Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels

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ABSTRACT

Stable carbon isotope ratios were determined for the OC and EC fractions of PM$_{2.5}$ collected from 14 Chinese cities in January and June/July of 2003. The period-averaged isotope values ($\delta^{13}$C) varied from $-26.90_{\pm0.50}$ to $-23.08_{\pm0.50}$% for OC and $-26.63_{\pm0.54}$ to $-23.27_{\pm0.54}$% for EC. A strong correlation ($R^2 = 0.70, p < 0.0001$) between $\delta^{13}$COC and $\delta^{13}$CEC was found in winter but not summer. Winter vs. summer differences for $\delta^{13}$COC and $\delta^{13}$CEC were greater for the seven northern cities ($\sim 1$ to $3_{\%}$) than the seven southern cities ($<1_{\%}$). Comparisons with isotopic signatures of putative sources suggest that the carbonaceous PM$_{2.5}$ was mainly from fossil fuels, especially coal combustion and motor vehicle emissions; the northern cities in particular were strongly impacted by coal combustion during winter. Studies of stable carbon isotopes in OC and EC are potentially useful for identifying sources for carbonaceous PM$_{2.5}$, and this approach may be a useful new tool for the study of air pollution.

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1. Introduction

Stable carbon isotopes ($^{13}$C and $^{12}$C) have proven to be useful geochemical markers, and these isotopes were first applied to studies of air pollution beginning in the 1980s (e.g., Chessett et al., 1981). Cachier et al. (1985, 1986) used carbon isotopes and studies of air pollution beginning in the 1980s (e.g., Chesselet geochemical markers, and these isotopes were first applied to aerosols from Chinese cities). The present study, stable carbon isotope abundances were determined for the OC and EC fractions of particulate matter with aerodynamic diameters less than 2.5 $\mu$m (PM$_{2.5}$) from fourteen cities in China. The studies were conducted to (1) evaluate spatial variations and summer versus winter differences in carbonaceous PM$_{2.5}$ and (2) identify the most probable sources for this material.

2. Experimental

2.1. Sampling sites and sample collection

Fourteen cities, including several megacities, in China were selected to represent aerosol populations from economically developed and developing regions of the country; these cities covered most of the country’s non-mountainous urban regions (Fig. 1). The cities included seven in northern China: Beijing, Changchun, Jinchang, Qingdao, Tianjin, Xi’An, and Yulin; and seven in southern China: Chongqing, Guangzhou, Hong Kong, Hangzhou, Shanghai, Wuhan, and Xiamen. Detailed descriptions of these sites can be found in Cao et al. (2007).

In each city, 24 h PM$_{2.5}$ sampling was performed both in the winter (January 6 to 20) and summer (June 3 to July 30) of 2003. Samples were collected on 405 pre-combusted (900 °C, 3 h) 47 mm diameter QM-A quartz-fiber filters (Whatman Ltd, Maidstone, UK) using a mini-volume air sampler (Airmetrics, Eugene, OR, USA) which operated at a flow rate of 5 L min$^{-1}$.

2.2. Carbon and stable isotope analyses

PM$_{2.5}$ samples were first analyzed for the OC and EC fractions following the IMPROVE (Interagency Monitoring of PROtected Visual Environments) thermal/optical reflectance (TOR) protocol.
These analyses were conducted using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., California, CA, USA). Due to the insufficient carbon loadings on single filters, composites of two to six samples were prepared for isotopic analysis based on the OC and EC contents of the individual samples. In preparing the samples for the analysis, carbonate was removed from the filters by treatment with hydrochloric acid. The carbon remaining on the substrates, which included both OC and EC, was then oxidized to CO$_2$ by dry combustion at 375 °C for 3 h. A series of cold traps was used to collect the CO$_2$ produced from OC by this treatment, and the CO$_2$ was quantified by manometry. The stable carbon isotope composition of the CO$_2$ was then determined as $\delta^{13}$COC (see below) with the use of a Finnigan MAT-251 ratio mass spectrometer (Ho et al., 2006). These analyses were conducted using a DRI EC, was then oxidized to CO$_2$ by dry combustion at 375 °C for 3 h; the CO$_2$ produced by this treatment was quantified as the EC fraction and its isotopic composition determined as $\delta^{13}$CEC. Samples were analyzed at least in duplicate, with a maximum difference in carbon isotopes of 0.3‰ between replicates.

