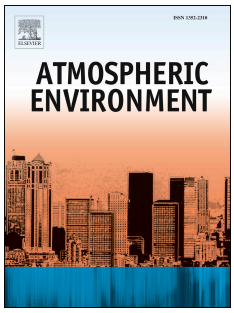
Accepted Manuscript



Top-Down Methane Emissions Estimates for the San Francisco Bay Area from 1990 to 2012

David Fairley, Marc L. Fischer

PII: S1352-2310(15)00088-6

DOI: 10.1016/j.atmosenv.2015.01.065

Reference: AEA 13583

To appear in: *Atmospheric Environment*

Received Date: 10 November 2014

Revised Date: 28 January 2015

Accepted Date: 29 January 2015

Please cite this article as: Fairley, D., Fischer, M.L., Top-Down Methane Emissions Estimates for the San Francisco Bay Area from 1990 to 2012, *Atmospheric Environment* (2015), doi: 10.1016/j.atmosenv.2015.01.065.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

Top-Down Methane Emissions Estimates for the San Francisco Bay Area from 1990 to 2012

David Fairley[1] and Marc L. Fischer[2]

[1] Planning, Rules and Research Division, Bay Area Air Quality Management District, 939 Ellis St., San Francisco, CA, 94109. 415-749-4656. fairley@baaqmd.gov (corresponding author)

[2] Energy and Environmental Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

Abstract

Methane is a potent greenhouse gas (GHG) that is now included in both California State and San Francisco Bay Area (SFBA) bottom-up emission inventories as part of California's effort to reduce anthropogenic GHG emissions. Here we provide a top-down estimate of methane (CH4) emissions from the SFBA by combining atmospheric measurements with the comparatively better estimated emission inventory for carbon monoxide (CO). Local enhancements of CH_4 and CO are estimated using measurements from 14 air quality sites in the SFBA combined together with global background measurements. Mean annual CH_4 emissions are estimated from the product of Bay Area Air Quality Management District (BAAQMD) emission inventory CO and the slope of ambient local CH_4 to CO. The resulting top-down estimates of CH_4 emissions are found to decrease slightly from 1990 to 2012, with a mean value of 240 +/- 60 $GgCH_4\ yr^{-1}$ (at 95 % confidence) in the most recent (2009-2012) period, and correspond to reasonably a constant factor of 1.5-2.0 (at 95 % confidence) times larger than the BAAQMD CH_4 emission inventory. However, we note that uncertainty in these emission estimates is dominated by the variation in CH_4:CO enhancement ratios across the observing sites and we expect the estimates could represent a lower-limit on CH_4 emissions because BAAQMD monitoring sites focus on urban air quality and may be biased toward CO rather than CH_4 sources.

Keywords: methane emissions, emissions inventory, greenhouse gas, inventory verification, top-down estimates

1. Introduction

From global to local scales, greenhouse gas (GHG) emission inventories are an essential element of efforts to address climate change. In California, USA, the State legislated mandatory reductions in GHG emissions to meet 1990 emissions levels by 2020 (AB-32 2006). The San Francisco Bay Area of California has GHG emissions that are reported as greater than those of Austria, Peru or Portugal (WRI 2014, BAAQMD 2014). According to the current inventory of the Bay Area Air Quality Management District (BAAQMD), the Bay Area emitted 125,500

metric tons of methane in 2011, or 3.5 million tons CO_2-equivalent, assuming a 100 yr. global warming potential (GWP = 28) from the IPCC 5th assessment (IPCC 2013, Table 8.A.1).

Currently, regional, state, and federal agencies, including the BAAQMD, estimate GHG emissions using bottom-up inventory methods that rely on a combination of activity data, emission factors, biogeochemical models and other information. Recent emission evaluation based on ambient measurements show that methane emissions for the US as a whole (e.g., Miller et al. 2013) and in California (e.g., Wennberg *et al*. 2009, Hsu *et al.* 2010, Singh *et al.* 2010, Jeong *et al*. 2013, Peischl *et al*. 2013) are underestimated by ~ 50% or more depending upon the area. Specific to oil and gas sector methane emissions, two meta-analyses, one for the US (Brandt *et al*. 2014) and another for California (Jeong *et al*. 2014) reached similar conclusions. Relevant to urban areas, the US-EPA recently released a report identifying uncertainty in methane emissions from the natural gas distribution system as an area in need of further research (US-EPA, 2014). For the Bay Area, which has a number of refineries and extensive natural gas use, a 50% underestimation would imply additional annual emissions of about 3.5 million tons CO_2-equivalent.

