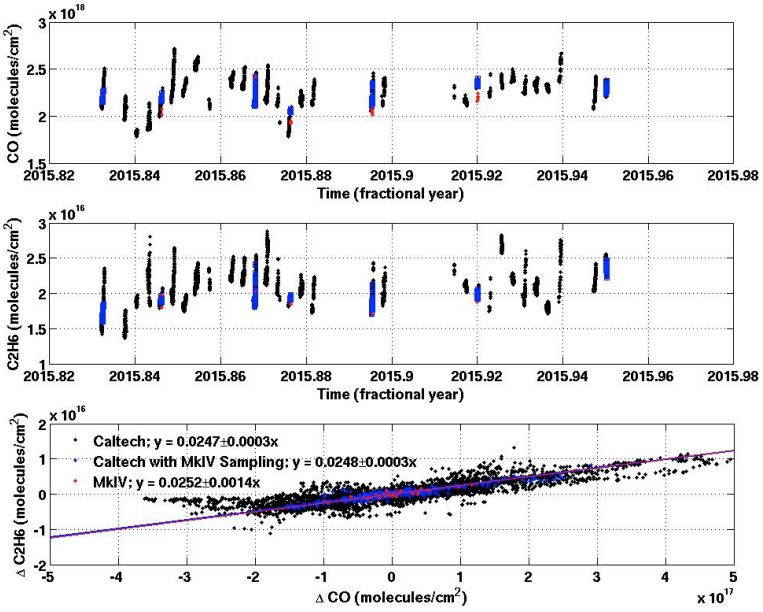
Response to Anonymous Referee #1

We thank the referee for their valuable comments, which substantially improved the paper.

Referee comments are in ***red italics***, our responses are in black text.

Observations from two different spectrometers are used in this work, the MkIV spectrometer covering a much longer period, but with sparser observations, and the Caltech TCCON spectrometer. I am a bit concerned with respect to the compatibility of the derived gas anomalies. The point is not primarily the spectral measurement itself, but the significantly different sampling strategies of the measurements (MkIV observations are constrained to local noon). It would be instructive to demonstrate that an analysis of a reduced TCCON dataset (local noon observations only) generates compatible gas anomaly values, or whether the sampling strategy can introduce a significant bias.

The figure below demonstrates that there should not be a significant bias induced into the tracer-tracer slopes. Shown below are a subset of the time series from MkIV and Caltech, filtered both datasets appropriately (removed plumes, cloudy data, etc.), and then subselected the Caltech data to points within 15 minutes of the MkIV measurements. The black dots below are all the filtered Caltech data; blue are the Caltech data time-matched with MkIV; red dots are the MkIV data themselves. Slopes of the tracer-tracer anomalies in the third panel below show a small bias between the Caltech and MkIV data that is well within the uncertainties in the slopes.

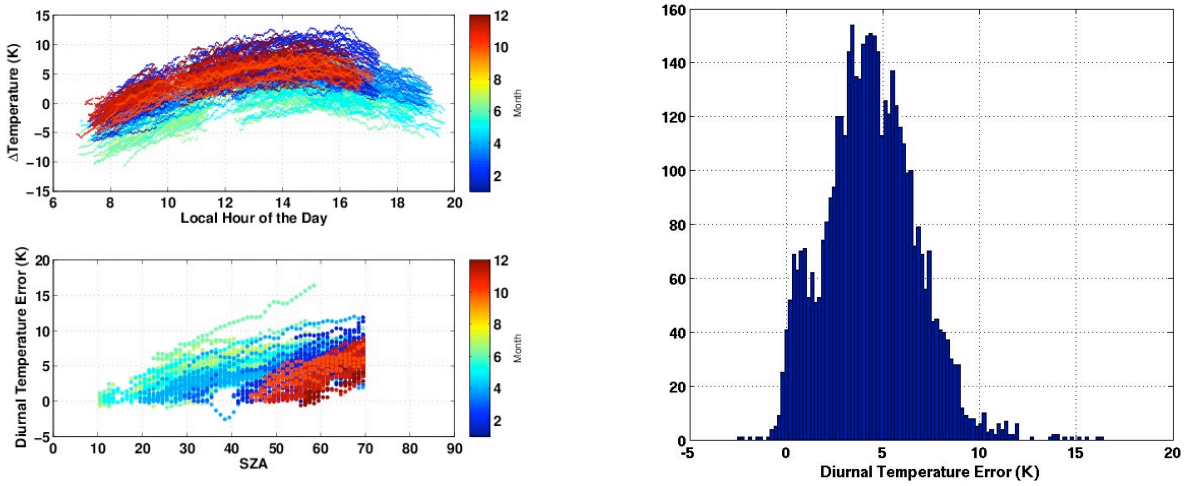


The determination of gas anomaly values from the difference of afternoon and morning values is in principle a convincing approach. However, as small changes are derived from differences of much larger column values, I wonder whether the heating of the boundary layer during the day might also mimic a gas anomaly contribution? Is the analysis performed assuming a constant temperature profile? Is the heating effect a significant disturbance?

The analysis uses a single *a priori* temperature profile throughout each day, that is representative of the local noon temperature profile, derived from the NCEP/NCAR reanalysis data. There is a systematic increase in surface temperature throughout the day; typically a 5K error between mid-morning and mid-afternoon at the surface (see histogram below); temperature changes aloft should be smaller and thus the integrated temperature error throughout the PBL should be smaller than 5K.

To minimize the temperature sensitivity of our retrievals, we chose windows in which the target absorption lines have average ground-state energies of around 300 cm-1. For example, we use the entire CO and CH4 bands in the near infrared, which have roughly the same number of high-j and low-j lines, reducing the temperature sensitivity. C2H6 is measured in its Q-branches between 2976 and 2997 cm-1. Based on performing C2H6 retrievals using correct and incorrect (perturbed) temperature profiles under a range of different conditions (temperature, humidity), we know that the retrieved C2H6 amount will change by <1% for a temperature perturbation of 5K at the surface, decreasing to zero at 3.5 km altitude. Since a typical diurnal change between mid-afternoon and mid-morning in the retrieved C2H6 is ~20%, the temperature-induced affect is comparatively small.

A sensitivity study for CH4 was performed by Hedelius et al. [2016] that showed <0.05% errors arising from 10K temperature perturbations between the surface and 700 hPa for lower resolution FTS instruments, and thus the sensitivity should be smaller for the higher-resolution TCCON instrument. This is also smaller than the <1% diurnal variations in CH4.



I have problems to understand that in Figure 2 the slope of the red dashed line differs between the top and bottom panels. If the slope is a function of time, why then is the slope in the upper panel so well defined (it encompasses data from several years, correct?).

The slopes of the red dashed lines in the quantile-quantile plots are not particularly important and the slope is not (necessarily) related to time. These plots were meant to show how we distinguished ambient SoCAB air from plumes. The bottom plot is for the time period when the Aliso Canyon leak was ongoing; the top panel is from the other time period. In this type of plot, data that are derived from a statistically similar set appear linear; that is, when the CO and CH4 vary simultaneously, their quantile-quantile plot will be linear. When they do not co-vary (i.e. when there is a plume of CH4),

their quantile-quantile plot will be nonlinear. We plotted the two times separately simply because the Aliso Canyon plumes will dominate the later data, and thus we wanted to be able to choose the filters that delineate between plumes and ambient air differently.

The error bars on the symbols in Figure 3 are difficult to read. It seems that while the 2013 and 2015 results from MkIV and the TCCON spectrometer agree nicely, the discrepancy in 2014 is much larger than the indicated error bars. Is this a sampling issue (dates of observations used?)

The Caltech annual mean slopes are calculated for September through August. If we calculate the mean 2014 monthly slope from the Caltech data for January-December, the slope increases from 2.1+/-0.4% (for September 2013 -August 2014) to 2.3+/-0.5%. (Closer to the 2.5+/-0.1% from MkIV.) We have also updated this figure to show the Caltech mean monthly slopes with the standard deviations as the uncertainties. (Previously we computed annual slopes and reported the slope errors, but we feel that was more complicated than necessary, and that the standard deviation of the monthly slopes provides a better estimate of the uncertainties.)

The scatter of the FTS deduced ethane to methane ratios in Figure 5 is large. The error bars on the individual data points are quite variable and especially in 2015, the scatter between the data points is much larger than the individual error bars. Why? Does this imply that the uncertainty budget is dominated by a sampling statistics issue?

Indeed, the variability in the FTS-deduced ethane to methane ratios is large. We would also point out that this is also true of the ratios in the delivered natural gas, which are very precise and accurate, and have very small error bars. This suggests to us that the delivered gas itself is quite a bit more variable than the reported withdrawn gas ratios from the Playa Del Rey storage facility, and our atmospheric measurements are able to detect that.

What is the level of significance for the derived slope value? Does the regression fit take into account a weighting of data points accoring to the individual error bars?

The slope of the ethane to methane ratios has an uncertainty of ~15%. The regression fit to the FTS data does take x and y errors into account, using the York et al. (2001) formulation.

York, D., N. M. Evensen, M. L. Martinez, and J. De Basabe Delgado (2004), Unified equations for the slope, intercept, and standard errors of the best straight line, Am. J. Phys., 72(3), 367, doi:10.1119/1.1632486.

The figure might suggest a superimposed peak of high ratio values in the mid of 2013.

We also noticed the mid-2013 peak, but given the large uncertainty, we're uncomfortable making any strong claims about that.

In Figure 7, the claimed steady rise of the slope during the observation period is hardly recognizable (due to the overlap of data points), perhaps a subdivision in several panels spanning fractions of the whole period would improve the readability.

We've updated the figure to show the slopes for each year overlaid.

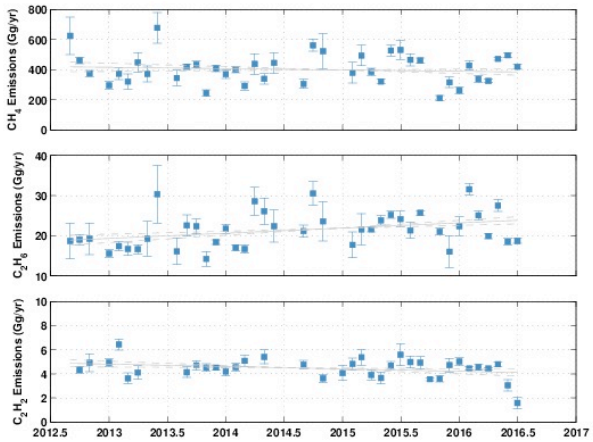
Response to Anonymous Referee #2.

We thank the referee for their valuable comments, which substantially improved the paper.

Referee comments are in ***red italics***, our responses are in black text.

The authors should consider and discuss the statistical significance of the reported trends in observed C1 and C2. The confidence intervals around the annual averages in Table 1, for example, suggest the annual averages across the 3-years shown are not statistically different. On the other hand, assuming the error bars shown in Figure 3 are correct, the 2015 values for C2 emissions seem to be statistically higher than those during 2006-2010. The authors should consider whether the monthly C1 and C2 emission time series in Figure 6 provide an alternative basis to determine the existence of a significant trend (e.g., are the slopes statistically different than zero?).

We have computed slopes for the monthly emissions. There is no statistically significant trend in the methane emissions during the 2012-2016 period (-9+/-14Gg/yr), and a very slight decrease in acetylene (-0.20+/-0.15Gg/yr). There is a statistically significant increase in the ethane emissions during this period of (1.3+/-0.6Gg/yr). We also looked back at data from two other temporary TCCON stations in the SoCAB (2007-2008 and 2011-2013) for which we can compute methane emissions (but not ethane



or acetylene). Between 2007-2015, there is a (very) slight decrease in methane emissions (-5+/-4 Gg/yr), which is in good agreement with the Wong et al. (2016) estimate of -5+/-4 Gg/yr.

Wong, K. W., T. J. Pongetti, T. Oda, P. Rao, K. R. Gurney, S. Newman, R. M. Duren, C. E. Miller, Y. L. Yung, and S. P. Sander (2016), Monthly trends of methane emissions in Los Angeles from 2011 to 2015 inferred by CLARS-FTS observations, Atmos. Chem. Phys. Discuss., (April), 1–29, doi:10.5194/acp-2016-232.

Wunch et al (2009) used CO2 instead of CO as the basis to estimate CH4. Also,Wunch et al (2009) pointed out the possible underestimation of CH4 if it was computed from CO emissions, given their differing diurnal profiles (CO emissions primarily influenced by traffic, which was believed to be a stronger daytime source than methane). This new discussion manuscript does not address these issues. The authors should clarify how potential differences in the diurnal profiles of CO, CH4, and C2H6 could affect the emissions estimates calculated with Equation 4.

Subsequent work has better agreed with the (lower) emissions estimates calculated using CO using aircraft and other remote sensing techniques. A sentence to this effect has been added to the Methods section:

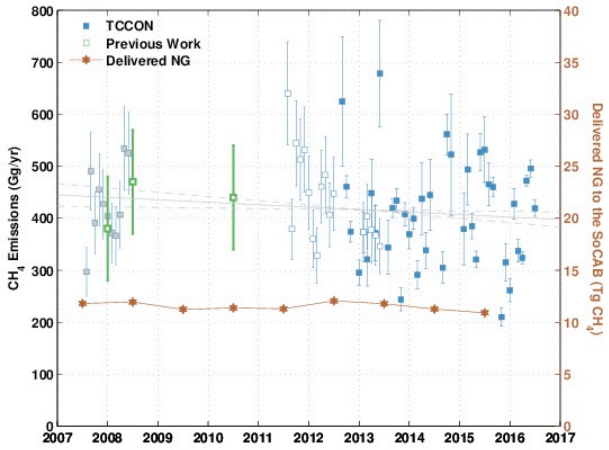
Wunch2009 suggested that using CO instead of CO2 to compute emissions may underestimate the emissions due to different diurnal emissions patterns, but subsequent studies have shown better agreement with the CH4 emissions estimates computed using its relationship with CO [Wennberg2012,Peischl2013,Wong2016].

The authors should emphasize the importance to their analysis of the changing C2:C1 ratio in pipeline gas. This trend appears to serve as tracer of opportunity, a unique fingerprint that allows attribution of the total observed C1 signal to infrastructure associated with handling, storage, delivery and use of pipeline quality natural gas. This is done indirectly in line 220, but the scientific novelty and utility of the trend deserves greater attention.

Agreed!

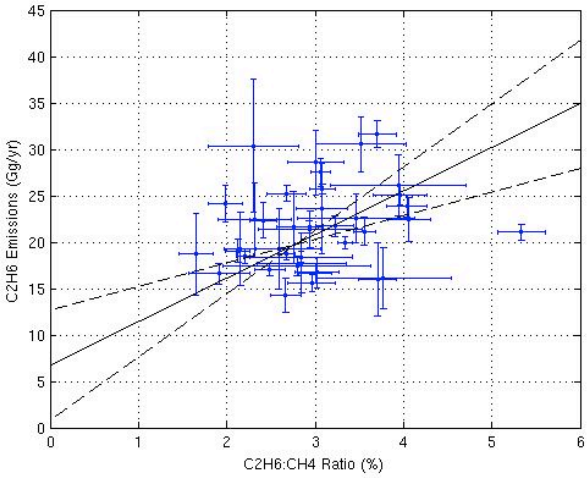
The manuscript's impact would be improved if the authors could provide a more complete picture about the contribution of specific source types to the observed C1 and C2 trends. Having partitioned the fraction of total methane signal due to pipeline gas (possible due to its increasing ethane content), can the authors further delve into the individual methane and ethane trends and provide a conceptual model that explains the recent trends or patterns in monthly/annual C1 and C2 emissions. [It would seem the C2 emissions might be reducible to a 2-source model (pipeline gas and associated gas/geologic seepage) with appropriate adjustment for vehicle emissions. Similarly, C1 emissions might be reducible to a 3-source model, by adding a generic third term for biogenic C1 sources.] At a minimum, the authors should clearly indicate whether the increasing C2:C1 ratio in pipeline gas is, by itself, sufficient to explain the potentially increasing C2 trend in Fig 3 and 6? Or can the balance of the C2 budget not explained by pipeline gas losses be explained: for example, given likely associated gas compositions, could the local oil/gas production to which Peischl attributed 32 Gg C1 also account for the excess C2 that is not explained by losses of pipeline quality gas? Alternatively, are other causes required?

