

Quantifying sources of methane using light alkanes in the Los Angeles basin, California

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Abstract

Methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and $\text{C}_2\text{--C}_5$ alkanes were measured throughout the Los Angeles (L.A.) basin in May and June 2010. We use these data to show that the emission ratios of CH_4/CO and CH_4/CO_2 in the L.A. basin are larger than expected from population-apportioned bottom-up state inventories, consistent with previously published work. We use experimentally determined CH_4/CO and CH_4/CO_2 emission ratios in combination with annual State of California CO and CO_2 inventories to derive a yearly emission rate of CH_4 to the L.A. basin. We further use the airborne measurements to directly derive CH_4 emission rates from dairy operations in Chino, and from the two largest landfills in the L.A. basin, and show these sources are accurately represented in the California Air Resources Board greenhouse gas inventory for CH_4 . We then use measurements of $\text{C}_2\text{--C}_5$ alkanes to quantify the relative contribution of other CH_4 sources in the L.A. basin, with results differing from those of previous studies. The atmospheric data are consistent with the majority of CH_4 emissions in the region coming from fugitive losses from natural gas in pipelines and urban distribution systems and/or geologic seeps, as well as landfills and dairies. The local oil and gas industry also provides a significant source of CH_4 in the area. The addition of CH_4 emissions from natural gas pipelines and urban distribution systems and/or geologic seeps and from the local oil and gas industry is sufficient to account for the differences between the top-down and bottom-up CH_4 inventories identified in previously published work.

1. Introduction

In California, methane (CH_4) emissions are regulated by Assembly Bill 32, enacted into law as the California Global Warming Solutions Act of 2006, requiring the state's greenhouse gas (GHG) emissions in the year 2020 not to exceed 1990 emission levels. To this end, the California Air Resources Board (CARB) was tasked with compiling and verifying an inventory of GHG emissions for the state. Two published works [*Wunch et al.*, 2009; *Hsu et al.*, 2010] have concluded that atmospheric emissions of CH_4 in the Los Angeles (L.A.) area were greater than expected from a per capita apportionment of the statewide 2006 CARB GHG inventory and from a bottom-up accounting of CH_4 sources, respectively.

Several recent works have estimated CH_4 emissions to the South Coast Air Basin (SoCAB; Fig. 1a), which are summarized in Table 1. *Wunch et al.* [2009] used a Fourier transform infrared spectrometer at the Jet Propulsion Laboratory (JPL) in Pasadena, California to measure vertically-integrated total column enhancement ratios of CH_4 relative to CO and to CO_2 . The observed column enhancement ratios, multiplied by CARB inventory values of CO for 2008 and an average of 2006 CARB GHG inventory and 2005 Emission Database for Global Atmospheric Research (EDGAR) for CO_2 , were used to derive a lower limit to CH_4 emissions of 400 ± 100 Gg CH_4/yr (based on CO) or 600 ± 100 Gg CH_4/yr (based on CO_2) for the SoCAB. One reason for the discrepancy in their top-down analysis was that their observed CO/ CO_2 enhancement ratio of 11 ± 2 ppb CO/ppm CO_2 was greater than the 8.6 ppb CO/ppm CO_2 calculated from the inventories. *Wunch et al.* [2009] contrasted these top-down assessments to a bottom-up estimate of 260 Gg CH_4/yr using the statewide 2006 CARB GHG inventory

apportioned by population after removal of agricultural and forestry emissions, and concluded that 140 – 340 Gg CH₄/yr were not accounted for in the CARB CH₄ inventory for the SoCAB.

Hsu et al. [2010] took a similar top-down approach and used observed atmospheric enhancement ratios of CH₄ to CO from *in situ* whole air samples taken at Mt. Wilson (34.22° N, 118.06° W, 1770 m above sea level), scaled by the projected CARB CO inventory for 2008, to derive CH₄ emissions of 200 ± 10 Gg CH₄/yr for just the Los Angeles (L.A.) County (Figure 1b) portion of the SoCAB (L.A. County ∩ SoCAB). They used methods prescribed by the Intergovernmental Panel for Climate Change (IPCC) to create the CARB GHG inventory and reached a bottom-up estimate of 140 Gg CH₄/yr, or 60 Gg less than their top-down calculation for the L.A. County portion of the SoCAB. *Hsu et al.* [2010] used higher spatial resolution emissions data from CARB to construct their bottom-up inventory, and therefore did not have to rely on population apportionment methods used by *Wunch et al.* [2009].

The difference between the top-down CH₄ emissions reported by *Wunch et al.* [2009] and by *Hsu et al.* [2010] (400 Gg and 200 Gg, respectively, both based on the CARB CO inventory) are in part due to the different geographic areas for which they calculate CH₄ emissions, and in part due to differences in observed CH₄/CO enhancements between these two studies: 0.66 ± 0.12 mol/mol for *Wunch et al.* [2009] [*Wennberg et al.*, 2012] and 0.52 ± 0.02 mol/mol for *Hsu et al.* [2010]. Both works suggested that fugitive losses of natural gas (NG) could be the source of the CH₄ missing from the bottom-up inventories.

More recently, *Townsend-Small et al.* [2012] analyzed stable CH₄ isotope ratios in atmospheric samples taken at Mt. Wilson and elsewhere in the western L.A. basin and showed they were consistent with isotope ratios in natural gas sources.

Wennberg et al. [2012] used the different atmospheric ethane/CH₄ enhancement ratios observed from research aircraft during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) field project in 2008 and the California Research at the Nexus of Air Quality and Climate Change (CalNex) field project [*Ryerson et al.*, in review] in 2010 to estimate an upper limit of 390 Gg CH₄/yr from natural gas leakage in the SoCAB. Further, their top-down analysis resulted in a calculated total emission of 440 Gg CH₄/yr in the SoCAB.

Wennberg et al. [2012] also recalculated the data used by *Hsu et al.* [2010] to derive CH₄ emissions for the entire SoCAB, and calculated a SoCAB CH₄ emission from 2008 using data from ARCTAS. The results are summarized in Table 1.

Here we use ambient measurements in the SoCAB taken in May and June 2010 aboard the National Oceanic and Atmospheric Administration (NOAA) P-3 research aircraft during the CalNex field study to derive CH₄ emissions from the SoCAB using methods different from *Wennberg et al.* [2012]. We further examine CH₄ emissions from landfills and dairy farms in the SoCAB identified in the bottom-up CH₄ inventories reported by *Hsu et al.* [2010] and *Wennberg et al.* [2012]. We then expand on these previous studies by examining light alkane emissions from Los Angeles area data sets. In addition to CH₄ and ethane, we examine propane, *n*- and *i*-butane, and *n*- and *i*-pentane measurements to derive emissions of each of these light alkanes in the SoCAB, and use them in a system of linear equations to further quantify the source apportionment of CH₄ in the L.A. basin.

2. Measurements

We use trace gas measurements from a subset of platforms and sites from the CalNex field study. The NOAA P-3 research aircraft flew all or parts of 16 daytime flights in and around the L.A. basin. Two independent measurements of CH₄ and CO₂ were made aboard the aircraft by wavelength-scanned cavity ring-down spectroscopy (WS-CRDS; Picarro 1301-m) [Peischl *et al.*, 2012], and by quantum cascade laser direct absorption spectroscopy (QCLS) [Kort *et al.*, 2011]. Imprecision of the 1-Hz Picarro CH₄ measurement is ± 1.4 ppbv (all uncertainties herein are 1- σ) and inaccuracy is estimated at ± 1.2 ppbv. Imprecision of the 1-Hz QCLS CH₄ measurement is ± 1 ppbv and inaccuracy is estimated at ± 15 ppbv. Imprecision of the 1-Hz Picarro CO₂ measurement is ± 0.14 ppmv and inaccuracy is estimated at ± 0.12 ppmv. Imprecision of the 1-Hz QCLS CO₂ measurement is ± 0.05 ppmv and inaccuracy is estimated at ± 0.10 ppmv. All CH₄ and CO₂ measurements are reported as dry air mole fractions. For this work, CH₄ and CO₂ data from the Picarro instrument are used, and QCLS CH₄ data from May 8 are used when the Picarro instrument was not operating. The 1-Hz CO data used in this analysis were measured by vacuum ultraviolet fluorescence spectroscopy [Holloway *et al.*, 2000]. Imprecision of the 1-Hz CO data is ± 1 ppbv; inaccuracy is estimated at $\pm 5\%$. C₂ to C₅ alkanes, and their structural isomers, were measured in whole air samples [Colman *et al.*, 2001], periodically filled during flight. Imprecision of these alkane measurements is $\pm 5\%$; inaccuracies are estimated at $\pm 10\%$. Wind measurements were derived from various sensors aboard the NOAA P-3; the uncertainty of the 1-Hz wind speed is estimated to be ± 1 m/s. Sensors aboard the NOAA P-3 also measured relative humidity, ambient temperature, and potential temperature with an estimated 1-Hz uncertainty of $\pm 0.5^\circ$ C, $\pm 0.5^\circ$ C, and ± 0.5 K, respectively.

At the CalNex Pasadena ground site, located on the California Institute of Technology (Caltech) campus, measurements of C₂–C₅ alkanes were made by a gas chromatograph-mass spectrometer (GC-MS) on 5 minute integrated samples taken every half hour [Gilman *et al.*, 2010]. Imprecision of these measurements are ±8% for ethane and ±6% for propane; inaccuracy is estimated at ± 15% for each. Data from the ground site were taken between 15 May and 15 June, 2010. CH₄ was not measured at the Pasadena ground site.

Additionally, whole-air flask samples were taken twice daily at the Mount Wilson Observatory (MWO) for most days during May and June 2010, and analyzed for a variety of trace gas species, including CH₄, CO₂, CO, and hydrocarbons [Dlugokencky *et al.*, 2011; Conway, *et al.*, 2011; Novelli *et al.*, 2010]. Imprecision of the CH₄ measurement is ± 1 ppb; imprecision of the CO₂ measurement is ± 0.1 ppm; imprecision of the CO measurement is ± 1 ppbv, and inaccuracy of CO measurement is estimated to be ± 5%.

We also analyze alkane data from whole air samples taken in the L.A. basin prior to 2010. Ethane and propane were measured in whole air samples taken on four flights in L.A. aboard an instrumented National Aeronautics and Space Administration (NASA) DC-8 research aircraft during ARCTAS in June 2008 [Simpson *et al.*, 2010]. Ethane and propane were also measured on one flight in L.A. aboard the NOAA P-3 during the Intercontinental Transport and Chemical Transformation (ITCT) study in May 2002 [Schauffler *et al.*, 1999].

3. Methods

To ensure sampling from the L.A. basin, we consider aircraft data collected between 33.6 and 34.3° N latitude and 118.5 and 116.8° W longitude (Figure 1d, dashed box) in the following analysis. Aircraft data were further limited to samples taken between 1000 and 1700 PST,

between 200 and 800 m above ground, and below 1400 m above sea level, to ensure daytime sampling was within the well-mixed boundary layer, which averaged 1000 ± 300 m above ground level for the daytime L.A. flights [Neuman *et al.*, 2012]. Ground-based measurements at Pasadena were retained between 1000 and 1700 PST to ensure sampling of a well-mixed daytime boundary layer. For MWO measurements, afternoon samples, which typically occurred between 1400 and 1500 PST, were retained to capture upslope transportation from the L.A. basin [Hsu *et al.*, 2010]. Linear fits to the data presented below are orthogonal distance regressions [Boggs *et al.*, 1989] weighted by instrument imprecision [Bevington, 1969] (weighted ODR). The total uncertainty in the fitted slope is calculated by quadrature addition of the fit uncertainty and the measurement uncertainties.

For flux determinations, crosswind transects were flown downwind of known point sources. Enhancements of CH_4 above background levels were integrated along the flight track, and a flux was calculated using the following equation:

$$\text{flux} = v \cos(\alpha) \int_{z_0}^{z_1} n(z) dz \int_{-y}^y X_m(y) dy \quad (1)$$

where $v \cos(\alpha)$ is the component of the average wind velocity normal to the flight track, n is the number density of the atmosphere, z_0 is the ground level, z_1 is the estimated boundary layer height, and X_m is the measured mixing ratio enhancement above the local background along the flight track [White *et al.*, 1976; Trainer *et al.*, 1995; Ryerson *et al.*, 1998; Nowak *et al.*, 2012]. Boundary layer heights are estimated from vertical profiles of relative humidity, ambient temperature, and potential temperature made prior to and after the crosswind transects.

