

Greenhouse Gas Measurements at Walnut Grove Tower

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GLOSSARY OF TERMS, ACRONYMS AND SYMBOLS

Glossary of Terms and Acronyms

| | |
|------------------------|---|
| AB-32 | Assembly Bill 32 |
| AGL | above ground level |
| BAAQMD | Bay Area Air Quality Management District |
| Bayesian inverse model | an inverse modeling approach that uses a “prior” (guess before observations are taken into account) probability and a "likelihood function" derived from a statistical model (e.g., a normal probability distribution) for the observed data. |
| CARB | California Air Resources Board |
| CALGEM | California Greenhouse Gas Emission Measurements |
| CEC | California Energy Commission |
| CH ₄ | methane |
| CL | confidence level |
| CO | carbon monoxide |
| CO ₂ | carbon dioxide |
| EPA | Environmental Protection Agency |
| ESRL | Earth System Research Laboratory |
| Gg | giga gram, 10 ⁹ g |
| GHG | greenhouse gas |
| GWP | global warming potential; a relative measure of how much heat a greenhouse gas traps in the atmosphere, typically compared to the amount of heat trapped by a similar mass of carbon dioxide |
| in-situ | a measurement system where instrumentation is located directly at the site and in contact with the air |
| inverse model | mathematical estimation technique to calculate the causal factors (e.g., most probable emissions in this study) from a set of observations |
| IPCC | Intergovernmental Panel on Climate Change |
| LBNL | Lawrence Berkeley National Laboratory |
| LGR | Los Gatos Research |
| μmol | micromole (10 ⁻⁶ mole) |
| mixing ratio | number of moles of a gas per mole of air or volume of a gas per volume of air; henceforth calculated per mol or volume of dry air |
| nmol | nanomole (10 ⁻⁹ mole) |
| NOAA | National Oceanic and Atmospheric Administration |
| PBL | planetary boundary layer; also known as the atmospheric boundary layer (ABL), the lowest part of the atmosphere directly influenced by its contact with a land surface. |
| PBLH | planetary boundary layer height |
| per mil | parts per thousand |

| | |
|------|----------------------------|
| ppb | parts per billion |
| ppm | parts per million |
| RMS | root-mean-square |
| SFBA | San Francisco Bay Area |
| UTC | Coordinated Universal Time |

Symbols

| | |
|-----------------------|--|
| C | mixing ratio of gas |
| $\Delta^{14}\text{C}$ | radiocarbon to ^{12}C ratio relative to std: $(^{14}\text{C}:^{12}\text{C}/^{14}\text{C}_{\text{std}}:^{12}\text{C}_{\text{std}} - 1) * 1000$ |
| z_i | boundary layer height |

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ABSTRACT

California has committed to an ambitious plan to reduce greenhouse gas (GHG) emissions to 1990 levels by 2020 through Assembly Bill 32 (AB-32). This has led to efforts to measure, quantify, and mitigate emissions of a variety of key GHGs. Over the past decade a variety of studies have estimated GHG emissions in different regions of California using measurements from ground towers, aircrafts, and satellites. Notably, many of the studies have used data from a tall-tower near Walnut Grove, in central California (henceforth WGC). We report a project with the objective of providing data for GHG emission estimates in central California. Here, we conducted a two-year measurement study of GHG concentrations from the WGC tower, which we combined with previous measurements to estimate temporal trends in multiple GHGs over the past decade. Results include a measurement record from October, 2007 to June, 2017 including hourly resolved time series measurements of primary GHG species (CO_2 , CH_4 , N_2O and CO) at 91 and 483 m above ground level, and flask measurements near 2 pm PST every other day for the above species, the radiocarbon isotope, $^{14}\text{CO}_2$, several important industrially produced GHGs, and other volatile organic compounds that might be used as tracers for anthropogenic activities. Using the flask measurements, we estimated temporal trends in the primary GHG species that show continued increases in atmospheric concentrations that are broadly similar to those observed at mid-Pacific oceanic site but with greater variability, indicating influence from local-regional sources. The resulting decadal record provides information on GHG concentrations for central California that could be used to estimate regional emissions when combined with other information in an inverse model context. We conclude by recommending that estimates of GHG emissions in the future will require continued long-term observations at multiple sites in emitting air basins

EXECUTIVE SUMMARY

Background

California has committed to an ambitious plan to reduce greenhouse gas (GHG) emissions to 1990 levels by 2020 through Assembly Bill 32 (AB-32). This has led to efforts to measure, quantify, and mitigate emissions of a variety of key GHGs. Over the past decade a variety of studies have estimated GHG emissions in different regions of California using measurements from ground towers, aircrafts, and satellites. Notably most of the studies have used data from a tall-tower near Walnut Grove, in central California (henceforth WGC).



Figure 1. California Air Resource Board GHG measurement network showing the location of the Walnut Grove tower (red). (<https://ww2.arb.ca.gov/sites/default/files/inline-images/ghgnetworkmap.png>)

Objectives and Methods

The objective of this project is to provide data for current and future GHG emission estimates in central California.

We conducted a two-year (2015-2017) measurement study of GHG measurements from the WGC tower, which we combined with previous measurements at the site to estimate temporal trends in multiple GHGs over the 2007-2017 period. This yielded a nearly decadal record of GHG data from Walnut Grove.

The measured data include both hourly resolved time series measurements of primary GHG species (CO₂, CH₄, N₂O and CO) at 91 and 483 m above ground level, and flask measurements near 2 pm PST every other day for the above species, including the radiocarbon isotope, ¹⁴CO₂, industrially produced GHGs, and other volatile organic compounds that might be used as tracers for anthropogenic activities.

We then used the measurements to perform an analysis long-term trends in GHG concentration for the California Central Valley and San Francisco Bay Area region over the 10-year period from 2007-2017 and then compare those trends with trends in GHG measurements obtained at the NOAA sampling site on Mauna Loa, HI (henceforth MLO).

Results

- We produced a measurement record from October, 2007 to June, 2017 including hourly resolved time series measurements of primary GHG species (CO₂, CH₄, N₂O and CO) at 91 and 483 m above ground level, and flask measurements near 2 pm PST every other day for the above species, the radiocarbon isotope, ¹⁴CO₂, industrially produced GHGs, and other volatile organic compounds that might be used as tracers for anthropogenic activities.
- The temporal trends determined for most of the GHG species show continued increases in atmospheric concentrations that are broadly similar to those observed at the Mauna Loa, HI, mid-Pacific oceanic site but with greater variability, indicating influence from local-regional sources.

Conclusions and Recommendations

- The estimated trends in atmospheric concentrations are roughly consistent with trends estimated for measurements at Mauna Loa
- Estimation of State-total GHG emissions in the future will benefit from continued long-term observations at multiple sites in emitting air basins

PROJECT REPORT

1. Introduction

California has committed to an ambitious plan to reduce greenhouse gas (GHG) emissions to 1990 levels by 2020 through Assembly Bill 32 (AB-32). This has led to efforts to measure, quantify, and mitigate emissions of a variety of key GHGs. At present, the California Air Resources Board provides comprehensive inventory estimates of GHG emissions by gas, and categorical source sectors that are based on detailed activity data, emission factors and industry reporting of major emitters at the annual timescale [CARB, 2017]. Because the inventory is subject to uncertainty in activity data, emission factors, or under-reporting, it is also valuable to make independent estimates of emissions across scales from an individual facility in a given hour to the entire state averaged over an entire year.

Over the past decade a variety of studies have estimated GHG emissions in different regions of California using measurements from ground towers, aircrafts, and satellites. Notably most of the studies have used data from a tall-tower near Walnut Grove, in central California (henceforth WGC). For fossil fuel CO₂ (ffCO₂), initial modeling suggested the need for a tower measurement network [Fischer et al., 2005], long-term atmospheric measurements were reported for a single site in southern California using isotope measurements Newman et al. [2013; 2016], more recent modeling identified the need for highly resolved emission maps [Feng et al., 2016], and a recent state-wide study applied radiocarbon measurements from 10 sites to estimate ffCO₂ emissions across California [Graven et al., 2018].

