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Source contributions to carbonaceous species in $PM_{2.5}$ and their uncertainty analysis at typical urban, peri-urban and background sites in southeast China

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ABSTRACT

Determination of ^{14}C and levoglucosan can provide insights into the quantification of source contributions to carbonaceous aerosols, yet there is still uncertainty on the partitioning of organic carbon (OC) into biomass burning OC (OC_{bb}) and biogenic emission OC (OC_{bio}). Carbonaceous species, levoglucosan and ^{14}C in $PM_{2.5}$ were measured at three types of site in southeast China combined with Latin hypercube sampling, with the objectives to study source contributions to total carbon (TC) and their uncertainties, and to evaluate the influence of levoglucosan/OC_{bb} ratios on OC_{bb} and OC_{bio} partitioning. It was found reliably that fossil fuel combustion is the main contributor (62.90–72.23%) to TC at urban and peri-urban sites. Biogenic emissions have important contribution (winter, 52.98%; summer, 45.71%) to TC at background site. With the increase in levoglucosan/OC_{bb} ratios, the contribution of OC_{bio} is increased while OC_{bb} is decreased in a pattern of approximate natural logarithm at a given range.

1. Introduction

Carbonaceous species is a ubiquitous component of particulate matter, contributing 25–54% to the mass of $PM_{2.5}$ (particles with an aerodynamic diameter less than or equal to 2.5 μm) (Cao et al., 2007). They are generally divided into elemental carbon (EC) and organic carbon (OC), having important effects on climate change (Jacobson, 2001; Liousse et al., 1996; Menon et al., 2002; Sun and Ariya, 2006; Yu, 2000; Yu et al., 2001; Vasconcelos et al., 1994) and human health (Mauderly and Chow, 2008). Thus, knowledge of the carbonaceous aerosols is the key to understand the links between the aerosols, climate and environment.

In view of the significance of carbonaceous aerosols, information about the origin of carbonaceous species in aerosols is fundamental to devise the strategies for abating their effects. EC is essentially a primary pollutant originated from incomplete burning processes, while OC may be directly from the burning or indirectly formed through gas-to-particle conversion processes of volatile organic compounds (VOCs) (Seinfeld and Pandis, 1998). Sources of carbonaceous aerosols include fossil combustion (eg. gasoline, diesel, coal, natural gas, etc.), biomass burning (eg. woods, branches, leaves, cereal straws, cowdung patties, etc.), primary biogenic emissions (eg. plant debris, pollen, fungal spores, bacteria, etc.) and secondary organic aerosol formed from biogenic VOC (eg. isoprene, terpenes, terpenoid alcohols, n-carbonyls, etc.). Unfortunately, the detailed source partitioning and quantification is still poorly understood in China due to the complexity of sources (Bauer et al., 2002; Kanakidou et al., 2005; Schauer et al., 1996).

Recently, source specific tracers have provided new insights into the studies of source contributions to carbonaceous aerosols. Radiocarbon (^{14}C) analysis could differentiate the contemporary and fossil carbon in aerosol because ^{14}C has been depleted in fossil fuels, and ^{14}C in the contemporary carbonaceous sources has the similar or higher levels than those in CO_2 in the present-day atmosphere (Currie, 2000). This isotopic method has been used successfully in the partitioning of carbonaceous aerosols between contemporary and fossil carbonaceous sources in China (Huang et al., 2010), Japan (Fushimi et al., 2011), Nordic region (Genberg et al., 2011; Szidat et al., 2009; Yttri et al., 2011a,b), Spain (Minguillón et al., 2011) and Switzerland (Szidat et al., 2006). Levoglucosan (Lev) is a thermal degradation product of cellulose during the biomass burning, and is widely used as a molecular tracer for carbonaceous emission from

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the biomass burning (Fraser and Lakshmanan, 2000). The contemporary organic carbonaceous sources can be further quantitatively partitioned into biomass burning and biogenic emissions combined the determination of Lev with the appropriate ratios of Lev/OC_{bb} (OC from biomass burning). Those pioneering insights give a comprehensive understanding to the studies of source apportionment of carbonaceous aerosols. Nevertheless, there are still some uncertainties on the quantification of OC_{bb} and biogenic emissions OC (OC_{bio}) by the ratios of Lev/OC_{bb}.

