

High resolution atmospheric monitoring of urban carbon dioxide sources

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[1] Estimates of fossil fuel emissions on local to regional spatial scales and hourly to weekly temporal scales are increasingly useful in studies of the carbon cycle and mass and energy flow in cities. We used a tunable diode laser absorption spectrometer (TDL) to measure CO₂ mixing ratios and carbon isotope composition of CO₂ in order to estimate the contribution of gasoline versus natural gas combustion to atmospheric CO₂ in Salt Lake City. The results showed a pronounced diurnal pattern: the proportional contribution of natural gas combustion varied from 30–40% of total anthropogenic CO₂ during evening rush hour to 60–70% at pre-dawn. In addition, over a warming period of several days, the proportional contribution of natural gas combustion decreased with air temperature, likely related to decreased residential heating. These results show for the first time that atmospheric measurements may be used to infer patterns of energy and fuel usage on hourly to daily time scales. **Citation:** Pataki, D. E., D. R. Bowling, J. R. Ehleringer, and J. M. Zobitz (2006), High resolution atmospheric monitoring of urban carbon dioxide sources, *Geophys. Res. Lett.*, *33*, L03813, doi:10.1029/2005GL024822.

1. Introduction

[2] The future magnitude of CO₂ emissions from human activities such as fossil fuel burning is one of the largest uncertainties in projections of atmospheric CO₂ concentrations. While there has been a great deal of emphasis in carbon cycle science on natural sources and sinks of carbon, the fossil fuel component of the carbon budget is also uncertain, particularly at increasingly smaller spatial and temporal scales [Wofsy and Harris, 2002; Blasing et al., 2005]. Atmospheric budget approaches that utilize CO₂ mixing ratios and the isotopic composition of CO₂ to infer carbon sources and sinks rely on robust estimates of the magnitude and isotopic composition of anthropogenic emissions. As these approaches are applied on local to regional scales with increasing temporal resolution, fossil fuel emissions estimates must be refined to address geographic variability as well as high frequency, diurnal scale variations. At finer spatial and temporal scales, studies of fossil fuel emissions may be used to understand underlying

patterns and drivers of energy and fuel use that will impact the future trajectory of atmospheric CO₂.

[3] We have previously shown a large seasonal cycle in the isotopic composition of CO₂ emissions in the Salt Lake Valley, Utah, as well as in the contributions of CO₂ sources derived from gasoline combustion, natural gas combustion, and biological respiration as estimated from atmospheric measurements [Pataki et al., 2003, 2005b]. In addition, isotopes of organic matter in urban areas have been used to assess time-integrated fossil fuel-derived CO₂ in the atmosphere [Lichtfouse et al., 2003]. Repeated in varying geographic regions, isotopic measurements can provide information about magnitudes and sources of fossil fuel emissions in urban areas, and can quantify temporal variability on time scales of days to weeks and years. However, while other pollutant tracers have been measured at high temporal frequency [e.g., Hurst et al., 1997; Fraser et al., 1999] there is a limit to the temporal variability in isotopes of CO₂ that can be resolved with both conventional flask sampling and emissions inventory approaches. While diurnal patterns in energy and gasoline use by urban residents are likely, they have not previously been studied from atmospherically-based measurements.

[4] In this study we measured CO₂ mixing ratios and the stable carbon isotope composition ($\delta^{13}\text{C}$) of CO₂ in Salt Lake City, Utah with tunable diode laser absorption spectrometry (TDL) as well as conventional Isotope Ratio Mass Spectrometry (IRMS) and infrared gas analysis. TDL instruments offer a means of monitoring the isotopic composition (C and O) of atmospheric CO₂ at higher temporal resolution than has been practical with IRMS [Bowling et al., 2003; Griffis et al., 2004; Bowling et al., 2005; Griffis et al., 2006]. We used these measurements to detect high frequency variations in the isotopic composition of atmospheric CO₂ in Salt Lake City, and quantify the contribution of gasoline versus natural gas fossil fuel sources to atmospheric CO₂ on an hourly time-scale. The goal was to evaluate diurnal patterns in the contribution of gasoline and natural gas combustion to CO₂ in a region of large anthropogenic emissions. Applying atmospheric methods to determine CO₂ sources at high temporal resolution can contribute to our understanding of the dynamics of energy and fuel use in order to improve emissions inventories and future projections of the trajectory of CO₂ emissions.

