



# Atmospheric fossil fuel CO<sub>2</sub> traced by <sup>14</sup>CO<sub>2</sub> and air quality index pollutant observations in Beijing and Xiamen, China

Zhanchuan Niu<sup>1,2,3</sup> · Weijian Zhou<sup>1,2,3,4</sup> · Xue Feng<sup>5</sup> · Tian Feng<sup>1,2</sup> · Shugang Wu<sup>1,2</sup> · Peng Cheng<sup>1,2</sup> · Xuefeng Lu<sup>1,2</sup> · Hua Du<sup>1,2</sup> · Xiaohu Xiong<sup>1,2</sup> · Yunchong Fu<sup>1,2</sup>

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## Abstract

Radiocarbon (<sup>14</sup>C) is the most accurate tracer available for quantifying atmospheric CO<sub>2</sub> derived from fossil fuel (CO<sub>2ff</sub>), but it is expensive and time-consuming to measure. Here, we used common hourly Air Quality Index (AQI) pollutants (AQI, PM<sub>2.5</sub>, PM<sub>10</sub>, and CO) to indirectly trace diurnal CO<sub>2ff</sub> variations during certain days at the urban sites in Beijing and Xiamen, China, based on linear relationships between AQI pollutants and CO<sub>2ff</sub> traced by <sup>14</sup>C (CO<sub>2ff</sub>-<sup>14</sup>C) for semimonthly samples obtained in 2014. We validated these indirectly traced CO<sub>2ff</sub> (CO<sub>2ff-in</sub>) concentrations against CO<sub>2ff</sub>-<sup>14</sup>C concentrations traced by simultaneous diurnal <sup>14</sup>CO<sub>2</sub> observations. Significant ( $p < 0.05$ ) strong correlations were observed between each of the separate AQI pollutants and CO<sub>2ff</sub>-<sup>14</sup>C for the semimonthly samples. Diurnal variations in CO<sub>2ff</sub> traced by each of the AQI pollutants generally showed similar trends to those of CO<sub>2ff</sub>-<sup>14</sup>C, with high agreement at the sampling site in Beijing and relatively poor agreement at the sampling site in Xiamen. AQI pollutant tracers showed high normalized root-mean-square (NRMS) errors for the summer diurnal samples due to low CO<sub>2ff</sub>-<sup>14</sup>C concentrations. After the removal of these summer samples, the NRMS errors for AQI pollutant tracers were in the range of 31.6–64.2%. CO generally showed a high agreement and low NRMS errors among these indirect tracers. Based on these linear relationships, monthly CO<sub>2ff</sub> averages at the sampling sites in Beijing and Xiamen were traced using CO concentration as a tracer. The monthly CO<sub>2ff</sub> averages at the Beijing site showed a shallow U-type variation. These results indicate that CO can be used to trace CO<sub>2ff</sub> variations in Chinese cities with CO<sub>2ff</sub> concentrations above 5 ppm.

**Keywords**  $\Delta^{14}\text{C}$  · Fossil fuel CO<sub>2</sub> · Indirect tracer · CO · PM<sub>2.5</sub>

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✉ Weijian Zhou  
weijian@loess.llqg.ac.cn

<sup>1</sup> State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China

<sup>2</sup> Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an AMS Center, Xi'an, China

<sup>3</sup> Open Studio for Oceanic-Continental Climate and Environment Changes, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China

<sup>4</sup> Joint Center for Global Change Studies, Beijing Normal University, Beijing, China

<sup>5</sup> College of Urban and Environmental Sciences, Northwest University, Xi'an, China

## Introduction

Global atmospheric CO<sub>2</sub> concentrations exceeded 400 ppm in 2016 (GMD/ESRL 2017) and are still increasing. As the second most important greenhouse gas after water vapor, quantifying how much of the increased atmospheric CO<sub>2</sub> is derived from fossil fuel emissions is an important environmental issue and scientific question. Radiocarbon (<sup>14</sup>C) can be used as a tracer to quantify atmospheric fossil fuel-derived CO<sub>2</sub> (CO<sub>2ff</sub>) concentrations (Levin and Hesshaimer 2000; Levin et al. 2003) because of the marked differences in <sup>14</sup>C levels found in CO<sub>2</sub> derived from fossil fuels and other sources. <sup>14</sup>C is entirely depleted in fossil fuels, while its level in biological sources is close to that of ambient air (Naegler and Levin 2009; Turnbull et al. 2006). This tracer has been used widely to study spatial and temporal variations (Hsueh et al. 2007; Kuc et al. 2007; Levin et al. 1989, 2003, 2008; Niu et al. 2016a, b, c; Riley et al. 2008; Turnbull et al. 2006), flux (Levin et al. 2003; van der Laan et al. 2010), and source

apportionment of atmospheric CO<sub>2ff</sub> (Zondervan and Meijer 1996; Djuricin et al. 2010); to compare trends between top-down CO<sub>2ff</sub> measurements and bottom-up CO<sub>2</sub> emissions (Newman et al. 2016); and to evaluate uncertainties for point source fossil fuel CO<sub>2</sub> emissions (Turnbull et al. 2016).

