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

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Abstract. California's South Coast Air Basin (SoCAB) is a region in which the top-down methane emissions are underestimated by the bottom-up inventories. To provide insight into the sources of the discrepancy, we analyse a record 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 a rapid decline in ethane emissions at a much faster rate than decreasing vehicle exhaust or natural gas and crude oil production can explain. Between 2010 and 2015, ethane emissions have grown gradually from 13 ± 4.5 Gg $\cdot$ yr^{-1} to 25.8 ± 3.9 Gg $\cdot$ yr^{-1}, which is in contrast to the steady production of natural gas liquids over that time. Our methane emissions record begins in 2012 and shows an increase between 2012 and 2015 from 380 ± 78 Gg $\cdot$ yr^{-1} to 448 ± 91 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 Since 2012, ethane to methane ratios in the natural gas withdrawn from a storage facility within the SoCAB have been increasing; these ratios are tracked in our atmospheric measurements with about half of the rate of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. From this, we infer that about 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

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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; Wennberg et al., 2012; Peischl et al., 2013; Wong et al., 2015; Hopkins et al., 2016).

The SoCAB is a highly urbanized region centered on Los Angeles, with almost 17 million residents. The lower atmosphere over the SoCAB is well-confined: it is contained by mountains to the North and East, and open to the Pacific Ocean to the 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; 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. Hopkins et al. (2016) and Townsend-Small et al. (2012) conclude that most of the elevated methane is related to fossil fuels using spatial alkane measurements and isotope measurements, respectively.

In this paper, 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 ground-based Fourier transform spectrometers (FTS) located 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

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is not in the field elsewhere for intensive scientific campaigns. The second 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), and has been measuring ethane, methane and other trace gases with high temporal frequency (several hundred spectra per sunny day) since 2012 (Wennberg et al., 2014). 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 FTS instruments are direct solar-viewing and measure solar absorption by atmospheric trace gases; they are thus insensitive to atmospheric aerosol abundances. The data analysis for both 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 (Toon, 2014). The GGG2014 software produces column-averaged dry-air mole fractions of the trace gases of interest (X_{gas}), which is defined as:

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

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), or from precise measurements of the surface pressure (for the MkIV record):

$$\text{column dry air} = \frac{\text{column}_{\text{O}_2}}{0.2095} \tag{2}$$

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

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 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, and so one would expect the magnitude of X_{CH_4} to be 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

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described as follows. Because of the topography of the SoCAB and its predictable diurnal wind flow pattern, gases emitted into the basin, 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 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 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 airmass-dependent biases in the measurements from appearing as diurnal changes. We assume that the emissions into the lowest layers of the atmosphere cause the diurnal pattern in X_{gas} and thus 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. We aggregate MkIV ΔX_{gas} data for each year to calculate tracer-tracer anomaly slopes. Because the Caltech dataset is much denser, we aggregate both monthly and annual data.

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, 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). 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 $\mathrm{mol \cdot mol^{-1}}$, M_{gas} and M_{CO} are the molecular masses of the gas of interest and carbon monoxide, respectively, in $\mathrm{g \cdot mol^{-1}}$.

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). Uncertainty estimates on the

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emissions multiply the calculated emissions by the sum in quadrature 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. 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 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 billion cubic foot capacity (2.4 billion cubic meters) (AQMD, 2016; USEIA, 2016b); the Playa Del Rey facility can store only about 2 billion cubic feet (~2% 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 October 2015, they have 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 (https://www.alisoupdates.com/acu-aliso-canyon-air-sample-results). Other measurements 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.

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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 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 the bottom panel shows the data after October 22, 2015.

3 Results and Discussion

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 Gg $\cdot$ yr^{-1} in 2010. Since 2010, however, ethane emissions have doubled. There are three main sources of ethane emissions in the SoCAB: vehicle exhaust, the natural gas system, and oil and gas exploration and extraction. To distinguish between vehicle exhaust and fossil fuel sources, we use our coincident measurements of carbon monoxide and acetylene (C_2H_2), whose emissions track vehicle exhaust (Kirchstetter et al., 1996; Warneke et al., 2012). 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. This is consistent with the Warneke et al. (2012) analysis of ethane to acetylene ratios. 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 $\cdot$ yr^{-1}, CARB, 2009), 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.