2. Methods

[5] The study was conducted in the winter beginning on Dec. 15 2004 and ending on Jan. 20 2005. This period was chosen to span a long enough period to capture a variety of meteorological conditions including persistent atmospheric

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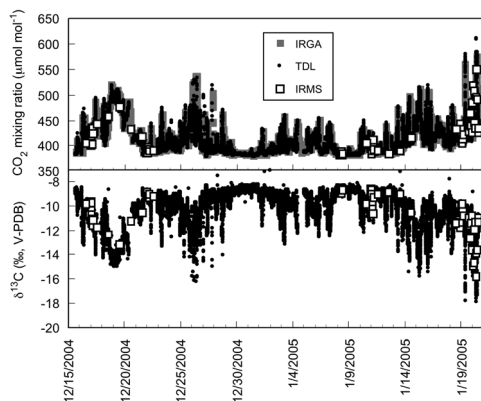


Figure 1. CO₂ mixing ratio and carbon isotope ratio ($\delta^{13}\text{C}$) during a month long period in Salt Lake City as measured with a Tunable Diode Laser (TDL), an Isotope Ratio Mass Spectrometer (IRMS) and an Infrared Gas Analyzer (IRGA).

temperature inversions, and because biological activity in the Salt Lake Valley in the winter is negligible such that the primary local influence on atmospheric $\delta^{13}\text{C}$ of CO₂ is derived from combustion [Pataki *et al.*, 2003].

[6] During this period air was sampled from an inlet on the roof of a four story building, approximately 18 m from the ground, on the campus of the University of Utah. The location of this site is shown as the “Eastern Foothills” site by Pataki *et al.* [2005b]. Sampled air flowed through polyethylene tubing (type 1300 Synflex, Saint-Gobain Performance Plastics, Mantua OH) to a TDL, an infrared gas analyzer, and a flask array as described below.

[7] The TDL used in this study was the TGA100 trace gas analyzer (Campbell Scientific, Logan, UT, USA); full details of this instrument are described in detail elsewhere [Bowling *et al.*, 2003, 2005]. The TDL was operated as described by Bowling *et al.* [2005] with the following two exceptions: first, a cycle of measurements involving four WMO-traceable (for CO₂) and VPDB-traceable (for $\delta^{13}\text{C}$) calibration gases and the unknown gas measurement was completed every 3 minutes rather than 6 minutes and second, calibrations were performed using a second-order rather than a linear polynomial (see Bowling *et al.* [2005] for details). Precision for CO₂ and $\delta^{13}\text{C}$ measurements during this period were $0.15 \mu\text{mol mol}^{-1}$ and 0.20% , respectively. Water vapor was removed using a Nafion counterflow assembly.

[8] CO₂ mixing ratios were also measured with an infrared gas analyzer (LI-7000, LI-COR, Inc., Lincoln, NE, USA). Air was passed through a cold trap to condense out water vapor and was introduced into the analyzer every 5 minutes. In addition, dry, CO₂-free air and WMO traceable calibration gas containing a known CO₂ mixing ratio were introduced into the analyzer hourly to correct mixing ratios with recorded zero and span values. Two-minute running averages of measured CO₂ mixing ratio were recorded every 5 minutes on a data logger (CR23x, Campbell Scientific Inc., Logan, UT, USA).

