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Quantification of long-term primary and secondary source contributions to carbonaceous aerosols

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ABSTRACT

Ambient fine particulate matter samples were collected during 2009–2013 in Chengdu, a megacity in western China, and the samples were speciated into organic carbon (OC), elemental carbon (EC), char-EC, soot-EC, eight carbon fractions, inorganic elements and water-soluble ions. Char-EC and soot-EC contribute to the better understanding of the sources and properties of EC. The highest levels of most carbon fractions were found in winter and May. The higher OC/EC ratio in winter suggests higher SOC fraction in winter, and higher char-EC/soot-EC ratio in May are the direct consequences of straw burning activities. Source contributions to $PM_{2.5}$ and carbonaceous aerosols were quantified using the ME2 receptor model. Major contributors to OC in $PM_{2.5}$ are vehicular exhaust (36.5%), coal combustion & straw burning (35.2%) and SOC (27.0%). The first two categories also contributed 51.4% and 49.3% of char-EC in $PM_{2.5}$. Vehicular exhaust dominated soot-EC, contributing 63.0% to soot-EC in $PM_{2.5}$. SOC contributed to high OC levels in winter due to the increase of precursor emissions and stable meteorological conditions. Coal combustion & straw burning show higher contributions to OC, char-EC and soot-EC in winter months and in May, which can be explained, in part, by increased coal consumption in winter and straw burning activities in May. Vehicular exhaust contributions are not strongly associated with monthly nor weekday-weekend patterns, resulting in that soot-EC vary insignificantly by month nor by weekday.

1. Introduction

The fractions of carbonaceous species in fine particulate matter ($PM_{2.5}$) are typically high, and are still growing in many areas due to stringent controls on sulfur and nitrogen oxides emissions which reduce inorganic and ionic species fractions (Zheng et al., 2002). Elemental carbon (EC) and organic carbon (OC) are two important categories of carbonaceous aerosols, largely due to their atmospheric abundance and direct/indirect impacts on the environment and health (Cooke et al., 1999; Lim et al., 2012; Crilley et al., 2016). BC (Black Carbon, generally is EC) is optically absorptive and can play an important role in climate change (IPCC, 2007; Novakov and Rosen, 2013; Bond et al., 2013; Lu et al., 2015). Light absorption by carbonaceous aerosols warms the atmosphere while reducing the amount of sunlight reaching surface (Kaufman et al., 2002; Niu et al., 2013), hence result in surface cooling (Ackerman et al., 2000; Rosenfeld, 2000; Nakajima et al., 2011; Ramanathan et al., 2001; Bréon et al., 2002). Another consequence, as suggested by recent studies, is flooding (Fan et al., 2015). OC is less absorptive than EC. However, OC may be comprised of thousands of different organic compounds, some of them are toxic and are even carcinogenic (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo−p−dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs)) (Cachada et al., 2012; Wei et al., 2014). As an important sub-category of OC, brown carbon (BrC) absorbs light, especially in the blue and ultraviolet (UV) region of the solar spectrum (Andreae and Gelencsér, 2006; Moosmüller et al., 2011). The sources of BrC include low-temperature combustion, biomass burning, and secondary organic aerosol formations (Kirchstetter et al., 2004).

To better characterize the environmental and health impacts of carbonaceous aerosols, a better understanding of their atmospheric

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behavior and formation pathways are critical. Carbonaceous aerosols are usually divided into different categories (Han et al., 2010). For example, by applying chemical measurement methods such as thermal optical reflectance (TOR) method, OC and EC can be separated and can be further subdivided into OC1, OC2, OC3, OC4, OP (used to correct OC and EC), EC1-OP, EC2, and EC3. The use of char-EC (equivalent to EC1-OP) and soot-EC (usually defined as EC2 + EC3) has also gained much attention because they can help explain the chemical/physical properties of EC (Cao et al., 2013). The ratio of Char-EC/soot-EC, normally varies with diverse source categories due to different combustion processes (Han et al., 2010), can be used to qualitatively identify possible sources of carbonaceous aerosols, and hence the environmental and climatic impacts of carbonaceous aerosols. In developing countries, related research are concentrated on the spatiotemporal variations of char-EC and soot-EC in urban areas (Kim et al., 2011) and exploring their source (Han et al., 2010), as well as using them to identify sources of other pollutants such as SOC (Diab et al., 2015). However, studies on char-EC and soot-EC study in developing counties are still scarce, due to the lack of long-term measurement data.

In this study, a long-term sampling campaign was carried out from 2009 to 2013 in Chengdu, a megacity in western China. $PM_{2.5}$ samples were collected in an urban sampling site. OC and EC fractions were measured, including OC1-4, EC1-3 and OP. Char-EC and soot-EC were also calculated accordingly. Such long term observational data sets are rare in developing countries, but are critically needed for understanding pollutant dynamics with respect to changing emissions.