We assume the plume is vertically homogeneous within the mixed layer at the point of measurement and the wind velocity is constant between emission and measurement. We estimate the uncertainty in these assumptions, combined with the uncertainties of the wind speed, wind direction, temperature, and integrated atmospheric enhancements, to be $\pm 50\%$ for the plumes studied here [Nowak *et al.*, 2012]. Weighted averages of the fluxes are calculated following Taylor [1997]. When calculating the CH₄ flux from dairies, CH₄ variability immediately upwind of the dairies is sufficiently large to complicate interpolation from the downwind local background. To account for this, we take the weighted ODR slope of CH₄/CO immediately upwind, multiply this ratio by the measured CO downwind of the dairies, and integrate the plume CH₄ enhancement calculated from CO ($\text{CO} \times [\text{CH}_4/\text{CO}]_{\text{upwind}}$), similar to the integrations performed by Nowak *et al.* [2012]. This assumes the dairies emit a negligible amount of CO.

As with previously published works [Wunch *et al.*, 2009; Hsu *et al.*, 2010; Wennberg *et al.*, 2012], we estimate total CH₄ emissions in the SoCAB by multiplying enhancement ratios of CH₄ to CO and CO₂ by inventory estimates of CO and CO₂ for that region:

$$E_{\text{CH}_4} = \left(\frac{\text{CH}_4}{X} \right)_{\text{ODR slope}} \times \left(\frac{MW_{\text{CH}_4}}{MW_X} \right) \times E_X \quad (2)$$

where E_{CH_4} is the emission of CH₄, X is either CO or CO₂, MW is the molecular weight, and E_X is the inventory emission value of either CO or CO₂. Although not necessarily emitted from the same sources, we assume emissions of CH₄, CO, and CO₂ are well-mixed by the time they are sampled from the NOAA P-3.

We use the following latest-available inventories for our analysis below: the 2010 CARB emissions inventory for CO projected from the base-year 2008 inventory (<http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php>), and the 2009 CARB GHG inventory (<http://www.arb.ca.gov/cc/inventory/data/data.htm>). Both inventories were accessed in November 2012.

CARB projects the total 2010 annually averaged CO emissions in the SoCAB at 979 Gg CO/yr (Table 2). We use the annually averaged CARB inventory that excludes biomass burning CO emissions because no known biomass burning events were observed in the L.A. basin during CalNex. This estimate is 4% less than the summertime CO inventory without biomass burning emissions, and approximately 6% less than the annually averaged CO inventory including biomass burning emissions used by *Wennberg et al.* [2012]. To estimate 2010 CH₄ emissions in the SoCAB using the 2009 CARB GHG inventory, we follow the method used by *Wunch et al.* [2009], and take the total statewide emission of 1525 Gg CH₄/yr, less agricultural and forestry CH₄ emissions of 898 Gg CH₄/yr, then apportion the remainder by population. In 2010, the SoCAB comprised 43% of California's population (http://www.arb.ca.gov/app/emsinv/trends/ems_trends.php). However, unlike *Wunch et al.* [2009], we include SoCAB dairy emissions of 31.6 Gg CH₄/yr, calculated in section 4.3 below. Therefore, we attribute a total of 301 Gg CH₄/yr to the SoCAB based on the 2009 CARB GHG inventory (Table 2).

According to CARB's mobile source emission inventory (EMFAC 2011) for the Los Angeles County portion of the SoCAB (http://www.arb.ca.gov/jpub/webapp//EMFAC2011WebApp/emsSelectionPage_1.jsp),

mobile source CO₂ emissions remained essentially unchanged between 2009 and 2010 (39.94 versus 39.95 Tg CO₂/yr). Additionally, the statewide CARB GHG inventory for CO₂, with out-of-state electricity generation emissions removed, decreased by less than 2% between 2008 and 2009. Therefore, we assume errors due to sampling year are negligible in examining the CO₂ emission inventories in the SoCAB from 2009–2010. To estimate 2010 CO₂ emissions in the SoCAB using the 2009 CARB GHG inventory, we take the total statewide emission of 465.7 Tg CO₂/yr, subtract out-of-state electricity generation of 47.9 Tg CO₂/yr, then apportion the remainder by population. We therefore attribute 180 Tg CO₂/yr to the SoCAB using the 2009 CARB GHG inventory (Table 2). We do not compare to the Vulcan CO₂ inventory [Gurney *et al.*, 2009] because at present it is only available for the 2002 reporting year.

4. Results and Discussion

4.1. Total derived emission of CH₄ in L.A. and comparison to inventories

In this section, we use P-3 measurements of CH₄, CO, and CO₂ to calculate enhancement ratios representative of the integrated emissions from the L.A. basin. We then use tabulated CO and CO₂ emissions taken from the CARB inventories to derive total CH₄ emissions based on enhancement ratios observed in CalNex, and compare to earlier estimates of total CH₄ emissions in L.A.

Figure 1c shows known stationary sources of CH₄ in the L.A. area, which include landfills, dairies, wastewater treatment facilities, and oil fields, as well as the location of measurement sites used in this study. Dairy sources are sized by estimated CH₄ emissions from enteric fermentation, as explained in section 4.3. Landfills are sized by CH₄ emissions from the 2008 CARB GHG inventory (L. Hunsaker, personal communication, 2011).

Point sources are sized by 2009 CARB individual facility CH₄ emissions (<https://ghgreport.arb.ca.gov/eats/carb/index.cfm>), but do not stand out in the map due to their low CH₄ emissions relative to the landfills and dairies. Figure 1d shows the locations of daytime boundary-layer CH₄ data from the P-3, colored by observed mixing ratio, that were retained for the analysis as described previously. The largest concentrations of CH₄ were typically encountered along the mountains at the north edge of the L.A. basin, likely driven by transport of air within the basin, as typical daytime winds in the L.A. basin were from the west and southwest during May and June 2010 [Washenfelder *et al.*, 2011]. CalNex CH₄ data are plotted against observed CO in Figure 2a. Weighted ODR fits to these data resulted in derived enhancement ratios of 0.74 ± 0.04 and 0.68 ± 0.03 ppbv CH₄/ppbv CO from the NOAA P-3 and MWO, respectively. We note that the same CH₄/CO enhancement ratio of 0.74 ± 0.03 was reported by Wennberg *et al.* [2012] using the CalNex P-3 data with different selection criteria. We include box and whisker plots in Figure 2a to show that the weighted ODR fit to the data is insensitive to the relatively few data points of higher CH₄. The ratio calculated from the CARB inventory (Table 2) is 0.54 ppb CH₄/ppb CO, and is displayed for comparison.

CalNex CH₄ data are plotted against observed CO₂ in Figure 2b. The slope from a weighted ODR of P-3 data is 6.70 ± 0.01 ppb CH₄/ppm CO₂ and of MWO data is 6.60 ± 0.04 ppb CH₄/ppm CO₂. The ratio of the CARB inventories from Table 2 is 4.64 ppb CH₄/ppm CO₂, and is displayed for comparison. In this case, because CH₄ and CO₂ are measured with high precision and accuracy, the largest uncertainties in interpreting the slope as an emissions ratio are likely determined by the extent of mixing of emissions from different sources within the Los Angeles air shed. Similarly, Figure 2c shows a correlation plot of CO against CO₂.

The slope from a weighted ODR of P-3 data is 9.4 ± 0.5 ppb CO/ppm CO₂ and of MWO data is 10.4 ± 0.5 ppb CO/ppm CO₂. The ratio of the CARB inventories from Table 2 is 8.5 ppb CO/ppm CO₂, and is plotted for comparison. We estimate a $\pm 7.5\%$ uncertainty in each of the CARB CO and CO₂ inventories, which is sufficient to explain the difference between the CO/CO₂ enhancement ratio measured from the NOAA P-3 and the ratio calculated from the CARB inventories. Quantitative agreement between emission ratios derived from P-3 and MWO data (Figures 2a–c) is likely due to the fact that the transport within the basin was driven by the land-sea breeze, meaning typical daytime winds in the Pasadena area near Mt. Wilson were from the southwest [*Washenfelder et al.*, 2011]. This transport, and the highest values of CH₄ and CO₂ in the P-3 data that are not seen at MWO (Figures 2a and b), also suggests that MWO preferentially samples the western part of the L.A. basin [*Hsu et al.*, 2009]. We therefore use enhancement ratios determined from the NOAA P-3 data to derive CH₄ emissions from the entire basin.

We note that the ratio of the latest CARB CO and CO₂ inventories (Table 2) are in better agreement with ambient enhancement ratios in the CalNex data than was the case for *Wunch et al.* [2009]. This is likely due to either improved CARB inventories, the present use of a basin-wide data set to determine basin-wide emission ratios, or both.

With the slopes and inventory values quantified, we next derive a CH₄ emission using equation (2). Using the CH₄/CO slope derived from the weighted ODR fit to the 2010 NOAA P-3 data and the projected 2010 CARB annually-averaged CO emission inventory in equation (2) yields an estimated SoCAB emission of 410 ± 40 Gg CH₄/yr. The stated uncertainty is the quadrature propagation of the measurement uncertainty, errors on the slope of the ODR fit to P-3

data, and an estimated uncertainty in the CARB CO inventory. We note our derived emission of 410 ± 40 Gg CH₄/yr is similar to that derived from the P-3 data by *Wennberg et al.* [2012], which was 440 ± 100 Gg CH₄/yr using different selection criteria. It is further consistent with the emission derived by *Wunch et al.* [2009] of 400 ± 100 Gg CH₄/yr, which assumed a CARB CO inventory uncertainty of 15%. We also determine CH₄ emissions using estimates of CO₂ emissions in the SoCAB. P-3 measurements of the CH₄/CO₂ enhancement ratio observed during CalNex and SoCAB CO₂ emissions inferred from the 2009 CARB GHG inventory result in a derived CH₄ emission rate of 440 ± 30 Gg CH₄/yr, with the stated uncertainties determined by quadrature propagation of the measurement uncertainty, errors on the slope of the ODR fit to P-3 data, and an estimated uncertainty in the CARB CO₂ inventory. This value, based on the CO₂ inventory, is consistent with that derived using P-3 measurements and the CO inventory, further supporting both our assessment of uncertainties in the CARB CO and CO₂ inventories, and our assumption of sampling well-mixed emissions in the SoCAB, since any outlying CH₄ data do not affect the overall emission estimates significantly.

The derived 2010 top-down SoCAB CH₄ emission of 410 and 440 Gg CH₄/yr reported here using the CARB CO or CO₂ inventories, respectively, are in quantitative agreement, in contrast to that reported for 2008 [*Wunch et al.*, 2009]. The 2010 estimates are a factor of 1.35 to 1.45 greater than the modified population-apportioned 2009 CARB GHG inventory value of 301 Gg CH₄/yr (Table 2). A concurrent inverse modeling study by *Brioude et al.* [2012] has found no statistical difference between the total SoCAB CO emissions reported by CARB for 2010 and a top-down approach that estimated CO emissions in the SoCAB region using the same CO measurements used in this paper. For this reason, and for consistency with published works [*Wunch et al.*, 2009; *Hsu et al.*, 2010; *Wennberg et al.*, 2012],

we use 410 ± 40 Gg CH₄/yr from the top-down CH₄ assessment based on 2010 P-3 measured CH₄/CO enhancement ratios and the CARB CO inventory for the remainder of our analysis.

4.2. Methane emissions from L.A. basin landfills

Landfills are the largest non-fossil fuel CH₄ emission source in the bottom-up inventories compiled by *Hsu et al.* [2010] and by *Wennberg et al.* [2012], but these two studies disagree on the magnitude of this source. *Hsu et al.* [2010] estimated annual emissions from landfills totaled 90 Gg CH₄/yr from the Los Angeles County portion of the South Coast Air Basin. *Wennberg et al.* [2012] reported landfill emissions of just 86 Gg CH₄/yr for the entire South Coast Air Basin. However, that number is too low due to an error in their gridded landfill emissions inventory [*P. Wennberg*, personal communication, 2012] and is discarded in the following analysis.

