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On the Sources of Methane to the Los Angeles Atmosphere

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ABSTRACT: We use historical and new atmospheric trace gas observations to refine the estimated source of methane (CH_4) emitted into California's South Coast Air Basin (the larger Los Angeles metropolitan region). Referenced to the California Air Resources Board (CARB) CO emissions inventory, total CH_4 emissions are 0.44 ± 0.15 Tg each year. To investigate the possible contribution of fossil fuel emissions, we use ambient air observations of methane (CH_4), ethane (C_2H_6), and carbon monoxide (CO), together with measured C_2H_6 to CH_4 enhancement ratios in the Los Angeles natural gas supply. The observed atmospheric C_2H_6 to CH_4 ratio during the ARCTAS (2008) and CalNex (2010) aircraft campaigns is similar to the ratio of these gases in the natural gas supplied to the basin during both these campaigns. Thus, at the upper limit (assuming that the only major source of atmospheric C_2H_6 is fugitive emissions from the natural gas infrastructure) these data are consistent with the attribution of most (0.39 ± 0.15 Tg yr^{-1}) of the excess CH_4 in the basin to uncombusted losses from the natural gas system (approximately 2.5−6% of natural gas delivered to basin customers). However, there are other sources of C_2H_6 in the region. In particular, emissions of C_2H_6 (and CH_4) from natural gas seeps as well as those associated with petroleum production, both of which are poorly known, will reduce the inferred contribution of the natural gas infrastructure to the total CH_4 emissions, potentially significantly. This study highlights both the value and challenges associated with the use of ethane as a tracer for fugitive emissions from the natural gas production and distribution system.

■ INTRODUCTION

Five to six hundred teragrams (Tg) of methane (CH_4) are currently released into the atmosphere each year.[1] Since 1750, the atmospheric abundance of CH_4 has increased from ~700 to 1800 ppb, yielding an increase in the globally averaged radiative forcing of ~0.5 W m^{-2}, or nearly 1/3 of the total estimated change.[1] The large change in the abundance of CH_4 has likely also altered the concentrations of atmospheric oxidants such as ozone and the hydroxyl radical.[2] While the total CH_4 budget and its trend are well constrained by atmospheric data recorded in situ or from air trapped in polar ice and snow, the individual contributions from its many sources (agriculture, natural wetlands, landfill gas release, energy production, and biomass burning) remain uncertain.[3]

Based on inventory analysis, or bottom-up methods, the United States Environmental Protection Agency (USEPA) estimates that US anthropogenic emissions of CH_4 to the atmosphere in 2009 were 32 Tg.[4] Top-down estimates using measurements of atmospheric CH_4 over the US suggest this number is likely too low by 20% or more.[5] Even using the lower USEPA number, CH_4 accounts for approximately 10% of all US greenhouse gas (GHG) emissions under EPA's assumption that CH_4 has a 100-year radiative forcing 21 times that of CO_2 by mass (~ 12% using IPCC's estimate of 25[1]).

One of the largest sources of CH_4 in the US are fugitive emissions from natural gas production and use (estimated to be 10 Tg or approximately 3% of the total gas produced).[4] Because CH_4 has such a large radiative forcing relative to CO_2, relatively small losses of CH_4 to the atmosphere can substantially increase the GHG forcing associated with this sector (e.g., 11% fugitive emission (mol/mol) doubles the 100-

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year radiative forcing compared to a system in which CH_4 is completely combusted to CO_2). To date, USEPA's evaluation of these fugitive emissions has focused primarily on losses sustained during energy production, while little attention has been paid to its storage, distribution, and end use.[4] Current inventory analysis suggests less than 1% is lost from transmission, storage, and distribution.[4] The California Air Resources Board (CARB) estimates fugitive emissions from the natural gas infrastructure account for only 0.093 Tg/yr or roughly 7% of the total CA CH_4 source of 1.36 Tg/yr.[6]

In this study, we follow up on the studies of Wunch et al. (2009)[7] and Hsu et al. (2010)[8] that pointed to large CH_4 emissions from within the greater Los Angeles basin. These reports add to a growing body of evidence for significant CH_4 emissions from urban regions.[9,10,11]

There are many possible sources of CH_4 within the greater Los Angeles metropolitan area. There are numerous landfills, some still active. In addition, the dairy industry in the east of the basin, wastewater treatment plants, and petroleum production and refineries as well as seeps of natural geogenic CH_4[12] contribute to the total emissions of CH_4 to the Los Angeles atmosphere. Previous measurements of CH_4, CO, and CO_2[7,8] cannot distinguish between the sources. Recent measurements of CH_4 isotopologues by Townsend-Small et al.[13] suggest, however, that fossil fuels are the main source of CH_4 to the Los Angeles atmosphere.