There has been a very small decline in the methane emissions over the past 8 years, but no statistically significant change since 2012, when the C2:C1 ratios began increasing. We've created a new figure to show this, that makes use of two TCCON stations that were temporarily in the SoCAB in 2007-2008 and 2011-2013. Overlaid on this plot is the natural gas delivered to SoCAB customers with the y-axis scaled to match the left y-axis if 2% of the natural gas is lost as fugitive emissions.



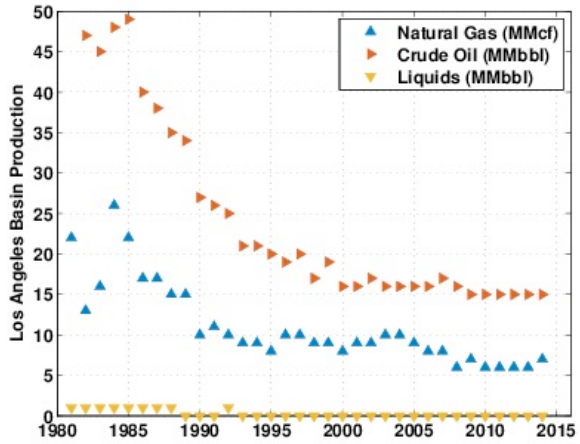
Assuming a constant methane emission over the 2012-2016 period, the C2:C1 ratio in the pipeline gas is sufficient to explain the increase in ethane since 2012: if we assume CH4 emissions are 413 Gg/yr, and roughly 240 Gg/yr from pipeline natural gas, we would infer C2H6 emissions of 11.6+/-4.4 Gg/yr in 2012-2013, 13.3+/-5.0 Gg/yr in 2013-2014, 15.0+/-5.7 Gg/yr in 2014-2015 using the increasing ethane to methane relationship. Adding this to the Peischl et al. 2010 estimate of C2H6 emissions from local oil and gas, vehicles, and the CARB "other" category (5.4+/-1.0 Gg/yr) results in 17.0+/-4.5 Gg/yr, 18.7+/-5.1 Gg/yr, and 20.4+/-5.7 Gg/yr for 2012-2013, 2013-2014, and 2014-2015, respectively. This falls well within the uncertainties of the ethane emissions estimates from the correlation with CO (19+/-4 Gg/yr 2012-2013; 21.4+/-4 Gg/yr 2013-2014; 23+/-3 Gg/yr 2014-2015).

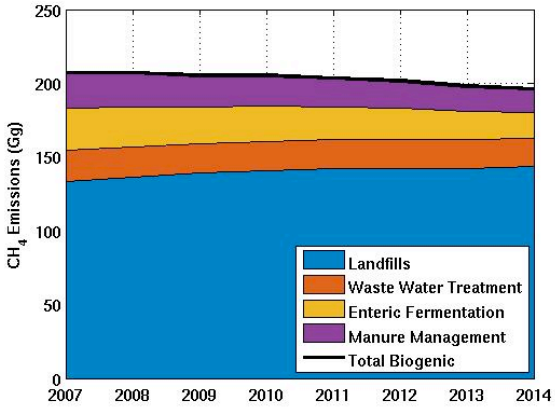
Attempts to extrapolate this relationship between ethane emissions and C2H6:CH4 ratio back to a regime in which the C2H6:CH4 ratio in the natural gas is zero (to get a sense of the magnitude of C2H6 in the SoCAB in the absence of natural gas C2H6 emissions) is not possible, due to the significant uncertainty on both the monthly C2H6:CH4 slopes and monthly C2H6 emissions. The y-intercept is 7+/-6 Gg/yr, implying that natural gas can explain anywhere from 1/3 to all of the C2H6 in the SoCAB atmosphere.



Once the C2 budget is determined, and knowing the C2:C1 ratio of pipeline gas, what can the authors say about the trend in C1 emissions due to losses of pipeline quality gas? It would be valuable if the authors could provide an assessment of whether the data indicates that downstream natural gas emissions in the region are changing.

We can say from our measurements that the methane emissions were roughly constant between 2007-2016 (changing by -5+/-4 Gg/yr), and no statistically significant decline is seen over the 2012-2016 period. According to the EIA, the oil and gas production in the Los Angeles Basin (somewhat larger than the SoCAB) has remained relatively constant over this period (left plot below). Biogenic emissions from the CARB statewide inventory scaled to the SoCAB totaled about 207 Gg in 2007, declining by about 1 Gg/yr due to a 2.8 Gg/yr livestock population change and a partially compensating increase in landfill emissions (right plot below). Thus the small decline we see in atmospheric CH4 emissions (-5+/-4 Gg/yr) might be partially attributable to the decline in biogenics, but the uncertainties are too small to be confident. The downstream natural gas emissions do not appear to be changing significantly.





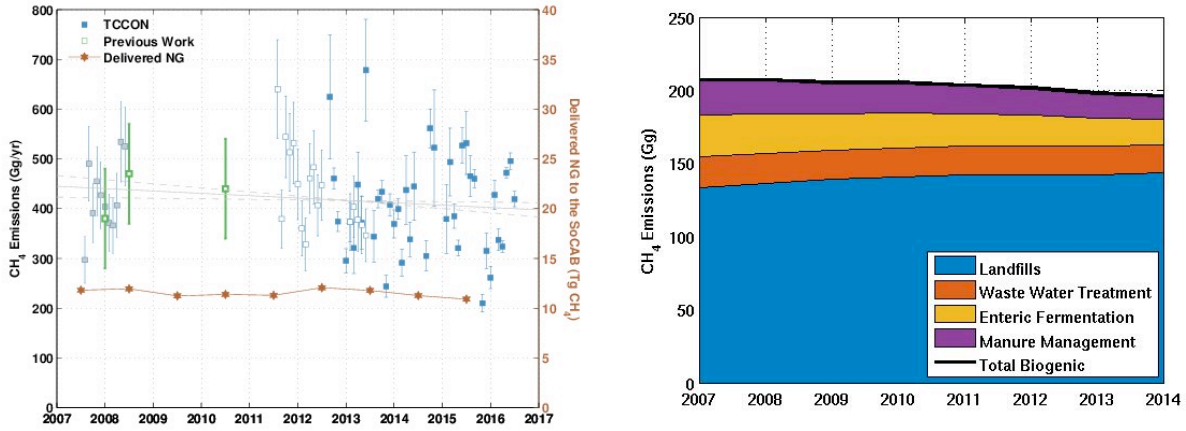
It is not clear from the text at line 225 and the reference cited how the authors derive the mass of C1 delivered by SoCalGas to customers within the SoCAB. It is also unclear why sales data going back to 2003 are relevant at this point of the discussion focused on the regional methane budget in 2015 (it would be more relevant – indeed desirable – to show historical gas deliveries in Figure 4). Southern California Gas' annual report (Sempra Energy 2015 Financial Report) reported annual volumes of gas sold in 2013, 2014 and 2015 of 999, 944 and 925 bcf (average 960 bcf, or 17.5 Tg assuming a methane content in gas of 95%). The authors should explain how they partition the SoCalGas' systemwide sales to isolate the customers solely within the SoCAB. Because not all of the gas sold by SoCalGas is consumed within the SoCAB and may or may not be transported through the SoCAB, the authors should report multiple metrics for the loss of pipeline quality gas that is sold or transported across the basin. One metric would be % of methane delivered that is emitted, and the other is the emissions as a percent of methane throughput in the SoCalGas system. The latter yields a loss rate for pipeline gas of 1.4% of potential throughput (242Gg/17.5Tg). The comparison to Wennberg et al's 2% loss rate should be done with caution, ensuring that the quantities in the numerator and denominator are apples-to-apples between this work and the previous work (it seems

the 2% in Wennberg would most appropriately be compared to 1.4%, as calculated above).

Agree this was unclear. SoCalGas have now published their 2015 delivery numbers, so historical data are no longer necessary. Here is the reworked paragraph:

Since the average total methane emissions in the SoCAB since 2007 have been roughly constant at 413+/-86 Gg yr^{-1}, the ~58\% attributable to the natural gas infrastructure is 240+/-78 Gg yr^{-1}. In 2015, the SoCalGas total throughput was 2559 MMcf day^{-1}, or 18 Tg CH4 total. We remove 3 Tg CH_4 from wholesales, and 0.2 Tg CH_4 from company use and ``lost and unaccounted for'' (LUAF) gas, giving 14.7 Tg CH4 delivered by SoCalGas. This suggests 1.6+/-0.5% losses as fugitive emissions from the total delivered. (However, only 74\% of the population served by SoCalGas lives in the SoCAB, and thus the fraction of the losses as fugitive emissions would represent a larger fraction of the delivered gas to SoCAB customers [Wennberg2012].)

Figure 4. The manuscript would be improved if the hydrocarbon production data provided was specific to the SoCAB rather than statewide (these are publicly available from state agencies). Additionally, since hydrocarbon production is only a small contributor to C1 and C2 emissions in the SoCAB, this figure would be much more useful if it presented publicly available activity trends for other chief sources – in particular, I would suggest SoCalGas' natural gas sales and livestock populations. Recent CH4 emissions data or landfills and waste water treatment plants may also be available through the US EPA Greenhouse Gas Reporting program or California state equivalents.



We have now included Los Angeles Basin production instead of statewide data, which simplifies this analysis somewhat. Furthermore, the left plot above shows the delivered natural gas to the SoCAB (right axis), which is about 11 Tg/year, and the roughly constant CH4 emissions we compute since 2007 (left axis) from our atmospheric measurements. If we assume 2% fugitive emissions, this delivered natural gas represents about 220 Gg/year. The right plot is the emissions from the CARB emissions database for California landfills and wastewater (scaled by SoCAB population relative to California), and enteric fermentation and manure management (scaled to the cattle and calve population in the SoCAB counties relative to California). As described earlier, these biogenics totaled about 207 Gg in 2007 and change only slightly in time. We have therefore added an inventory table that uses our measurements, the 2010 Peischl et al. inventory for biogenics, local oil and gas and vehicles, and included our pipeline natural gas emissions. We compare the sum of the inventory to our atmospheric estimates and the results agree within uncertainties.

The richest findings seem to derive from the more recent and denser Caltech FTS measurements, with the JPL MkIV FTS data providing corroboration and further insight about historical trends. The manuscript's flow and clarity might be improved with some reorganization of the results and discussion or more explicit delineation of how the two data sets are used to support the conclusions reached.

We reworked the paper with this in mind.

The results relating to Aliso Canyon are interesting and important, but are not central to the paper's main findings. I would recommend moving the Aliso Canyon discussion into a separate subsection.

Done.

Abstract Line 9. The introduction of "Our methane emissions record" here is confusing since line 4 refers to a record dating back to the 1980s.

Corrected and reorganized the abstract.

Abstract Lines 10-15. This wording might be misconstrued to imply that the source of the excess methane is the gas storage facility. In fact the gas storage facility is only mentioned since it is a reliable source of C2:C1 ratios. But the authors have a secondary data source (delivered gas) that yields a statistically indistinguishable trend line in Fig. 5. The authors should revise the language to indicate the comparison is between atmospheric measurements and measured C2:C1 of gas delivered and stored in the region. Additionally, the authors should more explicitly indicate the scope of natural gas infrastructure implicated in the final sentence – to indicate it includes gas delivery infrastructure including pipeline leaks (transmission and distribution), compression and storage facilities, and post-meter losses among others.

Reworked abstract.

Line 179. It was unclear how the statement about ethane to acetylene ratios followed from statements about C2:CO and acetylene:CO; please elaborate on the significance.

Updated text:

There are three main sources of ethane emissions in the SoCAB: vehicle exhaust, the natural gas system, and oil and gas exploration and extraction. Of these sources, only vehicle exhaust is not a significant source of CH4. To distinguish between vehicle exhaust and fossil fuel sources, we use our coincident measurements of carbon monoxide, which tracks sources of incomplete combustion (including mobile sources), and acetylene (C2H2), whose emissions more directly track vehicle exhaust [Kirchstetter1996,Warneke2012,Crounse2009]. The ratio of ethane to carbon monoxide in the SoCAB declined rapidly until the mid-1990s, and then slowly and steadily increased. The ratio of acetylene to carbon monoxide remained relatively constant throughout the time period, and thus the ethane to acetylene ratios follow the same trend as ethane to carbon monoxide. This implies that vehicle emissions are not driving the changes in ethane emissions. This is consistent with the Warneke2012 analysis, which showed an increase in ethane relative to acetylene after 1995, which they attributed to natural gas use and production.

Line 226. The statement attributing 242 Gg/yr C1 to natural gas infrastructure should be linked back to the prior paragraph's finding that 54% of total excess was due to natural gas (e.g. "242 Gg/yr, equal to 54% of the SoCab total. . .".

Done.

Lines 248-255. The specific value used for GWP100 should be stated (e.g., 25, 28, or 34). The choice of 100-yr GWP in this paragraph does not account for the greater short-term climate impacts of CH4. The authors should consider reporting a 20-yr CO2e value in addition to the 100-yr value. The reference to climate impact in the last sentence needs to explicitly distinguish short- and long-term impacts; if only 100-yr GWP comparisons are made, then the sentence should be clarified to refer to "longterm climate impact. . ."

Done.

Figure 1. The very rapid rise in C2 mole fraction in the most recent JPL MkIV FTS measurements should be explained (panel 3). Is this trend due to the increased C2:C1 ratio, the Aliso Canyon blowout or both? Should the C2 rise be accompanied by changes in C1?

Those six high C2 points are on a single day (November 10, 2015), and are due to the Aliso Canyon blowout plume having been advected over the line of sight of the MkIV instrument. The C2 rise is accompanied by a smaller (2.5%) increase in C1, which is difficult to see in the raw CH4 data due to natural variability, but by plotting CH4 versus N2O (see slide 14 of: http://mark4sun.jpl.nasa.gov/report/MkIV_ethene_Toon.pdf), the CH4 increase becomes much clearer.

Line 141. The word "are" appears twice.

Removed.

Figure 1. The black Mauna Loa data points are significantly obscured by the CO and C2 data points.

Revised figure.

Fig 3. The error bars are hard to make out and the symbol for the Peischl et al is not evident.

Figure clarified.

Response to Anonymous Referee #3.

We thank the referee for their valuable comments, which substantially improved the paper.

Referee comments are in ***red italics***, our responses are in black text.

In the paragraph starting on line 187, the authors relate the extraction of petroleum from the SoCAB to the production in the rest of the state. This seems likely to be a valid assumption, but it would be helpful here to provide some additional justification. Would the results of the analysis be substantially different if it is assumed that SoCAB petroleum extraction tracked regional or national trends? Lines 230-235 discuss how non-petroleum sources can close the methane budget. It would be helpful to discuss changes in these sources here to corroborate the conclusion that petroleum accounts for only half of the observed methane increase.

We have obtained Los Angeles Basin oil and gas production values from the EIA, and have replaced the discussion with the more relevant numbers. This has simplified the interpretation and discussion as it now seems likely that basin oil and gas production can explain the early ethane record from the MkIV measurements.

