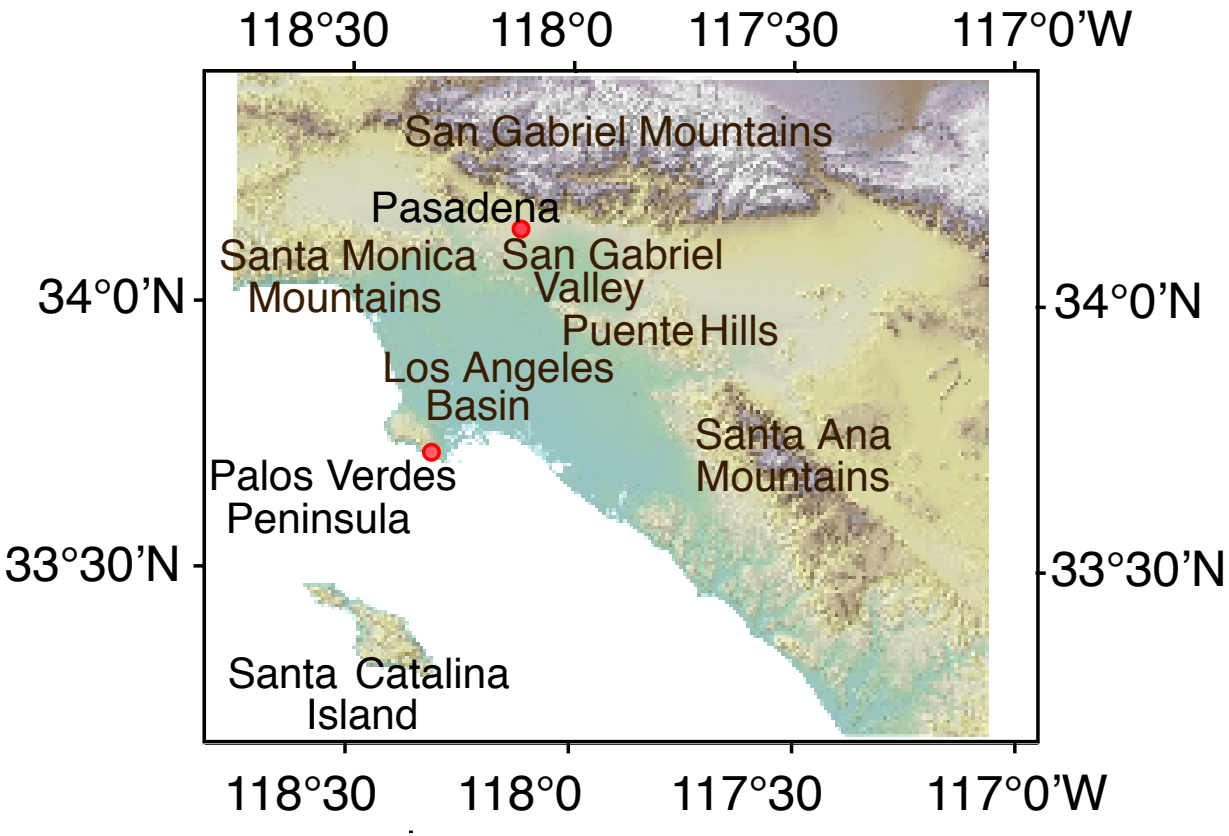
Trends in Atmospheric CO_2 in the Los Angeles Basin: Evidence of Anthropogenic Sources

Sally Newman, Caltech

Collaborators: Sam Epstein[1], Ed Stolper[1], Xiaomei Xu[2], Hagit Affek[3], Charles Miller[4], Yuk Yung[1], Sergio Alvarez[5], Bernhard Rappenglueck[5], Christine Haman[5], Barry Lefer[5]

[1]Caltech
[2]UC Irvine
[3]Yale
[4]JPL
[5]University of Houston


118°30
118°0
117°30
117°0'W
San Gabriel Mountains
Pasadena
Santa Monica Mountains
San Gabriel Valley
Puente Hills
Los Angeles Basin
Santa Ana Mountains
Palos Verdes Peninsula
Santa Catalina Island
34°0'N
33°30'N

8 January, 2009, 14:17
501 ppm CO_2
0.009 ppm O_3
1.1 ppm CO
0.035 ppm NO
0.049 ppm NO_2

16 January, 2009, 14:35
403 ppm CO_2
0.033 ppm O_3
0.2 ppm CO
0.003 ppm NO
0.008 ppm NO_2

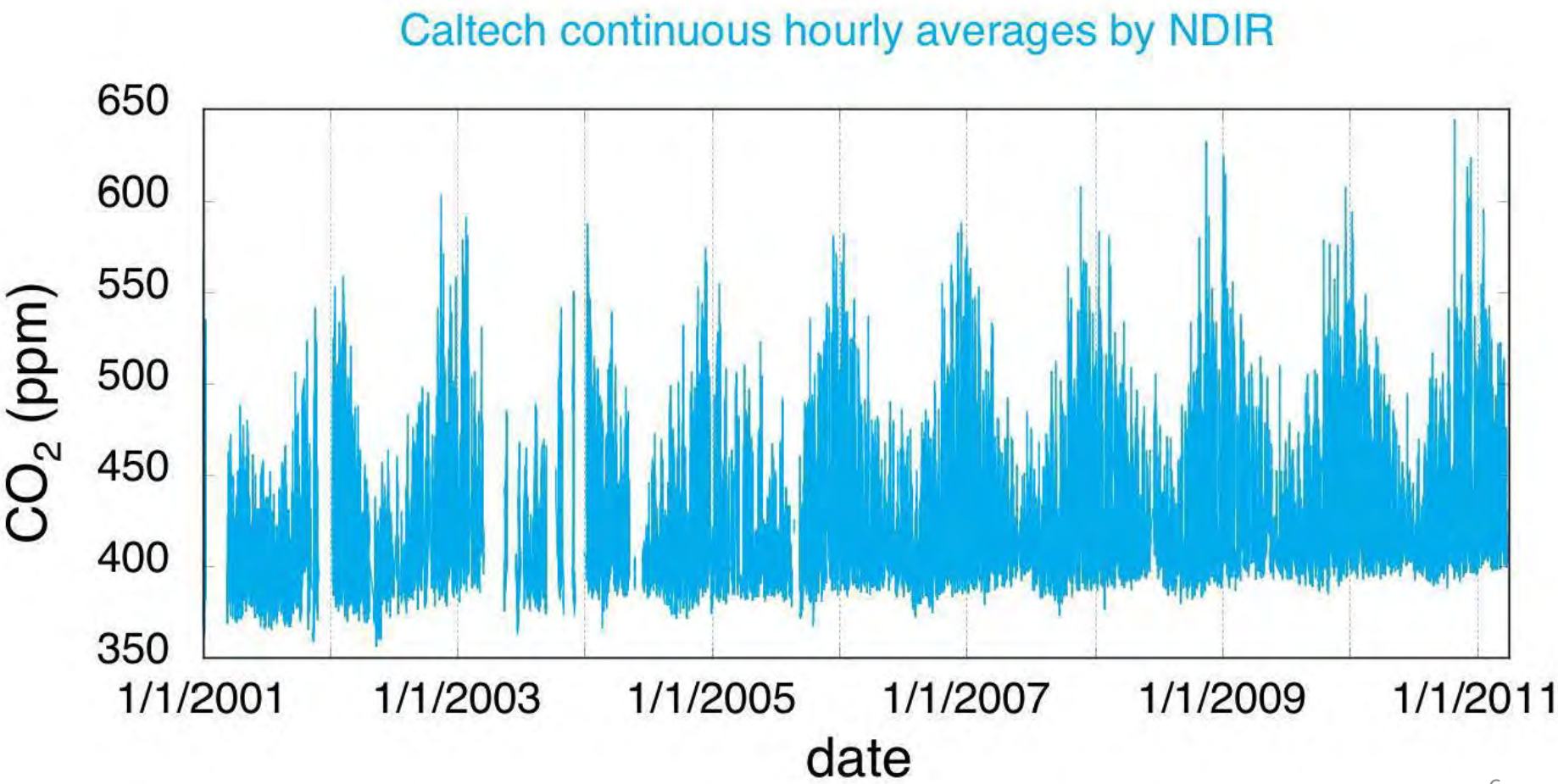
Outline

Using different types of CO_2 data to look at anthropogenic emissions on different time scales

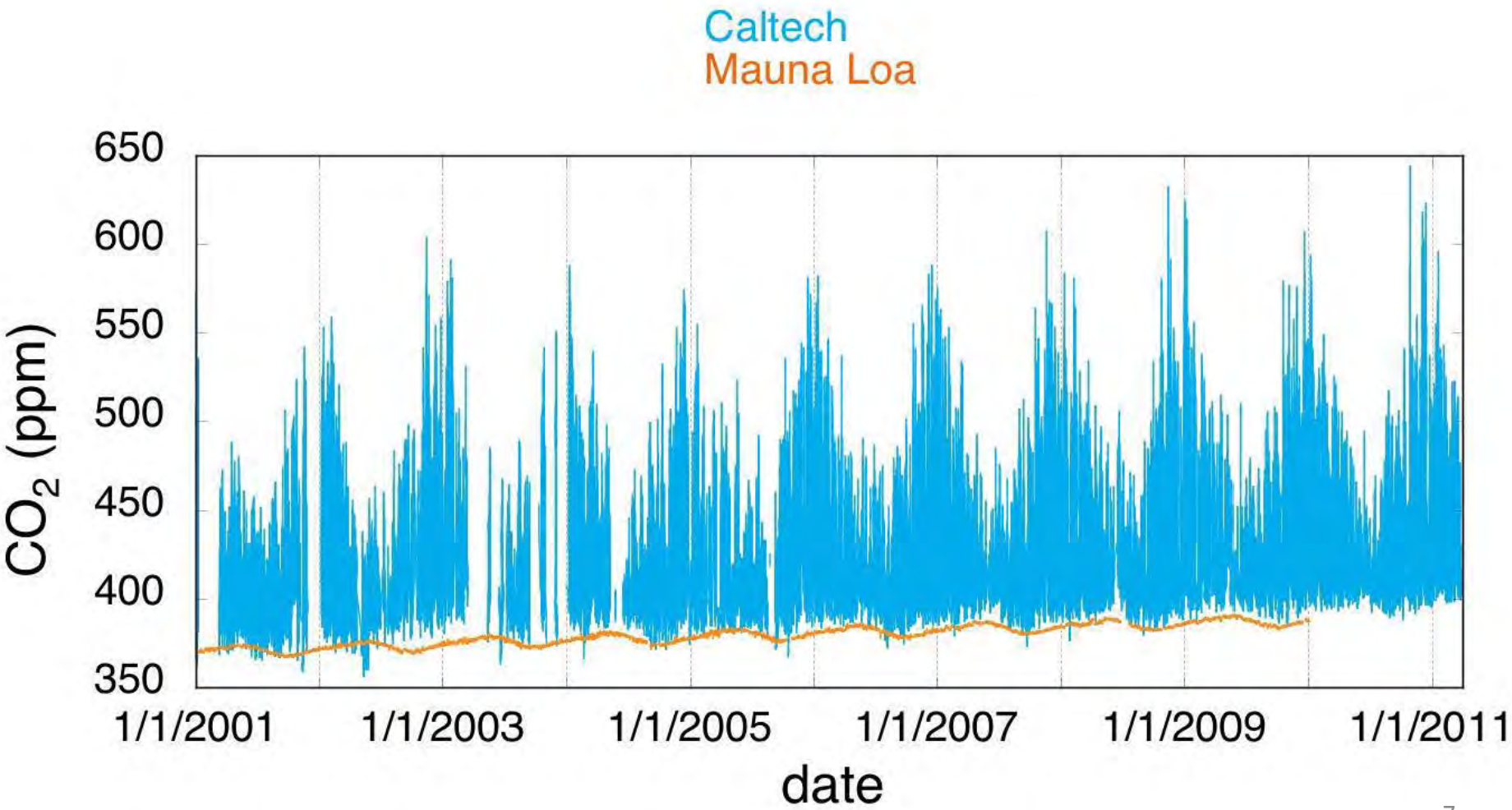
- Long term trends – Pasadena compared with clean air
- Periodicities in CO_2 trends compared with clean air and pollutants
- Lessons from the CalNex-LA ground campaign 15 May – 15 June, 2010

- **Long term trends – Pasadena compared with clean air**
  - CO_2
  - Using $\delta^{13}C$ to understand sources over long time periods
  - Using $\Delta^{14}C$ to understand intra-annual changes in sources

