

Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: Anthropogenic and biogenic effects

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[1] Atmospheric CO₂ mixing ratios and carbon and oxygen isotope composition were measured at 18 m above the ground in Salt Lake City, Utah, United States, for a one-year period. Mixing ratios were highest in the wintertime with maximum values approaching 600 μmol mol⁻¹ during atmospheric inversions. Nighttime carbon and oxygen isotope ratios of source CO₂ showed a seasonal pattern with isotopically depleted values in the wintertime and isotopically enriched values in the spring and summer. The effects of gasoline combustion, natural gas combustion, and biogenic respiration of plants and soils on CO₂ mixing ratio were quantified with a mass balance calculation using dual carbon and oxygen isotopic tracers. The calculations showed large contributions of natural gas combustion in the winter and significant nighttime biogenic respiration in the spring and late summer/early fall. The isotope-tracer technique used shows promise for quantifying the impacts of urban processes on the isotopic composition of the atmosphere and partitioning urban CO₂ sources into their component parts.

INDEX TERMS: 0315

Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: CO₂ mixing ratio, carbon isotopes, oxygen isotopes, urban pollution, biosphere-atmosphere interactions, Keeling plots

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1. Introduction

[2] The isotopic composition of atmospheric CO₂ contains information about the magnitude and distribution of sources and sinks of carbon. Photosynthetic uptake of CO₂, plant and soil respiration, biomass burning, and fossil fuel combustion impart carbon and oxygen isotope signals to the atmosphere that can be used as a tracer at various temporal and spatial scales [Francey *et al.*, 1985; Fung *et al.*, 1997; Keeling *et al.*, 1989]. The urban contribution to the isotopic composition of the atmosphere has generally been represented by combining estimates of the isotopic composition of fossil fuel types with energy-use statistics [Andres *et al.*, 2000; Tans, 1981]. Direct measurements of the isotopic composition of CO₂ emissions in urban areas have occasionally been conducted [e.g., Clark-Thorne and Yapp, 2003; Florkowski *et al.*, 1998; Friedman and Irsa, 1967; Takahashi *et al.*, 2002; Zondervan and Meijer, 1996] and can provide important information about 1) local processes, including biological contributions to urban CO₂ emissions, and 2) temporal and spatial variability in the isotopic composition of urban emissions.

[3] Biological and anthropogenic contributions to urban CO₂ mixing ratios have been evaluated in a handful of previous studies applying stable and radioisotopes of carbon

[Kuc and Zimnoch, 1998; Meijer *et al.*, 1997; Takahashi *et al.*, 2001, 2002; Zondervan and Meijer, 1996] and carbon and oxygen isotopes of CO₂ [Florkowski *et al.*, 1998]. These studies have distinguished between background CO₂ mixing ratio and CO₂ emitted from urban sources:

$$c_T = c_A + c_S \quad (1)$$

where c_T is the total CO₂ mixing ratio, c_A is the background CO₂ mixing ratio, and c_S is the mixing ratio originating from local sources. c_S has been further partitioned into anthropogenic (fossil fuel) and biogenic (plant/soil respiration) sources by utilizing the distinct ¹³C, ¹⁴C, and/or ¹⁸O isotopic composition of each component. Previous short-term applications of this approach have found significant contributions of biological respiration to total urban CO₂ mixing ratios [Meijer *et al.*, 1997; Takahashi *et al.*, 2001, 2002; Zondervan and Meijer, 1996].

[4] Here we use measurements of urban CO₂ mixing ratios and isotopic composition to examine an alternate form of the mass balance model for partitioning urban CO₂ emissions. In our initial approach, we have chosen to use the ¹³C and ¹⁸O tracers over ¹⁴C due to the relative feasibility and lower cost of stable isotope measurements in small gas volumes. Our application of these tracers differs from previous studies in that we apply the mass balance method of Keeling [1958, 1961] to estimate the carbon and oxygen isotopic composition of the integrated urban CO₂

source once a week for a one-year period. Thus, we derive the seasonal cycle of the impact of urban processes on the isotopic composition of the atmosphere. We then construct a mass balance model to partition the total CO₂ emission source into CO₂ produced by biological respiration and combustion, which have distinct oxygen isotope ratios, and further partition CO₂ produced by combustion into gasoline and natural gas components, which have distinct carbon isotope ratios.

2. Methods

2.1. Atmospheric Measurements

[5] In Salt Lake City, Utah, United States, CO₂ mixing ratios were continuously monitored at 18 m above the ground on the University of Utah campus with an infrared gas analyzer (LI 7000, LI-COR Inc., Lincoln, NE, United States). The measurement location was about 3.5 km east of downtown Salt Lake City. A 500 m radius around the CO₂ inlet mostly encompassed the University campus, as well as a residential neighborhood 300 m to the west. Sampled air was passed through a magnesium perchlorate (Mg(ClO₄)₂) desiccating trap. CO₂-free air and WMO traceable calibration gas containing a known CO₂ mixing ratio ranging from 400–420 μmol mol⁻¹ were separately introduced into the analyzer hourly to correct mixing ratios with recorded zero and span values. Two-minute running averages of CO₂ mixing ratio were recorded every 5 minutes from January–December, 2002 on a datalogger (CR23x, Campbell Scientific Inc., Logan, UT, United States).