Most of fossil CH_4 is derived from thermal decomposition of larger hydrocarbons. As a result, a suite of other gases, including C_2H_6, is typically associated with fossil CH_4. With few sources beyond fossil fuel emissions, C_2H_6 has been used extensively as a tracer of such emissions.[3,14] Over the past forty years large and increasing quantities of C_2H_6 have been removed from the US and Middle East natural gas for production of ethylene (which in turn is used as a chemical feedstock). As described below, C_2H_6 is declining in the natural gas supply in Los Angeles and now comprises ~2% of the volume. The low and declining ratio of C_2H_6 to CH_4 in the natural gas reflects the increasing value of C_2H_6 whose price is more closely tied with crude oil than natural gas. For example, between 1980 and 2010, US natural gas production increased by 35%, while US production of C_2H_6 increased by more than 300%.[15] In 2010, C_2H_6 production equaled 6% by mass or 3% by volume of natural gas CH_4.[16] As a result, reduction in the amount of C_2H_6 in natural gas supplied to consumers has been significant. Xiao et al. (2008)[14] estimated that US natural gas contains ~5% C_2H_6 at the wellhead. This suggests that 60% of the C_2H_6 is now removed prior to distribution. Thus, uncombusted losses from the natural gas infrastructure post liquid fuel processing (i.e., after the extraction of ethane, propane, etc.) may be an important contributor to the observed decrease in the atmospheric concentration of ethane.[3,17]

In contrast to fossil CH_4, biogenic production of CH_4 by anaerobic methanogens in landfills, wastewater treatment facilities, or in the guts of ruminants has essentially no associated C_2H_6 production.[14] Thus, simultaneous measurements of CH_4 and C_2H_6 offer one possible tool to partition enhanced CH_4 to either fossil or biogenic sources. Here, we use measurements of C_2H_6 and CH_4 as well as other tracers to investigate the sources of excess CH_4 within the greater Los Angeles Basin.

DATA SOURCES

In Situ Atmospheric Data. The aircraft in situ data used in this analysis were obtained during two sampling studies performed over the Los Angeles basin in 2008 and 2010. In June of 2008, air samples were collected from the NASA DC-8 aircraft during the California portion of the NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) field experiment.[18] The four ARCTAS flights included in this study (18, 22, 24, and 26 June) occurred during daytime hours and sampled the basin as illustrated in Figure 1. In May and June of 2010, samples were collected from NOAA's WP-3D aircraft during the California Research at the Nexus of Air Quality and Climate Change (CalNex) study as shown in Figure 1.

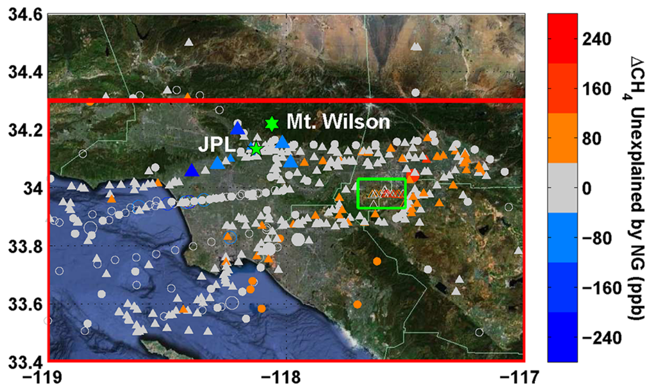

Figure 1. The locations of the ARCTAS (circles) and CalNex (triangles) measurements in the greater Los Angeles Basin overlaid on a Google Earth satellite image. The open symbols are measurements excluded from this analysis, either because they are samples that explicitly targeted dairy farms (green box), or because they were obtained in air with markedly different ratios of ΔCO to ΔCO_2 than the basin as a whole (see text). The colors represent the amount of ΔCH_4 'unexplained' by the putative source from natural gas (see text). Yellow and red colors represent an excess of ΔCH_4. The larger symbol sizes are measurements with ΔC_2H_6 in excess of 4 ppb. The green pentagram and hexagram are the locations of JPL and Mt. Wilson, respectively. The region bounding emission map sums is shown in red.