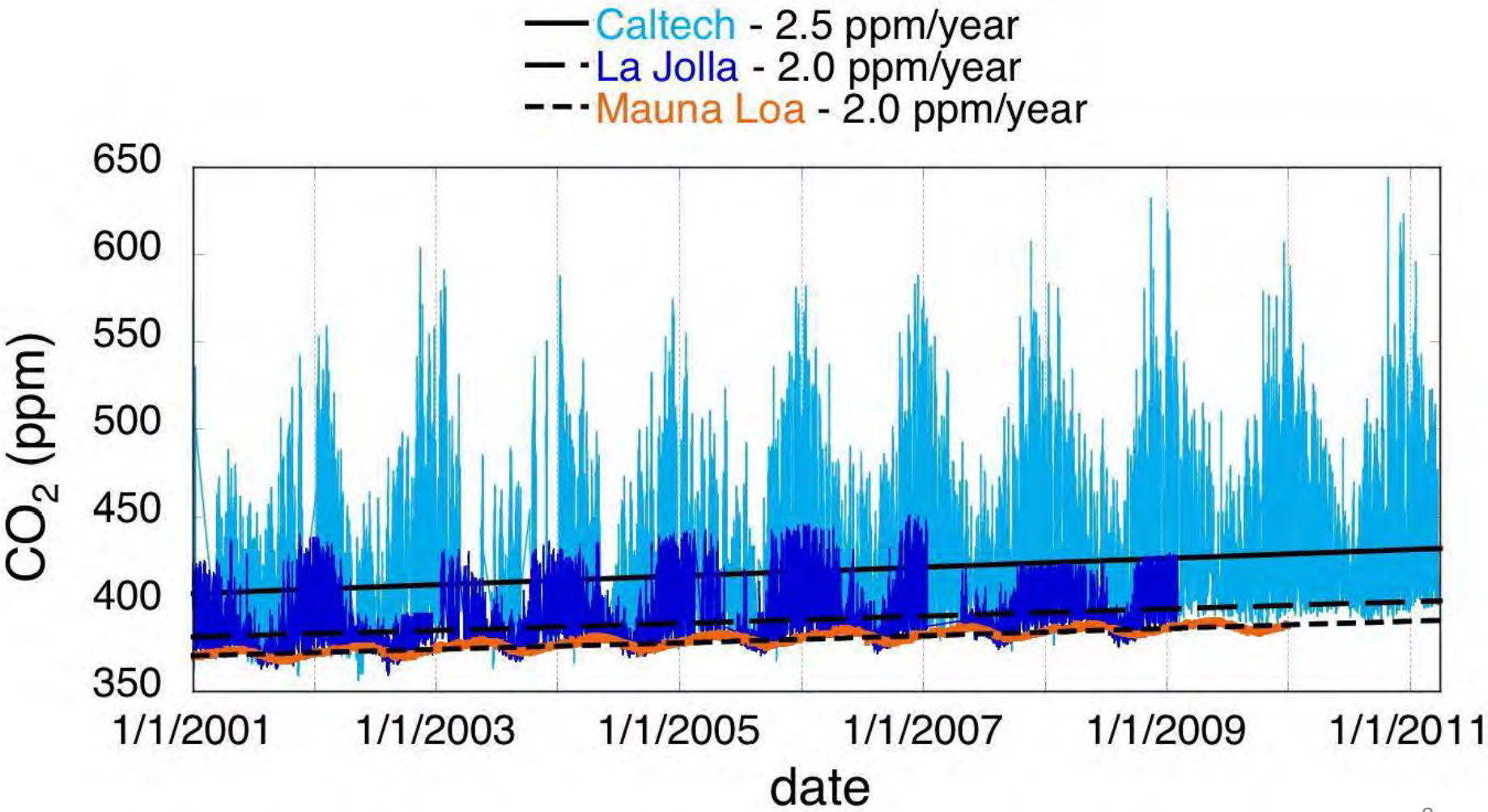
Caltech CO_2 mixing ratios



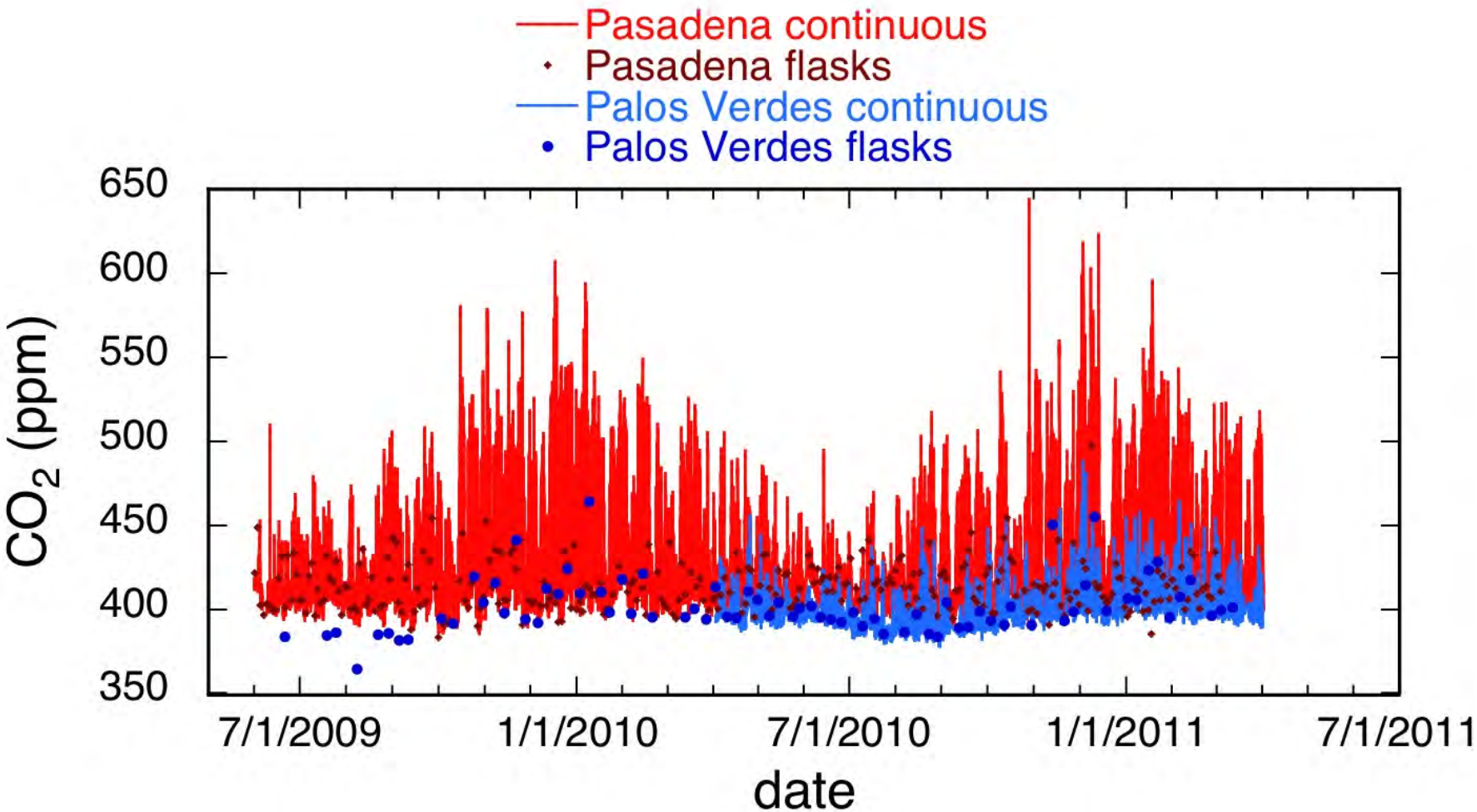
Caltech compared with Mauna Loa



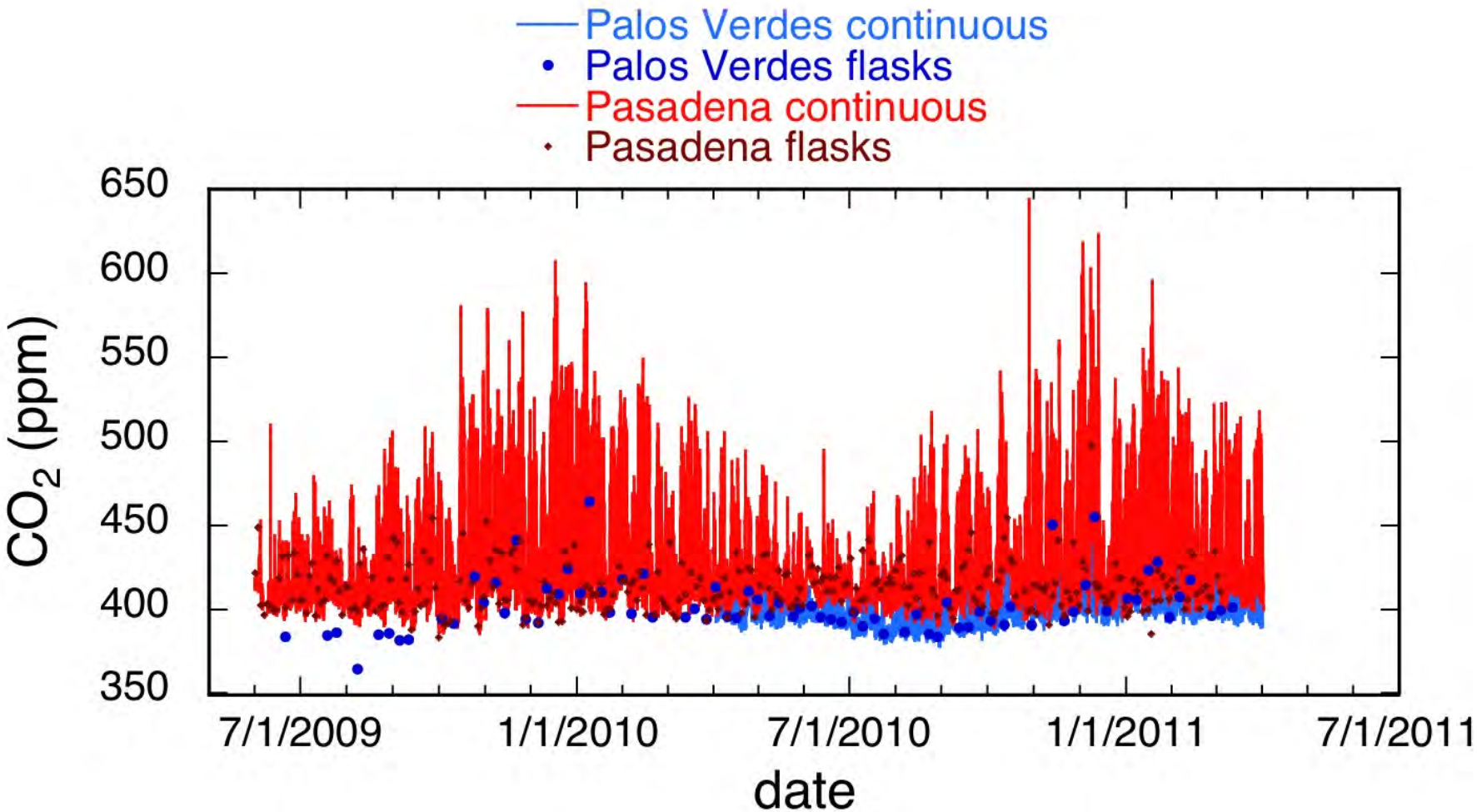
Caltech vs Mauna Loa and La Jolla



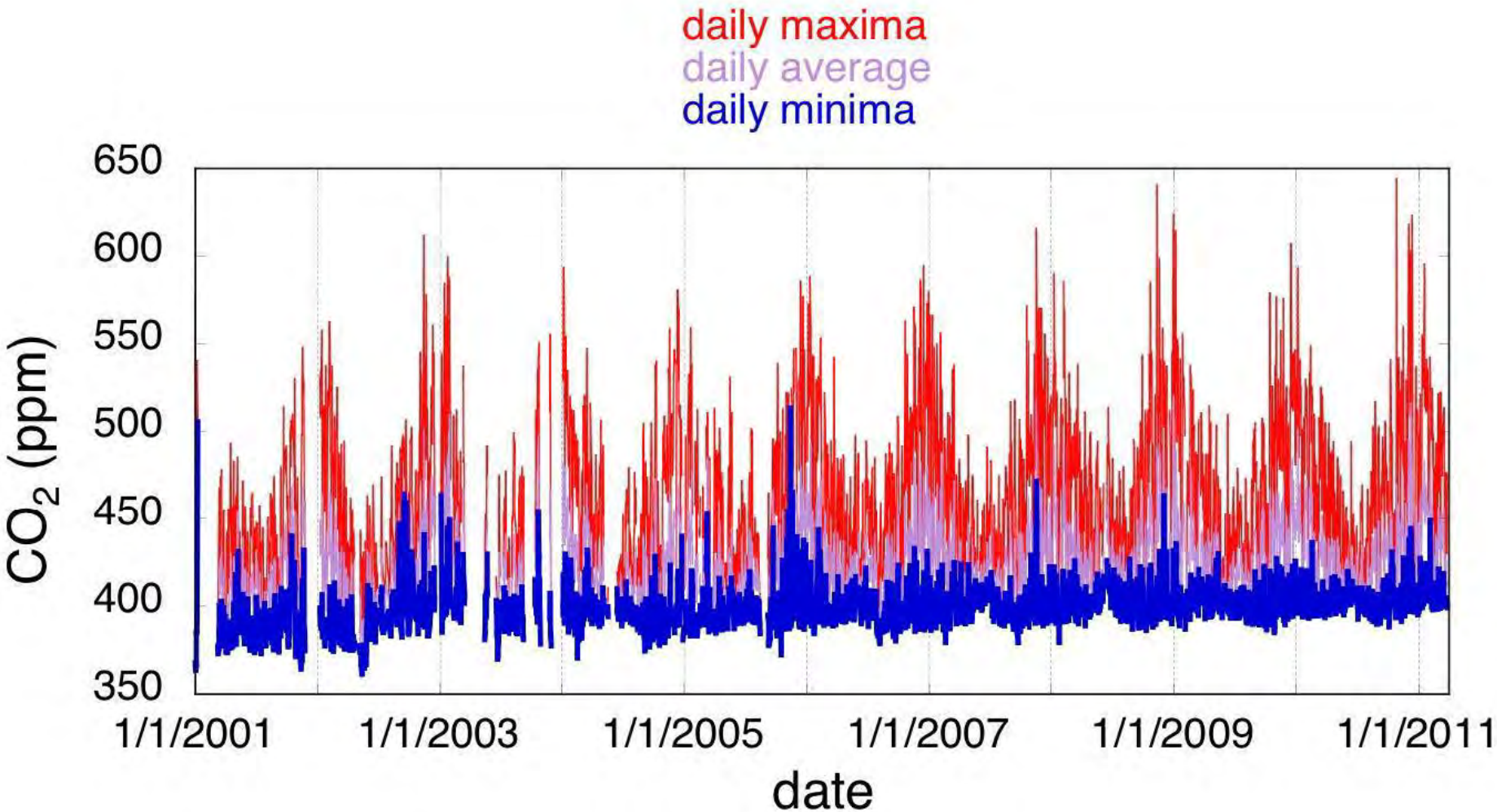
Comparison of Pasadena and Palos Verdes continuous and flask CO_2 data



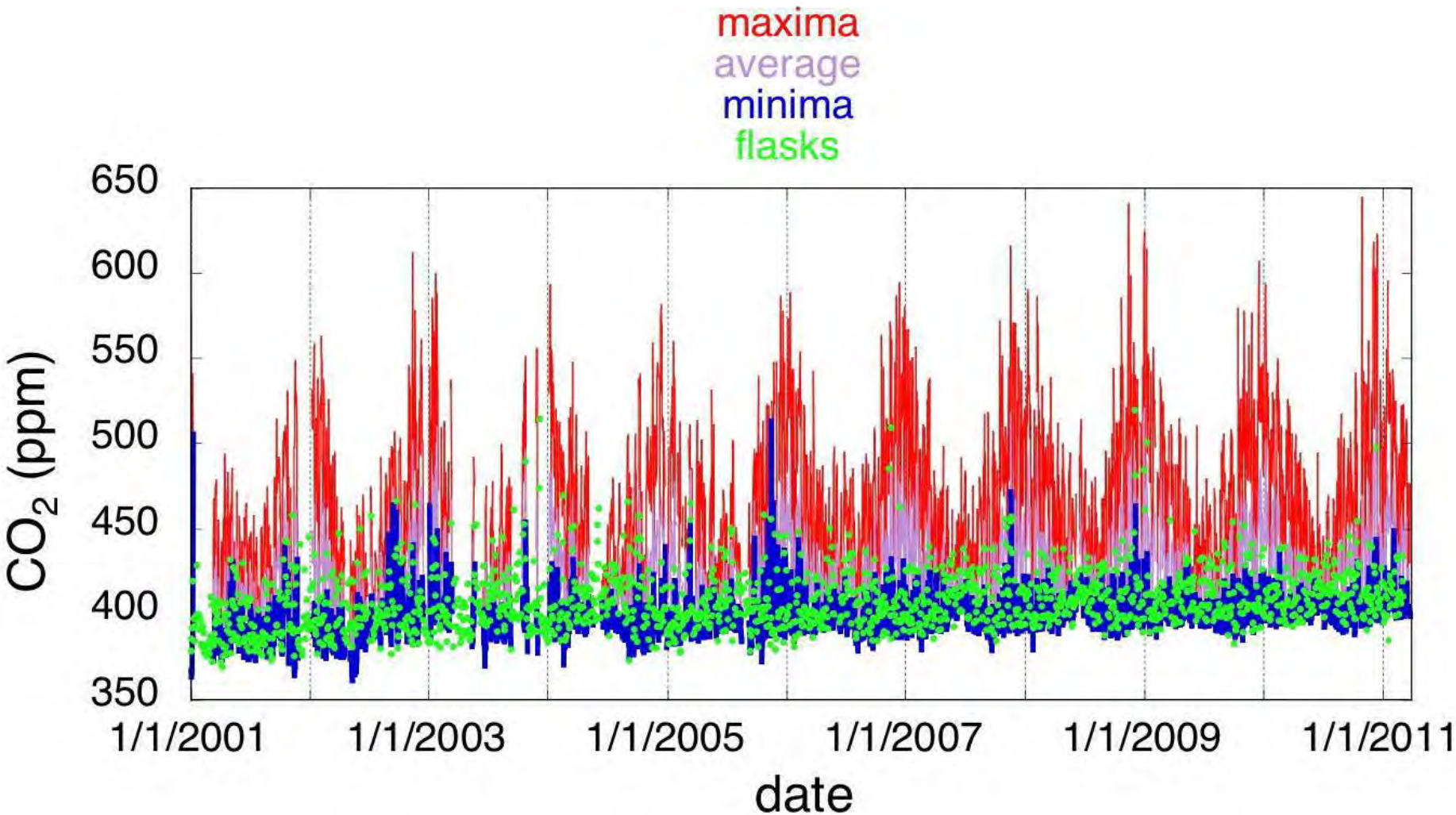
Comparison of Pasadena and Palos Verdes continuous and flask CO_2 data