[6] For isotopic analysis, fifteen 100-ml air samples were collected in glass flasks weekly with an automated sampler described by *Schauer et al.* [2003]. Air samples were obtained at 18 m height from an inlet adjacent to the CO₂ mixing ratio sampling described above. The sampler was programmed to fill flasks with dry sample air to obtain samples spanning a specified CO₂ mixing ratio range (30–50 μmol mol⁻¹ depending on the time of year) within a single nighttime period, generally from midnight to 6:00 MST. If the specified range was not obtained, the samples were flushed and the nighttime sampling began again the next day. For comparative purposes, some samples were collected during discrete daytime morning (5:00–10:00) or evening (17:00–21:00) rush-hour periods in the wintertime. Samples were analyzed for oxygen and carbon isotope ratios of CO₂ with an isotope ratio mass spectrometer (Delta S, Finnigan MAT, San Jose, CA, United States) as described by *Ehleringer and Cook* [1998]. CO₂ and N₂O were separated by gas chromatography, and resulting isotope values were corrected daily with known standards. The average daily precision of these measurements was 0.14‰ for carbon and 0.23‰ for oxygen. CO₂ mixing ratios of the flask samples were then measured as described by *Bowling et al.* [2001].

2.2. Mass Balance Approach

[7] *Keeling* [1958, 1961] applied isotopic mass balance to equation (1) and derived a linear mixing model between c_A and the mixing ratio of a CO₂ source (c_S):

$$\delta_T = c_A(\delta_A - \delta_S)(1/c_T) + \delta_S \quad (2)$$

where δ_T , δ_A , and δ_S are the isotope ratio of the total CO₂ mixing ratio, the background CO₂, and the CO₂ emitted from the source, respectively, expressed in δ notation:

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000 \text{ ‰} \quad (3)$$

where R is the molar ratio of heavy to light isotopes. In this study, carbon isotope ratio ($\delta^{13}\text{C}$) is expressed relative to the V-PDB standard and oxygen isotope ratio ($\delta^{18}\text{O}$) is expressed relative to V-SMOW.

[8] This “Keeling plot” method assumes that the isotopic composition of both the background and source CO₂ remain constant during the sampling period [*Miller and Tans*, 2003; *Pataki et al.*, 2003]. An advantage of this approach is that c_A , δ_A , and c_S need not be specified in order to solve the mass balance for δ_S .

[9] Equation (2) was used to estimate both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of source CO₂ for each set of 15 air samples collected. For simplicity, this analysis was limited to periods when photosynthesis was assumed to be negligible in wintertime and at night during the growing season. The Keeling plot intercept was calculated using geometric mean regression according to *Pataki et al.* [2003]. Outliers were removed if the absolute value of the residual for an individual data point was more than 3 standard deviations from the mean residual. Intercepts were discarded when the regression model was not significant at $\alpha = 0.01$ according to *Flanagan et al.* [1997] and *Bowling et al.* [2003b]. The standard error of the intercept was calculated by the ordinary least squares, “Model I” regression method [*Sokal and Rohlf*, 1995].

[10] We utilized the CO₂ isotope and mixing ratio data collected in Salt Lake City to evaluate the advantages and limitations of deriving the isotopic composition of urban source CO₂ with the Keeling plot method, and partitioning the total source into three component parts: gasoline combustion (c_G), combustion of natural gas (c_N), and biogenic respiration (c_R). We neglect the influence of coal in this application as there are no coal-fired power plants in Salt Lake City or the surrounding metropolitan area (Energy Information Administration, U.S. Department of Energy, <http://www.eia.doe.gov>). To solve for the contribution of the three remaining components, we applied the following mass balance:

$$f_R + f_G + f_N = 1 \quad (4)$$

$$\delta^{13}\text{C}_R f_R + \delta^{13}\text{C}_G f_G + \delta^{13}\text{C}_N f_N = \delta^{13}\text{C}_S \quad (5)$$

$$\delta^{18}\text{O}_R f_R + \delta^{18}\text{O}_G f_G + \delta^{18}\text{O}_N f_N = \delta^{18}\text{O}_S \quad (6)$$

where $f_R = c_R/c_S$, $f_G = c_G/c_S$, $f_N = c_N/c_S$, and $c_S = c_R + c_G + c_N$. The subscripts R , G , and N refer to respiration, gasoline combustion, and natural gas combustion, respectively. An assumption in this formulation is that f_R , f_G , and f_N remain constant during the sampling period for the determination of $\delta^{13}\text{C}_S$ and $\delta^{18}\text{O}_S$ from equation (2). If this condition is met, three urban sources of CO₂ can be distinguished without estimating the isotopic composition of background air from remote measurements. In this approach, all isotope ratios are