Cities are emission hotspots and urban levels of atmospheric CO<sub>2ff</sub> should be a focus of research efforts as more than 70% of global CO<sub>2ff</sub> emissions are concentrated in urban areas (Duren and Miller 2012). Atmospheric CO<sub>2ff</sub> is highly variable in cities, so we require widely temporal and spatial variability in the data in order to ensure accuracy and completeness of the CO<sub>2ff</sub> information we obtain. However, <sup>14</sup>C measurement is relatively expensive and time-consuming, which makes it difficult to support many sampling sites and frequent (e.g., hourly) observations. Consequently, other relatively cheap and easy tracers with emission patterns close to those of CO<sub>2ff</sub> are needed to quantify CO<sub>2ff</sub> concentrations in urban areas. Specifically, CO is often produced along with CO<sub>2ff</sub> during the combustion of fuels and a strong correlation between CO and CO<sub>2ff</sub> was observed by Zondervan and Meijer (1996) during pollution episodes at Kollumerwaard station in the Netherlands. CO has been used as an indirect method to trace atmospheric CO<sub>2ff</sub> in Heidelberg (Gamnitzer et al. 2006; Levin and Karstens 2007; Vogel et al. 2010), Paris (Lopez et al. 2013), New England, and Colorado (Turnbull et al. 2006). Additionally, CO<sub>2ff</sub> traced by CO has been compared with that traced by <sup>14</sup>C and SF<sub>6</sub> (Turnbull et al. 2006), and further validated by <sup>14</sup>C observations (Levin and Karstens 2007).

China is a significant CO<sub>2ff</sub> emitting country (Gregg et al. 2008); thus, research in this field in Chinese cities is of particular importance. However, there are more than 600 cities in China, and it is necessary to compromise between the cost of <sup>14</sup>C measurements and the accuracy of CO<sub>2ff</sub> data. Nowadays, the Air Quality Index (AQI) pollutants (including PM<sub>2.5</sub>, PM<sub>10</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>) are routine indexes monitored by the Ministry of Environmental Protection (MEP), China. These continuous data are easy to obtain and have wide coverage over cities; however, CO<sub>2ff</sub> data traced by CO are limited in China. Previous studies in Beijing and Xiamen showed that fossil fuel emissions were important sources of particulate matters (Huang et al. 2014; Niu et al. 2013; Song et al. 2006; Yu et al. 2013; Zhang et al. 2007, 2013). Additionally, CO<sub>2ff</sub> and PM<sub>2.5</sub> showed synchronous variation during the winter diurnal observations in Beijing (Niu et al. 2016b). Accurate determinations of atmospheric CO<sub>2ff</sub> concentrations can be used to understand the variability in the remaining biospheric CO<sub>2</sub>, and this crucial information can be used by the government to develop appropriate strategies on the reduction of carbon emissions. Thus: Can particulate matters and CO be used to trace CO<sub>2ff</sub> variations in Chinese cities? To answer this question, diurnal CO<sub>2ff</sub> variations at the urban sites in Beijing and Xiamen were indirectly traced by hourly AQI

pollutants, based on the linear relationships between AQI pollutants and CO<sub>2ff</sub> traced by <sup>14</sup>C (CO<sub>2ff</sub>-<sup>14</sup>C) for semimonthly samples acquired in 2014, and then validated by simultaneous diurnal CO<sub>2ff</sub>-<sup>14</sup>C.

## Material and methods

### Sampling strategy

Beijing and Xiamen were chosen to represent inland and coastal cities, respectively. The sampling site (40.01° N, 116.35° E) in Beijing is located on the roof (15 m) of a building at the Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences, in the Haidian District. The sampling site (24.48° N, 118.16° E) in Xiamen is located on the roof (18 m) of a building in Ruijing (RJ), a primary school in the Siming District on Xiamen Island. Both of the urban sites are surrounded by commercial, education, and residential areas. The sampling site in Beijing is more than 1 km from any motorways, 500 m from any other major roads, and 100 m from any streets or other potential sources of pollution. The urban site in Xiamen is more than 250 m from any main roads, and 100 m from any streets or other pollution sources.

Both diurnal and semimonthly air samples were collected. Diurnal samples were collected every 2 h from 8:00 AM (local time) until 6:00 AM (local time) on the next day on Jan 15–16, Jan 18–19, Jun 23–24, and Jun 28–29 at the site in Beijing; and on Jan 4–5, Jan 9–10, and Jun 20–22 at the site in Xiamen. Semimonthly samples were collected at 10:00 AM (local time) twice each month, from January to December, 2014. Sampling was conducted on days without rain or snow. Samples of approximate 5 L of air were collected in aluminum foil sampling bags (Delin Gas Packing Co., Ltd., Dalian, China) using a pump for 10–15 min. The bags were flushed with ambient air three times before samples were collected. The operators held their breath when turning on and off the switch and maintained a distance from the apparatus during sample collection. The differences in CO<sub>2</sub> concentrations between the bag samples and real-time Picarro analyzer (Picarro Inc., USA) measurements were below 0.4 ppm, and the bias resulting from that CO<sub>2</sub> concentration difference was 0.02 ppm for CO<sub>2ff</sub> calculations. After the sampling, the bags were immediately sent to the laboratory for analysis. In total, 144 urban air samples were collected, comprising 48 semimonthly samples and 96 diurnal samples.

