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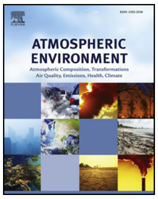

Stable carbon isotopes and levoglucosan for $PM_{2.5}$ elemental carbon source apportionments in the largest city of Northwest China

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ABSTRACT

Stable carbon isotopes provide information on aerosol sources, but no extensive long-term studies of these isotopes have been conducted in China, and they have mainly been used for qualitative rather than quantitative purposes. Here, 24 h $PM_{2.5}$ samples ($n = 58$) were collected from July 2008 to June 2009 at Xi'an, China. The concentrations of organic and elemental carbon (OC and EC), water-soluble OC, and the stable carbon isotope abundances of OC and EC were determined. In spring, summer, autumn and winter, the mean stable carbon isotope in OC ($\delta^{13}C_{OC}$) were −26.4 ± 0.6, −25.8 ± 0.7, −25.0 ± 0.6 and −24.4 ± 0.8‰, respectively, and the corresponding $\delta^{13}C_{EC}$ values were −25.5 ± 0.4, −25.5 ± 0.8, −25.2 ± 0.7 and −23.7 ± 0.6‰. Large $\delta^{13}C_{EC}$ and $\delta^{13}C_{OC}$ values in winter can be linked to the burning coal for residential heating. Less biomass is burned during spring and summer than winter or fall (manifested in the levels of levoglucosan, i.e., 178, 85, 370, 935 $ng\ m^{-3}$ in spring, summer, autumn, and winter), and the more negative $\delta^{13}C_{OC}$ in the warmer months can be explained by the formation of secondary organic aerosols. A levoglucosan tracer method combined with an isotope mass balance analysis indicated that biomass burning accounted for 1.6–29.0% of the EC, and the mean value in winter (14.9 ± 7.5%) was 7 times higher than summer (2.1 ± 0.4%), with intermediate values of 6.1 ± 5.6 and 4.5 ± 2.4% in autumn and spring. Coal combustion accounted for 45.9 ± 23.1% of the EC overall, and the percentages were 63.0, 37.2, 36.7, and 33.7% in winter, autumn, summer and spring respectively. Motor vehicles accounted for 46.6 ± 26.5% of the annual EC, and these contributed over half (56.7–61.8%) of the EC in all seasons except winter. Correlations between motor vehicle-EC and coal combustion-EC with established source indicators (B(ghi)P and As) support the source apportionment results. This paper describes a simple and accurate method for apportioning the sources of EC, and the results may be beneficial for developing model simulations as well as controlling strategies in future.

1. Introduction

Carbonaceous aerosols are important component of fine particulate matter ($PM_{2.5}$, particles ≤ 2.5 μm in diameter), and carbon-containing compounds concentrations can reach 20%–30% of the $PM_{2.5}$ mass in urban China (Cao et al., 2012). Carbonaceous aerosols are typically classified into organic carbon (OC) and elemental carbon/black carbon (EC/BC). In general, EC is a primary pollutant derived exclusively from the incomplete combustion of carbon-containing substances, especially fossil fuels and biofuels, and from forest and agricultural fires and other combustion related sources (Bond et al., 2013; Jacobson, 2001). In contrast, OC is a complex mixture of primary OC (POC) and secondary OC (SOC), which can be directly emitted from various combustion processes or produced from atmospheric reactions involving gaseous organic precursors (Pöschl, 2005; Turpin and Huntzicker, 1995). More than simply being components of $PM_{2.5}$, carbonaceous aerosols can substantially affect climate, air quality, visibility and impact human health. While it is important to investigate the spatial and temporal variations in these particles, they are derived from a variety of sources that can change over space and time, and as a result it can be challenging to identify their sources and even harder to quantify the impacts (Liu et al., 2013). This has led researchers to use increasingly

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sophisticated models or combined methods to quantify the contributions of individual sources to the aerosol populations.

For source apportionment studies, receptor-oriented models (positive matrix factorization models (PMF), chemical mass balance models (CMB) and UNMIX, etc.), source-specific marker method (also called Aethalometer method, quantified contributions based on light absorption coefficient in the earlier study by Sandradewi et al. (2008), but not confined to the Aethalometer data only) and various multivariate models are the conventional techniques. Among these, receptor models have been in broad use for the source types quantification/assessment works, which facilitate the source contributions based on atmospheric concentrations. The marker methods (e.g., levoglucosan or stable carbon isotopes/radiocarbon, etc.) are advantageous from the point of view that they do not require many samples or extensive data sets and are quite straightforward (Salma et al., 2017; Szidat et al., 2006).

Ratios of stable carbon isotopes measured as delta-^{13}C (δ^{13}C, see below for formula) can provide information about the sources of aerosols, and these isotopes have proven to be useful geochemical markers (López-Veneroni, 2009; Widory, 2006), while radiocarbon (^{14}C) provides information on the influence of fossil fuel, biomass burning and biogenic emissions on carbonaceous aerosols (Andersson et al., 2015; Szidat et al., 2006). In particular, they have been applied in various types of environmental studies to identify emission sources (Andersson et al., 2015; Cao et al., 2011, 2013; Kawashima and Haneishi, 2012; Liu et al., 2013; Salma et al., 2017; Zhang et al., 2015). For example, measurements of δ^{13}C in both OC and EC, led Cao et al. (2013) to conclude that fossil fuel combustion was the dominant source for carbonaceous $PM_{2.5}$ in Shanghai. Earlier studies by Cao et al. (2011) using the same approach showed that northern cities in China were strongly impacted by coal combustion during winter. To date, measurements of carbon isotopes and other substances have been combined to provide new insights into characteristics of atmospheric aerosols from different sources. For example, levoglucosan (1,6-anhydro-b-D-glucopyranose), which is a sugar anhydride produced during the combustion of cellulose (Simoneit et al., 1999), is a marker commonly used to indicate biomass burning (Liu et al., 2013). Some studies coupled ^{14}C and levoglucosan marker method for source apportionment of carbonaceous aerosols (Andersson et al., 2015; Liu et al., 2013, 2017; Salma et al., 2017). Some δ^{13}C studies have conducted during biomass burning episodes, and based on the assumption that the aerosols were only affected by biomass burning, it was possible to estimate the contributions from the burning of C3 versus C4 plants to the fine PM (Cao et al., 2016; Mkoma et al., 2014). Although source apportionments based on δ^{13}C data hold considerable promise, this approach is still being developed.