Natural gas and crude oil extraction in California decreased by ~30-40% between the mid-1980s and the mid-1990s, and dropped by ~20% between 1990 and 1995 (Figure 4, USEIA, 2016a). The California production of natural gas liquids, which includes ethane, propane and higher-order alkanes decreased at a similar rate during this period (Figure 4, USEIA, 2016b). If the production in the SoCAB tracks the state-wide production, this accounts for about a quarter of 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.

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Between the mid-1990s and 2010, the ethane emissions remained relatively constant (Figure 3) in contrast with the produced 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.

To explain the ethane increases in the latter period, we turn to measurements of ethane and methane available from the withdrawn natural gas composition of the Playa Del Rey storage facility, our measurements of the delivered natural gas composition to the laboratory, and our atmospheric measurements from the Caltech FTS. Figure 5 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. Our measurements of the ethane to methane ratio in the natural gas delivered to the laboratory 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 5) 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 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±20%) of that within the reported storage gas, suggesting that half of the excess atmospheric burden of methane in the western SoCAB is related 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 total methane emissions in the SoCAB in 2015 were $448 \pm 91\ \mathrm{Gg}\cdot\mathrm{yr}^{-1}$ (Figure 6; Table 1). Since 2003, SoCalGas has delivered (to within 5%) ~11.5 $\mathrm{TgCH_4}$ per year to customers within the SoCAB (California Gas and Electric Utilities, 2008, 2013). This ~242 $\mathrm{Gg}\cdot\mathrm{yr}^{-1}$ attributable to the natural gas infrastructure suggests 2.1±0.5% losses as fugitive emissions, a number in good agreement with the 2% estimate from Wennberg et al. (2012). The remaining ~206 $\mathrm{Gg}\cdot\mathrm{yr}^{-1}$ excess methane is likely from sources without an ethane signature with the same time dependence as the natural gas infrastructure. These likely sources are the SoCAB dairies (Viatte et al., 2016), feedlots and

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range cattle, landfills, waste-water treatment plants and – likely particularly important in the western part of the basin – oil and gas extraction. Peischl et al. (2013) estimate 182 ± 54 $\mathrm{GgCH_4 \cdot yr^{-1}}$ emitted from methane-dominant sources (i.e., dairies, landfills and wastewater treatment plants), and the oil and gas extraction to be 32 ± 7 $\mathrm{GgCH_4 \cdot yr^{-1}}$. Within the uncertainties of these sources, this closes the methane budget in the SoCAB.

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 $\mathrm{Gg\ CH_4}$ 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 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 with a slope of $4.28 \pm 0.07\%$ (Figure 7). From our atmospheric measurements, we calculate that the ethane emission from this leak is 7.7 ± 1.7 $\mathrm{Gg\ C_2H_6}$, which is about 30% of the annual SoCAB ethane emissions. This is also in good agreement with the 7.3 $\mathrm{Gg\ C_2H_6}$ 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. Furthermore, the annual methane emissions into the SoCAB (11.2 ± 2.3 $\mathrm{Tg\ CO_2e \cdot yr^{-1}}$, using the 100-year global warming potential) 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 $\mathrm{Tg \cdot yr^{-1}}$, CARB, 2015) to the population of the SoCAB. Thus, significantly reducing the 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 ethane emissions declined rapidly until the mid-1990s. After the mid-1990s, the ethane emissions are roughly constant until ~2010, and monotonically increase to twice the 2010 levels by 2015, which cannot be explained by the decreasing vehicular emissions or natural gas and oil production in the basin. After 2012, the methane emissions increased by ~20%. Since 2012, ethane to methane ratios in the stored and delivered natural gas have been increasing, and are tracked in our atmospheric measurements with a slope of about half the magnitude, implying that about half of the excess methane in the basin air is from losses in the natural gas infrastructure. These long-term measurements al-

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low 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 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 $\mathrm{Gg\ CH_4}$ into the SoCAB atmosphere in just 112 days, produced $7.7 \pm 1.7\ \mathrm{Gg\ C_2H_6}$, which represents about 30% of the annual ethane emissions in the basin. The emissions 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 ($N = 77396$) were filtered with several criteria to avoid biases in the slopes:

- 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 ΔX_{HF} changes 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 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 ($N = 1725$) than the Caltech FTS measurements, as the density of measurements is much lower.