Isotopic abundances were expressed relative to the international standard V-PDB as follows:

$$\delta^{13}C = \left( \frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1 \right) \times 1000$$

Total carbon (TC) was calculated as the sum of OC plus EC, and $\delta^{13}$CTC was calculated as follows:

$$\delta^{13}CTC = (OC/TC) \times \delta^{13}COC + (EC/TC) \times \delta^{13}CEC$$

3. Results and discussion

3.1. Variations in the stable carbon isotope ratios of carbonaceous aerosols

Average $\delta^{13}$C values in OC, EC and TC during the two sampling periods are summarized in Table 1. $\delta^{13}$COC varied by 3.54‰ during winter from −26.62‰ in Hong Kong to −23.08‰ in Changchun and by 1.61‰ during summer from −26.90‰ in Beijing and Xian to −25.29‰ in Wuhan. Compared with $\delta^{13}$CEC, the variations in $\delta^{13}$CTC were relatively small, differing by 2.83‰ during winter from −26.10‰ in Guangzhou to −23.27‰ in Changchun and by 1.36‰ in summer from −26.63‰ in Xiamen to −25.27‰ in Jinchang.

Studies by Ho et al. (2006) and Huang et al. (2006) have shown that the variations in $\delta^{13}$COC from urban atmospheres (~2 to 4‰) are usually larger than those of $\delta^{13}$CEC (~1‰), and this was the case in our study. Normally, EC is unreactive and so $\delta^{13}$CEC is likely to preserve the characteristics of the primary sources (Huang et al., 2006). On the other hand, OC can be modified by various reactions after emission, and so $\delta^{13}$COC values are expected to change with time.

In addition, the $\delta^{13}$CEC values were generally heavier (i.e., less negative) than the corresponding $\delta^{13}$COC values (Table 1). The differences between isotope ratios ($\delta^{13}$CEC-$\delta^{13}$COC) in Jinchang and Hong Kong were relatively large, close to 1‰ for both seasons. These findings can be explained by the results of a study by Ho et al. (2006) who found that photochemical reactions and the accumulation of biogenic materials both lead to lighter (i.e., less negative) $\delta^{13}$COC values.

A plot of $\delta^{13}$COC versus $\delta^{13}$CEC (Fig. 2a) shows that the isotopic composition of OC and EC in winter were strongly correlated ($R^2 = 0.71$, $p < 0.0001$). Furthermore, the slope of the $\delta^{13}$COC versus $\delta^{13}$CEC plot approaches unity, and this implies that the carbon isotope ratios of OC and EC in the wintertime samples are similar. Assuming that EC maintains the isotopic signature ($\delta^{13}$CEC) of the original emissions, one can conclude that the isotopic composition of OC was not significantly modified in the winter samples, and therefore OC and EC evidently originated from the same combustion sources during winter.

The relationship between $\delta^{13}$COC and $\delta^{13}$CEC did not hold in summer; in fact the summertime $\delta^{13}$COC and $\delta^{13}$CEC values were not correlated ($R^2 = 0.1$, $p = 0.072$). This can be explained by the impacts of secondary organic aerosol (SOA) formation on OC and its attendant effects on $\delta^{13}$COC. Along these lines, Cao et al. (2007) showed that SOA accounted for 45% of the OC in seven northern cities and 53% in seven southern cities in China during summer, but the percent contributions were considerably lower during winter (30% and 33%, respectively). There is some evidence for a light carbon preference for SOA; for example, Irie et al. (2006) reported that the $\delta^{13}$C of SOA produced in laboratory studies was in the range of −32.2‰ to −32.9‰. Therefore, the more negative $\delta^{13}$COC values in the northern cities during summer (Table 1), may be at least partly explained by the formation of SOA with a preference for the lighter carbon isotope.

3.2. Seasonal variations of the carbon isotopes in OC and EC

The distributions of $\delta^{13}$COC and $\delta^{13}$CEC in 14 cities can be seen to plot in two distinct areas (rectangles) in Fig. 2. In winter (Fig. 2a), most of

![Fig. 1. Locations of fourteen cities in China where samples were collected.](Image)
northern cities moved to Area II, and some of the 
values for the southern cities became even more negative than the 
values bounded by Area II. None of the summer time observations 
were higher than the average for the northern cities both in winter and summer, and winter-to-summer difference at Chongqing (0.7‰) was greater than for all of the southern cities except Xiamen. Okuda et al. (2002) used the 13C signal in polycyclic aromatic hydrocarbons (PAHs, $-22.9\%$ to $-27.2\%$) to demonstrate that emissions from coal combustion leave their signature in the atmosphere of Chongqing.

