

GEOSCIENCES

Special Topic: Air Pollution and Control

New insights into the sources and formation of carbonaceous aerosols in China: potential applications of dual-carbon isotopes

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Carbonaceous aerosols account for 20–50% of total fine particulate matter (PM_{2.5}, particles with a diameter of 2.5 μm or less) mass concentration in polluted urban atmospheres and can affect atmospheric chemistry, air quality, environmental health and Earth's radiation balance [1]. Bulk carbonaceous aerosol is usually divided into sub-fractions such as organic carbon (OC) and black carbon (BC) or elemental carbon (EC) [1]. OC is either directly emitted into the atmosphere as primary OC (POC) or formed via gas-to-particle conversion as secondary OC (SOC) [1]. EC arises almost exclusively from incomplete fossil-fuel combustion or biomass burning [1]. Recent studies have revealed that, in addition to secondary inorganic aerosol [e.g. (NH₄)₂SO₄, NH₄NO₃ and NH₄HSO₄], secondary organic aerosol (SOA) is an important, or sometimes even the dominant, contributor to PM_{2.5} during severe haze episodes in China [2].

¹⁴C-BASED SOURCE APPORTIONMENT IN CHINA

China, the largest global consumer of energy, is one of the most important source regions for carbonaceous aerosols, which make a significant contribution to particulate matter (PM) loading during haze events in Beijing and other Chinese megacities. Efforts to reduce atmospheric carbonaceous aerosols during haze events require knowledge of their sources and atmospheric formation processes. However, the complexity of these poses a significant challenge to both scientists and policy makers. Radiocarbon (¹⁴C)-based analyses provide

a powerful tool to quantitatively determine fossil and non-fossil sources of carbonaceous aerosols in different geographical locations; this methodology has been recently applied to fine aerosols in China, where PM_{2.5} levels may be up to an order of magnitude greater than those in many urban locations in Europe and USA. As shown in Fig. 1, fossil-fuel combustion is the most important contributor (average 67%) to the EC component of aerosols at urban study sites throughout China, regardless of seasonality. However, the fossil contribution to EC decreases to around 35% at background sites (e.g. Hainan, China), which is apparently influenced by seasonally varying biomass-burning emissions from South Asia and/or South China [3].

By combining ¹⁴C and organic marker measurements, the dominant fossil-fuel component may be determined, and is found to be significantly different between warm and cold periods [4]. During cold seasons in Beijing, coal combustion accounted for 33% of fossil EC with the remainder from liquid (e.g. gasoline) fossil-fuel combustion, whereas, in warm periods, more than 90% of fossil EC was related to traffic emissions [4]. In contrast to the source characteristics of EC, the ¹⁴C results demonstrate that non-fossil emissions generally are important (or even dominant) contributors to OC for almost all cases and seasons including the highly polluted and other places (e.g. Xi'an, Beijing, Wuhan, Shanghai and Guangzhou) with a mean contribution of 56%. Such high non-fossil contribution to OC has been recently also reported in China including several urban areas by a modelling study [5].

The abundant non-fossil components in urban organic aerosols may be associated with seasonally dependent biomass burning/biogenic emissions with primary and/or secondary origins as well as cooking activities (which is the subject of ongoing studies). A unique feature occurred during a wintertime haze episode in Beijing: fossil contributions to OC were greater than non-fossil ones. With multiple state-of-the-art analytical techniques (e.g. aerosol mass spectrometry, accelerator mass spectrometry and gas chromatography/time-of-flight mass spectrometry), we determined that this fossil OC is mostly secondary in nature [2], although the detailed atmospheric mechanisms responsible for the enhancement in fossil-derived SOA formation remain unclear.

FUTURE RESEARCH DIRECTIONS FOR ISOTOPE ANALYSIS OF AEROSOLS

Recent studies have shown that secondary inorganic and organic aerosol species are the most important components driving high levels of fine particulate matter in China. However, the chemical characteristics and formation mechanisms of SOA in China have not been well studied or documented in the literature. Here, we propose measurements of dual-carbon isotopes (¹⁴C and ¹³C) as a new approach to better understanding the sources and formation processes of organic aerosols:

- (i) The identification of a dominant modern source to OC, obtained from direct ¹⁴C analyses of OC or its