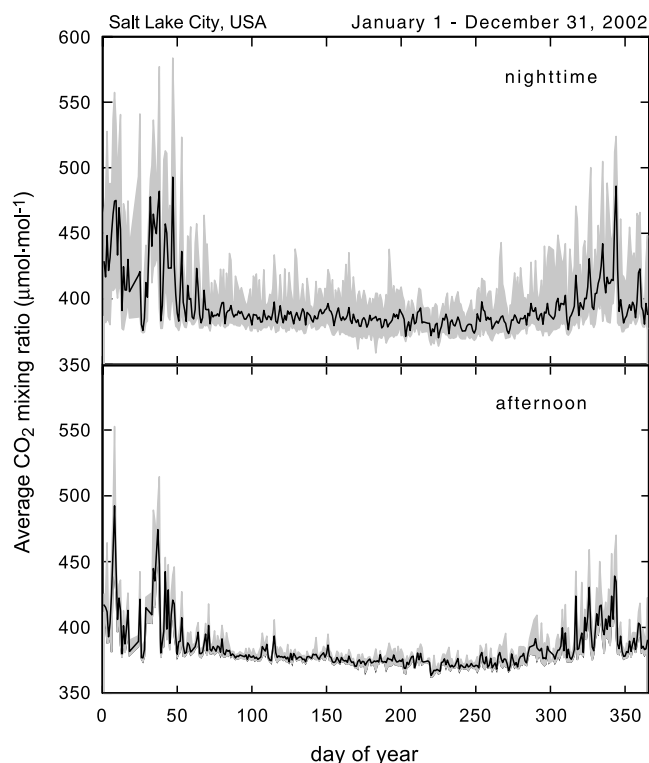


Figure 1. The average CO₂ mixing ratio measured at 18 m above the ground for nighttime (20:00–6:00) and afternoon (12:00–16:00) periods. The line shows the average value and the shaded area encompasses the minimum and maximum.

treated as known and are prescribed from direct measurements, models, or literature values.

3. Results and Discussion

[11] CO₂ mixing ratios were highest in the wintertime with nighttime maximal values reaching almost 600 $\mu\text{mol}\cdot\text{mol}^{-1}$ in January and February of 2002 (Figure 1). Peaks were observed during significant atmospheric inversion events. Nighttime average values ranged from approximately 390–480 $\mu\text{mol}\cdot\text{mol}^{-1}$ in the winter and 375–400 $\mu\text{mol}\cdot\text{mol}^{-1}$ in the spring and summer (Figure 1). Afternoon values in the spring and summer were commonly within 5 $\mu\text{mol}\cdot\text{mol}^{-1}$ of the background value of 372.2 $\mu\text{mol}\cdot\text{mol}^{-1}$ measured in Wendover, Utah, about 200 km west of Salt Lake City, in 2001 (U.S. National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory, Carbon Cycle Group).

[12] The nighttime buildup of CO₂ was used to derive $\delta^{13}\text{C}_S$ and $\delta^{18}\text{O}_S$ weekly by the Keeling plot intercept method throughout 2002. Representative Keeling plots for three time periods are shown in Figure 2. This figure illustrates a typical trend of greater variation and lower R-squared values in Keeling plots of $\delta^{18}\text{O}$ during the growing season than for $\delta^{13}\text{C}$, as is often observed when CO₂ is influenced by biogenic respiration [Flanagan *et al.*, 1997; Keeling, 1958, 1961]. $\delta^{13}\text{C}_S$ is shown for the one year period in Figure 3 in relation to the isotopic composition of CO₂ produced by potential local sources. Wintertime values were variable, which was partially explained by diurnal changes in CO₂ sources. $\delta^{13}\text{C}_S$ derived from data collected during rush-hour traffic conditions were 1.3‰ more