- 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.

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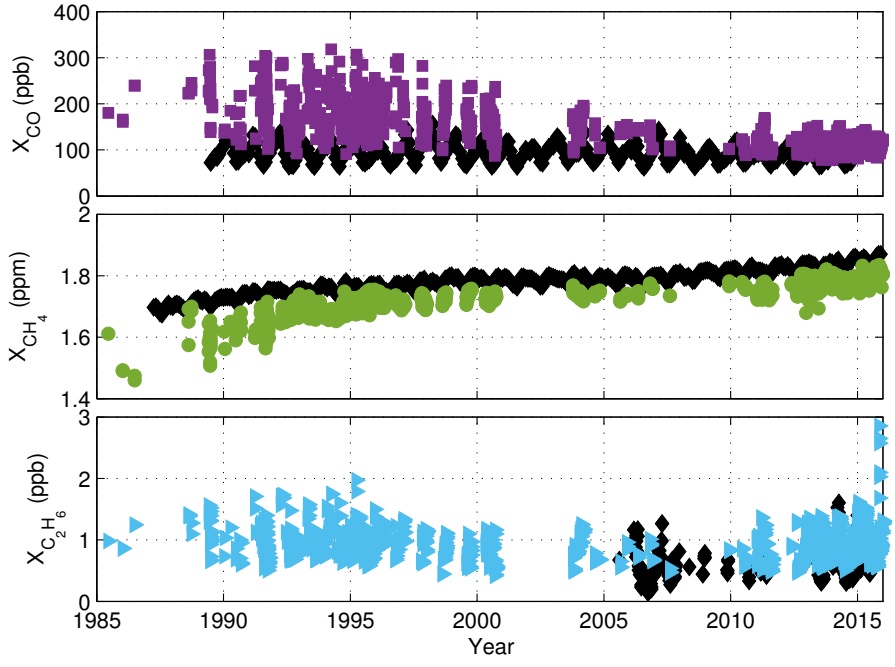

Figure 1. Time series from the MkIV FTS in the SoCAB. The black diamonds are the background surface *in situ* values measured atop Mauna Loa. The purple squares, green circles, and blue triangles indicate the MkIV FTS measurements of X_{CO} (top), X_{CH_4} (middle), and $X_{C_2H_6}$ (bottom), respectively. 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 $X_{C_2H_6}$.

Table 1. Annual methane and ethane emissions calculated from the Caltech TCCON measurements.

Time Period	CH_4 Emissions $Gg\,CH_4 \cdot yr^{-1}$	C_2H_6 Emissions $Gg\,C_2H_6 \cdot yr^{-1}$
201209-201308	380±78	17.8±3.6
201309-201408	352±71	19.2±3.8
201409-201508	448±91	25.8±5.2

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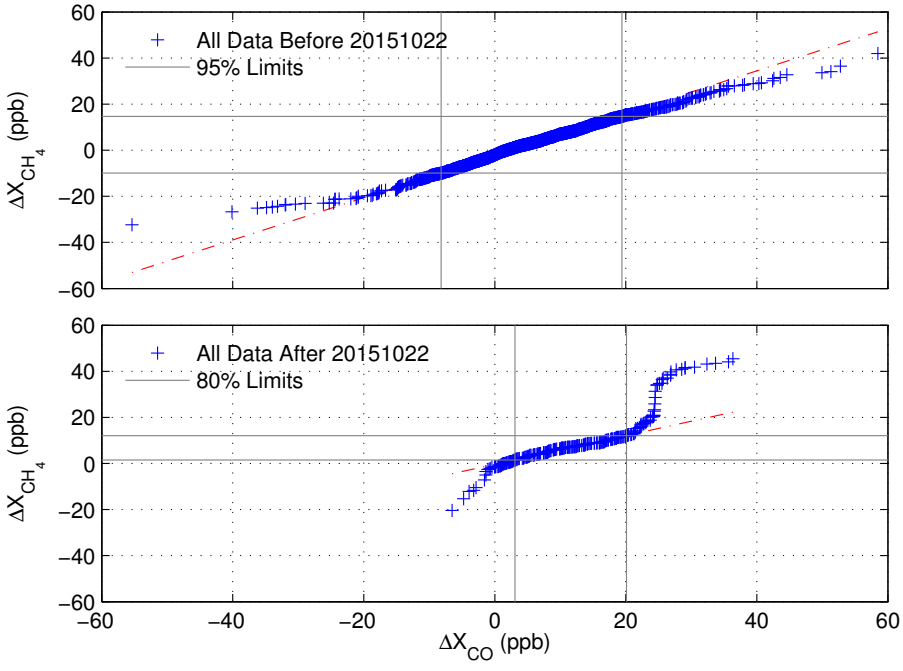