For methane (CH₄), Zhao et al. [2009] was the first to estimate central California emissions using WGC tower measurements, Wecht et al. [2014] estimated CH₄ emissions from California using a one-month aircraft campaign, and Jeong et al. [2016] estimated CH₄ emissions over California based on a year of measurements from 13 tower sites including WGC. At the sub-regional scale, many CH₄ studies have focused on the urban regions of southern California (e.g., Wunch et al. [2009]; Hsu et al. [2010]; Wennberg et al. [2012]; Peischl et al. [2013]; Wunch et al. [2016]).

For nitrous oxide fewer studies have been published, including initial work on central California using WGC [Jeong et al., 2012] and recently, measurements from WGC and a network of 5 other towers operated by CARB [Jeong et al., 2018]. Throughout these efforts WGC, has played a key role in producing high-quality GHG measurements for inverse model estimates of regional emissions in central California and acting as a key site for development of new techniques including multi-species estimation of source-specific emissions [e.g., Jeong et al. 2017].

In addition to the major GHG species, several different high global warming potential (HGWP) industrial gases are of potential importance. These include chemicals used as refrigerants, propellants, and foaming agents, such as the banned ozone depleting

substances (e.g., CFC-11, H1211) and their more modern replacements (e.g., HCFC-134a) (Gallagher, et al., 2014). In addition, the electrical insulator sulfur hexafluoride (SF₆) is still in use and of great concern, because SF₆ has the highest GWP of any ODS substitute, with a 100-year GWP of 22,800 (IPCC AR4) with emissions either relatively constant in the United States since 2012 (U.S. EPA, 2018), or increasing in the developing world (Zhou et al., 2018).

To maintain an ongoing record of high quality multi-species GHG measurements, we proposed a project with the following objectives:

1. Operate and maintain the Walnut Grove tower site to collect both continuous records of CO₂, CH₄, N₂O, and CO mixing ratios from 91 and 483 m, and flask samples from 91 m for analysis of all major GHG's, and associated tracers.
2. Perform data quality control, calibration and analysis:
 - a. data calibration and quality control to provide CARB with a three-year measurement record of continuous GHG species and NOAA-ESRL flask analyses of major GHG species and VOC tracers.
 - b. Long-term analysis of the GHG trends in the California Central Valley and San Francisco Bay Area region over a 10-year period using the data collected from this project as well as data collected through prior research efforts at this site.

To address the above objectives we conducted a two year study continuing GHG measurements at the WGC tower and then estimating temporal trends in multiple GHGs from nearly a decade record of WGC measurements. In the methods section below, we describe both the continuous measurements of primary gases (CO₂, CH₄, N₂O, and CO) made at the tower, periodic flask sampling and analysis of those gases, as well as others (radiocarbon ¹⁴CO₂, halo carbons, and other trace species), as well as methods for estimating the temporal trend in GHG mixing ratios. In results we report the time series of measured gases, estimate the trends in GHG concentration over time from WGC, and compare them with trends at an oceanic site (Mauna Loa Observatory, Hawaii). In the discussion we comment on the observations and trends and conclude with a recommendation for continued measurements.

2. Materials and Methods

2.1. Walnut Grove Tower Site

The CARB GHG measurement network, including the Walnut Grove site in central California (WGC; 38.27°N, 121.49°W, 0 m above current sea level), is shown in Figure 1. The site is an ~ 500m tall television transmitter tower located in a farm field at the eastern portion of the Sacramento River delta. The site receives air from both the San Francisco Bay area (SFBA), the Sacramento Valley, and the San Joaquin Valley, with flows to the site varying with the time of day, the season, and intermittent weather fronts. In general, winds are from the west during the day in spring and summer, but with both

northerly and southerly valley flows in other seasons, while boundary layer mixing heights vary from near the surface in winter mornings to 1.5-2 km on sunny dry days [Fischer et al., 2016; Bagley et al., 2017]. For example, the annually averaged daytime sensitivity to surface GHG emissions (or “footprint”) for air samples collected at 91 m above the ground in the June 2013 to May, 2014 period is drawn from the inverse modeling work reported by Jeong et al. (2016) is shown in Fig 2. Simply put, the footprint map provides a quantitative expression for how large a GHG concentration enhancement (ppm) is obtained per unit of surface GHG flux ($\mu\text{mol m}^{-2} \text{s}^{-1}$). Here, Fig 2 shows strong sensitivity to emissions in the region surrounding the WGC tower and for more than 100 km in the dominant upwind directions.

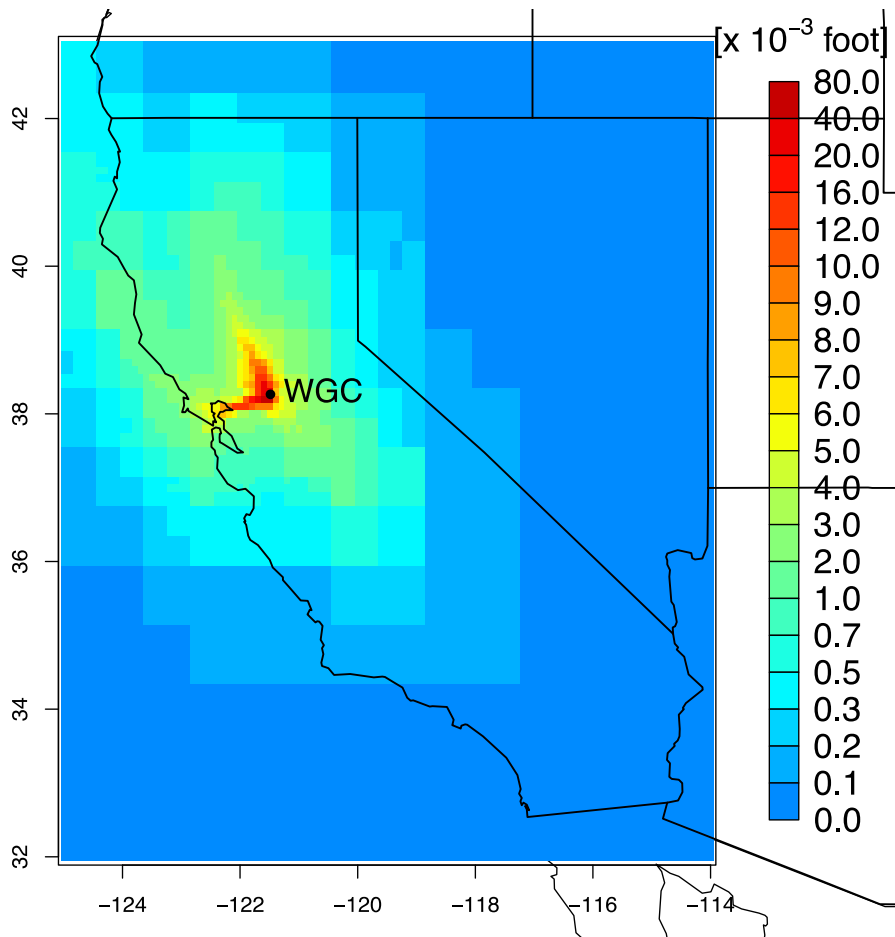


Figure 2. Map showing the annual averaged midday (11am to 5pm PST) sensitivity to surface emissions for observations at 91 m above the ground at the Walnut Grove field site for the June, 2013 to May, 2014 period (image courtesy S. Jeong, LBNL).