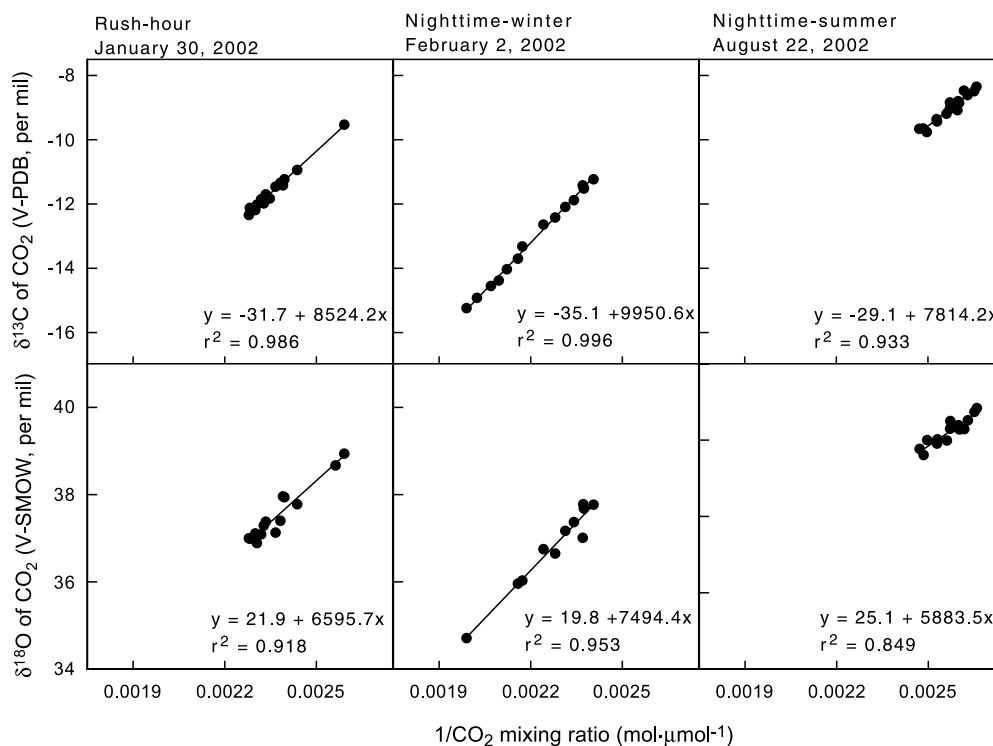


Figure 2. Representative Keeling plots of carbon and oxygen isotope ratio during three discrete sampling periods. The equation shown is derived from geometric mean regression.

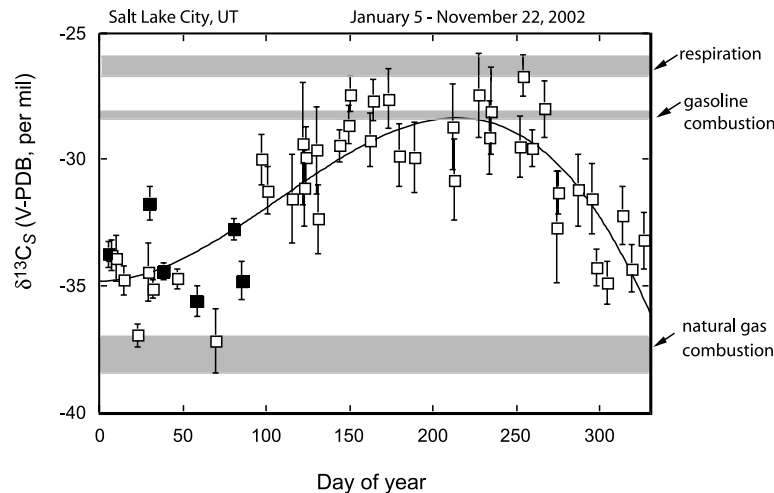


Figure 3. The carbon isotope ratio of the urban CO_2 source ($\delta^{13}\text{C}_S$) as estimated by the Keeling plot method. Open symbols were derived from nighttime data, and closed symbols were derived from rush hour data. Error bars show the standard error of the intercept. The shaded bars show the 95% confidence interval for the carbon isotope ratio of local CO_2 sources. Data for gasoline and natural gas combustion are taken from local measurements by S. Bush *et al.* (unpublished data), and data for ecosystem respiration are taken from Pataki *et al.* [2003]. The solid line is a 3rd order polynomial fit to the data.

enriched (more positive in $\delta^{13}\text{C}$) on average than $\delta^{13}\text{C}_S$ at night ($p = 0.05$, Student's *t*-test). Enriched ^{13}C values during rush hour are expected due to a larger influence of gasoline combustion on the total CO_2 source. Seasonally, $\delta^{13}\text{C}_S$ ranged from -30.0 to -37.2‰ in the winter and -27.4 to -32.4‰ in the spring/summer. A seasonal cycle was apparent, with depleted (more negative) values in the wintertime corresponding to increased combustion of natural gas, and enriched (more positive) values in the spring and summer that may be caused by either gasoline combustion or plant/soil respiration (the two are not distinguishable based on carbon isotopes alone).

