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

Jun-ji Cao [a,b,*], Judith C. Chow [a,c], Jun Tao [d], Shun-cheng Lee [e], John G. Watson [a,c], Kin-fai Ho [a], Ge-hui Wang [a,b], Chong-shu Zhu [a], Yong-ming Han [a]

[a] SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China
[b] Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China
[c] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, USA
[d] South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou, China
[e] The Hong Kong Polytechnic University, Hong Kong, China

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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‰ to −23.08‰ for OC and −26.63‰ to −23.27‰ for EC. A strong correlation ($R^2 = 0.70$, $p < 0.0001$) between $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ was found in winter but not summer. Winter vs. summer differences for $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ were greater for the seven northern cities (~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.

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., Chesselet et al., 1981). Cachier et al. (1985, 1986) used carbon isotopes and the ratio of elemental carbon (EC) to total carbon (TC) in aerosol particles to investigate emissions from biomass burning. More recent work (Ho et al., 2006; Huang et al., 2006; Fisseha et al., 2009) has explored the use of carbon isotopes in EC and organic carbon (OC) in source apportionment and atmospheric chemical transformation studies.

In 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 μm ($PM_{2.5}$) 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

* Corresponding author at: Institute of Earth Environment, Chinese Academy of Sciences (CAS), No. 10 Fenghui South Road, High-Tech Zone, Xi'an 710075, China. Tel.: +86 29 8832 6488; fax: +86 29 8832 0456.
E-mail address: cao@loess.llqg.ac.cn (J.-j. Cao).

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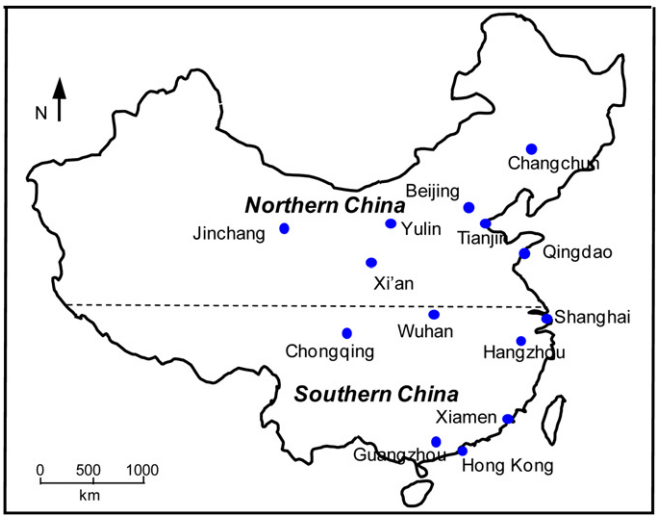

Fig. 1. Locations of fourteen cities in China where samples were collected.

Table 1
Average values of $\delta^{13}C$ for OC, EC and TC in 14 cities in China (unit: ‰).

	Winter (W)			Summer (S)			W–S[b]
	$\delta^{13}C_{OC}$	$\delta^{13}C_{EC}$	$\delta^{13}C_{TC}$[a]	$\delta^{13}C_{OC}$	$\delta^{13}C_{EC}$	$\delta^{13}C_{TC}$	$\delta^{13}C_{EC}$
North China							
Beijing	−25.17	−25.02	−25.14	−26.90	−26.62	−26.84	1.60
Changchun	−23.08	−23.27	−23.13	−26.41	−25.97	−26.33	2.70
Jinchang	−25.54	−24.51	−25.33	−26.67	−25.27	−26.45	0.76
Qingdao	−24.59	−24.47	−24.57	−26.46	−25.91	−26.33	1.44
Tianjin	−24.69	−24.44	−24.64	−26.33	−25.91	−26.26	1.47
Xi'an	−23.58	−23.61	−23.59	−26.90	−26.30	−26.79	2.69
Yulin	−24.54	−24.47	−24.53	−26.34	−25.88	−26.24	1.41
South China							
Chongqing	−26.05	−25.44	−25.94	−26.30	−26.14	−26.26	0.70
Guangzhou	−26.50	−26.10	−26.40	−25.50	−25.75	−25.55	0.35
Hong Kong	−26.62	−25.57	−26.20	−26.74	−25.82	−26.44	0.25
Hangzhou	−26.04	−25.64	−25.95	−26.02	−25.41	−25.92	0.23
Shanghai	−26.01	−25.66	−25.94	−25.54	−26.20	−25.65	0.54
Wuhan	−25.90	−25.33	−25.80	−25.29	−25.52	−25.32	0.19
Xiamen	−25.79	−25.68	−25.77	−26.30	−26.63	−26.3	0.95