C_2H_6 and other hydrocarbons were measured in so-called "whole-air canisters" collected in both campaigns and analyzed at the University of California − Irvine. The instrumentation and analysis methods are described by Colman et al.[19] CH_4 and CO were measured by tunable diode laser spectroscopy during ARCTAS,[20] while CO_2 was measured by a nondispersive IR instrument.[21] During CalNex, CO, CO_2, and CH_4 were measured by quantum-cascade laser absorption spectroscopy.[22]

We also make use of measurements from Mt. Wilson (34.22N, 118.06W, elevation 1735 m) previously reported by Hsu et al.[8] and Gorham et al.[23] In four campaigns in 2007 and 2008, continuous real-time monitoring of CH_4 and meteorological conditions, along with whole-air sampling of organic gases and CO analyzed at the University of California − Irvine, were obtained.

Remote Sensing Atmospheric Data. Total column measurement of atmospheric CO_2, CO, and CH_4 were measured with a ground-based Fourier transform spectrometer (FTS) located in Pasadena (on the campus of NASA's Jet Propulsion Laboratory) from the fall of 2007 through summer 2008. These data and the method of analysis are described in

Wunch et al.[7] Here, we extend the analysis to examine the seasonal variations in the ratio of CH_4 to CO (and CO_2).

Natural Gas Composition Analysis. The chemical composition of natural gas arriving to the Los Angeles Basin in the major pipelines is measured in situ semicontinuously by gas chromatography using Danalyzers (Daniel Division Headquarters - Houston, Texas, USA). Monthly averages of these data were provided to us by the dominant natural gas supplier to Los Angeles, Southern California Gas Company (May Lew, personal communication). Because we do not know the location of the monitors (each from a different pipeline feeding the basin), we have simply averaged the data for each sampling period to produce an estimate of the ratio of C_2H_6 to CH_4 in the supply gas. We use the mean reported ratio and assume that the true ratio in the natural gas supply as a whole is within 66% of the range of all the measured values (Table 1). During the period of ARCTAS, this ratio was 2.09 ± 0.27% while during CalNex the ratio was 1.65 ± 0.25%. Despite the large uncertainty in the absolute ratio, the reduction between 2008 and 2010 is a robust result as C_2H_6 to CH_4 decreased at all pipeline locations sampled (−20 ± 10%) while the fraction of total natural gas received from each pipeline was similar in 2008 and 2010.[24]

Table 1. Ratio of Ethane to Methane in Natural Gas (Mol:Mol) Delivered to Southern California Gas Company from Major Pipelines

SoCalGas sample ID#	June 2007 (%)	May−July 2008 (%)	April−June 2010 (%)
36817	1.76	2.14	1.36
36821	2.00	1.88	1.67
36824	1.72	1.74	1.33
36825	2.14	2.14	1.80
36836	2.59	2.56	2.10
mean	2.04	2.09	1.65
66% of range	±0.29	±0.27	±0.25

Analysis. All the aircraft data used in our analysis are obtained at altitudes less than 1.5 km within the basin (33.5−34.5° N; 117−119° W). To avoid the influence of fire, we only include data where the biomass burning tracer acetonitrile (CH_3CN) is less than 300 ppt. We define background concentrations for CO, CO_2, C_2H_6, and CH_4 for each flight using the average of the five samples with the lowest values of C_2H_6. These 'background' samples are typically from either offshore or at altitudes above the local boundary layer. For C_2H_6, the mean standard deviation of the background values (<110 ppt) is much smaller than the enhancements observed over the basin (1000s ppt). For all the samples taken in each flight, we determine the excess concentration of each gas, ΔX, relative to the background value

$$\Delta X = [X] - [X]_o$$

where X = CO, CO_2, C_2H_6, or CH_4, and $[X]_o$ denotes the background concentration of X. While improving the precision of the analysis, the calculation of anomalies relative to these background samples does not alter (within error) the slopes of the gas correlations.

To estimate basin-wide emissions of CH_4 we use the slope of the correlation between ΔCH_4 and ΔCO together with estimates of the CO emissions from CARB.[25] This method of estimating the emissions of a gas (using the correlation with CO) does not require that the same source is emitting both gases or even that emissions are geographically colocated. When the lifetimes of gases are long compared to the mixing time within the basin, gases whose sources are distinct will nonetheless be well correlated. Both CH_4 and CO are long-lived, and thus we expect that they will be well correlated - particularly in the afternoon after vertical mixing has helped homogenize the air in the basin. Indeed, previous excess ground-based remote sensing and in situ data from Mt. Wilson have demonstrated that CH_4 (and C_2H_6) are highly correlated with CO in the basin.[7,8,23]