In recent decade, the southeast coast of China has been undergoing a rapid pace of urbanization and industrialization, consequently accompanied by tremendous emissions of air pollutants and plummeting air quality (Chan and Yao, 2008; He et al., 2002). However, the paucity of the studies of source apportionment of carbonaceous aerosols in this region will constrain the formulation of effective air pollution abatement strategies. Therefore, typical urban, peri-urban and background sites were selected in southeast Fujian Province, China, aiming to study the source contributions to carbonaceous species in $PM_{2.5}$ and their uncertainties combined the determination of ^{14}C and Lev in aerosol with Latin hypercube sampling. Besides, the influence of the ratios of Lev/OC_{bb} on the quantification of OC_{bb} and OC_{bio} was also studied.

2. Methods

2.1. Site description

Three sites were selected in Fujian Province in southeast China (Fig. 1), representing typical urban, peri-urban and background sites respectively. The urban and peri-urban sites are located in Xiamen City, which has a sub-tropical oceanic monsoon climate with long and hot summers (29.3 ± 2.6 °C, relatively humidity 75.4 ± 11.1%) and short and mild winters (14.2 ± 3.4 °C, relatively humidity 80.7 ± 14.9%). Siming (SM) site (N 24.4768°, E 118.1519°) is on the roof of a building (18 m above ground) in a primary school in Siming District, Xiamen City, and this urban site is surrounded by schools, streets, residential and commercial districts. Jimei (JM) site (N 24.6103°, E 118.0594°) is on the roof (8 m above ground) of a building in Institute of Urban Environment, Chinese Academy of Sciences in Jimei District, Xiamen City. There are freeways, schools, residential districts, construction sites and Xinglin Bay around this peri-urban site. The background site (N 25.7131°, E 118.1052°) is on the top of a mountain (1653 m above ground) in Jiuxianshan (JXS) Scenic Area in Dehua Country, about 120 km to the north of Xiamen City. There is abundant subtropical vegetation in this sparsely populated mountainous region. The average temperature at the background site is 5.8 °C in winter and 18.4 °C in summer.

2.2. Sample collection

Twenty-four-hour (08:00 to 08:00, local time) $PM_{2.5}$ samples were collected on tandem-filters (one quartz fiber filter behind another) (Whatman Ø88 mm, UK) annealed previously at 800 °C for 2 h, using a medium-volume sampler (Tianhong TH-150C III, China) at a flow rate of 100 L min^{-1} at each site during winter (5–14 January, 2011) and summer (1–10 August, 2011). This sampler has two cutsizes of 10 and 2.5 μm, and only $PM_{2.5}$ was analyzed in this study. All the filters were weighed before and after the sampling to get the aerosol mass after equilibrating under constant temperature (25 ± 1 °C) and relative humidity (52 ± 1%) for 24 h. A total of 60 $PM_{2.5}$ samples were obtained during the sampling campaign, wrapped up with aluminum foils, sealed in plastic ziplock bags and stored at −20 °C prior to analysis. The meteorological parameters, including ambient temperature (T), relative humidity (RH) and wind speed (WS) were also recorded during the sampling campaign.

2.3. OC and EC analyses

OC and EC analyses were conducted on a 2.0 cm^2 quartz filter punch using a thermal optical transmittance (TOT) instrument (Sunset Lab Model-4, USA), operating following the National Institute for Occupational Safety and Health (NIOSH) protocol (Birch and Cary, 1996). Detailed analyzing process is presented in the paper of Niu et al. (2012). The concentrations of OC and EC in two blank filters were also measured, which was 0.2 μg C cm^{-2} and nearly zero, respectively. The positive sampling artifacts for OC were corrected, which was 29.04 ± 12.06% of the concentration in the front quartz filter. The artifact in this study was higher than those sampling at the roadside (7.5 ± 2.8%) and tunnel (12.9 ± 4.1%) in Taiwan (Chen et al., 2010).