Significance of the Walnut Grove Tower Site

A variety of studies have estimated GHG emissions in different regions of California over the past decade using measurements from ground towers, aircrafts, and satellites. Notably most of the studies have used data from the WGC tall tower site in central California. For fossil fuel CO₂ (ffCO₂), initial modeling suggested the need for a tower measurement network [Fischer et al., 2005], and WGC data was used in a recent state-wide study applied radiocarbon measurements from 10 sites to estimate ffCO₂ emissions across California [Graven et al., 2018]. For methane (CH₄), Zhao et al. [2009] was the first to estimate central California emissions using WGC tower measurements, and Jeong et al. [2016] estimated CH₄ emissions over California based on a year of measurements from 13 tower sites including WGC. For nitrous oxide fewer studies have been published, including initial work on central California using WGC [Jeong et al., 2012] and recently, measurements from WGC and a network of 5 other towers operated by CARB [Jeong et al., 2018]. Throughout these efforts WGC, has played a key role in producing high-quality GHG measurements for inverse model estimates of regional emissions in central California and acting as a key site for development of new techniques including multi-species estimation of source-specific emissions [e.g., Jeong et al. 2017]. However, as shown in previous studies (e.g., Jeong et al. [2012b, 2013, 2014]) emissions in California are still uncertain due to lack of activity data and incomplete understanding of emission processes, complicated by California's diverse emission sources, complex topography and weather patterns (e.g., land-sea breeze). Continued measurements at WGC ensure that GHG data are available for future studies and applications such as trend analysis, and emissions estimations using inverse modeling. This is particularly important for California's ambitious plan to reduce greenhouse gas (GHG) emissions to 1990 levels by 2020 through Assembly Bill 32 (AB-32), which requires accurate accounting of emissions for effective mitigation planning and verification of future emission reductions.

2.2. In-Situ Measurements

Measurements at WGC include semi-continuous in-situ measurements of CO₂, CO, CH₄ at three heights (30, 91, and 483 m AGL), automated measurements at two heights (91 and 483 m AGL) of N₂O and CO made by LBNL, and flask sampling (at 91m AGL) for the National Oceanic and Atmospheric Administration (NOAA).

A photograph of the instrument system is shown in Figure 3. As described by Andrews et al. (2014), air samples are drawn down from three heights on the tower by air pumps, pressurized to 10 psig (pounds per square inch gauge pressure), passed through 5 °C water traps, and supplied to a valve manifold. Air exiting the manifold is directed to separate temperature controlled membrane (Nafion) driers (one for the CO₂ and CH₄, and a 2nd for CO), which maintain the sample air streams at near -30°C dew point. Output of the driers is directed to a set of gas analyzers (Picarro 1301, Picarro Inc., Sunnyvale, CA) for CO₂, and CH₄; a Licor 4000 (Licor Inc., Lincoln NB) for CO₂; and a Thermo-Electron 48TC for CO). Air samples are switched between the three levels on the tower every 300 s, and the last 120 seconds of each sample used for further analysis. These instruments

are calibrated using 3rd order polynomial fit of measured instrument response to true gas mixing ratio every three hours using four gas standards provided by NOAA. However, as noted by Andrews et al. (2014), the Picarro instrument is sufficiently stable and linear that a single daily linear fit using two gas standards is sufficient to maintain instrument accuracy at levels limited by the accuracy of the calibration gas standards (~ 0.05 ppm for CO₂ and < 0.1 ppb for CH₄).



Figure 3. Photograph of instrument racks (left) and calibration gases (right) at the Walnut Grove field site.

Supporting this project we also measured N₂O and CO. A schematic of the gas processing and measurement system for N₂O and CO is shown in Figure 4. Here, we used the existing preconditioned (5°C dew point, 10 psig) air streams from two of the three levels (91 and 483 m AGL). Air was multiplexed through a pressure controller (at 800 Torr) to a membrane drier (Nafion), which maintained the dew point near -20°C, and then supplied it to a CARB supplied off-axis Integrated Cavity Output Spectrometer (LGR Model 907-0015; Los Gatos Research Inc., Los Gatos, CA). The multiplexer switched the sample air between the two heights on the tower every 400 s. Measurements were allowed to settle for 280 s, with only the last 120 s used for the measurement. Following a calibration protocol similar to that for the Picarro, the LGR instrument response was periodically fit to a linear function (offset and gain), and checked using two methods. The linear fit was performed using two working standards (tied to standards supplied by NOAA) to adjust the gain and offset of the instrument every 3 hours. As a primary check a third “target” standard was used to check the calibration at times midway between the linear fit calibrations. This produced target check measurements with differences from true values varying with root-mean-square (RMS) error of less than 0.1 ppb. Second, we also compared the calibrated in-situ N₂O measurements with results from the periodic flask measurements performed by NOAA. Here, the in-situ measurements (interpolated

to the time of the flask samples) varied from $\sim 0.3 - 0.5$ ppb, consistent with the expected variation in flask measurements (<https://www.esrl.noaa.gov/gmd/ccgg/flask.php>).

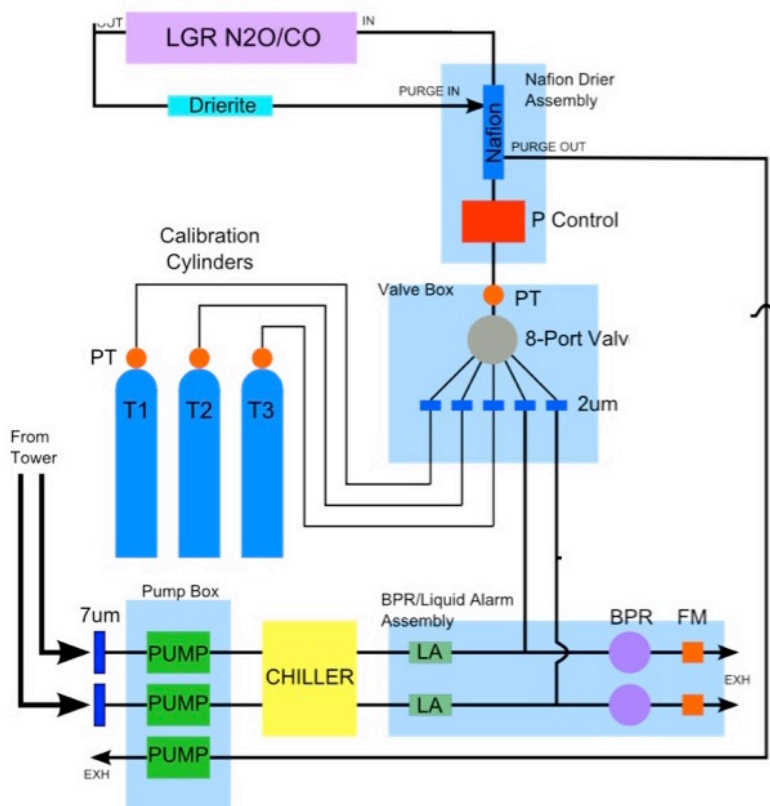


Figure 4. Schematic illustration of gas sampling handling sub-system used for N₂O/CO measurements at Walnut Grove field site. Gas samples enter system from tower, are dried in two stages (chiller and Nafion driers) and measured using a Los Gatos Research (LGR) gas analyzer. Instrument calibration is determined and checked periodically with known calibration gases.

2.3 Flask Sampling and Analysis

Flask samples are gathered from the 91 m level at 1400 PST (Pacific Standard Time) for approximately 5 minutes, roughly every other day and subsequently analyzed at NOAA for a suite of long-lived GHG (<http://www.esrl.noaa.gov/gmd/ccgg/>), selected halocarbons and volatile organic compounds (<http://www.esrl.noaa.gov/gmd/hats/>), and for stable isotope and radiocarbon ¹⁴CO₂ (<https://www.esrl.noaa.gov/gmd/ccgg/isotopes/>). All data were screened using quality control flags provided in the NOAA data output. In addition, periods with obvious contamination by regionally significant fires were excluded from trend analysis.

