phthalate esters. Sci. Total Environ. 541, 451–467.

Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C., Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta region, China during 2001 winter period. Atmos. Environ. 37 (11), 1451–1460.

Cao, J.J., Lee, S.C., Ho, K.F., Zou, S.C., Fung, K., Li, Y., Watson, J.G., Chow, J.C., 2004. Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China. Atmos. Environ. 38, 4447–4456.

Cao, J.J., Wu, F., Chow, J.C., Lee, S.C., Li, Y., Chen, S.W., An, Z.S., Fung, K.K., Watson, J.G., Zhu, C.S., Liu, S.X., 2005. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xian, China. Atmos. Chem. Phys. 5, 3127–3137.

Cao, J.J., Lee, S.C., Chow, J.C., Watson, J.G., Ho, K.F., Zhang, R.J., Jin, Z.D., Shen, Z.X., Chen, G.C., Kang, Y.M., Zou, S.C., Zhang, L.Z., Qi, S.H., Dai, M.H., Cheng, Y., Hu, K., 2007. Spatial and seasonal distributions of carbonaceous aerosols over China. J. Geophys. Res. 112 (D22S11), 1–9.

Cao, J.J., Chow, J.C., Tao, J., Lee, S.C., Watson, J.G., Ho, K.F., Wang, G.H., Zhu, C.S., Han, Y.M., 2011. Stable carbon isotopes in aerosols from Chinese cities: influence of fossil fuels. Atmos. Environ. 45 (6), 1359–1363.

Cao, J.J., Zhu, C.S., Tie, X.X., Geng, H.H., Xu, H.M., Ho, S.S.H., Wang, G.H., Han, Y.M., Ho, K.F., 2013. Characteristics and sources of carbonaceous aerosols from Shanghai, China. Atmos. Chem. Phys. 13 (2), 803–817.

Chen, Y., Cao, J.J., Zhao, J., Xu, H.M., Arimoto, R., Wang, G.H., Han, Y.M., Shen, Z.X., Li, G.H., 2014. N-alkanes and polycyclic aromatic hydrocarbons in total suspended particulates from the southeastern Tibetan plateau: concentrations, seasonal variations, and sources. Sci. Total Environ. 470–471, 9–18.

Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.H., Crow, D., Kohl, S.D., Engelbrecht, J.P., Green, M.K., 2004. Source profiles for industrial, mobile and area sources in the big bend regional aerosol visibility and observational (BRAVO) study. Chemosphere 54 (2), 185–208.

Chow, J.C., Watson, J.G., Chen, L.W.A., Chang, M.C.O., Robinson, N.F., Trimble, D., Kohl, S., 2007a. The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long term database. J. Air Waste Manage. Assoc. 57 (9), 1014–1023.

Chow, J.C., Yu, J.Z., Watson, J.G., Ho, S.S.H., Bohannan, T.L., Hays, M.D., Fung, K.K., 2007b. The application of thermal methods for determining chemical composition of carbonaceous aerosols: a review. J. Environ. Sci. Health A 42 (11), 1521–1541.

Cotham, W.E., Bidleman, T.F., 1995. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. Environ. Sci. Technol. 29 (11), 2782–2789.

Cui, H.Y., Chen, W.H., Dai, W., Liu, H., Wang, X.M., He, K.B., 2015. Source apportionment of PM$_{2.5}$ in Guangzhou combining observation data analysis and chemical transport model simulation. Atmos. Environ. 116, 262–271.

Dai, S., Bi, X.H., Chan, L.Y., He, J., Wang, B., Wang, X.M., Peng, P.A., Sheng, G.Y., Fu, J.M., 2015. Chemical and stable carbon isotopic composition of PM$_{2.5}$ from on-road vehicle emissions in the PRD region and implications for vehicle emission control policy. 2015. Atmos. Chem. Phys. 15, 3097–3108.

Duan, F.K., He, K.B., Liu, X.D., 2010. Characteristics and source identification of fine particulate n-alkanes in Beijing, China. J. Environ. Sci. 22 (7), 998–1005.

Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E.L., 2004. Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor-phase and PM$_{2.5}$ in Southern California urban and rural communities. Aerosol Sci. Technol. 38 (5), 447–455.

Feng, J.L., Hu, M., Chan, C.K., Lau, P.S., Fang, M., He, L.Y., Tang, X.Y., 2006. A comparative study of the organic matter in PM$_{2.5}$ from three Chinese megacities in three different climatic zones. Atmos. Environ. 40, 3983–3994.

Gao, D., Wen, Z.D., 2016. Phthaate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. Sci. Total Environ. 541, 986–1001.

Gao, B., Guo, H., Wang, X.M., Zhao, X.Y., Ling, Z.H., Zhang, Z., Liu, T.Y., 2012a. Tracer-based source apportionment of polycyclic aromatic hydrocarbons in PM$_{2.5}$ in Guangzhou, Southern China, using positive matrix factorization (PMF). Environ. Sci. Pollut. R. 20, 2398–2409.

Gao, B., Guo, H., Wang, X.M., Zhao, X.Y., Ling, Z.H., Zhang, Z., Liu, T.Y., 2012b. Polycyclic aromatic hydrocarbons in PM$_{2.5}$ in Guangzhou, Southern China: spatiotemporal patterns and emission source. J. Hazard. Mater. 239, 78–87.

Gao, B., Wang, X.M., Zhao, X.Y., Ding, X., Fu, X.X., Zhang, Y.L., He, Q.F., Zhang, Z., Liu, T.Y., Huang, Z.Z., Chen, L.G., Peng, Y., Guo, H., 2015. Source apportionment of atmospheric PAHs and their toxicity using PMF: impact of gas/particle partitioning. Atmos. Environ. 103, 114–120.

Guidotti, M., Colasanti, A., Chinzari, M., Ravaili, G., Vitali, M., 1998. Investigation on the presence of aromatic hydrocarbons, polycyclic aromatic hydrocarbons, persistent organochloride compounds, phthalates and the breathable fraction of atmospheric particulate in the air of Rieti urban area. Ann. Chim. 88 (5–6), 419–427.

Guo, Y., Kannan, K., 2011. Comparative assessment of human exposure to phthalate esters from house dust in China and the United State. Environ. Sci. Technol. 45, 3788–3794.

Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, S.C., 2003a. Particle associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmos. Environ. 37, 5307–5317.

Guo, Z.G., Sheng, L.F., Feng, J.L., Fang, M., 2003b. Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China. Atmos. Environ. 37, 1825–1834.

Guo, Z.G., Lin, T., Zhang, G., Hu, L.M., Zheng, M., 2009. Occurrence and source of polycyclic aromatic hydrocarbons and n-alkanes in PM$_{2.5}$ in the roadside environment of a major city in China. J. Hazard. Mater. 170, 888–894.

Hagler, G.S.W., Bergin, M.H., Salmon, L.G., Yu, J.Z., Wan, E.C.H., Zheng, M., Zeng, L.M., Kiang, C.S., Zhang, Y.H., Lau, A.K.H., Schauer, J.J., 2006. Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China. Atmos. Environ. 40, 3802–3815.

He, L.Y., Hu, M., Zhang, Y.H., Huang, X.F., Yao, T.T., 2008. Fine particle emissions from on-road vehicles in the Zhujiang Tunnel, China. Environ. Sci. Technol. 42, 4461–4466.

Ho, S.S.H., Yu, J.Z., 2004. In-injection port thermal desorption and subsequent gas chromatography–mass spectrometric analysis of polycyclic aromatic hydrocarbons and n-alkanes in atmospheric aerosol samples. J. Chromatogr. A 1059 (1–2), 121–129.

Ho, K.F., Lee, S.C., Cao, J.J., Li, Y.S., Chow, J.C., Watson, J.G., Fung, K., 2006. Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong. Atmos. Chem. Phys. 6, 4569–4576.