An advanced receptor model, ME2 (Multilinear Engine 2), was employed in this study, along with char-EC/soot-EC ratio method, for source identification. Back-trajectory analysis was also used to identify potential locations of emission sources. Retrievals from the Moderate Resolution Imaging Spectroradiometer (MODIS) onboard NASA satellites were used to estimate fire counts and identify emission events. This work is strengthened by two key attributes: (1) long-term characterization of the physicochemical characteristics of carbonaceous species (including OC, char-EC, soot-EC and eight carbon fractions), along with the inorganic element (Al, Si, K, etc.) and soluble ionic species (NH_4^+, SO_4^{2-}, NO_3^-, etc.) in ambient $PM_{2.5}$ collected during 2009–2013 in a megacity in western China; (2) application of multiple methods to identify and quantify the source contributions of EC and OC. The above two key attributes are used to understand the factors impacting the monthly and seasonal variations in EC, OC and SOC formation.

2. Method

2.1. Sampling

As mentioned previously, the urban sampling site in this study is located in a western city of China, Chengdu, which is well-known for pandas. Chengdu is the capital city of Sichuan province, with a rapidly growing population of over 14 million, and it is an important center of economy, communication and transportation in western China. The sampling site is located on top of the environmental protection agency building (104°04′E, 30°35′N), at a height of about 25 m above the ground (Bi et al., 2007; Tian et al., 2014). The building is located at a mixed residential and commercial area with no industrial emission sources of atmospheric pollutants nearby (Fig. S1). Chengdu is located inside the Sichuan Basin, and on the eastern edge of the Tibetan Plateau. The subtropical monsoon climate in Chengdu is characterized by distinct seasons. The meteorological parameters in four seasons are provided in Table S1. Because of the basin's terrain and meteorology, severe stagnations are frequent, leading to high PM levels. Straw burning around Chengdu exacerbated the problem, particularly in May.

During the sampling campaign, $PM_{2.5}$ and their components, were measured over a more than 4-year period from January 2009 to March 2013. A medium-volume air samplers (TH-150, Wuhan Tian Hong, China) was used at a flow rate of 100 L/min with polypropylene (90 mm dia., Beijing Synthetic Fiber Research Institute, China) and quartz fiber filters (90 mm dia, 2500AQT-UP, Pall Life Sciences). Detailed information are provided in supplementary materials.

2.2. Chemical analysis

Carbon analysis based on quartz fiber filters were performed using a Desert Research Institute (DRI) Model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA), employing the IMPROVE-A thermal/optical reflectance (TOR) protocol (Chow et al., 1993). For quality assurance/control (QA/QC), the first sample was reanalyzed every ten samples to assure the precision was better than 2%; the analyzer was calibrated every day before analyses, and sufficient blank test were also conducted. Further QA/QC procedures are available at (Cao et al., 2003). The IMPROVE protocol provides three EC fractions, OP and four OC fractions, and the EC fractions were used to calculate char-EC (EC1 minus OP) and soot-EC (EC2 plus EC3) (Han et al., 2007, 2009). The analysis performed conform to the requirements of Certified reference materials standards (CRM, produced by National Research Center for Certified Reference Materials, China).

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) (IRIS Intrepid II, Thermo Electron) was used to determine the elemental compositions of the collected samples on polypropylene filters (90 mm in diameter, Beijing Synthetic Fiber Research Institute, China), including Al, Si, Ca, V, Cr, Mn, Fe, Co, Cu, Zn, As and Pb. We also use pre-treated reference materials to ensure that the measurement accuracies of all target elements fell within 5% of certified values. Major water soluble ions (e.g., NO_3^-, SO_4^{2-}, Na^+, K^+ and Mg^{2+}) collected on quartz-fibers were quantified using ion chromatography (DX-120, DIONEX). Standard solutions were prepared accordingly before ion analysis and repetitively measured three times. Low standard deviations of the measurement were observed. Further details on pre-treatment, chemical analysis and QA/QC methods are described in our previous work and other related studies (Shi et al., 2009; Kong et al., 2010; Xue et al., 2010; Chuang et al., 2016), as well as in the supplementary materials.

2.3. Modeling approaches

The Multilinear Engine 2 (ME2) model is an advanced factor analysis method (Paatero, 1999). It can be used to describe the contributions from p independent sources to all chemistry species in a given samples:

$$x_{ik} = \sum_{j=1}^{p} g_{ij} f_{jk} + e_{ik} \quad (1)$$

where x_{ik} is concentration of the kth compound in the ith sample; g_{ij} represents contribution of the jth source to the ith sample; f_{jk} represents mass contribution of the kth compound from the jth source; and e_{ik} is the residual (Hopke, 2003; Paatero et al., 2014).

The purpose of ME2 is to calculate a minimized Q value. The Q_{main} is defined as:

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