[13] The seasonal cycle of $\delta^{18}\text{O}_S$ is shown in Figure 4 in relation to $\delta^{18}\text{O}$ produced by local CO_2 sources. In contrast to $\delta^{13}\text{C}_S$, $\delta^{18}\text{O}_S$ showed little variation in the winter, and highly enriched values in the spring and summer corresponding to the influence of plant and soil respiration. CO_2 released in plant and soil respiration equilibrates with leaf and soil water such that the $\delta^{18}\text{O}$ of respiration is predictable based on the Craig-Gordon model of evaporative enrichment and the equilibrium fractionation factor for exchange of oxygen between CO_2 and H_2O . The calculations of Craig and Gordon [1965] as modified by Flanagan *et al.* [1997] were followed here to model the isotopic composition of leaf and soil respiration. Model inputs were temperature and relative humidity measured at a MesoWest station on the University of Utah campus, a source water $\delta^{18}\text{O}$ value of -15‰ (the isotopic composition of the Salt Lake City municipal water supply and groundwater), and an average water vapor $\delta^{18}\text{O}$ value of -21‰ (data not shown). Because the urban forest in this semiarid region is sustained by irrigation and/or access to groundwater, we neglect the influence of local precipitation in this exercise. These calculations also neglect the influence of evaporative enrichment of soil water, which is dependent on the effective depth of CO_2 - H_2O equilibration. This depth was found to be 5–15 cm by Miller *et al.* [1999] but has seldom

been determined in other studies. We applied the theoretical kinetic fractionation in diffusion of CO_2 of 8.8‰ for plant and soil respiration rather than the value of 7.2‰ reported by Miller *et al.* [1999] in soil because of a similar lack of data for a variety of soils. For leaf water equilibration, we necessarily assumed steady-state conditions at night in the absence of other information such as leaf-level gas exchange data necessary to quantify Péclet and non-steady state effects [Cernusak *et al.*, 2002; Farquhar and Lloyd, 1993].

[14] Despite the number of assumptions required to model $\delta^{18}\text{O}$ of plant and soil respiration, our approach provides the upper and lower bounds on the oxygen isotope ratio of total ecosystem respiration, and has been shown to successfully capture field measurements of $\delta^{18}\text{O}$ of leaf water and ecosystem respiration [Bowling *et al.*, 2003a, 2003b; Flanagan *et al.*, 1997, 1999; J. P. H. Ometto *et al.*, Oxygen isotope ratios of waters and respired CO_2 in Amazonian forest and pasture ecosystems, submitted to *Ecological Applications*, 2003]. Here we apply these calculations toward interpreting $\delta^{18}\text{O}_S$ in Salt Lake City. In January and February of 2002, average nighttime air temperatures in Salt Lake City were -1.8°C . Biogenic respiration at these temperatures is unlikely to constitute a significant portion of urban CO_2 emissions relative to combustion, particularly aboveground. This is supported by the wintertime values for $\delta^{18}\text{O}_S$, which were $21.3 \pm 0.2\text{‰}$ (Figure 4). Interestingly, this value is not equivalent to the theoretical value for the oxygen isotope ratio of combustion, which is equal to $\delta^{18}\text{O}$ of atmospheric O_2 at 23.5‰ [Kroopnick and Craig, 1972]. The observed offset could be due to the influence of wintertime soil respiration or to fractionation of oxygen in combustion, which have not been well investigated.

[15] As a first-order attempt to solve equations (4)–(6), we applied the annual cycle of $\delta^{13}\text{C}_S$ and $\delta^{18}\text{O}_S$ as represented by the polynomial fits in Figures 3 and 4, and

