FOSSIL-FUEL-DERIVED CO_2 CONTRIBUTION TO THE URBAN ATMOSPHERE IN GUANGZHOU, SOUTH CHINA, ESTIMATED BY $^{14}CO_2$ OBSERVATION, 2010–2011

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ABSTRACT. From October 2010 to November 2011, the urban atmospheric CO_2 concentration in Guangzhou ranged from 550 to 460 ppm, with mean monthly concentration fluctuating between 530 and 470 ppm. A lower concentration was observed in summer and autumn, while a higher concentration occurred in spring and winter. The urban atmospheric CO_2 $\delta^{13}C$ value varied between –9.00 and –13.10‰, with mean monthly value fluctuating between –9.60 and –11.80‰. There was no significant relationship between the CO_2 concentration and $\delta^{13}C$ value, reflecting the influence from the fossil-fuel-derived CO_2 on the urban atmospheric CO_2. The urban atmospheric CO_2 $\Delta^{14}C$ value fluctuated dramatically from 29.1 ± 2.5‰ to –85.2 ± 3.1‰, with a mean annual value of –16.4 ± 3.0‰. A similar seasonal variation of $\Delta^{14}C$ value with the concentrations was observed: the higher $\Delta^{14}C$ values mainly appeared in summer and autumn (July to September), with a mean value of about –5.2 ± 2.9‰, while lower $\Delta^{14}C$ values occurred in spring and winter (December to April), about –27.1 ± 3.2‰ average. Based on the atmospheric $\Delta^{14}C$ values, the calculated fossil-fuel-derived CO_2 concentrations range between 1 and 58 ppm, with the mean annual concentration around 24 ppm. Similarly, a lower fossil-fuel-derived CO_2 concentration appeared in summer and autumn (July to September) with a mean value of ~17 ppm, while the higher fossil-fuel-derived CO_2 concentration occurred in spring and winter (December to April) with an average value of ~29 ppm. A comparison of the CO_2 concentrations before and after the Guangzhou Asian Games (in November 2010) and the Spring Festival of 2011 confirmed that human activities can greatly decrease the fossil-fuel-derived CO_2 emissions to the urban atmosphere in Guangzhou.

INTRODUCTION

Human activity is considered to be the main reason for the sharp increase in atmospheric CO_2 concentration since the Industrial Revolution and global warming (IPCC 2007). Reducing anthropogenic CO_2 emissions becomes the essential problem in the discussion of each international climate conference. After the Copenhagen Climate Change Conference in 2009, measuring and reporting atmospheric CO_2 concentration became necessary for the inspection of regional anthropogenic CO_2 emission and the evaluation of human impact on global warming. Monitoring of atmospheric CO_2 concentration has been conducted since 1950s (Keeling 1976), and a global air sampling network was established by the World Meteorological Organization (WMO) and the US National Oceanic and Atmospheric Administration (NOAA). The monitoring of atmospheric CO_2 in China was initiated relatively late. Most studies in China mainly concern seasonal or annual variations of atmospheric CO_2 concentration in the regional background stations (Wen et al. 1997; Wang and Li 1996; Wang GC et al. 2002; Wang YS et al. 2002; Wang CK et al. 2003).

Atmospheric $^{14}CO_2$ (usually reported as $\Delta^{14}C$) is considered the most sensitive tracer to monitor fossil-fuel-derived CO_2 contribution to the atmosphere (Levin et al. 1980, 2003; Gamnitzer et al. 2006; Turnbull et al. 2006; Hsueh et al. 2007). The carbon in fossil-fuel-derived CO_2 contains only ^{12}C and ^{13}C isotopes, so addition of CO_2 from fossil sources would dilute the ^{14}C value in the local atmosphere (Suess 1955). On the other hand, combustion of fossil fuel generates CO_2 with a ^{14}C of –1000‰ (Levin et al. 2003), thus a strongly negative shift in the ^{14}C of atmospheric CO_2. According to the differences in ^{14}C and CO_2 concentration relative to the background values, the fossil-fuel-derived CO_2 can be distinguished from autogenous CO_2 in the biosphere using mass balances

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of CO_2 and ^{14}C (Tans et al. 1979; Levin et al. 2003; Turnbull et al. 2006; Graven et al. 2009). For example, 1 ppm CO_2 generated from fossil fuel to the local atmosphere will cause a depletion of ^{14}C by approximately 2.8‰ (Turnbull et al. 2006). Therefore, observing the urban atmospheric CO_2 $\Delta^{14}C$ values could clearly reflect the impact of human activities on atmospheric CO_2 (Riley et al. 2008). Urban atmospheric CO_2 $\Delta^{14}C$ observation is also used to evaluate the influences on the remote rural atmospheric CO_2 and further the carbon isotopic composition of plants influenced by fossil fuel emission dispersion (Levin et al. 2003; Hsueh et al. 2007). Sampling air at different heights over a city or surrounding rural area and collecting annual plants such as corn leaves across a continent are proposed to be effective methods to trace fossil-fuel-derived CO_2 in the atmosphere (Levin et al. 2003; Hsueh et al. 2007; Wang and Pataki 2010). However, we still know little about atmospheric CO_2 ^{14}C in China, but preliminary work has been conducted on ^{14}C values of corn leaves across northern China (Xi et al. 2011, 2013).

To investigate the fossil-fuel-derived CO_2 in the urban atmosphere in China, air samples from Guangzhou, south China, were collected between October 2010 to November 2011. The ^{14}C values of urban atmospheric CO_2 in Guangzhou are presented herein and the fossil-fuel-derived CO_2 contribution to the urban atmosphere is calculated.