The AQI and concentrations of PM<sub>2.5</sub>, PM<sub>10</sub>, and CO during the sampling periods were obtained from the website (<http://www.aqistudy.cn/>). AQI values represent the maximum pollution sub-indices of six individual pollutants (PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, and CO); details of how AQI values are calculated are shown in the [supplementary material](#). The AQI, PM<sub>2.5</sub>, PM<sub>10</sub>, and CO data for Beijing were

obtained from the nearest national air monitoring station at Wanliu, about 4.5 km to the air sampling site. For Xiamen, they were obtained from the Hongwen national air monitoring station, which is the same site to the air sampling site. Particulate matters and CO were measured using a Thermo Scientific Model 5030 SHARP monitor and a Thermo Scientific Model 48i Carbon Monoxide Analyzer (Thermo Fisher, USA), respectively. All the instruments were maintained and routinely calibrated by China MEP to ensure data quality.

## CO<sub>2</sub> concentration measurements

The CO<sub>2</sub> concentrations of the air samples were measured by a Picarro G2131-I CO<sub>2</sub> Isotopic Analyzer (Picarro Inc.). This type of equipment employs cavity ring-down spectroscopy (CRDS) technology, which has high linearity, precision, and stability for CO<sub>2</sub> measurements (Chen et al. 2010; Crosson 2008). The precision in this study was better than 0.1 ppm. Briefly, the air samples in the bags were filtered, dried in an ethanol-liquid nitrogen cold trap (−90 °C), and then introduced into the Picarro analyzer. The optical absorbance of the samples, which is a function of CO<sub>2</sub> concentration, was determined by the light dissipation rate by the Picarro analyzer. Each sample was measured for 6 min. Because of the dead volumes remaining in the analyzer when switching to a new sample, only the data obtained during the last 4 min of analysis were averaged. The quantities of <sup>12</sup>CO<sub>2</sub>\_dry and <sup>13</sup>CO<sub>2</sub>\_dry were summed to get the total CO<sub>2</sub> concentration of an air sample. The instrument was calibrated by a standard gas (395.49 ± 0.02 ppm) obtained from the Chinese Academy of Meteorological Sciences. This standard gas is pressurized in a 29.5-L treated aluminum alloy cylinder (Scott-Marrin, Inc., California) fitted with high-purity, two-stage gas regulator, and calibrated with cylinders assigned by the WMO/GAW CO<sub>2</sub> Central Calibration Laboratory operated by NOAA/ESRL. A single-point calibration method was used in our study, details of which were shown in the study of Verhulst et al. (2017).

## Sample preparation and <sup>14</sup>C measurement

The air samples in the bags were transferred into a vacuum system at a flow rate of approximately 200 ml min<sup>−1</sup>, and then passed through a liquid nitrogen cold trap (−196 °C) to trap CO<sub>2</sub> and water. The trapped water was removed using an ethanol-liquid nitrogen cold trap (−90 °C) to obtain purified CO<sub>2</sub> (Turnbull et al. 2007). A zinc-iron method was used for the graphitization of CO<sub>2</sub>, with zinc particles and iron powder acting as the reductant and catalyst, respectively (Jull 2007; Slota et al. 1987). The graphite (1.0–1.2 mg) that resulted from the ambient air samples was pressed into an aluminum target holder for <sup>14</sup>C measurement. In addition, the gases produced

from the combustion of anthracite coal blanks were processed using the same procedure as the ambient air samples, and a vacuum system blank (−998.4 ± 0.1‰) was obtained. An aliquot of standard air (with a Δ<sup>14</sup>C value of 6.7 ± 2.3‰) obtained from the Chinese Academy of Meteorological Sciences was treated bimonthly with the same procedure as that applied to the bag air samples to assess the uncertainty of the chemical processing; an average uncertainty of 2.3‰ was obtained.

The <sup>14</sup>C levels in the air samples were measured using a 3-MV accelerator mass spectrometer (AMS) in Xi'an, China; details of these data are shown in the [supplementary material](#). The precision of a typical <sup>14</sup>C measurement was 3‰ (Zhou et al. 2006). Each batch contained 48 targets, comprising 38 air samples, six OX-II samples as primary standards, two Chinese sugar carbon (CSC) samples as secondary standards, and two anthracite coal samples as blanks. They were arranged in order in a sample-holding wheel, and then placed into the AMS ion source for <sup>14</sup>C measurement. Each sample recorded 300,000–400,000 <sup>14</sup>C counts, and on-line δ<sup>13</sup>C measurements were used for isotopic fractionation corrections. The <sup>14</sup>C levels in the samples were expressed as Δ<sup>14</sup>C, i.e., the per mil (‰) deviation from the absolute radiocarbon reference standard corrected by the convention of fractionation and decay (Stuiver and Polach 1977).

$$\Delta^{14}\text{C} = \left[ \frac{(^{14}\text{C}/^{12}\text{C})_{\text{SN}}}{(^{14}\text{C}/^{12}\text{C})_{\text{ABS}}} - 1 \right] \times 1000\text{‰} \quad (1)$$

where (<sup>14</sup>C/<sup>12</sup>C)<sub>SN</sub> is the <sup>14</sup>C/<sup>12</sup>C ratio of the sample normalized to a common δ<sup>13</sup>C value of −25‰, and (<sup>14</sup>C/<sup>12</sup>C)<sub>ABS</sub> is the absolute radiocarbon reference standard after the fractionation and decay corrections.