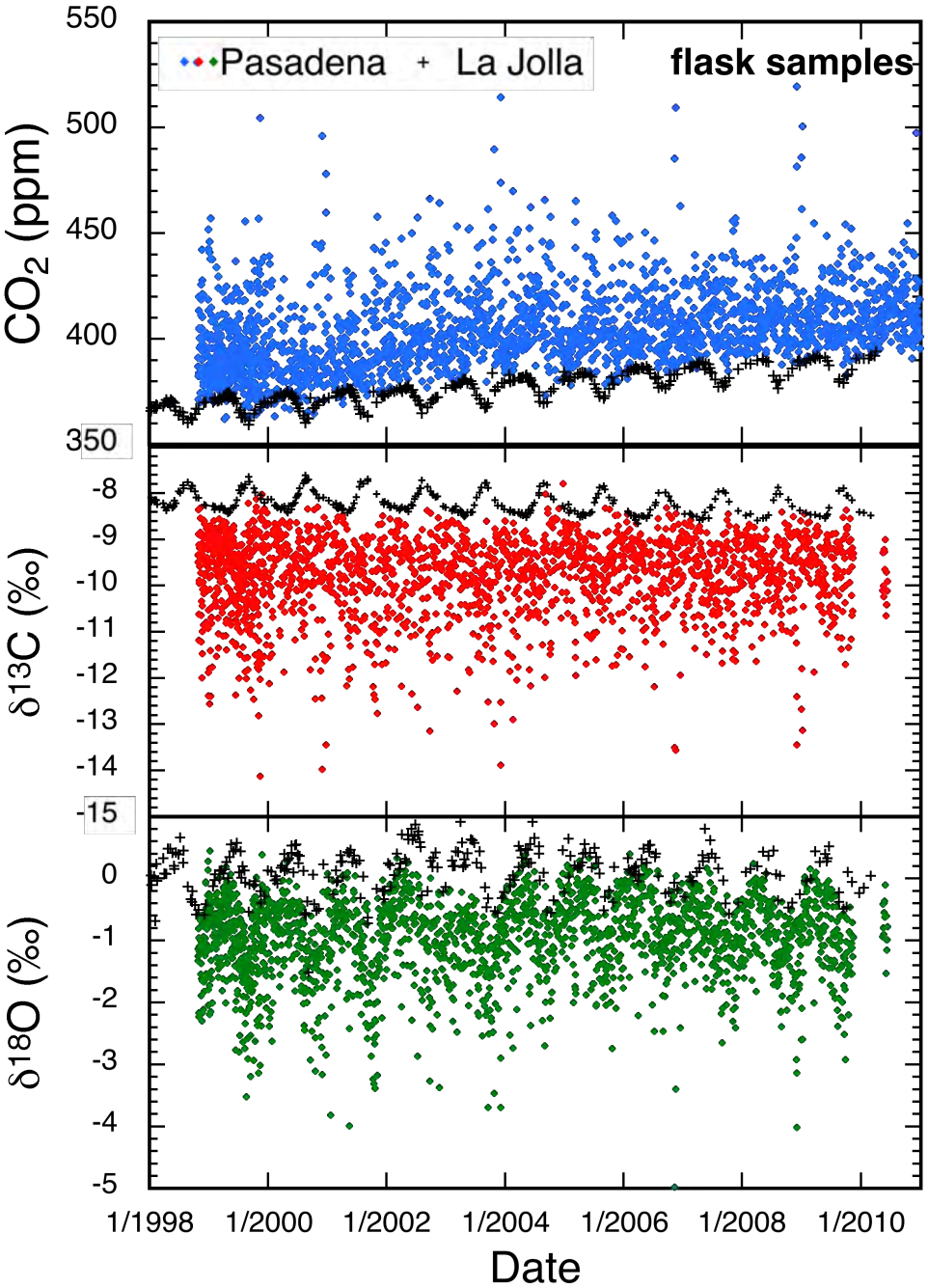


Caltech data



Including alternate afternoon flask samples

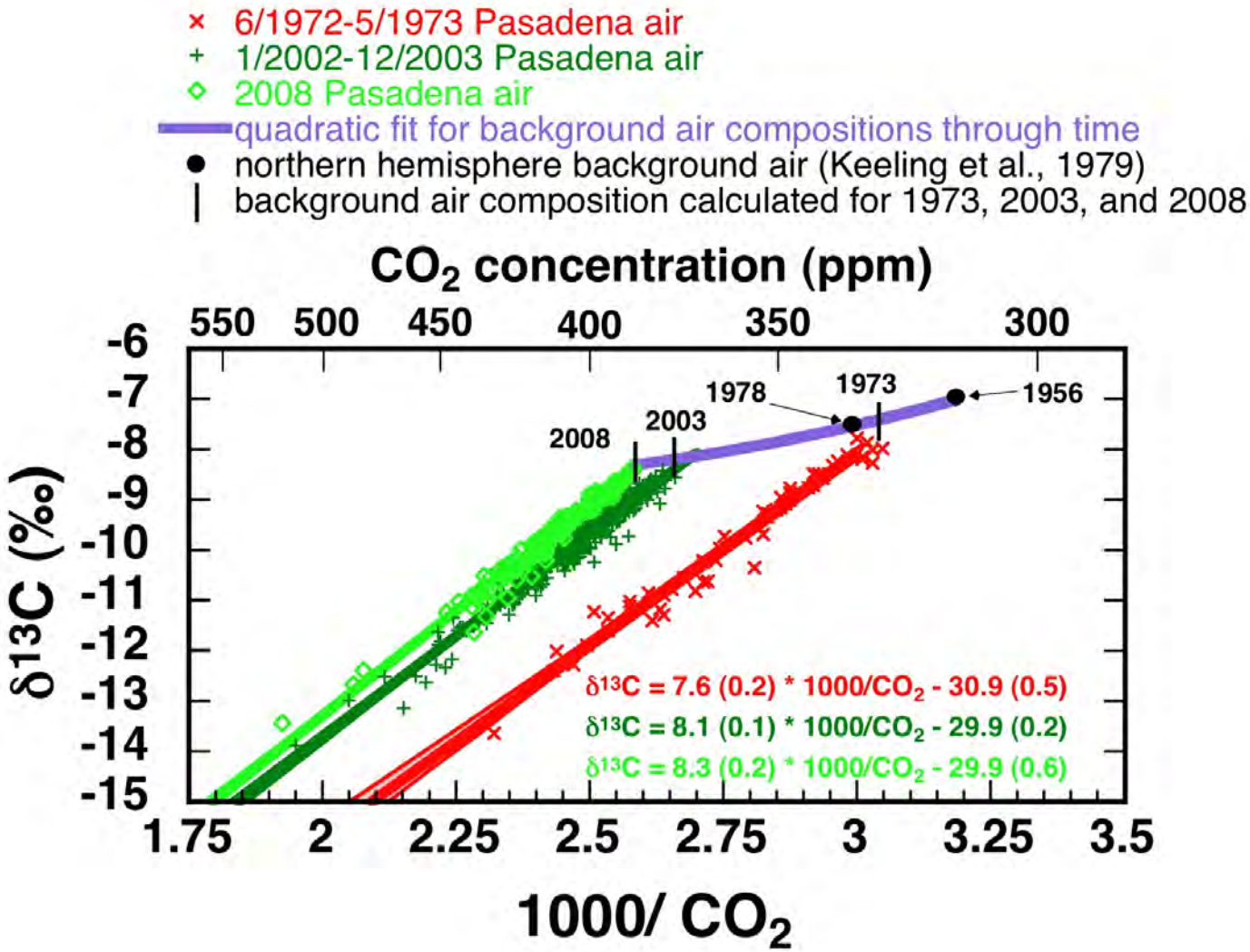




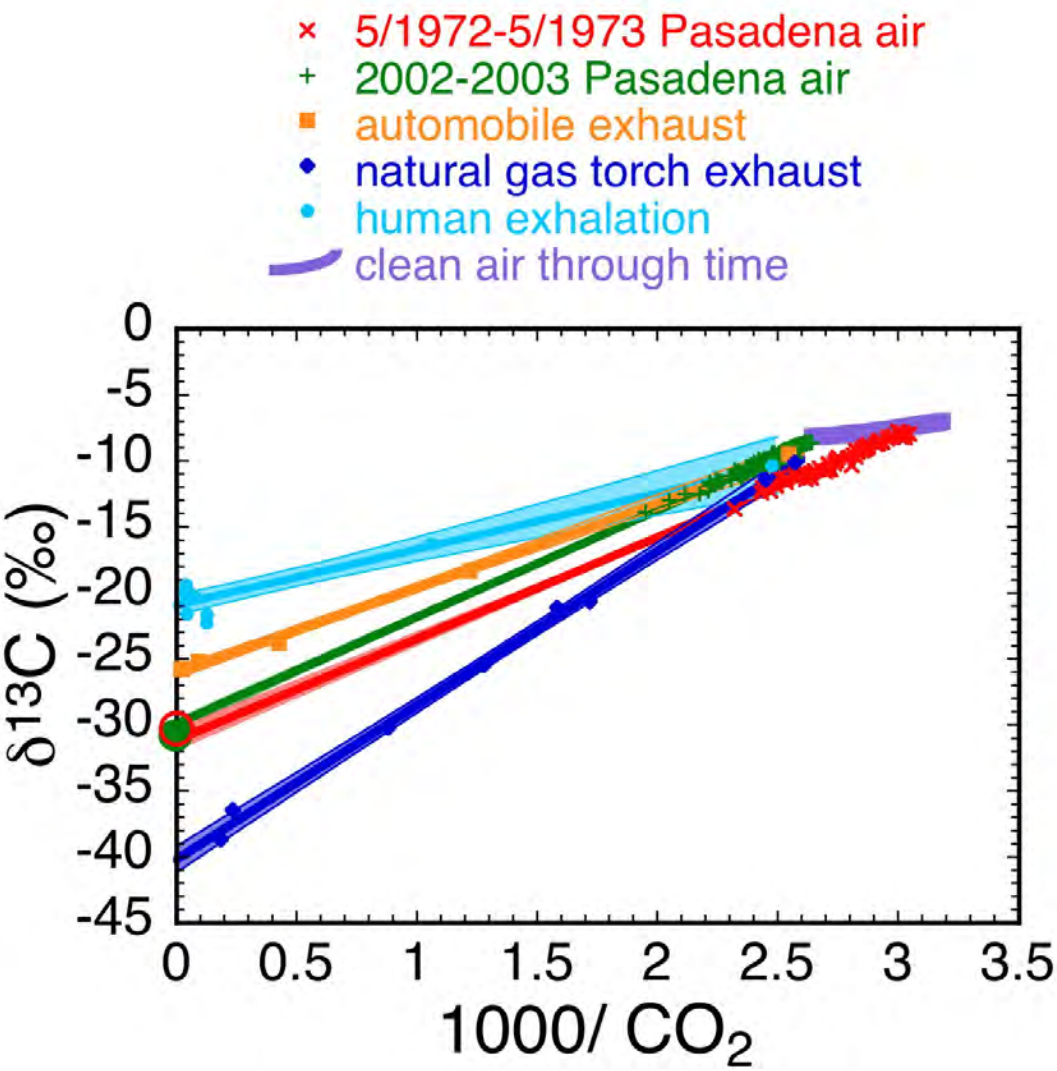
Mid-day flask samples from Caltech and La Jolla

La Jolla data from: C. D. Keeling, S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, and H. A. Meijer, Exchanges of atmospheric CO_2 and $^{13}CO_2$ with the terrestrial biosphere and oceans from 1978 to 2000. I. Global aspects, SIO Reference Series, No. 01-06, Scripps Institution of Oceanography, San Diego, 88 pages, 2001.

Keeling Plots for 2008, 2002-2003, and 1972-1973 Pasadena Flasks



Comparison of Pasadena data with possible sources of CO_2 emissions



$\delta^{13}C = 7.6\ (0.2) * 1000/CO_2 - \mathbf{30.9}\ (0.5)$

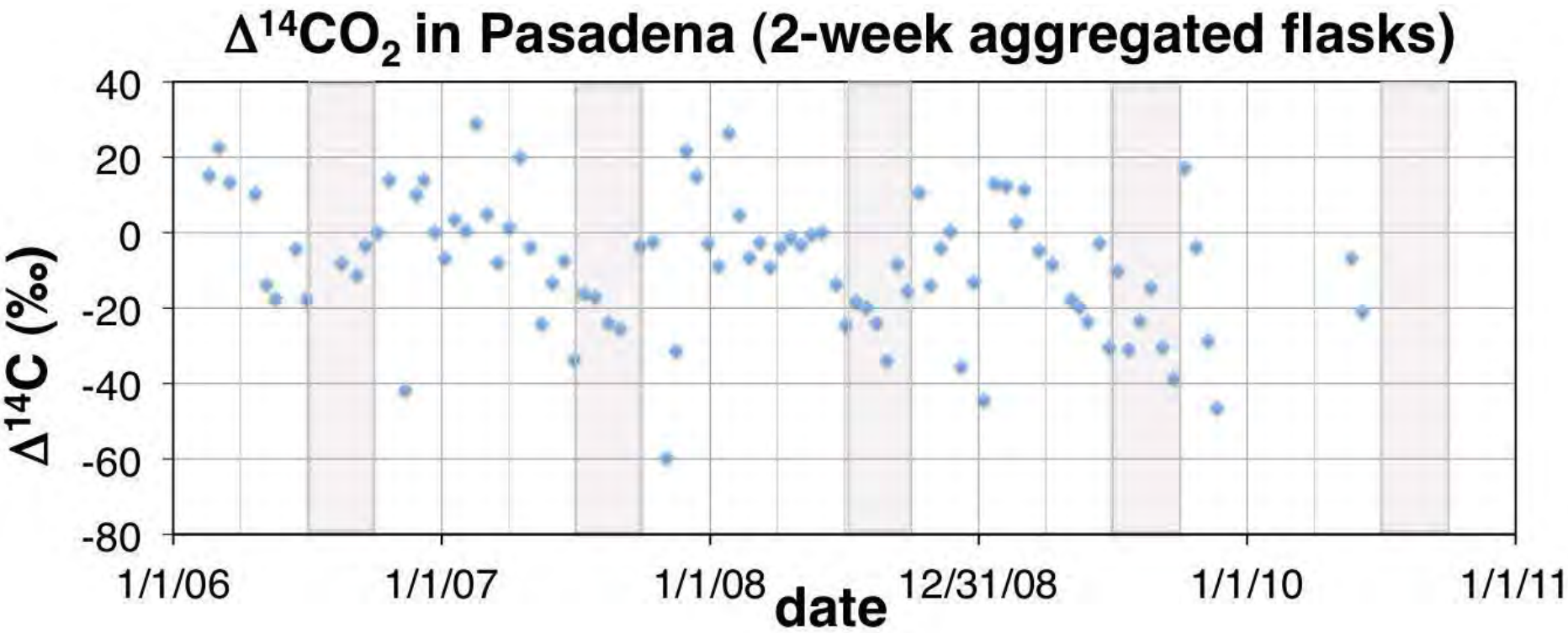
$\delta^{13}C = 8.1\ (0.1) * 1000/CO_2 - \mathbf{29.9}\ (0.2)$

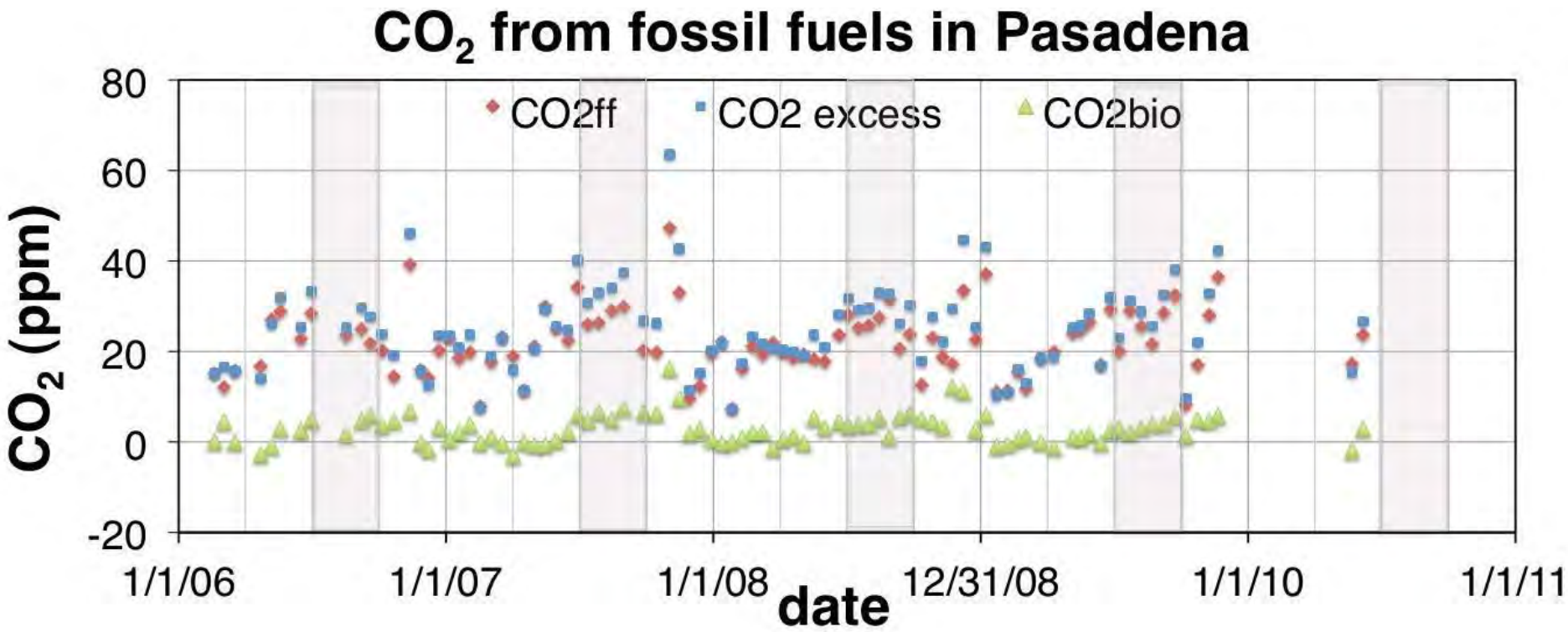
$\delta^{13}C = 6.4\ (0.2) * 1000/CO_2 - \mathbf{26.0}\ (0.2)$

$\delta^{13}C = 11.7\ (0.3) * 1000/CO_2 - \mathbf{40.2}\ (0.5)$

$\delta^{13}C = 4.2\ (0.5) * 1000/CO_2 - \mathbf{20.9}\ (0.4)$

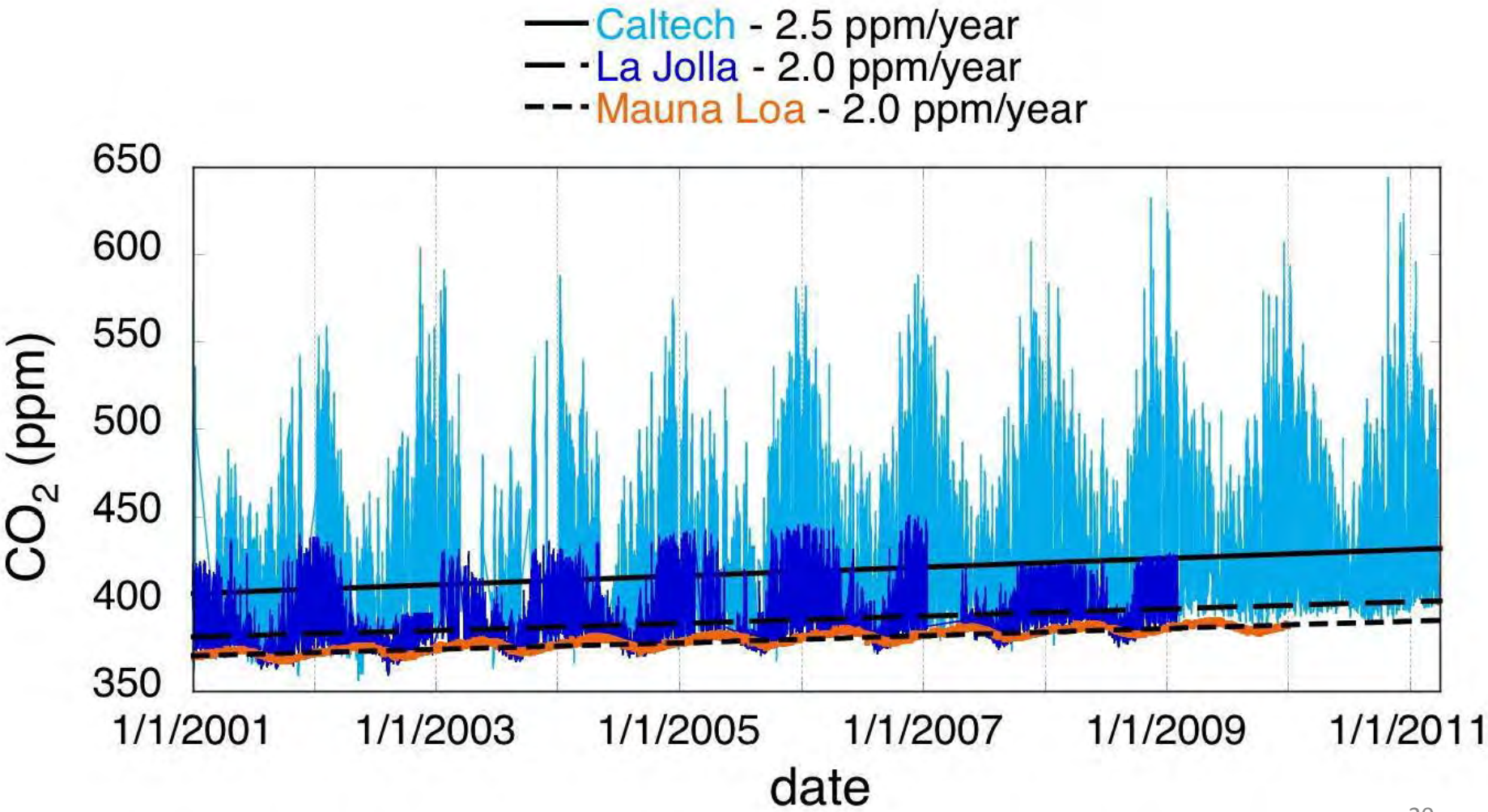
$^{14}CO_2$ is the gold standard for differentiating between modern and fossil sources of CO_2, because of its short half-life of 5730 years.


Δ14CO2 in Pasadena (2-week aggregated flasks)
Δ14C (‰)
40
20
0
-20
-40
-60
-80
1/1/06
1/1/07
1/1/08
12/31/08
1/1/10
1/1/11
date

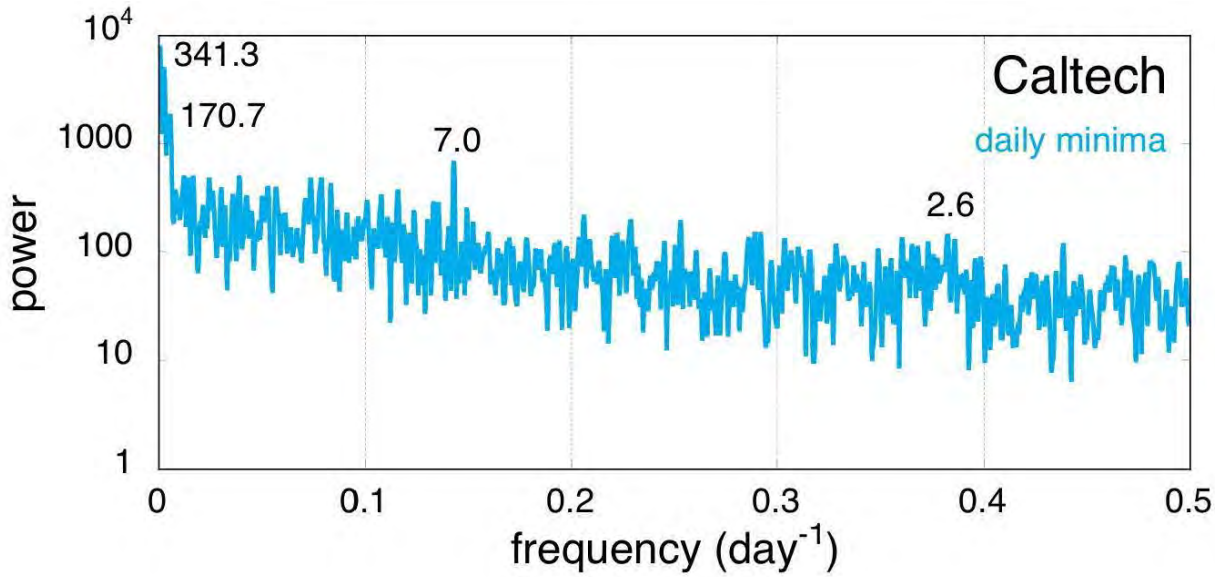

CO2 from fossil fuels in Pasadena
CO2ff
CO2 excess
CO2bio
CO2 (ppm)
80
60
40
20
0
-20
1/1/06
1/1/07
1/1/08
12/31/08
1/1/10
1/1/11
date

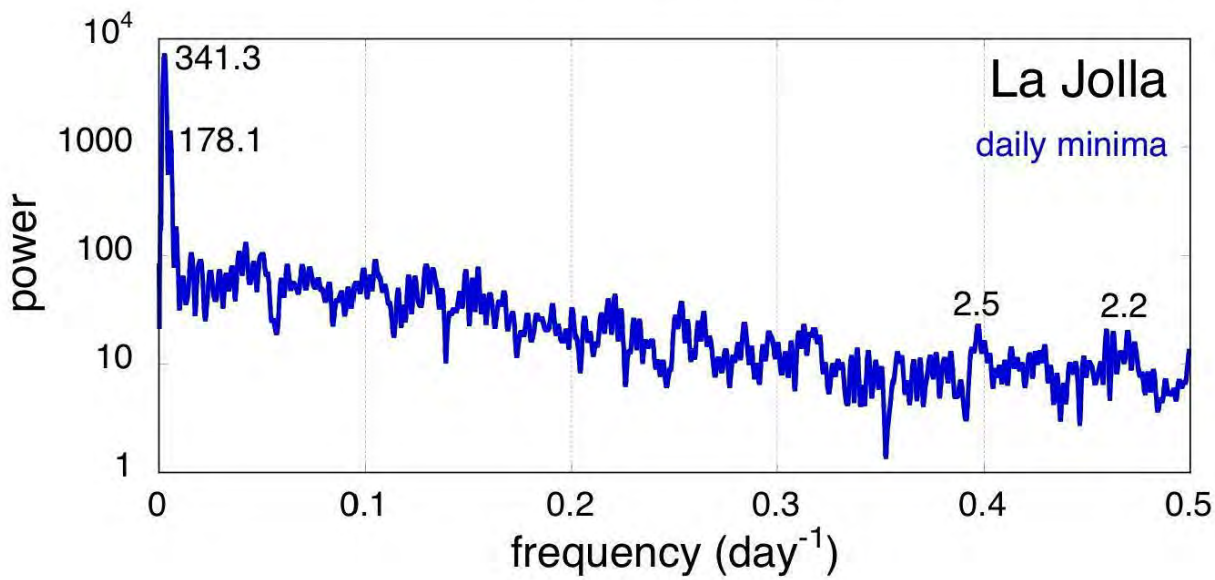
- **Periodicities in CO_2 trends compared with clean air and pollutants**
  - Annual and weekly cycles: CO_2, $\delta^{13}C$, $\delta^{18}O$
  - Diurnal cycles of CO_2
  - Influence of meteorology on diurnal variations