2.4 Trend Analysis

Long-term trends in GHG mixing ratios were estimated using software developed at NOAA that combines models containing both polynomial time dependence and average seasonal cycle harmonics with smoothing, which is named CCGCRV (Thoning et al., 1989; <https://www.esrl.noaa.gov/gmd/ccgg/mb/krvfit/krvfit.html>). In the procedure recommended by NOAA, outlying data points iteratively removed when their values exceeded 95% probability based on average residual error. Remaining points were fit to then fit to a linear model to determine the average trend over the decadal period from 2008 through 2016. Trends determined from measurements at the Walnut Grove site are also compared with trends determined from measurements at the NOAA sampling site on Mauna Loa, HI (henceforth designated as MLO).

3. Results and Discussion

3.1. In-situ Measurements at Walnut Grove

In-situ data were collected continuously in the 2015 to June, 2017 period and combined with data collected in previous work. Resulting dry-mole mixing ratios of CO₂, CH₄, CO, and N₂O are shown as a function of time during the 2007-2017 period in Figure 5. Complete time series data are provided as a separate electronic data file (“wgc-all-1hr-insitu.2007100100-2017063023.20171027.csv.zip”). In general, measurements are higher at night when planetary boundary layers (PBL) are lower than during the day, trapping surface emissions. In particular, this effect is more pronounced in winter when PBL are lower than during the summer. Note, N₂O measurements began in 2012. Periods with gaps indicate periods when different subsystems or instrument required maintenance. Episodic spikes in CO at 483 m (e.g., summer 2008) indicate periods with regionally significant fires.

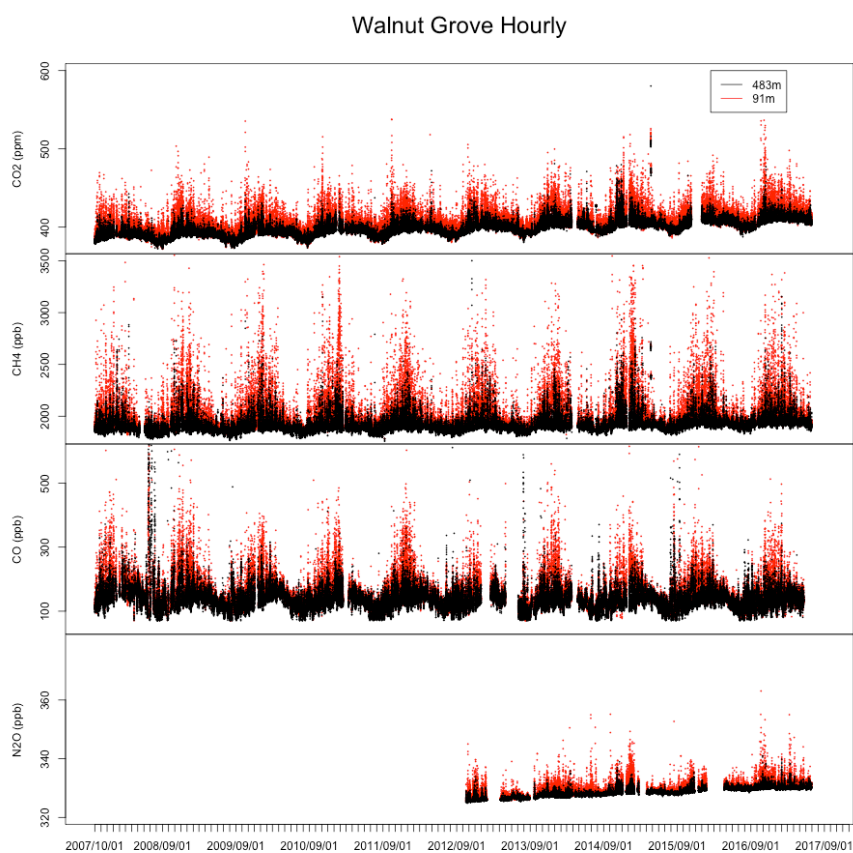
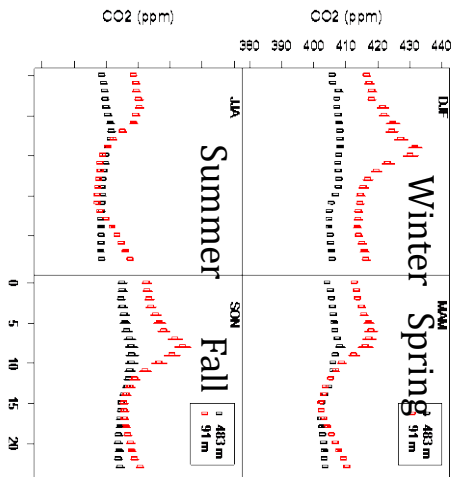


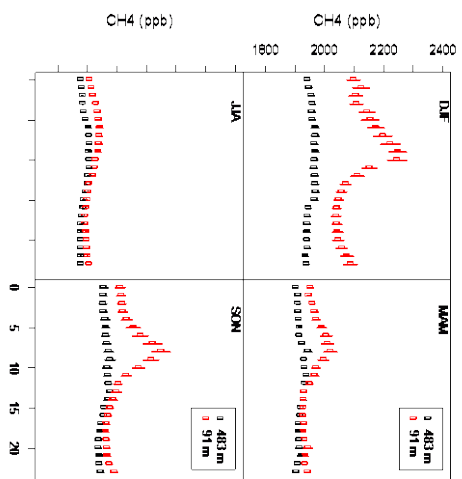
Figure 5. Hourly averaged measurements of CO₂, CH₄, CO, and N₂O mixing-ratios at the Walnut Grove (WGC) tower at 91 (red), and 483 (black) m AGL for the 2007-2017 period.

Using the diurnally resolved measurements, we examine the diurnal cycle of the primary GHGs and CO for the 91 and 483 m sampling heights on the tower. As shown in Figure 6, the highest concentrations and strongest vertical gradient generally occur at night when boundary layers depths and winds are lowest.

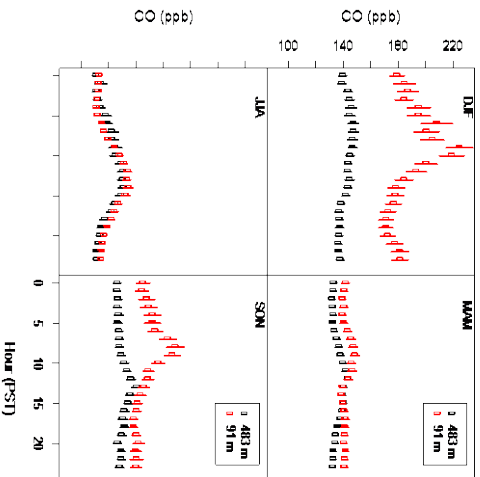
CO₂ (ppm)



CH₄ (ppb)



CO (ppb)



N₂O (ppb)

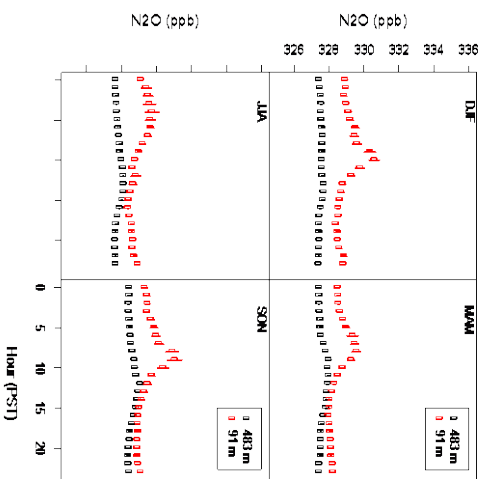


Figure 6. Mean seasonal diurnal cycles of primary GHGs and CO observed at WGC for 2014. Concentration maxima and greatest difference between 91m (red) and 483 m (black) concentrations generally occur at night when boundary layers depths and winds are lowest.