## Calculation of CO<sub>2ff-14C</sub> concentrations

The calculation of CO<sub>2ff-14C</sub> is based on the assumption that the ambient CO<sub>2</sub> (CO<sub>2a</sub>) is a mixture of three components, i.e., background CO<sub>2</sub> (CO<sub>2bg</sub>), CO<sub>2ff-14C</sub>, and other CO<sub>2</sub> (CO<sub>2other</sub>) (Levin et al. 2003; Vogel et al. 2010; Rakowski et al. 2008; Zhou et al. 2014). According to the mass balance of CO<sub>2</sub> and <sup>14</sup>C, the following two equations were obtained:

$$\text{CO}_{2a} = \text{CO}_{2bg} + \text{CO}_{2other} + \text{CO}_{2ff-14\text{C}} \quad (2)$$

$$\text{CO}_{2a}\Delta_a = \text{CO}_{2bg}\Delta_{bg} + \text{CO}_{2other}\Delta_{other} + \text{CO}_{2ff-14\text{C}}\Delta_{ff} \quad (3)$$

where Δ<sub>a</sub>, Δ<sub>bg</sub>, Δ<sub>other</sub>, and Δ<sub>ff</sub> are the Δ<sup>14</sup>C values for CO<sub>2a</sub>, CO<sub>2bg</sub>, CO<sub>2other</sub>, and CO<sub>2ff-14C</sub>, respectively, and Δ<sub>ff</sub> has a value of −1000‰. Based on the annual average of 17‰ at Waliguan station in 2015 (Niu et al. 2016c) and an annual decline of about 5‰ for Δ<sup>14</sup>CO<sub>2</sub> at Pt. Barrow, AK in recent years (Graven et al. 2012), a value of 22‰ (Niu et al. 2016b) was used for the Δ<sub>bg</sub> in this study.

From Eqs. 2 and 3,  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  can be calculated by the following equation:

$$\text{CO}_{2\text{ff}}^{-14}\text{C} = \frac{\text{CO}_2a(\Delta bg - \Delta a)}{\Delta bg - \Delta \text{ff}} + \frac{\text{CO}_2\text{other}(\Delta \text{other} - \Delta bg)}{\Delta bg - \Delta \text{ff}} \quad (4)$$

The second term on the right-hand-side in Eq. 4 is the bias ( $\beta$ ). Some researchers regard heterotrophic respiration as the main contributor to  $\beta$ , and take the view that if  $\beta$  is ignored,  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  will be underestimated by 0.2–0.3 ppm during the winter and 0.4–0.8 ppm during the summer (Turnbull et al. 2006, 2009; Miller et al. 2012). The  $\beta$  correction was used in this study, because it is quite consistent (on land) across most of the Northern Hemisphere (Turnbull et al. 2009). Nuclear power plants (NPP) contribute to  $\beta$ , with the correction from NPP ranging from –0.25 ppm over large regions and up to several ppm near nuclear sites (Graven and Gruber 2011; Vogel et al. 2013). However, since both the sampling sites are far from the NPP, a correction of –0.25 ppm was used for our  $\text{CO}_{2\text{ff}}$  calculations.

### Calculation of indirectly traced $\text{CO}_{2\text{ff}}$ concentrations by AQI pollutants

The concentrations of  $\text{CO}_{2\text{ff}}$  indirectly traced ( $\text{CO}_{2\text{ff-in}}$ ) by AQI pollutants were calculated by the following equation:

$$\text{CO}_{2\text{ff-in}} = \frac{A-b}{a} \quad (5)$$

where  $\text{CO}_{2\text{ff-in}}$  is the concentration of  $\text{CO}_{2\text{ff}}$  indirectly traced by each AQI pollutant separately;  $A$  is the value of each AQI pollutant;  $b$  is the intercept of the corresponding linear equation obtained from the correlation between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and the AQI pollutant, which is expected to agree with the continental background level; and  $a$  is the slope of the corresponding linear equation obtained from the correlation between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and each AQI pollutant.

### Data analysis

Pearson's correlation analyses were performed between the  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  concentrations and AQI pollutants (AQI,  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and CO) using SPSS statistical software (V. 17) (Norusis 2008). The significance of the correlations was judged by the correlation coefficient ( $R$ ) and the  $p$  value.