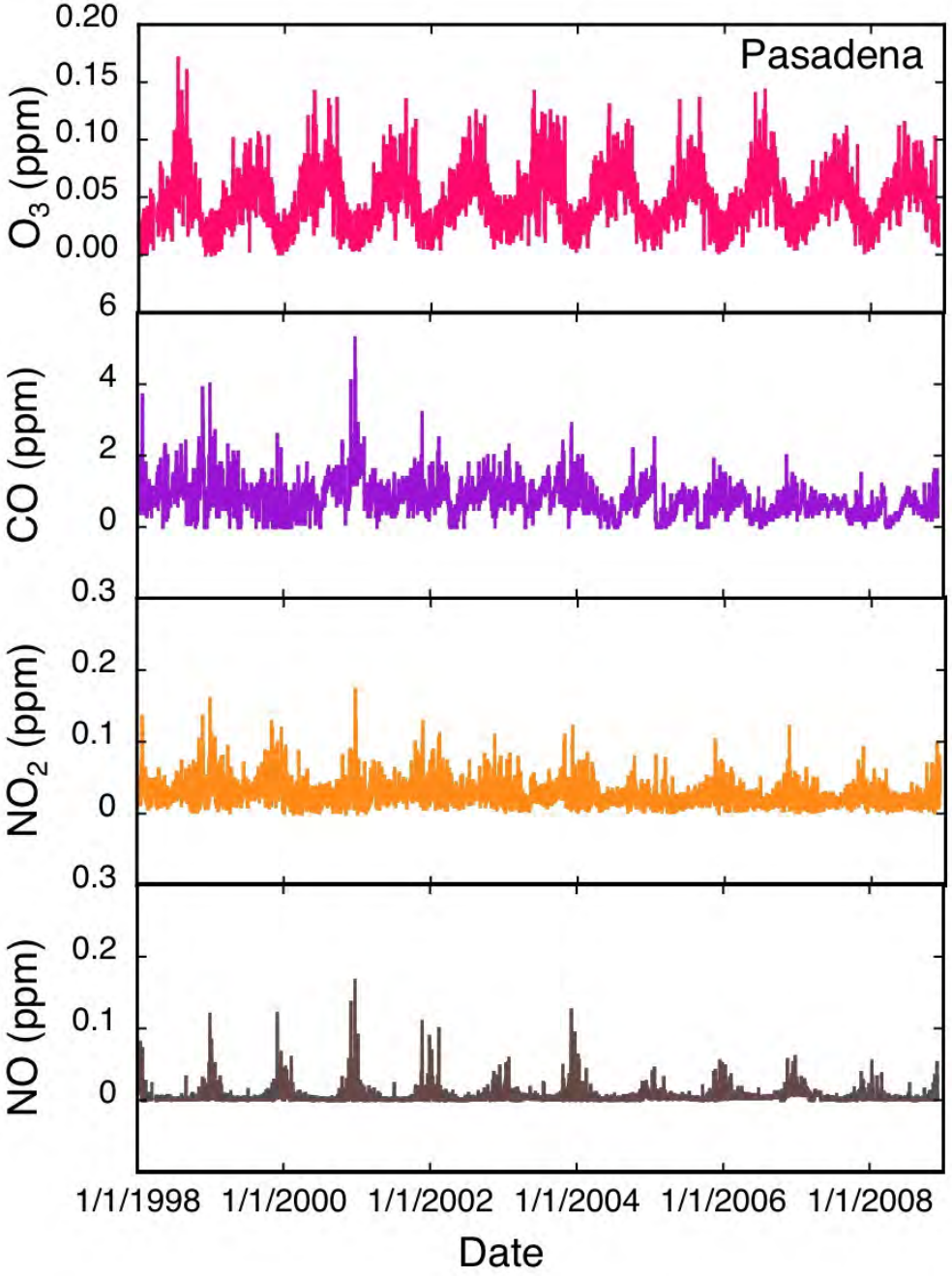
Caltech vs Mauna Loa and La Jolla



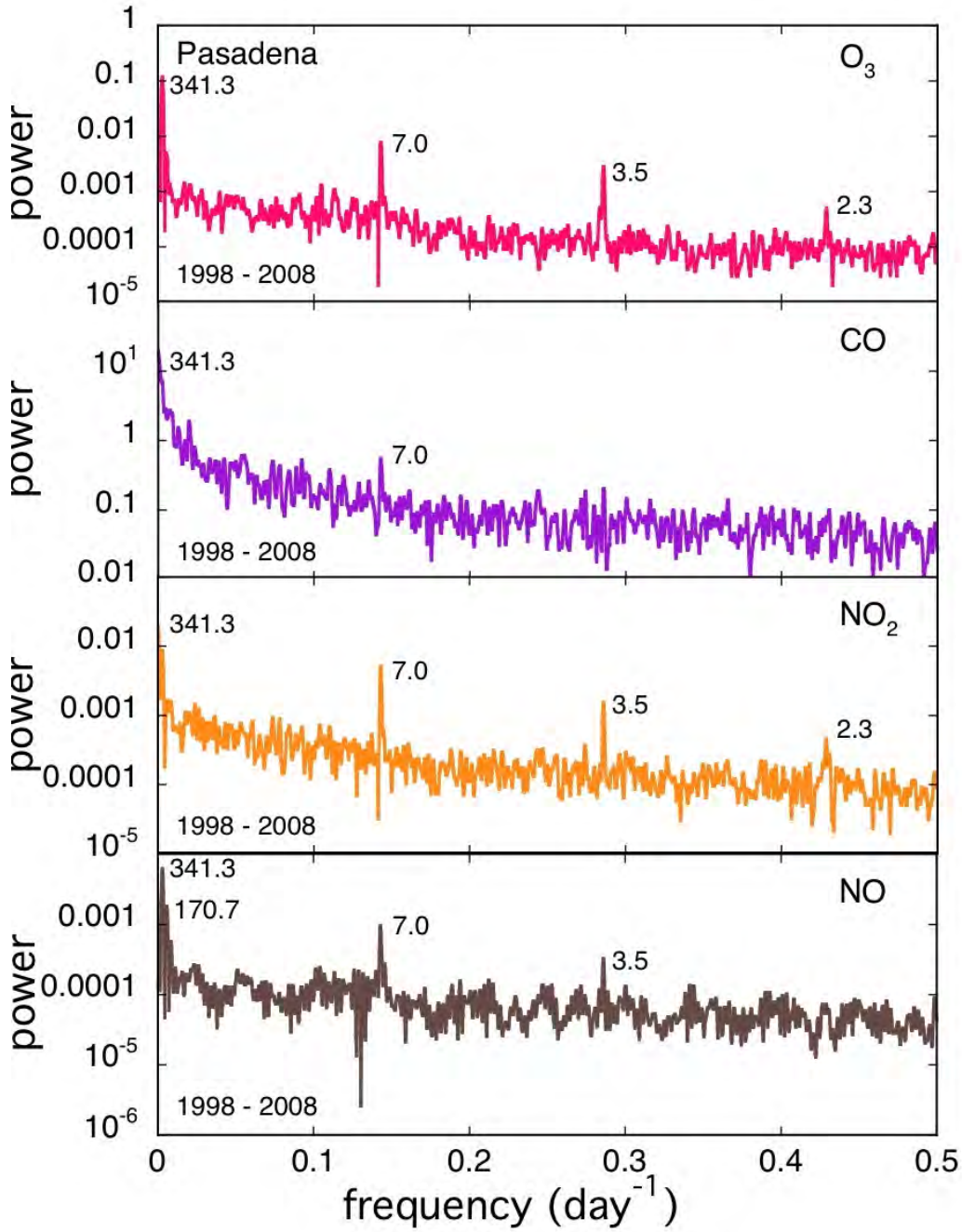
Comparison of periodicities in daily minimum CO_2 mixing ratios at Caltech and La Jolla





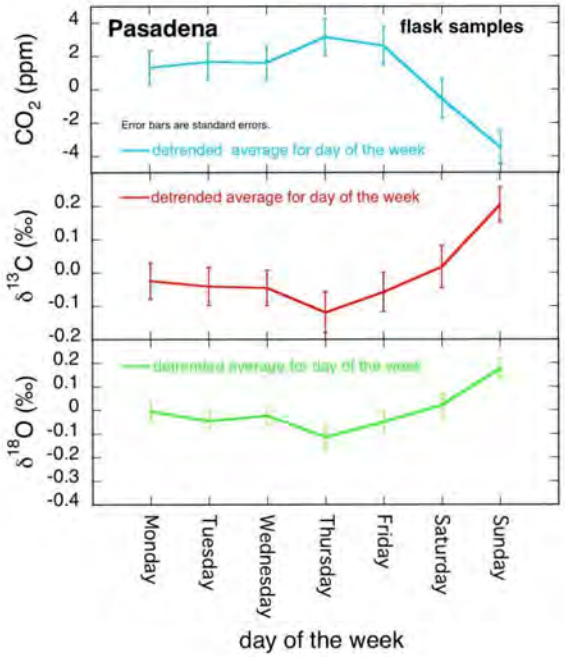


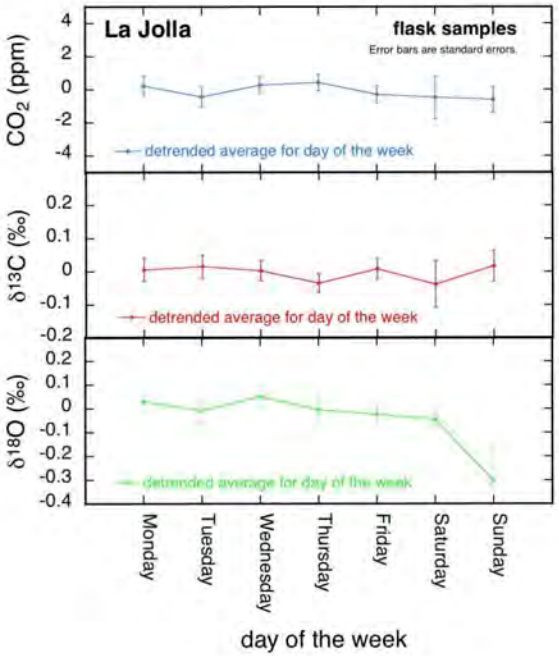
Mid-afternoon pollutant data from the Caltech campus, collected by the South Coast Air Quality Management District and the California Air Resources Board