[9] Air was also sampled periodically in 15 mL glass flasks preceded by a magnesium perchlorate (Mg(ClO₄)₂)

desiccating trap. $\delta^{13}\text{C}$ and mixing ratios of CO₂ in these samples were measured by continuous flow IRMS (Delta Plus, Finnigan MAT, San Jose, CA, USA) according to Schauer *et al.* [2005]. The precision of these measurements was 0.03% for $\delta^{13}\text{C}$ of CO₂ and $0.5 \mu\text{mol mol}^{-1}$ for mixing ratio.

[10] All mixing ratios and isotope ratios in this paper are expressed relative to the WMO CO₂ and V-PDB isotope ratio scales.

3. Results and Discussion

[11] CO₂ mixing ratios and $\delta^{13}\text{C}$ of CO₂ measured with the TDL, IRMS, and infrared gas analysis (mixing ratio only) agreed well (Figure 1). The 37-day data set showed short-term, diurnal-scale patterns as well as buildup of CO₂ over several day periods associated with persistent temperature inversions (Figure 1). Toward the end of the January measurement period, mixing ratios as high as $600 \mu\text{mol mol}^{-1}$ were recorded, which coincided with a large inversion event; air aloft at 350 m above the surface was 10°C warmer than air at the ground according to U. S. National Weather Service soundings taken at Salt Lake International Airport (data not shown).

[12] To utilize the distinct carbon isotope ratio of gasoline versus natural gas combustion to quantify the contribution of each fossil fuel source to atmospheric CO₂, we used the mass balance equations:

$$C_T = C_B + C_N + C_G \quad (1)$$

$$\delta_T C_T = \delta_B C_B + \delta_N C_N + \delta_G C_G \quad (2)$$

where C is mixing ratio, δ is isotope ratio expressed in conventional notation relative to the V-PDB standard, and the subscripts T , B , N , and G refer to the total CO₂ mixing ratio, and CO₂ from the background atmosphere, natural gas combustion, and gasoline combustion, respectively. δ_T and C_T were directly measured and are shown in Figure 1. δ_N and δ_G have been measured previously in the Salt Lake Valley by direct sampling and IRMS measurement of combustion exhaust from 8 residential furnaces and 80 idling, gasoline-powered vehicles. These measurements resulted in estimates of δ_N and δ_G of -37.1 ± 0.2 and $-27.9 \pm 0.1\%$, respectively [Pataki *et al.*, 2005a]. To derive C_N and C_G , δ_B and C_B of the background atmosphere must be specified.

[13] As a means of determining δ_B and C_B , we evaluated IRMS-based mixing ratios and $\delta^{13}\text{C}$ of CO₂ in air samples collected at midday on a daily basis over a two year period (Figure 2). This time of day was chosen to capture the period of maximum daytime convection and convective boundary layer height in order to minimize local effects. The results showed that in the winter in particular, local effects were often still considerable during inversion periods. However, if monthly minimum CO₂ mixing ratio and maximum $\delta^{13}\text{C}$ were plotted, a seasonal cycle was apparent (Figure 2) that closely resembled the smoothed seasonal cycle of C_B interpolated from measurements at a NOAA CMDL monitoring station in Wendover, Utah, about

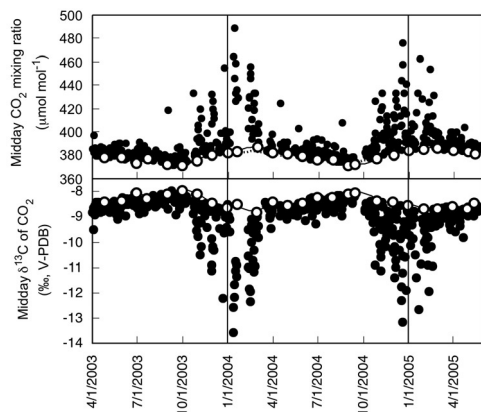


Figure 2. Closed symbols: CO₂ mixing ratio and carbon isotope ratio ($\delta^{13}\text{C}$) measured via IRMS from midday flask samples collected half-way between solar noon and sunset on a daily basis over a two year period. Open symbols: The monthly minimum CO₂ mixing ratio and maximum isotope ratio. Solid lines: A smoothed, annual harmonic function and second-order polynomial [Thoning *et al.*, 1989] fitted to the monthly minimum CO₂ mixing ratio and maximum isotope ratio. (top) Dashed line: Smoothed data from the NOAA CMDL flask monitoring station in Wendover, Utah [CMDL, 2005]. Vertical lines: Calendar years.

