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# Diurnal and Seasonal Attribution of Anthropogenic $CO_2$ Emissions Over Two Years in the Los Angeles Megacity

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## I. Introduction

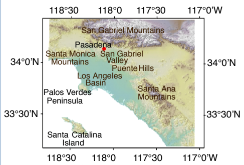


Figure 1. Map showing the location of the Pasadena site in the Los Angeles basin

In order to understand the role of anthropogenic greenhouse gases (GHGs), of which $CO_2$ is the most abundant, in climate change we must understand their sources. Since cities produce >70% of the anthropogenic GHGs, large signals there can be used to study the details of emission patterns. Treaties are being signed to regulate emissions, and there must be verification of compliance. The easiest way to get a broad picture of the distribution of $CO_2$ and its changes through time is to collect measurements of total column concentrations from space. Satellite-borne instruments measure during midday, but is the distribution of emissions among the sources the same at all times of day for all times of year? Understanding the diurnal variation of the sources is important for comparison with bottom-up inventories, modeling, and results from new instruments such as OCO-3 (Eldering et al., 2012, 2013) and the Geostationary Carbon Process Investigation (Xi et al., 2014) which will see more of a diurnal cycle. We have shown that $CO_2$, $\delta^{13}C$, and $\Delta^{14}C$ can be used to distinguish among gasoline combustion, natural gas combustion, and biosphere contributions to $CO_2$ in the atmosphere (Newman et al., 2015) in a top-down approach. Here we present in situ data for different times of day from the megacity of Los Angeles, CA, specifically from the Caltech campus in Pasadena (Figure 1), in order to understand this diurnal variation using this method with CO as a proxy for $\Delta^{14}C$, for morning, midday, and evening for June 2013 through May 2015.

## II. Data and Methods

- The data sets involved in this study include continuous measurements of $CO_2$ and $\delta^{13}C$ (Picarro Isotopic $CO_2$ Analyzer) and CO (LGR $N_2O$/CO EP Monitor) in Pasadena and background measurements on Mt. Wilson (CO, $CO_2$; flasks). $\Delta^{14}C$ compositions are determined for flask samples collected on alternate afternoons at 14:00 PST in Pasadena.
- We use multiple mass balance calculations on monthly averages to distinguish among the sources: fossil fuel combustion ($CO_2$ff), including gasoline ($CO_2$pet) and natural gas ($CO_2$ng), and the biosphere ($CO_2$bio).
- The $\Delta^{14}C$ values of the flask samples give the fraction of $CO_2$ff vs $CO_2$bio in the total local enhancement over background ($CO_2$xs) (Levin et al., 2003).
- We use the $CO_2$ff/$CO_2$xs from the flask $\Delta^{14}C$ measurements and COxs/$CO_2$xs from the continuous measurements for 13:00-15:00 to determine the emission ratio, RCO/$CO_2$ff, values for each month (Figure 4; e.g., Turnbull et al., 2006, 2011; Vogel et al., 2010; Miller et al., 2012). This assumes that RCOxs/$CO_2$ff does not vary diurnally, but only seasonally.
- The y-intercept of correlations between $\delta^{13}C$ and 1000/$CO_2$ (Figure 2; Keeling plots; Keeling, 1958, 1961) provide the composition of the high-$CO_2$, local enhancement of the $CO_2$. The summary of the daily morning, midday, and evening intercepts are shown in Figure 3. Since these can be quite scattered we filter the data by rejecting intercepts from correlations with $R^2$ < 0.90. Monthly averages of the retained intercepts are shown in Figure 5.
- The stable isotopic composition of the carbon in the $CO_2$ ($\delta^{13}C$, ‰ relative to the standard VPDB) is then used to distinguish between gasoline and natural gas combustion within $CO_2$ff.

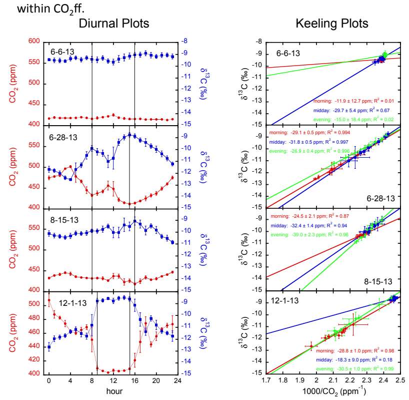


Figure 2. Examples of diurnal patterns (left column) and Keeling plots for morning, midday, and evening on individual days (right column). Keeling plot intercepts and correlation coefficients are shown for each correlation line. Vertical lines on the diurnal plots indicate the times chosen between morning and midday and evening.

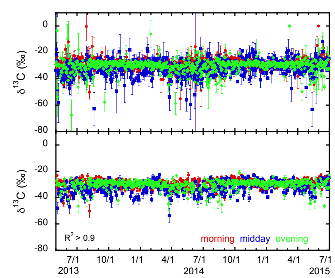


Figure 3. Top: all of the Keeling plot intercepts determined for Pasadena; morning values for correlations for hourly averages during 0:00-8:00, midday for 9:00-16:00, and evening for 17:00-23:00. Bottom: Keeling plot intercepts from the top panel that have been filtered by removing all results from correlations with $R^2$ < 0.9.