STUDY SITE

Guangzhou is located in the hinterland of the Pearl River Delta, one of the most economically developed areas in China. The city consumes more than 50 million tons of coal per year in comprehensive energy statistics. It is surrounded by hills and mountains except in the southeast where it borders the Pearl River Delta plain (Figure 1). A northern wind prevails in winter and spring, then comes from the south and southwest in summer and autumn. The average annual temperature is ~21 °C, and the annual average precipitation is between 1800~1900 mm. There are 2 peaks of precipitation during the rainy season (from April to September): 1) precipitation is brought by the East Asian summer monsoon from late spring to early summer; 2) from late summer to early autumn, the northwest Pacific summer monsoon causes tropical storms and typhoon to this area, and more than 80% of the rainfall occurs in this period (Wang and Lin 2002).

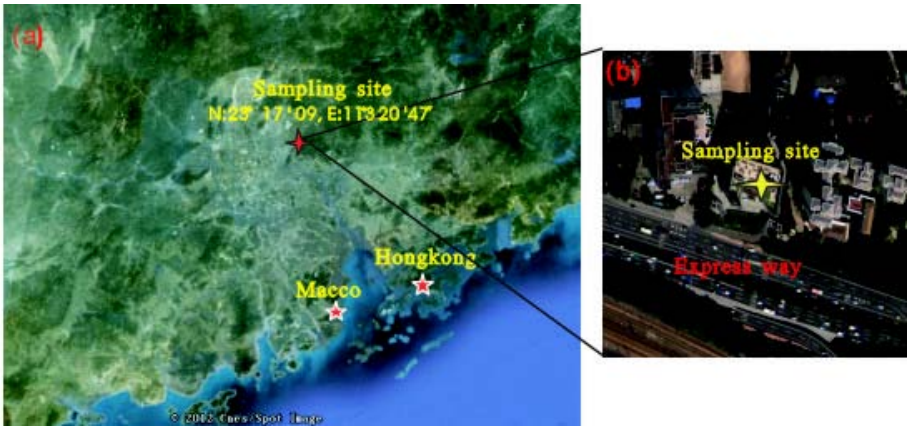

Figure 1 Location (a) and the detailed position (b) of the sampling site

METHODS

Collection of Air Samples

The sampling site (23°17′09″N, 113°20′47″E) is located on the rooftop of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS). The building is 30 m above the ground and ~80 m above sea level (asl), higher than the average altitude of 11 m asl of Guangzhou. In front of the building, ~80 m and 120 m away, there is an express way and a railway, respectively (Figure 1). Considering the location of the sampling site, it may be influenced by local signals rather than representing a general urban signal. The air samples were collected at 20:00, every Monday. The reason for the sampling time is that 18:00 to 19:00 is the "rush hour" of the city, and CO_2 emitted from the traffic and domestic activities such as cooking reaches its highest point at that time. Thus, the atmospheric CO_2 concentration is close to its peak in that time period (Wang CK et al. 2003).

The air samples were collected using the vacuum flask trapping method. The flask, 4.3 L in volume, was first vacuumed under 1.0×10^{-3} Torr for 4 hr, then the vacuumed and sealed flask was taken to the sampling site. Before collection, the flask mouth was set towards the prevailing wind direction for the corresponding season. It took about 45 min to collect the air sample in order to ensure the equilibrium of air in and out the flask had been reached. At the same time as the collection, a handheld CO_2 meter (GM 70, with a precision of ±20 ppm) was used to monitor the atmospheric CO_2 concentration. The equipment was calibrated by the real-time atmospheric temperature and pressure measured by 2 probers, respectively. Atmospheric CO_2 concentration was recorded when the of the handheld CO_2 meter readout was stable. In order to clarify the CO_2 ^{14}C value emitted from biological respiration, 6 newborn leaves as well as samples of secreted fluid from leaves of three 10-yr-old mango trees in the institute were sampled in August 2011.

Sample Preparation

CO_2 gas in the air sample was extracted and purified by flowing through a gas mass flow meter at a fixed rate of 120 mL/min under vacuum with a liquid nitrogen cold trap (–196 °C) and liquid nitrogen + alcohol cold trap (–90 °C). CO_2 concentration was calculated with a precision of 10 ppm by measuring the purified CO_2 pressure in a known volume with a microbarograph. The purified CO_2 was then divided into 2 portions, one containing 0.5–1.0 mg C for the graphitization using the method of Xu et al. (2007). The other portion was preserved for stable carbon isotope analysis.

The mango leaves were pretreated with a standard acid-base-acid (ABA) process (Santos et al. 2004). The secreted leaf fluid samples, however, were only treated with 0.5M HCl to remove any carbonate that may exist. After washing to neutral pH with deionized water, the leaf samples and leaf fluid samples were dried using a vacuum freeze-drier. The tree leaves and the secreted fluids were then combusted into CO_2 gas in the sealed vacuum tubes together with silver and copper oxide. The converted CO_2 was extracted and purified in the same way as described above.

Pretreatment and graphitization of air CO_2, tree leaves, and secreted fluids were carried out at the accelerator mass spectrometry (AMS) ^{14}C laboratory of the State Key Laboratory of Isotope Geochemistry (Guangzhou, China). The graphite targets were measured by a compact NEC 0.5 MeV AMS facility at the State Key Laboratory of Nuclear Physics and Technology, Peking University (Liu et al. 2007) with a precision better than 0.3% and background $^{14}C/^{12}C$ ratio below 4×10^{-16}. The $^{13}C/^{12}C$ ratio of the purified CO_2 gas was analyzed by a Finnigan MAT-251 mass spectrometer with a precision of ±0.02‰ in the State Key Laboratory of Loess and Quaternary Geology (Xi'an, China). Results were reported as $\delta^{13}C$ with the international Pee Dee belemnite (PDB) standard.

