Volume 25, issue 9, September 2010 ISSN 0883-2927

ELSEVIER

Applied Geochemistry

JOURNAL OF THE INTERNATIONAL ASSOCIATION OF GEOCHEMISTRY

Continued on outside back cover

Applied Geochemistry 25 (2010) 1339–1349

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Indoor and outdoor urban atmospheric CO_2: Stable carbon isotope constraints on mixing and mass balance

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ARTICLE INFO

Article history:
Received 3 December 2009
Accepted 5 June 2010
Available online 10 June 2010
Editorial handling by R.S. Harmon

ABSTRACT

From July to November 2009, concentrations of CO_2 in 78 samples of ambient air collected in 18 different interior spaces on a university campus in Dallas, Texas (USA) ranged from 386 to 1980 ppm. Corresponding $\delta^{13}C$ values varied from −8.9‰ to −19.4‰. The CO_2 from 22 samples of outdoor air (also collected on campus) had a more limited range of concentrations from 385 to 447 ppm (avg. = 408 ppm), while $\delta^{13}C$ values varied from −10.1‰ to −8.4‰ (avg.=-9.0‰). In contrast to ambient indoor and outdoor air, the concentrations of CO_2 exhaled by 38 different individuals ranged from 38,300 to 76,200 ppm (avg. = 55,100 ppm), while $\delta^{13}C$ values ranged from −24.8‰ to −17.7‰ (avg. = −21.8‰). The residence times of the total air in the interior spaces of this study appear to have been on the order of 10 min with relatively rapid approaches (~30 min) to steady-state concentrations of ambient CO_2 gas. Collectively, the $\delta^{13}C$ values of the indoor CO_2 samples were linearly correlated with the reciprocal of CO_2 concentration, exhibiting an intercept of −21.8‰, with $r^2 = 0.99$ and $p < 0.001$ ($n = 78$). This high degree of linearity for CO_2 data representing 18 interior spaces (with varying numbers of occupants), and the coincidence of the intercept (−21.8‰) with the average $\delta^{13}C$ value for human-exhaled CO_2 demonstrates simple mixing between two inputs: (1) outdoor CO_2 introduced to the interior spaces by ventilation systems, and (2) CO_2 exhaled by human occupants of those spaces. If such simple binary mixing is a common feature of interior spaces, it suggests that the intercept of a mixing line defined by two data points (CO_2 input from the local ventilation system and CO_2 in the ambient air of the room) could be a reasonable estimate of the average $\delta^{13}C$ value of the CO_2 exhaled by the human occupants. Thus, such indoor spaces appear to constitute effective "sample vessels" for collection of CO_2 that can be used to determine the average proportions of C_3 and C_4-derived C in the diets of the occupants. For the various groups occupying the rooms sampled in this study, C_4-derived C appears to have constituted ~40% of the average diet.

The average concentration of outdoor Dallas atmospheric CO_2 was ~17 ppm higher than the average of CO_2 concentrations measured on the same campus 10 a ago. In addition, Dallas outdoor CO_2 concentrations at both times were higher than the contemporaneous global atmospheric CO_2 concentrations. This observation, plus the fact that the increase of ~17 ppm in the average concentration of Dallas outdoor CO_2 was comparable to the global increase of ~18 ppm over the same 10-a interval, is consistent with a significant role for urban CO_2 "factories" in the global atmospheric CO_2 budget.

1. Introduction

A number of recent studies have examined patterns of C isotope variation in the CO_2 of urban atmospheres, which are concentrated sources of anthropogenic CO_2 (e.g. Clark-Thorne and Yapp, 2003; Widory and Javoy, 2003; Pataki et al., 2003, 2007; Zimnoch et al., 2004; Carmi et al., 2005; Newman et al., 2008). These studies of urban CO_2 are cast against the backdrop of rising global levels of tropospheric CO_2 from pre-industrial Holocene values of ~280 ppm (e.g. Friedli et al., 1989) to current concentrations of ~387 ppm (NOAA: http://www.esrl.noaa.gov/gmd/ccgg/trends/co2_data_mlo.html). Interest in the global increase in atmospheric CO_2 is centered on its implications for changes in Earth's climate (e.g. Petit et al., 1999; Hofmann et al., 2006, 2009).

Studies of urban outdoor and/or global tropospheric CO_2 consider processes in the C cycle that operate on various temporal and spatial scales with multiple sources and sinks of CO_2 (e.g. ocean–atmosphere CO_2 exchange, plant photosynthesis and respiration, combustion of fossil fuels, etc.). In contrast, the interiors of buildings and enclosed passenger compartments of vehicles of transport are important human "habitats" in which CO_2 mixing processes could be expected to operate on short time scales with a limited number of endmembers contributing to the CO_2 in the air of those spaces. Thus far, studies of indoor CO_2 have emphasized its concentration and the implications for health, performance efficiency, etc. (e.g.

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doi:10.1016/j.apgeochem.2010.06.004

Lee and Chang, 1999, 2000; Daisey et al., 2003; Shendell et al., 2004; Mendell and Heath, 2005; Roberson, 2006; Fromme et al., 2007; Santamouris et al., 2008; and references therein). To the best of the present authors' knowledge, little attention has been given to the relationship between the concentration and stable C isotope composition of indoor CO_2 (e.g., Widory and Javoy, 2003; Affek and Eiler, 2006).

If outdoor CO_2 and CO_2 respired by human occupants are the only CO_2 sources that mix in the air of an indoor environment, the CO_2 mixing process should manifest itself in easily understood variations of the concentrations and $^{13}C/^{12}C$ ratios of the indoor CO_2. These indoor CO_2 variations may in turn be used to deduce the average isotopic composition of the respired CO_2 and thus the average diets of the human occupants. In the current study, new data are presented on the concentration and C isotope composition of human-exhaled CO_2 and CO_2 in indoor and outdoor air. The data are interpreted in terms of the atom balance of simple mixing processes and the flux balances of open systems (i.e., ventilated rooms). The samples were collected on a university campus in Dallas, Texas, USA.

The new measurements of outdoor urban atmospheric CO_2 are compared with corresponding data measured ~10-a ago (Clark-Thorne and Yapp, 2003). The two sets of data are discussed briefly in the context of the change in the global concentration of tropospheric CO_2.

2. Methods

2.1. Collection of indoor and outdoor ambient air samples and extraction of CO_2

Samples of indoor and outdoor air were collected using evacuated vacuum flasks of known volume (1940 mL and 1948 mL) [e.g. Clark-Thorne and Yapp, 2003]. Indoor samples ($n = 78$) were collected at various locations on the campus of Southern Methodist University (SMU) in Dallas, Texas (Fig. 1). Specific locations of indoor samples are indicated by letters in Fig. 1 and Table 3. A total of 22 outdoor samples were collected at seven different sites around the SMU main campus as shown by numbers in Fig. 1 and Table 4. Samples were collected at different times of the day with variable environmental conditions (Table 4). All the indoor and the majority of the outdoor ($n = 17$) atmospheric CO_2 samples were collected about 1–2 m above local ground level (Tables 3 and 4). Five outdoor atmospheric CO_2 samples were collected on the roof of Moody parking garage (~18 m above ground level) located at the intersection of Airline Road and SMU Blvd. on the SMU campus (site 6 in Fig. 1). Temperature and relative humidity at the sites were measured for each sample. Other environmental variables such as wind direction and speed, and total atmospheric pressure were obtained from the web site (http://www.weather.gov/data/obhistory/KDAL.html) maintained by the National Weather Service at nearby Love-Field Airport, Dallas, Texas (Tables 3 and 4).

For measurement of concentration and isotopic composition, the method described by Clark-Thorne and Yapp (2003) was used to extract CO_2 from air collected in ~ 2 L vacuum flasks. For that work, the accuracy and precision of the extraction method (for CO_2 concentrations) were established by extracting CO_2 from artificial gas mixtures prepared with CO_2 and non-condensable gas in known proportions and found to be ±1 ppm (on a molar basis). Moreover, a precision of ±1 ppm was obtained for CO_2 in duplicate samples of outdoor air collected in ~2 L vacuum flasks (Clark-Thorne and Yapp, 2003).

For indoor CO_2 samples, there is an additional consideration in the determination of the molar mixing ratio (as ppm). According to the SMU Office of Facilities, Management and Sustainability, rooms (except for laboratories) in campus buildings are maintained at a very slight constant positive pressure relative to outdoor air. This indoor air pressure is only about 0.012% higher than outdoor air pressure. Thus, for indoor air samples, CO_2 concentrations (expressed as ppm) that were determined by normalizing a measured number of moles of CO_2 to the total moles of dry gas in a ~2 L flask (as calculated using outdoor air pressures) would result in a nominal value for the CO_2 concentration which was high by a factor of 1.00012. For nominal indoor CO_2 concentrations as high as ~2000 ppm, this would increase the uncertainty by ~0.2 ppm. This very small magnitude of additional uncertainty in the concentrations of indoor samples of CO_2 does not affect the conclusions of the study.