Figure 2. These quantile-quantile plots show the extent to which ΔX_{CH_4} and ΔX_{CO} anomaly data from the Caltech FTS are from the same probability distribution. When the distributions of the two datasets are similar, the points (blue '+') fall along the red dashed line. The top panel shows the quantile-quantile 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.

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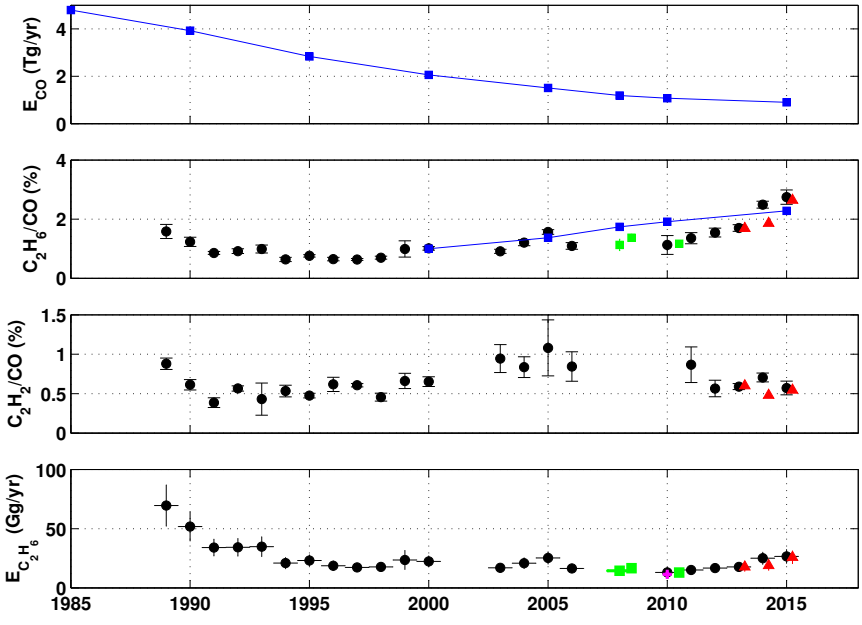

Figure 3. The top panel shows the estimated carbon monoxide emissions inventory for the SoCAB, published by the California Air Resources Board. The second panel shows the ethane to carbon monoxide anomaly slopes from the MkIV FTS (black circles), the Caltech FTS (red triangles) and previous studies (green squares). The blue line with blue squares 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 shows the inferred emissions of ethane from the MkIV FTS (black circles), the Caltech FTS (red triangles), previous estimates from Wennberg et al. (2012) (green squares), and Peischl et al. (2013) (magenta plus).