Xi'an, the largest city in northwest China, is located on the Guanzhong Plain, which is surrounded by Qingling Mountains to the south and loess plateau to the north. Recently, Xi'an has experienced some of the worst air pollution among China's cities (Cao et al., 2012). The Guanzhong Plain is one of the major agricultural production areas for wheat and corn in China, and agricultural biomass burning (especially the post-harvest burning of crop residues to clear farmland) and the burning of biomass for domestic purposes are common sources of pollutants in this region, especially in autumn and winter. Previous work showed that biomass burning contributed to 5.1–43.8% of the OC in Xi'an (Zhang et al., 2014a). In addition to biomass burning, emissions from the combustion of fossil fuels, such as coal, gasoline, and diesel, are among the major sources for the carbonaceous aerosols. For example, Cao et al. (2005) found that 44% of the total carbon was from the exhaust emitted by gasoline engines, and 44% was from coal burning during winter; these results were based on absolute principal component analysis of eight thermally-derived carbon fractions.

Although studies on stable carbon isotope analysis of aerosol have been conducted at several sites in China (Cao et al., 2011, 2013, 2016; Dai et al., 2015), no extensive, long-term observations have been made, and to this point, stable carbon isotope analyses of atmospheric particles have been used more for qualitative studies of sources rather than quantitative analysis. Here, we measured the concentrations of selected carbonaceous components and the stable carbon isotope abundances of OC and EC in $PM_{2.5}$ collected in Xi'an over an entire year. The objectives of this study were (1) to investigate seasonal variations of OC, EC, WSOC as well as stable carbon isotope composition; (2) to develop a combined ^{13}C stable isotope and levoglucosan tracer method in source apportionment for EC; and (3) to quantitatively apportion the contributions from different sources for EC mass loadings using this method and to characterize the seasonal changes in impacts from these sources.

2. Experimental

2.1. Sampling site and sample collection

The sampling site was located in the southeastern part of downtown Xi'an (34.23°N, 108.88°E) where there were no major industrial or constructive activities nearby. More detailed descriptions of the site may be found in previous publications (Xu et al., 2012; Zhang et al., 2014a). An air sampler (Model TE-6001-2.5-I-$PM_{2.5}$ SSI, Tisch Inc., USA) was deployed on the rooftop of the Institute of Earth Environment, Chinese Academy of Sciences, ~10 m above ground level. A total of 58 $PM_{2.5}$ filter samples were collected from July 2008 to June 2009. The high-volume air sampler operated at a flow rate of 1.1 $m^3\,min^{-1}$, and the sample substrates were 20 × 25 cm QM-A quartz-fiber filters (Whatman Ltd., Maidstone, UK), which were preheated in 900°Cmuffle furnace for at least 3 h to avoid inherent carbonaceous contaminants before using. Samples were collected every sixth day starting at 10:00 China standard time (UTC + 8), and each sample was run for 24 h.

Based on the meteorological characteristics and the dates of the traditional residential heating period (mid-November through mid-March), the period from 15 November to 14 March was designated as winter, spring was 15 March to 31 May, summer was 1 June to 31 August, and autumn was 1 September to 14 November (Zhang et al., 2014a,b). In addition, four filed blank filters in each season were collected by exposing filters in the sampler without drawing air through them; these were used to account for any artifacts introduced during the sample handling process.

2.2. Carbon and stable isotope analyses

Portions of the quartz filters (0.526 cm^2 punches) were analyzed for OC and EC using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., USA) following the IMPROVE_A protocol (Chow et al., 2007). The method detection limits (MDLs) for OC and EC were below 0.41 and 0.03 $\mu g\,cm^{-2}$, respectively. Replicate measurements were made for one in ten samples, and the difference between replicates was < 10% for both OC and EC. Quality assurance/quality control (QA/QC) procedures for these analyses have been described by Cao et al. (2003).

Another aliquot of the sample filters was extracted with 30 mL pure water under ultrasonic agitation/extraction for three times, and filtered through a polytetrafluoroethylene filter to remove the particles and filter debris. The water extract was analyzed for water-soluble organic carbon (WSOC) using a TOC-L CPH Total Carbon Analyzer (Shimadzu Corp., Japan). The difference between OC and WSOC was considered as water-insoluble OC (WIOC).

The stable carbon isotope composition of OC and EC was determined from carbon dioxide (CO_2) evolving at two temperatures and detected with a Finnigan MAT-251 ratio mass spectrometer (Thermo Electron Corporation, Burlington, ON, Canada). The isolation of OC and EC in the study followed up by our previous studies (Cao et al., 2011; Ho et al., 2006). Briefly, the particulate carbon captured on the quartz-fiber filters was oxidized to CO_2 with CuO catalyst grains by first combusted at 375 °C for 3 h (no oxygen under vacuum). The CO_2