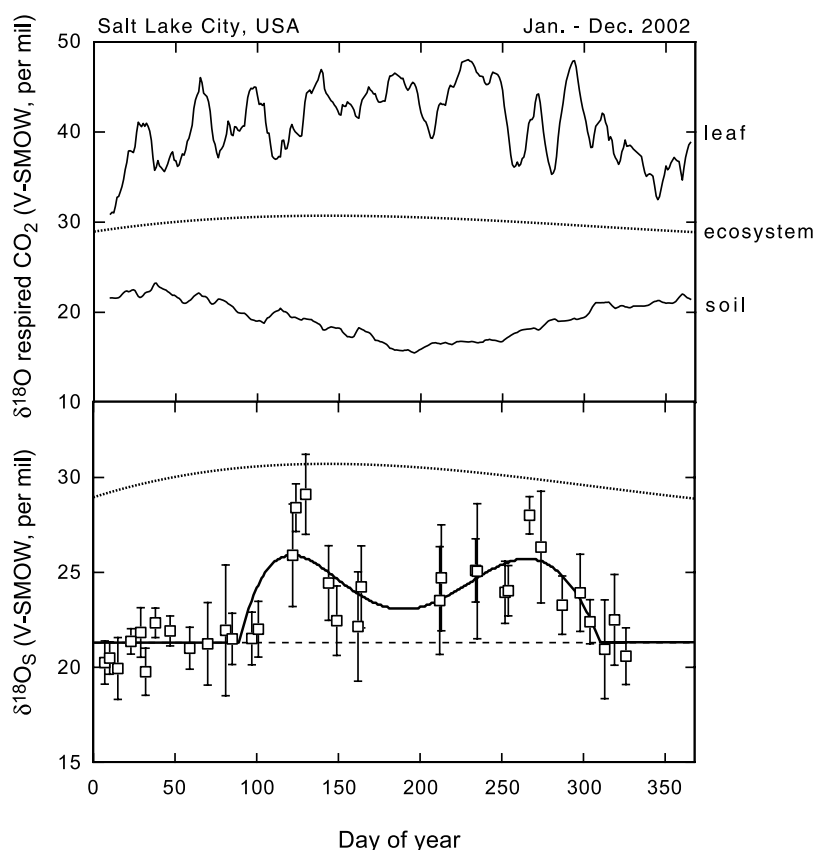


Figure 4. (top) A ten-day running average of the oxygen isotope ratio ($\delta^{18}\text{O}$) of leaf and soil respiration as modeled from local climate data assuming a source water value of -15‰ and a water vapor value of -21‰ . The dotted line shows the annual trend for ecosystem respiration if leaf and soil respiration contribute equally to the total. (bottom) The oxygen isotope ratio of the urban CO_2 source ($\delta^{18}\text{O}_S$) as estimated by the Keeling plot method. Error bars show the standard error of the intercept. The dashed line shows the wintertime average, and the dotted line is the annual trend for ecosystem respiration assuming equal contributions of leaf and soil respiration as shown in the top panel. The solid line is a 5th order polynomial fitted to day of year 90–310.

estimates of the isotopic composition of potential local sources of CO_2 . $\delta^{13}\text{C}_G$ and $\delta^{13}\text{C}_N$ were measured in Salt Lake City and found to be -28.3 ± 0.1 and $-37.7 \pm 0.3\text{‰}$, respectively (S. Bush et al., unpublished data). For simplicity, we assumed that $\delta^{18}\text{O}_G$ and $\delta^{18}\text{O}_N$ were equivalent to the $\delta^{18}\text{O}_S$ wintertime value of 21.3‰ and that wintertime soil respiration was negligible. $\delta^{13}\text{C}_R$ has been determined in a number of natural forests, but never in an urban ecosystem. Therefore we applied the average natural forest value of $-26.2 \pm 0.2\text{‰}$ from Pataki et al. [2003]. For $\delta^{18}\text{O}_R$, we applied an ecosystem respiration value consisting of 50% soil respiration and 50% leaf respiration, which is within the range of estimates from natural forests [e.g., Lavigne et al., 1997].

[16] The results of applying the above end-members to equations (4)–(6) are shown in Figure 5. Calculated values of f_R , f_G , and f_N were multiplied by c_S to evaluate the contributions of each CO_2 source to the total measured mixing ratio, c_T . The annual cycle of c_A was estimated from 2001 data collected by the NOAA CMDL Carbon Cycle Group in Wendover, Utah, 200 km west of Salt Lake City. The general trend of natural gas contributions to the nighttime CO_2 mixing ratio was consistent with the use of natural gas as a primary heating source. Approximately 60%

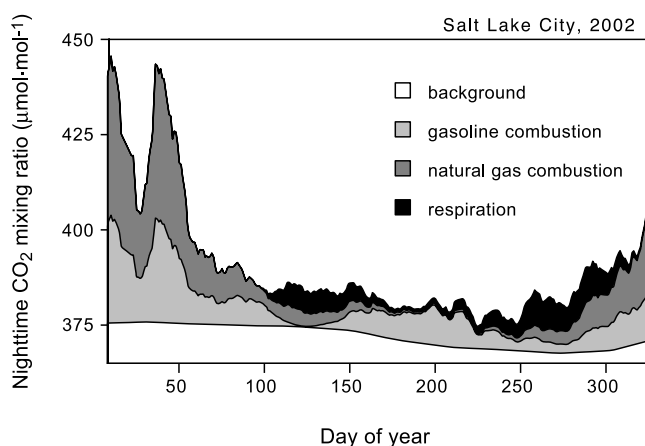


Figure 5. Components of the nighttime CO_2 mixing ratio, smoothed with a 10-day running average. The annual cycle of background CO_2 mixing ratio was estimated from monthly measurements in 2001 by the U.S. NOAA CMDL Carbon Cycle Group at the Wendover, Utah, flask network station. Contributions from gasoline combustion, natural gas combustion, and respiration were calculated from local CO_2 mixing ratio measurements and equations (4)–(6).

