

Seasonal and diurnal variations of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ in air: Initial observations from Pasadena, CA

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Abstract

The budget of atmospheric CO_2 is widely studied using records of temporal and spatial variations of concentrations, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. However, the number and diversity of sources and sinks prevents these alone from fully constraining the budget. Molecules containing two rare isotopes can serve as additional tracers and potentially provide additional, independent, constraints. We present data documenting seasonal and diurnal variations of CO_2 having a mass of 47 u (mostly $^{13}\text{C}^{18}\text{O}^{16}\text{O}$) in air from Pasadena, CA. We report these data using the ‘mass 47 anomaly’ (Δ_{47}), which is defined as the deviation of $R^{47} (= [47]/[44])$ from that expected for a random distribution of isotopologues. Between February 2004 and December 2005, Δ_{47} showed a seasonal pattern that differed significantly from that expected based on thermodynamic equilibrium. During the year 2004 Δ_{47} was 0.76‰ in winter, increased to 0.87‰ in summer and gradually decreased through the autumn to 0.81‰ at the end of the year. Δ_{47} then increased again through the winter and spring of 2005 to 0.97‰ in summer followed by a decrease to 0.88‰ at the end of 2005. The seasonal variations cannot be accounted for by variations in the relative contribution of local fossil fuel sources. Diurnal variations were the combined effect of both fuel combustion and respiration having Δ_{47} values of 0.41‰ and ca. 0.77‰, respectively. The seasonal cycle may be interpreted as a competition between low Δ_{47} values in respiration and higher Δ_{47} values resulting from CO_2 -water exchange in photosynthesis.

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1. INTRODUCTION

The budget of atmospheric CO_2 is widely studied using temporal and spatial records of concentration and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values combined with estimates of the values of these isotopic tracers associated with CO_2 fluxes (Francey and Tans, 1987; Francey et al., 1995; Ciais et al., 1995a,b, 1997; Peylin et al., 1999; Cuntz et al., 2003). In particular, $\delta^{13}\text{C}$ values are primarily used to partition marine from terrestrial fluxes (e.g., Ciais et al., 1995a) and $\delta^{18}\text{O}$ values are primarily used to separate terrestrial net photosynthesis from soil respiration (Yakir and Wang, 1996; Ciais et al., 1997; Peylin et al., 1999). Latitudinal gradients, long-term

change and seasonal variations are commonly used in isotopic mass balance models to partition fluxes. However, the diversity and variability of fluxes to and from the atmosphere prevents these alone from fully constraining the budget. Molecules containing two rare isotopes potentially provide additional, independent constraints. We present data documenting seasonal and diurnal variations of mass of 47 u (mostly $^{13}\text{C}^{18}\text{O}^{16}\text{O}$) in air from Pasadena, CA. We report these data using the ‘mass 47 anomaly’ (Δ_{47}), which reflects the deviation of the abundance of mass 47 isotopologues from that predicted for a random distribution of isotopes and is a measure of the preference of two heavy isotopes (^{13}C and ^{18}O) to ‘clump’ together in one chemical bond (Eiler and Schauble, 2004; Wang et al., 2004; Affek and Eiler, 2006).

Theoretical calculation (verified experimentally for the temperature range of 267–303 K; Eiler et al., 2003) suggest that at thermodynamic equilibrium the Δ_{47} value of CO_2 is temperature dependent (Eiler and Schauble, 2004; Wang

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et al., 2004). CO₂–H₂O isotope exchange drives CO₂ toward thermodynamic equilibrium and is likely to result in Δ₄₇ values that reflects the temperature of exchange, with Δ₄₇ of 0.95‰ at 25 °C (Eiler and Schauble, 2004). Fluxes that involve CO₂ equilibrium with water and whose δ¹⁸O values reflects these equilibria, such as exchange with ocean or leaf water, although never directly characterized for Δ₄₇, are expected to have Δ₄₇ values close to the thermodynamic equilibrium values. However, Δ₄₇ in human breath was observed to be 0.76‰ (Affek and Eiler, 2006), lower than the expected at thermodynamic equilibrium at body temperature (0.86‰ at 37 °C). CO₂ in car exhaust was found to have a Δ₄₇ value of 0.41‰, presumably reflecting higher temperature equilibrium quenched in the exhaust stream (Affek and Eiler, 2006).

Δ₄₇ values in ambient air must reflect a balance of CO₂ fluxes and their corresponding Δ₄₇ values, including both combustion sources and sources that involve exchange between the atmosphere and either ocean water or the land biosphere. The work presented here examined the stable isotope composition of urban air in Pasadena, CA, aimed at exploring the systematics and causes of temporal variation in Δ₄₇ values. The typical synoptic air pattern in the Los Angeles basin is a combination of sea-breeze and mountain flow that leads to air flow from the coast inland, pushing polluted urban air towards the San Gabriel mountains (Lu and Turco, 1995). Pasadena is located at the foothills of these mountains. It is therefore highly affected by the plume of polluted air, and the CO₂ in Pasadena air is likely to contain a significant component originating from combustion sources.

2. METHODS

2.1. Air sampling and isotopic analysis

We sampled air (a sample size of 5 L; air was dried by Mg(ClO₄)₂ during sampling) in Pasadena, CA, between February 2004 and December 2005. Samples were generally obtained at ~10am from a third floor balcony at the Caltech campus (34.137°N, 118.128°W), facing a courtyard in which the dominant vegetation is deciduous Sweetgum trees and lawn grass. The sampling time of day is shortly after the decrease in CO₂ concentration following the peak associated with morning traffic when the concentrations are already close to the diurnal minimum, suggesting minimal contribution from local sources. However, the air samples do not reflect background air (that is, air far from urban centers or vigorously active terrestrial ecosystems), because regional contributions from anthropogenic fluxes in the greater Los Angeles basin cannot be avoided at any time of the day. Diurnal variations were examined by collecting air every 3 h over a 24 h cycle in February 14, February 21 and March 24, 2006. In order to estimate the Δ₄₇ values in background air, samples from Cape Grim, Tasmania (40.68°S, 144.68°E) and Barrow, AK (71.32°N, 156.6°W) were analyzed. Cape Grim air was sampled between 1 and 4pm, when wind direction was west to south-west. Air in Barrow was sampled between 8am and 2pm, when the wind direction was west to south-west. CO₂ was

extracted from the collected air by freezing in liquid N₂ on a glass vacuum line (Affek and Eiler, 2006).

The isotopic composition of the extracted CO₂ was measured by a dual inlet gas source mass spectrometry using a Finnigan-MAT 253 isotope ratio mass spectrometer, configured to measure masses 44, 45, 46, 47, 48 and 49 to obtain δ¹³C, δ¹⁸O and Δ₄₇ values. Δ₄₇ is calculated as:

$$\Delta_{47} = \left[\frac{R^{47}}{2R^{13} \cdot R^{18} + 2R^{17} \cdot R^{18} + R^{13} \cdot (R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13} \cdot R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17}} + 1 \right] \cdot 1000 \quad (1)$$

and the Δ₄₇ calibration is obtained by measuring CO₂ heated to 1000 °C, which is assumed to have a stochastic distribution of isotopes among all isotopologues (Eiler and Schauble, 2004; a detailed description of the method is given in Affek and Eiler, 2006). Some of the air samples (during October 2004–December 2005) were analyzed also for ¹⁴C content at the University of California, Irvine (using the method described in Xu et al., 2007). We report seasonal data as monthly means (*n* = 1–9 samples sampled during 1–5 days per month for CO₂ concentrations, δ¹³C, δ¹⁸O and Δ₄₇ and *n* = 1–2 per month for Δ¹⁴C). The precision of Δ₄₇ measurements is estimated as 0.005‰ (standard error, *n* = 28) based on the reproducibility of measurement of cylinder CO₂ working standard (δ¹³C = –10.7‰, δ¹⁸O = 31.9‰, Δ₄₇ = 0.871‰) performed between November 2005 and April 2006 or as 0.015‰ (standard error, *n* = 8) based on the reproducibility of measurements of CO₂ produced by acid digestion of the carbonate standard NBS-19. Precision was slightly lower in the beginning of the seasonal time series. The typical standard error of Pasadena air Δ₄₇ monthly means is 0.024‰ (*n* = 1–9).