3.2. Flask Sampling at WGC

Flask samples were collected at approximately 2 pm PST every other day at WGC in the 2015- June, 2017 period, shipped to NOAA in Boulder, and analyzed for primary GHGs, radiocarbon ¹⁴C CO₂, a subset of industrially produced GHGs, and selected volatile organic tracers. Complete time series data are provided in a data file attachment as separate

electronic data file and will be posted on the research project website at https://www.arb.ca.gov/research/single-project.php?row_id=65248. For example, the time series of $\Delta^{14}\text{CO}_2$ (Figure 7), shows the gradual decline in the relative abundance of $^{14}\text{CO}_2$ with time, which is primarily due to global decay of bomb spike carbon $^{14}\text{CO}_2$, and additions of (radiocarbon free) fossil fuel CO_2 to the atmosphere (Turney et al. 2018; IPCC, 2007; 2014). However, as with the other primary GHG species, depressions of $^{14}\text{CO}_2$ in winter relative to summer are caused by local fossil fuel CO_2 emissions mixing into shallower boundary layers associated with weak atmospheric mixing.

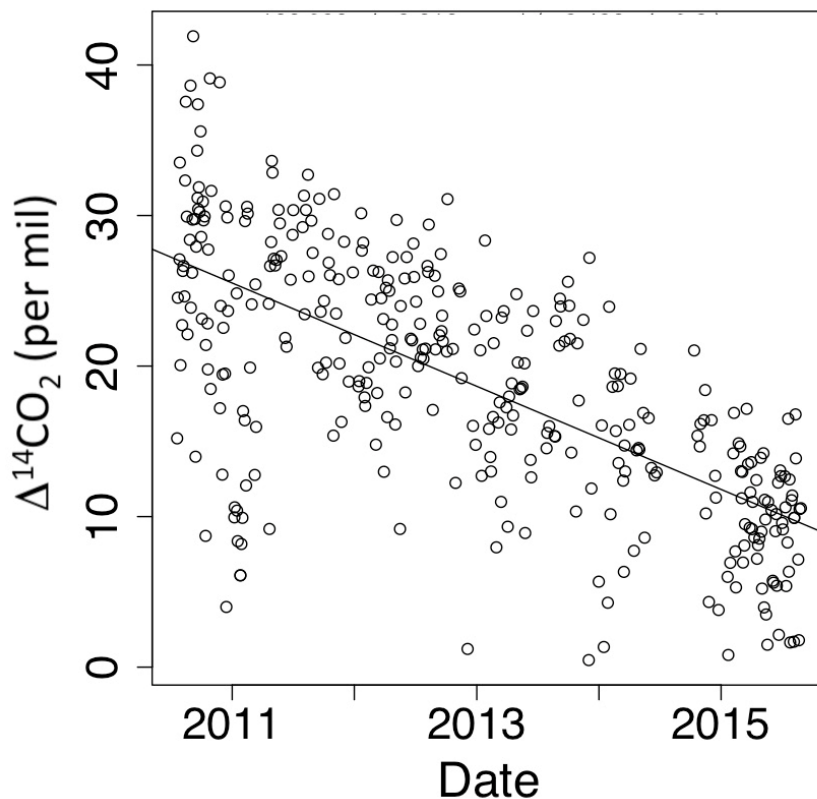


Figure 7. Time series of radiocarbon $\Delta^{14}\text{CO}_2$ for the 2009-2016 time period. The gradual decline is primarily due to global fossil fuel CO_2 additions to the atmosphere. The more occasional stronger depressions are due to local additions, which are accentuated in winter periods with weaker atmospheric mixing.

3.3. Estimated GHG Trends at Walnut Grove and Mauna Loa, HI

The PFP measurements, together with linear trends in primary GHGs and CO and selected high-GWP gases are shown for Walnut Grove in Figures 8 and 9, respectively. As a point of comparison, we also computed best-fit trends for primary GHGs and selected tracers that were measured at the NOAA marine observatory on Mauna Loa, Hawaii. Examples of the resulting trends for primary GHGs and high global warming potential gases are shown in Figure 10 and 11, respectively. For the primary GHGs, all mixing ratios are increasing, except for CO, which is approximately steady with time. For the high-GWP gases, some are clearly increasing due to continued global emissions,

while some are declining due gradual chemical removal following to phase-out for ozone protection under the Montreal protocol. These observed trends can be assumed to represent marine background values for that latitude and time, though we note that strong latitudinal gradients combined with varying long-range transport likely lead to variations in the background GHG mixing ratios for air reaching continental sites like WGC (e.g., Bruhwiler et al., 2017).

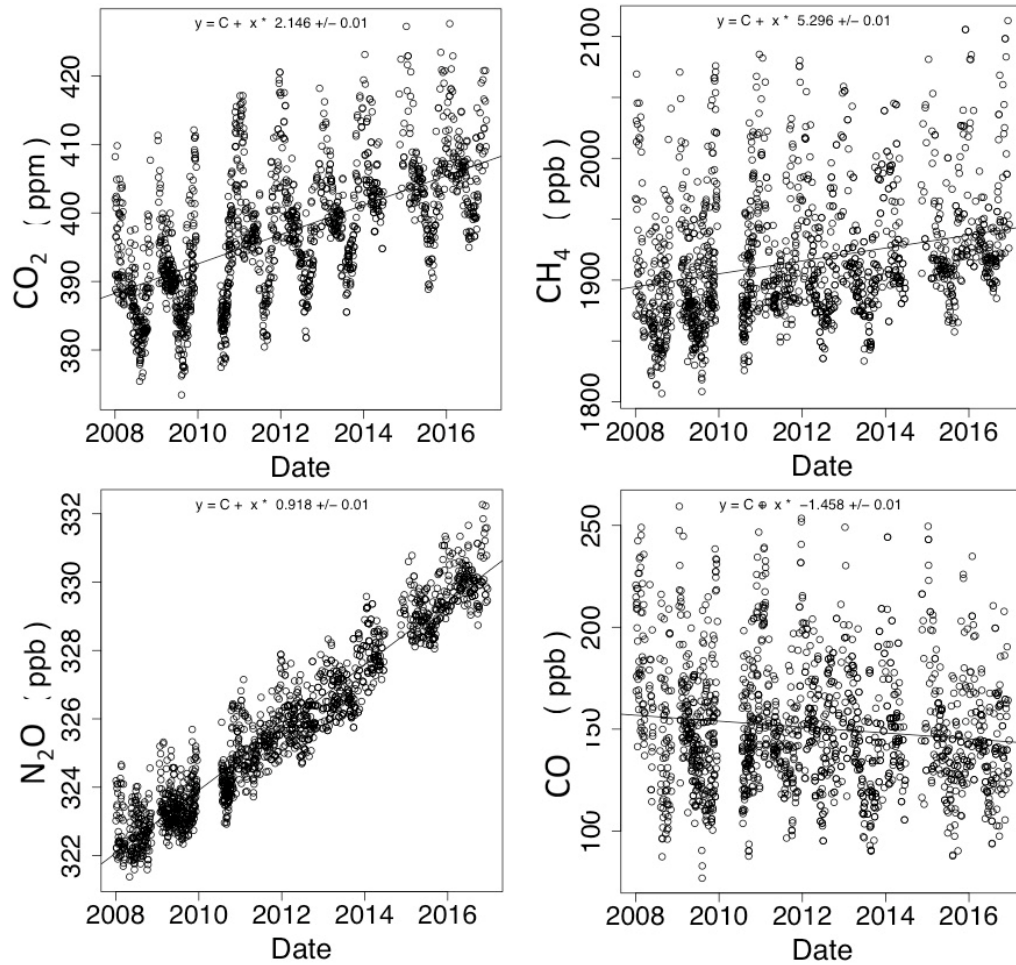


Figure 8. Time series of primary GHGs and CO measured at WGC after outlier removal and linear trend detection.