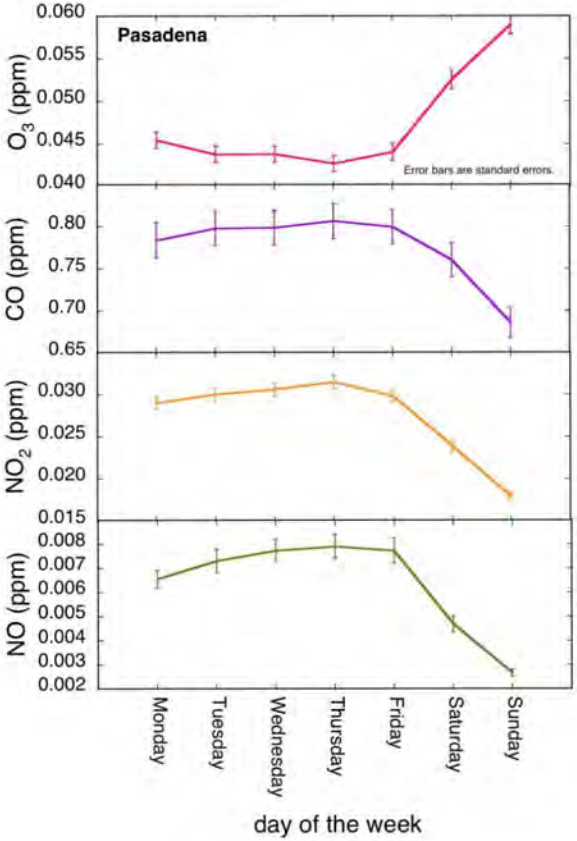


Periodicities for mid-afternoon Pasadena pollutants

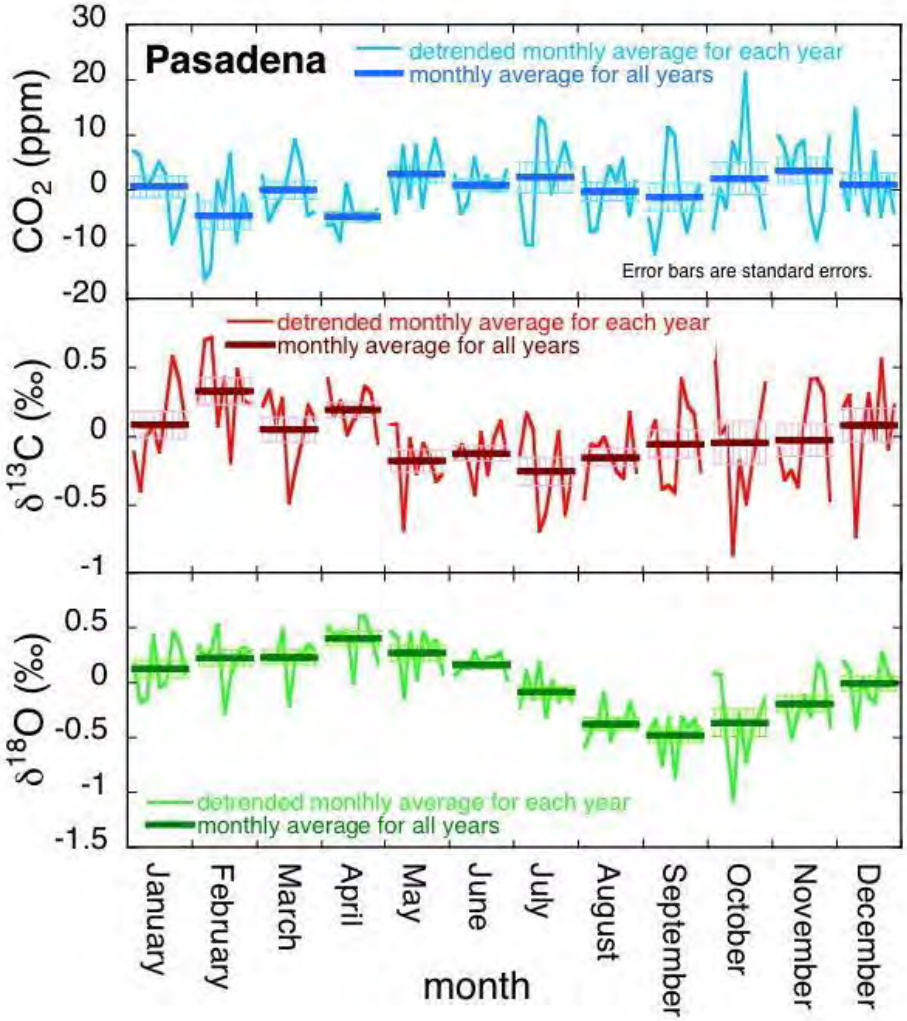
Weekly trends

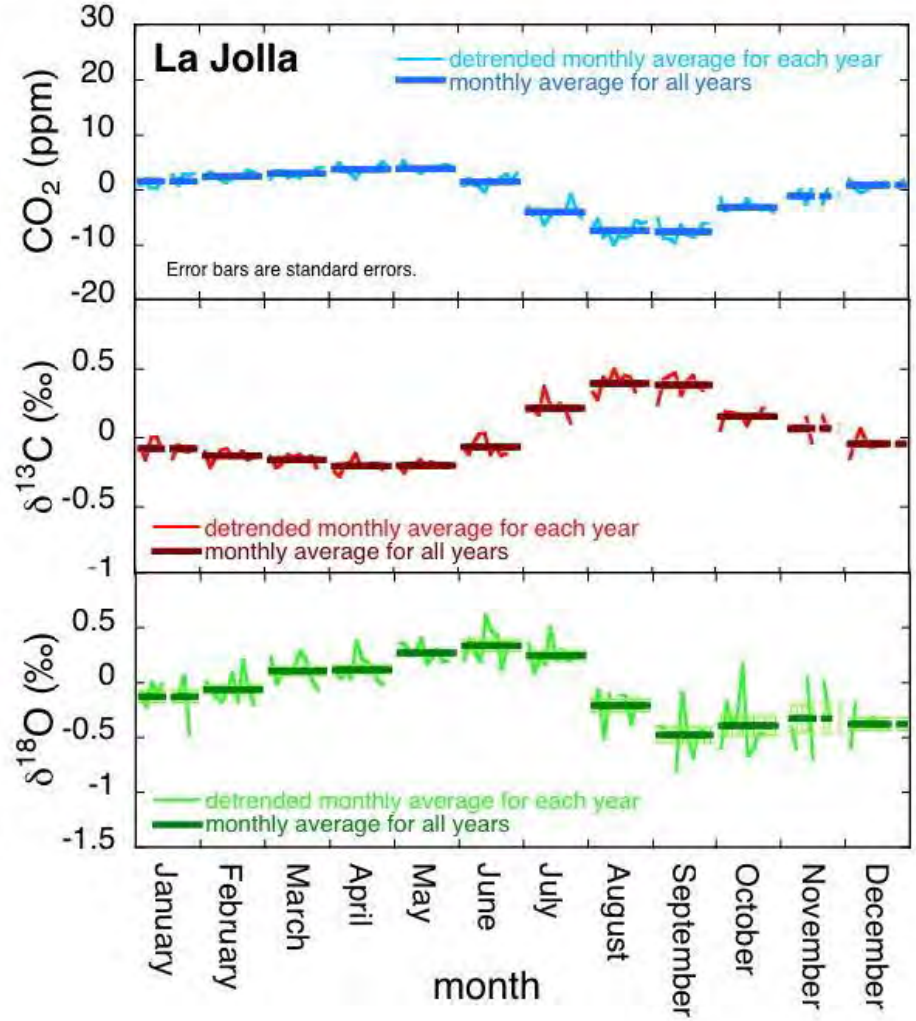






Comparison of seasonality in Pasadena and La Jolla





Note: 1. Very noisy annual CO_2 pattern, even though we see annual cycle in FFT

2. $\delta^{13}C$ in Pasadena out of phase relative to La Jolla

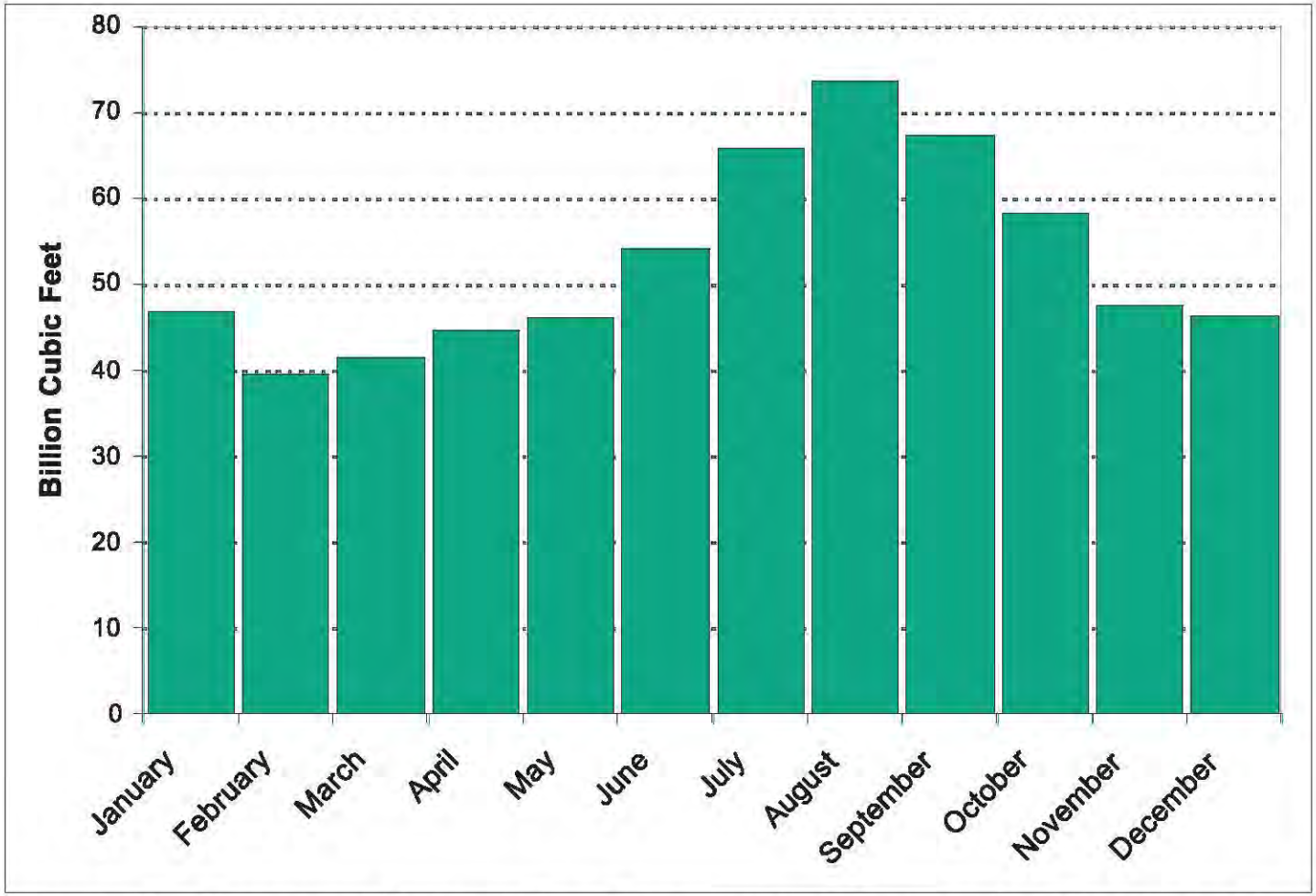
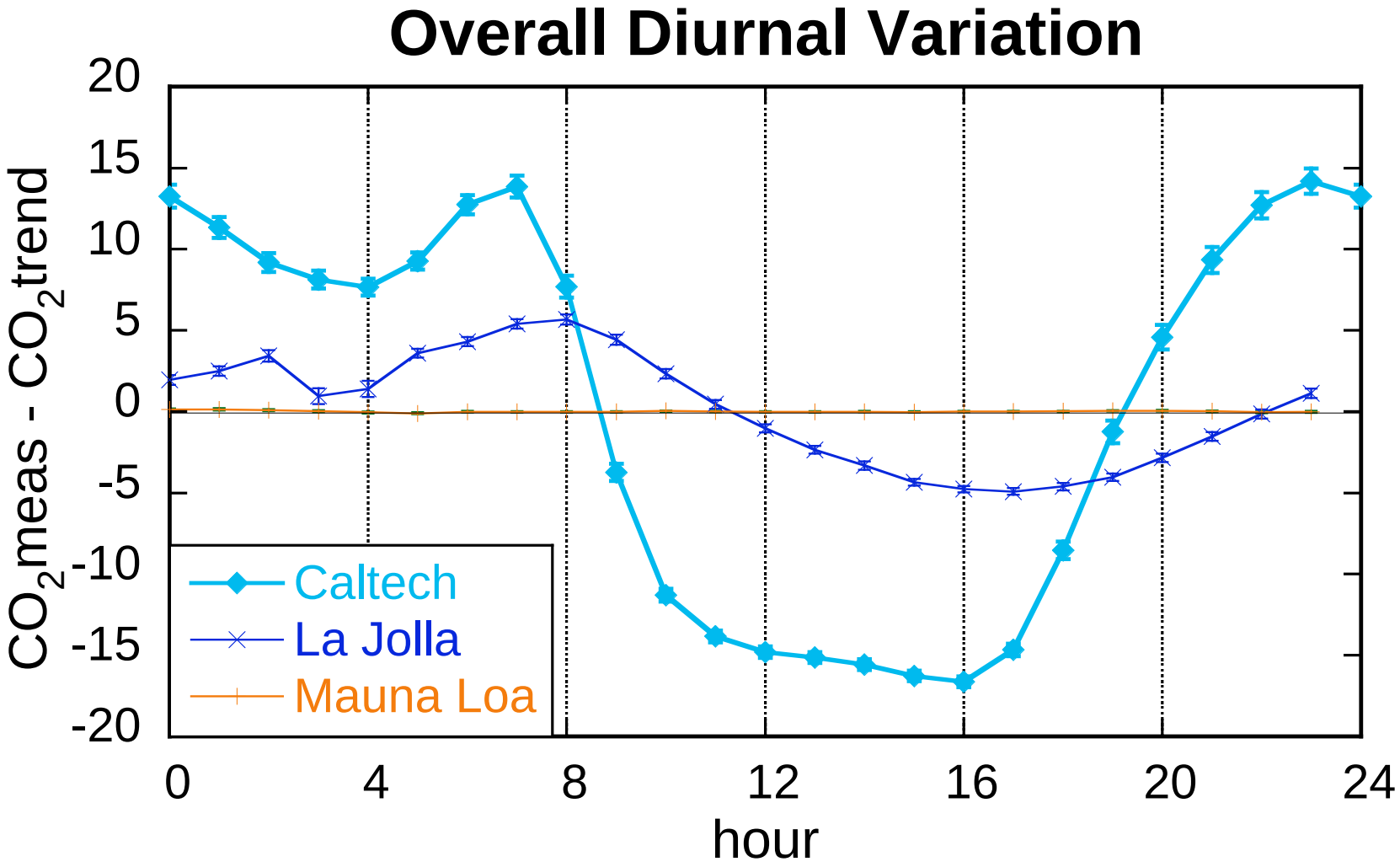
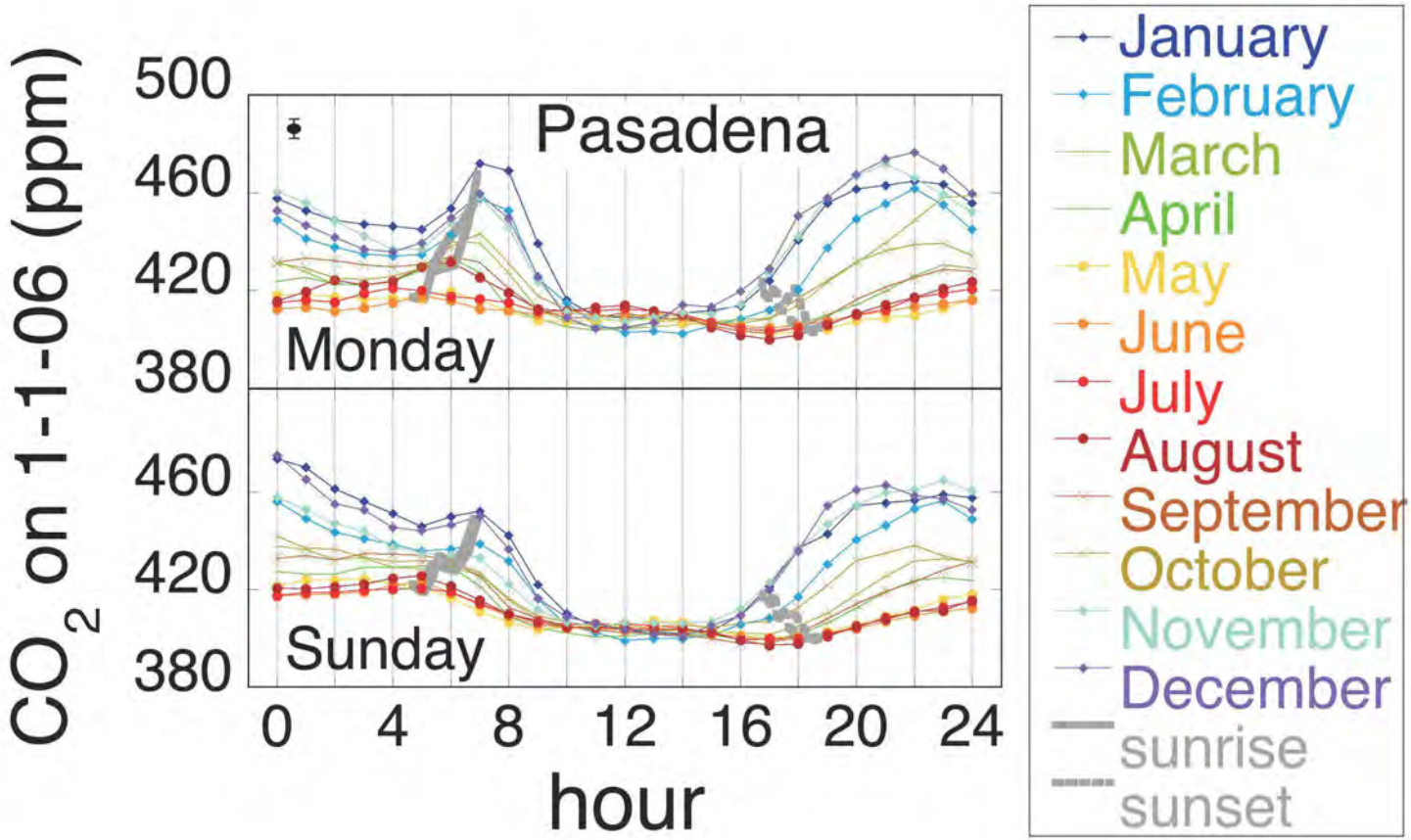


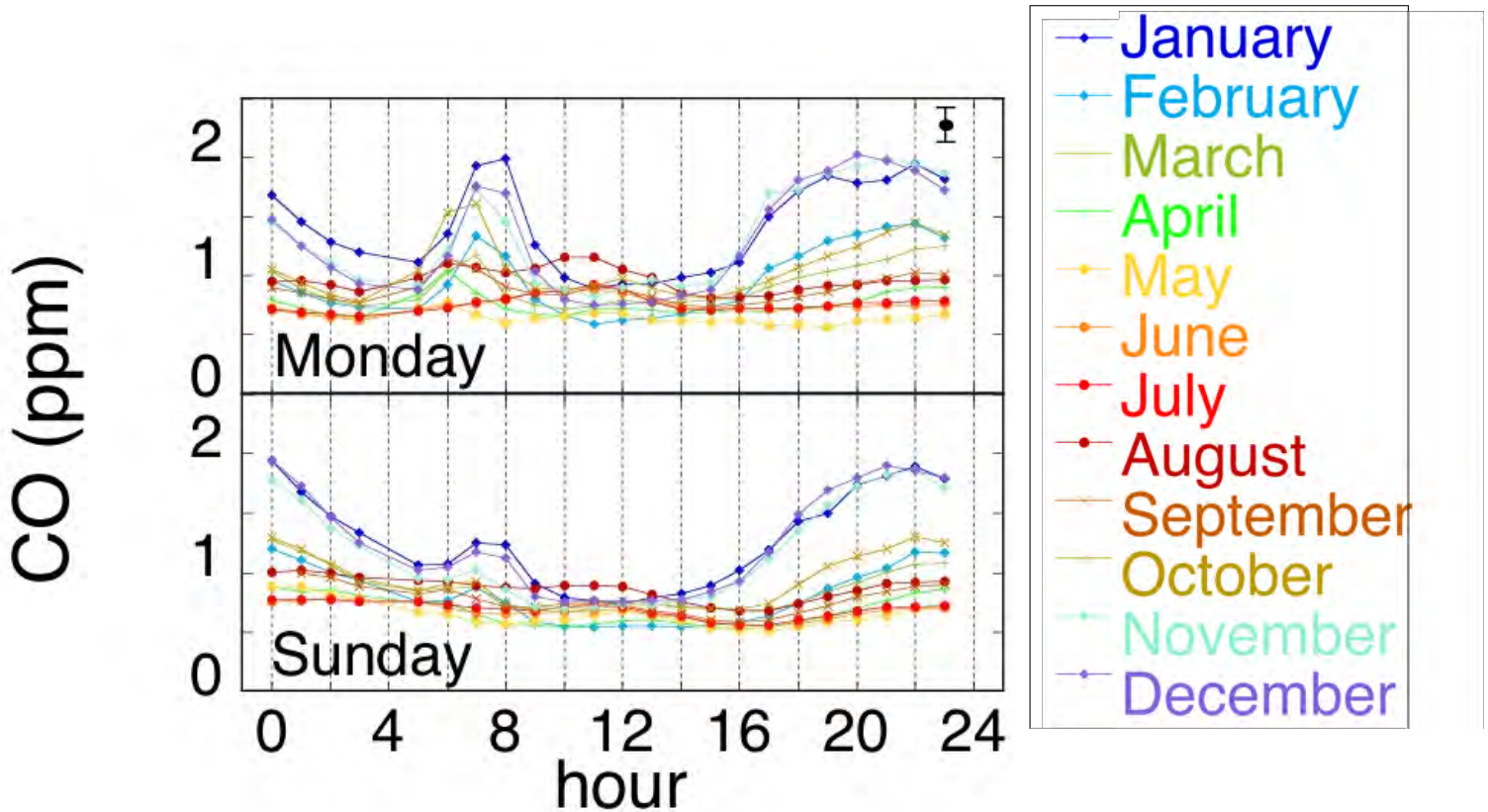
Figure 12: Seasonal Natural Gas Consumption Pattern for Electricity Generation
Source: California Energy Commission

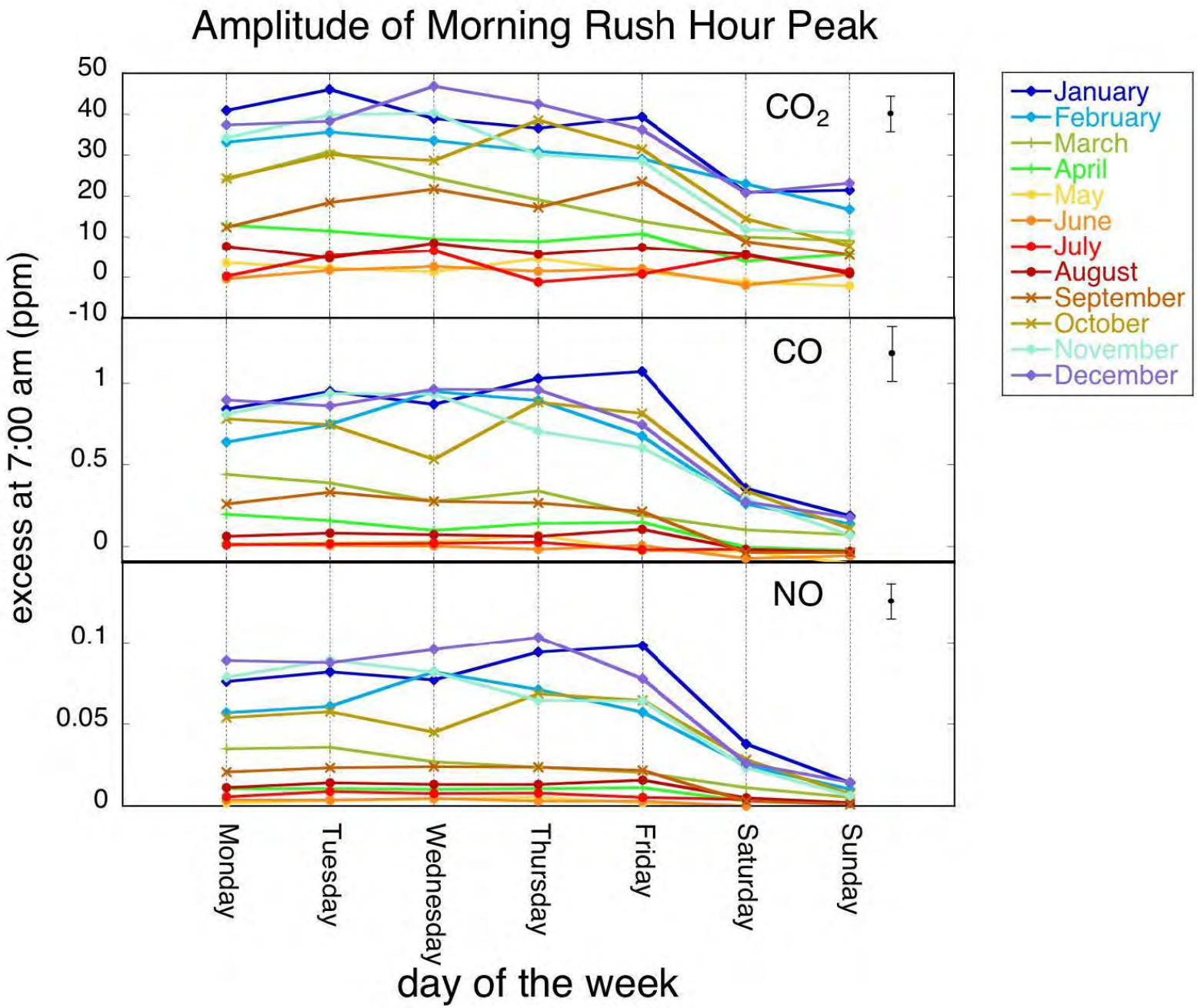

Overall Diurnal Variation
20
15
10
5
0
-5
-10
-15
-20
CO_2meas - CO_2trend
0
4
8
12
16
20
24
hour
Caltech
La Jolla
Mauna Loa

Seasonal and weekly variations in diurnal cycles of CO_2 in Pasadena, using continuous NDIR measurements for 2001-2009