In the CARB GHG inventory, CH₄ emissions are calculated for individual landfills using methods prescribed by the IPCC and summed over all landfills to estimate a statewide total. Annual CH₄ emission values for individual landfills were obtained directly from CARB [*L. Hunsaker*, personal communication, 2011] to facilitate direct comparison to the P-3 data from CalNex. We use the P-3 data to calculate emissions from two of the largest CH₄-emitting landfills in the statewide GHG inventory, both of which are located in the SoCAB.

The first landfill results we examine are from the Olinda Alpha landfill (33.934° N, 117.841° W) in Brea, Orange County, California. The NOAA P-3 flew five daytime boundary-layer transects on five different days downwind of this landfill (Figure 3), and a CH₄ emission flux was determined for each transect using equation (1). The results are summarized in Table 3.

For the three transects when both the WS-CRDS and QCLS CH₄ instruments were sampling ambient air, flux determinations using these independent CH₄ measurements agreed within 3%. In these cases, the flux was averaged and reported in Table 3. Three nearby CH₄ point sources are identified in the 2009 CARB GHG inventory: an oil and gas field power plant, which burns natural gas for fuel; the landfill power plant at Olinda Alpha, which burns landfill gas for fuel; and general stationary combustion from the landfill operations. Inventory data suggest that these three sources together emit between 0.0004 and 0.0015 Gg CH₄/yr, negligible amounts relative to CH₄ emitted directly from the landfill. On 19 May, the NOAA P-3 sampled plumes from the nearby oil and gas power plant and the landfill's power plant, both of which burn natural gas as fuel (Figure 3c). A large spike in CO₂, some CH₄, and perhaps a small amount of CO were encountered in the landfill power plant plume. However, downwind of the landfill in the large plume of CH₄, the CO₂ enhancement does not stand out significantly above the background variability. Therefore, our analysis of P-3 data supports the conclusion from the inventory that landfill CH₄ emissions dominate the observed plume enhancements downwind of Olinda Alpha landfill. Using NOAA P-3 CH₄ data from all five transects, we directly calculate a weighted average CH₄ emission flux via equation (1) of $(1.49 \pm 0.35) \times 10^{25}$ molecules/s, equal to 12.5 ± 2.9 Gg CH₄/yr assuming a constant emission, where the weights are the 50% uncertainty of each determination. For comparison, the CARB GHG inventory emission estimate from the Olinda Alpha landfill is 11.0 Gg/yr for 2008, showing agreement within the errors of the direct estimate using P-3 airborne data.

The second landfill results we examine in-depth are from the Puente Hills landfill (34.020° N, 118.006° W) in City of Industry, Los Angeles County, California. Of all California landfills, Puente Hills is the largest emitter of CH₄ in the 2008 CARB GHG inventory.

Nearby sources of CH₄ in the 2008 CARB GHG inventory include the Puente Hills power plant (0.00045 Gg CH₄/yr) and the Savage Hills Canyon landfill (1.1 Gg CH₄/yr), both of which are small relative to the CARB GHG inventory of 39 Gg CH₄/yr emission rate for Puente Hills. The NOAA P-3 conducted three daytime boundary layer plume transects from which we determine an average emission flux of $(4.06 \pm 1.18) \times 10^{25}$ molecules/s, which extrapolates to 34.0 ± 9.9 Gg CH₄/yr assuming a constant emission (Table 3). Similar to the findings for Olinda Alpha, the CARB GHG inventory of 39 Gg CH₄/yr for the Puente Hills landfill is in agreement within the errors of the direct estimate using P-3 airborne data.

Quantitative agreement between CH₄ flux estimates from the NOAA P-3 and the 2008 CARB GHG inventory for these two examples supports the use of that inventory to quantify total CH₄ emissions from landfills in the South Coast Air Basin. According to the 2008 CARB GHG inventory, CH₄ emissions from landfills totaled 117 Gg CH₄/yr in the L.A. County portion of the SoCAB, 30% higher than the 90 Gg CH₄/yr for the same geographic area using the CARB GHG inventory in 2008 reported by *Hsu et al.* [2010], which we attribute to different versions of the CARB GHG inventory.

The 2008 CARB GHG inventory further predicts an emission from landfills of 164 Gg CH₄/yr for the entire SoCAB. On the basis of the agreement with the CARB inventory described above for the emission rates from the two landfills quantified directly by the CalNex P-3 data (50 Gg CH₄/yr, or 30% of the inventory total for the SoCAB), we assume the remaining CARB landfill CH₄ emission estimates are accurate.

4.3. Methane emissions from L.A. basin dairies

Salas et al. [2008] published dairy locations in California for the year 2005, with an estimate of dairy cow population for each. The locations are plotted as filled yellow circles in Figure 1c, and sized by the expected CH₄ emission from enteric fermentation according to the 2009 CARB GHG inventory (144 kg CH₄ per cow per year). According to *Salas et al.* [2008], all dairies in San Bernardino and Riverside counties were also located in the SoCAB, and 87% of the dairy cows in the SoCAB in 2005 were located in the Chino area (the large grouping of dairies in Figure 1c). The Chino-area dairy operations, which at one time were distributed across the Riverside-San Bernardino county line in satellite images, now appear to be located mainly in San Bernardino County as the Riverside dairies have been converted to residential neighborhoods (*e.g.*, see Google Earth historical imagery since 2000). This declining number of dairies is confirmed by the United States Department of Agriculture (USDA) (http://www.nass.usda.gov/Statistics_by_State/California/Publications/County_Estimates/201005lvscef.pdf), which reports a decrease in dairy cows in San Bernardino and Riverside Counties from 200,000 head in 2005 to 137,500 head in 2010. In addition to dairy cows, dairies also stock immature heifers. Further, there are beef operations in the SoCAB, but these are negligible compared to the San Bernardino and Riverside dairy populations. According to the USDA, there were a total of 431,000 cattle in San Bernardino and Riverside counties in 2005, and 295,000 cattle in 2010. For both years, dairy cows represented approximately 46.5% of the cattle population in the SoCAB. From these dairy and cattle populations, we construct a bottom-up emissions inventory for the SoCAB using the same emission factors as the CARB GHG inventory.

We begin with CH₄ emissions from enteric fermentation. We assign to each of the 137,500 dairy cows in the SoCAB an emission factor of 144 kg CH₄/yr. We assume the remaining 157,500 head are dairy replacements, and assign each an emission factor of 57.7 kg CH₄/yr, or the average emission factor for 0–1 and 1–2 year old dairy replacements in the CARB GHG inventory. We calculate a total of 28.9 Gg CH₄/yr emitted solely from enteric fermentation in the SoCAB.

In addition to enteric fermentation, manure management practices have a substantial effect on CH₄ emissions from livestock operations. In the L.A. basin, dairies typically practice solid storage (http://www.aqmd.gov/rules/doc/r1127/pr1127_task1rpt_20020101.pdf and http://www.arb.ca.gov/planning/sip/sjv_report/addtl_resources.pdf), which emits relatively low levels of CH₄ (17 kg/yr per cow) according to the 2009 CARB GHG inventory. The tradeoff for this practice is that it emits larger amounts of NH₃ than other types of manure management (<http://www.epa.gov/ttn/chief/ap42/ch09/draft/draftanimalfeed.pdf>). Therefore, if we attribute dry manure management emissions to the SoCAB dairy cow population, and the dry lot emission rate of 2.1 kg CH₄/yr for the remaining heifers, we get an additional 2.7 Gg CH₄/yr from dairy operation manure management in the SoCAB. This results in a total of 31.6 Gg CH₄/yr from enteric fermentation and manure management for the SoCAB dairy operations. This is the emission from agriculture and forestry that we add back into the population-apportioned CARB CH₄ inventory above (Table 2).

Our estimate of 31.6 Gg CH₄/yr, based on inventory data, is less than half of the 76 Gg CH₄/yr estimated by *Wennberg et al.* [2012]. We attribute this difference in bottom-up inventories to the different assumptions of manure management practices.

Wennberg et al. [2012] scaled total California CH₄ emissions by livestock population, which also assumes the manure management practices from the San Joaquin Valley apply to the L.A. basin. For example, the anaerobic lagoons more commonly used in the San Joaquin Valley emit 325 kg CH₄ per cow per year according to the 2009 CARB GHG inventory, significantly higher than 17 kg CH₄ per cow per year from dry manure management practices typical of the L.A. basin.

Nowak et al. [2012] used P-3 data from CalNex to derive emissions of ammonia (NH₃) from dairy farms in the Chino area. From NOAA P-3 measurements, we determine a CH₄ flux from the Chino-area dairies for the same three downwind transects analyzed by *Nowak et al.* [2012]. Using the Chino to SoCAB population apportionment by *Salas et al.* [2008], we expect these same Chino-area dairies to emit approximately 28 Gg CH₄/yr. CH₄ fluxes determined from equation (1) range from 24 ± 12 to 88 ± 44 Gg CH₄/yr, and the average of the three transects is 49 ± 25 Gg CH₄/yr. This value derived from airborne flux determination lies between the 28 Gg CH₄/yr calculated from the inventory assuming dry manure management practices described above, and the estimate by *Wennberg et al.* [2012] of 76 Gg CH₄/yr (less livestock emissions from the SoCAB that are not in the Chino area) assuming mainly wet management practices. We attribute the differences to actual practices in the region, which are likely a mixture of the two manure management approaches. Satellite images of the area show what appear to be several anaerobic lagoons near Chino, California. Our flux determination is therefore consistent with our bottom-up CH₄ emission inventory, with room for a mixture of manure management practices, including some anaerobic lagoons, in the L.A. basin.

4.4. Spatial distribution of methane sources

Townsend-Small et al. [2012] concluded that the CH₄ emissions in the L.A. region had a stable isotope ratio similar to that of fossil-fuel CH₄. This conclusion was based on measurements made at the Mt. Wilson Observatory. A back-trajectory [*White et al.*, 2006; <http://www.esrl.noaa.gov/psd/programs/2010/calnex/traj/>] from MWO for 5 August 2009, the specific day that *Townsend-Small et al.* [2012] used to determine the excess CH₄ stable isotopic ratio, shows the prevailing winds to MWO were from the southwest, or from downtown L.A. and the coast west of downtown L.A. The trajectory tool also shows winds from the eastern basin on the previous day, which was excluded by *Townsend-Small et al.* [2012] due to lower correlation between the excess CH₄ and $\delta^{13}\text{C}$. We conclude that the MWO data interpreted by *Townsend-Small et al.* [2012] were dominated by emissions from the western basin only, and were not influenced by emissions from either the largest landfills (Puente Hills and Olinda Alpha), or from the dairies in the eastern part of the L.A. basin. This spatially-biased sampling is consistent with their conclusion that landfills do not contribute significantly to the total atmospheric CH₄ burden in L.A.

Evidence for the heterogeneous spatial distribution of CH₄ sources in the SoCAB can be seen in the NOAA P-3 data. Figure 4 shows that the correlation of ethane with CH₄ is dependent on the sample location in the L.A. basin. Also shown in Figure 4 is the slope used by *Wennberg et al.* [2012] to represent the ethane/CH₄ ratio (16.5 ± 2.5 ppt ethane/ppb CH₄) in pipeline-quality dry natural gas from the Southern California Gas Company (SoCalGas), the major provider of natural gas to the SoCAB, for 2010.

The chemical data in Figure 4 reflect the known source types shown on the map in Figure 1c: the large CH₄ sources in the eastern L.A. basin, primarily landfills and dairies, are not significant sources of ethane relative to CH₄.

We can reconcile the conclusions of *Townsend-Small et al.* [2012] and *Wennberg et al.* [2012] with the CARB GHG inventory by noting that fossil fuel CH₄ emissions predominate in the western basin, and that landfill and livestock CH₄ emissions predominate in the eastern basin. However, in contrast to the findings of *Wennberg et al.* [2012], we find that natural gas leaks from the SoCalGas and in-home pipelines are not the only possible source of fossil fuel CH₄ to the western basin, as described below.