In order to evaluate the overall performance of these indirect tracers, the normalized root-mean-square (NRMS) error and index of agreement (IOA) (Willmott 1981) were used in this study.

$$\text{NRMS} = \frac{\left[ \frac{1}{n} \sum_{i=1}^N (P_i - O_i) \right]^{\frac{1}{2}}}{\bar{P}} \quad (6)$$

$$\text{IOA} = 1 - \frac{\frac{1}{n} \sum_{i=1}^N (P_i - O_i)^2}{\frac{1}{n} \sum_{i=1}^N \left( |P_i - \bar{O}| + |O_i - \bar{O}| \right)^2} \quad (7)$$

where  $P_i$  and  $O_i$  are  $\text{CO}_{2\text{ff-in}}$  and  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  concentrations, respectively;  $\bar{P}$  and  $\bar{O}$  are the averages of  $\text{CO}_{2\text{ff-in}}$  and  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  concentrations, respectively; and  $N$  is the sample number used for comparisons. The IOA varies from 0 to 1, with high values indicating better agreement between  $\text{CO}_{2\text{ff-in}}$  and  $\text{CO}_{2\text{ff}}^{-14}\text{C}$ .

## Results and discussion

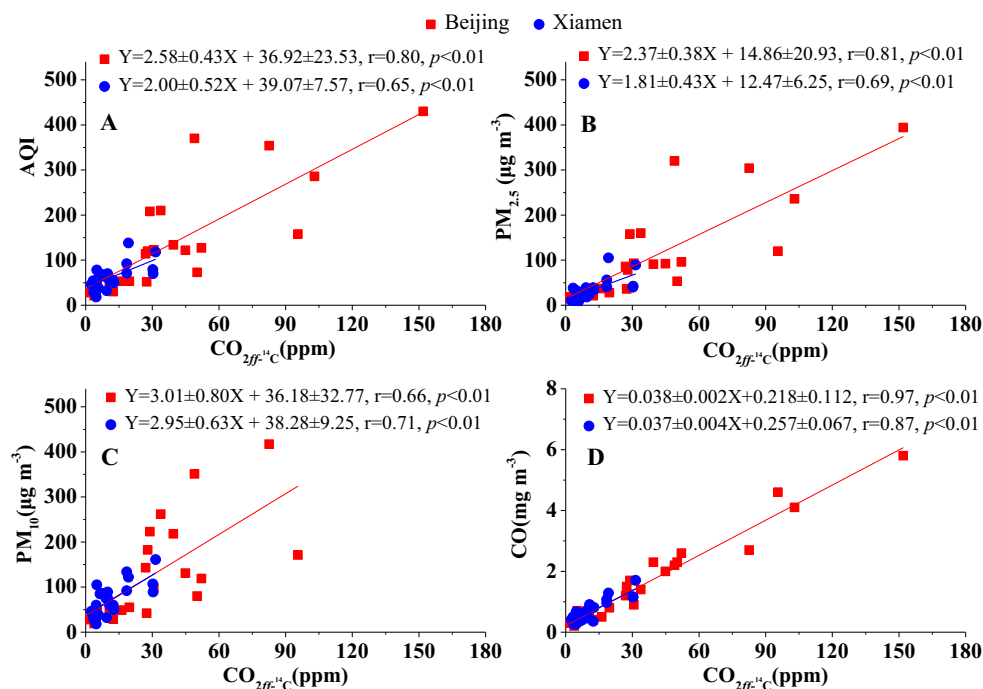
### Correlations between $\text{CO}_{2\text{ff}}^{-14}\text{C}$ and the AQI pollutants for the semimonthly samples

Correlation analyses were performed between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and the AQI pollutants for the semimonthly samples. Significant ( $p < 0.01$ ) correlations are observed between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and AQI values (Fig. 1a),  $\text{PM}_{2.5}$  (Fig. 1b),  $\text{PM}_{10}$  (Fig. 1c), and CO (Fig. 1d) at the sites in Beijing and Xiamen. The correlation coefficients for the AQI pollutants ranked CO ( $r = 0.97$ ) >  $\text{PM}_{2.5}$  ( $r = 0.81$ ) > AQI ( $r = 0.80$ ) >  $\text{PM}_{10}$  ( $r = 0.66$ ) at the site in Beijing, and CO ( $r = 0.87$ ) >  $\text{PM}_{10}$  ( $r = 0.71$ ) >  $\text{PM}_{2.5}$  ( $r = 0.69$ ) > AQI ( $r = 0.65$ ) at the site in Xiamen (Fig. 1). The strong correlations between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and particulate matters indicate that fossil fuel emissions are an important source of particulate matters in the two cities (Huang et al. 2014; Niu et al. 2013; Song et al. 2006; Yu et al. 2013; Zhang et al. 2007, 2013). Additionally, it was found that the haze in Beijing happened when there were high  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  concentrations. The strong correlation between  $\text{CO}_{2\text{ff}}^{-14}\text{C}$  and AQI obtained in this study resulted from that AQI was mainly determined by particulate matter concentrations.