From national to local scales, GHG emissions inventories are relatively new compared with the inventories for criteria pollutants. In particular, emissions of a primary criteria pollutant like carbon monoxide (CO) are estimated with greater accuracy. Here we estimate emissions of methane (CH_4) for the Bay Area using the top-down approach of Hsu et al. (2010), scaling the better estimated emissions of CO to CH_4 using the ratio of local enhancements, CH_{4local}:CO_{local}, where "local" indicates local atmospheric mixing ratio increments above the background inflow of CH_4 and CO to the region of interest.

We estimate CH_4 emissions from 1990 to 2012 using a record of CH_4 and CO measurements from a dozen sites across the Bay Area and background CO estimates. The following sections describe the data used to estimate the ratio of local enhancements—the change in concentration from the addition of local emissions—of CH_4 and CO, the quality of the CO emission inventory, the resulting estimates of CH_4 emissions, and a discussion of the limitations and implications of the study.

2. Methods

We follow a scaling ratio approach of CH_4: CO applied previously (e.g., Wennberg *et al*. 2009, Hsu *et al.* 2010, Singh *et al.* 2010), applying data from multiple sites for both local and background air. For oceanic background CH_4 and CO, we compare data from multiple sites, and then subtract the background CH_4 and CO from measurements at the Bay Area sites to estimate local enhancements. The resulting estimates of local CH_4 and CO are analyzed in 3 yr. periods,

and the resulting CH_4 emissions are estimated using the CH_4:CO ratios combined with the BAAQMD inventory estimates of CO emissions.

2.1 Bay Area CH_4 and CO Measurement Sites

The BAAQMD operated monitors that measured CH_4 hourly starting with 9 sites in 1980, peaking at 12 sites from 1986 to 1994, then tapering off to 7 sites in 2010 and none in 2013 (Figure 1). Two instruments were used to measure CH_4, a Bendix instrument (Model 8202A) that measured CH_4 and total hydrocarbons, and a Thermo Electron (TE-55), that measured CH_4 and non-methane hydrocarbons. Both instruments were calibrated to CH_4 using standard gas additions. While the focus of the measurements was on the non-methane hydrocarbons, the CH_4 measurements are reasonably consistent over time and among sites, and exhibit concentrations consistent with background for some sites. CO was measured with Thermo Electron (TE-48) CO monitors, calibrated following a US-EPA method (40 CFR 53), except for San Jose, where a trace-level CO analyzer (TE-48TC) was used. In this analysis, we estimate local mixing ratio enhancements for CH_4 and CO from 24-hour values for days with at least 18 hours of valid data. (The numbers of valid observations by year, site and pollutant are shown in supplementary materials S5.)