Table 1. Sensitivity Analysis of Calculations of the Mean Fractional Contribution of Respiration (f_R), Gasoline Combustion (f_G), and Natural Gas Combustion (f_N) to the Total CO₂ Source During Winter (January 1 to April 15) and the Growing Season (April 16 to November 15)^a

	January 1 to April 15			April 16 to November 15		
	f_R	f_G	f_N	f_R	f_G	f_N
Baseline	0.02	0.42	0.57	0.32	0.43	0.25
i) 1‰ depletion $\delta^{13}C_R$	0.02	0.42	0.56	0.32	0.47	0.21
ii) 1‰ depletion $\delta^{13}C_G$	0.02	0.47	0.52	0.32	0.48	0.19
iii) 1‰ depletion $\delta^{13}C_N$	0.02	0.47	0.51	0.32	0.46	0.22
iv) 30% soil respiration 70% plant respiration	0.01	0.42	0.56	0.26	0.51	0.23
v) 70% soil respiration 30% plant respiration	0.03	0.40	0.57	–	–	–
vi) 7.2‰ kinetic fractionation of soil diffusion	0.02	0.41	0.57	0.34 ^b	0.43 ^b	0.23 ^b
vii) 3‰ enrichment of soil water	0.02	0.42	0.57	0.35 ^b	0.40 ^b	0.25 ^b
viii) No enrichment of leaf water at night	0.00	0.42	0.58	–	–	–

^aCalculations are from equations (4)–(6). Baseline refers to the calculations shown in Figure 5 and described in the text. In analyses *i–iii*, the carbon isotope ratios of ecosystem respiration ($\delta^{13}C_R$), gasoline combustion ($\delta^{13}C_G$), or natural gas combustion ($\delta^{13}C_N$) were decreased by 1‰ from the baseline simulation. The remaining analyses are changes to the assumptions in the model of the oxygen isotope ratio of ecosystem respiration ($\delta^{18}O_R$). A dash indicates that a solution was less than 0 for much of the season; i.e., the solution was invalid.

^bValues of f_G were negative in April.

of c_S originated from natural gas combustion in the winter at this location, with the contribution becoming negligible in mid-summer. Gasoline combustion remained a large CO₂ source for much of the year. Biogenic plant and soil respiration had the largest effect in spring and late summer/fall, when respiration accounted for up to 60% of c_S . This result was driven by the pattern of $\delta^{18}O_S$ shown in Figure 4, which had a bimodal distribution. Although there was some scatter around this relationship and the polynomial fit shown approximates only the major features of the seasonal pattern, there may be a functional basis for a depression in biogenic respiration rates in mid-summer. This was an extremely hot and dry period when daytime vapor pressure deficits periodically exceeded 5 kPa and precipitation was negligible. The influence of high vapor pressure deficit on stomatal closure and soil evaporation in semiarid, yet irrigated, urban environments has not been well investigated. If the peaks in $\delta^{18}O_S$ values shown in Figure 4 are robust, this may indicate that the early and late growing season are the optimal periods for photosynthetic activity and soil decomposition in the Salt Lake City urban ecosystem, a hypothesis that can be tested with physiological and soil measurements.

[17] The results in Figure 5 are not intended to be a strict assessment of the contributions of combustion and respiration to the urban CO₂ mixing ratio in 2002. Rather, we used this exercise as a means to examine a potentially powerful tool for assessing the isotopic composition of urban CO₂ emissions and the contribution of biogenic processes to the urban carbon cycle. To assess the sensitivity of this technique to errors in the estimates of the isotopic composition of the CO₂ sources, we conducted a series of sensitivity analyses. For each analysis, values of f_R , f_G , and f_N were re-calculated and averaged for two time periods: January 1–April 15 when biological activity was low, and the growing season of April 16–November 15. In the first three analyses, $\delta^{13}C_R$, $\delta^{13}C_G$, or $\delta^{13}C_N$ were decreased by 1‰ - a relatively large change in the case of $\delta^{13}C_G$ and $\delta^{13}C_N$, which had small standard errors of 0.1 and 0.3, respectively, in local exhaust measurements (S. Bush et al., unpublished data). Shown in Table 1 are the results of these analyses

(numbered *i–iii*), in which the 1‰ depletion generally caused changes in f_R , f_G , and f_N of less than 15%, with the exception of the 1‰ change in $\delta^{13}C_G$ during the growing season. In this case, f_N decreased by 24%. This indicates that local measurements of $\delta^{13}C_G$ are an important component of this method, as the isotopic composition of petroleum shows significant geographical variation [Andres et al., 2000; Tans, 1981] and may not be captured adequately from mean literature values, leading to errors in the estimates of CO₂ source contributions.