4.5. Light alkane emissions from local natural gas production

Los Angeles was one of only three out of 28 cities characterized by propane and ethane levels within 10% of one another in the atmosphere [*Baker et al.*, 2008], consistent with an enhanced propane source term in L.A. Figure 5 shows correlations of propane vs. ethane in whole-air samples from various aircraft projects in the Los Angeles region (ITCT 2002, ARCTAS 2008, and CalNex 2010), as well as measurements from the CalNex Pasadena ground site in 2010. Also plotted are lines representing the composition ratios of other possible sources of ethane and propane in Los Angeles.

The L.A. basin is home to oil and gas operations (see Figure 1c); the composition ratios depicting possible emissions from local natural gas (gray lines) and local geologic seeps (salmon lines) in Figure 5 are those reported by *Jeffrey et al.* [1991]. The lower propane content relative to ethane seen in the seeps (*e.g.*, the La Brea tar pits) compared to the local natural gas is attributed to near-surface microorganisms forming shorter-chain alkanes from longer-chain

alkanes during the time the natural gas migrates toward the surface [Jeffrey *et al.*, 1991]. The average propane/ethane ratio for processed gas in SoCalGas pipelines [Wennberg *et al.*, 2012] is plotted as a dashed black line. Pipeline-quality dry natural gas has a low propane/ethane ratio because the natural gas has been processed (*i.e.*, the higher alkanes have been removed from the natural gas) before distribution. The SoCalGas ratio is representative of natural gas piped in from out of state (*e.g.*, from Texas, Wyoming, and Canada); approximately 90% of natural gas used in California is imported

(http://www.socalgas.com/regulatory/documents/cgr/2010_CGR.pdf). The on-road emissions are taken from a San Francisco Bay-area tunnel study by Kirchstetter *et al.* [1996], who reported a vehicular emission ratio of 0.13 mol propane/mol ethane roughly similar to those by Fraser *et al.* [1998] (0.27 mol propane/mol ethane) and by Lough *et al.* [2005] (0.06 – 0.18 mol propane/mol ethane). Vehicle engine exhaust typically contains small, decreasing amounts of CH₄, ethane, and propane due to incomplete combustion, as gasoline and diesel fuel do not contain significant amounts of these light alkanes. The on-road emissions, local geologic seeps, and the pipeline-quality dry natural gas from SoCalGas contain 3–5 times more ethane than propane, and therefore cannot alone explain the ambient ratios measured in the L.A. basin. The propane and ethane composition of unprocessed natural gas from local wells, on the other hand, closely matches the SoCAB ambient measurements from three aircraft campaigns, the CalNex ground site measurements, and the Baker *et al.* study [2008]. Propane and ethane were also typically enhanced at the same time, with the exception of one sample with elevated propane near the Long Beach area (Figure 1e).

The data in Figure 5 suggest that local oil and gas wells contribute significantly to the atmospheric propane burden in the SoCAB. However, Wennberg *et al.* [2012] invoked a large

source of propane from fugitive losses from the liquefied petroleum gas (LPG) industry (*i.e.*, propane tanks), in addition to leaks from the pipeline-quality dry natural gas distribution system in the L.A. basin. This would be consistent with past works that have found significant fugitive losses of propane in other cities, such as Mexico City [Blake and Rowland, 1995]. We therefore extend our analysis to incorporate ethane, propane, and C₄ (*n*- and *i*-butane) and C₅ (*n*- and *i*-pentane) isomers to better attribute and quantify the sources of light alkanes and CH₄ to the SoCAB atmosphere. Light alkanes are plotted in Figure 6, with lines depicting the composition of natural gas in SoCalGas pipelines [Wennberg *et al.*, 2012] and of on-road emissions [Kirchstetter *et al.*, 1996]. We neglect chemical processing of these long-lived alkanes ($\tau \geq 3$ days at OH = 1×10^6 molecules/cm³) as we find no detectable difference between daytime and nighttime enhancement ratios relative to CO, similar to the findings of Borbon *et al.* [2013] for *n*-butane and CO at the CalNex Pasadena ground site. Atmospheric enhancement ratios of propane, *n*-butane, and *i*-butane (Figures 6b–d) relative to ethane are consistent with emissions having the composition of local natural gas [Jeffrey *et al.*, 1991]. On-road emissions do not appear to contribute significantly to the CH₄, ethane, and propane in the L.A. atmosphere, and pipeline-quality dry natural gas and/or local geologic seeps do not appear to contribute significantly to the propane and *n*-butane relative to ethane in the L.A. atmosphere. Based on these observations, we conclude that the local natural gas industry contributes a significant fraction to the total atmospheric C₂-C₄ alkane abundances, including propane, in the L.A. basin. We infer CH₄ emissions from the local natural gas industry are non-negligible as well, as discussed below.

4.6. Source Attribution

Here we quantify total emissions of C_2 – C_5 alkanes in the L.A. basin by multiplying their observed enhancement ratios to CO by the CARB SoCAB emission inventory for CO. Figure 7 shows C_2 – C_5 alkanes plotted versus CO with their respective ODR fits. The slopes from these fits are used in equation (2) along with the projected 2010 CARB CO inventory to calculate annual alkane emissions in the SoCAB. We assume the slopes represent a direct emission with no chemical aging. These emissions are listed in the right-most column of Table 4. Also listed in Table 4 are the estimated contributions from mobile sources in the SoCAB, using C_1 – C_5 to CO emission ratios from *Kirchstetter et al.* [1996] (modified as discussed below) and CO emissions from the mobile sources category in the projected 2010 CARB CO inventory, equal to 920 Gg CO/yr, in equation (2).

Wennberg et al. [2012] attributed the inventory CH_4 shortfall [*Wunch et al.*, 2009; *Hsu et al.*, 2010] by ascribing much of the CH_4 and ethane enhancements to fugitive losses of processed pipeline-quality dry natural gas. They further suggest the majority of atmospheric propane is due to LPG industry/propane tank fugitive losses. Here, we consider other possible explanations of the sources of CH_4 and light alkanes in the L.A. basin for the following two reasons. First, the source attribution by *Wennberg et al.* [2012] leaves little room for CH_4 emissions from landfills, wastewater treatment plants, and dairies in the L.A. basin. This solution seems unlikely based on direct emissions flux estimates using the P-3 data downwind of landfills and dairies in the SoCAB, as described above. Second, the attribution by *Wennberg et al.* [2012] would leave a shortfall in both *n*- and *i*-butane emissions that cannot be explained by gasoline evaporation or emissions from mobile sources.

We use a multivariate approach based on a linear combination of the CH_4 and light alkane compositions from known sources in order to attribute and quantify total CH_4 and $\text{C}_2\text{--C}_5$ alkane emissions in the South Coast Air Basin.

We include 7 different source types (sectors) with distinct and known CH_4 and $\text{C}_2\text{--C}_5$ alkane compositions (Figure 8) in the following analysis: 1) Leaks of processed dry natural gas from pipelines, and/or emissions from local geologic seeps (this approach cannot distinguish between pipeline-quality dry natural gas and local seeps); 2) CH_4 -dominated emissions, such as from landfills, wastewater treatment plants, and dairies; 3) Leaks of unprocessed, local natural gas; 4) Leaks of liquefied petroleum gas from propane tanks; 5) On-road combustion emissions from mobile sources; 6) Emissions of CH_4 and $\text{C}_2\text{--C}_5$ alkanes in the SoCAB from other source sectors; and 7) Evaporative emissions from gasoline. These are described briefly below.

1. The South Coast Air Basin contains 14.8 million people, and SoCalGas delivers approximately 11 Tg/yr of natural gas to the Los Angeles area. Additionally, the Earth's natural degassing is a known source of CH_4 , ethane, and propane to the atmosphere [Etioppe *et al.*, 2008; Etioppe and Cicciole, 2009], and the L.A. basin contains abundant geologic hydrocarbon reserves [Jeffrey *et al.*, 1991]. We group fugitive losses from processed pipeline-quality dry natural gas with the emissions from local geologic seeps because the $\text{C}_1\text{--C}_4$ emissions from these sources are not sufficiently different to be treated separately in our linear combination analysis (illustrated by the similarity in slopes of the dashed black and salmon-colored lines in Figure 6).

Both pipeline-quality dry natural gas and local seep emissions contain similar amounts of CH₄ and ethane relative to one another, and have less C₃–C₅ alkanes relative to ethane than local, unprocessed natural gas. For pipeline-quality dry natural gas, most C₃₊ alkanes are removed during the processing stage, which is typically done close to the source, which for ~90% of the natural gas used in California is in Canada, Wyoming, and/or Texas. For local seeps, most C₃₊ alkanes are either preferentially adsorbed in shallow sediments compared to CH₄, or biodegraded by microbes in the earth's crust during the seepage of local natural gas to the surface [Jeffrey *et al.*, 1991]. We use SoCalGas samples of pipeline-quality natural gas from 2010 [Wennberg *et al.*, 2012] to represent this source, and estimate the uncertainty of the composition at 15%.

2. CH₄-dominant emission sources, which for this analysis include landfills, wastewater treatment plants, and livestock, emit CH₄ but no significant amounts of C₂–C₅ alkanes. This is represented in our analysis as a unit vector containing only CH₄.
3. From 2007–2009, the oil and gas industry in the L.A. basin produced roughly 12–13 billion cubic feet of natural gas per year, mostly associated gas from oil wells (http://www.conservation.ca.gov/dog/pubs_stats/annual_reports/Pages/annual_reports.aspx). We use an average of the samples reported by Jeffrey *et al.* [1991] weighted by 2009 gross natural gas production per field, and estimate the uncertainty of this composition at 25%.
4. Two types of LPG are sold in the Los Angeles area: one is almost completely composed of propane, the other has traces of *n*- and *i*-butane (http://www.arb.ca.gov/research/apr/past/98-338_1.pdf).

We use the ratios reported by *Blake and Rowland* [1995] from direct analysis of LPG in Los Angeles, which is consistent with an average of the two types of LPG sold in L.A., and estimate the uncertainty of the composition at 10%.

5. On-road combustion emissions are modified from the work of *Kirchstetter et al.* [1996] by multiplying emission ratios of alkanes to CO by the 925 Gg CO/yr from on-road sources in the projected 2010 CARB CO inventory. The C₄–C₅ emissions represent unburned fuel and are typically proportional to the fuel composition; the C₁–C₃ emissions typically represent incomplete combustion products. To account for differing fuel compositions since the time of the *Kirchstetter et al.* [1996] study, the *i*- and *n*-butane emissions calculated for mobile sources in the SoCAB (Table 4) have been scaled to the *i*-pentane emissions based on their relative abundance in gasoline [*Gentner et al.*, 2012].
6. There are additional sources of light alkanes in the SoCAB. We use the 2010 CARB speciated inventory for total organic gases (<http://arb.ca.gov/ei/speciate/interopt10.htm>) and projected 2010 total organic gas emissions (<http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php>) for the SoCAB to estimate emissions of light alkanes not specified in other source sectors. These include emissions from aerosol spray cans and other consumer products, coatings and solvents, adhesives and sealants, and fiberglass and plastics manufacturing. For example, propane, *n*- and *i*-butane are commonly used as propellants in aerosol spray cans, having replaced CFCs in the United States in the 1970s (*e.g.*, CARB estimates 0.6 Gg of aerosol antiperspirant vapors were emitted to the SoCAB in 2010, of which 0.14 Gg, 0.03 Gg, and 0.15 Gg were propane, *n*-, and *i*-butane, respectively).

These emissions are summed and listed in the “CARB other” column in Table 4. Emissions from natural gas leaks, petroleum refining, petroleum marketing (gas stations), landfills and composting, and mobile sources are not included in these totals, because they are accounted for elsewhere in other source sectors. We estimate a 25% uncertainty in the “CARB other” inventory.

7. Emissions ratios from evaporated gasoline were calculated from ten gasoline samples from five Pasadena gas stations in the summer of 2010, weighted by estimated sales of 80% regular and 20% premium [Gentner *et al.*, 2012]. Uncertainties are those reported by Gentner *et al.* [2012].