2.2. Collection of human-exhaled air and extraction of CO_2

The collection of human-exhaled air required a procedure that differed somewhat from the foregoing vacuum flask method. Therefore, somewhat more detailed descriptions of the procedure for collection and extraction of human-exhaled CO_2 are presented. Air exhaled by each of 38 individuals from the SMU community was collected using a 38.6 mL u-shaped Pyrex tube with a vacuum stopcock at each end. To purge the ambient air in the tube and replace it with CO_2-rich human respired air, each individual exhaled for 10 s through a disposable plastic beverage straw attached to the upstream side of the u-tube. When 10 s of slow, continuous exhalation through the u-tube had elapsed, the stopcock was quickly closed on the downstream side, the individual retreated from the straw, and the stopcock on the upstream side of the u-tube was then quickly closed. Thereafter, the closed u-tube was attached to a high vacuum extraction line via a ground glass joint connected to the downstream stopcock, and the u-tube portion of the sample vessel was immersed in a liquid N_2-filled dewar for 40 min to freeze CO_2 and H_2O out of the exhaled air sample. At the end of the 40-min interval (with the u-tube still maintained at the temperature of liquid N_2), non-condensable gases in the u-tube were slowly passed through a liquid N_2-cooled multiple coil trap to determine if any CO_2 and/or H_2O remained to be frozen out of the air sample. No CO_2 or H_2O were detected in the multiple coil trap in either of the extractions from two different samples of human-exhaled air. Thus, it was concluded that all detectable exhaled CO_2 and water is frozen in the u-tube during the 40 min at the temperature of liquid N_2. Subsequent extractions of CO_2 from air exhaled by people into the u-tube did not use the extra multiple coil trap as part of the extraction procedure. After pumping away non-condensable gases to separate them from the frozen CO_2 and H_2O, the CO_2 was processed as described by Clark-Thorne and Yapp (2003).

To calculate concentrations of human-exhaled CO_2 as molar ppm of dry air, it is necessary to know the volume of the collection tube (38.6 mL), the temperature of the sample air, the relative humidity of the sample air, and the total ambient air pressure. Relative humidity of the air exhaled by people into the u-tube was assumed to be 100%. Total ambient air pressure was determined from values of sea level corrected pressure reported by the United States National Weather Service at nearby Love Field, Dallas, Texas. The rationale for using this outdoor air pressure was presented in the preceding section. The approximate temperature of the exhaled air sample was estimated by a simple (although crude) expedient. An individual would closely blow on a thermometer, which was in the confining, approximately hemispheric volume of his/her cupped hand until the temperature indicated by the thermometer stopped rising. It should be noted that even if these measured temperatures are in error by as much as 6 °C, it would introduce an error of no more than about 2% of the nominal value of the calculated concentration of the exhaled CO_2. For the high concentrations of

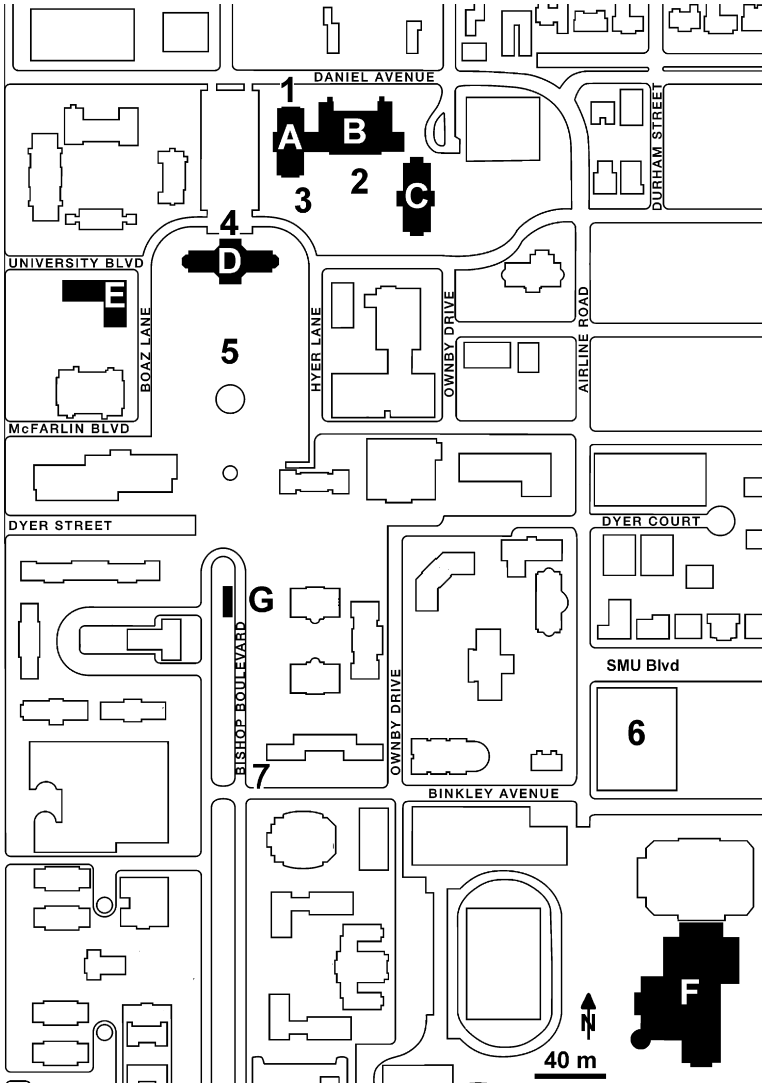

Fig. 1. Sample sites on the SMU campus. Outdoor atmospheric CO_2 samples are represented by numbers from 1 to 6. Indoor atmospheric CO_2 samples are represented by letters as follows: A – Heroy Building; B – Fondren Science; C – Dedman Life Sciences; D – Dallas Hall; E – Perkins Administration Building; F – Dedman Center for Lifetime Sports; G – SMU mustang express (shuttle bus).

human-respired CO_2 measured for this work, the impact of this magnitude of uncertainty in the concentrations of a presumed end-member is not an impediment to the characterization of the mixing and isotopic mass balance of CO_2 in indoor air.

The fact that 10 s of continuous exhalation was sufficient to purge the u-tube of ambient air was established by collecting different samples of air exhaled by a single individual for either 2 s, 5 s, 10 s, or 15 s purge intervals over the course of a single day (Fig. 2A; Table 1, section A). There was no substantial change in the measured concentration of CO_2 between the 5 s and 10 s purge times (from 48,100 ppm to 49,200 ppm; Table 1, section A). Therefore, a 10 s purge seemed adequate to insure that a sample of exhaled air was *not* contaminated by residual ambient air in the u-tube. It should be mentioned that because the 10 s exhalation time implies a somewhat longer residence time in the lungs than under normal conditions, the exhaled CO_2 collected for this study could exhibit higher concentrations than in "normal" breath. A longer residence time might account for the further increase in CO_2 concentration associated with the 15 s exhalation time (Fig. 2A; Table 1, section A).

The possibility that variations in the measured concentrations of CO_2 exhaled by different individuals might be, at least in part, a consequence of some unrecognized differences in the lengths of time for which breath was retained before exhalation into the u-tube was examined by collecting samples of air exhaled by a single individual. The concentration of exhaled CO_2 exhibits a progressive increase with increasing nominal retention times of ~1 s, 30 s, and 80 s (Table 1,section B; Fig. 2B), which mirrors the results of Epstein and Zeiri (1988) for consumption of O_2 during respiration.

During routine collection of exhaled air, individuals did not retain inhaled air for more than ~3 or 4 s before exhalation. Therefore, although variation in the concentrations of exhaled CO_2 among individuals may reflect some degree of differences in breath retention time, it is not thought to be a primary factor in the interpretation of the data of this study.

