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

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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
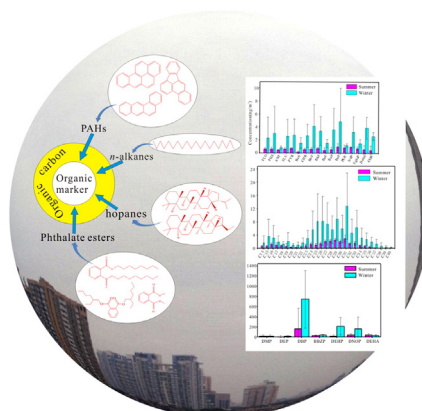
ABSTRACT

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

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Guangzhou
Source identification

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 m^3/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