The panels on Figures 2 and 3 have "squashed" aspect ratios that make them slightly difficult to read. The bottom panel of Figure 2, for example, compresses much of the data into a small region of the graph.

We have revised the plots.

In Figure 3, the presence of four panels in a single figure makes it difficult to see the trends described in the caption. Could some of these panels be merged and their axes modified to make the graphs taller?

Figure 3 has been reduced to three panels.

The error bars on the atmospheric ratios in Figure 5 are quite large and imply a large uncertainty in the calculated slope. Indeed, this uncertainty is reflected in the text as well. A visualization of this uncertainty in the figure would be beneficial. Line 219 reports the ratio of slopes as 54 ± 20%, which is thereafter referred to as "about half." However, the large uncertainty in the slope means that the atmospheric increase could be anywhere from not well explained by the changing storage ratios (about 1/3), to very well explained (over 2/3). Do the authors have speculation as to whether the percentage is on the high or low end of this range?

Error bars have been added to the slope. Since submitting this paper, we have recorded more Caltech measurements, which permitted more robust slopes to be computed. With the new data, we are now able report the mean slope (58%) with a smaller uncertainty (13%).

Editorial comments In line 244, the slope of the ethane/methane correlation is 4.28 ± 0.07%. This piece of information is in agreement with the storage "ratios exceeding 4%" in line 209. I suggest placing these pieces of information closer together to emphasize this connection, because it provides further evidence that the Aliso Canyon plume was detected.

We have linked these two numbers better in the revised draft.

The uncertainties are reported in an inconsistent manner in the text. Line 8 of the abstract contains the quantities 13 ± 4.5 and 25.8 ± 3.9; and line 234 of the text contains the quantity 32 ± 7. Some further discussion of how these different levels of uncertainty for these and other quantities reported in the text were chosen would be helpful.

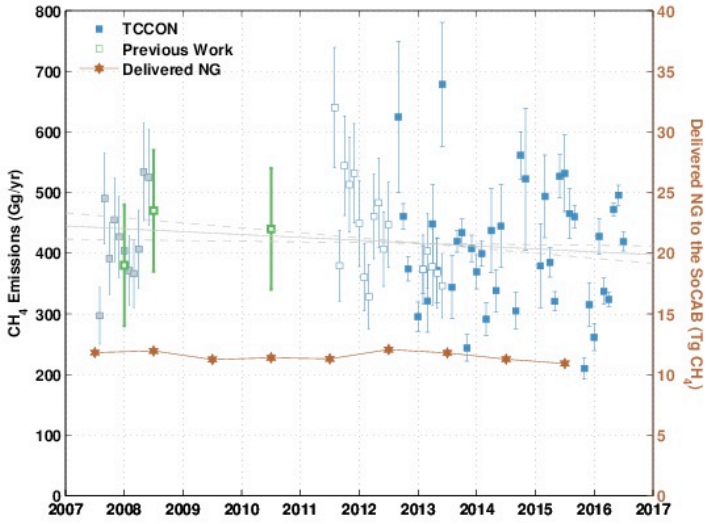
Uncertainties have been made more consistent and clearer in the revised draft.

Response to Anonymous Referee #4.

We thank the referee for their valuable comments, which substantially improved the paper.

Referee comments are in ***red italics***, our responses are in black text.

However, some of the conclusions seem to be at odds with another paper currently submitted to ACPD, Wong et al., that concludes that methane emissions in the SoCAB have been decreasing since 2011, albeit with a low confidence interval. Some discussion comparing and contrasting the conclusions of Wong et al. is warranted. For instance, how well does the Caltech FTS represent the entire SoCAB methane emission, compared to the multiple measurement locations described by Wong et al.?



We went back to TCCON measurements in the SoCAB starting in 2007 to look at longer-term trends in CH4 emissions. From those data, we compute a very small decrease in CH4 emissions of -5+/-4 Gg/yr, which agrees with the Wong et al. -5+/-4 Gg/yr value.

Line 42, the sampling location of Hopkins et al. and Townsend-Small et al. were heavily skewed toward the western SoCAB. How well do those studies represent emissions to the entire region?

Added in the introduction that these studies were focused on the western SoCAB.

Line 110, why do you subtract the daily mean of ethane, CO, and acetylene and not the lowest value?

We are interested in the daily anomalies, so either method would work. But subtracting off the daily mean has the advantage of producing anomalies with similar values to the Caltech analysis, in which we subtract morning from afternoon values.

Line 111-113, by aggregating for an entire year, how do you account for this slope not representing the seasonal variability instead of variability due to emissions?

We remove (to first order) the seasonal variability by computing emissions from diurnal anomalies.

Subtracting the daily means removes the seasonal changes in gas abundances.

Line 185, is there an earlier reference you could use to support your conclusion that ethane emissions from automobiles would not have accounted for the emissions decline in the late 1980s? The conclusions from the mid-90s on are well supported, but it is unclear they are relevant to the 1980s.

This is a good point, since many air quality control measures went into place in 1995. However, Kerchstetter et al. note that "... the remote sensors used at the time [of the 1988-1989 study of Bishop and Stedman (1990)] were not capable of measuring VOC or NOx emissions. Thus, the overall effects of oxygenated gasoline or in-use vehicle emissions remain uncertain."

We've added a statement in the revised paper about this:

Thus, emissions from vehicles are unlikely to be either a dominant source of ethane to the SoCAB atmosphere, or responsible for the significant decrease in ethane after 1995. Prior to 1995, there were fewer regulatory controls on air pollution from vehicles, and the exhaust composition is much less well-known [Kirchstetter1996].

Bishop, G. A., and D. H. Stedman (1990), On-road carbon monoxide emission measurement comparisons for the 1988-1989 Colorado oxy-fuels program, Environ. Sci. Technol., 24(6), 843–847, doi:10.1021/es00076a008.

Line 236, can you confirm with your data that the Aliso Canyon leak did not occur before October 23? There have been some reports of skeptical homeowners questioning that it may have been leaking before this date.

We see no peaks in our data before October 23, and this is now mentioned in the revised text.

Line 245, is the ethane emission from Aliso Canyon found by multiplying the 4.28% anomaly by the Conley et al. methane emission of 97.1 Gg? If so, this should be stated more clearly.

Yes. This has been clarified.

Line 250, please state which 100-yr global warming potential you used. 25?

Yes. Clarified in the revised paper.

Line 262, what is the uncertainty of the 20%? This would help in the comparison with Wong et al.

This has been removed and replaced by the figure above.

Line 72, equation 2, a subscripted "dry air" might fit better for the "column dry air", similar to how it is done for the molecular mass?

Fixed.

Line 143, Conley et al. state the facility has a capacity of 168 billion cubic feet, and a "working capacity" of 86 billion

Fixed.

Line 151-152, Suggest swapping "near the facility" and "from aircraft"

Done.

Line 167, change "represents" to "represent"

Done.

Line 282, please define "HF"

Done.

Figure 4 might look "cleaner" if you used the daily average production for a given month. The variability of the days in a month results in a 3% noise, which is close to the noise between 2003 and 2010.

This figure has been replaced by one for the Los Angeles Basin, which only has annual values and should look "cleaner".

Response to David Lyon.

Referee comments are in ***red italics***, our responses are in black text.

The observed increase in methane and ethane emissions may be partially attributable to decreased oxidation of methane and ethane by soil microbes. The surface flux of natural gas leaks can be reduced by microbial oxidation. GRI/EPA 1996 reports up to 40% of leak emissions can be oxidized within the soil. Several factors including moisture content and temperature affect the methane oxidation rate of the soil microbial community. Van den Pol-van Dasselaar 1998 report that methane oxidation in sandy grassland soils is highest at intermediate soil moisture and ceases below 5% moisture content. The severe, extended drought in southern California since 2012 might cause local distribution emissions to increase if inhibited microbial oxidation allows a greater fraction of underground leak emissions to reach the surface. It is possible that decreased microbial oxidation may also increase emissions from geologic seepage and biogenic sources. I recommend that you address this issue in your discussion.

http://link.springer.com/article/10.1007/BF00425043
https://www.epa.gov/gasstar/documents/emissions_report/9_underground.pdf
http://link.springer.com/article/10.1023/A:1004371309361
http://droughtmonitor.unl.edu

We thank Dr. Lyon for bringing this issue to our attention. It seems likely to be a small effect. A brief discussion has been added to the paper:

Droughts such as the one plaguing Southern California since 2012/2013 [Swain2014,Griffin2014] can reduce the ability of soil microbes to remove methane and ethane released underground into the soils [vandenPol-vanDasselaar1998,Adamse1972]. The constant CH4 emissions and growing C2H6 emissions since 2012 would require a compensating decrease in biogenic emissions of CH4 to offset this effect. However, biogenics are reported to have decreased by about 1% between 2012 and 2014 [CARB], so this effect is likely to be small.

Manuscript prepared for Atmos. Chem. Phys.
with version 2014/09/16 7.15 Copernicus papers of the LaTeX class copernicus.cls.
Date: 13 September 2016

Quantifying the Loss of Processed Natural Gas Within California's South Coast Air Basin Using Long-term Measurements of Ethane and Methane

Debra Wunch[1,2], Geoffrey C. Toon[2,3], Jacob K. Hedelius[2], Nicholas Vizenor[4], Coleen M. Roehl[2], Katherine M. Saad[2], Jean-François L. Blavier[2,3], Donald R. Blake[4], and Paul O. Wennberg[2,5]

[1]Department of Physics, University of Toronto, Canada
[2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA
[3]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA
[4]Department of Chemistry, University of California, Irvine, California, USA
[5]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California, USA

Correspondence to: Debra Wunch (dwunch@atmosp.physics.utoronto.ca)

Abstract. Methane emissions inventories for California's South Coast Air Basin (SoCAB) ~~is a region in which the top-down methane emissions are underestimated by the bottom-up inventories~~have underestimated emissions from atmospheric measurements. To provide insight into the sources of the discrepancy, we analyse ~~a record~~ records of atmospheric trace gas total column abundances in the SoCAB starting in the late 1980s~~. The gases measured include ethane and methane and provide insight into the sources of the excess methane found in the SoCAB. The early few years of the record show~~ , to produce annual estimates of the ethane emissions from 1989–2015, and methane emissions from 2007–2015. The first decade of measurements shows a rapid decline in ethane emissions ~~at a much faster rate than decreasing vehicle exhaust or~~ coincident with decreasing natural gas and crude oil production ~~can explain~~in the basin. Between 2010 and 2015, however, ethane emissions have grown gradually from ~~13 ± 4.5~~about 13 ± 5 $\mathrm{Gg \cdot yr^{-1}}$ to ~~25.8 ± 3.9~~about 23 ± 3 $\mathrm{Gg \cdot yr^{-1}}$, ~~which is in contrast to~~ despite the steady production of natural gas ~~liquids~~ and oil over that time ~~. Our~~ period. The methane emissions record begins ~~in 2012 and shows an increase between 2012 and 2015 from 380 ± 78 to 448 ± 91~~with one year of measurements in 2007 and continuous measurements from 2011–2016 and shows little trend over time, with an average emission rate of 413 ± 86 $\mathrm{Gg \cdot yr^{-1}}$. Since 2012, ethane to methane ratios in the natural gas withdrawn from a storage facility within the SoCAB have been increasing ~~; these ratios are tracked in our atmospheric measurements with about half of the rate of increase~~by $0.62 \pm 0.05\% \cdot \mathrm{yr^{-1}}$, consistent with the ratios measured in the delivered gas. Our atmospheric measurements also show an increase in these ratios, but with a slope of $0.36 \pm 0.08\% \cdot \mathrm{yr^{-1}}$, or $58 \pm 13\%$ of the slope calculated from the withdrawn gas. From this, we in-

fer that ~~about~~ more than half of the excess methane in the SoCAB between 2012–2015 is attributable to losses from the natural gas infrastructure.

1 Introduction

Anthropogenic sources of the potent greenhouse gas methane (CH_4) constitute about 60% of the global total CH_4 emissions, or nearly 350 $TgCH_4 \cdot yr^{-1}$ ~~(?)~~(Saunois et al., 2016). Urban regions are thought to be an important contributor to this flux (e.g., McKain et al., 2012), and thus quantification and attribution of these urban sources are crucial for fully understanding their causes and hence potentially regulating them. Southern California's South Coast Air Basin (SoCAB) has been the focus of several studies~~, due to its elevated methane and the disagreement between bottom-up inventories and the emissions determined using atmospheric measurements (Wunch et al., 2009; Hsu et al., 2010; Townsend-Small et al., 2012;~~ These studies have quantified the emissions from the basin and generally find that the SoCAB emissions are higher than the reported inventories (Wunch et al., 2009; Hsu et al., 2010; Townsend-Small et al., 2012; Wennberg et a

The SoCAB is a highly urbanized region centered on Los Angeles, with almost 17 million residents, representing 43% of the population of California. The lower atmosphere over the SoCAB is well-confined: it is contained by mountains to the ~~North and East~~north and east, and open to the Pacific Ocean to the ~~South-West~~south-west. Thus, urban emissions within the basin have long residence times and, under prevailing wind conditions, also have strong and predictable diurnal flow: out to the ocean at night, and inland during the day.

The many sources of methane in the SoCAB include oil and gas exploration and extraction, natural gas delivery pipelines and storage facilities, waste-water treatment plants, landfills, and dairies. Previous studies have shown that the atmosphere over the SoCAB contains significant CH_4 enhancements over the global background ~~(Wunch et al., 2009; Hsu et al., 2010; ?)~~(Wunch et al., 2009; Hsu et al., 2010; Wong et al., 2015). More recent work has attempted to attribute the sources of the enhanced methane using other tracers in the atmosphere that are co-emitted with particular sources. Wennberg et al. (2012) used simultaneous measurements of ethane (C_2H_6) and methane to separate ethane-containing sources of methane, such as natural gas and petroleum, from biogenic sources of methane which do not co-emit ethane, such as landfills, waste water treatment and ruminants. Wennberg et al. inferred that a significant fraction of the excess methane in the SoCAB atmosphere is likely emitted from the natural gas infrastructure, potentially post-consumer meter. Peischl et al. (2013) used co-emitted higher-order alkanes (including ethane) to suggest that oil and gas drilling and storage are significant contributors to the elevated methane ~~emissions. ?~~ and ethane emissions. Hopkins et al. (2016) and Townsend-Small et al. (2012) conclude that most of the elevated methane in the western SoCAB is related to fossil fuels using spatial alkane measurements and isotope measurements, respectively.

~~In this paper, we~~ We describe our data records and analysis methodology in §2, and, in §3, we discuss the change in the emissions of methane and ethane within the SoCAB. By comparing the

ethane to methane ratios measured in the atmosphere with the changing ratios in the withdrawn and delivered natural gas, we quantify the fraction of the excess methane in the atmosphere attributable to the natural gas infrastructure.

2 Methods

We use data from ~~two~~ four solar viewing ground-based Fourier transform spectrometers (FTS) ~~located~~ that have measured within the SoCAB. The first instrument, the JPL MkIV FTS (Toon, 1991), has measured ethane, methane and other trace gases from the Jet Propulsion Laboratory (JPL, NASA) since 1985 (Figure 1). The measurements have been made once or twice per week, for about 2 hours per day, when the instrument is not in the field elsewhere for intensive scientific campaigns. ~~The second~~ Two other instruments were temporarily stationed at JPL: JPL2007 (Wennberg et al., 2014c; Wunch et al., 2009) was operational between July 2007 and June 2008, and JPL2011 (Wennberg et al., 2014a) was operational between July 2011 and July 2013. These instruments measured CH_4 and other gases, but not C_2H_6, and are part of the Total Carbon Column Observing Network (TCCON, Wunch et al., 2011). The fourth instrument, which is located about 10 km from JPL at the California Institute of Technology (Caltech), is part of the ~~Total Carbon Column Observing Network (TCCON, Wunch et al., 2011)~~TCCON, and has been measuring ethane, methane and other trace gases with high temporal frequency (several hundred spectra per sunny day) since September 2012 ~~(?)~~(Wennberg et al., 2014b). The JPL MkIV FTS data are available from the MkIV website (http://mark4sun.jpl.nasa.gov/ground.html), and the ~~Caltech~~ TCCON data are available from the TCCON archive (http://tccon.ornl.gov/).