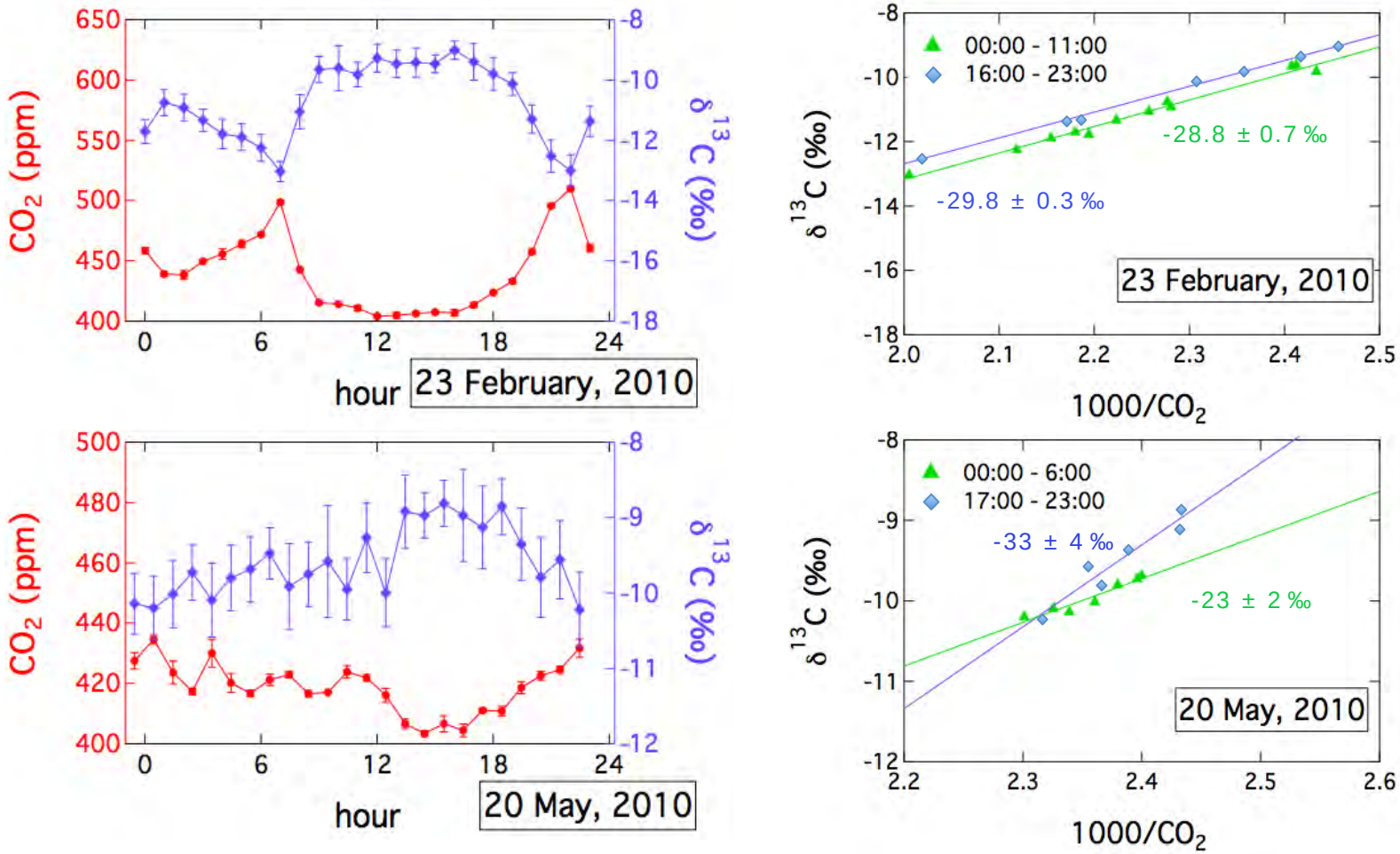


CO in Pasadena shows very similar patterns

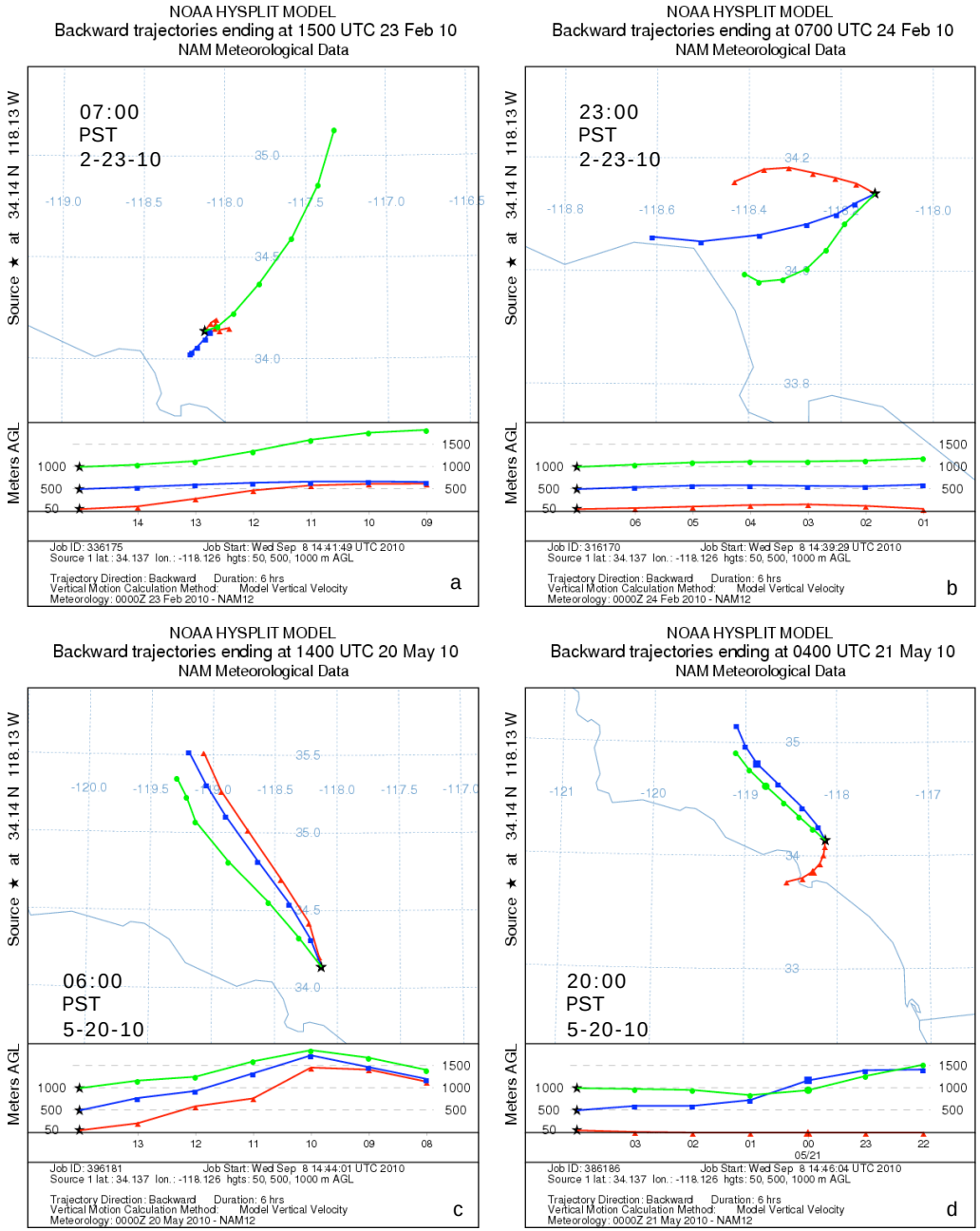



Amplitude of Morning Rush Hour Peak
excess at 7:00 am (ppm)
50
40
30
20
10
0
-10
CO2
1
0.5
0
CO
0.1
0.05
0
NO
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
day of the week
January
February
March
April
May
June
July
August
September
October
November
December

Looking at Keeling plots within single days

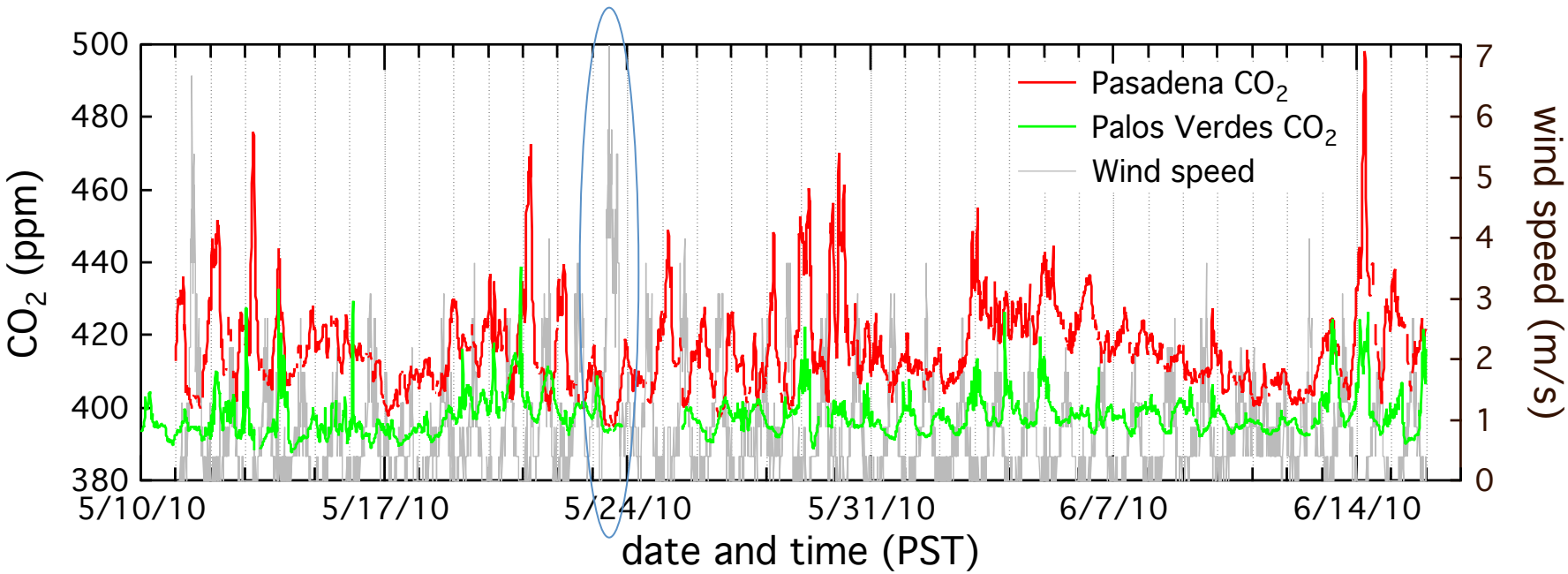


Diurnal cycles for CO_2 mixing ratios (red) and $\delta^{13}C$ (blue) (top plots) and Keeling plots (bottom plots) for 23 February and 20 May, 2010. Measurements were made in Pasadena by CRDS.

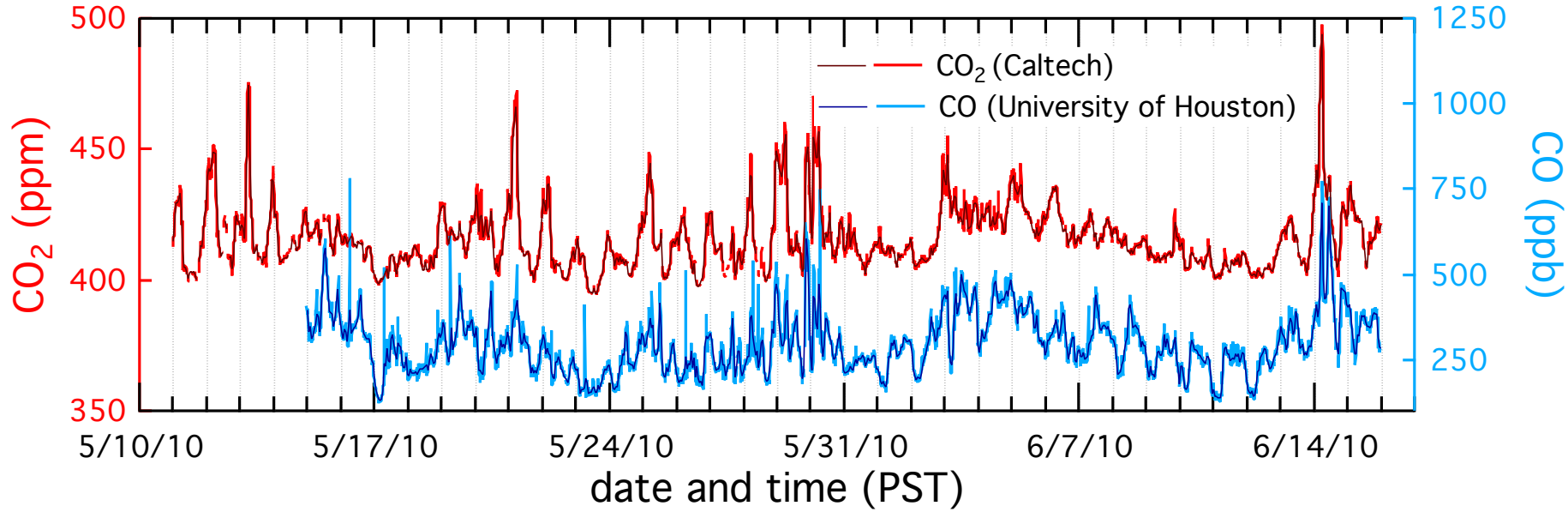


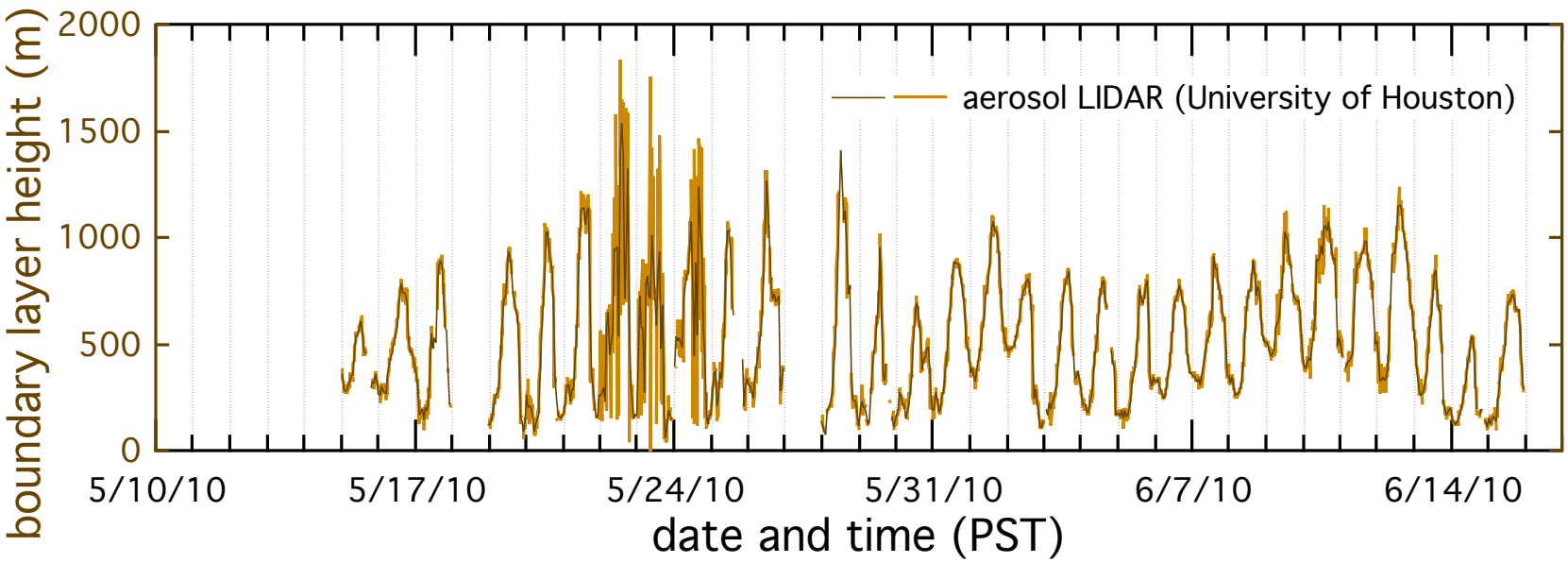
Back trajectories calculated by HYSPLIT for altitudes of 50, 500, and 1000 m from Pasadena (indicated by the star in each panel) for (a) 07:00 and (b) 23:00 on 23 February, 2010; and (c) 06:00 and (d) 20:00 on 20 May, 2010. Symbols on curves indicate 1-hour time increments.

Comparison of CO_2 in Pasadena and Palos Verdes with wind speed in Pasadena

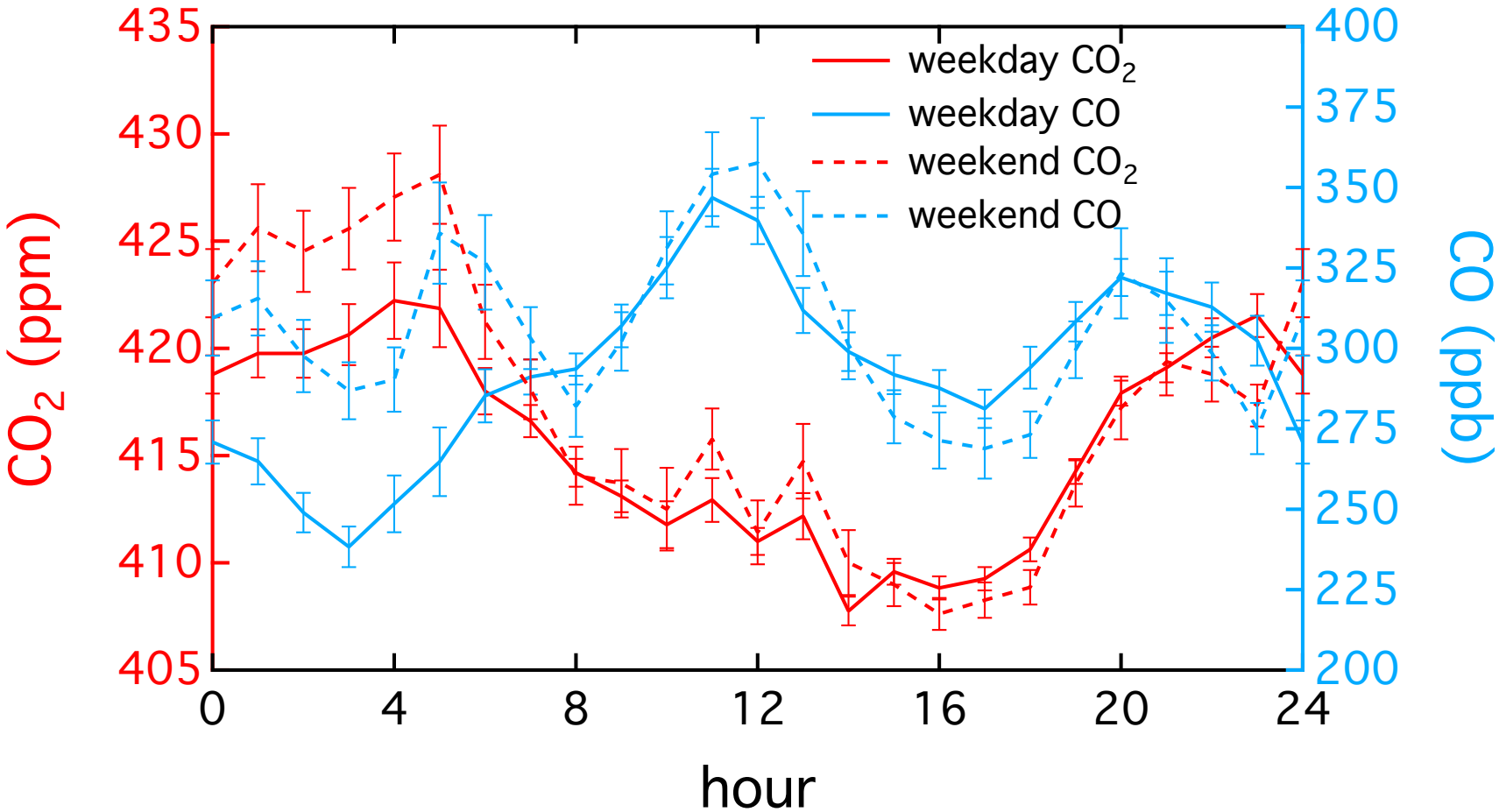


- **Lessons from CalNex-LA ground campaign 15 May – 15 June, 2010**
  - Combining CO, CO_2, and boundary layer height
  - Emission source allocation from CO/CO_2 ratios