[a] $\delta^{13}C_{TC} = (OC/TC) \times \delta^{13}C_{OC} + (EC/TC) \times \delta^{13}C_{EC}$.
[b] W–S refers to the differences of winter-to-summer average of $\delta^{13}C_{EC}$.

(Chow et al., 1993). These analyses were conducted using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, 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 isotopic composition of the CO_2 was then determined as $\delta^{13}C_{OC}$ (see below) with the use of a Finnigan MAT-251 ratio mass spectrometer (Ho et al., 2006). The carbon that remained on the filters was then combusted at 850 °C for 5 h; the CO_2 produced by this treatment was quantified as the EC fraction and its isotopic composition determined as $\delta^{13}C_{EC}$. 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:

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

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

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

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. $\delta^{13}C_{OC}$ 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 Xi'an to −25.29‰ in Wuhan. Compared with $\delta^{13}C_{OC}$, the variations in $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{OC}$ from urban atmospheres (~2 to 4‰) are usually larger than those of $\delta^{13}C_{EC}$ (<1‰), and this was the case in our study. Normally, EC is unreactive and so $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{OC}$ values are expected to change with time.

In addition, the $\delta^{13}C_{EC}$ values were generally heavier (i.e., less negative) than the corresponding $\delta^{13}C_{OC}$ values (Table 1). The differences between isotopic ratios ($\delta^{13}C_{EC}$–$\delta^{13}C_{OC}$) 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) $\delta^{13}C_{OC}$ values.

A plot of $\delta^{13}C_{OC}$ versus $\delta^{13}C_{EC}$ (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 $\delta^{13}C_{OC}$ versus $\delta^{13}C_{EC}$ 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 ($\delta^{13}C_{EC}$) 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 $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ did not hold in summer; in fact the summertime $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{OC}$. 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, Irei 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 $\delta^{13}C_{OC}$ 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 $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ in 14 cities can be seen to plot in two distinct areas (rectangles) in Fig. 2. In winter (Fig. 2a), most of

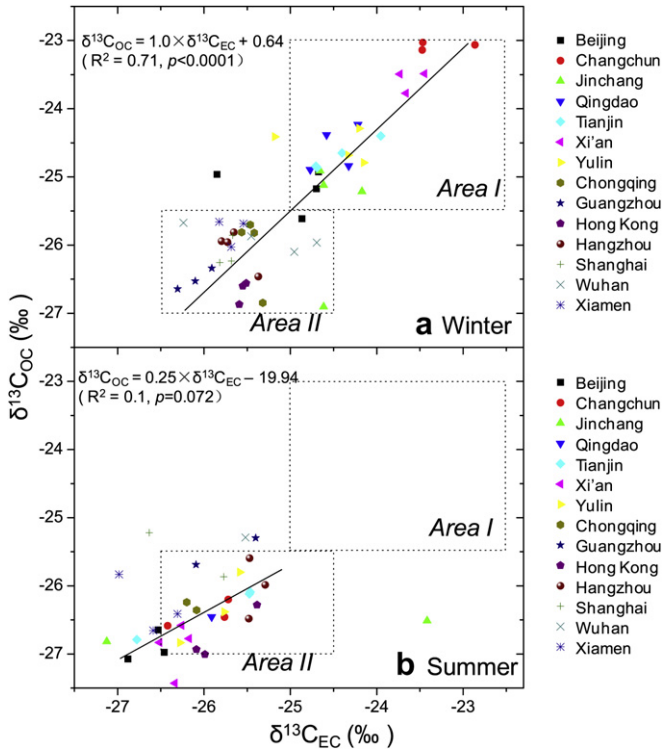

Fig. 2. Relationships between $\delta^{13}C_{EC}$ and $\delta^{13}C_{OC}$ in $PM_{2.5}$ from fourteen cities in China during winter and summer 2003. See text for description of Areas I and II.