Both the MkIV and ~~Caltech~~ TCCON FTS instruments are direct solar-viewing and measure solar absorption by atmospheric trace gases; ~~they~~ the retrievals are thus insensitive to atmospheric aerosol abundances. The data analysis for ~~both~~ these instruments makes use of the GGG2014 software package (Wunch et al., 2015). This includes a nonlinear least squares spectral fitting algorithm (GFIT) that scales an *a priori* profile for best fit, and a ~~linelist based on HITRAN (?)~~spectroscopic linelist (Toon, 2014) based on the HITRAN database (Rothman et al., 2013). The GGG2014 software produces column-averaged dry-air mole fractions of the trace ~~gases~~ gas of interest (X_{gas}), which is defined as:

$$X_{gas} = \frac{\text{column}_{\text{gas}}}{\text{column dry air}} \frac{\text{column}_{\text{gas}}}{\text{column}_{\text{air}}^{\text{dry}}} \tag{1}$$

The column of dry air, in units of $\text{molecules} \cdot \text{cm}^{-2}$, is computed either from retrieved oxygen (O_2) when available (for the ~~Caltech record~~TCCON records), or from precise measurements of the surface

pressure (for the MkIV record):

$$\text{column dry air}\text{column}_{\text{air}}^{\text{dry}} = \frac{\text{column}_{\text{O}_2}}{0.2095} \quad (2)$$

$$= \frac{P_s}{\{g\}_{air} m_{air}^{dry}} - \text{column}_{\text{H}_2\text{O}} \frac{m_{\text{H}_2\text{O}}}{m_{air}^{dry}} \quad (3)$$

The measured surface pressure (P_s) is converted to a dry surface pressure by subtracting the column amount of water ($\text{column}_{\text{H}_2\text{O}}$), where $\{g\}_{air}$ is the column-averaged gravitational acceleration, m_{air}^{dry} is the molecular mass of dry air, and m_{H_2O} is the molecular mass of water.

The MkIV time series plots shown in Figure 1 reflect the influence of local sources in addition to the large scale backgrounds for these gases. To show the global background trends, overlaid on Figure 1 are the surface *in situ* measurements of methane (Dlugokencky et al., 2016), carbon monoxide (CO, Novelli and Masarie, 2015), and ethane (Helmig et al., 2015) made atop Mauna Loa, Hawaii. The apparent "noise" in the MkIV time series is both from diurnal changes and from ~~seasonal changes, dominated by the~~ the larger seasonal changes. Note that the magnitude of the Mauna Loa free-troposphere *in situ* concentrations should not be expected to exactly match the MkIV total column-averaged dry-air mole fractions. In particular, the concentration of methane is significantly lower ~~aloft than in the troposphere~~above the tropopause, and so ~~one would expect the magnitude of~~ X_{CH_4} ~~to be~~ is generally lower than the free-tropospheric methane concentrations (Washenfelder et al., 2003; Saad et al., 2014; Wang et al., 2014).

To diagnose the contribution of SoCAB sources to the trace gas columns, we quantify the diurnally-varying gas ratios following the methodology described in detail in Wunch et al. (2009), and briefly described as follows. Because of the topography of the SoCAB and its predictable diurnal wind flow pattern, gases emitted into the basin atmosphere, even if they are not emitted by the same source, show similar diurnal patterns, with a peak in the total column around 2 pm local time, when the planetary boundary layer is thickest. Diurnal changes ~~can thus isolate~~ thus represent emissions into the SoCAB~~, as they are insensitive to seasonal or longer-term trends~~. To quantify the diurnal change in X_{gas} for the ~~Caltech FTS~~ TCCON data, we subtract morning values from afternoon values at the same solar zenith angles, producing ΔX_{gas}, a "gas anomaly" value. This ~~minimizes the potential for any~~ approach minimizes airmass-dependent biases in the measurements from appearing as diurnal changes~~.~~, but it does not remove the small temperature bias (as afternoons are systematically warmer than mornings). Sensitivity studies which perturb the assumed lower atmosphere temperature show that the retrieved C_2H_6 amount will change by <1% for a temperature perturbation of 5 K at the surface, a typical diurnal surface temperature change. Since a typical diurnal change in C_2H_6 between mid-afternoon and mid-morning is about 20%, the temperature-induced affect is comparatively small. Similar sensitivity studies for CH_4 (for lower spectral resolution instruments using the same absorption windows used here) show a much smaller temperature sensitivity, but also smaller diurnal variability, again resulting in an effect with a magnitude of about 5% (Hedelius et al., 2016).

We assume that the emissions into the lowest layers of the atmosphere cause the diurnal pattern in X_{gas} and thus we explicitly account for differences in the measurement sensitivity at the surface to each gas ~~. This is achieved~~ by dividing the ΔX_{gas} by the value of the column averaging kernel at the surface. We then compute the slope that relates anomalies of one gas to another. Our data filtering scheme, designed to minimize the impacts of non-basin air, fires, significant weather events, and instrument problems is described in §A.

The MkIV dataset is ~~relatively~~ temporally sparse, and the observation strategy was not intended for this kind of differential analysis: MkIV measurements are taken around solar noon, and only for one to two hours per day. While this observation strategy minimises airmass variation, columns measured only an hour apart tend to be similar, and so the computed anomalies are small and therefore noisy. A consequence of this is that MkIV methane measurements, which have smaller fractional diurnal variability than the other gases presented here, are not currently precise enough for anomaly analysis. Daily anomalies of ethane, carbon monoxide and acetylene are computed here by subtracting the daily mean value from each measurement, and applying the column averaging kernel in the same manner as for the ~~Caltech dataset~~TCCON datasets. We aggregate MkIV ΔX_{gas} data for each year to calculate tracer-tracer anomaly slopes. Because the ~~Caltech dataset is~~ TCCON datasets are much denser, we aggregate ~~both monthly and annual data.~~ monthly data. Subsampling the TCCON datasets to match the times of the MkIV measurements does not appear to bias the results.

To determine emissions of the gas of interest, we use tracer-tracer anomaly slopes ~~that relate it to a gas with known emissions in the SoCAB. We choose to relate the gas of interest~~ to carbon monoxide (CO), whose emissions in the SoCAB are well constrained by extensive, biannual, mandatory vehicle smog checks and oversight by the California Air Resources Board (CARB), and are published through the CARB webpage by air basin (http://www.arb.ca.gov/app/emsinv/emssumcat.php). Wunch et al. (2009) suggested that using CO instead of CO_2 to compute emissions may underestimate the emissions due to different diurnal emissions patterns, but subsequent studies have shown better agreement with the CH_4 emissions estimates computed using its relationship with CO (Wennberg et al., 2012; Peischl et al., 2013; Wong et al., 2016). To calculate the emissions of the gas of interest, we apply the following equation:

$$E_{gas}^{SoCAB} = \left(\alpha_{gas} \frac{M_{gas}}{M_{CO}}\right) E_{CO}^{SoCAB} \tag{4}$$

where E_{CO}^{SoCAB} is the emission of carbon monoxide in the SoCAB in units of TgCO, α_{gas} is the slope of the correlation between the gas of interest and carbon monoxide in $\mathrm{mol} \cdot \mathrm{mol}^{-1}$, M_{gas} and M_{CO} are the molecular masses of the gas of interest and carbon monoxide, respectively, in $\mathrm{g} \cdot \mathrm{mol}^{-1}$.

The uncertainty estimates on the tracer-tracer anomaly slopes are the standard deviation of many slopes calculated by bootstrapping ~~the linear fit (Efron and Gong, 1983)~~(Efron and Gong, 1983) a linear fit that takes x- and y-errors into account (York et al., 2004). Uncertainty estimates on the emissions ~~multiply~~ are determined by multiplying the calculated emissions by the sum in quadra-

ture of the fractional uncertainties of the slopes and the assumed uncertainty on the CARB carbon monoxide emissions (20%).

2.1 Ancillary Data

To determine the composition of the natural gas delivered to the SoCAB, we collected bi-weekly samples of the natural gas delivered to ~~the laboratory adjacent to the Caltech TCCON station~~Caltech by SoCalGas. Natural gas components were separated using gas chromatography on an HP-PLOT Q column. The abundance of each gas was measured using a flame ionization detector with appropriate calibrations. To ensure no drift in the chromatograph, a natural gas standard was also regularly analyzed. Prior to November 2014 the analysis was performed on site on the same day the sample was collected. Afterwards, samples were collected in canisters and analyzed in batches using an off-site gas chromatograph, also using a PLOT column and flame ionization detector.

To determine the composition of the natural gas stored within the SoCAB, we use data made ~~public~~ publicly available by the Southern California Gas Company (SoCalGas). There are four SoCalGas gas storage facilities (Aliso Canyon in Northridge, Honor Rancho in Valencia, Golita near Santa Barbara, and Playa Del Rey), two of which are within the SoCAB (Aliso Canyon and Playa Del Rey). Both the Aliso Canyon and Playa Del Rey facilities are ~~are~~ exhausted oil wells that were re-purposed to store natural gas. The Aliso Canyon facility is one of the largest depleted-well gas storage facilities in the United States, with an ~~86~~ 168 billion cubic foot capacity (~~2.4~~ 4.8 billion cubic meters) ~~(AQMD, 2016; ?)~~(AQMD, 2016; USEIA, 2016); the Playa Del Rey facility can store only about 2 billion cubic feet (~~~2~~~1% of the Aliso Canyon capacity). As the result of a 2007 legal settlement, SoCalGas publishes monthly withdrawn gas composition from the Playa Del Rey wells ~~(?)~~(SoCalGas, 2008). The data are freely obtained from their website (https://www.socalgas.com/stay-safe/pipeline-and-storage-safety/playa-del-rey-storage-operations). The Aliso Canyon facility does not regularly make their withdrawn gas composition publicly available. However, ~~since~~ between October 2015 ~~, they have~~ and February 2016, they made daily atmospheric measurements near the facility available on their website in response to the ~~large loss of gas following the~~ failure of one of the withdrawal wells resulting in a large loss of gas (https://www.alisoupdates.com/acu-aliso-canyon-air-sample-results). Other measurements from aircraft near the facility ~~from aircraft~~ have been recently published (Conley et al., 2016).

2.2 Defining local plumes within the data

Highly local plumes of methane are periodically observed throughout the Caltech FTS time record. We define these "plumes" as a diurnal change in methane that is not correlated with an associated change in carbon monoxide. Carbon monoxide is a heavily emitted gas within the SoCAB, but it has no significant common sources with methane, so correlations between carbon monoxide and

methane are due to the SoCAB's atmospheric dynamics and thus represents what we will refer to as the "ambient" SoCAB air.

To quantify this, we use quantile-quantile plots ~~(?)~~ (Wilk and Gnanadesikan, 1968) that determine whether two datasets draw from the same probability distribution. In these plots, a linear relationship indicates that the distributions are similar, and any deviations from linearity suggest that the distributions are different. We assume that the data in the linear region of the graph sample ambient SoCAB air, and the nonlinear regions are from the plumes. Figure 2 shows the quantile-quantile plots for anomalies in methane and carbon monoxide.

From these plots, we determine the regions of nonlinearity, marked by grey bars. We assume that the data that fall outside the grey bars ~~represents~~ represent air that is not well-mixed (i.e., "plume" air) and that the "ambient" air is contained in the box defined by the grey bars. The top panel shows the data prior to October 22, 2015 and after February 11, 2016, and the bottom panel shows the data ~~after October 22, 2015.~~ between those dates, during the period of sustained Aliso Canyon losses.

3 Results and Discussion

We have computed emissions estimates of C_2H_6 since 1989 (Figures 3, 4), and CH_4 emissions estimates since 2007 (Figure 5). The emissions of ethane in the basin decreased significantly from the late-1980s (Figure 3) from 70 ± 17 $Gg \cdot yr^{-1}$ to ~~13 ± 4.5~~13 ± 5 $Gg \cdot yr^{-1}$ in 2010. These 2010 emissions values agree well with previous studies (12.9 Gg, Wennberg et al. (2012); 11.4±1.6 Gg, Peischl et al. (2013)). Since 2010, however, ethane emissions have ~~doubled.~~ nearly doubled. Emissions of CH_4 are steady over the 2007–2016 period, with an average value of 413 ± 86 $Gg \cdot yr^{-1}$ and a slope of -5 ± 4 $Gg \cdot yr^{-1}$ (-1.2±1.0 $\% \cdot yr^{-1}$), in good agreement with the results from Wong et al. (2016), who have monitored CH_4 in various locations throughout the SoCAB since 2011.

There are three main sources of ethane emissions in the SoCAB: vehicle exhaust, the natural gas system, and oil and gas exploration and extraction. Of these sources, only vehicle exhaust is not a significant source of CH_4. To distinguish between vehicle exhaust and fossil fuel sources, we use our coincident measurements of carbon monoxide, which tracks sources of incomplete combustion (including mobile sources), and acetylene (C_2H_2), whose emissions more directly track vehicle exhaust ~~(??)~~(Kirchstetter et al., 1996; Warneke et al., 2012; Crounse et al., 2009). The ratio of ethane to carbon monoxide in the SoCAB declined rapidly until the mid-1990s, and then slowly and steadily increased. The ratio of acetylene to carbon monoxide remained relatively constant ~~(Figure 3)~~ throughout the time period (Figures 3, 4), and thus the ethane to acetylene ratios follow the same trend as ethane to carbon monoxide. This implies that vehicle emissions are not driving the changes in ethane emissions. This is consistent with the ~~? analysisof ethane to acetylene ratios~~Warneke et al. (2012) analysis, which showed an increase in ethane relative to acetylene after 1995, which they attributed to natural gas use and production. Using the motor vehicle gas composition measured by ~~?~~Kirchstetter et al. (1996),

and the reported SoCAB carbon monoxide emissions for 1995 by CARB for mobile sources ~~(2.114 Tg · yr^{-1}, **?**)~~(2.114 Tg · yr^{-1}, C we infer that ethane emissions from mobile sources account for only ~8% of the observed ethane, in agreement with the 5 – 10% estimate of Peischl et al. (2013) for the year 2010. Thus, emissions from vehicles are unlikely to be either a dominant source of ethane to the SoCAB atmosphere, or responsible for the significant decrease in ethane ~~in the late 1980s-early 1990s~~after 1995. Prior to 1995, there were fewer regulatory controls on air pollution from vehicles, and the exhaust composition is much less well-known (Kirchstetter et al., 1996).

Natural gas and crude oil ~~extraction in California decreased by ~30-40% between the mid-1980s and the mid-1990s, and dropped by ~20%~~ production from the Los Angeles Basin decreased by about a factor of two between 1990 and ~~1995 (Figure 6, **?**). The California production of~~ 2000 (USEIA, 2015c, a). The region's natural gas liquids production, which includes ethane, propane and higher-order alkanes~~decreased at a similar rate during this period (Figure 6, **?**). If~~ , is negligibly small and no production is reported after 1993 (USEIA, 2015b). The Los Angeles Basin and the SoCAB are not identical regions: the Los Angeles Basin encompasses the SoCAB except for the northwestern corner of Los Angeles County, but it additionally includes the eastern portions of San Bernardino and Riverside counties, and all of San Diego and Imperial counties. We assume that the production in the SoCAB tracks the ~~state-wide production, this accounts for about a quarter of~~ Los Angeles Basin production. The fractional decrease in natural gas and crude oil production is consistent with the drop in ethane emissions measured by the MkIV FTS between 1990 and ~~1995. It is not clear what has caused the remaining observed drop in emissions~~ 2000 (Fig. 6). However, the absolute abundance is inconsistent with the 17% losses from oil and gas extraction determined by Peischl et al. (2013) for 2010: it would account for less than half of the C_2H_6 emissions in 1990. This suggests that either extraction losses from oil and gas production in the 1990s were significantly higher, or that the ethane content of the gas was larger.