Ho, S.S.H., Yu, J.Z., Chow, J.C., Zielinska, B., Watson, J.G., Sit, E.H.L., Schauer, J.J., 2008. Evaluation of an in-injection port thermal desorption gas chromatography–mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples. J. Chromatogr. A 1200 (2), 217–227.

Ho, S.S.H., Chow, J.C., Watson, J.G., Ng, L.P.T., Kwok, Y., Ho, K.F., Cao, J.J., 2011. Precautions for in-injection port thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) as applied to aerosol filter samples. Atmos. Environ. 45 (7), 1491–1496.

Huang, R.J., Zhang, Y.L., Bozzetti, C., Ho, K.F., Cao, J.J., Han, Y.M., Daellenbach, K.R., Slowik, J.G., Platt, S.M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S.M., Bruns, E.A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z.S., Szidat, S., Baltensperger, U., Haddad, I.E., Prévôt, A.S.H., 2014. High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514 (7521), 218–222.

Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, G., Oyola, P., 1999. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. Atmos. Environ. 33, 4977–4986.

Khan, M.B., Masiol, M., Formenton, G., Gilio, A.D., de Gennaro, G., Agostinelli, C., Pavoni, B., 2016. Carbonaceous PM$_{2.5}$ and secondary organic aerosol across the Veneto region (NE Italy). Sci. Total Environ. 542, 172–181.

Kolarik, B., Bornehag, C.G., Naydenov, K., Sundell, J., Stavova, P., Nielsen, O.F., 2008. The concentrations of phthalates in settled dust in Belgarian homes in relation to building characteristic and cleaning habits in the family. Atmos. Environ. 42 (37), 8553–8559.

Kompalli, S.K., Babu, S.S., Moorthy, K.K., Manoj, M.R., Kumar, N.V.P.K., Shaeb, K.H.B., Joshi, A.K., 2014. Aerosol black carbon characteristics over Central India: temporal variation and its dependence on mixed layer height. Atmos. Res. 147, 27–37.

Kong, S.F., Ding, X., Bai, Z.P., Han, B., Chen, L., Shi, J.W., Li, Z.Y., 2010. A seasonal study of polycyclic aromatic hydrocarbons in PM$_{2.5}$ and PM$_{2.5-10}$ in five typical cities of Liaoning province, China. J. Hazard. Mater. 183, 70–80.

Kong, S., Ji, Y., Liu, L., Chen, L., Zhao, X., Wang, J., Bai, Z., Sun, Z., 2013. Spatial and temporal variation of phthalic acid esters (PAEs) in atmospheric PM$_{10}$ and PM$_{2.5}$ and the influence of ambient temperature in Tianjin, China. Atmos. Environ. 74, 199–208.

Li, J., Zhang, G., Li, X.D., Qi, S.H., Liu, G.Q., Peng, X.Z., 2006. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. Sci. Total Environ. 355, 145–155.

Li, W.F., Peng, Y., Bai, Z.P., 2010a. Distribution and sources of n-alkanes in PM$_{2.5}$ at urban, industrial and coastal sites in Tianjin, China. J. Atmos. Chem. 22 (10), 1551–1557.

Li, P.H., Wang, Y., Li, Y.H., Wang, Z.F., Zhang, H.Y., Xu, P.J., Wang, W.X., 2010b. Characterization of polycyclic aromatic hydrocarbons deposition in PM$_{2.5}$ and cloud/fog water at Mount Taishan (China). Atmos. Environ. 44, 1996–2003.

Li, J.N., Fan, R.F., Lu, S.Y., Zhang, D.R., Zhou, Y.X., Lv, Y.S., 2015. Exposure to polycyclic aromatic hydrocarbons (PAHs) could cause their oxidative DNA damage: a case study for college students in Guangzhou, China. Environ. Sci. Pollut. R. 22, 1770–1777.

Lin, Y., Ma, Y.Q., Qiu, X.H., Li, R., Fang, Y.H., Wang, J.X., Zhu, Y.F., Hu, D., 2015. Sources, transformation, and health implications of polycyclic aromatic hydrocarbons (PAHs) and their nitrated, hydroxylated, and oxygenated derivatives in fine particulate matter (PM$_{2.5}$) in Beijing. J. Geophys. Res. 120, 7219–7228.