RESULTS AND DISCUSSION

In this paper, $\Delta^{14}C$ is defined as $\Delta^{14}C = (A_{SN}/A_{abs} - 1) \times 1000‰$ (based on Stuiver and Polach 1977), where A_{SN} is the sample ^{14}C activity corrected by isotopic fractionation and A_{abs} is the absolute international standard ^{14}C activity, corrected both by isotopic fractionation and decay correction between 1950 and the year of the measurement. The weekly and monthly mean atmospheric CO_2 $\Delta^{14}C$ values are listed in Tables 1 and 2, respectively.

Table 1 The weekly urban atmospheric CO_2 concentration, $\delta^{13}C$ value, $\Delta^{14}C$ value, fossil-fuel-derived CO_2 concentration (C_{ff}) and inhalable particle (PM_{10}) concentration in Guangzhou, south China, from October 2010 to November 2011.

Date D-M-Y	CO_2 concentration (ppm)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Error ±	C_{ff} (ppm)	PM_{10} (μg/m^3)
4-Oct-10	559	–11.85	29.1	2.5	1	35
11-Oct-10	509	–9.75	–35.4	3.7	33	51
18-Oct-10	505	–10.17	25.9	3.6	3	42
25-Oct-10	528	–10.37	0.0	5.0	16	33
1-Nov-10	531	–10.40	–22.2	2.9	27	58
8-Nov-10	526	–10.16	–18.5	2.3	25	61
15-Nov-10	516	–11.40	–11.9	2.5	22	58
22-Nov-10	538	–9.27	19.1	3.0	7	58
29-Nov-10	495	–9.96	–32.2	3.0	31	56
6-Dec-10	531	–9.47	10.0	3.4	11	66
13-Dec-10	527	–13.10	–65.1	3.0	48	79
20-Dec-10	497	–12.30	–62.7	2.9	45	68
27-Dec-10	493	–10.50	–49.0	2.9	38	35
3-Jan-11	570	–11.40	7.1	3.4	13	63
10-Jan-11	560	–9.00	–15.8	2.9	25	64
24-Jan-11	552	–10.46	–33.5	3.0	34	51
30-Jan-11	550	–9.27	7.1	2.7	13	28
12-Feb-11	540	–10.68	–2.0	3.1	17	13
14-Feb-11	537	–9.00	11.2	2.5	11	6
21-Feb-11	493	–12.42	–71.7	2.7	49	54
28-Feb-11	511	–9.86	–15.6	3.4	23	63
7-Mar-11	551	–9.36	–12.6	2.9	23	60
13-Mar-11	522	–9.20	–6.7	3.0	19	78
20-Mar-11	481	–10.38	–28.9	2.7	28	59
27-Mar-11	519	–11.53	–85.2	3.1	57	67
4-Apr-11	508	–10.82	–28.5	2.5	29	82
11-Apr-11	542	–10.90	–40.5	2.7	37	67
18-Apr-11	498	–10.54	–27.1	2.9	29	43
2-May-11	497	–10.29	–16.1	3.4	24	53
9-May-11	539	–10.68	8.9	3.4	12	42
23-May-11	489	–10.73	–3.1	3.0	17	20
30-May-11	534	–9.78	–24.1	2.9	29	69
6-Jun-11	538	–9.64	7.0	2.9	13	22
13-Jun-11	515	–9.38	–8.6	3.4	21	24
20-Jun-11	506	–11.29	–85.1	2.9	58	34
27-Jun-11	510	–9.38	21.2	3.0	6	37
4-Jul-11	463	–9.40	7.6	2.7	12	33
11-Jul-11	503	–9.24	–26.3	3.1	29	40
18-Jul-11	486	–12.28	24.6	2.5	4	53
25-Jul-11	468	–10.11	–38.8	2.7	33	59
1-Aug-11	476	–10.21	3.7	2.9	14	56
7-Aug-11	509	–9.26	4.3	3.4	14	39
15-Aug-11	460	–9.42	–10.5	2.9	20	25

Table 1 The weekly urban atmospheric CO_2 concentration, $\delta^{13}C$ value, $\Delta^{14}C$ value, fossil-fuel-derived CO_2 concentration (C_{ff}) and inhalable particle (PM_{10}) concentration in Guangzhou, south China, from October 2010 to November 2011. *(Continued)*

Date D-M-Y	CO_2 concentration (ppm)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Error ±	C_{ff} (ppm)	PM_{10} ($\mu g/m^3$)
22-Aug-11	468	–10.11	7.2	3.0	12	29
29-Aug-11	484	–9.32	–13.4	2.7	22	36
5-Sep-11	468	–9.98	8.6	3.1	12	62
12-Sep-11	486	–10.00	15.7	2.5	8	35
19-Sep-11	478	–10.20	–23.6	2.7	27	50
26-Sep-11	479	–10.48	–14.5	2.9	23	55
3-Oct-11	495	–9.68	–2.3	3.4	17	24
10-Oct-11	471	–9.40	–35.9	2.9	32	45
17-Oct-11	471	–12.28	–47.1	2.7	37	53
24-Oct-11	473	–12.11	–51.8	2.5	40	76
31-Oct-11	504	–10.21	–43.4	3.0	38	50
7-Nov-11	479	–9.22	–25.9	3.0	28	38
14-Nov-11	477	–10.42	–3.7	3.4	17	50
21-Nov-11	474	–10.11	–8.6	3.0	20	41
28-Nov-11	456	–9.12	–7.4	2.7	19	68

Table 2 The monthly mean urban atmospheric CO_2 concentration, $\delta^{13}C$ value and $\Delta^{14}C$ value and fossil-fuel-derived CO_2 concentration (C_{ff}) in Guangzhou, south China, from October 2010 to November 2011.