To test for spatial representativeness in the aircraft data (i.e., well mixed air masses), we use the ratio of ΔCO to ΔCO_2. The sources of CO are overwhelmingly from automobiles, while those of CO_2 include all sectors in the basin (industrial, residential, mobile). During CalNex, the correlation of ΔCO with ΔCO_2 is high (R^2=75%) and $\Delta CO/\Delta CO_2$ = 0.82 ± 0.03%, a value broadly consistent with expectation from the basin-wide estimates of the emissions of these gases.[7] In contrast, the correlation of ΔCO with ΔCO_2 in the ARCTAS measurements that are colocated with the whole air samples are bifurcated (R^2=51%). Many of the ARCTAS samples were obtained in the morning at low altitude (<600 m) just offshore. This highly polluted air has a much lower $\Delta CO/\Delta CO_2$ (0.28 ± 0.05%). We believe this offshore plume results from advection of the shallow and highly polluted nocturnal boundary layer from the basin. This plume has very high concentrations of numerous hydrocarbons including very short-lived alkenes as well as CFCs and HCFCs. To avoid biasing our analysis by these nonrepresentative samples, we filter the data for $\Delta CO/\Delta CO_2$ > 0.70%. The locations of the samples that are removed from our analysis are shown as the open circles in Figure 1. The rest of the ARCTAS samples have a $\Delta CO/\Delta CO_2$ broadly consistent with the basin-wide emissions (0.86 ± 0.06%; R^2=88%). The ratio $\Delta CO/\Delta CO_2$ in 2007/8 is slightly larger

Table 2. Trace Gas Ratios and Estimated Emissions in Los Angeles

year	location	$\Delta CH_4/\Delta CO_2$ (%)	$\Delta CH_4/\Delta CO$	$\Delta C_2H_6/\Delta CO$ (%)	$\Delta C_2H_6/\Delta CH_4$ (%)	E_CO (Tg yr^{-1})[b]	E_C_2H_6 (Gg yr^{-1})	E_CH_4 (Tg yr^{-1})	E_{max}_CH_4 NG (Tg yr^{-1})
2007/8	Pasadena[7]	0.78 ± 0.08	0.66 ± 0.12[a]			1.20		0.4 ± 0.1	
2007/8	Mt. Wilson[8]	---	0.55 ± 0.03	1.13 ± 0.19	2.05 ± 0.30[c]	1.20	14.5	0.38 ± 0.1	0.38 ± 0.15
2008	ARCTAS	0.674 ± 0.058	0.761 ± 0.038	1.37 ± 0.12	1.70 ± 0.16	1.13	16.6	0.47 ± 0.1	0.38 ± 0.15
2010	CalNex	0.655 ± 0.029	0.743 ± 0.031	1.17 ± 0.08	1.50 ± 0.11	1.03	12.9	0.44 ± 0.1	0.40 ± 0.15

[a]The ratio and uncertainty are derived from the variation of the monthly data shown in Figure 2. [b]We use the inventory from the California Air Resources Board for 2008 and 2010. Estimate of the emissions in 2007 are interpolated between the 2005 and 2008 inventory.[32] [c]Hsu et al.[8] reported the ratio of methane to CO in flask samples obtained from Mt. Wilson; Gorham et al.[23] reported the ratio of ethane to methane in the same samples. Here we report the ratio of these ratios for the 4 sample periods described in Hsu et al.[8]

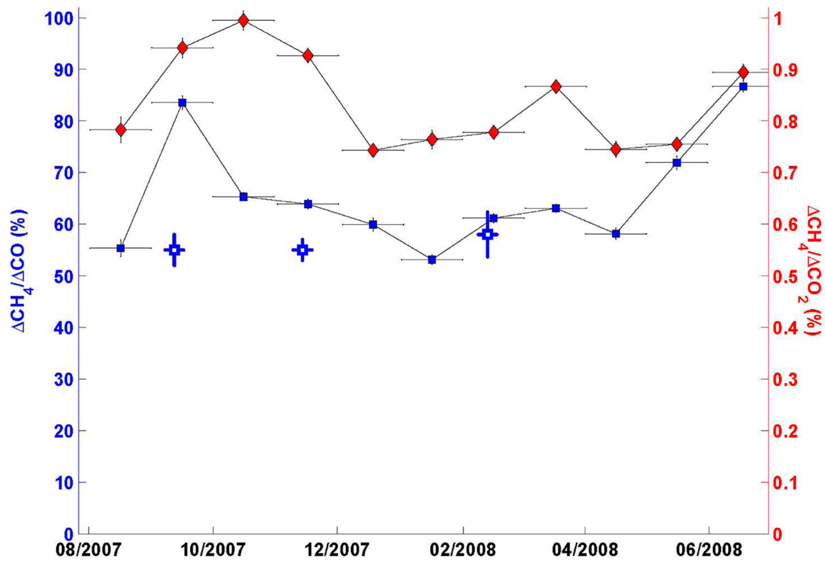

Figure 2. The monthly ratio of $\Delta CH_4/\Delta CO$ (blue squares, left axis) and $\Delta CH_4/\Delta CO_2$ (red diamonds, right axis) measured by a remote sensing technique at the campus of NASA's Jet Propulsion Laboratory (closed symbols) and at the top of Mt. Wilson (open symbols) by in situ sampling.