First, we start with estimated annual C_1 – C_5 emissions in the SoCAB (right-most column of Table 4), then subtract modified on-road emissions [Kirchstetter *et al.*, 1996] and projected emissions of C_1 – C_5 alkanes from other sources (source sector 6, above). Next, we place the remaining source sector characteristics into a matrix and solve for the fraction each source contributes to the remaining alkane observations for the L.A. basin based on each source’s relative abundances of various light alkanes. The matrix has five columns representing the five remaining source sectors, and seven rows containing C_1 – C_5 alkanes. We solve the equation [e.g., see §4.2 Kim *et al.*, 2011]

$$\mathbf{A}_{ij} \mathbf{x}_j = \mathbf{b}_i \quad (3)$$

where \mathbf{A}_{ij} is a matrix of the C_1 – C_5 alkane composition, i , for the source sectors, j , defined above; x_j is the fraction each source contributes to the total observed emissions, and b_i is the total observed emission of alkane i minus the contributions from the mobile and “other” source sectors (Table 4). The columns of the matrix \mathbf{A} are proportional to the first five columns of

Table 4. We use LAPACK (<http://www.netlib.org/lapack/>) to solve for the linear least squares solution that minimizes $(\mathbf{Ax} - \mathbf{b})$. Uncertainties in the derived \mathbf{x}_j are estimated by a sensitivity study, where we run the solution 1,000,000 times by randomly varying $\mathbf{A}_{i,j}$ and \mathbf{b}_i according to their estimated uncertainties, then use the standard deviation of the 1,000,000 \mathbf{x}_j determinations to estimate the uncertainty in the source attribution fraction. The source attribution fractions and their uncertainties are multiplied by the total estimated SoCAB emission for each alkane, then are summed with the uncertainties added in quadrature. CH_4 and $\text{C}_2\text{--C}_5$ alkane emissions totals, their uncertainties, and the contributions from each source type are given in Table 4. The source attribution solution solves the observed SoCAB alkane emission to within each alkane's emission uncertainty.

Our modeled source attribution differs from the alkane source distribution in the L.A. basin as set forth by *Wennberg et al.* [2012]. From a total calculated source of 410 ± 40 Gg CH_4/yr in the SoCAB, we determine that 47% comes from leaks of processed pipeline-quality dry natural gas and/or from local geologic seeps; 44% of the CH_4 comes from the sum of landfill, wastewater treatment, and dairy emissions; 8% from the leaks of unprocessed natural gas from production in the western L.A. basin; and 1% from mobile sources. The attribution is presented graphically in Figure 8. Figure 8a displays the total SoCAB emissions as a black horizontal line in each panel, with contributions from the different source sectors given below the line by the filled bars. Figure 8b shows the proportion that each source sector contributes to the derived total emissions of each alkane.

Our analysis attributes CH_4 emissions of 192 ± 54 Gg CH_4/yr to leaks of pipeline-quality dry processed natural gas and/or leaks from local geologic seeps, but does not distinguish further between these two different sources. This value is nearly a factor of 5 greater than the population-apportioned 2009 CARB GHG emissions inventory estimate of 40 Gg CH_4/yr lost from natural gas pipelines in the SoCAB. Our estimate of 192 Gg CH_4/yr is less than the maximum emission of 400 ± 150 Gg CH_4/yr estimated by *Wennberg et al.* [2012]. Our estimate would represent approximately 2% of the natural gas delivered to customers in the SoCAB and, including storage and deliveries to customers outside the SoCAB, 1% of the gas flowing into the basin [*Wennberg et al.*, 2012]. These percentages would decrease linearly with any CH_4 emissions attributed to local geologic seeps. *Farrell et al.* [*in press*, 2012] estimate up to 55 Gg CH_4/yr are emitted from the La Brea Tar Pits in western L.A. County alone; if accurate, this would imply pipeline leaks of only 0.7% of the gas flowing into the basin, or a factor of at least two lower than the 2% proposed by *Wennberg et al.* [2012].

Our analysis attributes 182 ± 54 Gg CH_4/yr in the SoCAB to emissions from landfills, wastewater treatment, and dairies. SoCAB landfills account for 164 Gg CH_4/yr in the 2008 CARB GHG inventory, a value supported by our analysis in section 4.2. In section 4.3, we estimated in a bottom-up inventory that SoCAB dairies emitted 31.6 Gg CH_4/yr . *Wennberg et al.* [2012] estimated an emission of 20 Gg CH_4/yr from wastewater treatment. These independent estimates sum to 216 Gg CH_4/yr and are consistent with our source apportionment using NOAA P-3 data.

CH₄ emissions of 31.9 ± 6.5 Gg CH₄/yr are ascribed to leaks of local, unprocessed natural gas, and would represent 17% of the local production in 2009, the latest year for which data are available

(http://www.conservation.ca.gov/dog/pubs_stats/annual_reports/Pages/annual_reports.aspx).

This number assumes a CH₄ composition of 72.5% by volume for natural gas produced in the South Coast Air Basin, which is calculated as an average from the samples reported by *Jeffrey et al.* [1991] weighted by 2009 production. Our derived value of 17%, although a surprisingly high amount of local production, is consistent with a nascent bottom-up estimate under way at CARB.

A new bottom-up inventory survey, conducted by CARB for the calendar year 2007 but not yet incorporated into the official GHG inventory, indicates that 109 Gg CH₄/yr, since revised to 95.5

Gg CH₄/yr [S. Detwiler, personal communication, October 2012], were emitted throughout

California by the oil and gas industry via combustion, venting, and fugitive losses (table 3-1,

<http://www.arb.ca.gov/cc/oil-gas/finalreport.pdf>). This updated value is a factor of 2.5 larger

than the current CARB GHG inventory tabulation of 38 Gg CH₄/yr from oil and gas extraction

for 2007 in California. CH₄-specific emissions for the South Coast Air Management District in

the new CARB survey report show 24.6 Gg CH₄/yr were emitted in the SoCAB [S. Detwiler,

personal communication, October 2012]. According to the survey, emissions in the SoCAB

accounted for 26% of the revised statewide total oil and gas operations CH₄ emission in 2007,

despite accounting for only 4.4% of statewide natural gas production in the basin that year

(http://www.conservation.ca.gov/dog/pubs_stats/annual_reports/Pages/annual_reports.aspx).

Thus, the survey responses suggest a CH₄ leak rate of 12% of local production in the L.A. basin.

Thus, our estimate of CH₄ emissions from local natural gas for 2010 based on P-3 data from CalNex is within a factor of 1.5 of the CARB bottom-up inventory currently in development based on the 2007 survey. According to the survey, other oil and gas producing regions in California show smaller CH₄ loss rates than that from the SoCAB. For instance, statewide losses of CH₄ represent approximately 2.1% of statewide production, and CH₄ losses from the San Joaquin Air Quality District represent approximately 1.4% of production (from Oil and Gas Districts 4 and 5). This indicates that losses from natural gas production are proportionally larger in the L.A. basin than elsewhere in the State of California.

A propane emission of 6.6 ± 2.9 Gg/yr from LPG/propane tanks would represent approximately 1% of sales (http://www.aqmd.gov/ceqa/documents/2012/aqmd/finalEA/PAR1177/1177_FEA.pdf), which is less than the ~4% calculated by *Wennberg et al.* [2012], and closer to the 0.6% estimated from the document cited.

Finally, our analysis suggests a resolution to the discrepancies noted above between previous top-down assessments and the bottom-up inventory calculations for CH₄ in the SoCAB [e.g., *Wunch et al.*, 2009; *Hsu et al.*, 2010; *Townsend-Small et al.*, 2012; *Wennberg et al.*, 2012]. We conclude the most probable source for the excess atmospheric CH₄ is likely due to a combination of primarily leaks, not accurately represented in the current CARB GHG inventory, from natural gas pipelines and urban distribution systems and/or from local geologic seeps, and secondarily leaks of unprocessed natural gas from local oil and gas production centered in the western L.A. basin.

This finding is based on the characteristic enhancement ratios of CH₄ and the various C₂–C₅ alkanes consistently observed in the L.A. atmosphere, and is further supported by the spatial information provided by P-3 samples during CalNex. Finally, the updated values for local oil and gas industry emissions in the recent GHG survey commissioned by CARB, when incorporated fully into the official CARB GHG record, will likely help to reduce this long-standing discrepancy between top-down assessments and bottom-up inventories.

5. Conclusions

We use aircraft measurements of CH₄, CO, and CO₂ during the CalNex field campaign to show that emissions of CH₄ to the L.A. basin are greater than can be explained by official state bottom-up inventories apportioned by population, consistent with published work. The ratio of the CARB CO and CO₂ inventories is in better agreement with our measurements of CO/CO₂ in the Los Angeles atmosphere than was the case for the analysis by *Wunch et al.* [2009], which we attribute either to improved CARB inventories, the present use of a basin-wide data set to determine basin-wide emission ratios, or both.

From crosswind plume transects downwind of the two largest landfills in the basin, we determine CH₄ fluxes that are consistent with the 2008 CARB GHG inventory values, which total 164 Gg CH₄/yr emitted from all landfills in the South Coast Air Basin. CH₄ emission fluxes were also determined for Chino-area dairies in the eastern L.A. basin. Flux estimates from these dairies ranged from 24 ± 12 to 87 ± 44 Gg CH₄/yr, and the average flux is consistent with a revised bottom-up inventory originally compiled by *Salas et al.* [2008] and with previous inventory estimates [*Wennberg et al.*, 2012].

Finally, we present a top-down assessment of C₂–C₅ alkane sources in the L.A. basin, then apportion CH₄ and the C₂–C₅ alkanes to specific source sectors in the region. Using this source apportionment approach, we estimate that 32 ± 7 Gg of CH₄/yr, or 8% of the total CH₄ enhancement observed in the SoCAB during CalNex, came from the local oil and gas industry. This number represents approximately 17% of the natural gas produced in the region, within a factor of 1.5 of that calculated from a recent survey that will be used to update the CARB bottom-up inventory. We estimate 182 ± 54 Gg CH₄/yr are emitted by landfills, dairies, and wastewater treatment, which is consistent with bottom-up inventories, and 192 ± 54 Gg CH₄/yr are emitted of processed pipeline-quality dry natural gas and/or from geologic seeps in the region. We further conclude that leaks of processed pipeline-quality dry natural gas and/or local geologic seeps, and unprocessed natural gas from local oil and gas production are the most likely major contributors to the previously noted discrepancy between CH₄ observations and State of California inventory values for the South Coast Air Basin. Our findings suggest that basin-wide mobile studies targeting CH₄ and C₂–C₅ alkane emissions from natural gas pipelines and urban distribution systems, geologic seeps, and local oil and gas industry production sites would be useful to further distinguish the sources of CH₄ in the L.A. basin.

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Table 1. Summary of past studies investigating CH₄ emissions in the L.A. basin.

| Study | Time of study | Geographic area | Percentage of California population in geographic area | CH ₄ Emission (Gg/yr) | Inventory referenced | Bottom-up CH ₄ emission inventory (Gg/yr) |
|-------------------------------|-------------------------|---------------------|--------------------------------------------------------|----------------------------------|------------------------------------------------------------|------------------------------------------------------|
| <i>Wunch et al.</i> [2009] | August 2007 – June 2008 | SoCAB | 43% | 400 ± 100 | CARB CO 2007 | 260 ^b |
| | | | | 600 ± 100 | (CARB CO ₂ 2006 + EDGAR CO ₂ 2005)/2 | |
| <i>Hsu et al.</i> [2010] | April 2007 – May 2008 | L.A. County ∩ SoCAB | 27% | 200 ± 10 | CARB CO 2007 | 140 |
| <i>Wennberg et al.</i> [2012] | April 2007 – May 2008 | SoCAB | 43% | 380 ^a ± 100 | CARB CO 2007 | --- |
| | June 2008 | SoCAB | 43% | 470 ± 100 | CARB CO 2008 | --- |
| | May 2010 – June 2010 | SoCAB | 43% | 440 ± 100 | CARB CO 2010 | --- |

^a *Wennberg et al.* [2012] recalculated the data reported by *Hsu et al.* [2010] to estimate a CH₄ emission from the entire SoCAB.