Between ~~the mid-1990s~~ 2000 and 2010, the ethane emissions remained relatively constant (Figure 3)~~in contrast with the produced~~ , consistent with the steady production of gas and oil~~, which continued to drop by more than 20%. The ethane emissions are also uncorrelated with the liquids production, which reduced until 2001, increased suddenly by 20% in 2002, and has since remained roughly constant, though quite variable since 2010. Because the carbon monoxide emissions have dropped significantly over the measurement time period, an increase in the ethane to carbon monoxide ratio is expected if ethane emissions remain constant. The ethane to carbon monoxide ratio increase that would result from a constant ethane source is overlaid in the second panel of Figure 3, and shows that ethane emissions dropped in 2006, and began to increase monotonically after 2010.~~ . After 2010, however, the calculated ethane emissions increase monotonically, in contrast with the near-constant oil and gas production.

To explain the ethane increases in the latter period, we ~~turn to~~ rely on our temporally denser atmospheric measurements from the Caltech FTS, combined with measurements of ethane and

methane available from the withdrawn natural gas composition of the Playa Del Rey storage facility, ~~our~~ and measurements of the delivered natural gas composition to ~~the laboratory, and our atmospheric measurements from the CaltechFTS~~Caltech. Figure 7 shows the time series of ethane to methane ratios since late 2009 from the Playa Del Rey storage facility. The ratios were roughly constant at around 2.3% until a minimum in spring 2012 of ~1.7%. Since that time, the ethane to methane ratios have increased at a rate of $0.62 \pm 0.05\% \cdot \mathrm{yr}^{-1}$ with ratios exceeding 4% by mid-2015. This significant increase in ethane content of the natural gas provides an unique opportunity to attribute the sources of CH_4 to the SoCAB atmosphere. Our measurements of the ethane to methane ratio in the natural gas delivered to ~~the laboratory~~ Caltech show values consistent with the stored natural gas at Playa Del Rey and at Aliso Canyon and a consistent change in ratio over time ($0.59 \pm 0.10\% \cdot \mathrm{yr}^{-1}$). The variability of the ratios measured in the delivered gas is much higher than that reported by SoCalGas (Figure 7) and commensurate with the variability seen in the atmospheric measurements. Since Caltech and Playa Del Rey are located ~45 km apart, this suggests that the Playa Del Rey withdrawn gas values provide a reasonable (if smoothed) approximation of the basin-wide natural gas ratios.

Measurements of the atmospheric ethane to methane emissions ratios using the Caltech FTS data ~~from the beginning of the record (September 2012) through September 2015 increase with a slope of about half (54~~increase by $0.36 \pm 20\%$ ~~) of that within the reported storage gas, suggesting that~~ $0.08\% \cdot \mathrm{yr}^{-1}$, which is $58 \pm 13\%$ of the change in the ratio of ethane to methane reported in the storage gas by SoCalGas at the Playa Del Rey storage facility. The linear relationship between the Caltech FTS ethane to methane ratios and the Playa Del Rey ratios has a slope of $58 \pm 12\%$ (Figure 8), providing confirmation of this value. This finding is consistent with more than half of the excess atmospheric burden of methane in the western SoCAB ~~is related~~ being attributable to emissions from the natural gas infrastructure. ~~The time period for calculating this slope was chosen to avoid biasing the slope due to any systematic seasonal cycle in the ratios, and to avoid data impacted by the large loss of natural gas from Aliso Canyon at the end of 2015 (discussed below).~~

~~The~~ Since the average total methane emissions in the SoCAB ~~in 2015 were 448 ± 91~~since 2007 have been roughly constant at 413 ± 86 $\mathrm{Gg} \cdot \mathrm{yr}^{-1}$ (Figure ~~4; Table ??). Since 2003, SoCalGas has delivered (to within 5%) ~11.5~~5; Table 1), the ~58% attributable to the natural gas infrastructure is 240 ± 78 $\mathrm{Gg} \cdot \mathrm{yr}^{-1}$. In 2015, the SoCalGas total throughput was 2559 $\mathrm{MMcf} \cdot \mathrm{day}^{-1}$, or 18 $\mathrm{TgCH_4}$ ~~per year to customers within the SoCAB (California Gas and Electric Utilities, 2008, 2013). This ~242~~total (California Gas and Electric Utilities, 2016). We remove 3 ~~attributable to the natural gas infrastructure suggests 2.1~~$\mathrm{TgCH_4}$ from wholesales, and 0.2 $\mathrm{TgCH_4}$ for company use and "lost and unaccounted for" (LUAF) gas, giving 14.7 $\mathrm{TgCH_4}$ delivered by SoCalGas. This suggests $1.6 \pm 0.5\%$ losses as fugitive emissions ~~, a number in good agreement with the 2% estimate from Wennberg et al. (2012)~~from the total delivered. (However, only 74% of the population served by SoCalGas lives in the SoCAB, and thus the fraction of the losses as fugitive emissions would represent a larger fraction of the

delivered gas to SoCAB customers (Wennberg et al., 2012).) The roughly constant total CH_4 emissions and delivered natural gas implies that downstream natural gas emissions were not likely changing during this period. The remaining ~206~173±56 $Gg \cdot yr^{-1}$ excess methane is likely from sources without lacking an ethane signature with the same time dependence as the natural gas infrastructurethat tracks the pipeline natural gas composition. These likely sources are the SoCAB dairies (Viatte et al., 2016), feedlots and range cattle, landfills, waste-water treatment plants septic systems (Wennberg et al., 2012), and – likely particularly important in the western part of the basin – oil and gas extraction. Peischl et al. (2013) estimate 182 ± 54 $GgCH_4 \cdot yr^{-1}$ emitted from methane-dominant sources (i.e., dairies, landfills and wastewater treatment plants), and the oil and gas extraction to be 32 ± 7 $GgCH_4 \cdot yr^{-1}$. Within the uncertaintiesof these sources, this closes the methane budget in the SoCABOur results are consistent with these previous studies within the uncertainties. Table 1 compiles these emissions for CH_4 between 2007-2015 and for C_2H_6 for 2012-2015. We assume constant total emissions of CH_4 during the 2007-2015 period and changing C_2H_6 emissions from the increasing ethane content in the pipeline-quality natural gas. Within the uncertainties, the increase in observed C_2H_6 emissions can be wholly explained by the increasing ethane content in the delivered natural gas. The other sources of C_2H_6 (vehicular exhaust, oil and gas exploration and production) are assumed to be constant.

Droughts such as the one plaguing Southern California since 2012/2013 (Swain et al., 2014; Griffin and Anchukaitis, 2014) can reduce the ability of soil microbes to remove methane and ethane released underground into the soils (van den Pol-van Dasselaar et al., 1998; Adamse et al., 1972). The constant CH_4 emissions and growing C_2H_6 emissions since 2012 would require a compensating decrease in biogenic emissions of CH_4 to offset this effect. However, biogenic emissions are reported to have decreased by about 1% between 2012 and 2014 (CARB, 2016), so this effect is likely to be small.

3.1 Aliso Canyon

A large gas loss from the Aliso Canyon Storage Facility to the SoCAB began on October 23, 2015 according to SoCalGas and reports from those living nearby. The failed well was finally plugged on February 11, 2016. Conley et al. (2016) estimate that approximately 97.1 Gg CH_4 were released into the atmosphere during the 112-day leak, about 25% of the typical annual SoCAB methane emissions. After October 23, 2015, we see several days with very large enhancements in atmospheric methane and ethane, typically in the afternoons when the plume is advected into the line of sight of the Caltech FTS. There are plumes that instruments. We see no evidence of such large plumes prior to October 23 in our measurements. The plumes from Aliso Canyon can be easily distinguished from the ambient SoCAB air during this period (Figure 2, lower panel), and in these plumes, the ethane and methane anomalies are very well-correlated well correlated with a slope of $4.28 \pm 0.07\%$ (Figure 9), in good agreement with the recent delivered natural gas ethane to methane ratios which exceed 4%. From our atmospheric measurements and the Conley et al. (2016) CH_4 emissions estimate, we calculate that the ethane emission from this leak is 7.7 ± 1.7 Gg C_2H_6, which is about 3040% of the annual

SoCAB ethane emissions. ~~This is also in good agreement with the~~ Conley et al. (2016) estimated a consistent 7.3 Gg C_2H_6 emissions ~~calculated by Conley et al. (2016)~~ using aircraft measurements.

While dramatic and important to prevent, the Aliso Canyon well failure represents only a small fraction of the SoCAB methane emissions over the long term (<3% of the emissions from the SoCAB between 2007 and 2015). Furthermore, the annual methane emissions into the SoCAB (~~11.2 ± 2.3~~10.3 ± 2.2 $\mathrm{Tg\,CO_2e \cdot yr^{-1}}$, using the 100-year global warming potential of 25) represent less than 7% of those of carbon dioxide (CO_2), which we estimate to be 167.4 $\mathrm{Tg \cdot yr^{-1}}$ by scaling the California Air Resources Board estimate for California's carbon dioxide emissions in 2013 ~~(386.6 $\mathrm{Tg \cdot yr^{-1}}$, **?**)~~ (386.6 $\mathrm{Tg \cdot yr^{-1}}$, CARB, 2015) to the population of the SoCAB. Thus, significantly reducing the long-term climate impact of the SoCAB's greenhouse gas emissions requires focusing efforts to reduce carbon dioxide emissions directly.

4 Conclusions

We have measured the total column atmospheric abundances of ethane, methane and other trace gases since the late 1980s in the South Coast Air Basin in Southern California, USA. ~~Early~~ We calculate that ethane emissions declined rapidly until the mid-1990s, coincident with the decline in Los Angeles Basin production of natural gas and crude oil, but the absolute abundances are inconsistent with recent estimates of natural gas emissions from the SoCAB oil and gas production. This may suggest that either extraction losses were higher in the 1990s than they are today, or that the ethane content of the gas was larger. After the mid-1990s, the ethane emissions are ~~roughly~~ relatively constant until ~2010, and ~~monotonically increase to twice the~~ then roughly double between 2010 ~~levels by 2015, which~~ and 2015. This increase cannot be explained by the ~~decreasing~~ (decreasing) vehicular emissions or (steady) natural gas and oil production in the basin~~. After 2012, the methane emissions increased by ~20%~~, but can be explained by the increasing ethane content of the natural gas delivered to the SoCAB. Methane emissions have remained steady since 2007 at 413 ± 86 $\mathrm{Gg \cdot yr^{-1}}$. Since 2012, ethane to methane ratios in the stored and delivered natural gas have ~~been increasing~~increased, and are tracked in our atmospheric measurements with a slope of about ~~half~~ $58 \pm 13\%$ the magnitude, implying that ~~about~~ over half of the excess methane in the basin air is from losses in the natural gas infrastructure. These long-term measurements allow us to monitor the atmospheric composition and attribute changes in the atmosphere to specific sources within the basin with unique time dependencies.

The Aliso Canyon Gas Storage facility well failure on October 23, 2015, was one of the biggest singular natural gas releases in US history. Our measurements indicate that this leak, which is estimated by Conley et al. (2016) to have released 97.1 Gg CH_4 into the SoCAB atmosphere in just 112 days, produced 7.7 ± 1.7 Gg C_2H_6, ~~which represents about 30~~about 40% of the typical annual ethane emissions in the basin. The ~~emissions~~ long-term climate impacts from the Aliso Canyon well

failure are much smaller than the accumulated background methane emissions, and minor compared with the direct carbon dioxide emissions in the SoCAB.

Appendix A: Data Filtering

Data from the Caltech FTS (~~$N = 77396$~~ $N = 73335$) were filtered ~~with several criteria~~ to avoid biases in the slopes using the following criteria:

- There must be at least 5 measurements during the day to calculate ΔX_{gas} anomalies.
- We filter out days on which the ΔX_{CO_2} changes by less than 1.5 ppm, as those are typically days during which the prevailing winds are so-called "Santa Anas," which bring relatively clean air from the Mohave Desert from the North into the SoCAB and hence are not representative of SoCAB air.
- We filter out days on which ~~the~~ hydrogen fluoride anomalies (ΔX_{HF} ~~changes~~) change by more than 10 ppt. ΔX_{HF} is a proxy for tropopause height, and large changes in it over the course of the day indicates a front or other significant weather change not representative of typical SoCAB air.
- We filter out days on which the biomass burning tracer ΔX_{HCN} changes by more than 0.5 ppt, because these data are likely contaminated with fire emissions.
- Each month of data must contain at least 15 ΔX_{gas} points for a slope to be calculated ~~in each~~ for that month. This avoids biasing the slopes based on a few non-representative measurements.
- Ethane and methane are measured on two separate detectors: ethane is measured with an InSb detector; methane with an InGaAs detector. Both detectors measure carbon monoxide, and so we ensure that the carbon monoxide measured on the two detectors are consistent. Any carbon monoxide measurements that are not within 2σ are excluded from further analysis.

Data from the MkIV FTS were filtered more loosely (~~$N = 1725$~~ $N = 1727$) than the Caltech FTS measurements, as the density of measurements is much lower, and measurements are manually initiated and terminated within a few hours of noon on clear, smoke-free days.

- There must be at least 5 ΔX_{gas} anomalies per year to calculate the tracer-tracer slopes.
- The change in X_{CO} must be sufficiently large ($5 \times 10^{17} \mathrm{molecules \cdot cm^2}$, or ~2%) in order to calculate a robust slope for each year.

Acknowledgements. Part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA. We thank the various people who have assisted with MkIV ground-based observations over the years. This research was supported by ~~NASA999~~NASA's Carbon Cycle Science program (NNX14AI60G).

References

Adamse, A. D., Hoeks, J., Bont, J. A. M., and Kessel, J. F.: Microbial activities in soil near natural gas leaks, Archiv fur Mikrobiologie, 83, 32–51, doi:10.1007/BF00425043, http://link.springer.com/10.1007/BF00425043, 1972.

AQMD: Aliso Canyon Update, Tech. rep., South Coast Air Quality Management District, http://www.aqmd.gov/home/regulations/compliance/aliso-canyon-update, 2016.

California Gas and Electric Utilities: 2008 California Gas Report, Tech. rep., https://www.socalgas.com/regulatory/documents/cgr/2008{_}CGR.pdf, 2008.

California Gas and Electric Utilities: 2013 California Gas Report Supplement, Tech. Rep. July, https://www.socalgas.com/regulatory/documents/cgr/2013-cgr.pdf, 2013.

California Gas and Electric Utilities: 2016 California Gas Report, Tech. rep., 2016.

CARB: Almanac Emission Projection Data, http://www.arb.ca.gov/app/emsinv/emssumcat.php, 2009.

CARB: Greenhouse Gas Emissions Inventory Summary [2000 - 2013], Tech. rep., California Air Resources Board, Sacramento, http://www.arb.ca.gov/app/ghg/2000{_}2013/ghg{_}sector{_}data.php, 2015.

CARB: Greenhouse Gas Emission Inventory Summary [2000-2014], Tech. rep., California Air Resources Board, Sacramento, http://www.arb.ca.gov/app/ghg/2000{_}2014/ghg{_}sector{_}data.php, 2016.