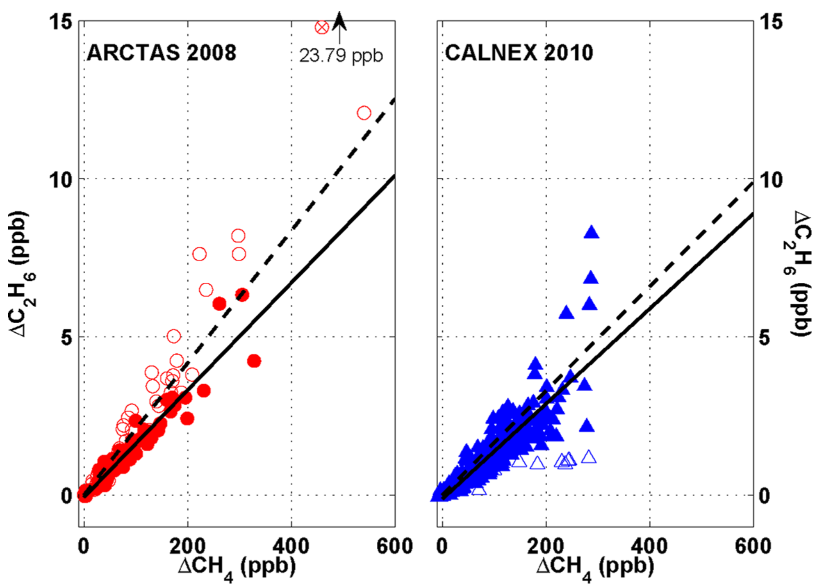

Figure 3. ΔC_2H_6 and ΔCH_4 during the ARCTAS 2008 and CalNex 2010 aircraft campaigns. The solid lines are the best fit lines to the data, and the dashed lines are the ratios of C_2H_6 to CH_4 in the natural gas delivered to the greater Los Angeles basin at the times of the measurements. The open symbols are measurements excluded from this analysis, either because they are samples that explicitly targeted dairy farms or because they were obtained in air with markedly different ratios of ΔCO to ΔCO_2 (see text).

than in 2010, not inconsistent with the CARB inventory which suggests that CO emissions declined by ~6–8% per year between 2005 and 2008 and by ~5% per year between 2008 and 2010 (see Table 2).

During CalNex, the aircraft heavily sampled the dairy area near Chino, CA (33.98 ± 0.05 N; 117.6 ± 0.10 W), shown in the small green box in Figure 1. This area is home to approximately 150,000 dairy cows, approximately 8% of the California dairy.[26] We excluded these data (shown as open symbols in Figure 1 and Figure 3) from our analysis to avoid spatial representativeness bias (e.g., to produce a sample set in 2008 and 2010 with a similar geographical distribution).

For a temporal representativeness test, we rely on the nearly continuous year-long total column measurements obtained at JPL in 2007/2008.[7] The slopes of ΔCH_4 vs ΔCO and ΔCO_2 (monthly average) are shown in Figure 2. There is little (±15%) variability in the slope of ΔCH_4 to ΔCO seasonally. Further, we see no difference in the correlation between weekdays and weekends (not shown). Thus, consistent with the Hsu et al. and Gorham et al. studies from Mt. Wilson, it appears that the CH_4 emissions do not have strong temporal variations. A similar lack of temporal variability in urban CH_4 emissions was noted by Gioli et al. in their study of Florence, Italy.[9]

In Table 2, we tabulate the observed slope of ΔCH_4 vs ΔCO and ΔC_2H_6 vs ΔCO (as well as slopes to ΔCO_2). We include in this table the previously reported data including ground-based in situ measurements obtained on Mt. Wilson, just north of Pasadena,[8] and ground-based remote sensing measurements.[7] For the remote sensing data, the error is derived from