2.2. Calculation of clean air Δ₄₇

The fraction of CO₂ from combustion sources was estimated from the observed Δ¹⁴C as *f*_{ff} = (Δ¹⁴C–60)/ (–960–60), where –960‰ is the Δ¹⁴C value observed in car exhaust and 60‰ is the Δ¹⁴C in clean air during 2004–2005 (the estimation assumes that the Δ¹⁴C associated with non fossil fuel sources is similar to the atmospheric background value). This was used to estimate the Δ₄₇ values in clean air by removing this contribution from local combustion sources, as Δ_{47-clean} = (Δ_{47-observed} – 0.41*f*_{ff})/(1 – *f*_{ff}) where 0.41‰ is the Δ₄₇ value observed in car exhaust (Affek and Eiler, 2006). This calculation assumes that CO₂ produced by combustion of natural gas in local power plants, whose Δ₄₇ value was not yet determined, is similar to that observed in car exhaust. As a sensitivity test for this assumption, we calculated Δ_{47-clean} with a Δ₄₇ value of zero for both combustion sources. This reduces the seasonal variations in Δ_{47-clean} but does not eliminate them and the values during October to December 2004 remained significantly lower than those during summer 2005.

Δ¹⁴C data were available for October 2004–December 2005. However, in the summer months (June to October)

of 2005 applying the above correction to estimate clean air Δ_{47} values would result in values that are significantly higher than the values reflecting thermodynamic equilibrium, which is unlikely given the current knowledge of the factors controlling Δ_{47} values (Eiler and Schauble, 2004; Affek and Eiler, 2006). Although a CO_2 source having Δ_{47} values significantly higher than those at thermodynamic equilibrium cannot be ruled out, it is more likely that during these months Δ_{47} values were modified by fast local exchange with water that eliminated the regional fossil fuel contribution to Δ_{47} values but did not affect the $\Delta^{14}\text{C}$. We therefore consider the clean air Δ_{47} values during June to October 2005 to be identical to the uncorrected values, resulting in a minimum estimate for the winter–summer 2005 difference in clean air.

3. RESULTS

3.1. Seasonal variations

Monthly averaged CO_2 concentrations, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47} and $\Delta^{14}\text{C}$ values are given in Fig. 1 and Table 1. During the two-year measurement period, CO_2 concentrations averaged $398 \pm 1 \mu\text{mol mol}^{-1}$ (average \pm SE, $n = 101$) with no clear seasonal trend, reflecting a contribution of approx-

imately $20 \mu\text{mol mol}^{-1}$ from fuel combustion and other sources in the Los Angeles basin.

Values of $\delta^{13}\text{C}$ were relatively low in winter 2004 ($-9.6 \pm 0.2\text{‰}$) and higher in summer ($-9.2 \pm 0.1\text{‰}$), in agreement with the seasonal trend observed in northern hemisphere clean, non-urban air—although the Pasadena values are lower at any given time due to local sources (mostly combustion). During 2005, variable contributions of local sources overcame the typical seasonal signal and no clear seasonal trend was observed in $\delta^{13}\text{C}$. The values of $\delta^{18}\text{O}$ averaged $41.2 \pm 0.1\text{‰}$ over the two years and showed pronounced minima during September 2004 ($40.3 \pm 0.1\text{‰}$) and August 2005 ($40.2 \pm 0.1\text{‰}$).

Δ_{47} value was lowest (0.75‰) in March 2004, increased to 0.89‰ in May 2004 and then decreased again to 0.80‰ in November. Δ_{47} values then increased gradually to the maximal observed value (1.01‰) in August 2005 followed by a decrease to 0.88‰ in December 2005. $\Delta^{14}\text{C}$ values varied between 51‰ in October 2004 and -30‰ in November 2005 with no clear seasonal trend.

3.2. Diurnal variations

Diurnal variations in CO_2 concentrations, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47} and $\Delta^{14}\text{C}$ are given in Fig. 2 and Table 2. On February

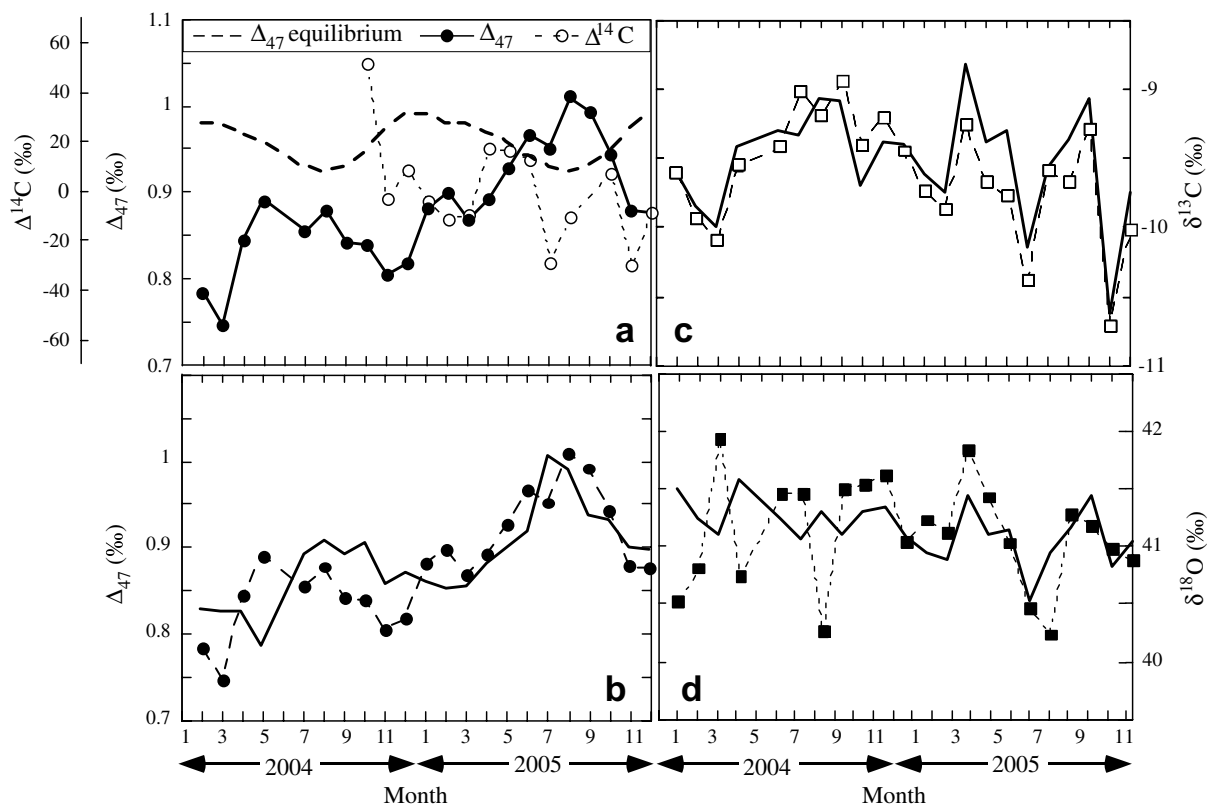


Fig. 1. (a) Seasonal variations (calculated as monthly averages) in Δ_{47} (bold circles with full line) and $\Delta^{14}\text{C}$ (empty circles with short-dashed line) for CO_2 in air sampled in Pasadena, CA, during the years 2004 and 2005. The long-dashed line depicts Δ_{47} values at thermodynamic equilibrium, based on the monthly mean temperatures in Pasadena, CA. (b) Observed seasonal variation in Δ_{47} (bold circles with dashed line) and modelled Δ_{47} (full line). (c) Monthly averaged seasonal variations in $\delta^{13}\text{C}$ (observation: empty squares with long-dashed line, model: full line) and (d) $\delta^{18}\text{O}$ (observation: bold squares with short-dashed line, model: full line). Note that the model results are more reliable after October 2004 (where $\Delta^{14}\text{C}$ data is available).

