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Source apportionment of fine particulate matter organic carbon in Shenzhen, China by chemical mass balance and radiocarbon methods☆

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ABSTRACT

Chemical mass balance (CMB) modeling and radiocarbon measurements were combined to evaluate the sources of carbonaceous fine particulate matter ($PM_{2.5}$) in Shenzhen, China during and after the 2011 summer Universiade games when air pollution control measurements were implemented to achieve air quality targets. Ambient $PM_{2.5}$ filter samples were collected daily at two sampling sites (Peking University Shenzhen campus and Longgang) over 24 consecutive days, covering the controlled and uncontrolled periods. During the controlled period, the average $PM_{2.5}$ concentration was less than half of what it was after the controls were lifted. Organic carbon (OC), organic molecular markers (e.g., levoglucosan, hopanes, polycyclic aromatic hydrocarbons), and secondary organic carbon (SOC) tracers were all significantly lower during the controlled period. After pollution controls ended, at Peking University, OC source contributions included gasoline and diesel engines (24%), coal combustion (6%), biomass burning (12.2%), vegetative detritus (2%), biogenic SOC (from isoprene, α-pinene, and β-caryophyllene; 7.1%), aromatic SOC (23%), and other sources not included in the model (25%). At Longgang after the controls ended, similar source contributions were observed: gasoline and diesel engines (23%), coal combustion (7%), biomass burning (17.7%), vegetative detritus (1%), biogenic SOC (from isoprene, α-pinene, and β-caryophyllene; 5.3%), aromatic SOC (13%), and other sources (33%). The contributions of the following sources were smaller during the pollution controls: biogenic SOC (by a factor of 10–16), aromatic SOC (4–12), coal combustion (1.5–6.8), and biomass burning (2.3–4.9). CMB model results and radiocarbon measurements both indicated that fossil carbon dominated over modern carbon, regardless of pollution controls. However, the CMB model needs further improvement to apportion contemporary carbon (i.e. biomass burning, biogenic SOC) in this region. This work defines the major contributors to carbonaceous $PM_{2.5}$ in Shenzhen and demonstrates that control measures for primary emissions could significantly reduce secondary organic aerosol (SOA) formation.

1. Introduction

Shenzhen is a rapidly developing and heavily urbanized coastal city in the Pearl River Delta (PRD) region of China. The economic growth of PRD cities has been accompanied by increased emission of air pollutants. Elevated levels of particulate matter (PM) have been attributed to primary emissions from industry and transportation and secondary aerosol formation (He et al., 2011; Huang

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et al., 2014; Yuan et al., 2006). High concentrations of PM pose risk to public health (Huang et al., 2012) and negatively affect visibility (Tan et al., 2009). Assessment of the chemical composition of PM and its contributing emission sources is therefore crucial to the implementation of effective air quality regulations.

To estimate source contributions to ambient PM in the PRD region, receptor models including positive matrix factorization (Dai et al., 2013; Kuang et al., 2015) and chemical mass balance (CMB) modeling (Wang et al., 2016; Zheng et al., 2011) have both been used. CMB has been widely used to apportion PM to its primary emission sources when source profiles are available (Kong et al., 2010). In Guangzhou, for instance, secondary organic carbon (SOC), coal combustion, and cooking sources were found to have contributed more than 20%, 14%, and 11% of fine particle ($PM_{2.5}$) organic carbon (OC), respectively (Wang et al., 2016). These results underscore the importance of combustion and secondary sources to $PM_{2.5}$ OC in the PRD.

To distinguish carbonaceous PM derived from fossil fuels from that devrived from contemporary sources, radiocarbon (^{14}C, $t_{1/2} = 5730$ years) measurements have been used (Gelencser et al., 2007; Gustafsson et al., 2009). ^{14}C is conserved with respect to emission conditions, atmospheric transport and chemical transformations (Szidat et al., 2004), making it a reliable tracer of modern carbonaceous matter. Using a combination of ^{14}C measurements and organic tracers in an industrial city in the PRD, Liu et al. (2014) demonstrated that fossil sources contributed 71% of the elemental carbon (EC) and 38% of OC detected. In a Chinese regional background site on Hainan Island (550 km from Shenzhen), radiocarbon analysis demonstrated that the contribution of fossil sources to EC was 51% and OC was 30% (Zhang et al., 2014), with fossil fuel emissions transported from regional industrial cities. These findings demonstrate strong influences from both modern and fossil fuel emissions on carbonaceous $PM_{2.5}$ in the PRD.