2.3. Generation of CO_2 from the ingredients in a cola beverage

A small volume (~10 mL) of the liquid in a newly opened container of a commercial cola was dried in air at 22 °C followed by vacuum desiccation at room temperature. A portion of the viscous residue was weighed by difference using a fragment of pure silica glass ("quartz" glass) as the sample platform. The ensemble of

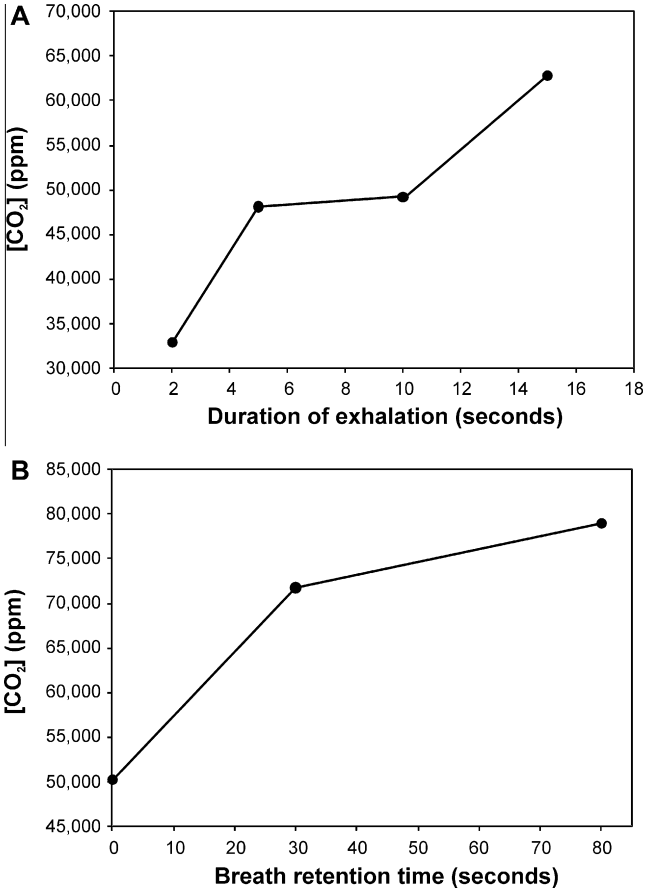

Fig. 2. Tests of exhaled CO_2 sampling strategy. (A) Individual #1 at rest conditions exhaled through the sampler for different times. (B) Individual # 9 delayed exhalation for different lengths of time before sampling.

quartz glass plus sample was combusted in a Vycor break-seal tube containing Cu oxide to yield CO_2 for isotopic analysis.

2.4. Stable isotope analysis

The C isotopic composition of CO_2 was measured on a dual-inlet Finnigan MAT 252 gas source isotope ratio mass spectrometer in the Huffington Department of Earth Sciences at SMU. All stable isotope results are reported in the usual δ notation:

$$\delta^{13}C = [(^{13}R_{sample}/^{13}R_{standard}) - 1] \times 1000‰$$

where $^{13}R = {}^{13}C/{}^{12}C$, and the standard is Vienna-Pee Dee Belemnite (V-PDB). $\delta^{13}C$ values of samples were measured with respect to a laboratory working standard of tank CO_2 and were then corrected to the V-PDB standard (hereafter referred to as PDB). Overall analytical precision of the $\delta^{13}C$ measurements was ±0.1‰.

3. Results

Carbon dioxide extracted from air samples collected from various interior spaces around the SMU main campus (Fig. 1) exhibited $\delta^{13}C$ values ranging from −19.4‰ to −8.9‰ (Table 3; Fig. 3A). The concentration of this indoor CO_2 ranged from 386 ppm to 1980 ppm (Table 3; Fig. 3B). The highest CO_2 concentrations and lowest $\delta^{13}C$ values are generally associated with larger numbers of people in a particular interior space (Table 3).

$\delta^{13}C$ values of outdoor atmospheric CO_2 samples collected at various sites around the SMU campus (Fig. 1) ranged from −10.1‰ to −8.4‰ (Table 4; Fig. 3C), with an average value of −9.0 ± 0.5‰. Concentrations of outdoor atmospheric CO_2 ranged from 385 ppm to 447 ppm (Table 4; Fig. 3D), with an average value of 408 ± 15 ppm.

The $\delta^{13}C$ values of 41 CO_2 samples exhaled under rest conditions by 38 individuals from the SMU community ranged from −24.8‰ to −17.7‰ (Table 2; Fig. 3E), with a mean value of −21.8 ± 1.6‰. The CO_2 concentration varied from 38,300 ppm to 69,500 ppm (Table 2; Fig. 3F), averaging 55,100 ± 6000 ppm. For the sample population, no significant gender or age-related differences were observed, and no samples of exhaled CO_2 were collected from individuals during times of vigorous physical activity. However, for a single individual, samples of exhaled CO_2 collected

Table 1
Variations of exhaled CO_2 for single individuals.

Sample ID	Date	Local time (CDT)	Individual	T (°C)	Conditions	$\delta^{13}C$‰ (PDB)	$[CO_2]$ (ppm)
(A) U-tube collection times							
MPX-366	11/12/2009	8:50 AM (CST)	1	34.2	2 s. exhaling	−22.7	32,900
MPX-367	11/12/2009	9:30 AM (CST)	1	31.2	5 s exhaling	−22.7	48,100
MPX-368	11/12/2009	10:30 AM (CST)	1	29.9	10 s exhaling	−22.9	49,200
MPX-369	11/12/2009	11:20 AM (CST)	1	29.6	15 s exhaling	−23.3	62,800
(B) Breath retention effect					*Retention before exhaling*		
MPX-287	10/13/2009	2:55 PM (CDT)	9	34.6	<1 s	−22.6	50,200
MPX-311	10/4/2009	10:55 AM (CDT)	9	33.4	~30 s	−21.9	71,800
MPX-312	10/4/2009	12:00 PM (CDT)	9	34.0	~80 s	−22.5	78,900
(C) Consumption of C_4 sugar (cola beverage: $\delta^{13}C$ = −11.8‰)							
MPX-334	10/23/2009	9:15 AM (CDT)	1	31.0	Before drinking	−23.0	57,000
MPX-335	10/23/2009	10:20 AM (CDT)	1	29.0	10 min after drinking	−21.0	62,900
MPX-336	10/23/2009	11:10 AM (CDT)	1	29.0	60 min after drinking	−17.7	55,200
MPX-337	10/23/2009	1:05 PM (CDT)	1	29.0	180 min after drinking	−20.1	60,700
(D) Variability for a single individual							
MPX-288	9/24/2009	5:30 PM (CDT)	1	35.0	At rest	−21.3	64,900
MPX-293	9/28/2009	5:55 PM (CDT)	1	30.4	At rest	−21.2	76,200
MPX-294	9/28/2009	8:15 PM (CDT)	1	34.6	At rest	−20.8	76,000
MPX-297	9/30/2009	8:55 AM (CDT)	1	30.2	At rest	−22.0	60,700
MPX-305	10/2/2009	7:35 AM (CDT)	1	33.2	At rest	−22.9	58,400
MPX-334	10/23/2009	9:15 AM (CDT)	1	31.0	At rest	−23.0	57,000
MPX-358	10/29/2009	7:50 PM (CDT)	1	29.8	At rest	−22.2	55,100
MPX-368	11/12/2009	10:30 AM (CDT)	1	29.9	At rest	−22.9	49,200

T: temperature; CDT: Central Daylight Time; CST: Central Standard Time.

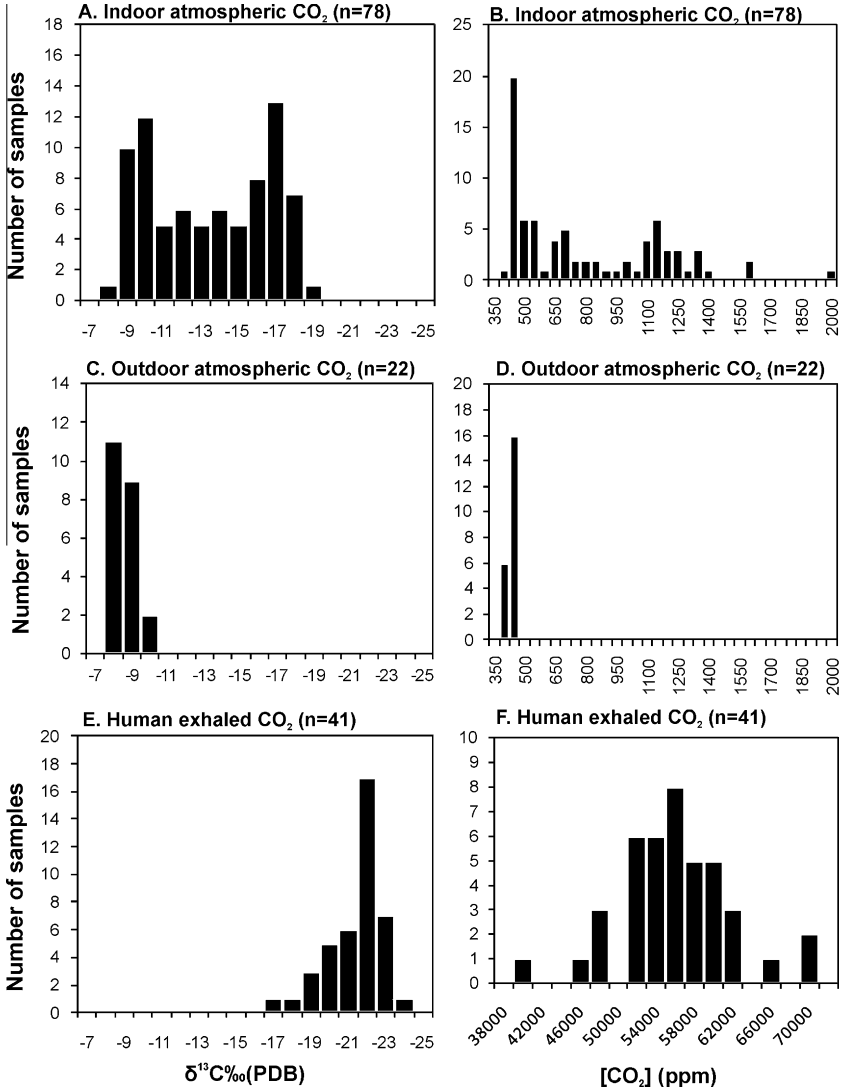

Fig. 3. Frequency distribution of the C isotopic composition (left column) and concentration (right column) of indoor CO_2 (A and B), outdoor CO_2 (C and D) and human breath CO_2 (E and F).