Before the implementation of Beijing Clear Sky project in 1999, coal burning was the major source for air pollutants in the city, but during ensuing two decades, the number of motor vehicles in Beijing has increased fourfold (from 1 million in 1998 to 4 million in 2008). This has shifted the urban air pollution pattern from one dominated by coal emissions to one more strongly affected by photochemically modified emissions from motor vehicles. Zhang et al. (2007) found that motor vehicle exhaust accounted for 74% of PM10 carbonaceous aerosols in Beijing during January 2004 while coal combustion accounted for the remaining 26%. Earlier studies in Beijing by Okuda et al. (2002) showed that motor vehicle exhaust was the predominant influence on the isotopic composition of PAHs ($-26.1\%$ to $-21.1\%$) during the summer and winter of 1998.

The winter-to-summer differences in 13C in the southern cities, Wuhan, Shanghai, Hangzhou, Guangzhou and Hong Kong (0.30‰ to 0.35‰) were less than the precision of this isotopic measurement, therefore it can be argued that no seasonal shift carbon isotopes occurred in these four cities. Most of these cities are relatively prosperous and the air pollution is mainly due to automotive emissions (Cao et al., 2004, 2006). The reason for the relatively large winter to summer difference in 13C in the samples from Xiamen (0.95‰) remains unclear.

### 3.3. Relationship between $\delta^{13}$C and the EC/TC ratio

Data for carbon isotopes and the ratio of EC to TC have been utilized to differentiate among biomass-burning emission sources (Cachier et al., 1989). In Fig. 3 we plot $\delta^{13}$C against the EC/TC ratio based as noted above EC retains the isotopic information of the original emission sources while OC does not. The correlations between 13C and EC/TC were not significant for either winter or summer (for both seasons, $R^2 = 0.09$), suggesting that the sources for EC varied but were likely dominated by emissions from fossil fuel combustion and not biomass burning.

Although the relationship between the stable carbon isotope fingerprints and EC/TC ratios was not statistically significant, $\delta^{13}$C tended to decrease with increasing EC/TC ratios (Fig. 3). Most of the $\delta^{13}$C data points had relatively heavy carbon values ($\delta^{13}C > -25.5\%$) when the EC/TC ratio was less than 0.2. For the subset of samples with EC/TC $< 0.2$, the OC/EC ratio averaged 4.0, and this ratio is indicative of emissions from coal combustion (Cao et al., 2007). However, as the EC/TC ratio increased from 0.2 to 0.5, the $\delta^{13}$C data points clustered along a zone between $-25.5\%$ and $-26.5\%$ (Fig. 3); and this is likely due to increasing contributions from motor vehicle exhaust: the EC/TC ratio for fresh vehicular exhaust is $\sim 0.5$ (Cao et al., 2006).

**Fig. 2.** Relationships between $\delta^{13}$OC and $\delta^{13}$EC in PM$_{2.5}$ from fourteen cities in China during winter and summer 2003. See text for description of Areas I and II.
3.4. Source identification

$\delta^{13}C$ values for major emission sources and ambient air samples from various urban regions are presented for comparison with the Xi’an PM data in Fig. 4. The upper panel of that figure shows that $\delta^{13}C_{TC}$ values for coal combustion ($-24.9_{\text{coal}}$ to $-21.0_{\text{coal}}$, Gleason and Kyser, 1984; Widory, 2006), are lighter than those for motor vehicle exhaust ($-28_{\text{exh}}$ to $-26_{\text{exh}}$, Widory, 2006). The isotopic composition of biomass burning products are highly variable due to (1) the different photosynthetic pathways used by plants, (2) the non-homogeneous characteristics of the fuels (e.g. leaves versus trunks), and (3) changes in emissions during the different stages of a fire (i.e. flaming versus smoldering). With reference to photosynthetic pathways, there is a large difference between the isotopic signatures of C3 plants (e.g., pines and conifers, $\delta^{13}C = -29_{\text{pine}}$ to $-32_{\text{pine}}$, Moura et al., 2008) and C4 plants (e.g., grasses, $\delta^{13}C = -11.5_{\text{grass}}$ to $-13.5_{\text{grass}}$, Martinelli et al., 2002) as illustrated in Fig. 4a.