Conley, S., Franco, G., Faloona, I., Blake, D. R., Peischl, J., and Ryerson, T. B.: Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA, Science, 2348, 2–7, doi:10.1126/science.aaf2348, 2016.

Crounse, J. D., DeCarlo, P. F., Blake, D. R., Emmons, L. K., Campos, T. L., Apel, E. C., Clarke, A. D., Weinheimer, A. J., McCabe, D. C., Yokelson, R. J., Jimenez, J. L., and Wennberg, P. O.: Biomass burning and urban air pollution over the Central Mexican Plateau, Atmospheric Chemistry and Physics, 9, 4929–4944, doi:10.5194/acp-9-4929-2009, www.atmos-chem-phys.net/9/4929/2009/, 2009.

Dlugokencky, E. J., Crotwell, A., Lang, P., and Mund, J.: Atmospheric Methane Dry Air Mole Fractions from quasi-continuous measurements at Mauna Loa, Hawaii, 1986-2015, Version: 2016-01-20, ftp://aftp.cmdl.noaa.gov/data/trace{_}gases/ch4/in-situ/surface/, 2016.

Efron, B. and Gong, G.: A Leisurely Look at the Bootstrap, the Jackknife, and Cross-Validation, The American Statistician, 37, 36, doi:10.2307/2685844, http://www.jstor.org/stable/2685844?origin=crossref, 1983.

Griffin, D. and Anchukaitis, K. J.: How unusual is the 2012 – 2014 California drought?, Geophysical Research Letters, 41, 9017–9023, doi:10.1002/2014GL062433.1., 2014.

Hedelius, J. K., Viatte, C., Wunch, D., Roehl, C. M., Toon, G. C., Chen, J., Jones, T., Wofsy, S. C., Franklin, J. E., Parker, H., Dubey, M. K., and Wennberg, P. O.: Assessment of errors and biases in retrievals of XCO2, XCH4, XCO, and XN2O from a 0.5 cm-1 resolution solar-viewing spectrometer, Atmospheric Measurement Techniques, 9, 3527–3546, doi:10.5194/amt-9-3527-2016, http://www.atmos-meas-tech.net/9/3527/2016/, 2016.

Helmig, D., Hueber, J., and Tans, P. P.: Non-Methane Hydrocarbons from the NOAA ESRL Surface Network, 2004-2015, ftp://aftp.cmdl.noaa.gov/data/trace{_}gases/voc/c2h6/flask/surface/c2h6{_}mlo{_}surface-flask{_}1{_}arl{_}event.txt, 2015.

Hopkins, F. M., Kort, E. A., Bush, S. E., Ehleringer, J. R., Lai, C.-T., Blake, D. R., and Randerson, J. T.: Spatial patterns and source attribution of urban methane in the Los Angeles Basin, Journal of Geophysical Research:

Atmospheres, 121, 2490–2507, doi:10.1002/2015JD024429, http://doi.wiley.com/10.1002/2015JD024429, 2016.

Hsu, Y.-K., VanCuren, T., Park, S., Jakober, C., Herner, J., FitzGibbon, M., Blake, D. R., and Parrish, D. D.: Methane emissions inventory verification in southern California, Atmospheric Environment, 44, 1–7, doi:10.1016/j.atmosenv.2009.10.002, http://linkinghub.elsevier.com/retrieve/pii/S1352231009008504, 2010.

Kirchstetter, T. W., Singer, B. C., Harley, R. A., Kendall, G. R., and Chan, W.: Impact of Oxygenated Gasoline Use on California Light-Duty Vehicle Emissions, Environmental Science & Technology, 30, 661–670, doi:10.1021/es950406p, http://pubs.acs.org/doi/abs/10.1021/es950406p, 1996.

McKain, K., Wofsy, S. C., Nehrkorn, T., Eluszkiewicz, J., Ehleringer, J. R., and Stephens, B. B.: Assessment of ground-based atmospheric observations for verification of greenhouse gas emissions from an urban region., Proceedings of the National Academy of Sciences of the United States of America, 109, 8423–8, doi:10.1073/pnas.1116645109, http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=3365165{&}tool=pmcentrez{&}rendertype=abstract, 2012.

Novelli, P. and Masarie, K.: Atmospheric Carbon Monoxide Dry Air Mole Fractions from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1988-2014, Version: 2015-08-04, ftp://aftp.cmdl.noaa.gov/data/trace{_}gases/co/flask/surface/, 2015.

Peischl, J., Ryerson, T. B., Brioude, J., Aikin, K. C., Andrews, A. E., Atlas, E., Blake, D. R., Daube, B. C., de Gouw, J. A., Dlugokencky, E. J., Frost, G. J., Gentner, D. R., Gilman, J. B., Goldstein, A., Harley, R. A., Holloway, J. S., Kofler, J., Kuster, W. C., Lang, P. M., Novelli, P. C., Santoni, G. W., Trainer, M., Wofsy, S. C., and Parrish, D. D.: Quantifying sources of methane using light alkanes in the Los Angeles basin, California, Journal of Geophysical Research: Atmospheres, 118, n/a–n/a, doi:10.1002/jgrd.50413, http://doi.wiley.com/10.1002/jgrd.50413, 2013.

Rothman, L., Gordon, I., Babikov, Y., Barbe, A., Chris Benner, D., Bernath, P. F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L. R., Campargue, A., Chance, K., Cohen, E., Coudert, L., Devi, V., Drouin, B., Fayt, A., Flaud, J.-M., Gamache, R., Harrison, J., Hartmann, J.-M., Hill, C., Hodges, J., Jacquemart, D., Jolly, A., Lamouroux, J., Le Roy, R., Li, G., Long, D., Lyulin, O., Mackie, C., Massie, S., Mikhailenko, S., Müller, H., Naumenko, O., Nikitin, A., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E., Richard, C., Smith, M., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G. C., Tyuterev, V., and Wagner, G.: The HITRAN2012 molecular spectroscopic database, Journal of Quantitative Spectroscopy and Radiative Transfer, 130, 4–50, doi:10.1016/j.jqsrt.2013.07.002, http://linkinghub.elsevier.com/retrieve/pii/S0022407313002859, 2013.

Saad, K. M., Wunch, D., Toon, G. C., Bernath, P. F., Boone, C., Connor, B. J., Deutscher, N. M., Griffith, D. W. T., Kivi, R., Notholt, J., Roehl, C., Schneider, M., Sherlock, V., and Wennberg, P. O.: Derivation of tropospheric methane from TCCON CH4 and HF total column observations, Atmospheric Measurement Techniques, 7, 2907–2918, doi:10.5194/amt-7-2907-2014, http://www.atmos-meas-tech.net/7/2907/2014/, 2014.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A.,

Joos, F., Kim, H.-S., Kleinen, T., Krummel, P., Lamarque, J.-F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., O'Doherty, S., Parmentier, F.-J. W., Patra, P. K., Peng, C., Peng, S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W. J., Saito, M., Schroder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thorton, B. F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D. B., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z., and Zhu, Q.: The Global Methane Budget: 2000-2012, Earth System Science Data Discussions, pp. 1–79, doi:10.5194/essd-2016-25, http://www.earth-syst-sci-data-discuss.net/essd-2016-25/, 2016.

SoCalGas: Playa del Rey natural gas storage operations, Tech. rep., Southern California Gas Company, https://www2.socalgas.com/documents/safety/pdr{_}storage.pdf, 2008.

Swain, D., Tsiang, M., Haugen, M., Singh, D., Charland, A., Rajaratnam, B., and Diffenbaugh, N. S.: The extraordinary California drought of 2013/2014: Character, context, and the role of climate change, Bulletin of the ..., p. 17, http://search.proquest.com/openview/437b06df38d374695901882dfac98766/1?pq-origsite=gscholar{&}cbl=31345, 2014.

Toon, G. C.: The JPL MkIV interferometer, Optics and Photonics News, 2, 19, doi:10.1364/OPN.2.10.000019, 1991.

Toon, G. C.: Telluric line list for GGG2014, http://dx.doi.org/10.14291/tccon.ggg2014.atm.R0/1221656, doi:10.14291/tccon.ggg2014.atm.R0/1221656, 2014.

Townsend-Small, A., Tyler, S. C., Pataki, D. E., Xu, X., and Christensen, L. E.: Isotopic measurements of atmospheric methane in Los Angeles, California, USA: Influence of "fugitive" fossil fuel emissions, Journal of Geophysical Research, 117, 1–11, doi:10.1029/2011JD016826, http://www.agu.org/pubs/crossref/2012/2011JD016826.shtml, 2012.

USEIA: California - Los Angeles Basin Onshore Crude Oil Estimated Production from Reserves (Million Barrels), http://tonto.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET{&}s=RCRR10RCAL{_}1{&}f=A, 2015a.

USEIA: Calif–Los Angeles Basin Onshore Natural Gas Plant Liquids, Reserves Based Production (Million Barrels), http://tonto.eia.gov/dnav/ng/hist/rl2r55rcal{_}1a.htm, 2015b.

USEIA: California - Los Angeles Basin Onshore Dry Natural Gas Reserves Estimated Production (Billion Cubic Feet), http://tonto.eia.gov/dnav/ng/hist/rngr20rcal{_}1a.htm, 2015c.

USEIA: Natural Gas Annual Respondent Query System (EIA-191 Field Level Storage Data (Annual) through 2014), http://www.eia.gov/cfapps/ngqs/ngqs.cfm?f{_}report=RP7, 2016.

van den Pol-van Dasselaar, A., van Beusichem, M. L., and Oenema, O.: Effects of soil moisture content and temperature on methane uptake by grasslands on sandy soils, Plant and Soil, 204, 213–222, doi:10.1023/A:1004371309361, http://link.springer.com/10.1023/A:1004371309361, 1998.

Viatte, C., Lauvaux, T., Hedelius, J. K., Parker, H., Chen, J., Jones, T., Franklin, J., Deng, A., Gaudet, B., Verhulst, K., Duren, R., Wunch, D., Roehl, C., Dubey, M., Wofsy, S. C., and Wennberg, P. O.: Methane emissions from dairies in the Los Angeles Basin, Submitted to Atmos. Chem. Phys. Discuss., 2016.

Wang, Z., Deutscher, N. M., Warneke, T., Notholt, J., Dils, B., Griffith, D. W. T., Schmidt, M., Ramonet, M., and Gerbig, C.: Retrieval of tropospheric column-averaged CH₄ mole fraction by solar absorption

FTIR-spectrometry using N₂O as a proxy, Atmospheric Measurement Techniques, 7, 3295–3305, doi:10.5194/amt-7-3295-2014, http://www.atmos-meas-tech.net/7/3295/2014/, 2014.

Warneke, C., de Gouw, J. A., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E., Blake, D. R., Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions, Journal of Geophysical Research: Atmospheres, 117, 1–10, doi:10.1029/2012JD017899, http://doi.wiley.com/10.1029/2012JD017899, 2012.

Washenfelder, R. A., Wennberg, P. O., and Toon, G. C.: Tropospheric methane retrieved from ground-based near-IR solar absorption spectra, Geophysical Research Letters, 30, 1–5, doi:10.1029/2003GL017969, http://www.agu.org/pubs/crossref/2003/2003GL017969.shtml, 2003.

Wennberg, P. O., Mui, W., Wunch, D., Kort, E. A., Blake, D. R., Atlas, E. L., Santoni, G. W., Wofsy, S. C., Diskin, G. S., Jeong, S., and Fischer, M. L.: On the sources of methane to the Los Angeles atmosphere., Environmental science & technology, 46, 9282–9, doi:10.1021/es301138y, http://www.ncbi.nlm.nih.gov/pubmed/22853880, 2012.

Wennberg, P. O., Roehl, C., Blavier, J.-F., Wunch, D., Landeros, J., and Allen, N.: TCCON data from Jet Propulsion Laboratory, Pasadena, California, USA, Release GGG2014R0, http://dx.doi.org/10.14291/tccon.ggg2014.jpl02.R0/1149297, doi:10.14291/tccon.ggg2014.jpl02.R0/1149297, 2014a.

Wennberg, P. O., Wunch, D., Roehl, C., Blavier, J.-F. L., Toon, G. C., and Allen, N.: TCCON data from California Institute of Technology, Pasadena, California, USA, Release GGG2014R1, http://dx.doi.org/10.14291/tccon.ggg2014.pasadena01.R1/1182415, doi:10.14291/tccon.ggg2014.pasadena01.R1/1182415, 2014b.

Wennberg, P. O., Wunch, D., Yavin, Y., Toon, G. C., Blavier, J.-F., Allen, N., and Keppel-Aleks, G.: TCCON data from Jet Propulsion Laboratory, Pasadena, California, USA, Release GGG2014R0, http://dx.doi.org/10.14291/tccon.ggg2014.jpl01.R0/1149163, doi:10.14291/tccon.ggg2014.jpl01.R0/1149163, 2014c.

Wilk, M. B. and Gnanadesikan, R.: Probability plotting methods for the analysis of data, Biometrika, 55, 1–17, doi:10.1093/biomet/55.1.1, http://biomet.oxfordjournals.org/cgi/doi/10.1093/biomet/55.1.1, 1968.

Wong, K. W., Fu, D., Pongetti, T. J., Newman, S., Kort, E. A., Duren, R., Hsu, Y. K., Miller, C. E., Yung, Y. L., and Sander, S. P.: Mapping CH4 : CO2 ratios in Los Angeles with CLARS-FTS from Mount Wilson, California, Atmospheric Chemistry and Physics, 15, 241–252, doi:10.5194/acp-15-241-2015, 2015.

Wong, K. W., Pongetti, T. J., Oda, T., Rao, P., Gurney, K. R., Newman, S., Duren, R. M., Miller, C. E., Yung, Y. L., and Sander, S. P.: Monthly trends of methane emissions in Los Angeles from 2011 to 2015 inferred by CLARS-FTS observations, Atmospheric Chemistry and Physics Discussions, pp. 1–29, doi:10.5194/acp-2016-232, http://www.atmos-chem-phys-discuss.net/acp-2016-232/, 2016.

Wunch, D., Wennberg, P. O., Toon, G. C., Keppel-Aleks, G., and Yavin, Y. G.: Emissions of greenhouse gases from a North American megacity, Geophysical Research Letters, 36, 1–5, doi:10.1029/2009GL039825, http://www.agu.org/pubs/crossref/2009/2009GL039825.shtml, 2009.

Wunch, D., Toon, G. C., Blavier, J.-F. L., Washenfelder, R. A., Notholt, J., Connor, B. J., Griffith, D. W. T., Sherlock, V., and Wennberg, P. O.: The total carbon column observing network., Philosophical transactions. Series A, Mathematical, physical, and engineering sciences, 369, 2087–

2112, doi:10.1098/rsta.2010.0240, http://rsta.royalsocietypublishing.org/content/369/1943/2087http://www.ncbi.nlm.nih.gov/pubmed/21502178, 2011.

Wunch, D., Toon, G. C., Sherlock, V., Deutscher, N. M., Liu, C., Feist, D. G., and Wennberg, P. O.: The Total Carbon Column Observing Network's GGG2014 Data Version, Tech. rep., California Institute of Technology, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. doi: 10.14291/tccon.ggg2014.documentation.R0/1221662, doi:10.14291/tccon.ggg2014.documentation.R0/1221662, http://dx.doi.org/10.14291/tccon.ggg2014.documentation.R0/1221662, 2015.

York, D., Evensen, N. M., Martinez, M. L., and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, American Journal of Physics, 72, 367, doi:10.1119/1.1632486, http://link.aip.org/link/AJPIAS/v72/i3/p367/s1{&}Agg=doi, 2004.