at various times over an interval of about 7 weeks during rest conditions had $\delta^{13}C$ values that ranged from −20.8‰ to −23.0‰ and CO_2 concentrations that ranged from 49,200 ppm to 76,200 ppm (Table 1, section D).

In addition, it was observed that the $\delta^{13}C$ values of CO_2 exhaled by a single individual after drinking a commercial cola that contained ~65 g of C_4 sugars ($\delta^{13}C$ = −11.8‰) increased from −23.0‰ before drinking to −17.7‰ 60 min after consuming the cola, with a subsequent decrease to −20.1‰ about 180 min after (Table 1, section C). No other foods or beverages had been consumed during the interval of 180 min. This apparently diet-induced, short-term variation in the $\delta^{13}C$ values (range = 5.3‰) of CO_2 exhaled by a single individual (Table 1, section C) is comparable to the range (7.1‰) of $\delta^{13}C$ values observed among CO_2 samples exhaled by 38 different individuals (Table 2).

4. Discussion

The SMU buildings in which air samples were collected are cooled or heated by piping in chilled water or steam. Consequently, CO_2 introduced into rooms by the ventilation system should arise from "outdoor" Dallas air. This condition suggests that the concentration and $\delta^{13}C$ values of outdoor air (Fig. 3C and D) can be considered likely endmembers in any CO_2 mixing processes that occurred in those interior spaces. The relatively small ranges of concentration and $\delta^{13}C$ values of outdoor CO_2 compared to indoor CO_2 (Fig. 3A–D) and the positions of the outdoor values at, or near, the low concentration end of the range of indoor values appear to support the validity of this endmember supposition.

4.1. Human-exhaled CO_2

The $\delta^{13}C$ of CO_2 in human breath seems to approximate the $\delta^{13}C$ values of the most recent food intake (e.g. Schoeller et al., 1980; Hedges et al., 2009). As noted, the $\delta^{13}C$ values measured for exhaled CO_2 in the current study range from −24.8‰ to −17.7‰. This suggests varying proportions of foods representing ingredients ultimately derived, directly or indirectly, from C_3 or C_4 plants (e.g. O'Leary, 1988).

It is worth noting that the average $\delta^{13}C$ value (−21.8‰) of the exhaled CO_2 is comparable to the mode of about −22‰ seen in the frequency distribution for these data (Fig. 3E). If this distribution is representative of the SMU community, it suggests that even relatively small numbers of people in a room might be expected to exhale CO_2 with an average $\delta^{13}C$ value near −21.8‰. If so, CO_2 in the air of the indoor environments on the SMU campus (in which

Table 2
Concentration and $\delta^{13}C$ values of CO_2 exhaled by individuals.

Sample ID	Date	Local time[a]	Individual	T (°C)	$\delta^{13}C$‰ (PDB)	$[CO_2]$ (ppm)
MPX-288	9/24/09	5:30 PM	1	35.0	−21.3	64,900
MPX-291	9/28/09	3:10 PM	2	32.0	−21.0	54,200
MPX-292	9/28/09	4:30 PM	3	29.0	−20.5	47,400
MPX-296	9/29/09	4:00 PM	5	30.0	−23.5	38,300
MPX-295	9/29/09	2:40 PM	4	29.0	−22.7	50,400
MPX-301	9/30/09	5:00 PM	6	29.0	−23.8	51,100
MPX-304	10/1/09	3:35 PM	7	32.6	−20.8	55,700
MPX-309	10/2/09	2:35 PM	8	34.0	−22.1	61,400
MPX-310	10/2/09	4:25 PM	2	28.0	−24.8	51,700
MPX-313	10/5/09	5:20 PM	10	30.2	−19.0	54,900
MPX-315	10/7/09	5:25 PM	12	32.0	−20.0	52,900
MPX-314	10/7/09	3:40 PM	11	27.0	−22.5	53,500
MPX-318	10/8/09	3:30 PM	13	33.0	−20.5	52,200
MPX-319	10/8/09	4:45 PM	14	32.2	−20.0	58,600
MPX-324	10/12/09	2:05 PM	16	35.0	−22.8	56,400
MPX-323	10/12/09	12:25 PM	15	32.2	−19.4	55,300
MPX-326	10/13/09	2:55 PM	9	34.6	−22.6	50,200
MPX-327	10/14/09	9:40 AM	17	27.6	−17.7	59,900
MPX-328	10/15/09	3:10 PM	18	31.6	−23.7	58,900
MPX-329	10/15/09	4:35 PM	19	33.9	−22.1	60,900
MPX-330	10/22/09	11:00 AM	20	31.0	−21.7	52,900
MPX-331	10/22/09	12:20 PM	21	31.0	−23.9	55,900
MPX-332	10/22/09	3:15 PM	22	30.6	−22.2	59,100
MPX-333	10/22/09	5:15 PM	23	29.0	−22.8	59,600
MPX-340	10/23/09	4:40 PM	25	28.2	−23.1	51,100
MPX-339	10/23/09	3:34 PM	24	34.2	−22.0	52,300
MPX-341	10/23/09	5:40 PM	26	31.2	−19.6	57,900
MPX-344	10/24/09	1:45 PM	27	30.0	−22.2	53,500
MPX-348	10/26/09	4:20 PM	29	30.8	−22.6	54,800
MPX-347	10/26/09	12:55 PM	28	33.2	−21.1	46,600
MPX-353	10/27/09	1:40 PM	31	28.2	−23.1	61,200
MPX-350	10/27/09	10:25 AM	17	25.0	−18.1	69,500
MPX-349	10/27/09	8:55 AM	30	32.4	−22.0	57,100
MPX-354	10/28/09	5:40 PM	32	32.8	−22.3	56,900
MPX-358	10/29/09	7:50 PM	1	29.8	−22.2	55,100
MPX-355	10/29/09	9:19 AM	33	31.0	−22.4	57,400
MPX-356	10/29/09	11:05 AM	34	33.0	−22.2	47,900
MPX-357	10/29/09	3:30 PM	35	32.6	−21.5	69,500
MPX-359	10/30/09	3:45 PM	36	28.8	−21.5	56,000
MPX-362	11/2/09	5:10 PM	37	31.8	−22.3	44,800
MPX-365	11/5/09	2:40 PM	38	29.0	−23.1	51,600

[a] All local times for days prior to November 1, 2009 are Central Daylight Time (CDT).

humans are expected to be the dominant *in situ* source of CO_2) could be considered to be a mixture of outdoor CO_2 (average $\delta^{13}C = -9.0‰$) supplied by the ventilation systems and CO_2 exhaled by people (average $\delta^{13}C = -21.8‰$) occupying the rooms.

Although, compared to the ambient indoor and outdoor CO_2 samples (Fig. 3B and D), there is a relatively large range in the absolute concentrations (as ppm) of human-exhaled CO_2 (Fig. 3F), the highest exhaled CO_2 concentration is only about a factor of 2 larger than the lowest exhaled value. This factor of two contrasts with the ratio of ~100–200 for the concentration of exhaled CO_2 relative to outdoor CO_2. Thus, the variations in concentrations of exhaled CO_2 are expected to have no significant effect on the mass balance of the indoor CO_2 mixture. Moreover, the distribution of the concentrations of exhaled CO_2 has a mode at 56,000 ppm (Fig. 3F), which is about the same as the average value (55,100 ppm). Consequently, even a relatively small number of people might exhale CO_2 with an average concentration near 55,000 ppm. The preceding discussion implies that mixing of CO_2 in indoor air on the SMU campus can be reasonably characterized with a simple two-endmember mixing model involving the measured concentrations and $\delta^{13}C$ values of the indoor CO_2.