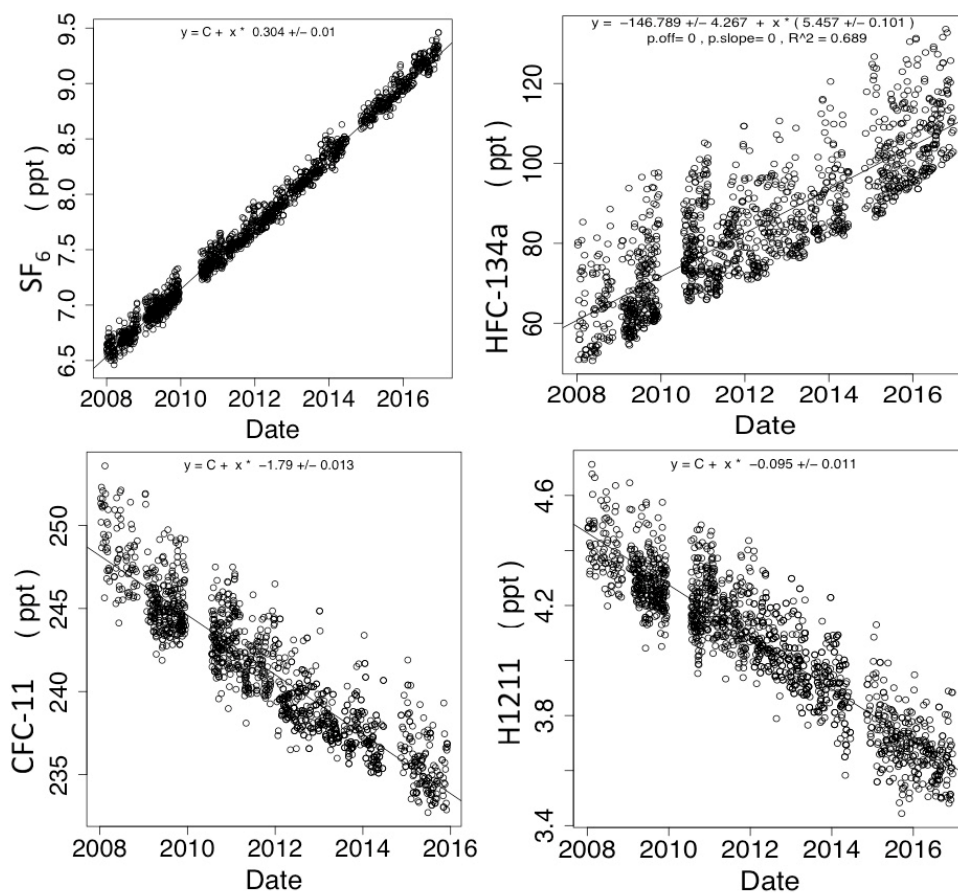


Figure 9. Time series of selected high-GWP GHGs measured at WGC after outlier removal and linear trend detection.

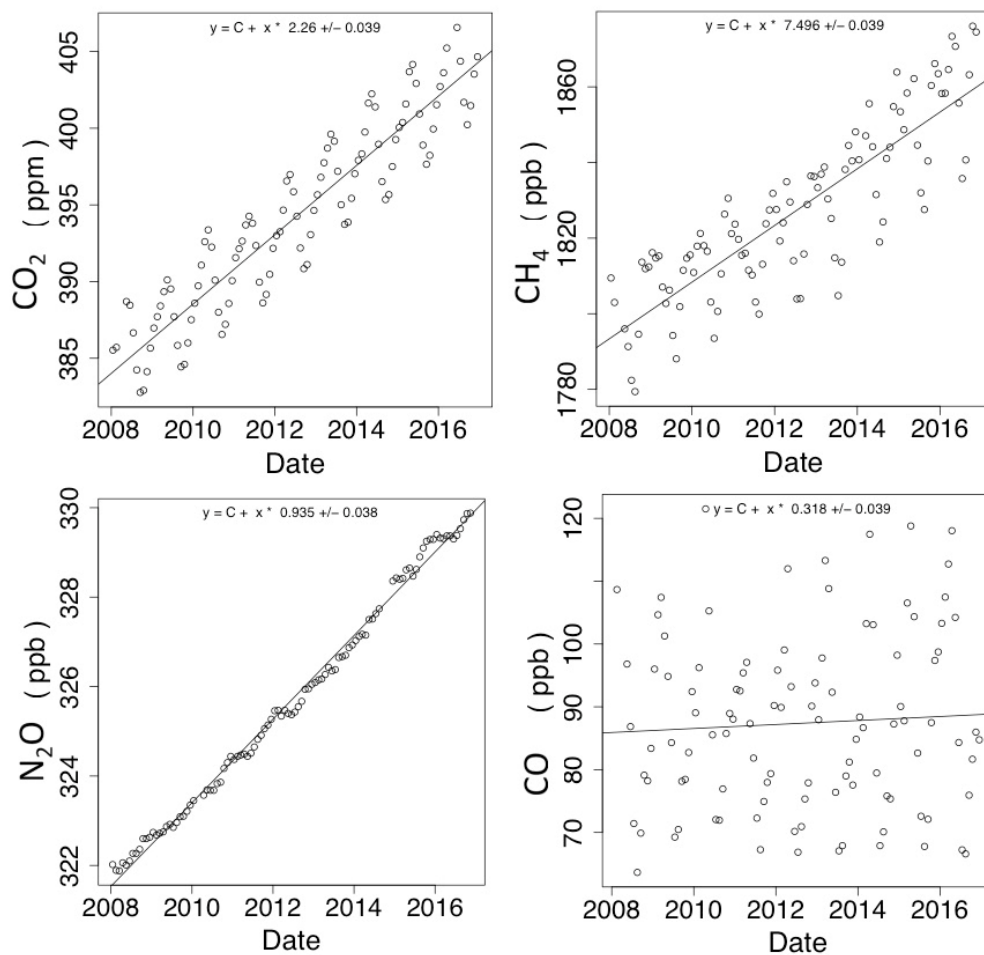


Figure 10. Time series of primary GHGs and CO measured at Mauna Loa, HI after outlier removal and linear trend detection.