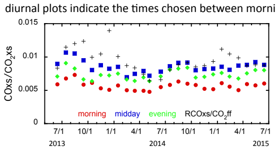


Figure 4. Monthly averages of COxs/$CO_2$xs for morning, midday, and evening on individual days (colored dots) and of emission ratios (RCO/$CO_2$ff; +) from $\Delta^{14}C$ data from midday flasks.

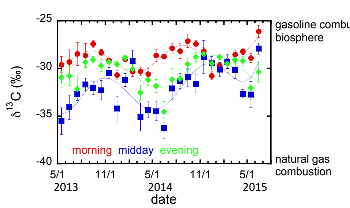


Figure 5. Monthly averages of the Keeling plot intercepts for morning, midday, and evening on individual days. The isotopic signatures of natural gas and petroleum/ biosphere are labeled to the right of the plot.

## III. Results

- The monthly averages of the Keeling plot intercepts (Figure 5) show significantly different patterns at different times of day, especially between early mornings and later. The lowest values of $\delta^{13}C$ are centered on warmer months during midday and evening, whereas they are centered in the fall in the morning. This suggests that gasoline combustion or the biosphere dominate the signal at different times of day.
- When these $\delta^{13}C$ values are combined with values of the fraction of $CO_2$ from fossil fuels in $CO_2$xs, this dichotomy propagates through to different patterns for the proportions of natural gas and gasoline combustion of total $CO_2$xs at different times of day (Figure 6 left). Although natural gas is the dominant source of local $CO_2$ emissions during the summer middays, when the satellite-borne instruments observe, gasoline combustion is the dominant source during summer mornings and evenings. Winter early morning emissions are mostly from the biosphere, very different from midday, when the biosphere contributes at most ~20%. As expected, the biosphere is a sink for $CO_2$ during the spring and summer, although this sink is much less intense than elsewhere.
- The absolute contributions in $CO_2$ ppm (Figure 6 right) are very similar to the patterns for the fractions for the morning period, but are higher for mornings and evenings than for middays, when the atmosphere is most well-mixed and therefore mixing ratios are closest to the background values, resulting in lower $CO_2$xs. The seasonal pattern for the evening absolute contributions is similar for all three sources.
- We have shown that the pattern of higher fossil fuel emissions observed in Pasadena during summer is due to the annual wind direction pattern (Newman et al., 2015). However, the different patterns for different times of day during the summer cannot be due to the winds, since the wind directions are the same at all time of day.

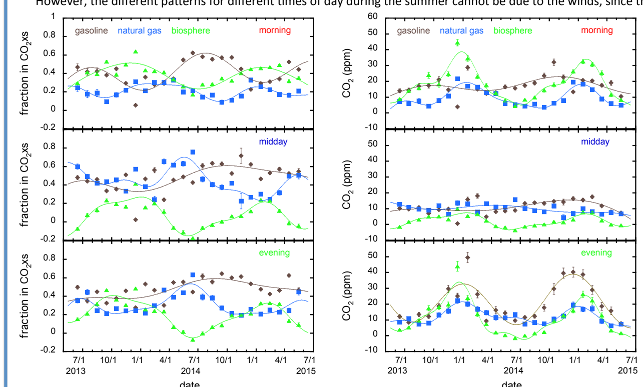


Figure 6. Source allocation as fraction of $CO_2$pet, $CO_2$ng, and $CO_2$bio in $CO_2$xs (left column) and as $CO_2$ (ppm; right column) contributed to the local atmosphere.

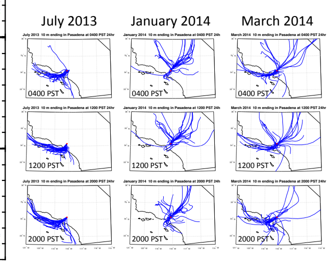


Figure 7. Wind back trajectories calculated using HYSPLIT (Draxler and Rolph, 2015) at different times of day showing seasonal, but not significant diurnal, variations in the source regions. The red dots indicate the location of Pasadena.

## IV. Conclusions

- The relative proportions of the different emission sources for $CO_2$ may not be the same at different times of day. At least during the summer, this is not obviously due to diurnal changes in wind direction bringing emissions from different regions.
- In the megacity of Los Angeles, the relative contribution from natural gas combustion is higher during the summers and lower during the winter at midday and during the evenings, when orbiting satellites take measurements, but is higher in winter-spring than in summer during mornings. This is probably because of shifting wind directions seasonally.
- The biosphere's contribution is higher during the cooler months than during the warmer months for all times of day, as expected for this low mid-latitude semi-arid region. However, the early mornings always have the highest biospheric contributions of the day.
- Emissions from gasoline combustion do not have a clear seasonal cycle for these two years, during midday and evening.
- To improve this analysis, we must determine the emission ratio (RCO/$CO_2$ff) for different times of day. We must also improve modeling at times other than mid-day, in order to quantitatively account for transport of emissions.

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