4.2. Two-endmember mixing of indoor atmospheric CO_2

The assumption that CO_2 from outdoor Dallas air and CO_2 exhaled by the human occupants of the interior spaces of interest on the SMU campus are the only significant contributors to the ambient indoor CO_2 leads to the following mass balance equation:

$$\delta^{13}C_m = \left[\left(\delta^{13}C_{OD} - \delta^{13}C_X\right)\left(\frac{C_{OD}}{10^4}\right)\right]\left[\frac{10^4}{C_m}\right] + \delta^{13}C_X \quad (1)$$

where, $\delta^{13}C_m$ = the measured $\delta^{13}C$ value of the indoor atmospheric CO_2 sample, $\delta^{13}C_{OD}$ = the $\delta^{13}C$ value of the outdoor atmospheric CO_2 sample, $\delta^{13}C_X$ = the $\delta^{13}C$ value of the human-exhaled CO_2, C_m = concentration (in ppm) of the measured indoor atmospheric CO_2, C_{OD} = concentration (in ppm) of the outdoor atmospheric CO_2. If $\delta^{13}C_{OD}$, $\delta^{13}C_X$, and C_{OD} are constant, Eq. (1) predicts that $\delta^{13}C_m$ will be a linear function of the reciprocal of the CO_2 concentration ($10^4/C_m$). The intercept of Eq. (1) would correspond to the $\delta^{13}C$ value of the human-exhaled CO_2. Values of $\delta^{13}C$ for indoor CO_2 from Table 3 are plotted against the corresponding reciprocal of the concentration in Fig. 4A. Linear regression of the data of Fig. 4A yields the following equation:

$$\delta^{13}C_m = 0.51(\pm 0.01)[10^4/C_m] - 21.8(\pm 0.1) \quad (2)$$

With $r^2 = 0.99$, and $p < 0.001$ ($n = 78$). This high degree of linearity characterizes samples from a variety of indoor locations with differing numbers of people (Table 3). This linearity plus the fact that the intercept of −21.8(±0.1)‰ in Eq. (2) is the same as the average value of −21.8‰ determined for the CO_2 exhaled by 38 different individuals implies that the air in the sampled interior

Table 3
Concentration and $\delta^{13}C$ values of indoor atmospheric CO_2 at locations on the SMU main campus.

Sample ID	Date	Local time[a]	Site	Sampled area	Room location	Time (min)[b]	# of people	T (°C)	RH (%)	Pressure (mb)[c]	$\delta^{13}C‰$ (PDB)	CO_2 (PPM)
MPX-270	9/12/2009	8:10 AM	A	2nd floor hall			1	22.2	55	1012.1	−13.1	556
MPX-275	9/16/2009	2:20 PM	A	2nd floor hall			4	23.2	56	1011.0	−11.0	481
MPX-209	7/30/2009	11:55 AM	A	4st floor hall			1	23.1	53	1012.5	−9.8	412
MPX-208	7/30/2009	11:45 AM	A	Basement hall			3	22.0	56	1012.5	−10.0	431
MPX-364	11/2/2009	5:25 PM	A	Elevator with doors closed			5	24.0	73	1021.6	−16.5	1030
MPX-363	11/2/2009	5:15 PM	A	Elevator with doors open			5	24.0	73	1021.6	−15.7	842
MPX-321	10/9/2009	6:15 PM	A	Lab 338	Back		2	21.4	72	1017.8	−10.9	458
MPX-217	8/5/2009	9:55 AM	A	Room 153	Back		1	22.8	55	1015.9	−9.8	433
MPX-218	8/5/2009	10:05 AM	A	Room 153	Front		1	22.5	55	1015.9	−10.3	386
MPX-225	8/10/2009	6:00 AM	A	Room 153	Back		1	22.2	51	1014.0	−9.3	416
MPX-226	8/10/2009	6:10 AM	A	Room 153	Front		1	22.4	51	1014.0	−9.4	420
MPX-268	9/11/2009	12:45 PM	A	Room 153	Back	45	70	23.9	62	1015.2	−18.0	1310
MPX-269	9/11/2009	12:47 PM	A	Room 153	Front	47	70	23.9	62	1015.2	−18.0	1330
MPX-278	9/18/2009	12:35 PM	A	Room 153	Front	35	55	23.2	65	1015.4	−17.6	1160
MPX-279	9/18/2009	12:45 PM	A	Room 153	Back	45	55	23.0	65	1015.4	−17.6	1160
MPX-222	8/7/2009	2:35 PM	B	3rd floor hall			3	25.4	53	1013.4	−10.3	443
MPX-281	9/21/2009	10:15 AM	B	3rd floor hall			7	23.8	58	1011.6	−14.0	655
MPX-221	8/7/2009	2:20 PM	B	Basement hall			5	23.8	52	1014.0	−9.7	413
MPX-280	9/21/2009	10:05 AM	B	Basement hall			4	23.0	55	1011.6	−11.9	511
MPX-227	8/17/2009	9:30 AM	B	Room 130	Front		1	22.1	44	1015.1	−9.7	420
MPX-228	8/17/2009	9:40 AM	B	Room 130	Back		1	22.1	44	1015.1	−9.8	429
MPX-242	8/26/2009	11:50 AM	B	Room 130	Back		9	23.8	45	1014.6	−17.6	1200
MPX-243	8/26/2009	11:50 AM	B	Room 130	Back		9	23.8	45	1014.6	−17.8	1260
MPX-249	8/31/2009	12:00 PM	B	Room 130	Front	60	7	24.0	45	1021.3	−18.2	1210
MPX-250	8/31/2009	12:10 PM	B	Room 130	Back	70	7	23.9	45	1021.3	−17.4	1060
MPX-253	9/2/2009	11:00 AM	B	Room 130	Front		9	24.6	51	1019.1	−18.4	1320
MPX-254	9/2/2009	12:15 PM	B	Room 130	Front	75	9	24.4	44	1018.6	−17.6	1140
MPX-264	9/9/2009	12:00 PM	B	Room 130	Front	60	6	25.0	52	1014.5	−18.6	1570
MPX-265	9/9/2009	12:10 PM	B	Room 130	Back	70	10	24.8	44	1014.5	−18.3	1380
MPX-271	9/14/2009	10:55 AM	B	Room 130	Back	60	24	22.6	62	1010.5	−18.6	1560
MPX-272	9/14/2009	12:05 PM	B	Room 130	Back	65	9	22.0	57	1010.7	−17.6	1220
MPX-201	7/23/2009	5:00 PM	B	Room 133	Front		2	22.0	54	1013.9	−12.8	620
MPX-202	7/23/2009	9:10 PM	B	Room 133	Front		1	22.1	63	1014.3	−10.7	480
MPX-205	7/27/2009	8:30 PM	B	Room 133	Front		1	21.0	71	1011.8	−10.1	428
MPX-229	8/18/2009	9:45 AM	B	Room 133	Front		1	22.8	67	1016.4	−9.8	428
MPX-230	8/18/2009	9:55 AM	B	Room 133	Back		1	23.0	67	1016.4	−10.1	440
MPX-255	9/3/2009	10:55 AM	B	Room 133	Back		20	23.5	59	1014.6	−16.7	971
MPX-256	9/3/2009	12:00 PM	B	Room 133	Back	60	67	23.0	57	1014.6	−17.0	1100
MPX-262	9/8/2009	12:00 PM	B	Room 133	Front	60	64	24.5	57	1013.7	−17.0	1110
MPX-263	9/8/2009	12:05 PM	B	Room 133	Back	65	64	23.6	58	1013.7	−17.1	1120
MPX-351	10/27/2009	12:40 PM	B	Room 133	Back	10	120	22.9	73	1011.1	−16.7	1070
MPX-352	10/27/2009	1:20 PM	B	Room 133	Back	40	120	22.5	73	1011.1	−16.7	1170
MPX-206	7/28/2009	7:28 PM	B	Room 153	Front		2	21.3	62	1007.5	−10.0	439
MPX-207	7/28/2009	7:28 PM	B	Room 153	Front		2	21.3	62	1007.5	−10.1	435
MPX-231	8/19/2009	9:35 AM	B	Room 153	Front		1	22.0	57	1012.4	−9.5	411
MPX-232	8/19/2009	9:45 AM	B	Room 153	Back		1	22.2	57	1012.4	−9.4	421
MPX-244	8/27/2009	9:10 AM	B	Room 153	Back		23	22.6	53	1015.2	−15.2	782
MPX-251	9/1/2009	9:00 AM	B	Room 153	Front	60	25	21.6	52	1021.7	−14.3	669
MPX-252	9/1/2009	9:10 AM	B	Room 153	Back	70	25	23.0	51	1021.7	−15.2	744
MPX-266	9/10/2009	9:05 AM	B	Room 153	Front	65	23	21.9	57	1015.2	−14.7	683
MPX-267	9/10/2009	9:10 AM	B	Room 153	Back	70	23	23.0	56	1015.2	−15.3	752
MPX-215	8/4/2009	9:40 AM	C	1st floor hall			2	24.4	49	1015.3	−10.6	447
MPX-216	8/4/2009	9:55 AM	C	3rd floor hall			5	23.8	43	1015.3	−11.2	484
MPX-211	8/1/2009	9:05 AM	C	Rm 131	Front		1	21.6	49	1014.7	−10.0	435
MPX-212	8/1/2009	9:15 AM	C	Rm 131	Back		1	21.2	49	1014.7	−12.9	545
MPX-233	8/20/2009	9:05 AM	C	Rm 131	Front		1	22.9	47	1010.3	−8.9	401
MPX-234	8/20/2009	9:15 AM	C	Rm 131	Back		1	22.8	47	1010.3	−10.0	439
MPX-245	8/28/2009	9:35 AM	C	Rm 131	Front		43	23.2	51	1014.8	−16.5	950
MPX-246	8/28/2009	9:40 AM	C	Rm 131	Back		43	23.4	49	1014.8	−16.2	895
MPX-257	9/4/2009	9:40 AM	C	Rm 131	Front	40	40	23.4	51	1015.8	−17.6	1090
MPX-258	9/4/2009	9:45 AM	C	Rm 131	Back	40	40	23.5	50	1015.8	−16.4	917
MPX-213	8/3/2009	9:25 AM	D	1st floor hall			8	23.8	49	1014.7	−11.6	487
MPX-247	8/28/2009	7:30PM	D	1st floor hall			3	22.8	52	1012.0	−12.4	549
MPX-273	9/15/2009	1:55 PM	D	1st floor hall			20	23.0	52	1012.4	−17.2	1140
MPX-214	8/3/2009	9:40 AM	D	3rd floor hall			3	25.5	47	1015.4	−11.6	499
MPX-248	8/28/2009	7:40 PM	D	3rd floor hall			1	25.0	47	1012.0	−12.4	537
MPX-274	9/15/2009	2:05 PM	D	3rd floor hall			10	23.5	52	1012.4	−16.8	1080
MPX-276	9/17/2009	10:40 AM	E	1st floor hall			5	21.9	52	1011.6	−13.5	615
MPX-289	9/28/2009	10:00 AM	E	1st floor hall			15	22.2	72	1017.5	−12.3	543
MPX-277	9/17/2009	10:45 AM	E	3rd floor hall			4	23.0	51	1011.6	−13.6	627