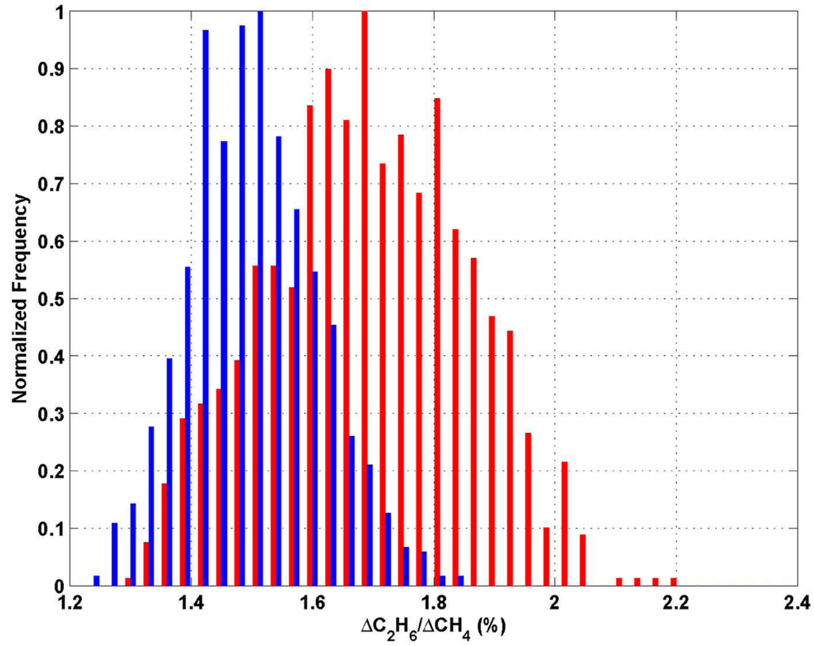

Figure 4. Histograms of the distributions of the slopes of the possible linear fits to the data in Figure 3 from the bootstrap analysis. The data in red (to the right) are computed from the ARCTAS measurements, and the data in blue (to the left) are from CalNex.

the observed month-to-month variability shown in Figure 2. Uncertainty in the Mt. Wilson data is as reported by the authors of these studies.

Using the CARB CO inventory, the unweighted mean and standard deviation of the resulting CH_4 emissions estimates are 0.44 ± 0.04 Tg. Additional sources of error include unaccounted for spatial and temporal representation error (perhaps <10% given the consistency of these different approaches) and uncertainty in the emissions of CO (~10%), suggesting that total annual emissions of CH_4 to the basin are 0.44 ± 0.15 Tg. Similarly, C_2H_6 annual emissions are estimated to be 14 ± 4 Gg.

A scatter plot of ΔC_2H_6 plotted as a function of the ΔCH_4 is shown in Figure 3 for both the ARCTAS and CalNex campaigns. The observed slopes of ΔC_2H_6 vs ΔCH_4 are listed in Table 2 and shown as the solid line on Figure 3. Errors, listed in Table 2 and illustrated in Figure 4, are calculated using the bootstrap method.[27]

DISCUSSION

Bottom Up Inventory. Shown in Table 3 is an estimate of the sources for CH_4 and C_2H_6 to the Los Angeles Air Basin by sector for 2008. The basin-level CH_4 emissions are estimates calculated by summing 0.1 degree (~10 km) spatial resolution maps of California's estimated annual average emissions[28] for different source sectors over the red box (−119 < longitude < −117, 33.4 < latitude < 34.3) that captures the LA Basin (Figure 1). The emissions from landfills are derived from estimates of individual landfills following established methods.[29] Emissions from livestock are estimated by scaling livestock density to 2008 total emissions reported of California livestock.[6,30] Emissions from wetlands are derived from Potter et al.[31] For wastewater, we use the CARB inventory[32] for statewide domestic wastewater treatment multiplied by the fraction of state residents using either septic systems or central waste treatment.[33] Of the 3.5 million California residents using septic systems, 28% live in the Los Angeles basin (mostly in the east of the basin) yielding 0.010 Tg/yr, while 45% of the California residents using central waste treatment live in the basin yielding 0.009 Tg/yr. In addition, we add 50% of the emission due to statewide wastewater treatment associated with petroleum refining (0.001 Tg/yr). The remainder of the statewide wastewater inventory is associated with agriculture, particularly paper pulp processing; we assume none of the emissions are in the basin. As we have filtered our atmospheric data to avoid biomass burning, we do not include any such emissions here.