200 km to the west [Climate Monitoring and Diagnostics Laboratory, 2005].

[14] We chose a period in which C_T was consistently greater than C_B by at least $20 \mu\text{mol mol}^{-1}$ (January 14–20, 2005) to analyze the relative contribution of different CO₂ combustion sources. C_B and δ_B were derived from data in Figure 2 with a 2nd order polynomial and annual harmonic smoothing function [Thoning *et al.*, 1989], and were used to directly solve equations 1 and 2. A large diurnal cycle in the proportion of non-background CO₂ derived from gasoline combustion ($C_G/[C_T - C_B]$) was observed (Figure 3). However, sensitivity analyses indicated that the mass balance calculation was highly sensitive to the choice of δ_B : varying δ_B by only 0.1‰ resulted in a 20% change in the estimate of C_G . Given that the precision of the TDL measurements during the study period was 0.2‰, additional constraints were required to have confidence in our results.

[15] We attempted to compensate for random measurement error by averaging 3-minute TDL measurements over hourly periods. We also used a Bayesian inversion method to estimate the unknown quantities, C_G , C_N , C_B , and δ_B by assuming the parameters and measured data are random variables [Gubbins, 2004; Raupach *et al.*, 2005; Tarantola, 2005]. To briefly describe the method, in addition to equations (1) and (2) and analytical uncertainties in the measured data C_T and δ_T , we also prescribed prior values and uncertainties on the parameters C_B , C_N , C_G , and δ_B based upon previous studies (see above discussion). A solution was obtained by minimizing a quadratic cost function. The quadratic cost function included the model-data residual (left hand side minus the right hand side of equations (1) and (2)) and the differences between param-

eters and their prior values. This cost function was scaled by the analytical uncertainties in the measured data and the prior parameter uncertainties respectively. For the optimization, we selected fixed-in-time prior values and errors for all parameters and fixed-in-time errors on all measurements. Prior values for δ_B , C_B , $\%C_N$, and $\%C_G$ were specified as -8.4‰ , $380 \mu\text{mol mol}^{-1}$, 0.5, and 0.5, respectively. We allowed a 1‰ error in δ_B , a $10 \mu\text{mol mol}^{-1}$ error in C_B , and an error in C_G and C_N of $(C_T - C_B)$. C_T and δ_T were allowed a $0.25 \mu\text{mol mol}^{-1}$ and 0.25‰ error to account for TDL measurement error.

[16] The optimization resulted in slightly higher estimates for the contribution of natural gas to fossil fuel-derived CO₂ than specifying background δ_B and C_B with midday measurements, but overall the two approaches yielded similar results (Figure 3). The posterior reduction in error on the optimized parameters led to approximately a 25% reduction in uncertainty estimates (Table 1). For both calculations, there was a diurnal pattern of relatively larger contributions of natural gas combustion in early morning, pre-dawn hours representing about 60–70% of total fossil fuel-derived CO₂, and smaller contributions of about 30–40% during late afternoon and evening rush hour. This is consistent with greater natural gas use during cold nighttime hours and increased gasoline combustion during evening rush hour. There was also a pattern of decreasing relative contributions of natural gas combustion over the week-long measurement period that corresponded to increasing ambient air temperature. This likely corresponded to reduced natural gas usage for residential heating during a warming period. In general, the results agree with monthly CO₂ emissions calculated for Salt Lake County from state inventory data [U.S. DOE EIA, <http://www.eia.doe.gov>] and scaled to the county with demographic data [U.S. Environmental Protection Agency, 1998]: in January 2005,