(*continued on next page*)

Table 3 (*continued*)

Sample ID	Date	Local time[a]	Site	Sampled area	Room location	Time (min)[b]	# of people	T (°C)	RH (%)	Pressure (mb)[c]	$\delta^{13}C$‰ (PDB)	CO_2 (PPM)
MPX-290	9/28/2009	10:10 AM	E	3rd floor hall			10	22.4	73	1017.5	−12.0	547
MPX-282	9/21/2009	7:00 PM	F	Tread mill area			80	23.8	50	1007.8	−15.5	837
MPX-285	9/23/2009	3:45 PM	F	Tread mill area			55	22.8	73	1021.5	−13.9	658
MPX-286	9/23/2009	3:50 PM	F	Tread mill area			55	22.2	73	1021.5	−14.5	696
MPX-302	10/1/2009	9:45 AM	G	Shuttle bus			7	21.2	70	1009.1	−14.8	704
MPX-303	10/1/2009	10:15 AM	G	Shuttle bus			12	18.6	66	1009.1	−17.0	1100
MPX-316	10/8/2009	10:35 AM	G	Shuttle bus			3	17.8	67	1010.6	−13.4	601
MPX-317	10/8/2009	10:55 AM	G	Shuttle bus			32	19.2	66	1010.6	−19.4	1980

T: temperature; RH: relative humidity; # number.
[a] All local times for days prior to November 1, 2009 are Central Daylight Time (CDT).
[b] Time elapsed since the start of class (in minutes).
[c] Total pressure (sea level corrected) data from NWS station at Love-Field Airport.

spaces was reasonably well-mixed and that the average $\delta^{13}C$ value of the CO_2 exhaled by those 38 individuals was representative of the larger SMU community. Note also that the outdoor CO_2 samples scatter tightly at one end of the indoor CO_2 data array in Fig. 4A, which is also consistent with the model assumption that outdoor air is one of the two end members of the mixed air found indoors.

The agreement of the average $\delta^{13}C$ value of the exhaled CO_2 with the value predicted by the intercept of Eq. (2) not only emphasizes the validity of the two-endmember mixing model represented by Eq. (1), but also the dominant role of human-respired CO_2 in producing variations in the abundance and isotopic composition of CO_2 in the interior spaces of this study. Although this sort of "Keeling mixing curve" behavior is not unexpected, the data array in Fig. 4A demonstrates its simple realization in these indoor spaces. Furthermore, for any interior space that satisfies the assumptions put forward here, the simple binary mixing model implies that concentrations and $\delta^{13}C$ values of CO_2 in a pair of samples of indoor and outdoor air might be used in combination to obtain a relatively rapid and credible estimate of the average $\delta^{13}C$ value of CO_2 exhaled by people occupying a room, thereby providing information about the role of C_3 and C_4-type foods in the average diet of that local population. For any of the various groups occupying the sampled SMU rooms of this study, a simple mass balance calculation (for a C_4 endmember $\delta^{13}C$ value of −13‰ and a C_3 endmember value of −27‰, e.g. O'Leary, 1988) suggests that C_4-derived C was ~40% of the average diet.

A possible example of the use of a binary mixing model for ambient CO_2 in another indoor venue is represented by some of the data of Widory and Javoy (2003). These authors analyzed concentrations and $\delta^{13}C$ values of samples from five indoor sites on the Jussieu campus of the Université de Paris, France (i.e., one classroom and four laboratories). Widory and Javoy (2003) noted that their laboratory air probably included CO_2 contributed by CH_4-burning torches used for routine glass blowing in the laboratories. However, the reported concentrations and $\delta^{13}C$ values of laboratory CO_2 do not differ greatly from those of their "open country" samples. Therefore, the four laboratory data points plus the single classroom point of Widory and Javoy (2003) are plotted in Fig. 4B. Although the distribution of the data of Widory and Javoy (2003) is not substantively different from an array containing only two points, a linear regression of those data is represented by the line and corresponding equation in Fig. 4B. The intercept of that best-fit line has a value of −25.8‰. If this intercept value is indicative of the average $\delta^{13}C$ value of CO_2 exhaled by the people in those Paris rooms, it indicates a lower proportion (~10%) of C_4-derived C in their diet than the proportion (~40%) in the diet of the people in the SMU community in Dallas. These types of dietary differences between Europeans and Americans were observed previously by direct measurements of $\delta^{13}C$ values of CO_2 in human breath (e.g. Schoeller et al., 1980).

4.3. Steady state and time scales for mixing of SMU indoor air

Data on the maximum fluxes of air provided by the ventilation systems to certain rooms on the SMU campus were obtained from the SMU Office of Planning, Design, and Construction. Those volumes and ventilation rates are listed in Table 5. Since the air pressure in the rooms does not vary dramatically, it is assumed that input and output fluxes of air via the ventilation systems are equal and that the volumes (amounts) of air in the rooms can be considered to be at steady state and equal to the measured volumes of the rooms themselves. This assumption allows calculations of residence times for the air in some of the rooms sampled in this study. Residence time is defined as follows:

$$\tau = \frac{V_{rm}}{f_{in}} \tag{3}$$

where τ = residence time (min); V_{rm} = volume (m^3) of air in the room; f_{in} = flux (m^3/min) of air into the room. The calculated residence times for the rooms for which data are available are listed in Table 5 and range from ~2.0 to 10.2 min. These relatively short residence times suggest that CO_2 extracted from air samples collected about 30–60 min after the beginning of a class session should represent a close approximation to steady-state conditions, if the number of people in the room remained relatively constant and the doors to the room were closed. This can be formally expressed by the following flux balance equation for the CO_2:

$$\frac{dn_{rm}}{dt} = F_{in} + F_x - F_{out} \tag{4}$$

t = time (min). n_{rm} = moles of CO_2 in the room air. F_{in} = flux (moles/min) of CO_2 introduced into the room by the ventilation system. F_X = the flux (moles/min) of exhaled CO_2 introduced into the room air by the human occupants. F_{out} = flux (moles/min) of CO_2 that leaves the room via the ventilation system. It is assumed that no other fluxes are of significance to the CO_2 mass balance in these systems. $F_{in} = C_{in}\, f_{in}$ Where, C_{in} = concentration of CO_2 (moles/m^3) in the input ventilation air. f_{in} is as defined for Eq. (3). F_{out} = flux (moles/min) of CO_2 out of the room via the ventilation system. $F_{out} = C_{rm} f_{out}$ and C_{rm} = concentration of CO_2 (moles/m^3) in the room air at some time t. Also, the assumption of steady state requires that $f_{out} = f_{in}$ (see discussion before Eq. (3)). Finally, it is assumed that $F_x = kN_x$ where "k" (mole/min/person) is a proportionality constant (the average individual respiration rate of the occupants in a room) and N_x = the number of people in a room during the time of interest. The average value of "k" is an unknown for the current study. With the preceding terms, Eq. (4) can be rewritten as:

Table 4
Outdoor atmospheric CO_2 concentration and $\delta^{13}C$ values on the SMU main campus.