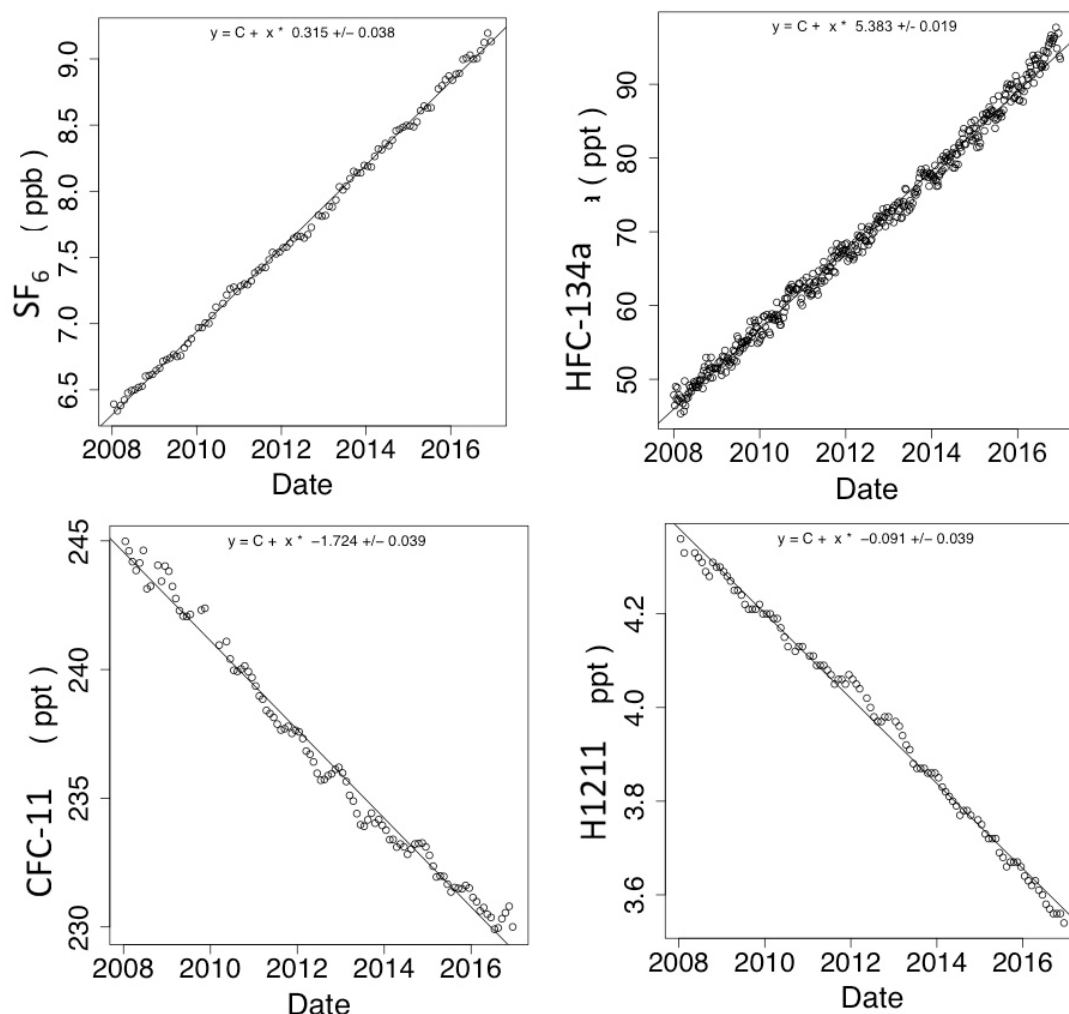


Figure 11. Time series of selected high-GWP GHGs measured at Mauna Loa, HI after outlier removal and linear trend detection.

Table 1 lists best-fit slopes with uncertainties for both Walnut Grove and Mauna Loa. Here we note the trends in primary GHGs at Walnut Grove are generally consistent with those obtained from those obtained for Mauna Loa, with the possible exceptions of CH_4 and CO , which at WGC may be growing more slowly (CH_4) or declining more rapidly (CO). However, as noted above, the strong latitudinal gradients in CH_4 (and likely other GHGs), coupled with inter-annually long-range transport would need to be evaluated before concluding that any differences in trend necessarily reflect changing emissions in California. For the high-GWP GHGs, we do not detect any significant differences, particularly given possible variations in large scale transport mentioned above.

| Gas | WGC trend | uncert | units | MLO trend | uncert |
|------------------|-----------|--------|--------|-----------|--------|
| CO ₂ | 2.1465 | 0.0097 | ppm/yr | 2.2604 | 0.0392 |
| CH ₄ | 5.2959 | 0.0099 | ppb/yr | 7.4959 | 0.0391 |
| CO | -1.4576 | 0.0099 | ppb/yr | 0.3178 | 0.0389 |
| N ₂ O | 0.9176 | 0.0099 | ppb/yr | 0.9346 | 0.0384 |
| SF ₆ | 0.3038 | 0.0096 | ppt/yr | 0.3146 | 0.0379 |
| HFC-134a | 5.5455 | 0.0108 | ppt/yr | 5.3827 | 0.0186 |
| CFC-11 | -1.7896 | 0.0134 | ppt/yr | -1.7237 | 0.0390 |
| H1211 | -0.0946 | 0.0107 | ppt/yr | -0.0908 | 0.0386 |

Table 1. Comparison of best-fit linear trends (slopes) in GHG mixing ratio obtained for Walnut Grove, CA (WGC) and Mauna Loa, HI (MLO).

4. Summary, and Conclusions

This study continued high-accuracy multi-species measurements of CO₂ and CH₄ and other selected GHGs and tracers at a tall tower near Walnut Grove, CA, yielding a nearly decadal record from 2007 to 2017. In addition, this study augmented the in-situ WGC measurements with an instrument on loan from ARB to perform accurate continuous measurements of nitrous oxide (N₂O) and carbon monoxide (CO). In the past researchers including CARB, have used GHG data from WGC to estimate GHG emissions using inverse model techniques.

In addition to the measurements, this study includes time series analyses of both the measurements from WGC and NOAA measurements from Mauna Loa, HI. Comparing results from the two sites show that:

1. The primary GHGs (CO₂, CH₄, N₂O) continued to rise at WGC, consistent with global background, though containing additional fine scale information that can likely be used to estimate California emissions in the context of regional atmospheric inversions.
2. Linear-trends at WGC are approximately consistent with trends observed at Mauna Loa for primary the GHGs and some high-GWP GHGs, though variations in background air reaching the two sites does not allow clear attribution to trends in local emissions.

In conclusion, continued GHG observation at WGC and other sites across CA will provide data that can be used for future analyses of trends, and to estimate emissions using applications such as inverse model techniques.

REFERENCES

- A. E. Andrews, J. D. Kofler, M. E. Trudeau, J. C. Williams, D. H. Neff, K. A. Masarie, D. Y. Chao, D. R. Kitzis, P. C. Novelli, C. L. Zhao, E. J. Dlugokencky, P. M. Lang, M. J. Crotwell, M. L. Fischer, J. T. Lee, D. D. Baumann, A. R. Desai, C. O. Stanier, S. F. J. de Wekker, D. E. Wolfe, J. W. Munger, M. J. Parker, and P. P. Tans (2014), CO₂, CO and CH₄ measurements from the NOAA Earth System Research Laboratory's tall tower greenhouse gas observing network: instrumentation, uncertainty analysis and recommendations for future high-accuracy greenhouse gas monitoring efforts, *Atmospheric Measurement Techniques*, 6, 1461–1553.
- Bruhwiler, L. M., et al. (2017), U.S. CH₄ emissions from oil and gas production: Have recent large increases been detected?, *J. Geophys. Res. Atmos.*, 122, 4070–4083, doi:[10.1002/2016JD026157](https://doi.org/10.1002/2016JD026157).
- CARB (2017), California Greenhouse Gas Emissions Inventory. California Air Resources Board Staff Report, Accessed April 2018 (<https://www.arb.ca.gov/cc/inventory/data/data.htm>).
- Dye, T. S., C. G. Lindsey, and J. A. Anderson (1995), Estimates of mixing depth from “boundary layer” radar profilers. Preprints from the 9th Symposium on Meteorological Observations and Instrumentation, Charlotte, NC, March 27-31, 156-160 (STI-94212-1451).
- Fairley, D. and M. L. Fischer (2015). Top-Down Methane Emissions Estimates for the San Francisco Bay Area from 1990 to 2012, *Atmospheric Environment*, doi:10.1016/j.atmosenv.2015.01.065.
- Feng, S., T. Lauvaux, S. Newman, P. Rao, R. Ahmadov, A. Deng, L. I. Díaz-Isaac, R. M. Duren, M. L. Fischer, C. Gerbig, K. R. Gurney, J. Huang, S. Jeong, Z. Li, C. E. Miller, D. O'Keeffe, R. Patarasuk, S. P. Sander, Y. Song, K. W. Wong and Y. L. Yung (2016). Los Angeles megacity: a high-resolution land-atmosphere modelling system for urban CO₂ emissions. *Atmos. Chem. Phys.* **16**(14): 9019-9045. DOI: 10.5194/acp-16-9019-2016.
- Fischer, M.L., W.J. Riley, and S. Tonse. 2005. Development of an Implementation Plan for Atmospheric Carbon Monitoring in California. California Energy Commission, PIER Energy-Related Environmental Research. CEC-500-2005-123 (LBNL-57485).
- Fischer, M.L., Jeong, S., Zhang, J., and S. Newman (2016) Atmospheric Measurement and Inverse Modeling to Improve Greenhouse Gas Emission Estimates. California Air Resources Board. Report # 11-306. <https://www.arb.ca.gov/research/apr/past/11-306.pdf>.
- Fischer, M. L., N. Parazoo, K. Brophy, X. Cui, S. Jeong, J. Liu, R. Keeling, T. E. Taylor, K. Gurney, T. Oda and H. Graven (2017). Simulating Estimation of California Fossil Fuel and Biosphere Carbon Dioxide Exchanges Combining In-situ Tower and Satellite Column Observations. *Journal of Geophysical Research: Atmospheres*. DOI: 10.1002/2016JD025617.
- Gallagher, G.; Zhan, T.; Hsu, Y.-K.; Gupta, P.; Pederson, J.; Croes, B.; Blake, D. R.; Barletta, B.; Meinardi, S.; Ashford, P. (2014) High-Global Warming Potential F-gas Emissions in California: Comparison of Ambient-Based versus Inventory-Based Emission Estimates, and Implications of Refined Estimates. *Environmental science & technology*, 48, (2), 1084-1093; DOI: [dx.doi.org/10.1021/es403447v](https://doi.org/10.1021/es403447v).