the $\delta^{13}C$ values for OC and EC in the seven northern cities plotted in Area I ($-25‰ < \delta^{13}C_{EC} < -22.5‰$; $-25.5‰ < \delta^{13}C_{OC} < -23‰$) while most of the $\delta^{13}C$ values in the seven southern cities fell within Area II ($-26.5‰ < \delta^{13}C_{EC} < -24.5‰$; $-27‰ < \delta^{13}C_{OC} < -25.5‰$). In contrast, in summer (Fig. 2b) most of the $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ values for the northern cities moved to Area II, and some of the $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ values for the southern cities became even more negative than the values bounded by Area II. None of the summertime observations plotted in Area I (Fig. 2b).

In northern China, large quantities of coal are burned for heat, and there is a formal residential "heating season" that extends from November of one year to March of the following year (Cao et al., 2007). The heavier values of $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ we observed in the January samples from the northern cities relative to the June/July samples can be linked to the coal burned for residential heating. For example, the average winter $\delta^{13}C_{EC}$ in Beijing was $-25.02‰$ compared with $-26.62‰$ in summer, a winter-to-summer difference of 1.6‰. The stable carbon isotopes in coal produce $\delta^{13}C$ values between $-21‰$ and $-24.9‰$ (Gleason and Kyser, 1984; Widory, 2006). Assuming the isotopes do not fractionate when the coal is burned, the particles from this combustion source should have an isotopic composition similar to if not identical to that of coal (Widory, 2006), and this was the case for both $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ from the northern cities in winter.

Differences in the average winter versus summer $\delta^{13}C_{EC}$ values (Table 1) indicate that the major sources for EC from the northern cities change with season. The largest winter-to-summer differences in $\delta^{13}C_{EC}$ were found at Changchun and Xi'an (~2.70‰), followed by Beijing (1.60‰), and this again reflects the pervasive influence of coal combustion on the atmospheric aerosol in those cities during winter (Cao et al., 2005, 2007). The winter-to-summer differences in $\delta^{13}C_{EC}$ for most other northern cities (e.g., Tianjin, Qingdao, and Yulin) were also high (1.41 to 1.47‰), supporting the notion that coal burned for residential heating influences those cities as well.

Little or no coal is burned for residential heating in summer, even in the northern China, and although there are still sizable emissions of particles from coal burned for industrial purposes, the overall influence of coal combustion on $\delta^{13}C$ evidently decreases in summer. This is manifest as more negative $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ values in summer (Table 1). The winter-to-summer differences in both $\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$ for the southern cities were relatively small (<1‰), and this can be interpreted to mean that the sources for OC and EC are less variable in the southern part of the country than the north.

Chongqing, a heavily industrialized city in the southern zone, is an interesting case because large quantities of coal are burned there even though the city has no formal residential heating season (Cao et al., 2007). The $\delta^{13}C_{EC}$ at Chongqing was slightly more negative 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 $\delta^{13}C$ 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 PM_{10} 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 $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{EC}$ in the samples from Xiamen (0.95‰) remains unclear.

3.3. Relationship between $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{EC}$ against the EC/TC because as noted above EC retains the isotopic information of the original emission sources while OC does not. The correlations between $\delta^{13}C_{EC}$ 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, $\delta^{13}C_{EC}$ tended to decrease with increasing EC/TC ratios (Fig. 3). Most of the $\delta^{13}C_{EC}$ 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 $\delta^{13}C_{EC}$ 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 ~0.5 (Cao et al., 2006).