Table 1

CO₂ concentrations ($\mu\text{mol mol}^{-1}$), $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47} ($\pm\text{SE}$) and $\Delta^{14}\text{C}$ (‰) observed in air sampled in Pasadena, CA, during the years 2004 and 2005

Month (<i>n</i>)	[CO ₂]	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Δ_{47}	$\Delta^{14}\text{C}$	% Fuel ^a	% Local contribution ^b
Jan-04							
Feb-04 (2)	391 ± 2	-9.61 ± 0.08	40.52 ± 0.17	0.784 ± 0.015			3.2
Mar-04 (2)	399 ± 1	-9.94 ± 0.04	40.81 ± 0.01	0.746 ± 0.028			5.0
Apr-04 (2)	404 ± 0.2	-10.10 ± 0.10	41.92 ± 0.08	0.844 ± 0.112			5.8
May-04 (2)	383 ± 1	-9.55 ± 0.21	40.74 ± 0.02	0.890 ± 0.019			0.7
Jun-04							
July-04 (2)	399 ± 2	-9.43 ± 0.23	41.45 ± 0.25	0.854 ± 0.013			5.3
Aug-04 (1)	403	-9.03	41.45	0.877			6.8
Sept-04 (6)	392 ± 3	-9.19 ± 0.08	40.26 ± 0.14	0.842 ± 0.027			4.5
Oct-04 (3)	396 ± 2	-8.94 ± 0.26	41.49 ± 0.78	0.838 ± 0.006	51.4	0.8	5.4
Nov-04 (8)	400 ± 2	-9.41 ± 0.06	41.53 ± 0.07	0.804 ± 0.020	-2.6	6.1	6.0
Dec-04 (8)	396 ± 4	-9.20 ± 0.11	41.62 ± 0.33	0.817 ± 0.017	8.6	5.0	4.6
Jan-05 (9)	395 ± 3	-9.45 ± 0.20	41.04 ± 0.33	0.880 ± 0.008	-3.7	6.2	4.1
Feb-05 (6)	400 ± 3	-9.74 ± 0.15	41.22 ± 0.28	0.898 ± 0.014	-11.2	7.0	4.9
Mar-05 (9)	404 ± 4	-9.87 ± 0.19	41.11 ± 0.23	0.868 ± 0.012	-9.0	6.8	5.6
Apr-05 (9)	387 ± 1	-9.26 ± 0.13	41.84 ± 0.10	0.891 ± 0.013	17.3	4.2	1.3
May-05 (8)	400 ± 5	-9.67 ± 0.23	41.42 ± 0.13	0.927 ± 0.029	16.9	4.2	4.4
Jun-05 (6)	398 ± 4	-9.78 ± 0.26	41.03 ± 0.36	0.965 ± 0.017	13.1	4.6	3.9
July-05 (2)	410 ± 2	-10.38 ± 0.01	40.46 ± 0.01	0.951 ± 0.020	-28.6	8.7	7.1
Aug-05 (3)	398 ± 1	-9.59 ± 0.03	40.23 ± 0.06	1.008 ± 0.060	-10.0	6.9	4.7
Sept-05 (2)	396 ± 2	-9.68 ± 0.09	41.27 ± 0.06	0.991 ± 0.028			4.8
Oct-05 (3)	389 ± 2	-9.29 ± 0.01	41.18 ± 0.01	0.943 ± 0.001	7.6	5.1	3.0
Nov-05 (5)	420 ± 2	-10.71 ± 0.06	40.97 ± 0.07	0.878 ± 0.014	-29.8	8.8	9.8
Dec-05 (2)	403 ± 2	-10.02 ± 0.06	40.87 ± 0.05	0.876 ± 0.020	-8.4	6.7	5.7
Monthly mean SE	2	0.12	0.17	0.024			
Car exhaust sample		-25.03	30.37	0.361	-959		

Data is given as monthly averages, with the number of samples per month $n = 1-9$ per month over 1-5 days per month.

^a % Fuel refers to the amount of CO₂ in Pasadena air originating from fossil fuel combustion, based on $\Delta^{14}\text{C}$ data and calculated as: % fuel = $(\Delta^{14}\text{C}-60)/(-960-60)\cdot 100$.

^b % Local contribution refers the net effect of local CO₂ fluxes, estimated based on the CO₂ concentration difference between Pasadena, CA and Mauna Loa, HI (Mauna Loa data from the NOAA CMDL flask network, <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>).

14th, CO₂ concentrations varied from 499 $\mu\text{mol mol}^{-1}$ at 5am to 398 $\mu\text{mol mol}^{-1}$ between 8 and 11pm. $\delta^{13}\text{C}$ values were a mirror image of the concentration trend, varying between -9.0 and -13.0‰ with a 'Keeling plot' intercept of $-29.4 \pm 0.5\text{‰}$ ($R^2 = 0.996$). Δ_{47} values varied in a similar fashion from 0.818 $\pm 0.004\text{‰}$ between 2am and 2pm and $0.87 \pm 0.01\text{‰}$ between 5pm and 11pm. The $\Delta^{14}\text{C}$ values were highly correlated with the $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} = (0.034 \pm 0.001)\Delta^{14}\text{C} - (10.16 \pm 0.06)$; $R^2 = 0.992$) and varied between -80‰ at 5am and 41‰ at 11pm. The $\Delta^{14}\text{C}$ 'Keeling plot' intercept was -569‰ ($R^2 = 0.986$).

On February 21st, CO₂ concentrations were high at night and low around midday, as is typically observed in the region (Newman et al., 2004). They varied between 453 $\mu\text{mol mol}^{-1}$ at 6am and 392 $\mu\text{mol mol}^{-1}$ at 3pm. $\delta^{13}\text{C}$ values varied between -8.7 and -11.7‰ with a 'Keeling plot' whose intercept was $-33 \pm 1\text{‰}$ ($R^2 = 0.978$). Δ_{47} values were high ($0.88 \pm 0.02\text{‰}$) between noon and 6pm and low ($0.80 \pm 0.01\text{‰}$) in early morning and late evening. The $\Delta^{14}\text{C}$ trend was a mirror image of the CO₂ concentrations and varied from -50‰ at 6am to 47‰ at 3pm with a 'Keeling plot' intercept of -638‰ ($R^2 = 0.962$). The relationship between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ was similar to the other two days, though the correlation was not as clear ($\delta^{13}\text{C} = (0.019 \pm 0.009)\Delta^{14}\text{C} - (9.8 \pm 0.3)$; $R^2 = 0.480$).

On March 24th, CO₂ concentrations were high at night and low around midday, between 467 $\mu\text{mol mol}^{-1}$ at 5am and 406 $\mu\text{mol mol}^{-1}$ at 11am. $\delta^{13}\text{C}$ values varied between -9.6 and -11.8‰ with a 'Keeling plot' intercept of $-28 \pm 1\text{‰}$ ($R^2 = 0.985$). The Δ_{47} pattern was generally similar to that of February 21st though with a less clear trend and varied between 0.73‰ (at 8am) and 0.93‰ (at 11am). The $\Delta^{14}\text{C}$ trend was a mirror image of CO₂ concentrations and varied between -57‰ at 8am and 17‰ at 2am with a 'Keeling plot' intercept of -660‰ ($R^2 = 0.922$). Correlation was observed between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ ($\delta^{13}\text{C} = (0.024 \pm 0.004)\Delta^{14}\text{C} - (10.2 \pm 0.1)$; $R^2 = 0.822$). In all 3 days the $\delta^{18}\text{O}$ diurnal pattern was similar to that of $\delta^{13}\text{C}$ but the correlation with concentrations was weaker (a 'Keeling plot' correlation coefficient of 0.503 for all 3 days, as compared to $R^2 = 0.975$ for $\delta^{13}\text{C}$).