The ratios of  $\text{CO}:\text{CO}_{2\text{ff}}^{-14}\text{C}$  were calculated from the slopes of the linear equations of CO and  $\text{CO}_{2\text{ff}}^{-14}\text{C}$ . The ratios at the sampling sites in Beijing ( $30.4 \pm 1.6$  ppb  $\text{ppm}^{-1}$ ) and Xiamen ( $29.6 \pm 3.2$  ppb  $\text{ppm}^{-1}$ ) were lower than the winter  $\Delta\text{CO}:\text{CO}_{2\text{ff}}^{-14}\text{C}$  ratio ( $47 \pm 2$  ppb  $\text{ppm}^{-1}$ ) recorded at the Shangdianzi regional background station in China (Turnbull et al. 2011), but much higher than both the ratio ( $9.8 \pm 1.4$  ppb  $\text{ppm}^{-1}$ ) from Kollumerwaard station in the Netherlands (Zondervan and Meijer 1996), and a long term  $\Delta\text{CO}:\text{CO}_{2\text{ff}}^{-14}\text{C}$  ratio ( $15.5 \pm 5.6$  ppb  $\text{ppm}^{-1}$ ) in Heidelberg, Germany (Vogel et al. 2010). Biomass burning and domestic coal combustion usually show higher CO emission factors than natural gas and fuel oil (Streets et al. 2006), and no  $\text{CO}_{2\text{ff}}$  emits from biomass burning. Although coal is the main



**Fig. 1** Correlations between  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  and AQI (a),  $\text{PM}_{2.5}$  (b),  $\text{PM}_{10}$  (c), and CO (d) for the semimonthly samples at the sampling sites in Beijing and Xiamen



fuel in China, the burning of biomass is widespread in rural Chinese areas; natural gas and fuel oil are the main fuels in Western Europe. It is likely that the variations in fossil fuel types between the sites caused the differences in  $\text{CO}:\text{CO}_{2\text{ff}}$  ratios above.

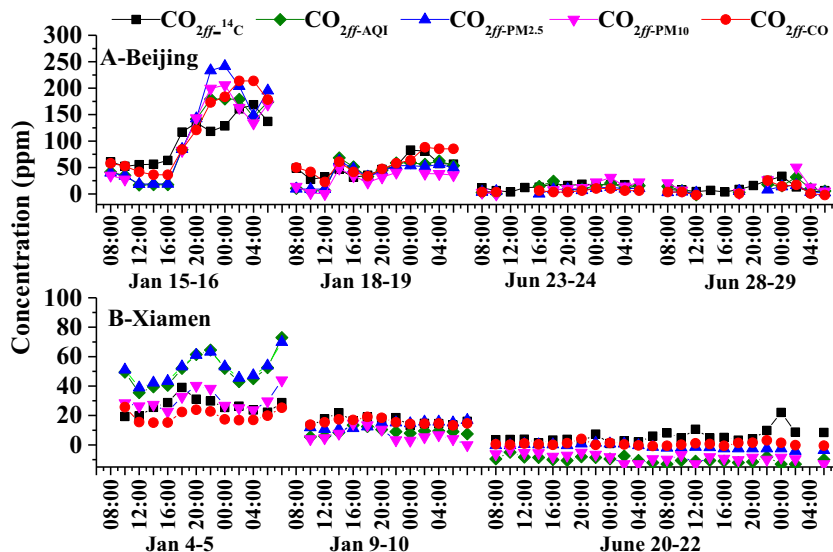
The intercepts of the best-fit lines fitted to the data displayed in Fig. 1 are expected to agree with the continental background levels of the relevant pollutants. For example, the intercept values ( $14.86 \pm 20.93 \mu\text{g m}^{-3}$  and  $12.47 \pm 6.25 \mu\text{g m}^{-3}$ ) of the best-fit lines for  $\text{PM}_{2.5}$  are close to the background  $\text{PM}_{2.5}$  level of  $12.6 \pm 12.0 \mu\text{g m}^{-3}$  at Waliguan station (Yang et al. 2017). For the CO equations, the intercepts ( $176 \pm 88 \text{ ppb}$  and  $200 \pm 56 \text{ ppb}$ ) are close to that ( $190 \pm 30 \text{ ppb}$ ) reported by Zondervan and Meijer

(1996), which they state agrees with the expected continental background conditions.

### Indirect tracing of diurnal $\text{CO}_{2\text{ff}}$ and validation by simultaneous $^{14}\text{CO}_2$ observations

Based on the linear equations (Fig. 1) obtained from the semi-monthly samples, diurnal  $\text{CO}_{2\text{ff}}$  concentrations on particular days were indirectly traced by the corresponding AQI pollutants. These diurnal concentrations of each separate  $\text{CO}_{2\text{ff-in}}$  and  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  are shown in Fig. 2. The trends of diurnal variation of each separate  $\text{CO}_{2\text{ff-in}}$  are similar to those of  $\text{CO}_{2\text{ff}}-^{14}\text{C}$