Sample ID	Date	Local time[a]	Location	T (°C)	RH (%)	Pressure (mb)[bc]	Wind speed & direction (mph)[c]	$\delta^{13}C‰$ (PDB)	CO_2 (PPM)
MPX-204	7/27/2009	8:30 PM	2	24.2	91	1011.8	NE at 6	−9.5	429
MPX-210	7/31/2009	1:30 PM	2	29.8	58	1017.2	E at 8	−8.4	387
MPX-219	8/6/2009	9:15 AM	1	28.0	86	1016.0	SE at 10	−10.1	447
MPX-220	8/6/2009	9:30 AM	5	30.0	71	1016.3	SE at 8	−9.7	415
MPX-223	8/8/2009	2:30 PM	3	34.0	49	1014.5	S at 18 G25	−8.4	395
MPX-224	8/8/2009	2:20 PM	2	34.2	51	1014.5	S at 18 G25	−8.4	385
MPX-235	8/21/2009	9:55 AM	4	23.8	80	1016.0	N at 6	−9.2	404
MPX-236	8/21/2009	10:05 AM	2	24.4	84	1016.0	N at 6	−9.0	404
MPX-237	8/22/2009	10:05 AM	1	27.8	65	1017.2	N at 6	−9.5	419
MPX-238	8/22/2009	10:20 AM	5	30.0	56	1017.2	N at 6	−9.3	412
MPX-239	8/24/2009	9:00 AM	2	26.5	77	1015.5	SE at 14	−9.6	392
MPX-240	8/24/2009	9:10 AM	2	26.3	79	1015.5	SE at 14	−9.5	413
MPX-241	8/25/2009	1:20 PM	4	34.4	54	1014.6	SW at 6	−8.9	414
MPX-259	9/5/2009	8:55 AM	7	23.2	88	1017.0	S at 6	−10.0	436
MPX-261	9/5/2009	7:05 PM	7	30.4	54	1014.3	E at 3	−9.0	407
MPX-283	9/22/2009	3:00 PM	4	19.8	70	1018.0	N at 12	−8.5	411
MPX-284	9/22/2009	3:05 PM	1	18.8	66	1018.0	N at 12	−8.5	391
MPX-338	10/23/2009	3:25 PM	6	21.4	77	1013.0	NW at 15 G 22	−8.6	412
MPX-342	10/24/2009	2:25 PM	6	22.8	73	1012.4	S at 12 G 22	−8.6	403
MPX-343	10/24/2009	2:25 PM	6	22.8	73	1012.4	S at 12 G 22	−8.6	401
MPX-345	10/25/2009	3:20 PM	6	25.5	77	1009.3	S at 14 G 22	−8.7	399
MPX-346	10/25/2009	3:20 PM	6	25.5	77	1009.3	S at 14 G 22	−8.7	408

T: temperature; RH: relative humidity.
[a] All local times for days prior to November 1, 2009 are Central Daylight Time (CDT).
[b] Total pressure (sea level corrected).
[c] Weather variables collected from NWS station at Love-Field Airport.

$$\frac{dC_{rm}}{dt} = \left(C_{in}\frac{f_{in}}{V_{rm}} + \frac{kN_x}{V_{rm}}\right) - \left(\frac{f_{in}}{V_{rm}}\right)C_{rm} \quad (5)$$

Eq. (5) derives from the fact that $C_{rm} = n_{rm}/V_{rm}$. For constant C_{in}, f_{in}, V_{rm}, k, and N_x in any particular interior space for some time of interest, Eq. (5) can be integrated to yield:

$$C_{rm} = \left[C_{in} + \frac{kN_x}{f_{in}}\right] - \left[\left(C_{in} + \frac{kN_x}{f_{in}}\right) - C_{rm_0}\right]e^{-\left(\frac{f_{in}}{V_{rm}}\right)t} \quad (6)$$

C_{rm0} = the concentration of CO_2 in a room when $t = 0$. For ambient air residence times of ~10 min, Eq. (6) suggests that ~30 min after $t = 0$ the CO_2 system should exhibit an approximately 95% approach to steady state. This implies that the assumption of steady state may be reasonable for many of the samples. From Eq. (6), the equation for the steady state concentration of CO_2 is:

$$C_{rm_{SS}} = \left[C_{in} + \frac{kN_x}{f_{in}}\right] \quad (7)$$

If f_{in} for a particular room is constant, Eq. (7) predicts that C_{rm} should be a linear function of N_x. Plots of C_{rm} against N_x are shown in Fig. 5 for three interior spaces in which the number of people was different enough at various sampling opportunities to constitute a useful test of Eq. (7). For all three spaces, C_{rm} increases with increasing N_x. However, of the three interior spaces in Fig. 5, only the data from the SMU shuttle bus (Fig. 5C) exhibit an apparently linear relationship between the concentration of CO_2 and the number of people in that space.

The absence of linearity in the data (Fig. 5A and B) for rooms 130 and 133 in the Fondren Science building could indicate that steady state was not uniformly achieved and/or that f_{in} was not constant in those rooms. This latter possibility is supported by information from the SMU Office of Planning, Design, and Construction that the ventilation in Fondren Science is variable flow in response to thermal demands placed on the rooms by the occupancy. Therefore, once some number of people (N_x) has been established in such a room, f_{in} should settle on some value related to N_x. Thus, in view of the previous discussion about the maintenance of the very small constant pressure difference between room air and outdoor air, if f_{in} is some function of N_x, Eq. (7) (a steady state equa-

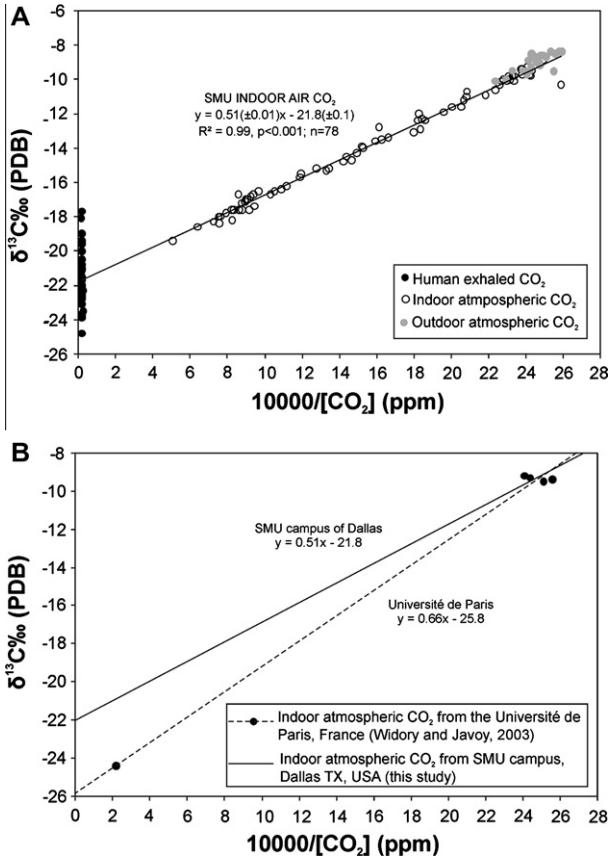

Fig. 4. (A) Carbon isotopic composition of SMU indoor air CO_2 samples (white circles), outdoor atmospheric CO_2 samples (gray circles) and human-respired CO_2 samples (black circles) plotted against the reciprocal of the atmospheric CO_2 concentration (ppm). The solid line represents the linear regression of the SMU indoor data of this study. (B) Data for indoor CO_2 of the Jussieu campus, Université de Paris, France, measured by Widory and Javoy (2003). The dashed line and associated equation represent the linear regression of the data of Widory and Javoy (2003). The SMU mixing line (solid line) and equation from 4A are also shown in 4B for comparison.

Table 5
Volumes and ventilation rates for some rooms on the SMU campus, Dallas, Texas, USA.