The different daily pattern among the three days was probably due to different weather patterns that reflect potential variations in the trajectories of the air observed. February 14th was a clear day that turned cloudy between 4 and 5pm. The minimal and maximal temperatures were 9 and 21 °C, respectively. Early morning (before 8am) was characterized by light North-westerly wind (wind data is based on measurements in a private station located at 34.136N, 118.124W, and reported in the Weather Under-

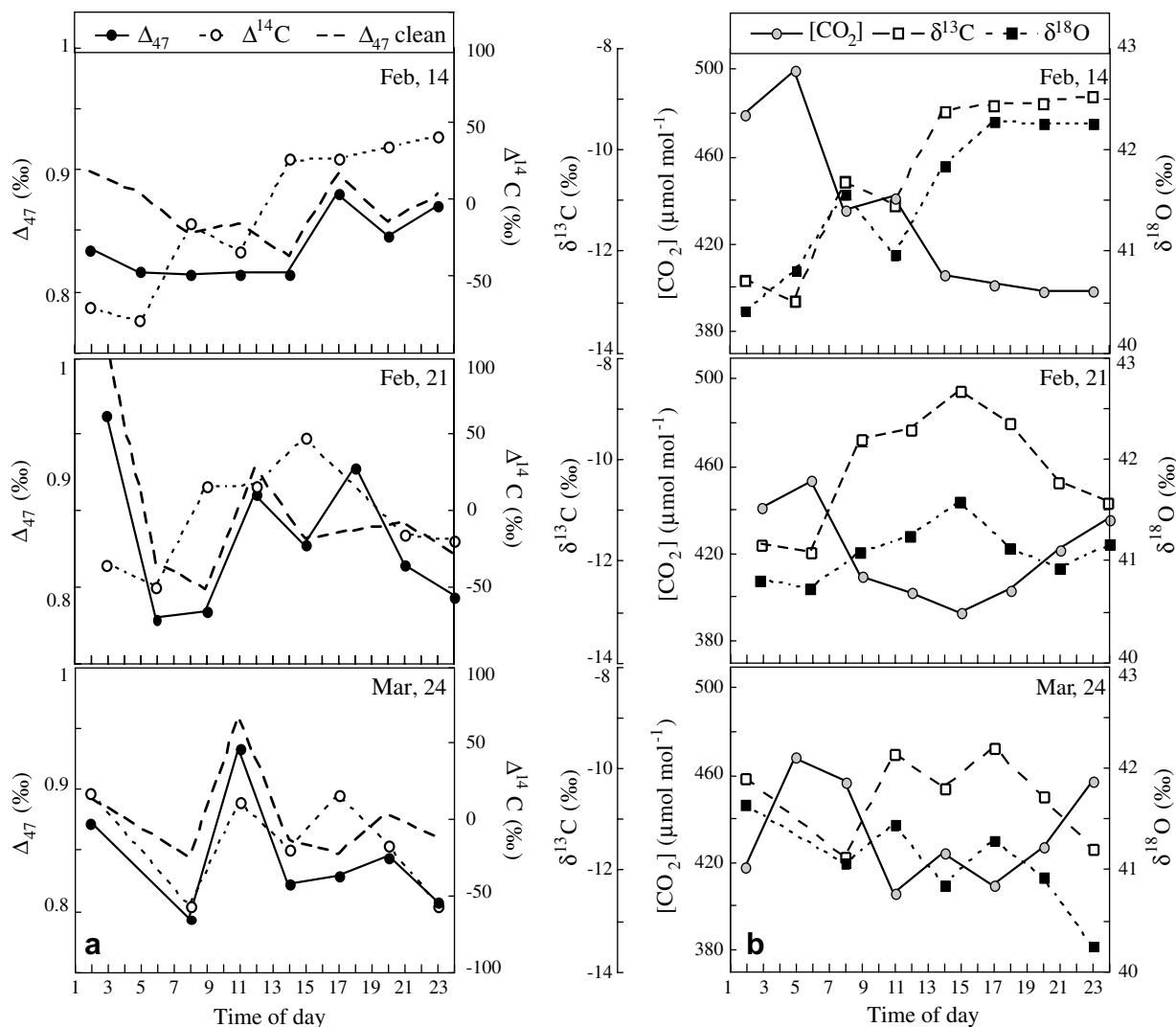


Fig. 2. (a) Diurnal variations in Δ_{47} (bold circles with full line) and $\Delta^{14}\text{C}$ (empty circles with short-dashed line) in air sampled on February 14, February 21 and March 24, 2006 in Pasadena, CA. The long-dashed line depicts Δ_{47} values estimated for “corrected” clean air. (b) Diurnal variations in CO_2 concentrations (grey circles with full line), $\delta^{13}\text{C}$ (empty squares with long-dashed line), and $\delta^{18}\text{O}$ (bold squares with short-dashed line).

ground web page: <http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCAPASAD5>). After 8am slightly stronger wind blew from the Southeast. February 21st was a clear and chilly day with minimal and maximal temperatures of 3 and 18 °C, respectively. Early morning (before 8am) wind direction was North-westerly, followed by 3 h of South easterly winds. From midday till midnight winds were stronger with alternating direction between Northeast and Northwest. March 24th was partly cloudy with minimal and maximal temperatures of 8 and 25 °C, respectively. Early morning (before 8am) and late night (after 8pm) wind direction was North-westerly. Winds intensified during the day and changed gradually from South easterly before noon and South westerly after noon. Sunrise occurred between 5:50 and 6:20am. Sunset occurred between 5:35 and 6:10 pm.

4. DISCUSSION

4.1. Seasonal variations

Previous interpretations of the $\delta^{18}\text{O}$ value of atmospheric CO_2 have emphasized the dominant influence of fluxes that involve exchange equilibria between CO_2 and ocean water, leaf water and soil water. This interpretation implies, *a priori*, that the Δ_{47} value of these CO_2 fluxes should also reflect thermodynamic equilibrium at the temperature of that exchange because a system in equilibrium with respect to CO_2 - H_2O exchange will also be in equilibrium with respect to homogeneous equilibria among CO_2 isotopologues (as for $\delta^{18}\text{O}$ (Gillon and Yakir, 2000), approximately 15 hydration steps are necessary for full exchange that would result in equilibrium Δ_{47} values). At thermodynamic equilibrium, the value of Δ_{47} varies due

Table 2

CO₂ concentrations (μmol mol⁻¹), δ¹³C, δ¹⁸O, Δ₄₇, and Δ¹⁴C (‰) observed in air sampled in Pasadena, CA, over a 24 h cycle during February 14th, February 21st, and March 24th, 2006