Month (M-Y)	CO_2 concentration (ppm)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Error ±	C_{ff} (ppm)
Oct-10	499	–10.54	4.9	3.7	13.3
Nov-10	495	–10.24	–13.1	2.8	22.1
Dec-10	512	–11.34	–41.7	3.0	35.5
Jan-11	530	–10.03	–8.7	3.0	20.9
Feb-11	494	–10.49	–19.5	2.9	24.8
Mar-11	492	–10.12	–33.4	2.9	31.9
Apr-11	499	–10.75	–32.0	2.7	31.7
May-11	515	–10.37	–8.6	3.1	20.5
Jun-11	517	–9.92	–16.4	3.0	24.3
Jul-11	480	–10.26	–8.2	2.8	19.5
Aug-11	479	–9.66	–1.7	3.0	16.4
Sep-11	478	–10.07	–3.5	2.8	17.2
Oct-11	483	–10.49	–35.4	2.9	35.5
Nov-11	472	–9.72	–11.4	3.0	20.8

Variation of CO_2 Concentration and $\delta^{13}C$ Value

CO_2 measurements obtained using the handheld CO_2 meter were in good agreement with the calculated results within ±10 ppm except for a few data (see Figure 2a). Values ranged from 550 ± 10 to 460 ± 10 ppm from October 2010 to November 2011 (Figure 2a), with a monthly mean CO_2 concentration between 530 ± 10 and 470 ± 10 ppm (Figure 3). The maximum CO_2 concentration appeared during winter, from December to January, while the minimum concentration appeared in summer from July to September. The variation was consistent with the natural fluctuation of atmospheric CO_2 concentration caused by biospheric photosynthesis and respiration (Amundson et al. 1998). A subpeak in CO_2 concentration was observed during March to June when the urban atmospheric CO_2 concentration increased by 40 ppm. However, it decreased sharply by 50 ppm in July. In the same

month but different year, e.g. October and November in 2010 and 2011, respectively, the urban atmospheric CO_2 concentration showed a fluctuation of 20 to 30 ppm.

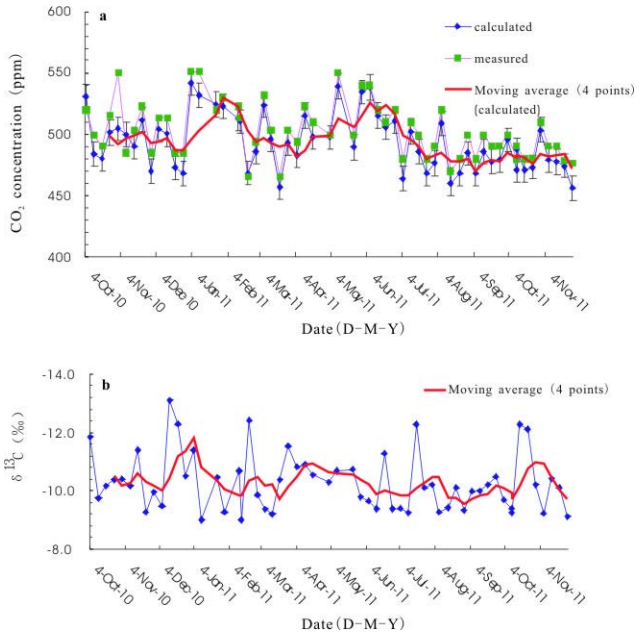

Figure 2 Variations of the urban atmospheric CO_2 concentration (a) and $\delta^{13}C$ values (b) in Guangzhou from October 2010 to November 2011.

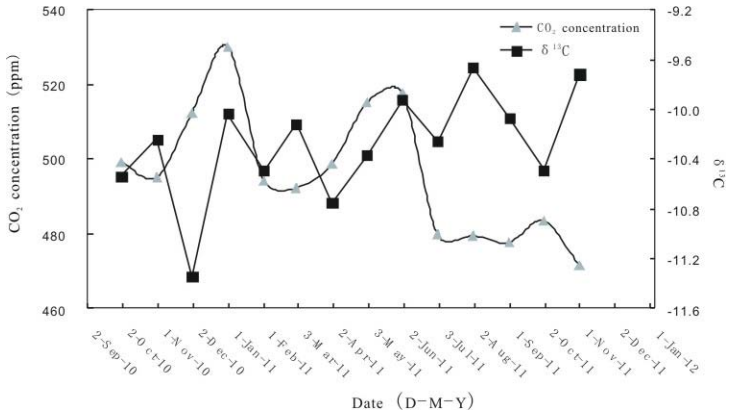

Figure 3 Variations of the monthly mean urban atmospheric CO_2 concentration and $\delta^{13}C$ values in Guangzhou from October 2010 to November 2011.