For petroleum, the inventory is derived from mandatory reporting of oil extraction and refining to the CARB. In addition, we include the CARB statewide mobile emissions associated with the basin.[30] For natural gas, we use an estimate of the fraction of the "Lost-and-Unaccounted-For Gas" from either known fugitive emissions or unaccounted for losses as communicated to us by the Southern California Gas Company (0.02 Tg CH_4/yr or approximately 0.1% of deliveries, M.A. Bermel, Southern California Gas Company, personal communication). As only 0.01 Tg of natural gas was produced in the basin in 2009 (in production not associated with petroleum extraction), we neglect this sector.

For C_2H_6, we assume that only the petroleum and natural gas sectors have associated emissions. For petroleum, we assume that the ratio of C_2H_6 to CH_4 is 10%,[14,34] while for the natural

Table 3. 2008 Sector Based Inventory for Emissions of CH_4 and C_2H_6 into the Atmosphere of the South Coast Air Basin

sector	CH_4 emissions (Tg/yr)	C_2H_6 emissions (Gg/yr)
landfills	0.086	–
livestock	0.076	–
wastewater	0.020	–
petroleum	0.007	1.3
wetlands	0.001	–
natural gas	0.022	0.9
SUM	0.212	2.2

gas sector we use the measured C_2H_6:CH_4 ratio in 2008 from the Southern California Gas Company (Table 1).

In sum, while the bottom-up CH_4 inventory (0.212 Tg/yr) accounts for 35−73% of the inferred total emissions to the basin, these sources explain a much smaller fraction of the excess C_2H_6 (~15%). To simultaneously close the budget of both gases requires a 0.23 Tg source of CH_4 with a C_2H_6:CH_4 molar ratio of 2.6%, a ratio consistent with a source from fossil fuels.

Fossil Fuel Emissions of Methane and Ethane in the Basin. There are two fossil CH_4 sources to the basin that need to be better quantified: 1) emissions from underlying geological resource and 2) emissions associated with the imported natural gas.

The Los Angeles Basin overlays a large number of petroleum and gas rich sediments.[12b] In 2009, 0.22 Tg of natural gas was produced in the basin (approximately 2% of the gas consumed) − the vast majority associated with petroleum production.[35] In addition, there are numerous capped wells from historical gas and oil production.[34] The CARB inventory suggests, however, that the methane (and, by inference, the C_2H_6) emissions from this sector are small (Table 3).[8] If the emissions from petroleum production or from emissions of capped wells are much higher than reported, this sector could be an important contributor to both the C_2H_6 and CH_4 budgets.

In a heterogeneous environment such as Los Angeles, it is not straightforward to find unique tracers of the geological gas emissions. For example, while the ratio of propane to C_2H_6 in Los Angeles air[23] (~1) is similar to the ratio measured in many of the gas and petroleum fields[34] and much higher than in the natural gas supply (~0.17), large amounts of propane are sold in Los Angeles (~0.6 Tg/yr).[36] Gorham et al. estimate of 71 tons of propane emitted into the basin each day[23] thus represents only ~4% of the supply. Indeed, elevated propane is found in many cities that have no known geological sources.[37]

Emissions from the natural gas infrastructure are estimated by the Southern California Gas Company to be very small. Nevertheless, it is striking how similar the slope of ΔC_2H_6 vs ΔCH_4 is to the ratio of these gases in the natural gas supply (shown as dashed lines in Figure 3). In addition, the change in the observed ratio between 2008 (ARCTAS) and 2010 (CalNex) is of the same sign and magnitude as the reduction in the amount of C_2H_6 in the natural gas.

To estimate the upper limit to the contribution of emissions from the imported natural gas to the total sources of methane, we use the ratio of ethane to methane in ambient air and in the gas supply. Assuming that the only significant source of C_2H_6 to the Los Angeles atmosphere is fugitive emissions of natural gas, the maximum emissions of CH_4 into the atmosphere from natural gas, NG, are

$$E_{max}(CH_{4,NG}) = E(CH_4) \times (\beta/\alpha)$$

where α is the ratio of C_2H_6 to CH_4 in the natural gas (Table 1), and β is the same ratio in ambient air. The values of β are reported in Table 2. Clearly, if the only emissions of C_2H_6 are from uncombusted natural gas supplied to the basin, most of the ΔCH_4 in the basin is also derived from this source. The average $E_{max}(CH_{4,NG})$ is 0.39 ± 0.15 Tg where the error is dominated by the systematic uncertainty in α (Table 2).