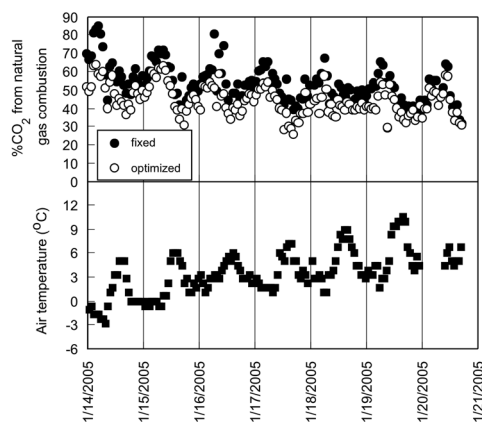


Figure 3. (top) The percent of CO₂ above background mixing ratios derived from natural gas combustion (versus gasoline combustion), calculated using equations (1) and (2) in the text. “Fixed” values refer to the analytical solution of the mass balance obtained by specifying all values except C_N and C_G . “Optimized” values refer to the parameters obtained via Bayesian inversion. (bottom) Mean hourly air temperature for the same period. Vertical lines mark midnight on each measurement day.

Table 1. Comparison of the Reduction in Error for Optimized Parameters Obtained Via Bayesian Inversion^a

Parameter	Prior Error	Posterior Error
C _G	C _T - C _B μmol mol ⁻¹	(0.66 ± 0.15) · (C _T - C _B) μmol mol ⁻¹
C _N	C _T - C _B μmol mol ⁻¹	(0.71 ± 0.14) · (C _T - C _B) μmol mol ⁻¹
C _B	10 μmol mol ⁻¹	7.9 ± 1.6 μmol mol ⁻¹
δ _B	1‰	0.6 ± 0.2‰

^aThe second column is the fixed-in-time prior errors on the parameters and the third column is the mean and standard deviation of the posterior error over the sampling period in Figure 3. Abbreviations are as denoted in the text.

gasoline combustion released an estimated 85 kT C while natural combustion released 115 kT C. During deep, persistent inversions such as the Jan. 14–20 period, the measurement footprint and the spatial extent of the Salt Lake Valley mountain basin are approximately equivalent [Pataki *et al.*, 2005b].

4. Conclusions

[17] Monitoring fossil fuel emissions near large anthropogenic CO₂ sources such as cities is a very useful application of atmospheric measurements, as estimates of fossil fuel combustion are most commonly available on a fairly coarse temporal and spatial scale from energy and fuel use statistics. For the first time, we have detected the diurnal pattern of fossil fuel combustion from natural gas versus gasoline sources from the atmosphere. This pattern reflects diurnal changes in the proportion of residential energy use and traffic-based emissions of CO₂. Increasingly, energy use and fossil fuel emissions data at this temporal scale can be applied to atmospheric mass balance studies as well as urban ecosystem studies that utilize local to regional scale footprints in order to gain a mechanistic understanding of patterns and processes in the carbon cycle. Partitioning fossil fuel emissions into gasoline and natural gas components can provide a means of validating fossil fuel emissions inventories, as well as a mechanistic understanding of the drivers and dynamics of fuel usage in regions of large fossil fuel emissions.

[18] As atmospheric and urban carbon cycle measurement techniques are refined, high resolution monitoring of CO₂ sources can provide additional levels of detail. For example, optical instruments that measure both δ¹³C and δ¹⁸O of CO₂ can be used to resolve the contribution of biological sources of CO₂ during the growing season, as well as partitioning anthropogenic fossil fuel sources. While the current analysis was restricted to a strong inversion when the measurement footprint was very large, analyses during other periods of more localized atmospheric influence may provide information on a neighborhood-type scale. Combined with traffic and household energy use survey data, these analyses can provide insight into urban energy use patterns and drivers. Atmospheric measurements can contribute to carbon cycle and energy use studies by providing a useful tool for monitoring both short- and long-term trends in human activities and their impacts on the physical environment.

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