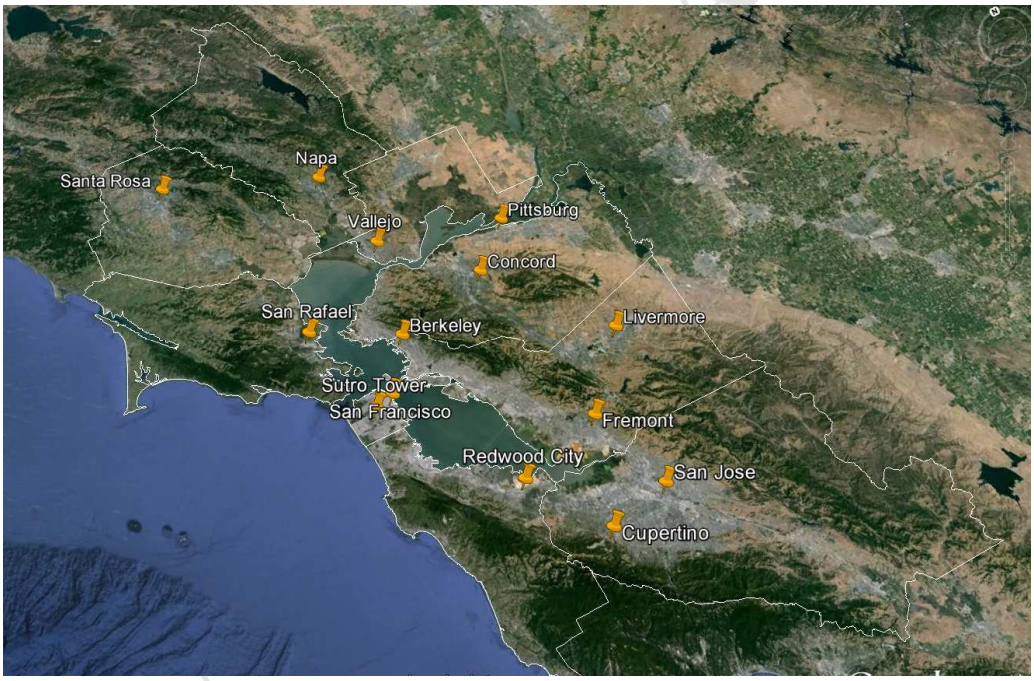


Figure 1. Locations of CH_4 and CO sampling sites in the Bay Area used for this study.

2.2 Drift in CO instruments

The TE-48 CO instruments were subject to drift on the order of 200 ppb, typically on the timescale of weeks. Instruments were re-zeroed after this amount of drift based upon

measurements of CO-free air made every two days. These measurements were available in digital form from 2009 through 2012. Subtracting these zero measurements from the CO measurement appeared to correct much of the drift. Because of the limited availability of zero-air measurements, this adjustment could only be made in the most recent, 2009-2012, period. Applying the drift correction had little effect on the estimated ratios of local CH_4:CO. (See supplemental materials S4 for details.)

2.3 Estimating Seasonal Background CH_4 and CO

Ambient atmospheric CH_4 concentrations are typically enhanced by small fractions above oceanic background inflow to the Bay Area. In contrast, ambient CO is more strongly enhanced by local emissions. In both cases, background CH_4 and CO concentrations were estimated and subtracted from Bay Area measurements to estimate local enhancements.

To estimate inflow of CH_4 and CO to the Bay Area, we use long-term measurements from the National Oceanographic and Atmospheric Administration's Global Monitoring Sites on Mauna Loa (MLO), Hawaii, Trinidad Head (THD), California, and a shorter (2008-present) record from 232 m above ground at Sutro Tower (STR), in San Francisco, California (NOAA, 2014). In all cases, either single hour- or averages of multiple hour-measurements for a day were compared with that day's daily averages of the measurements from Bay Area sites. For years when THD data were available, regressions were used to estimate the annual mean. For earlier years, the mean was estimated as the MLO mean plus the average difference between the THD and MLO means. See supporting material (S1) for more detail.

Annually averaged Bay Area and background CH_4 and CO measurements are shown in Figures 2 and 3. Figure 2 shows a generally increasing trend in CH_4, except for reductions in the early 1990s. There is considerable individual site variation, but show similar long-term patterns. CH_4 background estimates capture the long-term pattern of trends, and are generally lower than, measurements from the SFBA. Figure 3 shows a decline in Bay Area CO concentrations of about 70%. The pattern is matched consistently at Bay Area sites. Background CO, in contrast, has decreased, but only slightly.

As described in supporting materials, we found that NOAA flask measurements from STR in the 2009-2012 period compare closely with data from THD for times when winds for both sites are derived from clear air sectors. Specifically, for hours where the mean u-component from winds measured at Fort Funston in San Francisco from the previous 5 hours was ≥ 4 knots, the median STR-THD difference in methane was -3 ppb with a 95% (Wilcoxon) confidence interval of -4.5 ppb to -2.5 ppb, based on 513 paired hours between 2007 and 2012. For CO, few paired observations were available. The difference in the STR and THD seasonal curves for CO was -

1.5 ppb. As these differences were small relative to the magnitude of the observations, the THD-derived curves were used without adjustment. (See supporting material S1 for more details.) We note that two sites (Santa Rosa and San Francisco) show small negative (likely instrumental) offsets relative to the NOAA background that were subtracted before estimating CH_4:CO slopes.