Liu, Y., HE, K.B., Shi, Z.B., Chen, Y.J., Xie, M.S., 2006. Study progress of atmospheric particulate in the Pearl River Delta Region. Environ. Protec. Sci. 32 (5), 1–5.

Liu, D.M., Gao, S.P., An, X.H., 2008. Distribution and source apportionment of polycyclic aromatic hydrocarbons from atmospheric particulate matter PM$_{2.5}$ in Beijing. Adv. Atmos. Sci. 25 (2), 297–305.

Liu, J.W., Li, J., Zhang, Y.L., Liu, D., Ding, P., Shen, C.D., Shen, K.J., He, Q.F., Ding, X., Wang, X.M., Chen, D.H., Szidat, S., Zhang, G., 2014. Source apportionment using radiocarbon and organic tracers for PM$_{2.5}$ carbonaceous aerosols in Guangzhou, South China: contrasting local- and regional-scale haze events. Environ. Sci. Technometrics 48, 12002–12011.

Lohmann, R., Northcott, G.L., Jones, K.C., 2000. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs and PAHs to the UK atmosphere. Environ. Sci. Technol. 34 (14), 2892–2899.

Marr, L.C., Kirchatetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., Hammond, S.K., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhast emissions. Environ. Sci. Technol. 33, 3091–3099.

Marr, L.C., Dzepina, K., Jimenez, J.L., Reisen, F., Bethel, H.L., arey, J., Gaffney, J.S., Marley, N.A., Molina, L.T., 2006. Source and transformations of particle-bound polycyclic aromatic hydrocarbons in Mexico City. Atmos. Chem. Phys. 6, 1733–1745.

Martellini, T., Giannoni, M., Lepri, L., Katsoyiannis, A., Cincinelli, A., 2012. One year intensive PM$_{2.5}$ bound polycyclic aromatic hydrocarbons monitoring in the area of Tuscany, Italy. Concentrations, source understanding and implications. Environ. Pollut. 164, 252–258.

Meng, X.Z., Wang, Y., Xiang, N., Chen, L., Liu, Z.G., Wu, B., Dai, X.H., Zhang, Y.H., Xie, Z.Y., Ebinghaus, R., 2014. Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: implication for risk assessment of sludge applied to soil. Sci. Total Environ. 476, 242–249.

Miguel, A.H., Kirchstetter, T.W., Harley, R.A., Hering, S.V., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environ. Sci. Technol. 32, 450–455.

Myridakis, A., Fthenou, E., Balaska, E., Vakinti, M., Kogevinas, M., Stephanou, E.G., 2015. Phthalate esters, parabens and bisphenol A exposure among mothers and their children in Greece (Rhea cohort). Environ. Int. 83, 1–10.

Oanh, N.T.K., Nghiem, L.H., Phyu, Y.L., 2002. Emission of polycyclic aromatic hydrocarbons, toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood, and kerosene. Environ. Sci. Technol. 36, 833–839.

Panther, B.C., Hooper, M.A., Tapper, N.J., 1999. A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments. Atmos. Environ. 33, 4087–4099.

Pleil, J.D., Vette, A.F., Rappaport, S.M., 2004. Assaying particle-bound polycyclic aromatic hydrocarbons from archived PM$_{2.5}$ filters. J. Chromatogr. A 1033, 9–17.

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. J. Air Waste Manage. Assoc. 56, 709–742.

Rakkestad, K.E., Dye, C.J., Yttri, K.E., Holme, J.A., Hongslo, J.K., Schwarze, P.E., Becher, R., 2007. Phthalate levels in Norwegian indoor air related to particle size fraction. J. Environ. Monit. 9 (12), 1419–1425.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921.

Salgueiro-González, A., M.J., Lopez deAlda, Muniategui-Lorenzo, S., Prada-Rodríguez, D., Barceló, D., 2015. Analysis and occurrence of endocrine-disrupting chemicals in airborne particles. Trends Anal. Chem. 66, 45–52.