Based on the atmospheric CO_2 concentrations from 4 background stations (Table 3), the background value of atmospheric CO_2 concentration in China is ~383 ppm during 2006 to 2007 (Liu et al. 2009). The international background of atmospheric CO_2 concentration increases by 1.93 ppm per year (WMO 2007). Therefore, the background of atmospheric CO_2 concentration in China during 2010 to 2011 would be ~390 ppm. Obviously, the monthly mean urban atmospheric CO_2 concentration in Guangzhou was higher than the background by 70 to 160 ppm. A large difference was also seen in

the urban atmospheric CO_2 concentration in Beijing (Wang CK et al. 2003). As indicated by the atmospheric CO_2 concentration during 1993 to 2000, which ranged between 441 to 367 ppm with an amplitude ~74 ppm in a suburb of Beijing, the urban atmospheric CO_2 concentration in Beijing would be higher than 460 ppm during 2010 to 2011 considering the urbanization.

Table 3 Atmospheric CO_2 concentrations from 6 regional stations in China: # International background station (2006~2007), * national background station in China (2006~2007).

Station	Lat. (N)	Long. (E)	m asl	Distance to city (km, city)	Monthly max. (ppm, month)	Monthly min. (ppm, time)	Reference
Waliguan#	36°17′	100°54′	3816	150, Xilin	387, April	374, Oct/Nov	Liu et al. 2009
Shangdianzi*	40°39′	117°07′	293	150, Beijing	391, April	364, Oct/Nov	Liu et al. 2009
Lin'an*	30°18′	119°44′	138	50, Hangzhou	393, February	375, July	Liu et al. 2009
Longfengshan*	44°44′	127°36′	330	180, Harbin	395, February	358, Oct/Nov	Liu et al. 2009
Beijing	39°58′	116°22′	84	0, Beijing	430, February	369, Oct/Nov	Wang et al. 2003
Guangzhou	23°17′	113°20′	80	0, Guangzhou	530, January	470, Oct/Nov	This work

The urban atmospheric CO_2 $\delta^{13}C$ value in Guangzhou varied between –9.00 and –13.10‰ from October 2010 to November 2011 (Figure 2b). The monthly mean $\delta^{13}C$ value ranges between –9.60 and –11.80‰ with a shift of ~2.20‰ in amplitude (Figure 3). More positive $\delta^{13}C$ values appeared in summer and autumn, and reached a maximum of –9.60‰ in August. In winter and spring, the $\delta^{13}C$ value was more negative, with a minimum of –11.80‰ appearing in December. Based on the data from Waliguan, an international background station (Zhou et al. 2006), the background value of atmospheric CO_2 $\delta^{13}C$ varied between –7.80 and –8.40‰ in 2002, and decreased by 0.04‰ per year from 1992 to 2002. According to the data above, the calculated CO_2 $\delta^{13}C$ value of atmospheric CO_2 $\delta^{13}C$ of Waliguan from 2010 to 2011 would range between –8.16 and –8.56‰. The urban atmospheric CO_2 $\delta^{13}C$ value in Guangzhou was obviously lower by 1.44 to 3.24‰ than that of Waliguan.

Long-term observations show a significant inverse relationship between atmospheric CO_2 concentration and $\delta^{13}C$ value (Amundson et al. 1998; Zhou et al. 2006). The inverse relationship reflects a strong influence from the biosphere to the atmosphere. However, the inverse relationship has not been indicated in the urban atmospheric CO_2 concentration and $\delta^{13}C$ value in Guangzhou. As shown in Figure 4, these was no relationship between CO_2 concentration and $\delta^{13}C$ value in the urban atmosphere of Guangzhou (Figure 4a) despite a weak inverse correlation ($r^2 = –0.32$, $p < 0.001$, $n = 14$) in the monthly mean value (Figure 4b).

Although the similar variations of atmospheric CO_2 concentration and $\delta^{13}C$ value with the atmospheric background measurements are partly reflected in the urban atmosphere of Guangzhou, the great difference of the values and correlation implies an unusual urban atmosphere. A huge addition of fossil-fuel-derived CO_2 to the urban atmosphere would be responsible for the difference. Additional fossil-fuel-derived CO_2 depleted in ^{13}C and ^{14}C did not only significantly increase the urban atmospheric CO_2 concentration and decrease the urban atmospheric CO_2 $\delta^{13}C$ value, but also disturbed the correlation between the CO_2 concentration and $\delta^{13}C$ value.

$\Delta^{14}C$ and Fossil-Fuel-Derived CO_2

The atmospheric CO_2 ^{14}C fluctuated significantly from 29.1 ± 2.5‰ to –85.2 ± 3.1‰ with a mean value of –16.4 ± 3.0‰ from October 2010 to November 2011 in Guangzhou (Figure 5a). The monthly mean ^{14}C values, however, showed a more narrow range between 4.9 ± 3.0‰ and –41.7 ± 2.7‰ (Figure 5b). Higher ^{14}C values appeared in the summer and autumn (July to September), with

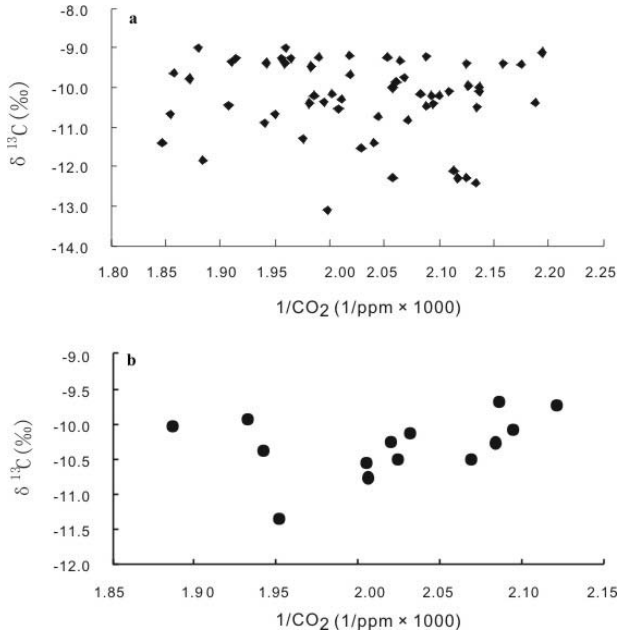

Figure 4 Correlations between weekly and monthly urban atmospheric CO_2 concentration and $\delta^{13}C$ value in Guangzhou.

a mean of –5.2 ± 2.9‰, while the lower ^{14}C values were concentrated in winter and spring (December to April), with a mean value of –27.1 ± 3.2‰.