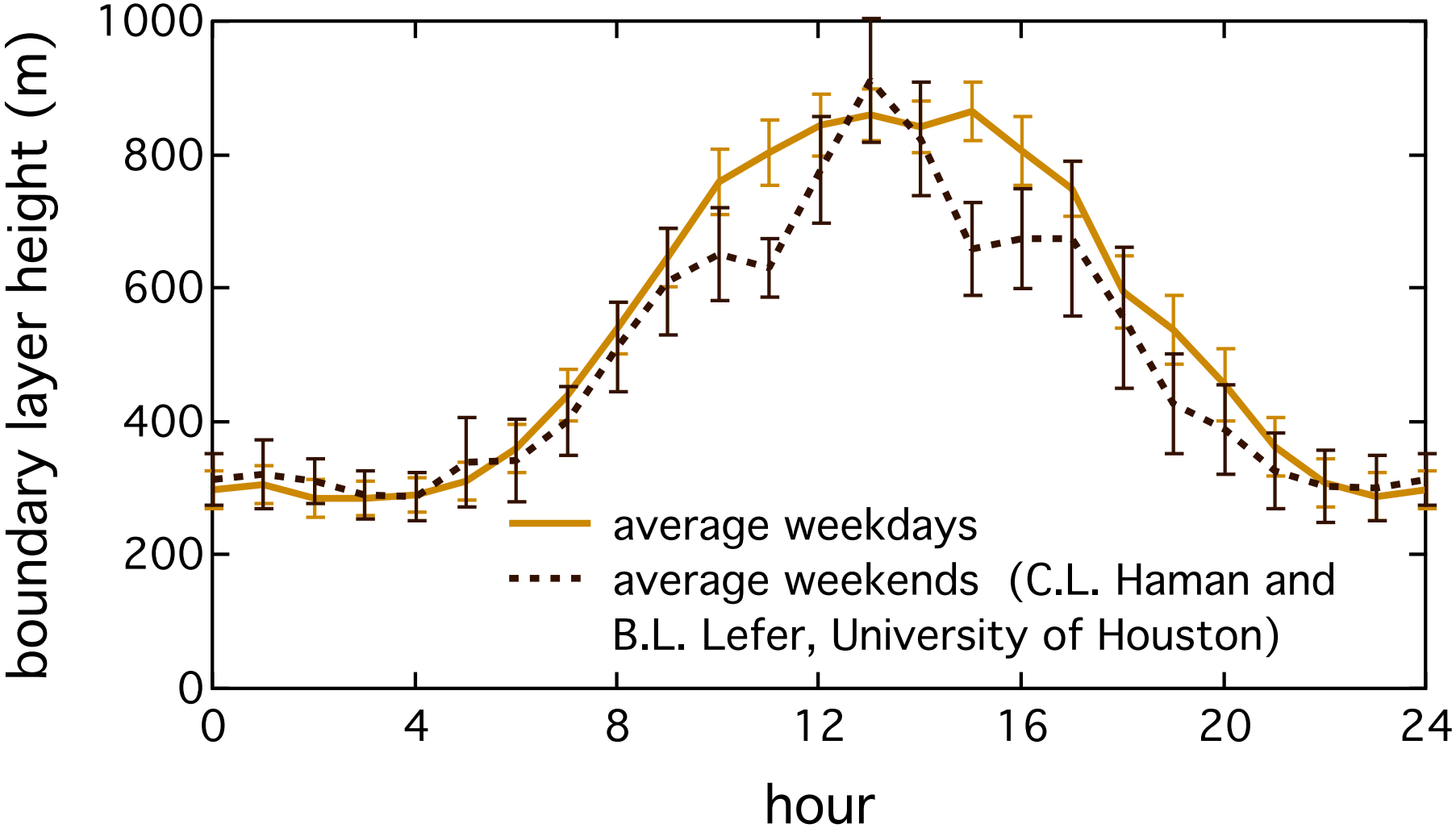

500
450
400
350
CO_2 (ppm)
1250
1000
750
500
250
CO (ppb)
CO_2 (Caltech)
CO (University of Houston)
5/10/10
5/17/10
5/24/10
5/31/10
6/7/10
6/14/10
date and time (PST)

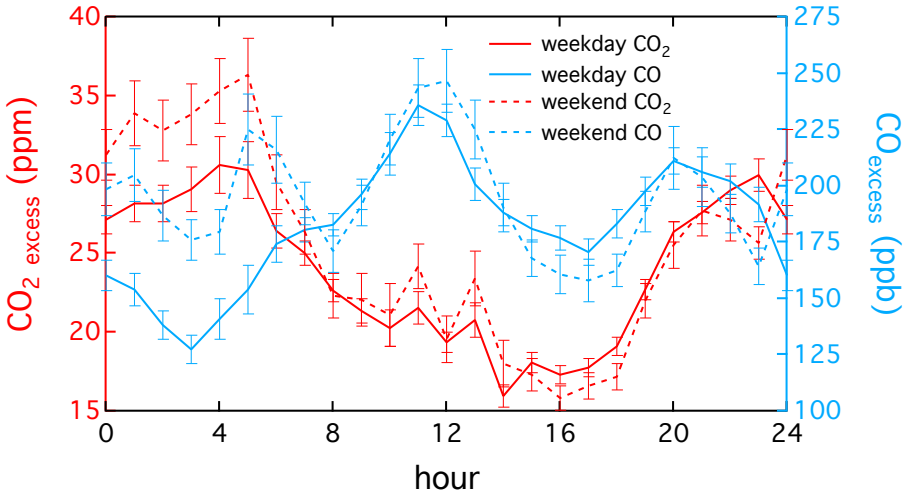

2000
1500
1000
500
0
boundary layer height (m)
aerosol LIDAR (University of Houston)
5/10/10
5/17/10
5/24/10
5/31/10
6/7/10
6/14/10
date and time (PST)

Weekday and Weekend Diurnal Variation of CO_2 and CO Mixing Ratios

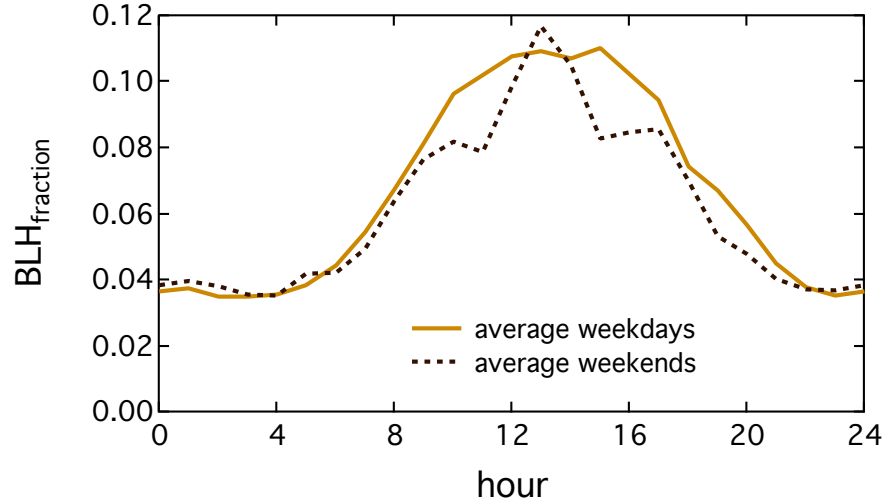


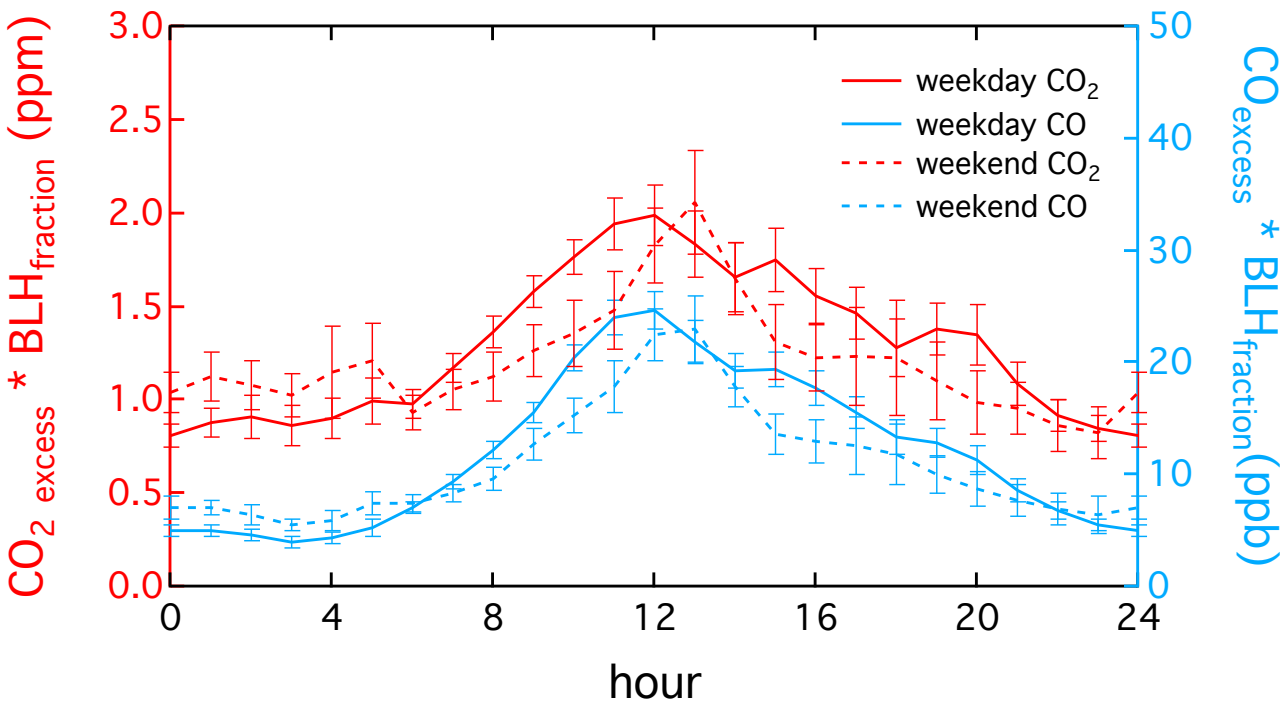
Weekday and Weekend Diurnal Variation of Boundary Layer Height above Ground Level



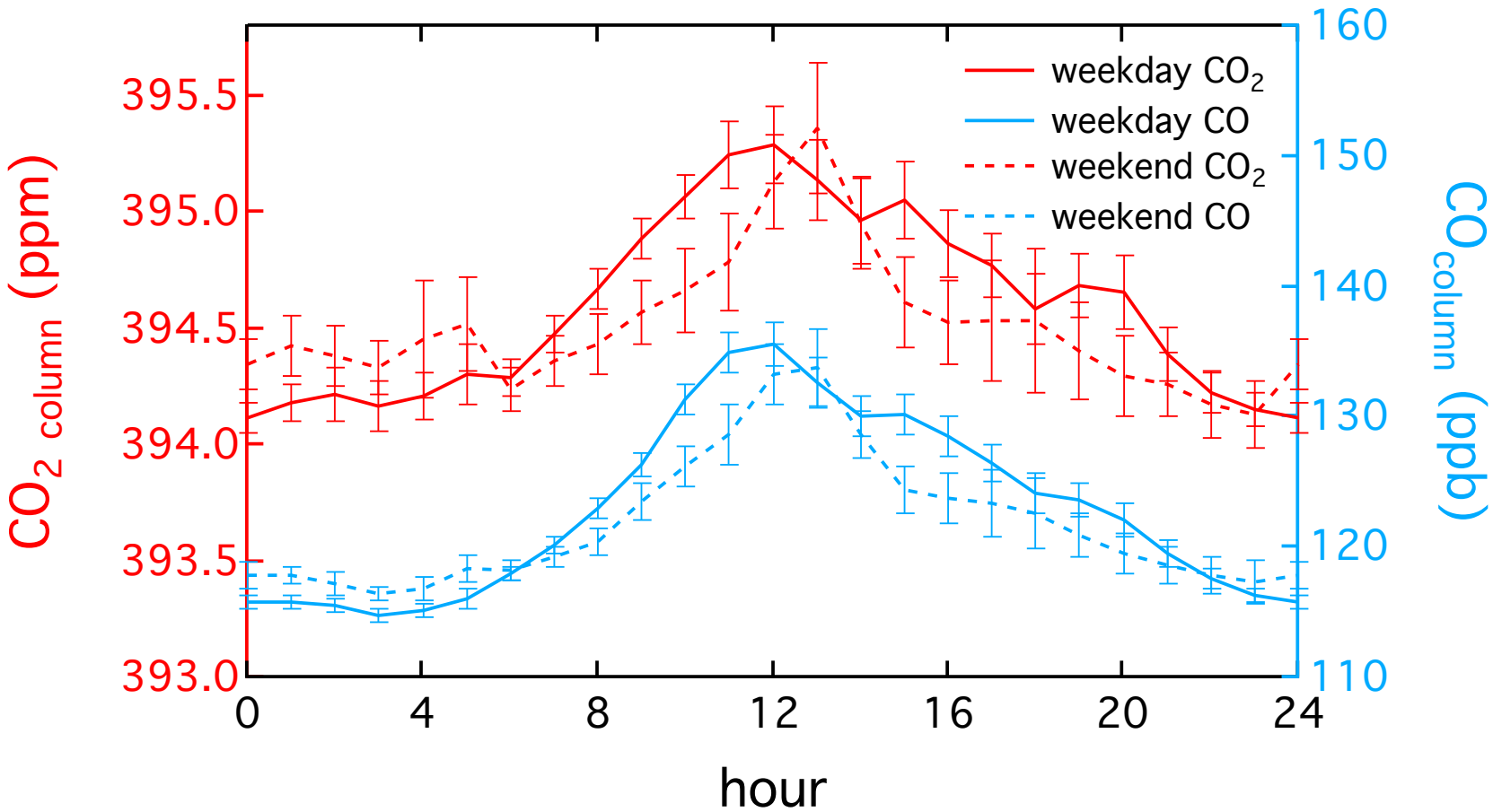

weekday CO_2
weekday CO
weekend CO_2
weekend CO
$CO_{2\ excess}$ (ppm)
CO_{excess} (ppb)
hour

*


average weekdays
average weekends
$BLH_{fraction}$
hour

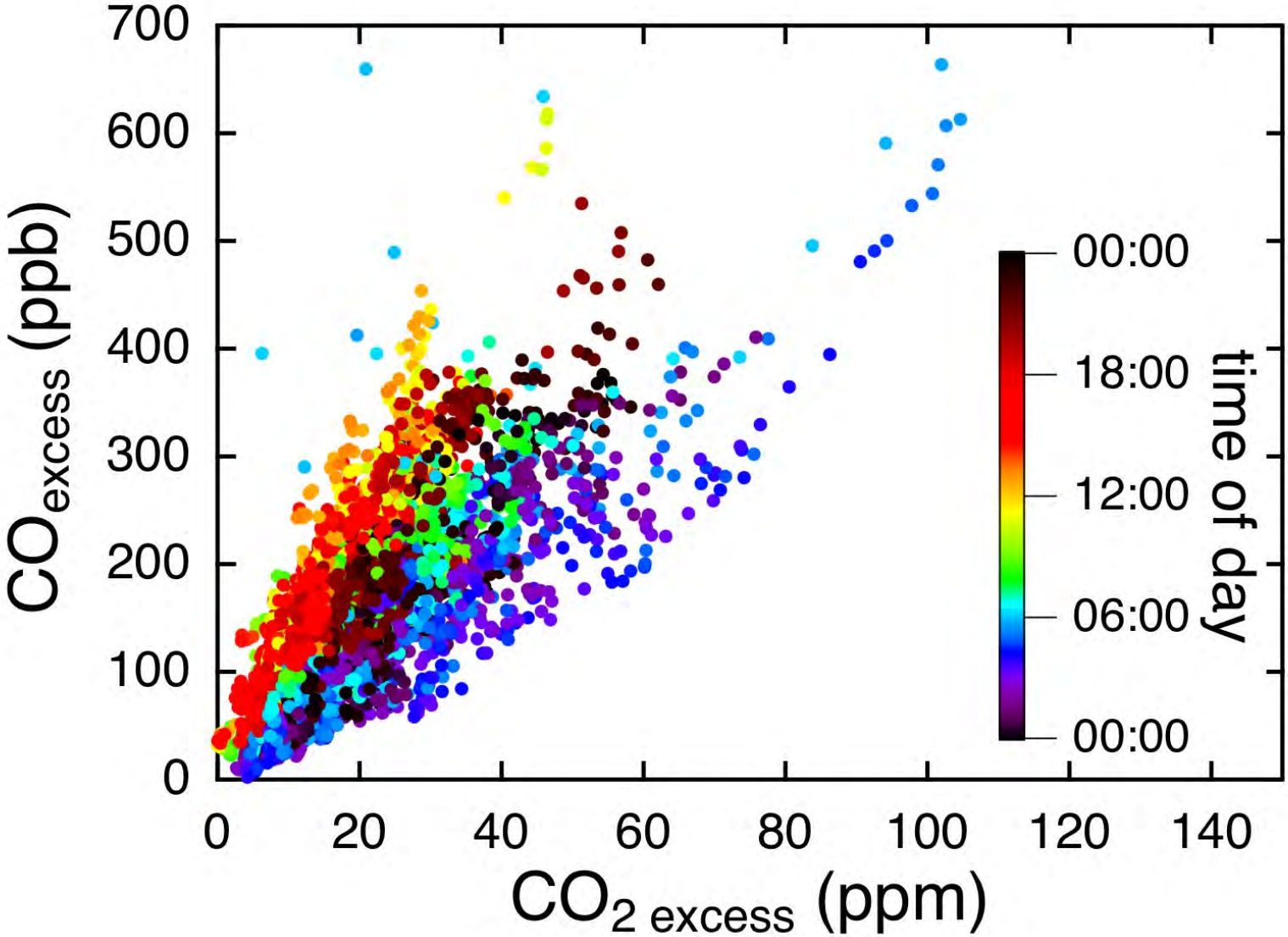

weekday CO_2
weekday CO
weekend CO_2
weekend CO
$CO_{2\ excess}$ * $BLH_{fraction}$ (ppm)
CO_{excess} * $BLH_{fraction}$ (ppb)
hour

Weekday and Weekend Diurnal Variation of CO_2 and CO Mixing Ratios Corrected for Boundary Layer Height Variations