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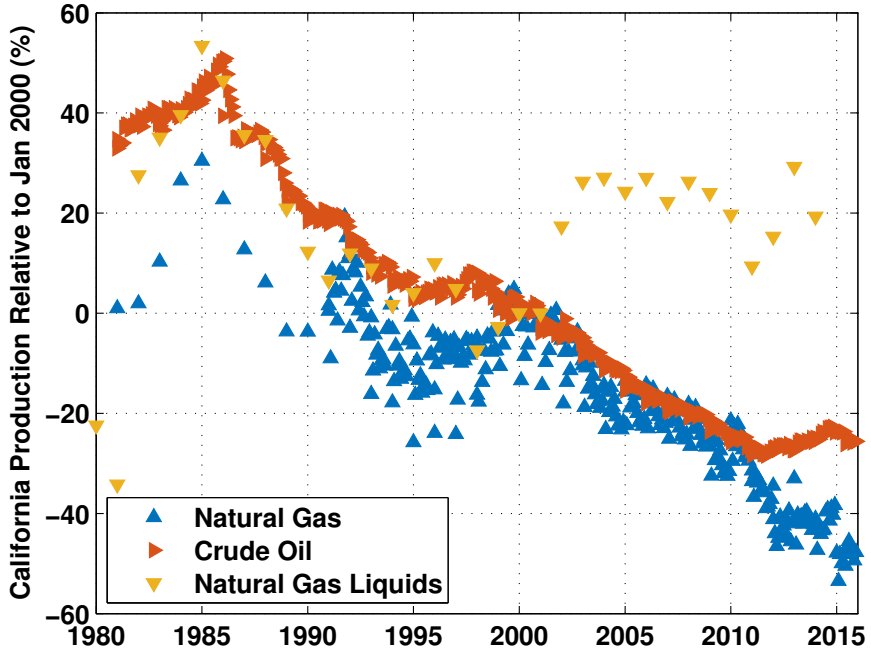

Figure 4. Natural gas, crude oil, and natural gas liquids production in California, reported by USEIA (2016a, b). Natural gas data prior to 1991 are reported annually, and after 1991 are reported monthly. The production is scaled to illustrate the changes in production relative to January 2000.

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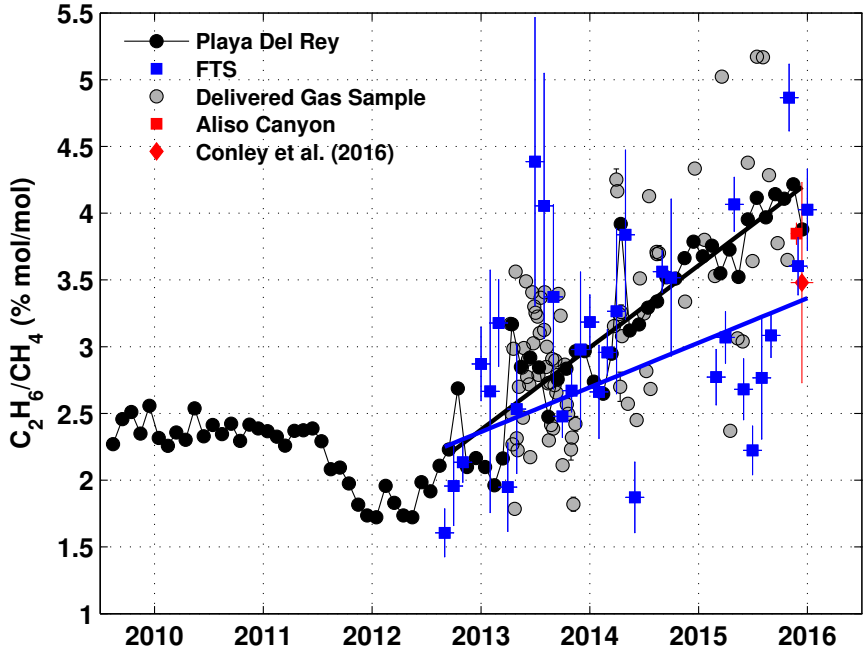

Figure 5. This time series shows the ethane to methane ratios in the Playa Del Rey gas storage facility (black circles), in the natural gas delivered to the laboratory (grey circles) and in gas anomalies measured with the Caltech FTS (dark blue squares). The slope of the Playa Del Rey ratios is shown in black; the slope of the Caltech FTS ratios is in blue. 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, and the value measured from an aircraft platform by Conley et al. (2016) is indicated by the red diamond.