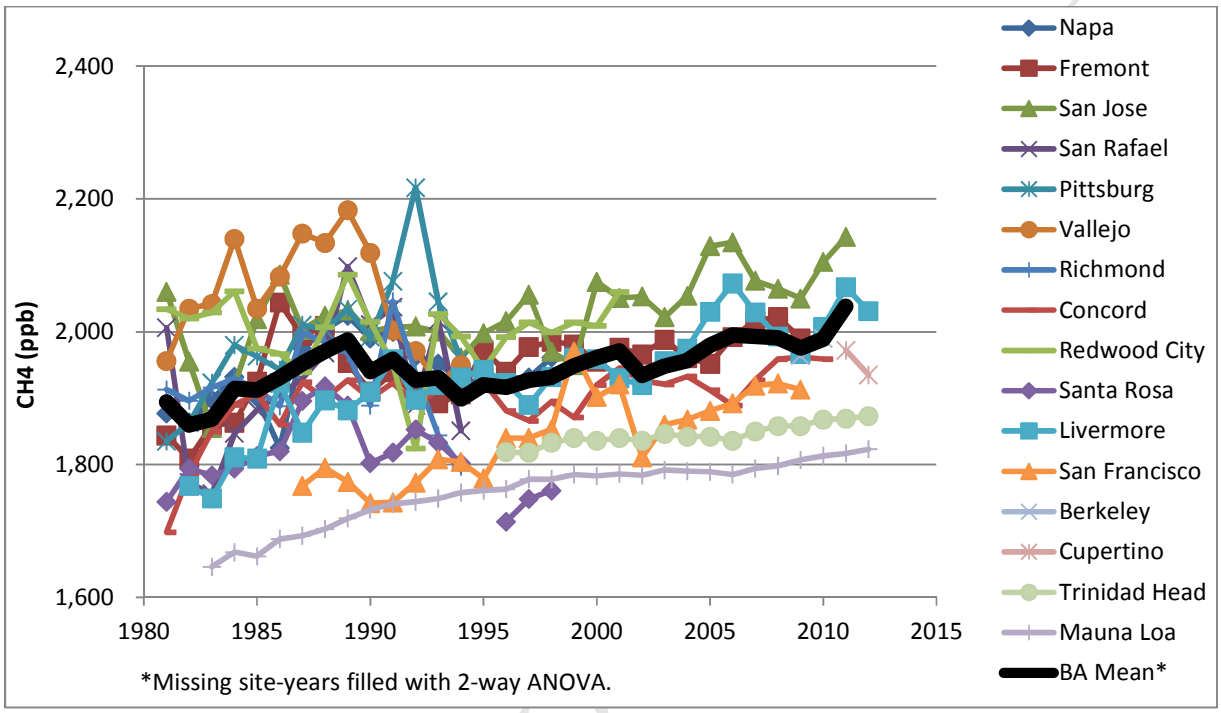


Figure 2. Methane Trends 1981-2011 Annual Means: SF Bay Area and Background Sites