2.4. Lev analysis

Molecular tracer (Lev) was analyzed according to the method described by Wan and Yu (2006). In brief, 1/8 of the quartz fiber filter was extracted by a 10 mL methanol in an ultrasonic bath for 40 min. The extract was filtered through a 0.45 μm Teflon filter, and then was evaporated to dryness in a gentle nitrogen atmosphere. The residue was redissolved by a 1 mL aqueous solution of 5 mM ammonium acetate. A volume of 100 μL sample solution was injected into a high performance liquid chromatography (LC-20AD, Shimadzu, Japan)-tandem a triple quadrupole/linear ion trap mass spectrometer (API 3200 Q-TRAP, Applied Biosystems, USA), equipped with an electrospray ionization (ESI) source, to quantify the concentrations of molecular tracer operated in the positive ion mode. The column for separation was a C_{18} column (4.6 mm i.d. × 100 mm length, 2.6 μm), which was kept at a temperature of 30 °C, and a flow rate of 0.5 mL min^{-1}. Isocratic elution was carried out in a mobile phase consisting of 92% 2.2 mM aqueous ammonium acetate and 8% methanol. The $[M + Na]^+$ ions were selected for monitoring and quantification.

The standard of Lev was purchased from the J&K Scientific, China. Calibration curve was obtained by different concentrations (0, 5, 10, 20, 50 and 100 ng g^{-1}) of Lev standard solutions. The blank filters spiked with known masses of standard

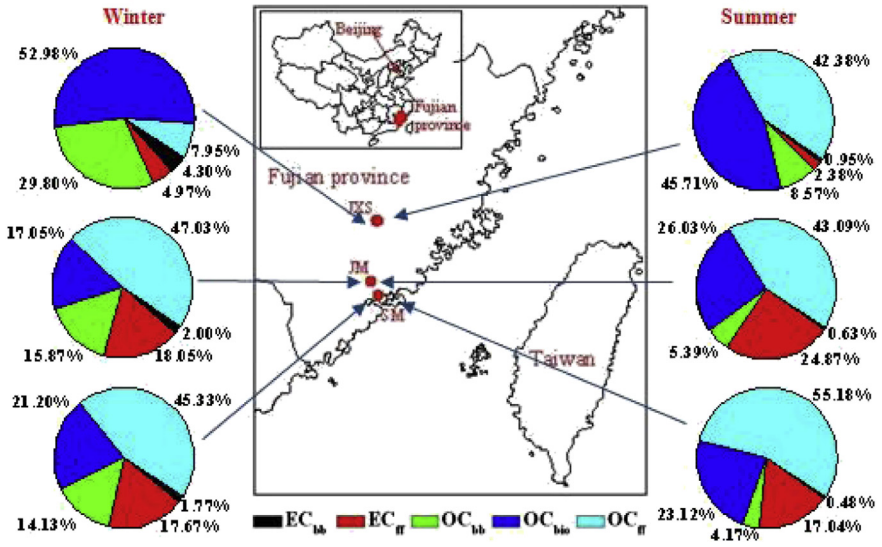

Fig. 1. Best estimated contributions of different carbonaceous components to TC at the urban (SM), peri-urban (JM) and background (JXS) sites in winter and summer. Best estimated contributions indicate the 50th percentile of the data obtained from the Latin hypercube sampling with the performance of 3000 random sets of variables (the same below). EC_{bb} and EC_{ff} indicate elemental carbon (EC) contributed from biomass burning and fossil fuel combustion, respectively. OC_{bb}, OC_{bio} and OC_{ff} indicate organic carbon (OC) contributed from biomass burning, biogenic emission and fossil fuel combustion, respectively (the same below).