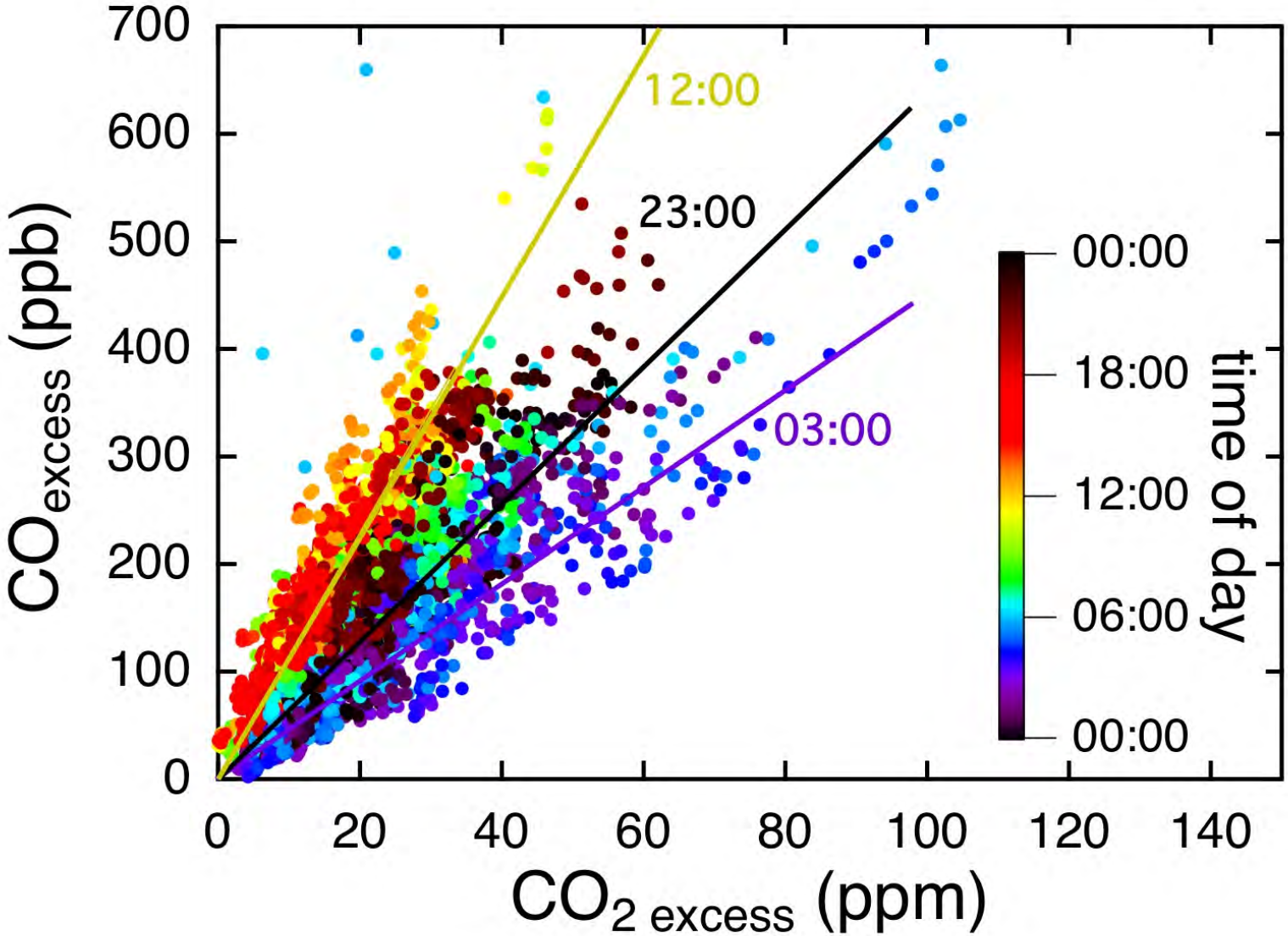


Can we use the ratio of these two components to give a meaningful source allocation to the local contributions?

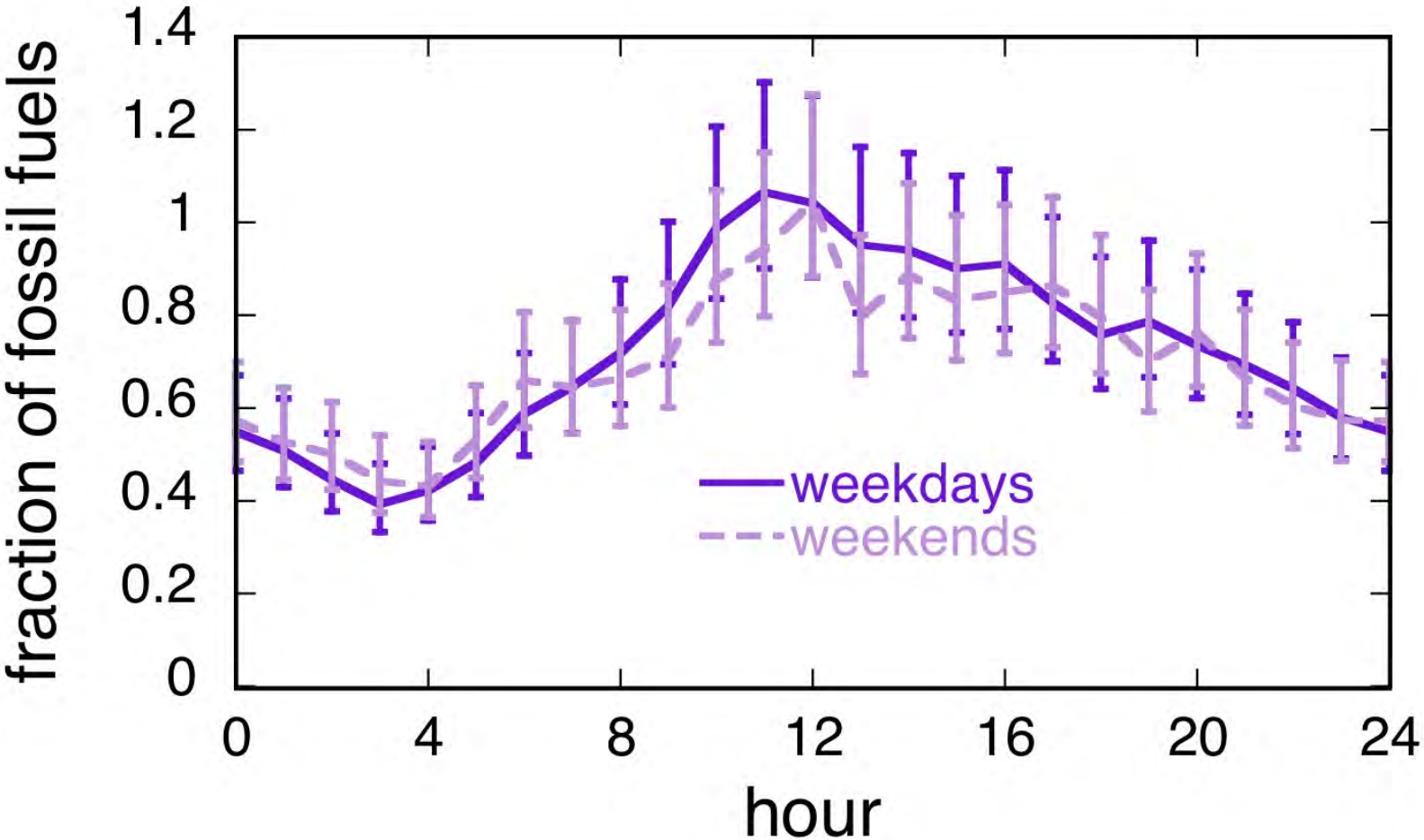
CO vs CO_2 in excess of background vs time of day



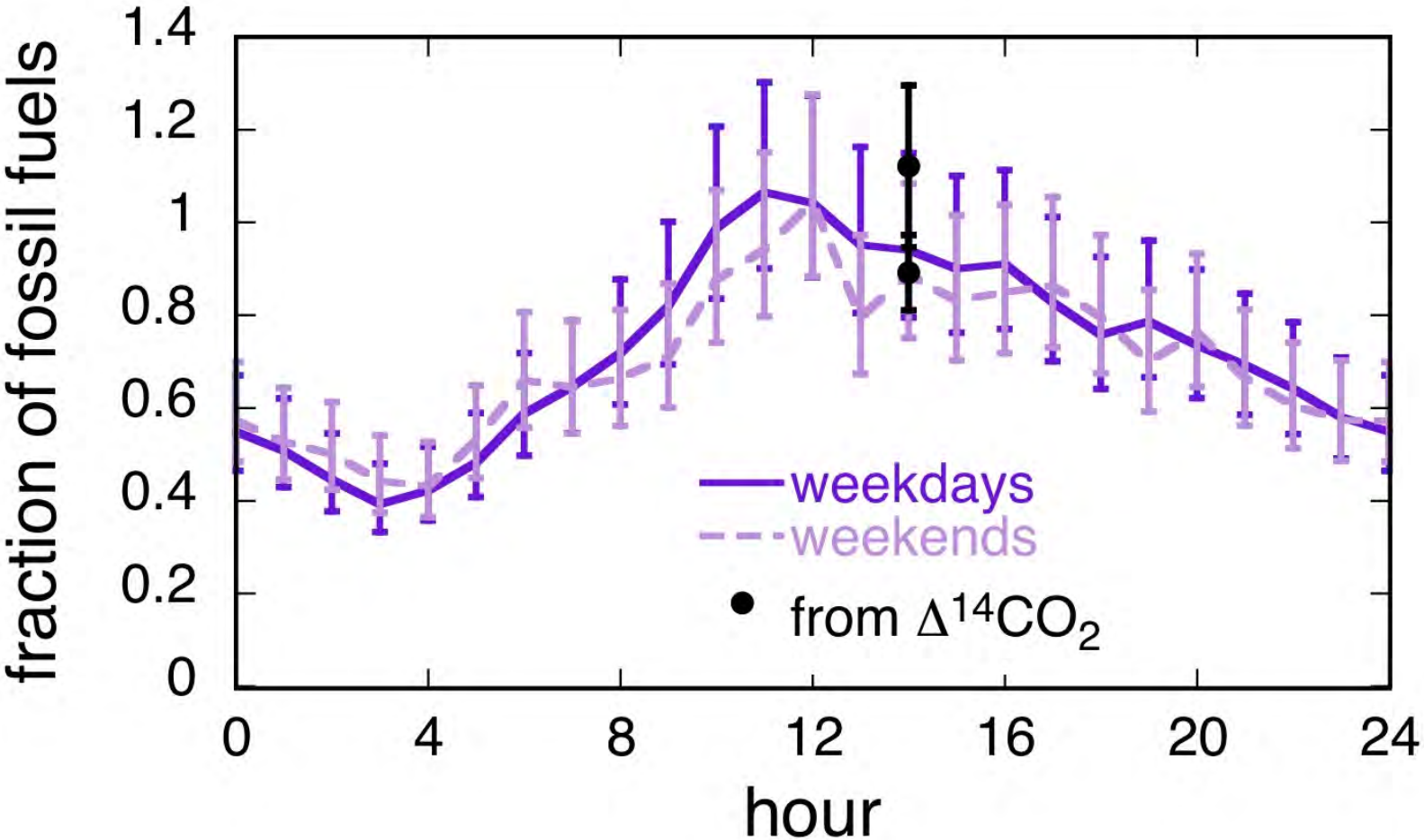
CO vs CO_2 in excess of background vs time of day



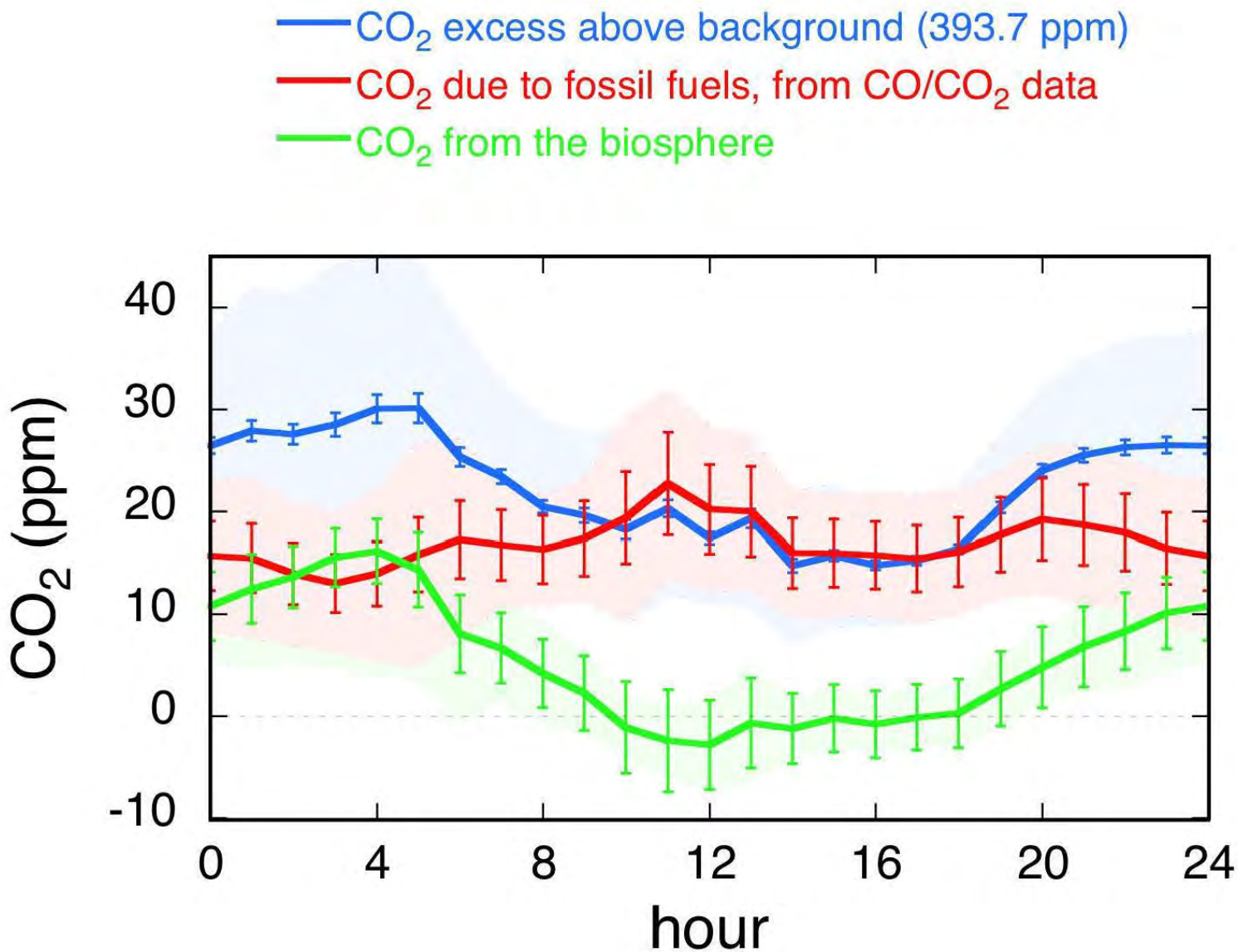
Fraction of fossil fuel combustion products in the local CO_2 emissions from these $CO_{excess}/CO_{2\ excess}$ ratios



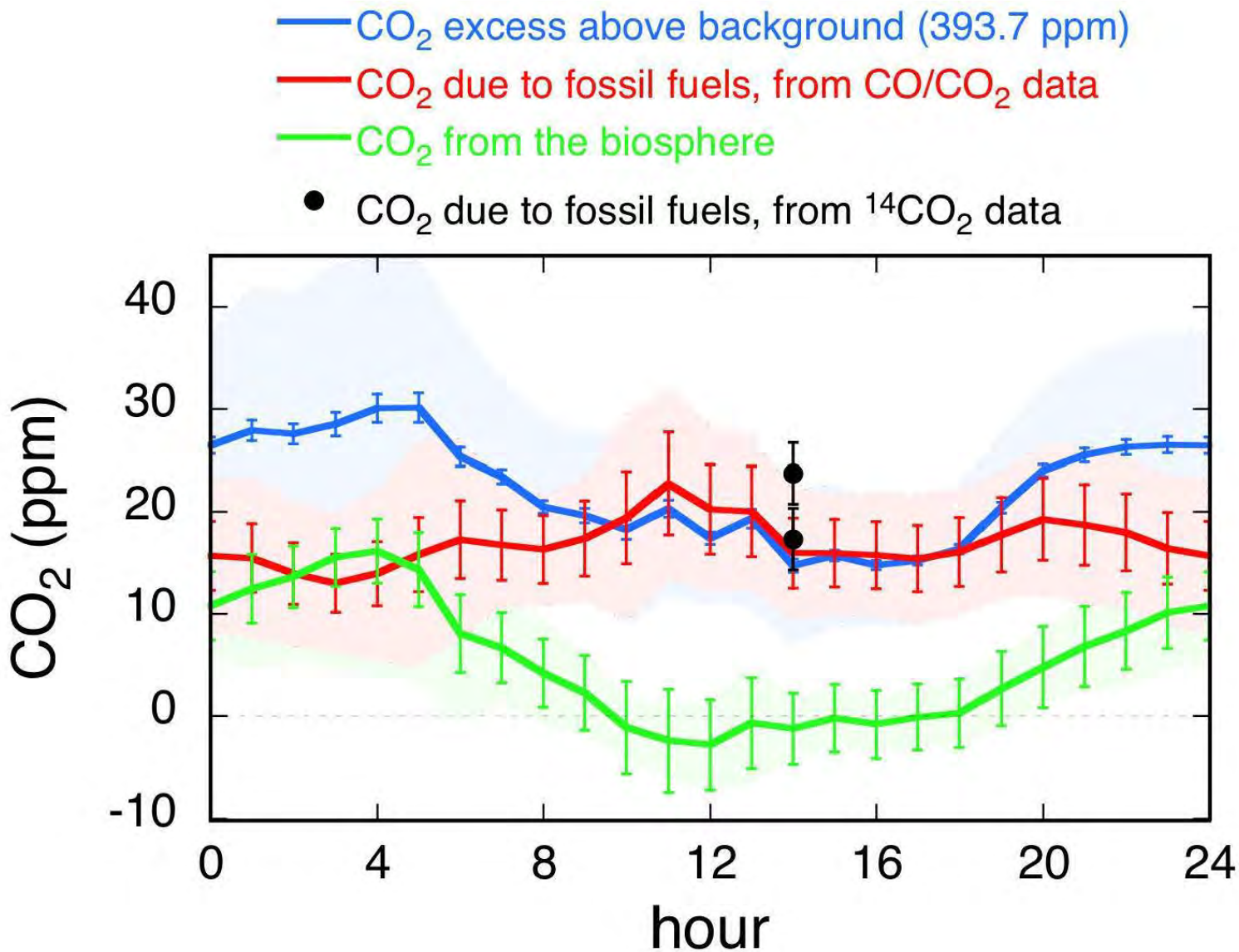
$\Delta^{14}CO_2$ results are consistent with the CO/CO_2 results



Amount of the local emissions of CO_2 from different sources



Compare with $\Delta^{14}CO_2$ results



Conclusions - 1

- Long term trends show that the yearly increase in CO_2 in Pasadena is in general similar to that in clean air.

- Periodicities of 1 and 0.5 years are seen in clean air, whereas there is a significant anthropogenic period of 1 week seen in Pasadena.

Conclusions - 2

- Stable carbon isotope ratios are consistent with inventories indicating a long term mixture of ~60:40 petroleum:natural gas burned. Less than 20% biogenic emissions are allowed by the errors.

- Radiocarbon indicates seasonal variations in the local contributions of both anthropogenic and biogenic sources.

Conclusions - 3

- Diurnal patterns are due mainly to variations in boundary layer height, with superimposed anthropogenic and meteorologic influences.

- Using CO/CO_2 ratios we can derive the diurnal cycle of both anthropogenic and biogenic emissions.