Time	[CO ₂]	δ ¹³ C	δ ¹⁸ O	Δ ₄₇	Δ ¹⁴ C
<i>February, 14</i>					
2:00	479	-12.57	40.41	0.834	-71.0
5:00	499	-13.01	40.80	0.815	-80.1
8:00	435	-10.67	41.56	0.813	-16.3
11:00	441	-11.07	40.96	0.814	-34.3
14:00	406	-9.25	41.83	0.814	25.9
17:00	401	-9.14	42.26	0.880	26.5
20:00	398	-9.09	42.25	0.845	34.6
23:00	398	-8.97	42.25	0.870	41.2
<i>February, 21</i>					
3:00	441	-11.68	40.80	0.953	-35.5
6:00	453	-11.87	40.73	0.786	-50.0
9:00	409	-9.64	41.08	0.792	15.2
12:00	402	-9.44	41.24	0.888	16.1
15:00	392	-8.69	41.57	0.846	47.0
18:00	403	-9.32	41.12	0.910	
21:00	422	-10.48	40.92	0.830	-16.1
23:59	435	-10.85	41.15	0.804	-19.9
<i>March, 24</i>					
2:00	418	-10.22	41.63	0.872	17.1
5:00	467				
8:00	457	-11.78	41.05	0.793	-57.1
11:00	406	-9.74	41.44	0.932	11.1
14:00	424	-10.41	40.84	0.822	-19.6
17:00	409	-9.62	41.29	0.828	15.9
20:00	427	-10.59	40.92	0.844	-17.1
23:00	457	-11.62	40.24	0.807	-56.7

to a temperature-dependent tendency to ‘clump’ ¹³C and ¹⁸O into bonds with each other leading to higher Δ₄₇ values at low equilibrium temperatures (Eiler and Schauble, 2004; Wang et al., 2004). Under such conditions, the global mean Δ₄₇ value should reflect a flux-weighted average of global temperatures. Local values are likely to be a mixture of background air values with Δ₄₇ values of local fluxes that in turn would reflect the local temperatures of exchange. In the extreme case in which all the CO₂ undergoes exchange locally, the predicted seasonal variations, based on long-term monthly mean temperatures in Pasadena, CA, would be between a winter maximum Δ₄₇ value of 0.99‰ (T = 13 °C) and a summer minimum of 0.92‰ (T = 25 °C; Fig. 1a). Under more realistic conditions, in which only part of the CO₂ interacts with local water, seasonal variations in Δ₄₇ are expected to be even smaller.

Monthly mean Δ₄₇ values of atmospheric CO₂ in Pasadena, CA, exhibit a temporal variation (Fig. 1a; Table 1) that has pronounced seasonality but is different in three respects from that predicted for thermodynamic equilibrium: The observed values are lower in winter and higher in summer—opposite to the predicted seasonal trend; the seasonal amplitude is larger than predicted; and there is a pronounced, unexpected inter-annual trend. This seasonal pattern and inter-annual trend differs from those for δ¹³C and δ¹⁸O (Fig. 1c and d).

Our results suggest that seasonal variations are the result of variations in the balance between several end-members,

some of which have Δ₄₇ values close to thermodynamic equilibrium, resulting from full CO₂–H₂O exchange, or even slightly above the predicted equilibrium values, and at least one flux that has a Δ₄₇ value substantially lower than the equilibrium value. Furthermore, Δ₄₇ values are closest to predicted equilibrium values during the summer and furthest away during winter, suggesting that the fluxes that dominate the summer budget reflect isotopic equilibrium (presumably mediated by exchange with water) or possibly have Δ₄₇ values slightly above that at equilibrium, whereas one or more of the local fluxes important to the winter budget have low Δ₄₇ values.

We would therefore expect the Δ₄₇ values of CO₂ in the major fluxes to and from the atmosphere (respiration, photosynthesis and ocean gas exchange) to be between ca. 0.9 and 1.0‰ (Eiler and Schauble, 2004; Wang et al., 2004). Such values are consistent with the summer maximum observed in our results, but are inconsistent with the lower values observed in winter. One possible explanation is that the low Δ₄₇ values characteristic of winter Pasadena air reflect a greater proportion of CO₂ from automobile exhaust and other combustion sources, which are known to have average Δ₄₇ values near 0.41‰ (Affek and Eiler, 2006). The extent of local transportation is not likely to vary strongly with season and emissions from local power generation is significantly higher in summer than in winter (E. Klinkner, Pasadena Water and Power, personal communication, 2006). However, relative anthropogenic contribution might be higher if the mixed layer is shallower in winter or if the trajectory of the air reaching Pasadena in winter leads to increased urban contribution. We tested this hypothesis by analyzing some of our air samples for Δ¹⁴C (Fig. 1a; Table 1), which can identify CO₂ produced from fossil fuel combustion (Zondervan and Meijer, 1996; Levin et al., 2003; Turnbull et al., 2006). Correlation between the Δ¹⁴C and Δ₄₇ values over the seasonal cycle (primarily through the winter) would suggest that anthropogenic emissions control the seasonal variation in Δ₄₇ values and are the cause for the low Δ₄₇ values observed in winter. CO₂ in clean air has a Δ¹⁴C value of ca. 60‰ (i.e., the value of 65‰ reported for the beginning of 2004 (Turnbull et al., 2006) decreased by the mean rate of ~5‰/y (Levin et al., 2003)). CO₂ from local car exhaust has a Δ¹⁴C value of -960‰ (Table 1, the value is not -1000‰ probably due to a few percent of ethanol, having modern Δ¹⁴C values, added to the gasoline). During the period of October 2004 to December 2005, the Δ¹⁴C values of CO₂ in Pasadena air varied between 51‰ and -30‰. This suggests that the contribution of CO₂ from fossil fuel combustion varied between 1% and 9%, averaging 6% (Table 1). No seasonal trend was observed in the Δ¹⁴C values, suggesting that there is no strong seasonality in the anthropogenic CO₂ contribution in Pasadena and hence probably no significant seasonal shift in the air trajectory that would lead to more urban air arriving to Pasadena in either season. No correlation was observed between the Δ¹⁴C and Δ₄₇ values (Fig. 4) indicating that fossil fuel combustion is not a major control on the seasonal trend in Δ₄₇ values.

We can use the Δ¹⁴C data to “correct” the measured Δ₄₇ values for the contribution from local combustion sources

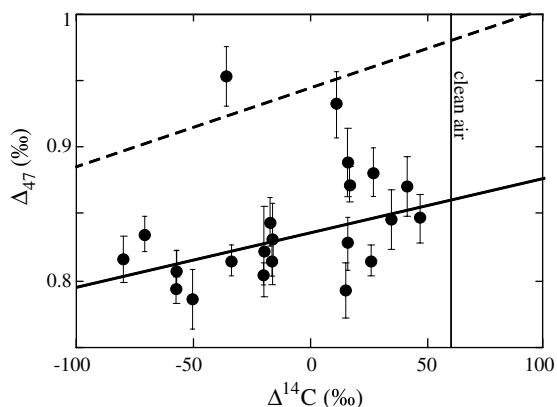


Fig. 3. Correlation between Δ_{47} and $\Delta^{14}\text{C}$ values observed in samples collected as part of our study of diurnal variations. The full line is a fit to the combined data of all 3 days (excluding 2 outliers) and yields the line: $\Delta_{47} = (0.0004 \pm 0.0001)\Delta^{14}\text{C} + (0.834 \pm 0.006)$, which implies $\Delta_{47} = 0.86 \pm 0.03\text{‰}$ for clean air (based on $\Delta^{14}\text{C} = 60\text{‰}$ in clean air). This line crosses the observed composition of car exhaust ($\Delta_{47} = 0.41\text{‰}$, $\Delta^{14}\text{C} = -960\text{‰}$). The dashed line reflects a mixing line between the measured composition of car exhaust and a hypothetical composition of clean air if it were at thermodynamic equilibrium (0.98‰ for a monthly mean local temperature of 15°C in February and March). The error bars are the standard error in 5 measurement of each sample (approximately 0.02‰), the error in $\Delta^{14}\text{C}$ is estimated as $\sim 2\text{‰}$.