The atmospheric CO_2 in Guangzhou is assumed to mainly come from background (C_{bg}), terrestrial biosphere exchange (C_{bio}), and fossil fuel combustion (C_{ff}). Oceanic emission is neglected because Guangzhou is not a coastal city and the sampling site is low in altitude. Based on the conservation equation, the atmospheric CO_2 concentration can be expressed as follows (Levin et al. 2003):

$$C_m = C_{bg} + C_{bio} + C_{ff} \quad (2)$$

Atmospheric CO_2 $\Delta^{14}C$ ($\Delta^{14}C_m$) also contains 3 different components: $^{14}C_{bg}$, $^{14}C_{bio}$, and $^{14}C_{ff}$. According to the conservation principles, the following equation could be expressed as (Levin et al.2003):

$$C_m\Delta^{14}C_m = C_{bg}\Delta^{14}C_{bg} + C_{bio}\Delta^{14}C_{bio} + C_{ff}\Delta^{14}C_{ff} \quad (3)$$

Based on the Equations 2 and 3, the following equation could be derived:

$$C_{ff} = \frac{C_m(\Delta^{14}C_m - \Delta^{14}C_{bio}) + C_{bg}(\Delta^{14}C_{bio} - \Delta^{14}C_{bg})}{\Delta^{14}C_{ff} - \Delta^{14}C_{bio}} \quad (4)$$

where $\Delta^{14}C_{ff}$ = –1000‰ and C_{bg}= 390 ppm determined from the equations above. The $\Delta^{14}C$ background values adopted are different in different regions of the world. A background interval of about 35‰ to 45‰ was suggested for the Pt. Barrow station during May to September 2009 (XM Xu, personal communication). According to the measured $\Delta^{14}C$ values of annual plant corn leaves in 2010 from Qinghai, Gansu Province, and Tibet, where the human activity can be neglected, the mean

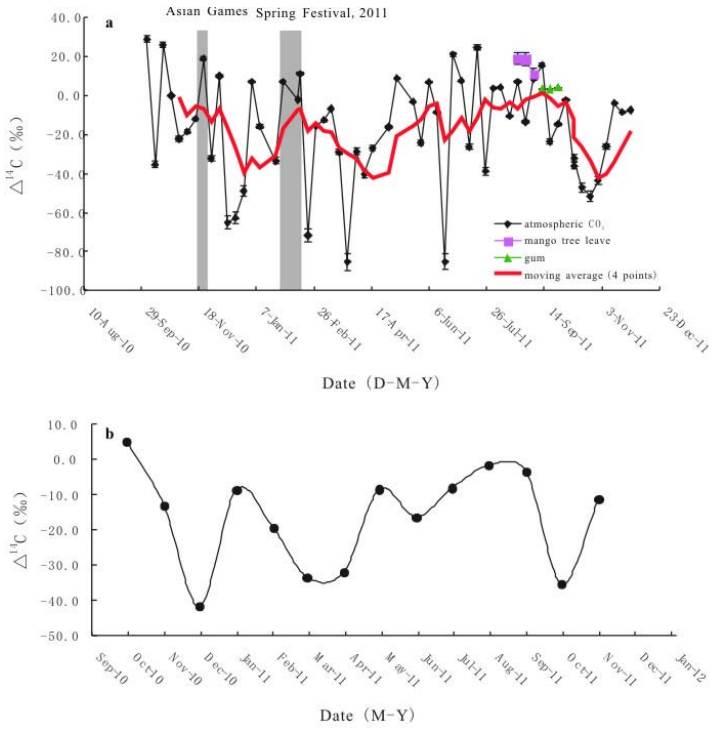

Figure 5 Weekly (a) and monthly (b) variations of urban atmospheric CO_2 $\Delta^{14}C$ during October 2010 to November 2011 in Guangzhou.

$\Delta^{14}C$ value of 37.5 ± 3.0‰ was taken as the background $\Delta^{14}C$ value of 2010 in China (Xi et al. 2012), $\Delta^{14}C_{bg}$ = 37.5‰. To obtain the $\Delta^{14}C_{bio}$ value, a simple assumption was made that the CO_2 emission from soil respiration could be neglected since most of the Guangzhou city area was covered by concrete. The biospheric CO_2 emission is mostly derived from plant respiration, which has a similar $\Delta^{14}C$ value with plants. Measured leaves and secreted fluids from three 10-yr-old mango trees in the Institute suggested a $\Delta^{14}C$ value ranging from 4.8 ± 2.8‰ to 26.1 ± 3.10‰, with a mean value of 15.0 ± 3.0‰ in 2011. The mean value of 15.0‰ was thus taken as the $\Delta^{14}C$ value of the biospheric CO_2 in Guangzhou, $\Delta^{14}C_{bio}$= 15.0‰. Using $\Delta^{14}C_{bg}$ = 37.5‰ and $\Delta^{14}C_{bio}$=15.0‰ in Equation 4, the fossil-fuel-derived CO_2 concentration (C_{ff}) was calculated and shown in Figure 6.