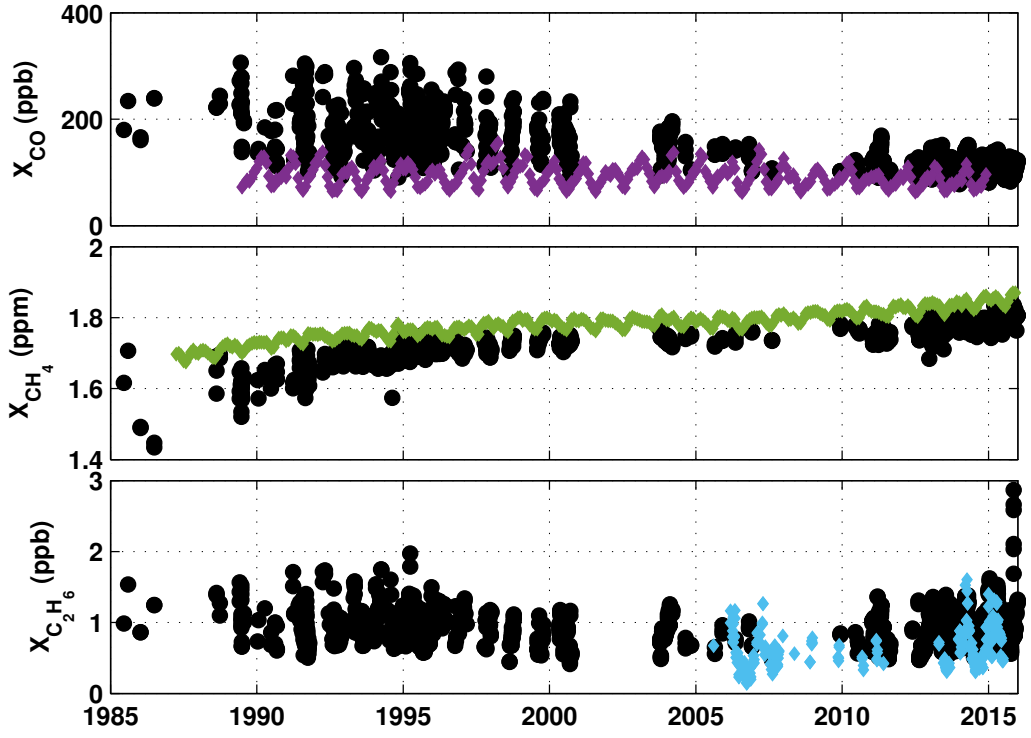


Figure 1. Time series from the MkIV FTS in the SoCAB. The ~~black~~ colourful diamonds are the background surface *in situ* values measured atop Mauna Loa. The ~~purple squares, green~~ black circles ~~, and blue triangles~~ indicate the MkIV FTS measurements of X_{CO} (top), X_{CH_4} (middle), and $X_{C_2H_6}$ (bottom)~~, respectively~~. There is a marked decrease in both the day-to-day variability and median value in X_{CO} over time, an increase in X_{CH_4} in line with the global trends, and non-monotonic, seasonal changes in $X_{C_2H_6}$.

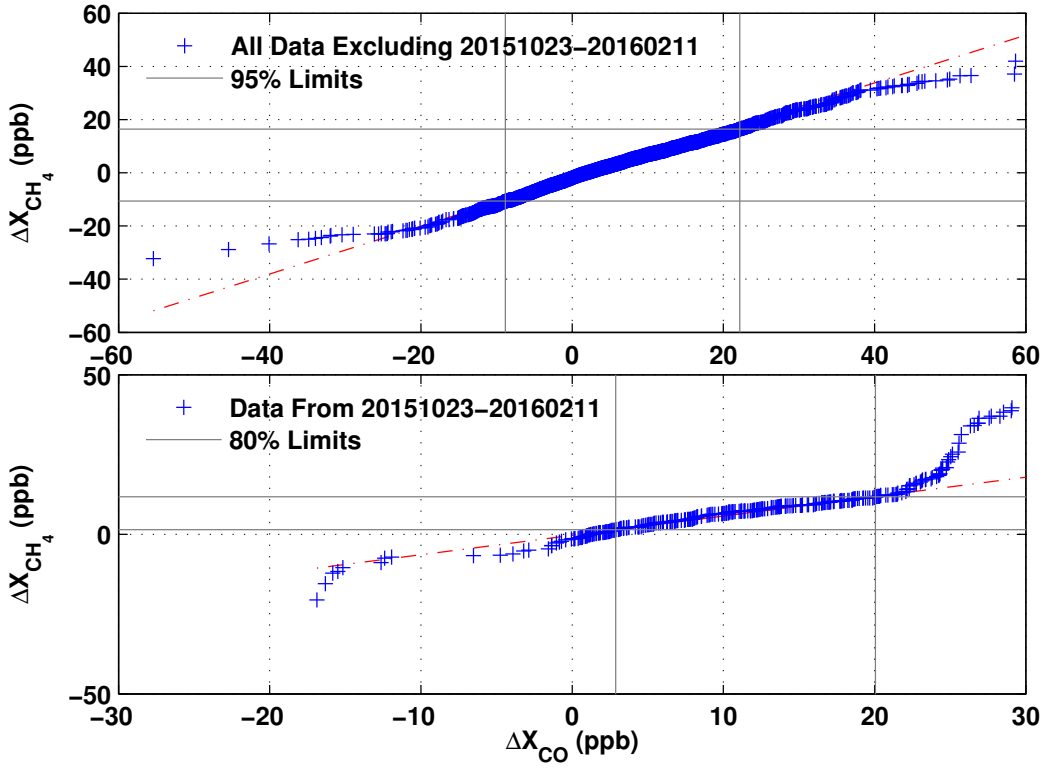


Figure 2. These quantile-quantile plots show the extent to which ΔX_{CH_4} and ΔX_{CO} anomaly data from the Caltech FTS are from the same probability distribution. When the distributions of the two datasets are similar, the points (blue '+') fall along the red dashed line. The top panel shows the quantile-quantile plot of methane and carbon monoxide from data prior to the Aliso Canyon gas leak, which started on October 23, 2015. The plot is linear between the grey lines which indicate the 95% quantiles of ΔX_{CO} and ΔX_{CH_4}. We use these limits to define air that is representative of "ambient" SoCAB air from air that contains plumes during that time period. The bottom panel shows the quantiles of ΔX_{CH_4} and ΔX_{CO} anomaly data for the time period after the Aliso Canyon gas leak began. For this time period, 80% quantiles were chosen to distinguish between ambient and plume air.

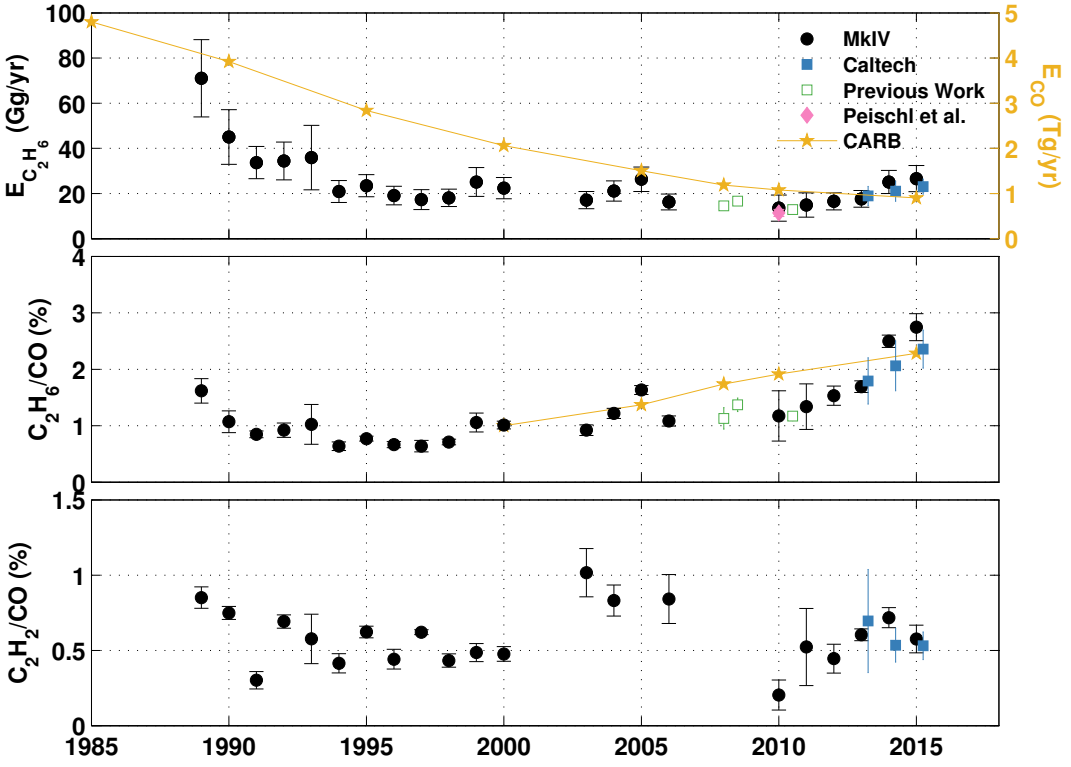


Figure 3. The top panel right axis shows the estimated carbon monoxide emissions inventory for the So-CAB, published by the California Air Resources Board (CARB). The top panel left axis shows the inferred emissions of ethane from the MkIV FTS (black circles), the Caltech FTS (blue squares), previous estimates from Wennberg et al. (2012) and Hsu et al. (2010) (green squares), and Peischl et al. (2013) (pink diamond). The second panel shows the ethane to carbon monoxide anomaly slopes from the MkIV FTS (black circles), the Caltech FTS (~~red triangles~~blue squares) and previous studies (green squares). The ~~blue~~ gold line with ~~blue squares~~ gold stars represents what the ethane to carbon monoxide anomaly slope would be if ethane in the atmosphere remained constant at 1% of the year 2000 carbon monoxide emissions from 2000 onward. The third panel shows the acetylene to carbon monoxide anomaly slopes, which are reasonably invariant over the time series.~~The fourth panel~~

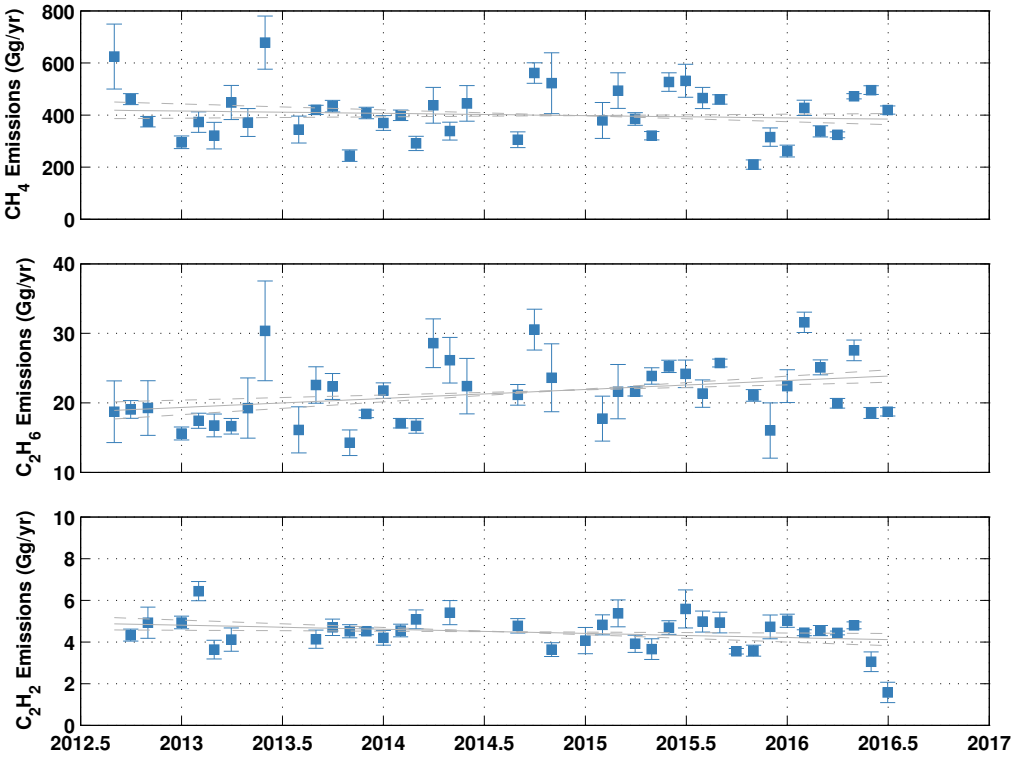
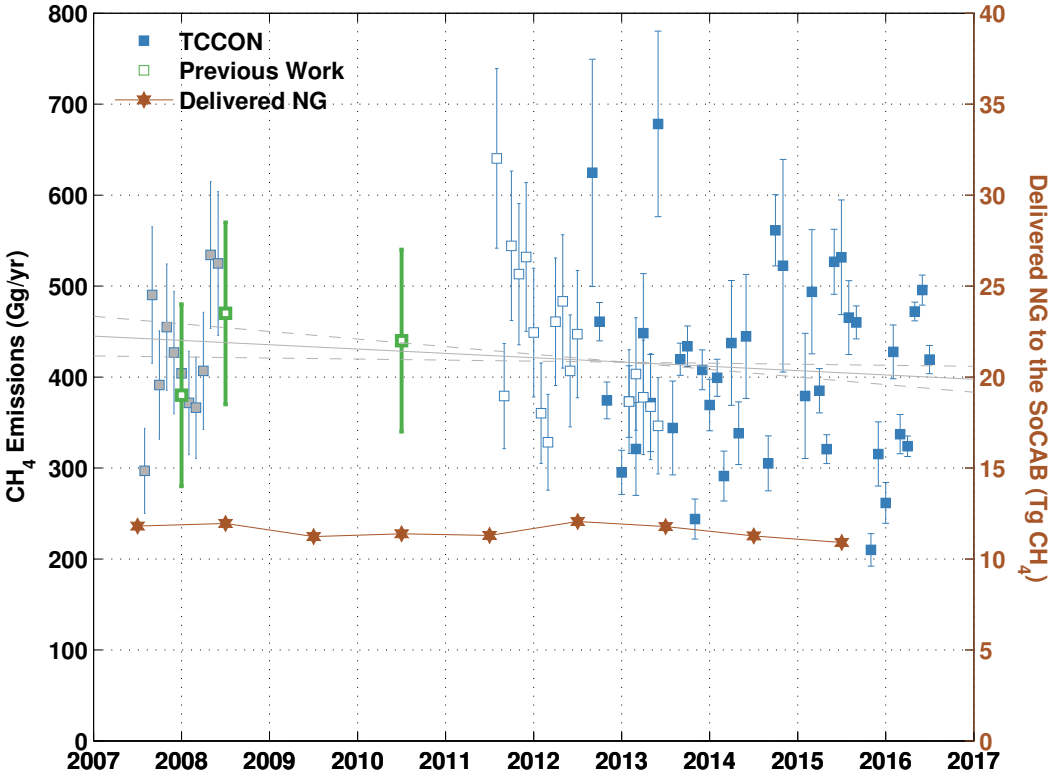


Figure 4. This plot shows the ~~inferred emissions of ethane from the MkIV FTS~~ monthly methane (~~black circles~~top), ~~the Caltech FTS~~ ethane (~~red triangles~~middle), ~~previous estimates from Wennberg et al. (2012)~~ and acetylene (~~green squares~~bottom) ~~, and Peischl et al. (2013)~~ emissions measured in the atmosphere by the Caltech FTS (~~magenta plus~~blue squares). Grey solid lines indicate the best-fit slopes with standard errors indicated by the grey dashed lines.