Saxena, P., Hildemann, L.M., 1996. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. J. Atmos. Chem. 24, 57–109.

Sheesley, R.J., Schauer, J.J., Chowdhury, Z., Cass, G.R., Simoneit, B.R.T., 2003. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. J. Geophys. Res. Atmos. 108, 4285–4299.

Simoneit, B.R.T., 1999. A review of biomarker compounds as source indicators and tracers for air pollution. Environ. Sci. Pollut. Res. 6, 159–169.

Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural western United States. Atmos. Environ. 16, 2139–2159.

Smith, D.J.T., Harrison, R.M., 1998. Polycyclic aromatic hydrocarbons in atmospheric particles. In: Harrison, R.M., R., Van Grieken, (Eds.), Atmospheric Particles. Wiley.

Song, M., Chi, C.C., Guo, M., Wang, X.Q., Cheng, L.X., Shen, X.Y., 2015. Pollution levels and characteristics of phthalate esters in indoor air of offices. J. Environ. Sci. 28, 157–162.

Streets, D.G., Gupta, S., Waldhoff, S.T., Wang, M.Q., Bond, T.C., Yiyun, B., 2001. Black carbon emissions in China. Atmos. Environ. 35 (25), 4281–4296.

Takahashi, K., Tsugane, S., Nakazawa, H., Inoue, K., Tsukino, H., Wang, P., Zhang, S., Yoshimura, M., Hanaoka, T., Pan, G., 2006. Decreased serum free testosterone in workers exposed to high levels of di-n-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP), a cross-sectional study in China. Environ. Health Perspect. 114 (11), 1643–1648.

Tao, J., Ho, K.F., Chen, L.G., Zhu, L.H., Han, J.L., Xu, Z.C., 2009. Effect of chemical composition of PM$_{2.5}$ on visibility in Guangzhou, China, 2007 Spring. Particuology (7), 68–75.

Tham, Y.W.F., Takeda, K., Sakugawa, H., 2008. Exploring the correlation of particulate PAHs, sulfur dioxide, nitrogen dioxide and ozone, a preliminary study. Water Air Soil Pollut. 194 (1–4), 5–12.

Tiwari, S., Pipal, A.S., Hopke, P.K., Bisht, D.S., Srivastava, A.K., Tiwari, S., Saxena, P.N., Khan, A.H., Pervez, S., 2015. Study of the carbonaceous aerosol and morphological analysis of fine particles along with their mixing state in Delhi, India: a case study. Environ. Sci. Pollut. Res. 22, 10744–10757.

Venkataraman, C., Reddy, C.K., Josson, S., Reddy, M.S., 2002. Aerosol size and chemical characteristics at Mumbai, India, during the INDOEX-IFP (1999). Atmos. Environ. 36, 1979–1991.

Villalobos, A.M., Barraza, F., Jorquera, H., Schauer, J.J., 2015. Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013. Sci. Total Environ. 512-513, 133–142.

Wang, G.H., Kawamura, K., 2005. Molecular characteristics of urban organic aerosols from Nanjing: a case of a mega-city in China. Environ. Sci. Technol. 39 (19), 7430–7438.

Wang, J.Z., Ho, S.S.H., Cao, J.J., Huang, R.J., Zhou, J.M., Zhao, Y.Z., Xu, H.M., Liu, S.X., Wang, G.H., Shen, Z.X., Han, Y.M., 2015a. Characteristics and major sources of carbonaceous aerosols in PM$_{2.5}$ from Sanya, China. Sci. Total Environ. 530, 110–119.

Wang, Q.Q., Hilda Huang, X.H., Zhang, T., Zhang, Q.Y., Feng, Y.M., Yuan, Z.B., Wu, D., Lau, A.K.H., Yu, J.Z., 2015b. Organic tracer-based source analysis of PM$_{2.5}$ organic and elemental carbon: a case study at Dongguan in Pearl River Delta, China. Atoms. Environ. 118, 164–175.