The isotopic patterns observed in our study (Fig. 4b) are more similar to the signatures from coal combustion and motor vehicle emissions than those from biomass burning. The lightest observed values for $\delta^{13}C_{OC}$ ($-26.9_{\text{Xi’an}}$) were found in Xi’an and Beijing in summer, and the lightest value for $\delta^{13}C_{EC}$ ($-26.6_{\text{Xi’an}}$) was in Beijing during summer. These signals are similar to the $\delta^{13}C$ values for motor vehicle exhaust reported by Widory (2006). Heavy $\delta^{13}C_{OC}$ ($-23.0_{\text{Changchun}}$) and $\delta^{13}C_{EC}$ ($-23.2_{\text{Changchun}}$) values in Changchun during winter are consistent with values cited above for coal burning. The combustion of C3 and C4 plants can be discounted as dominant sources for carbonaceous aerosols in the Chinese urban atmosphere because representative $\delta^{13}C$ values for C3 plants were much lighter than the observed values and the $\delta^{13}C$ values for C4 plants were much heavier (Fig. 4). Biomass combustion was legally prohibited in urban areas of China beginning in 1998, and other investigations based on methods different than those used in our study provide support for the suggestion that fossil fuels are a more important

![Fig. 3. Scatter plots of EC/TC ratio versus $\delta^{13}C_{EC}$.](image)

![Fig. 4. Comparison of $\delta^{13}C$ values for major emission sources and selected urban areas. a) $\delta^{13}C$ of major emission sources including coal-combustion (Gleason and Kyser, 1984; Widory, 2006), biomass burning from C3 and C4 plants (Martinelli et al., 2002; Moura et al., 2008), and motor vehicle exhaust (Widory, 2006). b) $\delta^{13}C$ in TC, OC, and EC at various urban regions: Vancouver, Canada (Huang et al., 2006); Tuscany, Italy (Grassi et al., 2007); Rio de Janeiro, Brazil (Tanner and Miguel, 1989); Mexico city, Mexico (Lopez-Veberoni, 2009); Paris, France (Widory et al., 2004); Zurich, Switzerland (Szidat et al., 2004); Wroclaw, Poland (Gorka and Jedrysek, 2004). Stippled area represents the range of $\delta^{13}C$ for carbonaceous aerosols in Chinese cities.](image)
source for carbonaceous aerosols than biomass burning (He et al., 2001; Ye et al., 2003; Cao et al., 2003, 2004, 2005, 2007).

The contribution of south Asia to the global EC budget is similar in magnitude to the EC emissions from China (Menon et al., 2002), and radiocarbon-based studies have indicated that unlike the situation in China, the major source for carbonaceous aerosols in south Asia is biomass burning (Gustafsson et al., 2009). Hansen et al. (2005) argued that the net climate-related effect of carbonaceous particles from fossil fuel combustion is one of warming, while biomass burning products tend to produce a cooling effect. Hence, reductions in carbonaceous emissions in China and south Asia, especially in India, may have counter-balancing effects on climate due to the differences in sources for the particles and the types of EC emitted.

The data from our study of Chinese urban atmospheres also are compared with results of studies at other urban locations worldwide in Fig. 4b. Obviously, the range of $\delta^{13}C$ in OC, EC and TC for the cities in China was large compared with the other sites, and this is likely due to (1) varying contributions from coal combustion and motor vehicle exhaust and (2) the relatively large number of cities included in our study. Most of the studies in other urban locations worldwide were from a single city (Gorka and Jedrysek, 2004; Huang et al., 2006; Lopez-Veneroni, 2009). It is also important to note that the carbonaceous particles from many of these other study sites originated mainly from liquid fuels rather than coal and other solid fuels.

4. Conclusions

Stable carbon isotope ratios were determined for OC and EC in PM$_{2.5}$ from fourteen selected cities in China. The $\delta^{13}C_{OC}$ values varied between $-26.9\%e$ and $-23.08\%e$ and $\delta^{13}C_{EC}$ varied between $-26.63\%e$ and $-23.27\%e$. The isotopic signatures indicate that coal combustion and emissions from motor vehicles were the major sources for the carbonaceous aerosols. The urban air in seven northern cities was strongly impacted by coal burned for residential heating during winter. Our results show that stable carbon isotope data can be useful for distinguishing among major sources for carbonaceous PM$_{2.5}$, and the results of our studies are consistent with source assessments based on other methods. Once representative source profiles and the isotopic compositions of major emission sources are established, studies of stable carbon isotope ratios may make it possible to more accurately quantify the impacts of combustion sources on PM$_{2.5}$.

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