~~Natural gas, crude oil, and natural gas liquids production in California, reported by ??. Natural gas data prior to 1991 are reported annually, and after 1991 are reported monthly. The production is scaled to illustrate the changes in production relative to January~~



~~2000.~~

Figure 5. The left-hand axis shows methane emissions measured in the atmosphere by three TCCON FTS instruments that were located in the SoCAB since 2007. The grey solid line indicates the best-fit slope with standard errors indicated by the grey dashed lines. Previous measured emissions are indicated by green squares. The right-hand axis shows the delivered natural gas to the SoCAB, and is scaled such that if 2% of the delivered gas is released into the atmosphere, the atmospheric burden would be equal to the numbers (in Gg) on the left-hand axis.

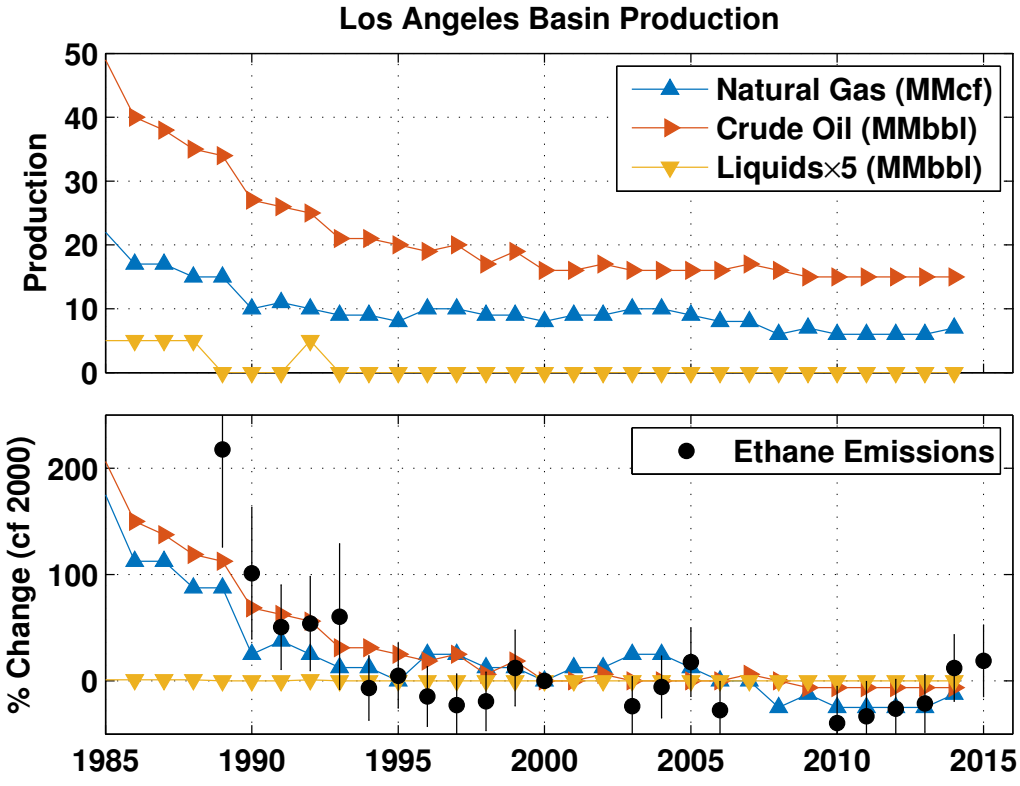


Figure 6. Natural gas, crude oil, and natural gas liquids production in the Los Angeles Basin, reported by USEIA (2015c, a, b) are shown in the top panel. The natural gas liquids production values are multiplied by 5 for scale. In the lower panel, the production is scaled to illustrate the changes in production relative to 2000. The MkIV C_2H_6 emissions relative to 2000 (black circles) are added for reference.

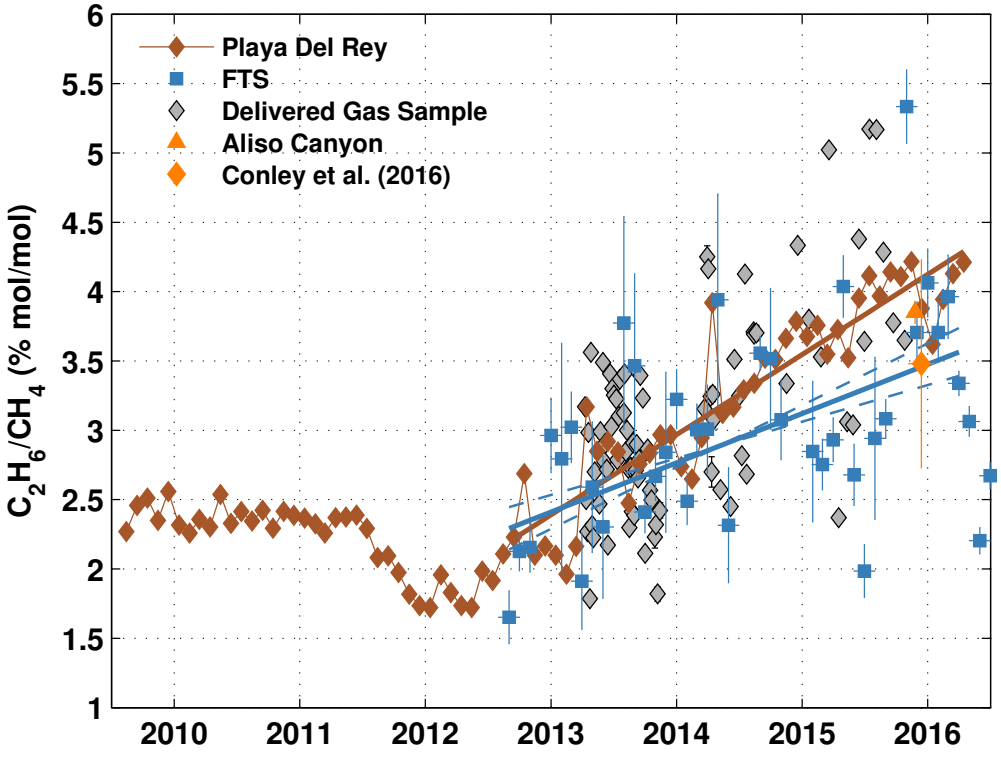


Figure 7. This time series shows the ethane to methane ratios in the Playa Del Rey gas storage facility (~~black circles~~brown diamonds), in the natural gas delivered to the laboratory (grey ~~circles~~diamonds) and in gas anomalies measured with the Caltech FTS (~~dark~~ blue squares). The slope of the Playa Del Rey ratios is shown in ~~black~~brown; the slope of the Caltech FTS ratios is in blue with dashed lines indicating the slope uncertainty. The slope of the delivered gas samples is not shown, but is statistically indistinguishable from the Playa Del Rey slope. The median ethane to methane anomaly ratio measured by SoCalGas in the air near the Aliso Canyon gas leak is indicated by the ~~red square~~orange triangle, and the value near Aliso Canyon measured from an aircraft platform by Conley et al. (2016) is indicated by the ~~red~~ orange diamond.

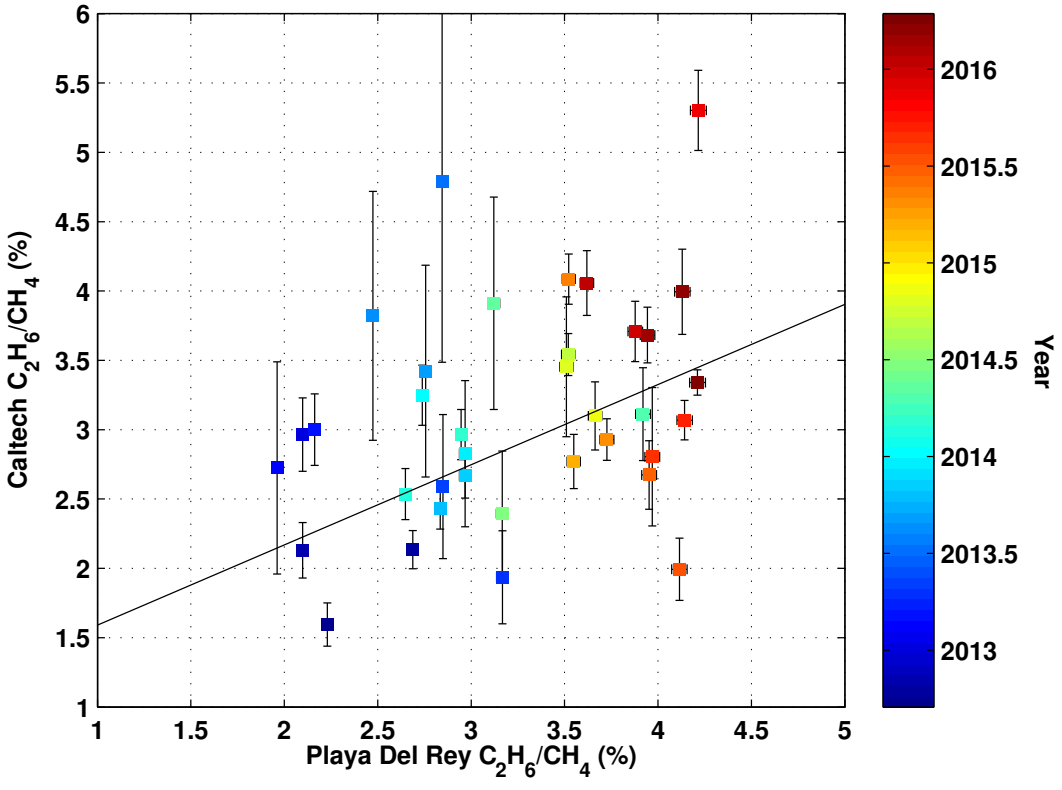


Figure 8. This ~~plot~~ figure shows the ~~monthly methane (top),~~ ethane ~~(middle),~~ to methane ratios from the Caltech FTS data on the y-axis and ~~acetylene (bottom) emissions measured in~~ from the ~~atmosphere~~ Playa Del Rey gas storage facility on the x-axis between September 2012 and March 2016. The colours indicate the date of the measurements. The slope of the relationship is indicated by the ~~Caltech FTS (~~black ~~triangles~~line (0.58 ± 0.12) ~~. The red circles show~~ and is consistent with the ~~median annual emissions~~slope derived from Figure 7.

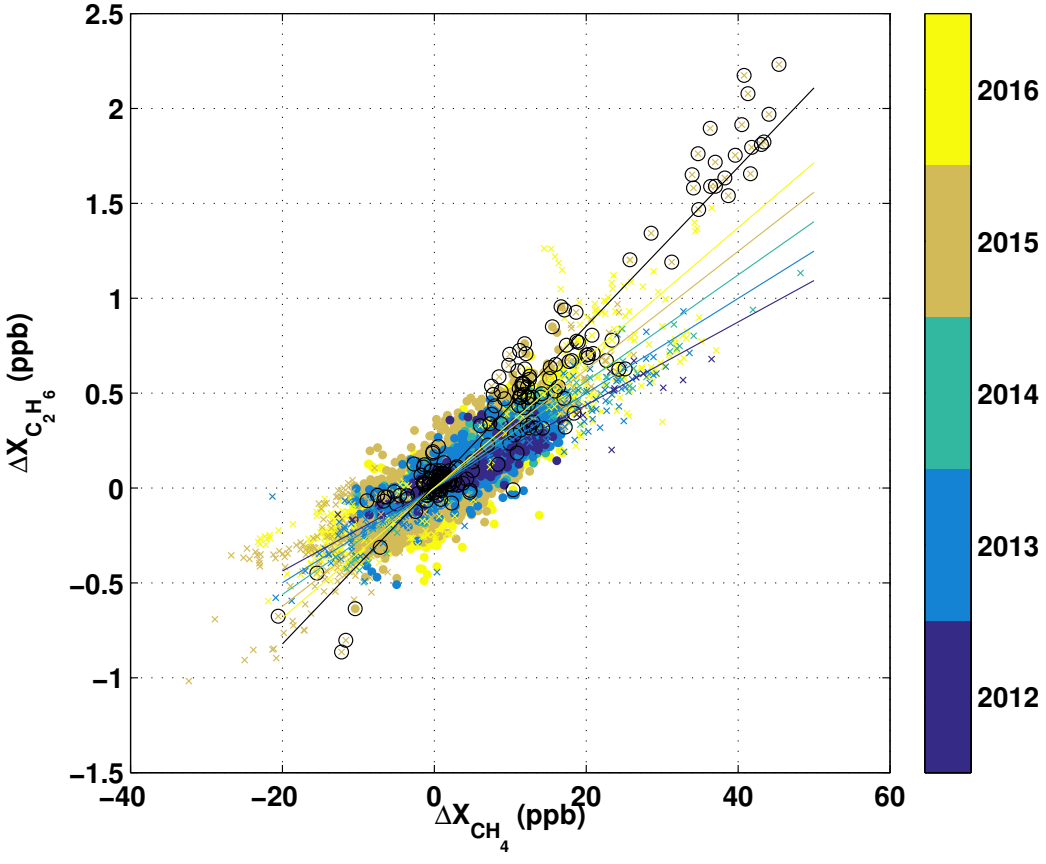


Figure 9. This figure shows the ethane and methane anomalies ~~for three different time periods:~~ during the Caltech TCCON record. The entire time series ~~(~~is represented by filled circles~~)~~, the plume data ~~(~~is represented by 'x' symbols~~)~~, and the measurements of the plume originating from the Aliso Canyon gas leak ~~(~~are circled in black~~open circles)~~. The colours represent the ~~time at~~ year during which the ~~measurement was~~ measurements were recorded. The average ambient slopes from figure 7 are indicated with solid lines, and show a time dependence consistent with the slopes from plumes. The ethane to methane slope in the Aliso Canyon plume data (black line) shows a high degree of correlation ($R^2 = 0.95$) and a slope of $4.28 \pm 0.07\%$. Note that the ethane to methane ratios in the ambient air were rising throughout the record.

Table 1. ~~Annual~~ Emissions Inventories for CH_4 and C_2H_6. Only one methane emission value is included which is the mean emissions over the 2007-2015 measurement period. Ethane emissions are from the Caltech measurements only, and each column of the table contains data from September through August. Emissions marked with a dagger (†) are from Peischl et al. (2013) for 2010. The Pipeline Natural Gas emissions of ethane are computed by multiplying the methane emissions ~~calculated~~ from the pipeline natural gas (58% of the measured total CH_4) by the increasing slope fitted to the ethane to methane ratios measured by the Caltech ~~TCCON measurements~~instrument. Uncertainties on the "Measured" emissions are the standard deviations of the monthly emissions computed for the time range.

~~Time Period~~	CH_4 Emissions $Gg\,CH_4 \cdot yr^{-1}$	~~Emissions~~	C_2H_6 Emissions $Gg\,C_2H_6 \cdot yr^{-1}$	
Source	2007–2015	2012-2013	2013-2014	2014-2015
~~201209-201308~~ Biogenics	~~380~~182±~~78~~ 54†	~~17.8~~—	—	—
Local Oil and Gas	32±~~3.6~~ 7†	4.5±1.0†	4.5±1.0†	4.5±1.0†
~~201309-201408~~ Vehicles and "Other"	~~352~~—	0.9±~~71~~ 0.1†	~~19.2~~0.9±~~3.8~~ 0.1†	0.9±0.1†
~~201409-201508~~ Pipeline Natural Gas	~~448~~240±73	11.6±4.4	13.3±5.0	15.0±5.7
Inventory Total	453±91	~~25.8~~17.0±~~5.2~~ 4.5	18.7±5.1	20.4±5.7
Measured	413±86	19±4	21±4	23±3