^b *Wunch et al.* [2009] apportioned the statewide CARB GHG inventory for CH₄, less agriculture and forestry emissions, by population

Table 2. Inventories used in current analysis

| Emission | Inventory | Year | Geographic Area |
|----------------------------|-----------------------|------|--------------------|
| 180 Tg CO ₂ /yr | CARB GHG ^a | 2009 | SoCAB ^c |
| 979 Gg CO/yr | CARB ^b | 2010 | SoCAB ^c |
| 301 Gg CH ₄ /yr | CARB GHG ^a | 2009 | SoCAB ^c |

^a 2009 CARB CO₂ and CH₄ emissions (<http://www.arb.ca.gov/cc/inventory/data/data.htm>)

^b projected 2010 CARB CO emissions
(<http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php>)

^c statewide inventory apportioned by SoCAB population

Table 3. Landfill emission fluxes determined aboard the NOAA P-3 in 2010 from downwind plume transects.

| Landfill | Transect Date | Flux, 10^{25} molecules/s | Flux, Gg/yr | 2008 CARB GHG inventory, ^a Gg/yr |
|-----------------|----------------------------|-----------------------------------|-------------------|------------------------------------------------------|
| Olinda Alpha | 8 May | 1.13 | 9.5 | 11.0 |
| | 14 May | 1.45 | 12.2 | |
| | 16 May | 1.74 | 14.6 | |
| | 19 May | 1.61 | 13.5 | |
| | 20 June | 2.90 | 24.3 | |
| | average^b | 1.49 ± 0.35 | 12.5 ± 2.9 | |
| Puente Hills | 8 May | 4.29 | 36.0 | 38.8 |
| | 19 May | 3.62 | 30.4 | |
| | 20 June | 4.48 | 37.6 | |
| | average^b | 4.06 ± 1.18 | 34.0 ± 9.9 | |

^a data from CARB [L. Hunsaker, personal communication, June 2011]

^b weighted average, assuming a 50% uncertainty in the individual flux determinations [Taylor, 1997]

Table 4. Derived emissions in the South Coast Air Basin (in Gg/yr) for 2010 from each source sector used in linear analysis.

| | Pipeline-quality dry NG/ local seeps | CH ₄ -dominant (landfills, dairies, etc.) | Local NG | LPG/propane | Evaporated gasoline | Mobile sources | CARB other | Summed source totals | Estimated SoCAB total ^a |
|-------------------|-----------------------------------------|---------------------------------------------------------|--------------|------------------|---------------------|----------------|----------------|----------------------|------------------------------------|
| CH ₄ | 192 ± 54 | 182 ± 54 | 32 ± 7 | --- | --- | 4.9 ± 1.3 | 1.2 ± 0.3 | 411 ± 77 | 411 ^b ± 37 |
| ethane | 5.9 ± 1.7 | --- | 4.5 ± 1.0 | 0.05 ± 0.02 | 0.0 ± 0.0 | 0.6 ± 0.1 | 0.3 ± 0.1 | 11.4 ± 1.9 | 11.4 ^b ± 1.6 |
| propane | 1.5 ± 0.4 | --- | 9.9 ± 2.0 | 6.6 ± 2.9 | 0.006 ± 0.001 | 0.1 ± 0.0 | 1.6 ± 0.4 | 19.8 ± 3.6 | 19.8 ± 2.7 |
| <i>n</i> -butane | 0.3 ± 0.1 | --- | 5.9 ± 1.2 | 0.02 ± 0.01 | 0.5 ± 0.1 | 0.3 ± 0.1 | 1.4 ± 0.4 | 8.5 ± 1.3 | 8.3 ± 1.2 |
| <i>i</i> -butane | 0.3 ± 0.1 | --- | 2.2 ± 0.5 | 0.13 ± 0.06 | 0.08 ± 0.02 | 0.04 ± 0.01 | 1.8 ± 0.5 | 4.6 ± 0.6 | 5.1 ± 0.7 |
| <i>n</i> -pentane | 0.07 ± 0.02 | --- | 2.2 ± 0.5 | --- | 2.6 ± 0.4 | 1.0 ± 0.1 | 0.3 ± 0.1 | 6.6 ± 0.6 | 6.5 ± 0.9 |
| <i>i</i> -pentane | 0.11 ± 0.03 | --- | 2.4 ± 0.5 | 0.003 ± 0.001 | 7.6 ± 1.0 | 3.9 ± 0.5 | 0.03 ± 0.01 | 14.1 ± 1.2 | 14.1 ± 1.8 |

^a includes measurement, ODR fit, and inventory uncertainty

^b Wennberg *et al.* [2012] estimate emissions to the SoCAB of 440 ± 100 Gg CH₄/yr and 12.9 ± 0.9 Gg ethane/yr

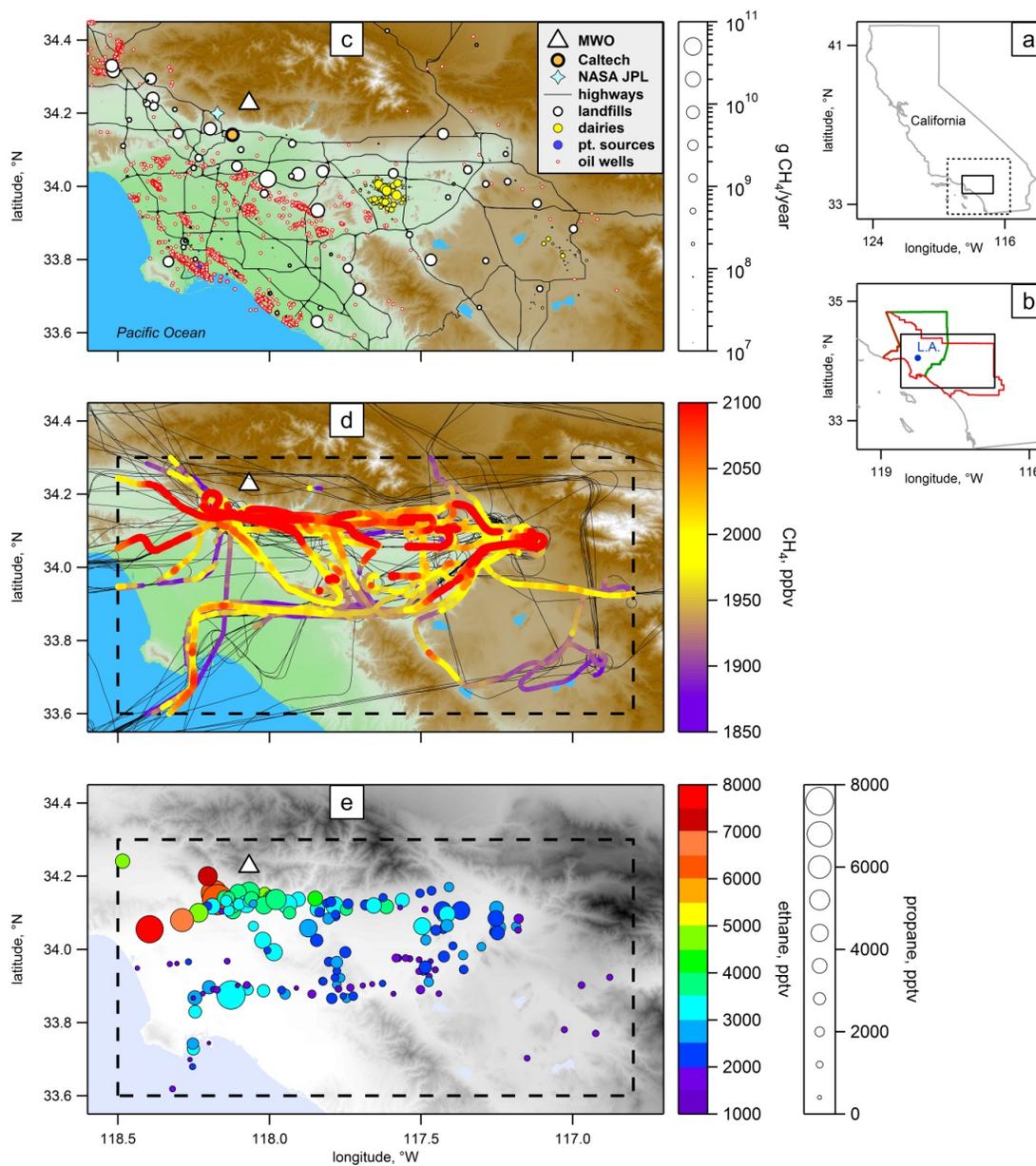


Figure 1. **a)** Map of California. The dashed box shows the inset for panel (b), the solid box shows the extent of the map boundaries for panels (c) – (e). **b)** Map of southern California showing the location of downtown L.A. (blue dot), the Los Angeles County boundary (green), the South Coast Air Basin boundary (red), and the extent of the map boundaries for panels (c) – (e) (black box). **c)** Map of the L.A. region showing known sources of CH_4 in the L.A. basin. The white triangle shows the location of the Mt. Wilson Observatory, where ground-based measurements were made by *Hsu et al.* [2010] and in this study. The light blue star shows the location of the Jet Propulsion Laboratory, where *Wunch et al.* [2009] made their measurements. The CalNex Pasadena ground site was located on the California Institute of Technology (Caltech) campus, located at the orange filled circle. Landfills (white circles) and CH_4 point sources (filled blue circles; negligibly small) are sized by emissions in the 2008 CARB greenhouse gas inventory. Dairies (filled yellow circles) are sized by the estimated emissions from the number of cows from *Salas et al.* [2008] multiplied by the 2009 CARB GHG inventory annual CH_4 emission per cow from enteric fermentation. **d)** Same map of the Los Angeles region as in (c), with flight tracks from 16 daytime flights of the NOAA P-3 (thin black lines). CH_4 measurements from the daytime boundary layer are color-coded atop these tracks according to the legend to the right. **e)** Locations of whole air samples in the L.A. basin, colored by ethane mixing ratio and sized by propane mixing ratio as indicated in the legends to the right.