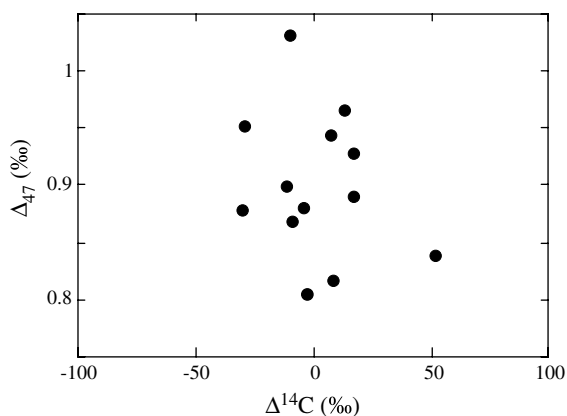


Fig. 4. Lack of correlation between Δ_{47} and $\Delta^{14}\text{C}$ measured between October 2004 and December 2005.

in order to estimate Δ_{47} values of nominally clean local air. This clean air is not identical to background atmosphere, as it is air free of local fossil fuel emissions but not free of the contribution of other local fluxes, such as photosynthesis and respiration by local ecosystems. The resulting Δ_{47} values for clean air are higher by 0.02‰ to 0.05‰ than the measured values, yielding an average Δ_{47} value of 0.94‰ for 2005 (Fig. 1b). The correction does not substantially change the seasonal trend, suggesting that local anthropogenic CO_2 sources affect the mean Δ_{47} value of Pasadena air but have only a minor effect on the temporal variations and are not the cause of the seasonal cycle. The fossil fuel contribution derived from $\Delta^{14}\text{C}$ is similar to the local con-

tribution to CO_2 concentration (5% in average; Table 1) estimated based on the difference of monthly mean concentrations between Pasadena and Mauna Loa (data from the NOAA/ESRL flask network, <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>) indicating that the net contribution of the local ecosystem is small. However, Δ_{47} , just like $\delta^{18}\text{O}$, is likely to be affected by gross fluxes and therefore might be influenced by local processes far more than suggested by concentration variations alone.

The combined constraints of $\Delta^{14}\text{C}$ and Δ_{47} require that one or more of the CO_2 sources other than anthropogenic emissions have a Δ_{47} value lower than expected for thermodynamic equilibrium over the range of local temperatures. Our results are most consistent with this low- Δ_{47} source being dominant in winter; based on previous studies of Δ_{47} in CO_2 from natural and anthropogenic sources (Eiler and Schauble, 2004; Affek and Eiler, 2006), this source must also make up a large fraction of all fluxes to the atmosphere because no known flux differs in Δ_{47} from average atmospheric CO_2 by more than ca. 0.5‰ . Ecosystem respiration (both plants and soil) is the most obvious source of this CO_2 , though ocean-air exchange cannot be ruled out *a priori*. If so, atmospheric CO_2 would be dominantly influenced by respiration (or ocean exchange) in winter, and drawn towards equilibrium with leaf water between late spring and early fall, when photosynthesis dominates.

To assess the possibility that the low Δ_{47} values of winter background air might reflect a possible kinetic isotope effect associated with atmosphere-ocean exchange (whose Δ_{47} values have not yet been characterized), we examined CO_2 in air from Cape Grim, Tasmania, and Barrow, Alaska. Both sites are considered remote enough from anthropogenic point sources so that air is likely to reflect global (or hemispheric) background air, not affected by local anthropogenic sources. Air in Cape Grim was sampled when the wind direction was west to south-west, suggesting probable marine influence. If Δ_{47} values of global background air or in ocean-air exchange were significantly lower than equilibrium values, we would expect these air samples to reflect these low values. However, Δ_{47} values of marine air collected at Cape Grim and Barrow during 2005 averaged $0.92 \pm 0.01\text{‰}$ (Table 3), higher than the values we observed in winter-time Pasadena air, not supporting this hypothesis. Thus, respiration seems like the most plausible source of low Δ_{47} values in nominally clean air.

4.2. Diurnal variations

We further explored the isotopic composition of respired CO_2 by examining the diurnal variations in Δ_{47} in Pasadena air, expecting that respired CO_2 would be dominant at night and therefore lead to lower night-time Δ_{47} values (note that due to the high sensitivity of Δ_{47} to even small amounts of water, direct sampling of soil or leaf respired CO_2 using conventional incubation methods is problematic, forcing us to use this indirect approach). This approach does not distinguish between soil and dark plant respiration. Measurements of this kind are likely to be influenced by variations in the relative contribution of all local sources, including anthropogenic ones, due to diurnal

Table 3
Isotopic composition of air sampled in Cape Grim, Tasmania (40.68S, 144.68E) and Barrow, AK (71.32N, 156.6W)

Sampling date	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Δ_{47}
<i>Cape Grim</i>			
February, 9, 2005	−8.15	42.29	0.948
February, 9, 2005	−8.16	42.76	0.906
April, 26, 2005	−8.10	42.68	0.853
May, 5, 2005	−8.14	42.70	0.934
June, 28, 2005	−8.15	42.71	0.902
July, 11, 2005	−8.14	42.48	0.883
July, 18, 2005	−8.11	42.41	0.972
July, 26, 2005	−8.14	42.65	0.848
August, 4, 2005	−8.20	42.31	0.992
August, 10, 2005	−8.18	42.67	0.889
August, 15, 2005	−8.13	42.84	0.987
August, 22, 2005	−8.24	42.53	0.886
Average \pm SE	-8.15 ± 0.01	42.59 ± 0.05	0.917 ± 0.013
<i>Barrow</i>			
February, 11, 2005	−8.62	40.39	0.948
April, 1, 2005	−8.54	41.25	0.915
April, 6, 2005	−8.65	40.24	0.934
June, 3, 2005	−8.50	40.74	0.896
June, 10, 2005	−8.72	39.19	0.942
June, 17, 2005	−8.54	40.12	0.928
June, 27, 2005	−8.25	40.29	0.870
August, 12, 2005	−7.62	40.68	0.905
August, 19, 2005	−7.95	40.51	0.928
Average \pm SE	-8.34 ± 0.12	40.45 ± 0.19	0.918 ± 0.008

variations in atmospheric mixing as a result of the typically shallow mixed layer at night (analogous to the “rectifier effect”; Denning et al., 1996). Similar effects have been previously observed in diurnal measurements of urban air and were manifested as a lack of correlation between source strength and CO_2 concentrations and $\delta^{13}\text{C}$ values near the surface (Reid and Steyn, 1997; Grimmond et al., 2002; Nemitz et al., 2002; Pataki et al., 2005; Moriwaki et al., 2006). To control for anthropogenic contributions and normalize the effect of varying synoptic conditions and mixed layer depth, we compared Δ_{47} diurnal variations to those in $\Delta^{14}\text{C}$ (since those physical atmospheric parameters would control both tracers in a similar fashion).

The values of Δ_{47} and $\Delta^{14}\text{C}$ vary inversely with concentrations over a 24-h cycle for 3 separate days during winter 2006 (Fig. 2 and Table 2). The values of Δ_{47} and $\Delta^{14}\text{C}$ are generally correlated with one another (Fig. 3; excepting the data for air collected at 3am on February 21st and 11am on March 24th). A likely explanation of this correlation is diurnal variations in atmospheric mixing, so that CO_2 from both fossil fuel combustion and respiration is concentrated near the surface at night and is mixed deeper in the atmosphere during the day.

The concentration pattern during February 21st and March 24th is the pattern observed typically in Pasadena (Newman et al., 2004). It is associated with the typical wind pattern in the Los Angeles basin with wind blowing seawards (Northerly wind) in early morning and blowing from sea to inland in the afternoon (Neiburger, 1969) and return-

ing to seaward direction in the evening. In February 14th, on the other hand, sea breeze persisted through the evening and night, leading to the observed evening cloud cover, which is typically accompanied with low CO_2 concentrations (S. Newman, personal communication, 2007). Although the sea breeze is likely to bring to Pasadena urban air from Los Angeles this wind direction is not necessarily associated with higher concentrations and larger anthropogenic contribution, suggesting that the boundary layer height and local surface fluxes are more important than wind direction to the local Pasadena CO_2 diurnal pattern.