Secondary organic aerosols (SOA) that are important contributors to PM mass are produced in the atmosphere through the photooxidation of VOCs from biogenic and anthropogenic precursors (Kroll and Seinfeld, 2008). The contributions of some precursors to SOA can be estimated using a SOA tracer approach, developed by Kleindienst et al. (2007), in which SOA is estimated based on the ambient concentration of SOA tracers by way of SOA tracer-to-SOA (or tracer-to-SOC) mass ratios determined in smog chambers. In this way, aromatic precursors (i.e. toluene) have been shown to contribute two-thirds of the total estimated SOC in the PRD region (Ding et al., 2012). This dominance reflects the significance of anthropogenic activities on SOA production in the PRD, with a minor contribution from biogenic VOCs like isoprene and monoterpenes.

The effects of short-term pollution control on the concentration and composition of atmospheric PM have been the focus of prior field studies in China. Vehicular and industrial emission controls were enforced during the 2008 Beijing Olympic Games, reducing PM_{10}, nitrogen oxides (NO_x), sulfur dioxide (SO_2), and non-methane VOC by 55%, 47%, 41%, and 57%, respectively (Wang et al., 2010). Simultaneously, black carbon (45%), OC (31%), and polycyclic aromatic hydrocarbons (PAH) decreased (Wang et al., 2011). Benzene, toluene, ethylbenzene, and xylenes (BTEX) decreased by $\geq$ 47% (Liu et al., 2009). In addition to emission controls, Gao et al. (2011) suggested that wind direction and precipitation also contributed to air pollutant reductions during this period. In another effort at reducing air pollution during sporting events, during the 16th Asian Games in 2010 in Guangzhou, emissions from power plants, industry, mobile sources, and construction activities were restricted and $PM_{2.5}$ decreased by 26%, while both SO_2 and NO_x dropped by >40% (Liu et al., 2013). These studies, focused predominantly on primary air pollutants, underscore the importance of controlling emission sources for improving air quality. However, the effect of pollution controls on the relative abundances of SOC from biogenic and anthropogenic origins has not previously been evaluated.

In 2011, Shenzhen hosted the 26th summer Universiade, an international sporting event, during which strict controls on emission sources were implemented to improve air quality, including reduction of: (i) emission of NO_x from power plants, commercial and industrial boilers, and motor vehicles; (ii) SO_2 emission by controlling fuel sulfur content, the flue gas from desulphurization units, and coal-fired power plants (iii) VOC emissions from industries including printing, adhesives, and furniture; (iv) PM and other air pollutants from construction sites, open biomass burning, and on-road vehicles (Dewan et al., 2016; Wang et al., 2014). In addition to the controls on emission sources in Shenzhen, industrial activities in neighboring cities were minimized. These conditions provided a unique opportunity to examine the effect of anthropogenic activities on the absolute and relative levels of primary and secondary $PM_{2.5}$ sources in Shenzhen.

In this study, we assess $PM_{2.5}$ concentrations, composition, and sources, both under strict emission controls (the "controlled period"), and after Universiade, when the controls were lifted (the "uncontrolled period"). Organic molecular markers and SOA tracers were measured in $PM_{2.5}$ collected over 24 days. $PM_{2.5}$ OC was apportioned by a molecular marker-driven CMB model (Schauer et al., 1996) and the SOC tracer method (Kleindienst et al., 2007). Tracers included levoglucosan for biomass burning (Simoneit et al., 1999), PAH and hopanes for fossil fuels including coal combustion (Zhang et al., 2008) and vehicle emissions (Schauer et al., 2002), odd-numbered n-alkanes for vegetative detritus (Rogge et al., 1993), and SOA products identified in chamber studies for biogenic-and aromatic-VOC derived SOA (Kleindienst et al., 2007). The resulting contributions of fossil and modern sources to OC and elemental carbon (EC) were compared to radiocarbon measurements of fossil and modern carbon over the same time period. This study examines differences in $PM_{2.5}$ and its sources during and after Universiade in 2011, providing new insight to the effect of primary emission controls on SOC.

2. Methods

2.1. Sampling

$PM_{2.5}$ samples were simultaneously collected from two sampling locations in Shenzhen, China from 12 August to 4 September 2011. Teflon and quartz filters (47 mm, Whatman) were used to collect $PM_{2.5}$ samples for mass and organic speciation, respectively. The Longgang (LG) site is located in the Longgang district of Shenzhen (22.70°N, 114.21°E, 161 m) on top of a 31-floor residential building at a height of 90 m from the ground level, about 500 m north of the main Universiade stadium. The Peking University (PU) site is located at Nanshan district of Shenzhen (22.60°N, 113.97°E, 50 m, 45 hm north of the LG site) atop of a graduate building at a height of 16 m. The samplers' heights provided well-mixed air masses at the point of sample collection. Detailed descriptions for both sampling site and sampling techniques are provided elsewhere (Dewan et al., 2016). Wind and visibility data during this study were obtained from the weather forecast at Shenzhen Bao'an International Airport (SGSZ), approximately 18 and 48 km east of PU and LG sampling sites, respectively. The difference in the altitudes of the two sites could have affected PM collected, so throughout this report we emphasize differences between controlled and uncontrolled periods at each site, rather than comparisons across the two sites.