Wang, X.M., Chen, W.H., Chen, D.H., Wu, Z.Y., Fan, Q., 2016. Long-term trends of fine particulate matter and chemical composition in the Pearl River Delta Economic Zone (PRDEZ), China. Front. Environ. Sci. Eng. 10 (1), 53–62.

Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C., Frazier, C.A., Neuroth, G.R., Robbins, R., 1994. Differences in the carbon composition of source profiles for diesel- and gasoline powered vehicles. Atmos. Environ. 28 (15), 2493–2505.

Weschler, C.J., 1980. Characterization of selected organics in size-fractionated indoor aerosols. Environ. Sci. Technol. 14 (4), 428–431.

Xu, H.M., Tao, J., Ho, S.S.H., Ho, K.F., Cao, J.J., Li, N., Chow, J.C., Wang, G.H., Han, Y.M., Zhang, R.J., Watson, J.G., Zhang, J.Q., 2013. Characteristics of fine particulate non-polar organic compounds in Guangzhou during the 16th Asian Games: effectiveness of air pollution controls. Atmos. Environ. 76, 94–101.

Yang, Y.Y., Guo, P.R., Zhang, Q., Li, D.L., Zhao, L., Mu, D.H., 2010. Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China. Sci. Total Environ. 408, 2492–2500.

Yao, L., Li, X.R., Guo, Y.Q., Liu, X.R., Wang, Y.S., 2009. Pollution characteristics of n-alkanes in atmospheric fine particles during Spring Festival of 2007 in Beijing. Environ. Sci. 30 (2), 589–593.

Yu, H.A., Yu, J.Z., 2011. Size distributions of polycyclic aromatic hydrocarbons at two receptor sites in the Pearl River Delta Region, China: implications of a dominant droplet mode. Aerosol Sci. Technol. 45, 101–112.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2000. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33 (4), 489–515.

Zhang, Y.X., Schauer, J.J., Zhang, Y.H., Zeng, L.M., Wei, Y.J., Liu, Y., Shao, M., 2008. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. Environ. Sci. Technol. 42, 5068–5073.

Zhang, L.B., Wang, F.M., Ji, Y.Q., Jiao, J., Zou, D.K., Liu, L.L., Shan, C.Y., Bai, Z.P., Sun, Z.R., 2014. Phthalate esters (PAEs) in indoor $PM_{10}/PM_{2.5}$ and human exposure to PAEs via inhalation of indoor air in Tianjin, China. Atmos. Environ. 85, 139–146.

Zhang, Y.L., Huang, R.J., Haddad, I.E., Ho, K.F., Cao, J.J., Han, Y.M., Zotter, P., Bozzetti, C., Daellenbach, K.R., Canonaco, F., Slowik, J.G., Schwikowski, M., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Baltensperger, U., Prévôt, A.S.H., Szidat, S., 2015. Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013. Atmos. Chem. Phys. 15, 1299–1312.

Zheng, M., Fang, M., Wang, F., To, K.L., 2000. Characterization of the solvent extractable organic compounds in $PM_{2.5}$ aerosols in Hongkong. Atmos. Environ. 34, 2691–2702.

Zheng, L., Porter, E.N., Sjödin, A., Needham, L.L., Lee, S., Russell, A.G., Mulholland, J.A., 2009. Characterization of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Atlanta-Seasonal variations at urban, suburban, and rural ambient air monitoring sites. Atmos. Environ. 43, 4187–4193.

Zheng, M., Cheng, Y., Zeng, L.M., Zhang, Y.H., 2011. Developing chemical signatures of particulate air pollution in the Pearl River Delta region, China. J. Environ. Sci. 23 (7), 1143–1149.

Zhou, J.M., Zhang, R.J., Cao, J.J., Chow, J.C., Watson, J.G., 2012. Carbonaceous and ionic components of atmospheric fine particles in Beijing and their impact on atmospheric visibility. Aerosol and Air Quality Resear. 12 (4), 492–502.