The correlation in Fig. 3 can be fit with a line that crosses the observed car exhaust $\Delta^{14}\text{C}$ value of -960‰ at a Δ_{47} value of 0.41‰ —identical to the Δ_{47} value measured in car exhaust in the Pasadena area (Affek and Eiler, 2006). This result strongly indicates that one cause of diurnal variations in $\Delta^{14}\text{C}$, Δ_{47} and $\delta^{13}\text{C}$ is concentration of car exhaust in boundary layer air at night. On the other hand, given a $\Delta^{14}\text{C}$ value of 60‰ for clean air, this line suggests a Δ_{47} value of $0.86 \pm 0.03\text{‰}$ for clean air (i.e., not including the local fossil fuel component). This value is significantly lower than that at thermodynamic equilibrium (0.98‰ for the mean local temperature in February and March) indicating, as discussed above for the seasonal variations, that the clean air end member does not reflect equilibrium and that at least one of the non-fossil-fuel CO_2 fluxes driving diurnal variability is characterized by lower Δ_{47} values.

As with the seasonal data, we used $\Delta^{14}\text{C}$ values to “correct” the measured Δ_{47} values for the contribution of combustion sources in order to estimate diurnal variations of Δ_{47} from other sources. The “corrected” values are all higher than the raw measured values, but the pattern of diurnal variability changed only slightly (Fig. 2). One explanation of this result is that the shallow mixing also concentrates respired CO_2 into boundary layer air at night, and that local respired CO_2 is characterized by a Δ_{47} value lower than expected for thermodynamic equilibrium. This interpretation is consistent with our suggested interpretation of the seasonal cycle; i.e., competition between low Δ_{47} values in respiration and higher Δ_{47} values resulting from $\text{CO}_2\text{--H}_2\text{O}$ (leaf or surface) exchange are responsible for seasonal variations in Δ_{47} , and the diurnal cycle in urban air reflects accumulation of both low- Δ_{47} respiration CO_2 and very low- Δ_{47} combustion CO_2 in night-time boundary layer air.

We estimate the Δ_{47} and $\Delta^{14}\text{C}$ values for the respiration component that we hypothesize contributes to diurnal variability in Pasadena air using the observed, uncorrected, diurnal data in a ‘Keeling plot’ approach (Keeling, 1958). The intercept of the $\Delta^{14}\text{C}$ ‘Keeling plot’ is $-595 \pm 29\text{‰}$, indicating that the source of night-time CO_2 is a combination of 64% combustion CO_2 and 36% modern carbon, which we attribute to respiration. The Δ_{47} ‘Keeling plot’ intercept is $0.54 \pm 0.10\text{‰}$, implying a Δ_{47} value of $0.77 \pm 0.28\text{‰}$ for the putative respiration end-member. The error estimate for the respiration Δ_{47} value is large, probably because of the indirect approach we had to take in estimating it through diurnal variations as well as due to the complication in using urban air. Future work must be devoted to detailed respiration measurements in a clean environment, such as agricultural settings, in order to get a

more precise estimate of the Δ_{47} value associated with respiration. Nevertheless, this value is indistinguishable from the value of 0.76‰ observed for human breath (Affek and Eiler, 2006). Human breath obviously constitutes a trivial fraction of all respired CO_2 , but it is possible that similar biological kinetic isotope effects are responsible for the lower than equilibrium value in both types of respiration. At this stage we can only hypothesize as to the cause for this low respiration value. This value is clearly out of equilibrium for CO_2 but might be the result of a kinetic isotope effect either in the CO_2 production or in its escape from the leaf or the soil. This might be combined with a possibility that the respired CO_2 still carries some of the original Δ_{47} signature of the carboxyl group from which it was formed (W. Guo, personal communication, 2007), which due to the lower bond order (as compared to CO_2) is expected to have a lower Δ_{47} value at equilibrium (Schauble et al., 2006).

4.3. Mass balance model

We can consider the plausibility and implications of the apparent Δ_{47} value of respired CO_2 by examining its ability to explain the observed seasonal cycle, using a single box model. We used the isoflux mass-balance approach (Tans et al., 1993), with the flux rates constrained by our Pasadena air CO_2 concentration, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ measurements, with concentrations and $\delta^{13}\text{C}$ values measured in Mauna Loa (data from the NOAA/ESRL flask network, <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>) used as background air values. We then used estimates of Δ_{47} values associated with CO_2 sources to reconstruct the observed Δ_{47} seasonal variations.

The mass balance relations used in this model are:

$$M(c_a - c_b) = F_{\text{ff}} + R + F_{\text{la}} - F_{\text{al}} \quad (2)$$

$$M(c_a\delta_a - c_b\delta_b) = F_{\text{ff}}\delta_{\text{ff}} + R\delta_R + F_{\text{la}}\delta_{\text{la}} - F_{\text{al}}(\delta_b - \varepsilon) \quad (3)$$

where c_a and c_b are CO_2 concentrations in ambient Pasadena air and in background (Mauna Loa) air, and δ_a and δ_b are the respective isotopic compositions (referring to either $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\Delta^{14}\text{C}$ or Δ_{47}); M is the mass of air in the footprint covered by the observations, namely the size of the box in the model, so that Mc_a is the pool size of CO_2 in the box (we have no way to estimate the size of M in the local footprint, therefore all calculated flux rates are normalized to the box size, namely given as F/M , see below); F_{ff} is the flux of CO_2 from local fossil fuel combustion, R is ecosystem respiration flux, F_{al} and F_{la} are fluxes of leaf gas-exchange (from air to leaf and from leaf to air, respectively). δ_i (or Δ_i) values are the isotopic compositions associated with the respective fluxes, and ε is the isotopic fractionation associated with CO_2 uptake in photosynthesis (taken as 18‰ (Bowling et al., 2001) for $\delta^{13}\text{C}$ and zero for the other isotopic tracers).

First, we constructed a steady-state single box model of the annual budget based on isoflux mass balance equations (Eqs. (2, 3)) for Δ_{47} , assuming the ratio between the local flux rates to be the same as in global annual flux rates. We consider that $F_{\text{la}} = A_n(c_c/(c_a - c_c))$, where A_n is net photosynthesis rate, c_a is atmospheric CO_2 concentration and c_c

is the CO_2 concentration in the chloroplasts, and that c_c/c_a is typically 2/3, yielding: $F_{\text{la}} = 2A_n$ and $F_{\text{al}} = 3A_n$, and $R = A_n$ and we assume that $F_{\text{ff}} = 0.1A_n$. For Δ_{47} we adopt the value $\Delta_{47-\text{ff}} = 0.41‰$ (Affek and Eiler, 2006), and $\Delta_{47-R} = 0.77‰$ (based on diurnal variation analysis above) and $\Delta_{47-b} = 0.92‰$ (based on values observed in Cape Grim and Barrow air). We assume that ocean exchange fluxes are not involved directly in the local Pasadena air mass balance, but only affect it through possible variations in background air Δ_{47} values. We further assume that CO_2 uptake in photosynthesis (F_{al}) does not include a Δ_{47} isotopic effect ($\varepsilon = 0$ in Eq. (3)). Given these assumptions we calculate a Δ_{47} value of 0.97‰ for the flux out of leaves (F_{la}). This value is equivalent to an equilibration temperature of 16 °C, very close to the mean yearly local temperature of 18 °C, and it provides the high Δ_{47} end-member of the local Δ_{47} balance.

We can use these end-member Δ_{47} values to reconstruct the observed seasonal cycle. We first used the concentration and $\Delta^{14}\text{C}$ records to estimate flux rates that would fit the observed $\delta^{13}\text{C}$ seasonal record in Pasadena. We then use the obtained flux rates to fit the observed Pasadena air $\delta^{18}\text{O}$ and Δ_{47} trends.