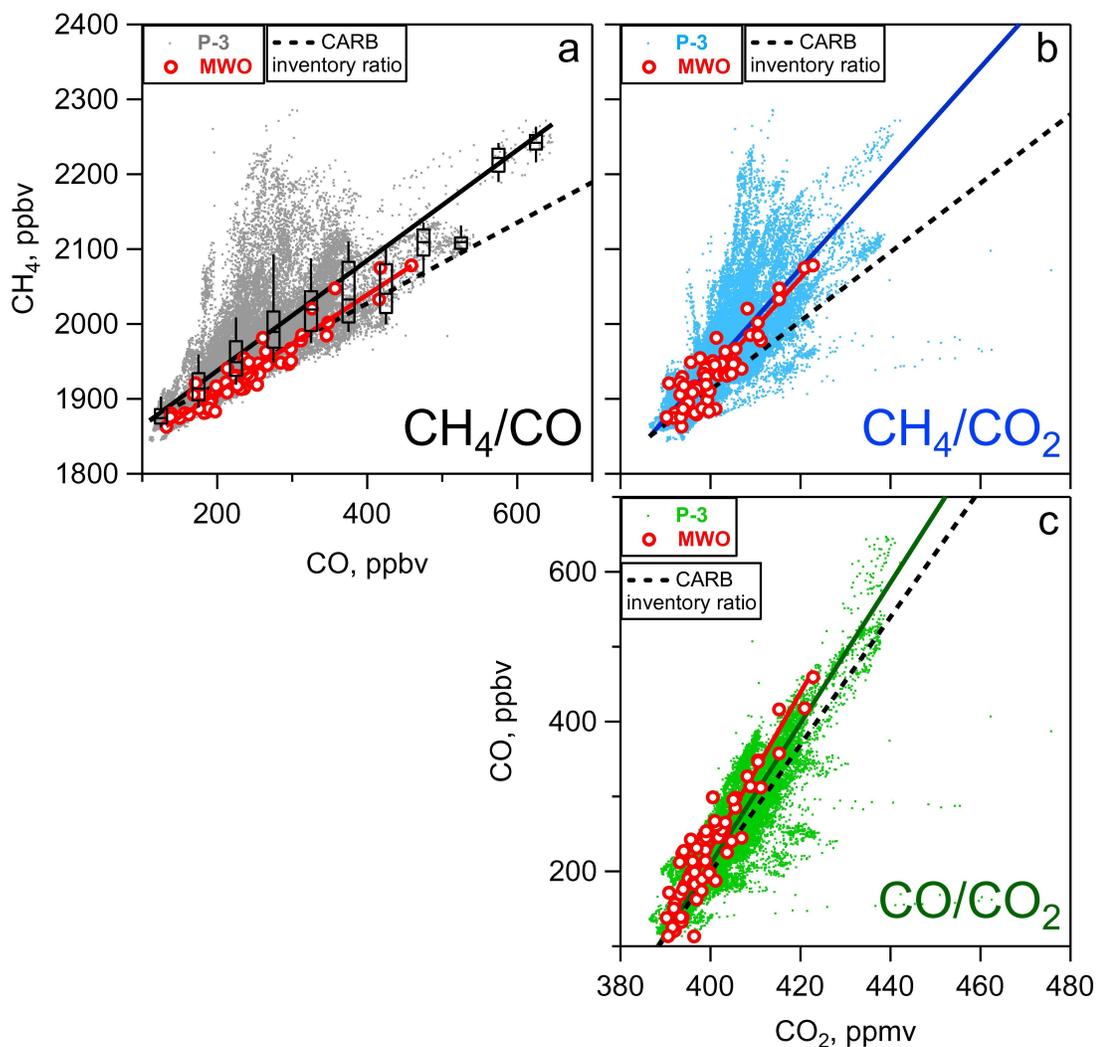


Figure 2. Scatter plots of CH₄, CO₂, and CO from all 1-second data points along flight track highlighted in Figure 1. Dots are from the NOAA P-3, while red circles are from NOAA GMD flask samples taken at the Mt. Wilson Observatory during CalNex. Weighted ODRs (solid lines) result in slopes of (a) 0.74 ± 0.04 and 0.68 ± 0.04 ppb CH₄/ppb CO; (b) 6.70 ± 0.01 and 6.60 ± 0.04 ppb CH₄/ppm CO₂; and (c) 9.4 ± 0.5 and 10.4 ± 0.5 ppb CO/ppm CO₂ from the NOAA P-3 and Mt. Wilson Observatory, respectively. The black dotted lines represent molar ratios of the CARB inventories listed in Table 2: CH₄:CO = 0.54, CH₄:CO₂ = 4.64×10^{-3} , and CO:CO₂ = 8.5×10^{-3} , where the background values used are the same as those determined from the fitted slopes. Also plotted in Figure 2a are boxes (25th–75th percentiles), whiskers (10th–90th percentiles), and the median (horizontal line) for distributions of CH₄ data calculated for 50 ppbv-wide bins from the NOAA P-3 CO data.

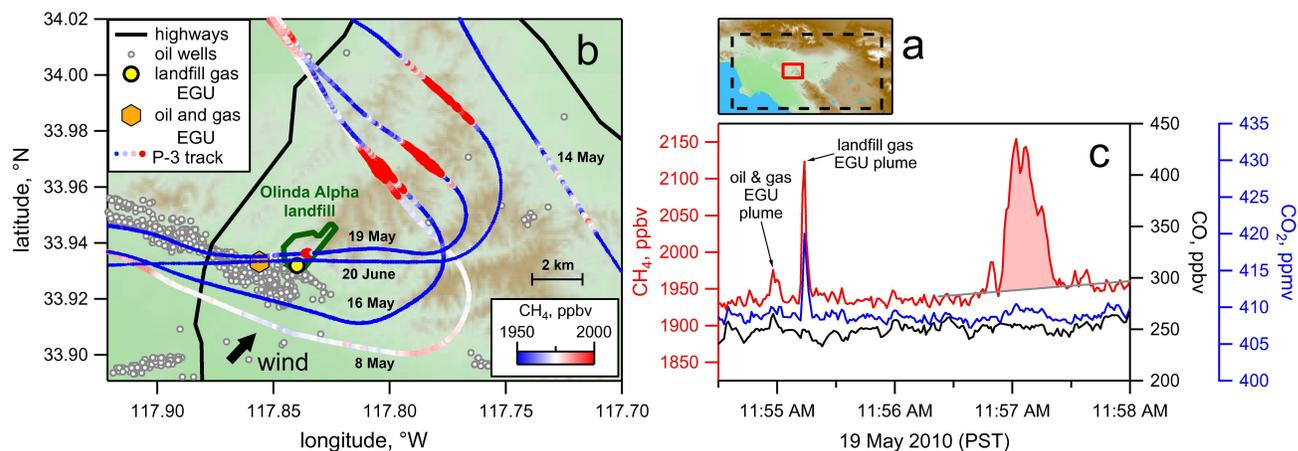


Figure 3. **a)** The map from Figure 1c–e shows the inset for part (b) in red. **b)** Five downwind transects, sized and colored by CH₄ mixing ratio, showing enhancements in CH₄ downwind of the Olinda Alpha landfill (green outline). Winds were from the southwest, except on 14 May, when they were from the west-southwest. **c)** Example of integration of the CH₄ plume from the 19 May flight. The filled pink area is integrated above the surrounding background (gray line). The upwind transect on this day passed downwind of two power plant (EGU) plumes.

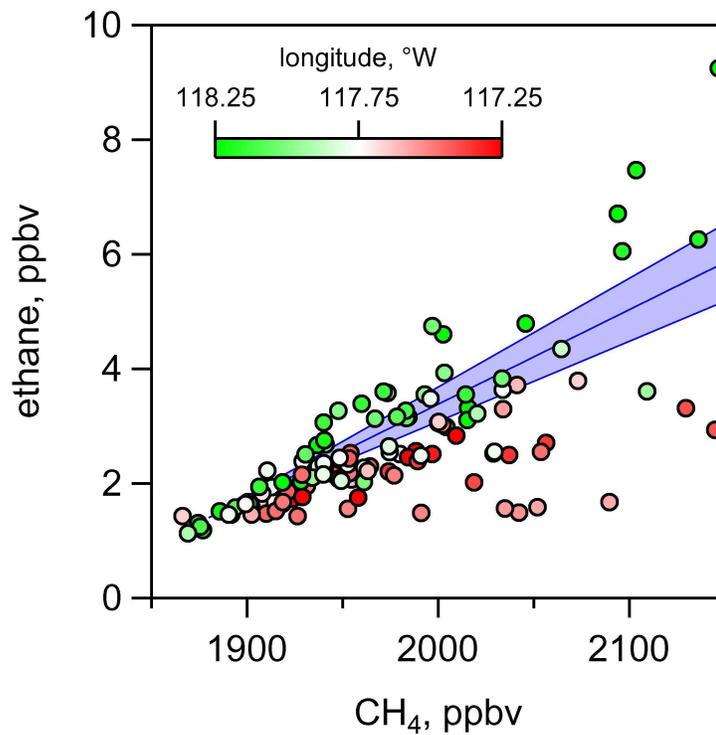


Figure 4. Scatter plot of ethane vs. CH₄ from the NOAA P-3 data in the L.A. basin. Data points are colored by longitude to show the different distributions of ethane to CH₄ in the eastern (red) and western (green) parts of the basin. The blue line represents the slope of 1.65 ± 0.25 % used by *Wennberg et al.* [2012] to represent the estimated ethane/CH₄ ratio of pipeline-quality dry natural gas from the Southern California Gas Company's pipelines.

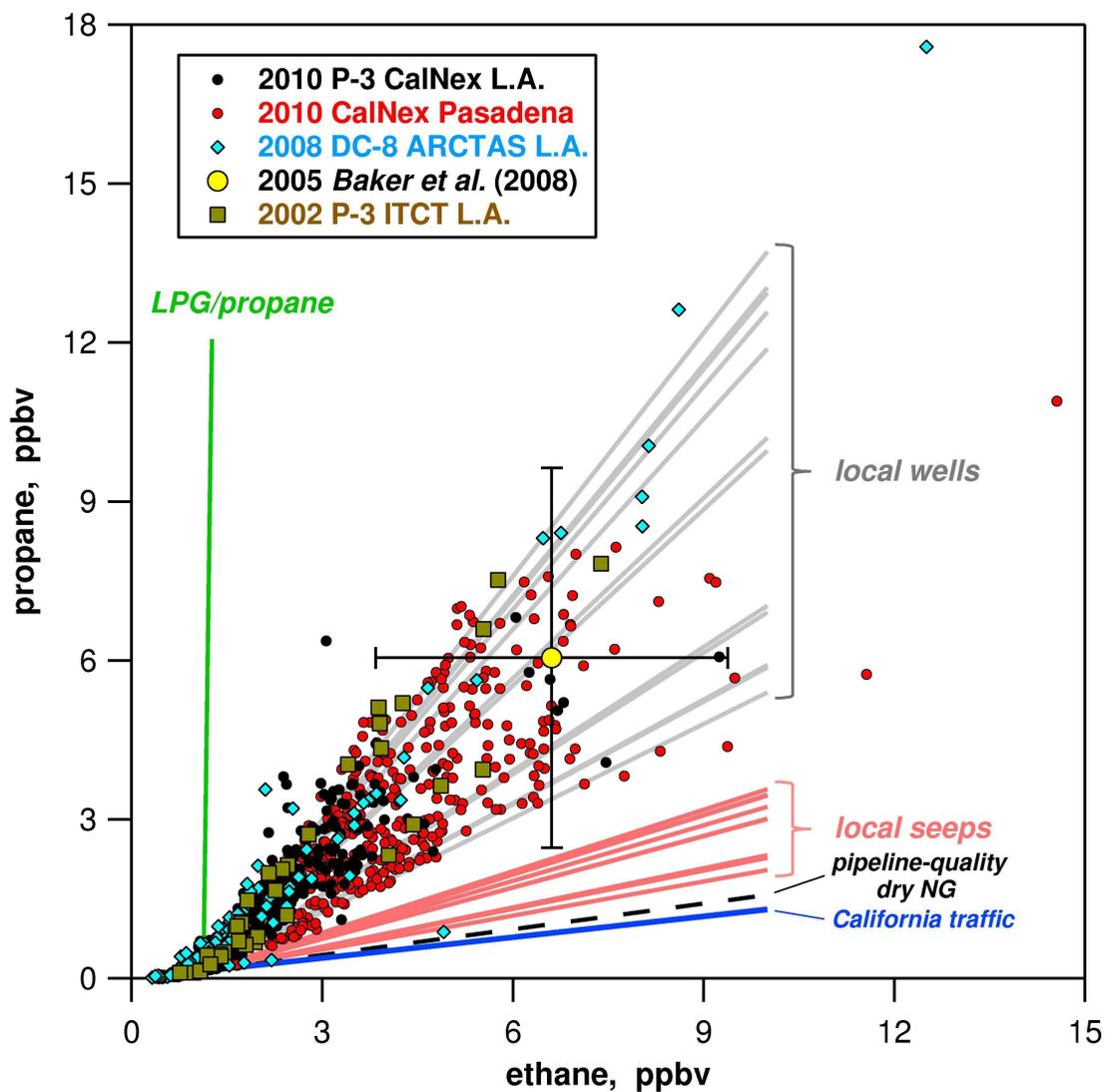


Figure 5. Correlation plot of propane vs. ethane from four Los Angeles datasets. Also plotted are composition ratios of local wells (gray lines) and local seeps (salmon lines) reported by *Jeffrey et al.* [1991], the composition ratio of pipeline-quality dry natural gas (black dashed line), the propane/ethane emission ratio from a San Francisco Bay-area tunnel study reported by *Kirchstetter et al.* [1996], and the average composition ratio of liquefied petroleum gas (LPG), or propane (green line).