**Fig. 2** Diurnal variations in  $\text{CO}_{2\text{ff}}$  during certain days in 2014 traced by  $^{14}\text{C}$ , AQI,  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and CO at the sampling sites in Beijing (a) and Xiamen (b)



at each site. The agreements between  $\text{CO}_{2\text{ff-in}}$  and  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  at the sampling site in Beijing (IOA 0.88–0.94) were higher than those in Xiamen (IOA 0.46–0.68), and the poorer agreement at the site in Xiamen might be a result of lower  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  concentrations. The CO tracer showed the highest IOA of the diurnal variations at the site in Beijing, while the  $\text{PM}_{2.5}$  tracer showed the highest IOA at the site in Xiamen, followed by CO. The IOA values for diurnal variations in winter were about 0.2 higher than those in summer at the sampling site in Beijing, but the IOA differences between winter and summer diurnal variations were much higher at the sampling site in Xiamen. These results indicate that diurnal  $\text{CO}_{2\text{ff-in}}$  agree better with  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  during winter-time, as did the diurnal  $\text{CO}_{2\text{ff}}$  traced by CO ( $\text{CO}_{2\text{ff-CO}}$ ) in Heidelberg (Vogel et al. 2010), whereas the study of Turnbull et al. (2006) showed surprisingly good agreement during summer.

CO tracer showed the lowest NRMS errors among the indirect tracers for the diurnal variations at the sampling sites in Beijing (41.7%) and Xiamen (70.9%). The NRMS errors for other tracers of AQI (49.4%),  $\text{PM}_{2.5}$  (69.1%), and  $\text{PM}_{10}$  (56.4%) were relatively higher at the sampling site in Beijing, but they were much higher at the sampling site in Xiamen (AQI 172.8%,  $\text{PM}_{2.5}$  90.7%, and  $\text{PM}_{10}$  226.1%). It is well known that the sources of particulate matters are complex, comprising primary emissions and secondary formation. Additionally, precipitation will significantly reduce the concentration of particulate matters, but it is unlikely to reduce levels of CO. These factors may cause relatively higher NRMS errors for particulate matter tracers than the CO tracer.

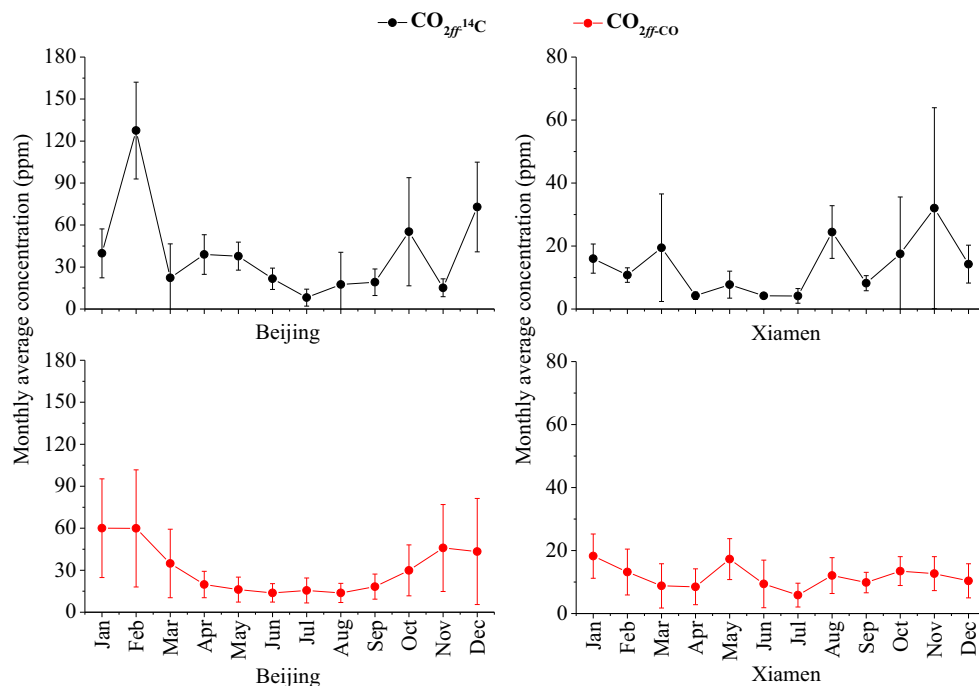
The high NRMS errors for diurnal variations at the sampling site in Xiamen resulted from low  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  concentrations in this

coastal city, especially in the summer with an average  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  concentration of 5.5 ppm. High NRMS errors due to low  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  concentrations (below 5 ppm) were also presented in the study of Levin and Karstens (2007). After the removal of summer diurnal samples, the NRMS errors for winter diurnal variations for the tracers of AQI,  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and CO at the sampling site in Beijing dropped to 40.6%, 54.6%, 46.8%, and 31.6% respectively—they fell to 64.2% (AQI), 58.1% ( $\text{PM}_{2.5}$ ), 49.9% ( $\text{PM}_{10}$ ), and 36.2% (CO) for the site in Xiamen. These NRMS errors for the CO tracer for winter diurnal variations are comparable to the uncertainties shown in other CO tracing studies (Gamnitzer et al. 2006; Levin and Karstens 2007; Vogel et al. 2010).