We use $\Delta^{14}\text{C}$ data to estimate the fossil fuel local contribution as:

$$\frac{F_{\text{ff}}}{M} = \frac{\Delta^{14}\text{C}_a - \Delta^{14}\text{C}_b}{\Delta^{14}\text{C}_{\text{ff}} - \Delta^{14}\text{C}_b} \cdot c_b \quad (4)$$

using $\Delta^{14}\text{C}_{\text{ff}} = -960‰$ and $\Delta^{14}\text{C}_b = 60‰$ (Levin et al., 2003; Turnbull et al., 2006) and assuming that $\Delta^{14}\text{C}_R \approx \Delta^{14}\text{C}_{\text{la}} \approx \Delta^{14}\text{C}_b$. We then assume that the concentration excess ($C_E = c_a - c_b$) in Pasadena with respect to Mauna Loa reflects the sum of local anthropogenic and biogenic fluxes, so that the difference between that excess and F_{ff}/M is the effect of the net local ecosystem flux (with $A_n/M = 10F_{\text{ff}}/M$ and $R/M = 10F_{\text{ff}}/M + C_E$). We then use $\delta^{13}\text{C}_{\text{ff}} = -31‰$, (based on a weighted average of $\delta^{13}\text{C}$ values for the fossil fuel sources used in California, Newman et al., 2004), $\delta^{13}\text{C}_{\text{la}} = \delta^{13}\text{C}_b + \varepsilon$ (with $\varepsilon = 18‰$) and $\delta^{13}\text{C}_R = -26.5‰$ to reconstruct the $\delta^{13}\text{C}$ seasonal variations in Pasadena. In February to September 2004, where $\Delta^{14}\text{C}$ data is not available, we vary F_{ff}/M to fit the observed $\delta^{13}\text{C}$ values (Fig. 1c).

The resulting flux rates are given in Table 4. In 2004 the fossil fuel local contribution seem to be high in winter and low in summer (note, however, that in the absence of $\Delta^{14}\text{C}$ data till October 2004, our analysis is more reliable for 2005). The local anthropogenic influence on $\delta^{13}\text{C}$ was therefore in phase with the global $\delta^{13}\text{C}$ variations in background air, resulting in a seasonal pattern that is similar to the global pattern, though shifted to more depleted values. In 2005 the average fossil fuel contribution was the same as in 2004 but it was distributed rather evenly through the year, resulting in the observed absence of a clear seasonal pattern in $\delta^{13}\text{C}$. During 2005 the fossil fuel component was slightly higher than the CO_2 concentration excess when comparing Pasadena concentrations to the corresponding Mauna Loa concentrations, suggesting net CO_2 uptake in photosynthesis year round. In 2004, on the other hand, net respiration flux

Table 4
Parameters and results of mass balance box model

Month	F_{ff}/M	R/M	F_{al}/M	F_{la}/M	Δ_{47-b}
Jan-04					
Feb-04	40	373	1200	800	0.92
Mar-04	40	380	1200	800	0.92
Apr-04	40	383	1200	800	0.92
May-04	60	543	1800	1200	0.92
Jun-04					
July-04	10	111	300	200	0.92
Aug-04	2	45	60	40	0.92
Sept-04	10	108	300	200	0.92
Oct-04	3	51	100	67	0.92
Nov-04	25	245	737	491	0.92
Dec-04	20	199	602	401	0.92
Jan-05	25	243	756	504	0.92
Feb-05	28	275	852	568	0.92
Mar-05	28	271	829	553	0.92
Apr-05	17	157	507	338	0.92
May-05	17	169	505	337	0.85
Jun-05	18	182	554	369	0.82
July-05	36	353	1080	720	0.82
Aug-05	28	269	835	557	0.8
Sept-05	20	197	594	396	0.8
Oct-05	20	196	615	410	0.82
Nov-05	37	371	1101	734	0.88
Dec-05	27	269	818	546	0.88
$\delta^{13}\text{C}$ end-members	-31	-26.5	$\delta^{13}\text{C}_b-18$	$\delta^{13}\text{C}_b-18$	
$\delta^{18}\text{O}$ end-members	30	31.5	$\delta^{18}\text{O}_b$	47	
$\Delta^{14}\text{C}$ end-members	-960	60	60	60	
Δ_{47} end-members	0.41	0.77	Δ_{47-b}	0.97	

Flux rates are normalized to the air pool size and are given in units of $\mu\text{mol mol}^{-1}$. Isotopic values are given in units of ‰. Concentrations, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ in background air values are taken as the values observed in Mauna Loa (of the NOAA CMDL flask network, <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>).

was obtained in summer. This inter-annual variations in respiration and photosynthesis fluxes might be attributable to recent local climate variability: 2005 was one of the rainiest years on record in Southern California, encouraging high photosynthetic rates in this usually arid environment, whereas 2004 was significantly drier.

To reconstruct the observed $\delta^{18}\text{O}$ trend we use $\delta^{18}\text{O}_{ff} = 30\text{‰}$ (Affek and Eiler, 2006) but have no independent estimate of the local biospheric $\delta^{18}\text{O}$ end members. We therefore use the flux estimate derived from $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ and vary the biospheric end members to yield a best fit of the model results to the $\delta^{18}\text{O}$ observations (Fig. 1d; the values used for the end-members are given in Table 4). This results (Fig. 1d) in a satisfactory reconstruction of the observed trend in variations in 2005. In 2004 we were able to model the average $\delta^{18}\text{O}$ value but not the details of the variations. The large amount of rainfall in Southern California during 2005 is likely to result in small variations in the ^{18}O end-members, thus enabling us to reconstruct the observed variations. In 2004, on the other hand, potential variations in the mixture of water sources used for irrigation probably resulted in complex variations of $\delta^{18}\text{O}$ values of the end-member values. These

variations are not known and therefore not included in our analyses, preventing good reconstruction of the 2004 seasonal pattern.

Finally, we use these flux estimates with the Δ_{47} end-members (given above) to reconstruct the seasonal variations observed in Δ_{47} (Fig. 1b). The resulting modelled Δ_{47} seasonal curve is therefore independent of the observed Δ_{47} data and depends only on the observed concentrations, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values and provides a test for the end-member values obtained. The flux rates used yielded a good reconstruction of the seasonal Δ_{47} amplitude in 2004 due to relatively large seasonal variations in flux rates. In 2005 flux rates varied much less and resulted in smaller amplitude than observed. A sensitivity test, performed by applying small changes in the Δ_{47} end-members, was unable to yield the observed seasonal amplitude. A good fit to the seasonal pattern of 2005 was obtained only by allowing variations in the Δ_{47} values of the background air entering the footprint included in our measurements, with slightly lower (0.80 to 0.88 instead of 0.92; Table 4) values in the summer and autumn of 2005. Such variations may be the result of changes in Δ_{47} values associated with ocean gas exchange, which are not yet characterized.

Pasadena air is typical of air in urban areas and its isotopic values therefore reflect a complex combination of both anthropogenic and natural local CO_2 fluxes, on top of the global variations. In spite of these complications, our results indicate that Δ_{47} values do not reflect only the expected effect of anthropogenic combustion sources but are affected also by local or regional natural gross fluxes, with a competition between ecosystem respiration and CO_2 uptake and retro-flux in photosynthesis. Furthermore, the local Δ_{47} values reflect also variation in background air Δ_{47} values, due to either a change in global background values or to a regional shift in the source of the background air parcels.

This work identifies the existence of measurable temporal, seasonal and diurnal, variations in Δ_{47} in atmospheric CO_2 , which is a prerequisite for it being used as a new isotopic tracer. Although further work must be performed to better characterize the Δ_{47} values associated with all the relevant end-members, the preliminary estimates presented here of low Δ_{47} values in respiration, very low Δ_{47} values in combustion (Affek and Eiler, 2006) and high values in photosynthetic retro-diffusion, suggest that Δ_{47} has the potential to be useful in partitioning photosynthesis, respiration, and fossil fuel combustion, all inseparable using the more common isotopic tracers, such as $\delta^{13}\text{C}$.

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