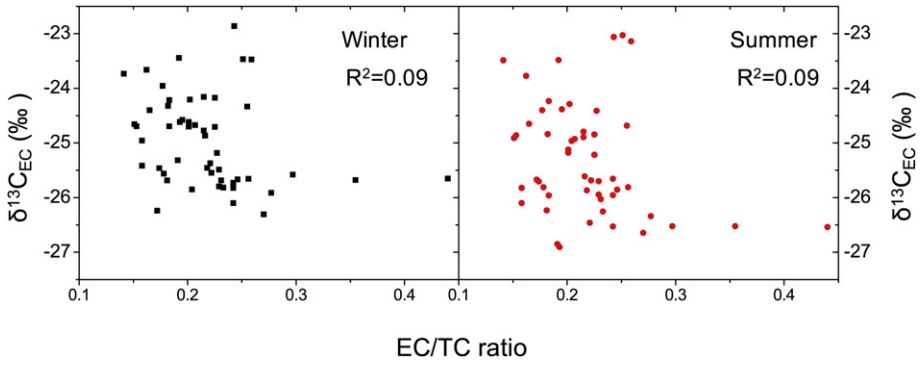

Fig. 3. Scatter plots of EC/TC ratio versus $\delta^{13}C_{EC}$.

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‰ to −21‰, Gleason and Kyser, 1984; Widory, 2006), are lighter than those for motor vehicle exhaust (−28‰ to −26‰, 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, $\delta^{13}C = -29‰$ to −32‰, Moura et al., 2008) and C4 plants (e. g., grasses, $\delta^{13}C = -11.5‰$ to −13.5‰, 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 $\delta^{13}C_{OC}$ (−26.90‰) were found in Xi'an and Beijing in summer, and the lightest value for $\delta^{13}C_{EC}$ (−26.62‰) was in Beijing during summer. These signals are similar to the $\delta^{13}C$ values for motor vehicle exhaust reported by Widory (2006). Heavy $\delta^{13}C_{OC}$ (−23.08‰) and $\delta^{13}C_{EC}$ (−23.27‰) 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

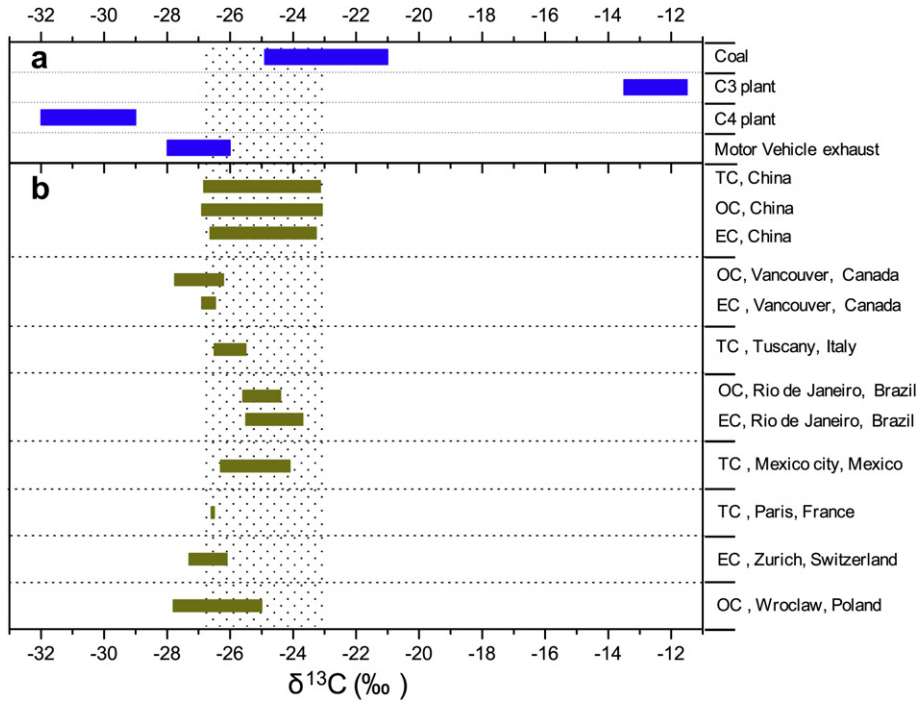

Fig. 4. Comparison of $\delta^{13}C$ values for major emission sources and selected urban areas. a) $\delta^{13}C$ of major emission sources including coal-combustion (Gleason and Kyser, 1984; Widory, 2006), biomass burning from C3 and C4 plants (Martinelli et al., 2002; Moura et al., 2008), and motor 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-Veneroni, 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.

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‰ and −23.08‰ and $\delta^{13}C_{EC}$ varied between -26.63‰ and −23.27‰. 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 isotopes may make it possible to more accurately quantify the impacts of combustion sources on $PM_{2.5}$.

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