[18] Sensitivity analyses were also conducted on several assumptions in the estimation of $\delta^{18}O_R$. A large uncertainty in this method is in the proportions of above- and below-ground respiration, which have varying isotopic compositions due to the influence of evaporative enrichment of leaf water on aboveground respiration. The contribution of each component to total $\delta^{18}O_R$ was varied from equal contributions in the initial calculations to 30% soil respiration and 70% aboveground plant respiration, and vice-versa. These results are shown in Table 1 as analyses *vi–v*. In the first case, applying an assumption of 30% soil respiration caused a 19% reduction in the contribution of f_R during the growing season. However, such small proportions of soil respiration to total ecosystem respiration are not typical in natural ecosystems [Goulden et al., 1996; Lavigne et al., 1997; Law et al., 1999, 2001; Xu et al., 2001], although we cannot exclude this possibility in an urban ecosystem. Contributions of soil respiration of up to 70% and greater have been reported in the literature [Goulden et al., 1996; Law et al., 1999, 2001; Xu et al., 2001]; however, applying 70% soil respiration to our calculations violated mass balance during growing season; that is, $\delta^{18}O_S$ was more enriched than the most enriched possible source of CO₂ for much of this period. This occurred because soil respiration is much less enriched in ¹⁸O than leaf respiration, and the measurements of $\delta^{18}O_S$ indicate that an enriched source must be present in this ecosystem.

[19] We also altered the value of kinetic fractionation of soil CO₂ from the theoretical value of 8.8‰ to 7.2‰ as reported by Miller et al. [1999] in analysis *vi* and applied an assumption of 3‰ evaporation enrichment of shallow soil

moisture in analysis *vii*. Neither of these changes had large effects on the results, although both violated mass balance early in the growing season (Table 1). Finally, because the extent of steady-state evaporative enrichment of leaf water at night is not well known, we examined the end-member case of no evaporative enrichment in analysis *viii*. This assumption caused $\delta^{18}\text{O}_R$ to be less enriched than $\delta^{18}\text{O}_S$, violating the mass balance for much of the growing season (Table 1). Therefore, an analysis of the valid solutions to this mass balance approach can provide some constraints on the acceptable range of values for unknowns with a high degree of error.

[20] A number of the uncertainties in utilizing $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ to partition urban CO_2 sources can be further overcome with additional research. Measurements of the carbon isotope ratio of urban plant/soil respiration and the oxygen isotope ratio of leaf, stem, and soil water may be used to validate the assumptions and modeling of $\delta^{13}\text{C}_R$ and $\delta^{18}\text{O}_R$. Measurements of the absolute rates of above- and below-ground respiration coupled with bottom-up estimates of natural gas and gasoline combustion from fuel use statistics and traffic data can be used to validate the results of the mass balance calculation. Such a comparison may also help determine whether current approaches for estimating the isotopic composition of regional and global fossil fuel emissions sufficiently capture temporal and spatial variability at the scales necessary for carbon cycle modeling. Previous studies have found mismatches between local bottom-up inventories and atmospheric integration of fuel combustion [Kuc and Zimnoch, 1998] that illustrate the need for further comparisons in a number of different regions, and for different locations within the same region. Given the heterogeneous nature of land cover in urban areas, evaluating the spatial heterogeneity in these results is a necessary next step.

4. Conclusions

[21] In this study, the seasonal cycle of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 emissions were characterized weekly for a one-year period at the University of Utah campus in Salt Lake City. Both isotopes showed depletion in the winter and enrichment in the summer due to changes in the proportions of natural gas combustion, gasoline combustion, and biogenic respiration at different times of the year. These effects were quantified with a mass balance calculation that solved for the proportional contribution of each component to the total CO_2 source. The results conformed well to expected trends of greater natural gas combustion in the winter and biogenic respiration in the spring and summer.

[22] The strengths of utilizing the Keeling plot method for partitioning urban CO_2 emissions are the potential to evaluate the integrated effect of these emissions on the atmosphere without the need to determine the isotopic composition of background air. As has been noted in the original application of the Keeling plot method, this approach works well with $\delta^{13}\text{C}$ but cannot always be applied to $\delta^{18}\text{O}$ [Keeling, 1958, 1961]. Varying proportions of CO_2 sources containing distinct isotope ratios violate the assumptions of the 2-ended mixing model and are more common with oxygen than carbon isotopes, causing poor relationships between $\delta^{18}\text{O}_T$ and $1/c_T$. In this study, several

Keeling plots were excluded from the analysis when $P > 0.01$, reducing the sample size available for evaluating the seasonal cycle of $\delta^{18}\text{O}_S$. However, the alternative to the Keeling plot method is to specify $\delta^{18}\text{O}_A$ from remote, non-urban measurements, which may be problematic due to its spatial and temporal variability [Zondervan and Meijer, 1996]. Where Keeling plot sampling can be limited to short periods under steady-state conditions in the proportion of CO_2 sources, determination of $\delta^{18}\text{O}_S$ provides a viable alternative.

[23] Different forms of the mass balance model are plausible and should be evaluated for their utility in using the atmosphere as an integrator of urban processes. As interest in the global carbon cycle and also regional and local processes in urban and urbanizing regions further develops, atmospheric isotope data will provide critical information, particularly when combined with terrestrial measurements. The methods described here are a potential starting point for the application of long-term atmospheric monitoring in urban areas.

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