Results showed that the fossil-fuel-derived CO_2 concentration shifted between 1 and 58 ppm during 2010 to 2011 (Figure 6a), with an annual mean value of 24 ppm in Guangzhou. The monthly average fossil-fuel-derived CO_2 concentration also fluctuated dramatically, from 13 to 36 ppm (Figure 6c). Similar to the variation of CO_2 concentration, the lower fossil-fuel-derived CO_2 concentration appeared in the summer and autumn (July to September), with a mean concentration of 17 ppm, while the higher fossil-fuel-derived CO_2 concentration was observed in winter and spring (December to April), with a mean value of 29 ppm. A high fossil-fuel-derived CO_2 concentration also appeared in the urban atmosphere of Beijing. According to the $\Delta^{14}C$ values of corn leaves, the highest fossil-fuel-derived CO_2 concentration was a ~25 ppm in the atmosphere of Beijing in 2009 (Xi et al. 2009). The farther from the city, the lower the fossil-fuel-derived CO_2 concentration. The lowest fossil-fuel-derived CO_2 concentration of 4 ppm was found in a mountainous outer suburban area of Beijing. Furthermore, in Qinghai, Gansu, Inner Mongolia, and Tibet, areas far away from indus-

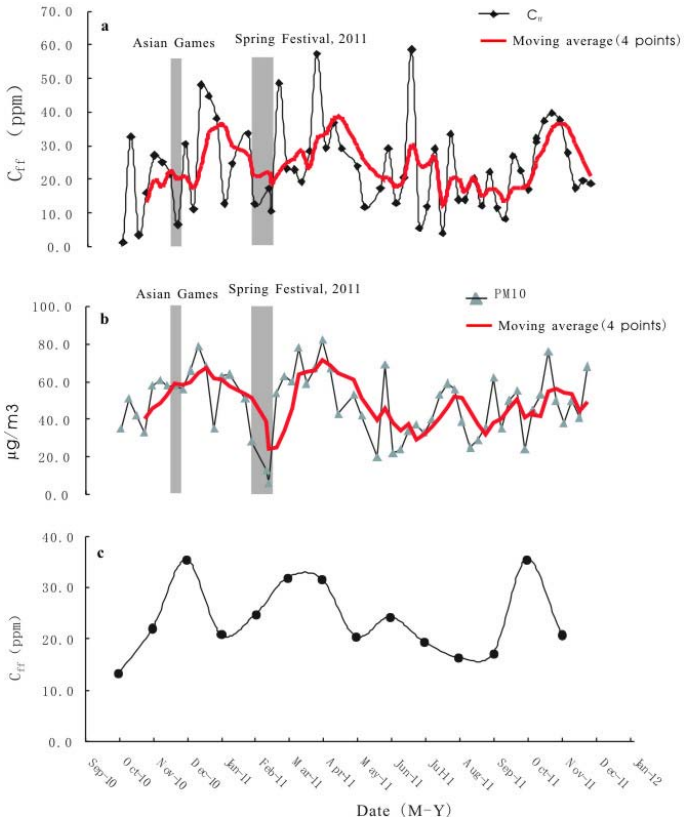

Figure 6 Weekly (a) and monthly (c) variations of C_{ff}, and weekly variation of inhalable particle concentration (PM_{10}) (b) during October 2010 to November 2011 in Guangzhou.

try and traffic, the fossil-fuel-derived CO_2 concentration was calculated to be only 1 ppm (Xi et al. 2013). For comparison, an obviously lower fossil-fuel-derived CO_2 concentration was observed long term in an urban station in Heidelberg, Germany, which had only 14 ppm in winter and 6.5 ppm in summer in the atmosphere (Levin et al. 2003), almost half that of Guangzhou.

Compared to the high CO_2 enrichment in the urban atmosphere, the lower concentration of fossil-fuel-derived CO_2 indicated a huge contribution of biogenic CO_2 to the atmosphere. This could be derived from biomass burning, such as wood and other biofuel used for heating and cooking (Turnbull et al. 2011), or human respiration (Wang and Pataki 2010) and soil and plant respiration (Scheimel 1995). The main source of biogenic CO_2 in the observation site was inferred to link with the combustion of plant litter such as leaves and branches that were collected as garbage every day. It was quite difficult to quantify the amount of biogenic CO_2 derived from the combustion of the plant garbage. As reported, the mean density of plant carbon is 15.9 t/hm^2 in Guangzhou city, so the plant litter derived from regeneration would be close to that amount. It was not clear whether the plant garbage is combusted all over Guangzhou, but it was indeed combusted in the sampling region. Biogenic CO_2 from human respiration could also not be neglected. As measured by a handheld CO_2 meter in the office building, the CO_2 concentration reaches 600 ppm, which is mostly derived from human respiration within the building. The diffusion of the high CO_2 concentration from the office building somehow increases the atmospheric CO_2 concentration around the building.