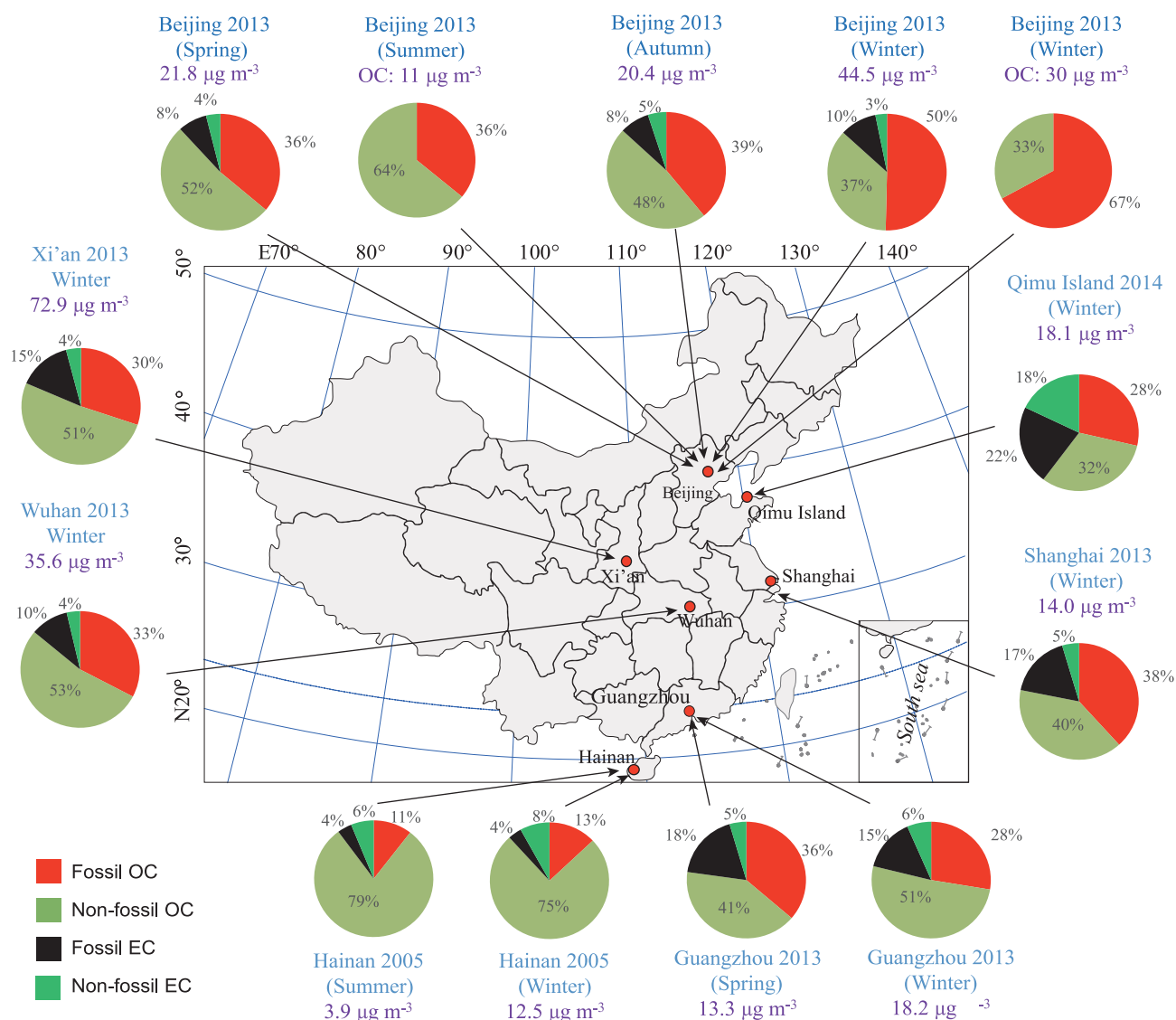


Figure 1. Fossil and non-fossil contributions to OC and EC in $\text{PM}_{2.5}$ samples from different locations of China. Total carbon (TC) mass concentrations are also shown here. Data are obtained from previous studies on ^{14}C -based source apportionment across China [2,3,6–9].

sub-fractions such as water-soluble OC, seems to contradict the concept of anthropogenic pollution as the most important source to carbonaceous aerosols, as identified by ^{14}C measurement of EC and other high time-resolution studies (e.g. aerosol mass spectrometry-related studies). This discrepancy may be explained by enhancement of SOA formation from biogenic/biomass burning precursors by anthropogenic emissions, which should be a focus of future studies. An obvious distinction of SOA between fossil and non-fossil precursors can be obtained using a combination of aerosol

mass spectrometry data and high time-resolution (e.g. 1–3 h) ^{14}C analyses. In addition, ^{14}C measurements of SOA tracer compounds (e.g. oxalic acid) and other classes of compounds with either primary or secondary nature (e.g. HUmic Like Substances or HULIS) will provide direct constraint on their origins.

(ii) Current atmospheric models continue to underestimate the mass concentration of secondary OC, especially within the polluted atmospheric boundary layer. A likely cause of this discrepancy between observation and model is difficulties in understanding the complex

and mixed atmospheric processes (e.g. aging, SOA formation in the gaseous or aqueous phase). ^{13}C measurements at a molecular level, together with traditional techniques (e.g. measurement of inorganic and organic markers), provide a powerful tool to characterize the sources, atmospheric-formation processes and fates of organic aerosols [10]. The stable carbon isotopic composition ($\delta^{13}\text{C}$) will change according to the (so-called) kinetic isotope effects (KIEs) inherent in different processes, such as volatilization, chemical reaction, aging and gas-particle

partitioning, in which lighter and heavier isotopes differ (slightly, but measurably) in their behaviour. ^{13}C measurements in bulk or individual organic compounds (e.g. oxalic acid, levoglucosan, lipid compounds and 2-methyltetrols) from experimental and/or field studies can differentiate various atmospheric processes and determine the degree of atmospheric aging of organic aerosols. For instance, $\delta^{13}\text{C}$ values of low-molecular-weight dicarboxylic acids were heavily enriched compared to those of high-molecular-weight dicarboxylic acids in aerosols from the East Asian continental outflow [11]. Such a trend suggests that smaller dicarboxylic acids are not produced from photochemical breakdown of longer-chain diacids or fatty acids, but from the aqueous-phase processing of precursors or intermediates and the subsequent gas-particle partitioning [11]. However, the sources of dicarboxylic acids that are often subject to aqueous processing remain unknown. Here, we propose that the dual measurements of ^{13}C and ^{14}C isotopes at a molecular level (e.g. dicarboxylic acids) could provide detailed insights into the

sources and chemical processes of organic aerosols.

Therefore, dual-carbon (^{14}C and ^{13}C) isotope analysis of bulk and individual compounds in atmospheric aerosols have the potential to significantly enhance source apportionment and improve our understanding of air-pollution-formation mechanisms, which can be further integrated in atmospheric models to reduce the uncertainty in air-quality models.

FUNDING

This work was supported by the National Natural Science Foundation of China (91644103, 41603104, 41625014).

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National Science Review

4: 804–806, 2017

doi: 10.1093/nsr/nwx097

Advance access publication 11 August 2017