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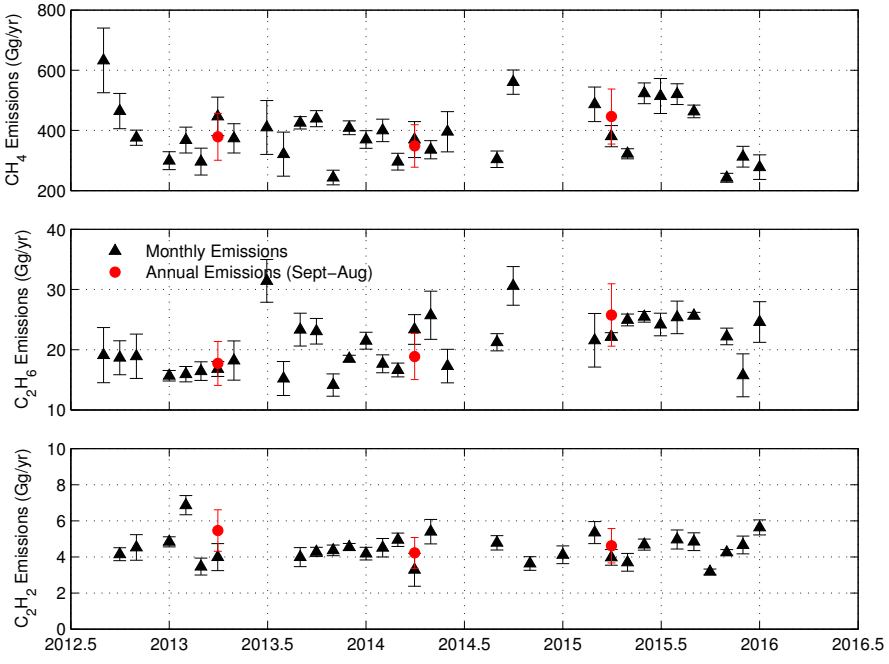

Figure 6. This plot shows the monthly methane (top), ethane (middle), and acetylene (bottom) emissions measured in the atmosphere by the Caltech FTS (black triangles). The red circles show the annual emissions.

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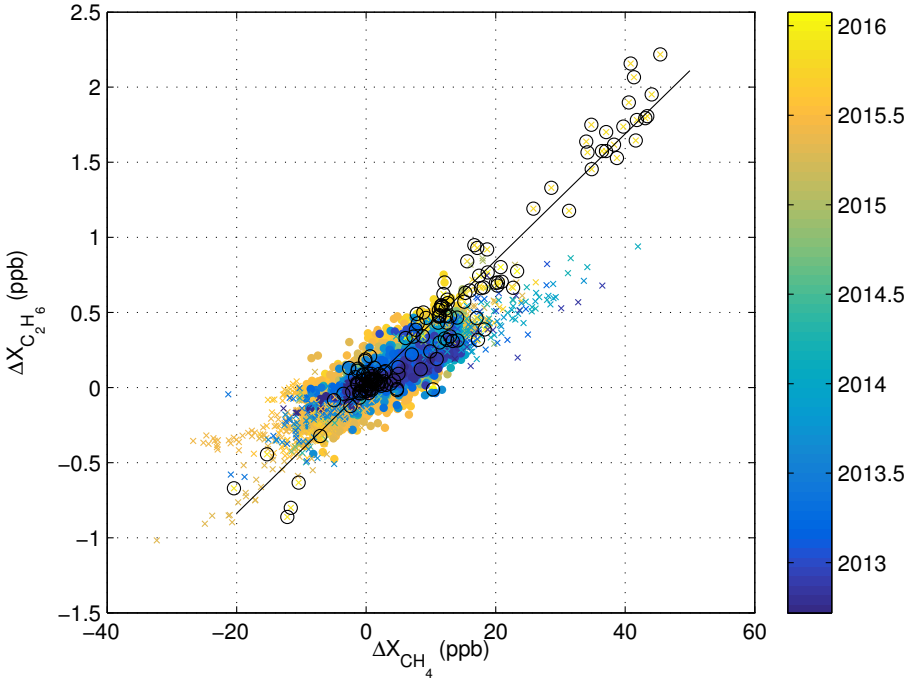

Figure 7. This figure shows the ethane and methane anomalies for three different time periods: the entire time series (filled circles), the plume data ('x' symbols), and the measurements of the plume originating from the Aliso Canyon gas leak (black open circles). The colours represent the time at which the measurement was recorded. The ambient slopes 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.