### Monthly averages of $\text{CO}_{2\text{ff}}$ traced by monthly averages of CO

Members of the publics and government sometimes focus on the average values of  $\text{CO}_{2\text{ff}}$  as an indication of fossil fuel emissions. Figure 3 shows the monthly averages of  $\text{CO}_{2\text{ff}}$  traced by two  $^{14}\text{C}$  data and those traced by the monthly averages of continuous CO observations at the urban sites in Beijing and Xiamen in 2014. The monthly averages of  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  varied greatly during 2014 at the sites in Beijing and Xiamen. In Beijing, they showed extremely high values in February and abnormally low values in November, while at the Xiamen site, the values of  $\text{CO}_{2\text{ff-}^{14}\text{C}}$  were abnormally high in August. However, the variation in monthly  $\text{CO}_2$  flux in Beijing (Liu et al. 2012) is roughly symmetrical and slightly concave. Similar variation was also observed for the monthly

**Fig. 3** Monthly averages of  $\text{CO}_{2\text{ff}}$  traced by two  $^{14}\text{C}$  data ( $\text{CO}_{2\text{ff-}^{14}\text{C}}$ , black dot) and those traced by monthly continuous CO observations ( $\text{CO}_{2\text{ff-CO}}$ , red dot) at the sampling sites in Beijing and Xiamen in 2014. The curve of monthly  $\text{CO}_{2\text{ff-CO}}$  averages at the Beijing site shows a shallow U-type variation



$\text{CO}_{2\text{ff}}-^{14}\text{C}$  averages in an inland city of Kraków, Poland (Kuc et al. 2007). The concave nature of the curve implies that there will be a large error in the monthly  $\text{CO}_{2\text{ff}}$  average if only two  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  data are used in  $\text{CO}_{2\text{ff}}$  calculation each month.

The results above show that CO is the most accurate AQI pollutant tracer to quantify  $\text{CO}_{2\text{ff}}$  at the sampling sites in Beijing and Xiamen; thus, the monthly  $\text{CO}_{2\text{ff}}$  averages in 2014 at the sites in Beijing and Xiamen were traced by the monthly averages of continuous CO observations, together with the linear equations for CO shown in Fig. 1. The curve of monthly  $\text{CO}_{2\text{ff}}\text{-CO}$  averages at the site in Beijing shows a shallow U-type variation, as can be seen in Fig. 3. Compared to the  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  curve in Fig. 3, the  $\text{CO}_{2\text{ff}}\text{-CO}$  curve at the Beijing site is more similar to the variations in monthly  $\text{CO}_2$  flux in this city (Liu et al. 2012), which also showed a shallow U-type variation. The monthly  $\text{CO}_{2\text{ff}}\text{-CO}$  average in August at the Xiamen site is relatively lower compared to the abnormally high monthly  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  average in this month. Thus, these monthly  $\text{CO}_{2\text{ff}}$  averages traced by continuous CO observations might be closer to the actual monthly averages compared with those traced by limited  $^{14}\text{C}$  data.

## Conclusions

This study investigated the correlations between AQI pollutants and  $\text{CO}_{2\text{ff}}-^{14}\text{C}$  for semimonthly samples collected from urban sites in Beijing and Xiamen. We indirectly traced the diurnal  $\text{CO}_{2\text{ff}}$  variations for various days by AQI pollutants based on these correlations, and then validated indirectly traced  $\text{CO}_{2\text{ff}}$  by simultaneous diurnal  $^{14}\text{CO}_2$  observations. Finally, we traced the monthly  $\text{CO}_{2\text{ff}}$  averages by monthly continuous CO observations. From this study, we obtained the following conclusions:

1. The highest correlation coefficients between  $\text{CO}_{2\text{ff}}$  and AQI pollutants were found for CO tracer. Relatively higher  $\text{CO}:\text{CO}_{2\text{ff}}-^{14}\text{C}$  ratios were found in some Chinese sites compared with the ratios in some European sites, which might be due to higher Chinese CO emissions from burning coal and biomass. The intercepts of linear equations for  $\text{PM}_{2.5}$  and CO agreed with the continental background levels of  $\text{PM}_{2.5}$  and CO, respectively.
2. Trends in diurnal variations of  $\text{CO}_{2\text{ff}}$  traced by each of the separate AQI pollutants were similar to those traced by  $^{14}\text{C}$  at the two urban sites. The CO tracer generally showed good agreement (with IOA value of 0.94 for the Beijing site and 0.62 for the Xiamen site) and low NRMS errors among these indirect tracers of AQI pollutants, but it showed high NRMS errors for samples with low  $\text{CO}_{2\text{ff}}$  concentrations (below 5 ppm).
3. Monthly  $\text{CO}_{2\text{ff}}$  averages traced by CO observations were closer to the actual monthly  $\text{CO}_{2\text{ff}}$  averages than those

traced by limited  $^{14}\text{C}$  data. The monthly  $\text{CO}_{2\text{ff}}$  averages at the Beijing site showed a shallow U-type variation.

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