H. Graven, M.L. Fischer, T. Lueker, S. Jeong, T.P. Guilderson, R.F. Keeling, R. Bambha, K. Brophy, W. Callahan, X. Cui, C. Frankenberg, K.R. Gurney, B.W. LaFranchi, S.J. Lehman, H. Michelsen, J.B. Miller, S. Newman, W. Paplawsky, N.C. Parazoo, C. Sloop, S.J. Walker. 2018. Assessing Fossil Fuel CO₂ Emissions in California Using Atmospheric Observations and Models. *Environmental Res. Lett.* (in press)

Hsu, Y.-K., T. VanCuren, S. Park, C. Jakober, J. Herner, M. FitzGibbon, D. R. Blake, and D. D. Parrish (2010), Methane emissions inventory verification in southern California, *Atmos. Environ.*, 44, 1 – 7, doi:10.1016/j.atmosenv.2009.10.002.

Intergovernmental Panel on Climate Change (IPCC, 2007), Fourth Assessment Report.. <http://ipcc.ch/report/ar4/>

Intergovernmental Panel on Climate Change (IPCC, 2014), Fifth Assessment Report. <http://ar5-syr.ipcc.ch/>.

Jeong, S., C. Zhao, A. E. Andrews, E. J. Dlugokencky, C. Sweeney, L. Bianco, J. M. Wilczak, and M. L. Fischer (2012), Seasonal variations in N₂O emissions from central California. *Geophys. Res. Lett.*, 39, L16805, doi:10.1029/2012GL052307.

Jeong, S., Y.-K. Hsu, A. E. Andrews, L. Bianco, P. Vaca, J. M. Wilczak, and M. L. Fischer (2013), A multitower measurement network estimate of California's methane emissions, *J. Geophys. Res. Atmos.*, 118, 11,339–11,351, doi:10.1002/jgrd.50854.

Jeong, S., X. Cui, D. R. Blake, B. Miller, S. A. Montzka, A. Andrews, A. Guha, P. Martien, R. P. Bambha, B. LaFranchi, H. A. Michelsen, C. Clements, P. Glaize and M. L. Fischer (2016). Estimating methane emissions from biological and fossil-fuel sources in the San Francisco Bay Area. *Geophysical Research Letters*, 43, ^[1]_[SEP]DOI: 10.1002/2016GL071794.

Montzka, S. A., E. J. Dlugokencky, and J. H. Butler (2011), Non-CO₂ greenhouse gases and climate change. *Nature*, 476, 43-50.

Newman, S., X. Xu, H. P. Affek, E. Stolper, and S. Epstein (2008), Changes in mixing ratio and isotopic composition of CO₂ in urban air from the Los Angeles basin, California, between 1972 and 2003, *J. Geophys. Res.*, 113, doi:10.1029/2008JD009999.

Newman, S., S. Jeong, M. L. Fischer, X. Xu, C. L. Haman, B. Lefer, S. Alvarez, B. Rappenglueck, E. A. Kort, A. E. Andrews, J. Peischl, K. R. Gurney, C. E. Miller, and Y. L. Yung (2013), Diurnal tracking of anthropogenic CO₂ emissions in the Los Angeles basin megacity during spring 2010, *Atmos. Chem. Phys.*, 13, 4359–4372, doi:10.5194/acp-13-4359-2013.

Peischl, J., et al. (2013), Quantifying sources of methane using light alkanes in the Los Angeles basin, California, *J. Geophys. Res. Atmos.*, 118, doi:10.1002/jgrd.50413.

Thoning, K.W., P.P. Tans, and W.D. Komhyr, 1989, Atmospheric carbon dioxide at Mauna Loa Observatory, 2. Analysis of the NOAA/GMCC data, 1974 1985., *J. Geophys. Res.*, 94, 8549 8565.

Turnbull, J., J. Miller, S. Lehman, P. Tans, R. Sparks and J. Southon (2006), Comparison of ¹⁴CO₂, CO, and SF₆ as tracers for recently added fossil fuel CO₂ in the atmosphere and implications for biological CO₂ exchange, *Geophys Res Lett.*, 33(1), L01817.

U.S. EPA (2018). United States Environmental Protection Agency (U.S. EPA). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2016. <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks>.

Wecht, K. J., Jacob, D. J., Sulprizio, M. P., Santoni, G. W., Wofsy, S. C., Parker, R., Bösch, H., and Worden, J. (2014) Spatially resolving methane emissions in California: constraints from the CalNex aircraft campaign and from present (GOSAT, TES) and future (TROPOMI, geostationary) satellite observations, *Atmos. Chem. Phys.*, 14, 8173-8184, doi:10.5194/acp-14-8173-2014.

Wennberg, P. O., W. Mui, D Wunch, E. A. Kort, D. R. Blake, E. L. Atlas, G. W. Santoni, S. C. Wofsy, G. S. Diskin, S. Jeong, and M. L. Fischer (2012), On the Sources of Methane to the Los Angeles Atmosphere. *Environ. Sci. Technol.*, 46 (17), 9282 - 9289, doi:10.1021/es301138y.

Turney, C. S. M.; Palmer, J.; Maslin, M. A.; Hogg, A.; Fogwill, C. J.; Southon, J.; Fenwick, P.; Helle, G.; Wilmshurst, J. M.; McGlone, M.; Bronk Ramsey, C.; Thomas, Z.; Lipson, M.; Beaven, B.; Jones, R. T.; Andrews, O. Hua, Q. (2018), Global Peak in Atmospheric Radiocarbon Provides a Potential Definition for the Onset of the Anthropocene Epoch in 1965. *Scientific Reports* 8(1): 3293. DOI: 10.1038/s41598-018-20970-5.

Zhou, S., Teng, F., Tong, Q., “Mitigating Sulfur Hexafluoride (SF6) Emission from Electrical Equipment in China” (2018). *Sustainability*, 10, 2402; doi:10.3390/su10072402. <https://www.mdpi.com/2071-1050/10/7/2402/pdf>.