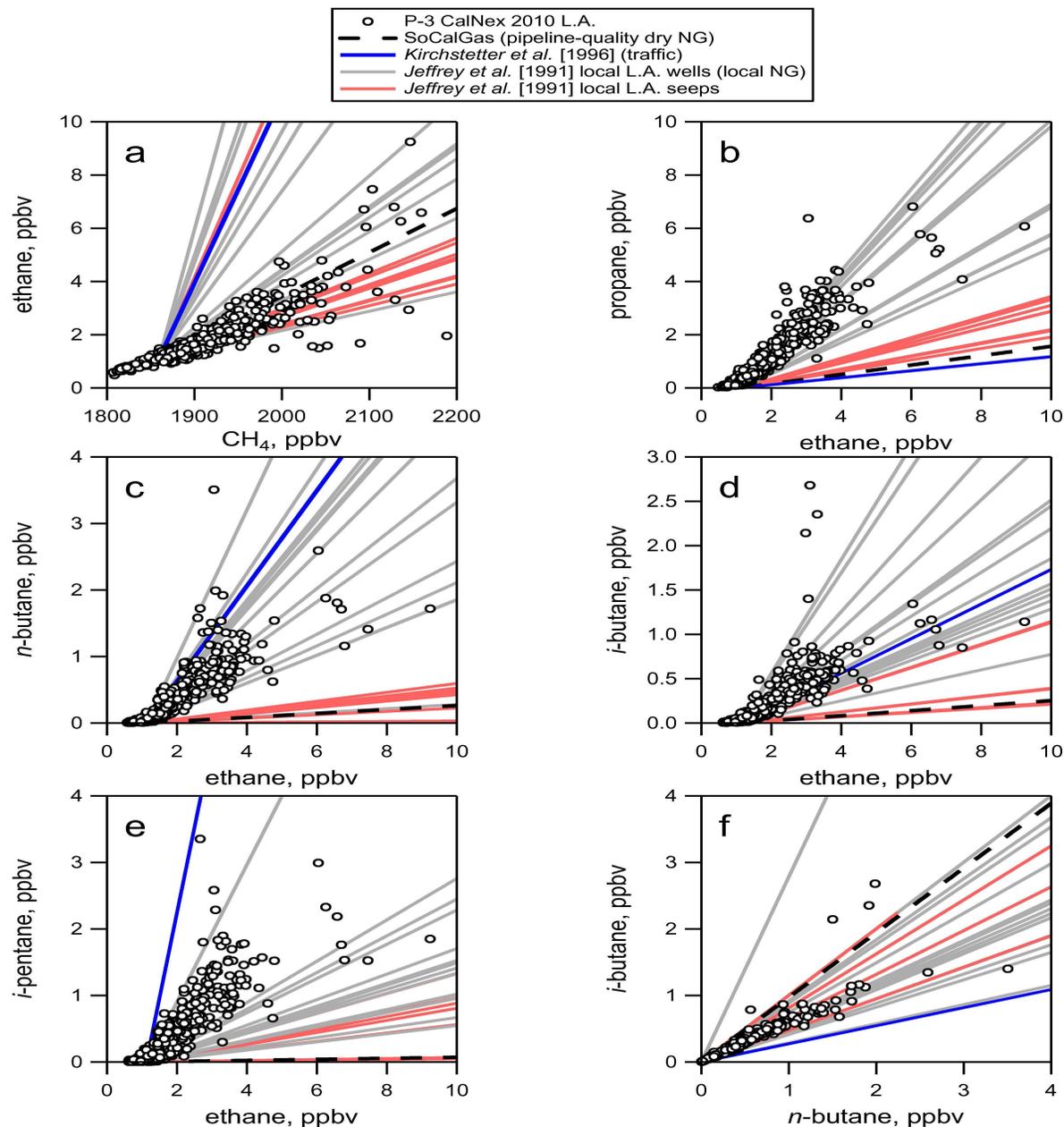


Figure 6. Plots of CH₄ and C₂–C₅ alkanes from the NOAA P-3 CalNex data set, selected for the SoCAB (black circles). Nighttime and high-altitude data are included. Also included for reference are the emission ratios of mobile sources from *Kirchstetter et al.* [1996] (blue line), composition ratios measured by *Jeffrey et al.* [1991] for local natural gas (gray lines) and local geologic seeps (salmon lines), and composition ratios from pipeline-quality dry natural gas (NG) delivered by SoCalGas (dashed black line). These ratios were plotted from daytime background levels.

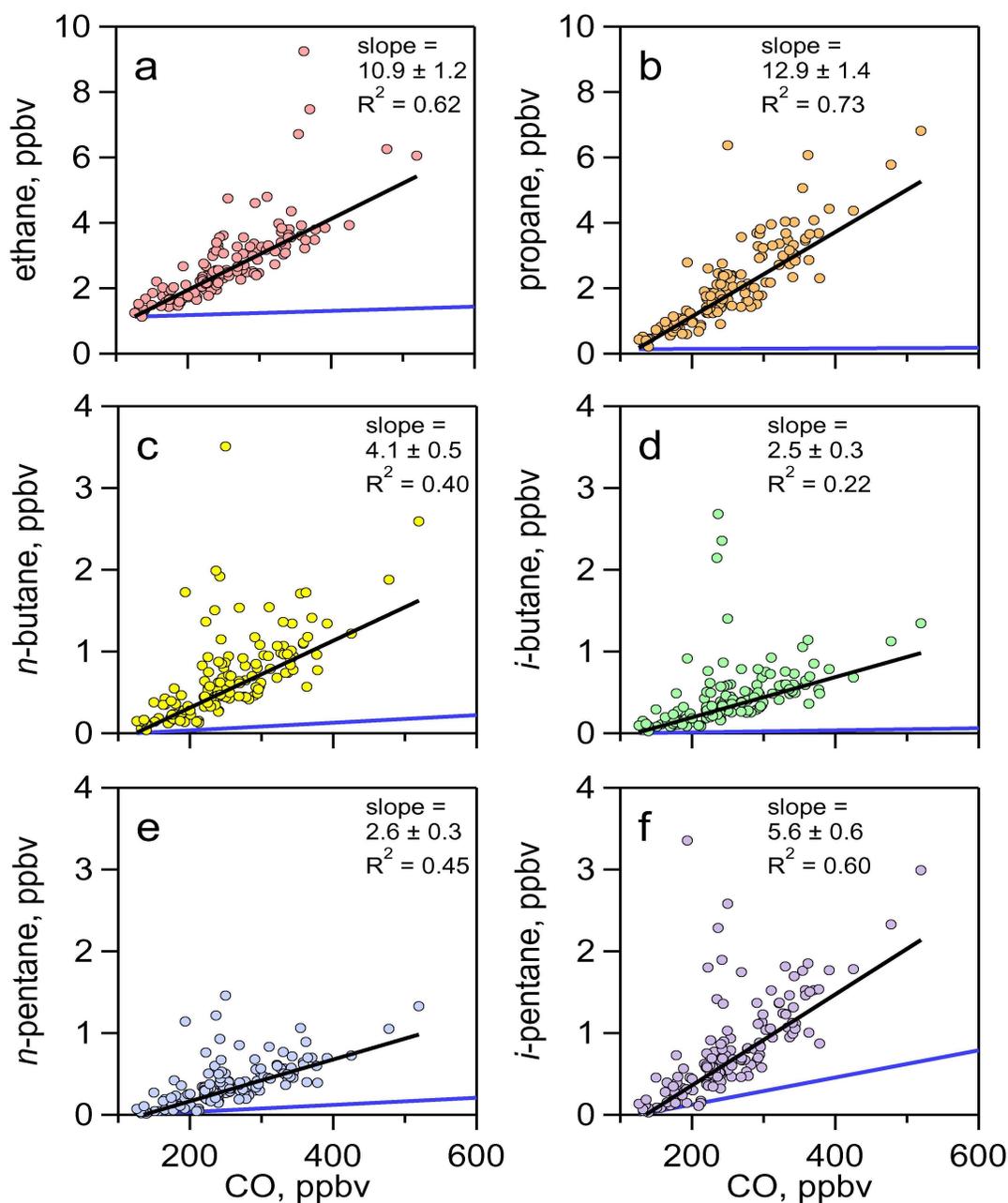


Figure 7. a–f) Daytime measurements of alkanes vs. CO from the NOAA P-3 in the L.A. basin during CalNex are plotted as filled circles. For comparison, the alkane/CO emission ratios from a San Francisco Bay-area tunnel study [Kirchstetter *et al.*, 1996] are plotted as a solid blue line, which extends to the edge of the right axis. The slope from a weighted ODR (given as ppt alkane/ppb CO), total slope uncertainty, and R^2 are given in each panel.

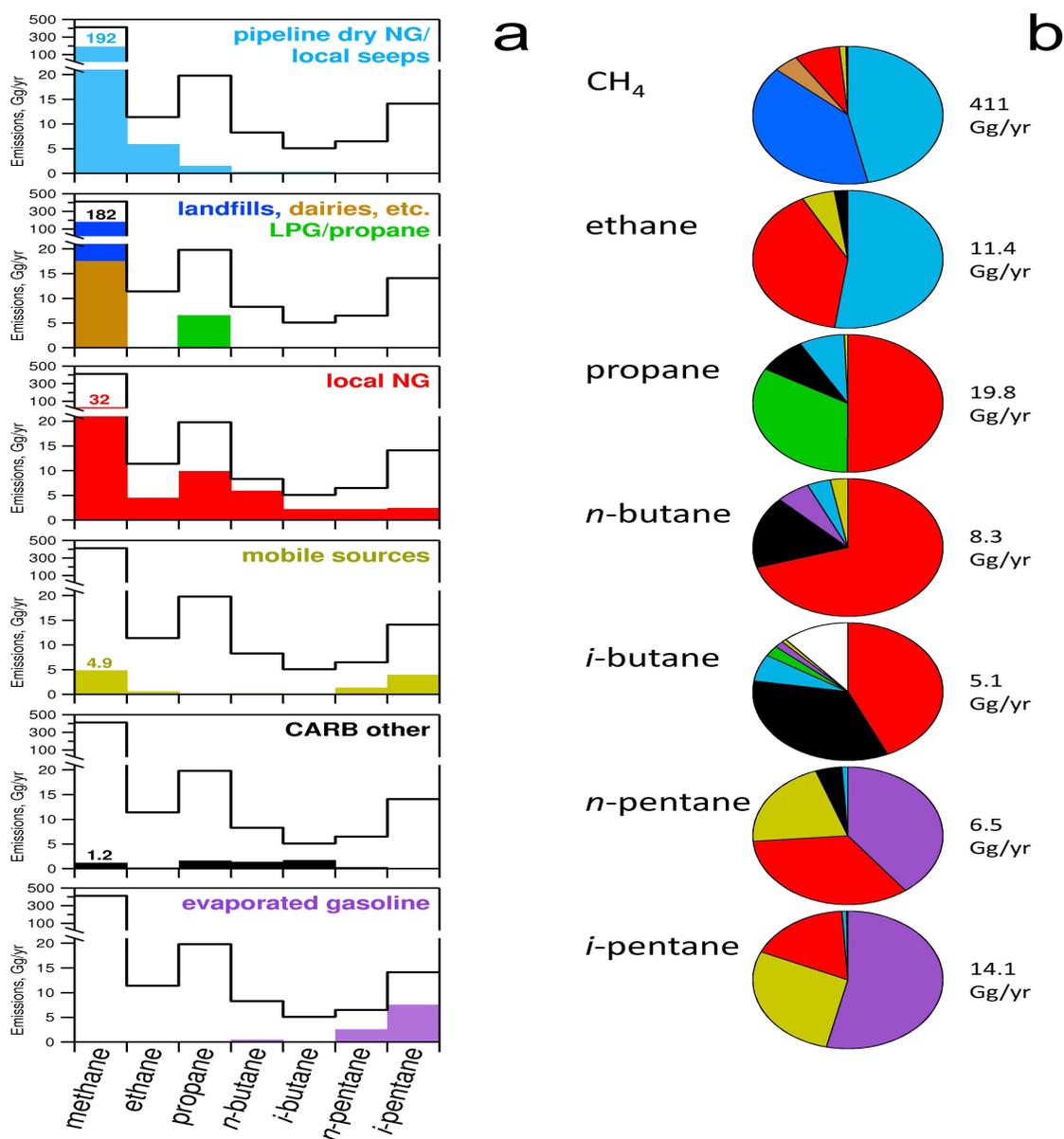


Figure 8. **a)** Results from a linear least squares solution to a combination of six sources and seven trace gas species in the SoCAB. The thick black line represents the estimated total annual emission to the SoCAB for seven hydrocarbons (CH₄ and C₂–C₅). The colored bars represent the fraction of the total contributed by each of the six source sectors used in the linear analysis. CH₄ emissions are written above the bar. **b)** Pie charts for the same data in (a) showing the relative contributions from each source for each of seven alkanes, colored as in part (a). The white region in the *i*-butane pie chart represents the 11% shortfall between our source attribution and our estimated emission to the SoCAB, though it is within the uncertainties of these two values. The total emission of the alkane to the SoCAB is given to the right of each pie chart.