Another possibility for the lower fossil-fuel-derived CO_2 contribution is linked to the $\Delta^{14}C_{bio}$ selected in the C_{ff} calculation where the soil respiration was neglected. According to Ding et al. (2010), who studied soil $^{14}CO_2$ in south China, the ^{14}C value of the soil CO_2 ranges from 100‰ to 107‰. Given that soil respiration contributes 10% CO_2 to the atmospheric CO_2 per year, or about 39–40 ppm in total, the equation could be expressed as:

$$C_m\Delta^{14}C_m = C_{bg}\Delta^{14}C_{bg} + C_{bio}\Delta^{14}C_{bio} + C_{ff}\Delta^{14}C_{ff} + C_s\Delta^{14}C_s \quad (5)$$

where C_s and $\Delta^{14}C_s$ are CO_2 concentration and its $\Delta^{14}C$ value from soil respiration, respectively. The recalculated results show that C_{ff} has increased by 3 to 5 ppm. This means C_{ff} should be larger since there was a great amount of biogenic CO_2 with variable sources and these higher $\Delta^{14}C$ sources fluxed into atmosphere.

The ^{14}C distribution in one region is related to local natural conditions, such as geographical and meteorological conditions, and human activities, such as population density, traffic, and industrial emissions (Wang and Pataki 2010). The Nanling Mountains to the north of Guangzhou greatly hinder the convection of the lower air, resulting in a low diffusion rate of fossil source CO_2 in the weak monsoon seasons. In spring and early summer, the weak summer monsoon could not disperse the urban atmospheric CO_2 concentration, which led to a subpeak of fossil source CO_2 concentration. Although the winter monsoon is strong, the Nanling Mountains dramatically reduced the intensity before the wind reached in Guangzhou. Additionally, the short duration of winter, generally from December to January, is also an important reason for the limited influence of the winter monsoon on decreasing fossil source CO_2 concentration in the urban atmosphere in Guangzhou. Thus, the fossil-fuel-derived CO_2 concentration reached its maximum in December. The winter and spring are also a period full of dust-haze in Guangzhou, with dust-haze days reach 22 days per month during this time (Li et al. 2008). On the contrary, during the late summer to early autumn, from July to September in general, tropical storms and typhoons accelerate the convection of lower air (Wang and Lin 2002), resulting in a significant decrease of fossil-fuel-derived CO_2 concentration.

Guangzhou consumes more than 50 million tons of standard coal per year in comprehensive energy statistics. Thus, the emissions from human activities including daily domestic life, traffic, and industrial contribute a huge amount of fossil-fuel-derived CO_2 to the urban atmosphere. Controlling the human activities would be an effective way to reduce the fossil-fuel-derived CO_2 emission. During the Gaungzhou Asian Games, from 12 to 27 November 2010, traffic was limited by the government. The traffic amount decreased by nearly half and significantly improved the urban atmospheric CO_2 $D^{14}C$ value from –11.9‰ on November 15 to 19.1‰ on 22 November 2010. When the traffic controls were lifted on 29 November 2010, the CO_2 $\Delta^{14}C$ value quickly reached –32.2%. Correspondingly, the fossil source CO_2 concentration decreased from 22 to 7 ppm when the traffic was controlled, and then increased to 30 ppm when the traffic returned to normal. During the Spring Festival of 2011, from 30 January to 14 February 2011, when a great number of residents moved out of Guangzhou city, the traffic flow decreased by more than 70% during the 3-week period. The sharp decrease in traffic flow resulted in an obviously higher mean CO_2 $\Delta^{14}C$ value of 5.4 ± 3.0‰ than the average value of –27.1 ± 3.2‰ in this season. The calculated fossil-fuel-derived CO_2 was only 13 ppm, significantly lower than the average value of ~29 ppm in this season. However, when the Spring Festival was over, residents came back to the city and the CO_2 $\Delta^{14}C$ value measured –71.7‰ while the fossil-fuel-derived CO_2 climbed to 49 ppm on 21 February 2011. Similarly, the variation of the concentration of the inhalable particle fraction (PM_{10}), which mainly derives from traffic and industrial emissions, also showed a clear reduction during the Guangzhou Asian Games in 2010 and the Spring Festival of 2011 (Figure 6b).

SUMMARY AND CONCLUSION

The atmospheric CO_2 concentration ranged from 550 to 460 ppm during 2010 to 2011 in Guangzhou. The higher urban atmospheric CO_2 concentration mainly appears in winter and spring, while lower concentrations mainly occur in summer and autumn, partly reflecting the natural variation of atmospheric CO_2 concentration. The atmospheric CO_2 $\delta^{13}C$ values spanned from –9.00 to –13.10‰, obviously more negative than the background $\delta^{13}C$ value ranging between –8.16 and –8.56‰ in China. There was no correlation between the urban atmospheric CO_2 concentration and $\delta^{13}C$ value, reflecting a strong impact from fossil-fuel-derived CO_2 to the urban atmosphere in Guangzhou. Contrary to the seasonal variation of CO_2 concentration, the urban atmospheric CO_2 $\Delta^{14}C$, which ranged from 29.1 ± 2.5‰ to –85.2 ± 3.1‰ with a mean value of –16.4 ± 3.0‰, has higher $\Delta^{14}C$ values in summer and autumn (July to September) with a mean value of about –5.2 ± 2.9‰, and lower $\Delta^{14}C$ values in winter and spring (December to April) with a mean value of about –27.1 ± 3.2‰. The atmospheric CO_2 $\Delta^{14}C$ values indicate a significant influence of the fossil-fuel-derived CO_2 contributing to the urban atmosphere. Based on the conservation equations, the fossil-fuel-derived CO_2 concentration in the urban atmosphere in Guangzhou fluctuated between 1 and 58 ppm, with an annual average value around 24 ppm. Based on the fossil-fuel-derived CO_2 concentrations measured during and after the Guangzhou Asian Games, controlling human activities, especially automotive traffic, can greatly decrease CO_2 emissions to the urban atmosphere in Guangzhou.

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