We show in Figure 1 the mixing ratio of ΔCH_4 *not* explained by ΔC_2H_6, $[\Delta CH_4]^*$

$$[\Delta CH_4]^* = \Delta CH_4 - 1/\alpha(\Delta C_2H_6)$$

The circles are from 2008 while the triangles are from 2010. The larger symbols are locations where ΔC_2H_6 is greater than 4 ppb. The only obvious source of CH_4 not associated with ΔC_2H_6 is in the east of the basin near Chino, California (red open triangles within the green box), where a large concentration of dairy farms is located. Samples obtained near landfills (e.g., Scholl Canyon (34.16N,118.19W)) and near the large Hyperion wastewater treatment plant (33.92N,118.43W) show no obvious CH_4 enhancements above those explained by C_2H_6, though the sampling is admittedly sparse and wind will certainly advect these emissions away from their source.

Southern California Gas Company delivers natural gas to the Los Angeles Basin and the surrounding area. Approximately 30% of its gas is delivered to residential customers (5.4 Tg/yr), 30% to industrial and commercial customers (5.6 Tg/yr), 37% to electric utilities (6.9 Tg/yr), and the remainder to natural gas vehicles and enhanced oil recovery steaming (0.5 Tg/yr).[38] Assuming that this distribution of gas is the same inside the Los Angeles Basin (which includes Los Angeles, San Bernardino, Orange, and Riverside Counties), an emission of 0.39 Tg represents approximately 3.5% of the gas delivered to customers in the basin (~11 Tg in 2007).[38] Southern California Gas Company also delivers to Fresno, Imperial, Kern, Kings, Santa Barbara, San Luis Obispo, Tulare, and Ventura Counties, which are less densely populated, are not located in the basin, and consume an additional 1 Tg for residential customers and 6 Tg for nonresidential customers. Southern California Gas Company,[24] however, operates several large storage facilities within the basin. Thus, using the total volume flowing through pipelines in the basin as a denominator, 0.39 Tg represents approximately 2% of the gas flowing into the basin.

As mentioned above, however, mass balance estimates by Southern California Gas Company suggest that only ~0.1% of the natural gas is lost between the city gates and the customer meters (M. A. Bermel, Southern California Gas Company, personal communication). This suggests that if the methane emissions in Los Angeles are associated with the natural gas infrastructure, such losses must occur post consumer metering. Losses of gas within both homes and businesses are certainly one possible explanation for our findings. Steady but very small leaks from gas fittings and valves could contribute a significant fraction of the total gas used in these settings. Indeed, it is highly likely that the vast majority of all valves and fittings between the gas wells and the end-use gas appliances are located at the very end of the delivery system, e.g. in customers' homes and businesses. For example, the first author's home (constructed in 1914) contains no fewer than 100 gas fittings, seven ball valves, and, within the appliances themselves, eight control/throttle valves; several had obvious leaks. Yet, the duty cycle of appliance use is very low − just a few percent of the time is any gas appliance in use. Thus, small steady leaks could amount to a few percent of the total consumed. Such leaks would produce only a small enhancement in methane in the home and would not be detectable by smell or constitute, in any way, a health or fire hazard. For example, consider a 150 m^2 home that uses 1000 m^3 of gas annually and has one air exchange each hour. If 5% of the annual natural gas usage is lost unburned into the home (less than the use of a typical pilot light), methane concentrations would only be about 12 ppm higher than in the ambient air outside the home; the odorant concentration would be orders of magnitude below the threshold necessary to smell the gas. If such high leakage rates occurred across the US, losses within the distribution system would represent a source of more than 6 Tg/year.[4] This additional source of CH_4 would go a substantial way toward reconciling the top-down and inventory estimates of total US CH_4 sources.[39] Electronic gas metering is currently being installed throughout Southern California Gas Company's service area, and these data may provide a rapid and noninvasive method of evaluating whether some or many customers have unrealistically large and steady natural gas consumption.

Outlook for Future Studies. Emissions of methane from Los Angeles are substantial and considerably larger than current inventories suggest. The correlation between methane and ethane within the basin point suggest fossil fuel emissions as the likely source of much of the unaccounted for source. We are unable, however, to definitively determine whether these emissions are associated with imported gas or emissions from the underlying geological resource. The obvious next step is to undertake in situ sampling to seek out sources of methane within Los Angeles and more broadly in a cross section of urban centers, in an extended version of the work by Baker et al.[26] These measurements should include a suite of hydrocarbons and perhaps sulfur compounds together with an associated inventory of possible sources, including natural gas.

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Notes

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■ NOTE ADDED IN PROOF

A recent study for the California Air Resources Board suggests that the CARB inventory of emissions from the petroleum industry is underestimated by a factor of two. (Y. K. Hsu, personal communication).

■ NOTE ADDED AFTER ASAP PUBLICATION

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