Building	Building ID	Room number	Volume (m^3)	Ventilation rate (m^3/min)	Residence time (min)
Heroy	A	153	298.5	151.2	2.0
Dedman Life Sciences	C	131	468.9	60.0	7.8
Fondren Science	B	130	288.8	28.3	10.2
Fondren Science	B	133	944.6	141.6	6.7
Fondren Science	B	153	322.2	31.4	10.2

tion) implies that even a nonlinear data array (such as those in Fig. 5A and B) could represent a locus of steady-state conditions. However, if it should happen that steady-state conditions were not attained in all instances, the highly coherent data array of Fig. 4A would not be affected. Furthermore, the results in Figs. 4A and 5A–C, taken together, support an assumption that the mixing processes in all of the interior spaces of this study were generally efficient.

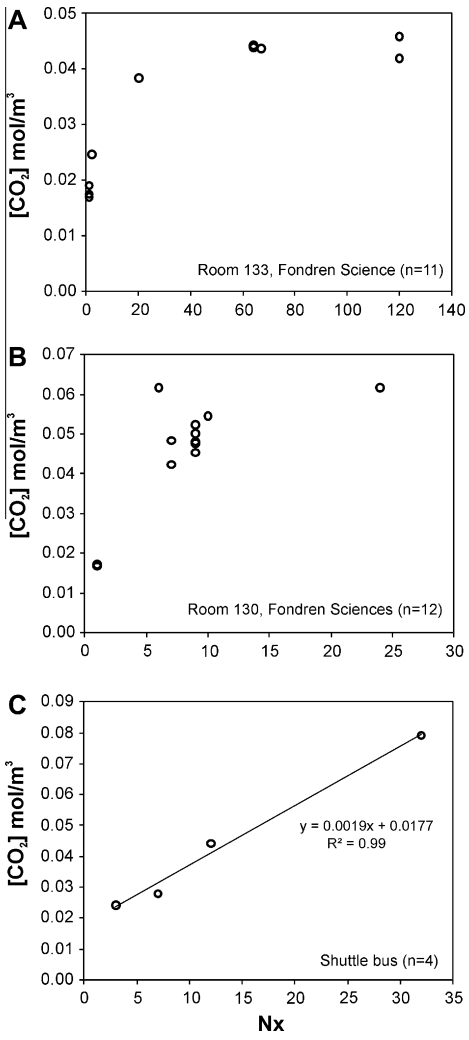

Fig. 5. Concentration (mol/m^3) [of indoor atmospheric CO_2 in classrooms (A and B) and of CO_2 in the air inside the passenger compartment of a shuttle bus (C)] plotted against number of people (N_x). See text.

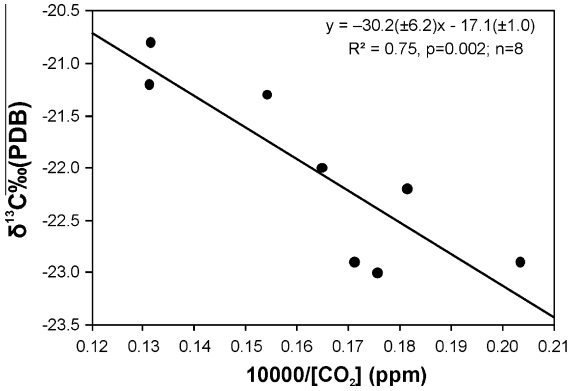

Fig. 6. $\delta^{13}C$ values of the respired CO_2 plotted against the reciprocal of the CO_2 concentration for a single individual at different times under rest conditions.

4.4. Concentration and $\delta^{13}C$ values of single-source human-exhaled CO_2

An apparent relationship between the $\delta^{13}C$ of CO_2 and the reciprocal of concentration (ppm) was observed for a suite of CO_2 samples exhaled by a single individual (Fig. 6) under rest conditions over an interval of 7 weeks (Table 1, section D). A linear regression of the data of Fig. 6 is represented by the line in the Figure for which $r^2 = 0.75$ and $p = 0.002$ ($n = 8$). At present, the authors have no explanation for the apparent linearity of the relationship, but it is suggestive of some type of mixing process. The results are presented here to call attention to the observation. The generality of this observation remains to be investigated.

4.5. Outdoor urban atmospheric CO_2

Clark-Thorne and Yapp (2003) analyzed the isotopic composition of outdoor atmospheric CO_2 that was collected about 10 a ago in the Dallas metropolitan area and evaluated the impact of fossil fuel combustion on the urban atmospheric CO_2 budget. $\delta^{13}C$ values of their CO_2 samples are plotted against the reciprocal of the CO_2 concentration in Fig. 7 (restricted to the outdoor samples collected on the SMU campus). Fig. 7 also contains outdoor CO_2 data obtained in the current work (Table 4). At present, the average concentration of outdoor CO_2 on the SMU campus is ~17 ppm higher than the average concentration measured 10 a ago. In contrast, the average $\delta^{13}C$ values of the two data sets

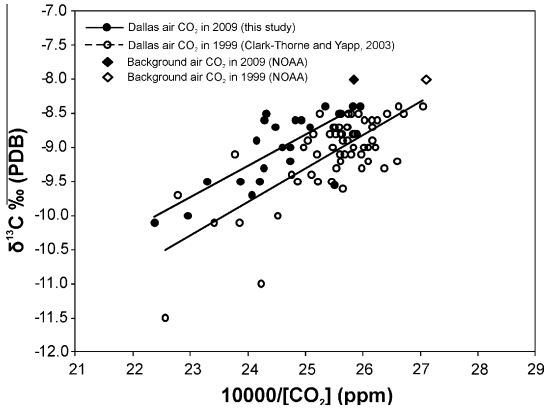

Fig. 7. Carbon isotopic composition of the outdoor atmospheric CO_2 on the SMU campus plotted against the reciprocal of the CO_2 concentration for the 1999 and 2009 data sets. Also, included are the corresponding global "background" CO_2 data. See text.

are essentially unchanged at ~−9‰. This local increase in the concentration of urban atmospheric CO_2 is comparable to the increase of ~18 ppm in the concentration of global atmospheric CO_2 observed at Mauna Loa Observatory over the last 10 a. The Mauna Loa data are represented by diamond symbols in Fig. 7 (NOAA: http://www.esrl.noaa.gov/gmd/ccgg/trends/co2_data_mlo.html). The intercepts of the regression lines for the SMU data sets in Fig. 7 differ by 1.3‰ (−21.6‰ for the 1999 data and −20.3‰ for the 2009 data), which reflects the increase in the average concentration of CO_2 with no significant change in the average $\delta^{13}C$ value.

This magnitude of change in the concentration of the Dallas area atmospheric CO_2 over a 10 a interval compares to a 25-a increase of about 30 ppm observed on the Caltech campus in Pasadena, California by Newman et al. (2008). The increase of ~30 ppm in the Pasadena, California, CO_2 concentration was set against a global increase of 47 ppm during that interval. Newman et al. (2008) also found that there was no substantial change in the $\delta^{13}C$ values of the ambient urban CO_2.

5. Conclusions

The outdoor urban atmospheric CO_2 samples analyzed for this Dallas study exhibit an average increase in concentration of ~17 ppm relative to samples measured in a study of Dallas CO_2 performed 10 a ago. At both times, the average concentration of CO_2 in the Dallas atmosphere was higher than the concurrent global averages. This observation, plus the fact that the temporal increase in the urban CO_2 concentration mimicked the global increase in concentrations of atmospheric CO_2 reported over the same interval, emphasizes the role of urban fossil fuel combustion as a source term in the global atmospheric CO_2 budget.

Carbon dioxide exhaled by human beings is clearly manifested in the isotopic mass balance of CO_2 in the air of interior spaces. The simple binary mixing model that describes this mass balance suggests that samples of indoor air can be used to deduce the average isotopic characteristics of food in the diets of people that occupy an interior space for times on the order of 30 min. Thus, interior spaces may serve as effective "sample vessels" for rapidly assessing differences in the average diets (C_3 vs. C_4 contributions) of large numbers of people at various times and places using measurements of CO_2 in the ambient air.

Acknowledgements

This research was partially supported by the Huffington Department of Earth Sciences at SMU. Special thanks go to the Ministry of Science and Innovation (MICCIN) of the Spanish Government for support of Y.Yanes as a postdoctoral researcher at SMU. We thank Kurt Ferguson and Stephanie Thomas (SMU) for assistance with isotopic analyses; Larry Helpert of the SMU Office of Planning, Design, and Construction and Rocky Nana of the SMU Office of Facilities, Management, and Sustainability for important information about the building ventilation systems; and all those in the SMU community who exhaled CO_2. We also extend our appreciation to two anonymous reviewers for their comments.

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