ACCEPTED

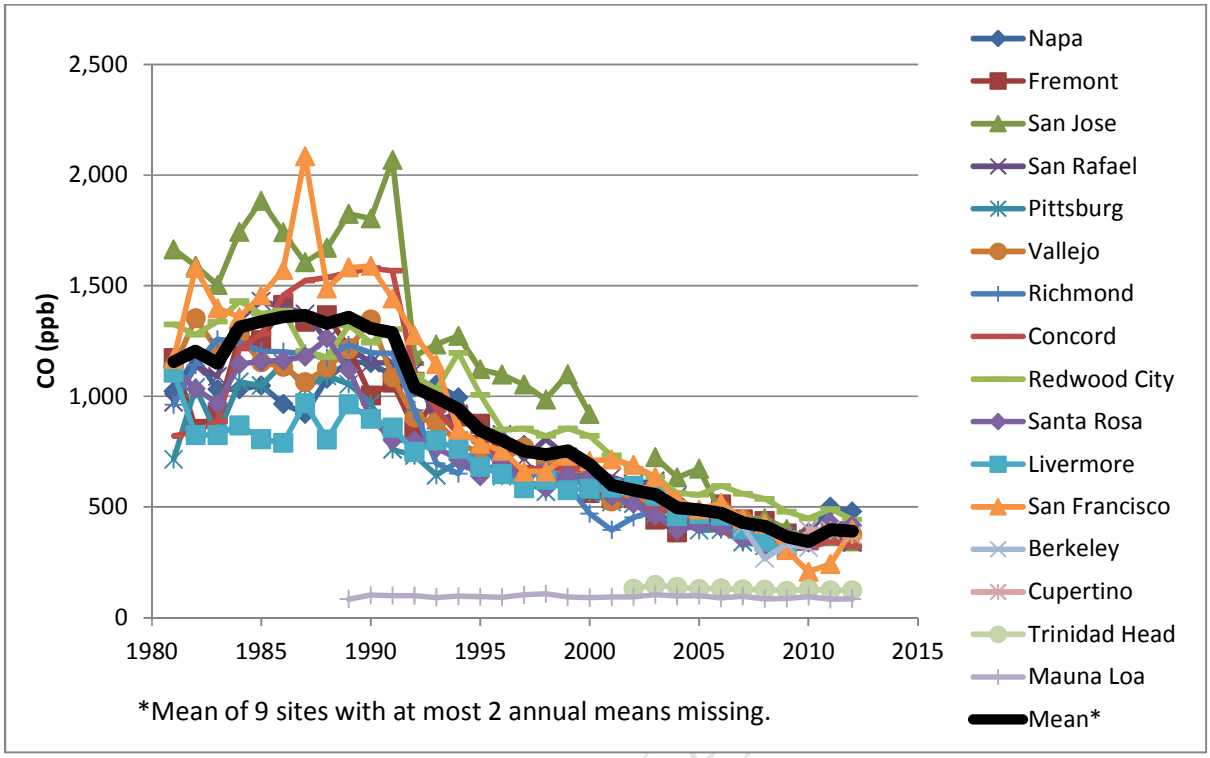


Figure 3. Trends in Bay Area and Background CO, 1981-2011

We estimated CH4 and CO enhancements by subtracting the estimated background:

$CH4_{local,it} = CH4_{it} - CH4_{background,it}$, for year i and day t, and similarly for CO. (1)

2.4 Emissions Inventory

The BAAQMD maintains and regularly updates emissions inventories for both criteria pollutants and greenhouse gases. Bay Area-wide annual CO emissions estimates were obtained from the latest county-level inventory (BAAQMD 2014 (1)). This inventory includes back-casting of CO emissions from previous years.

While BAAQMD does not report an uncertainty for the CO emissions inventory (EI), the EI has been carefully vetted for many years in the process of planning to achieve the national and state CO standards. Trends in CO emissions closely correlate with ambient concentrations. Figure 4 shows emissions along with Bay Area mean enhancement above background, computed from equation (1). Note that the mean enhancement shown in Figure 4 equals the difference between the mean CO shown in Figure 3 and the estimated background (approximately equal to the Trinidad Head or Mauna Loa concentrations). The correlation is 0.99. Error bars represent one standard error (s.e.), where the s.e. is computed from second differences in the annual mean, to

account for the year-to-year variation caused by all factors, including meteorology and measurement error. (See Supplementary materials for an explanation of estimating standard errors from second differences.) For on-road motor vehicles, which produce the majority of Bay Area CO according to the EI, a recent study showed a very close match for Bay Area emissions of CO between the EMFAC-model-based approach used in the EI (728.2 short tons/day for 2011), and a fuel –based approach (714.1 short tons/day for 2010) (McDonald and Harley 2013, Tables S5 and S6).

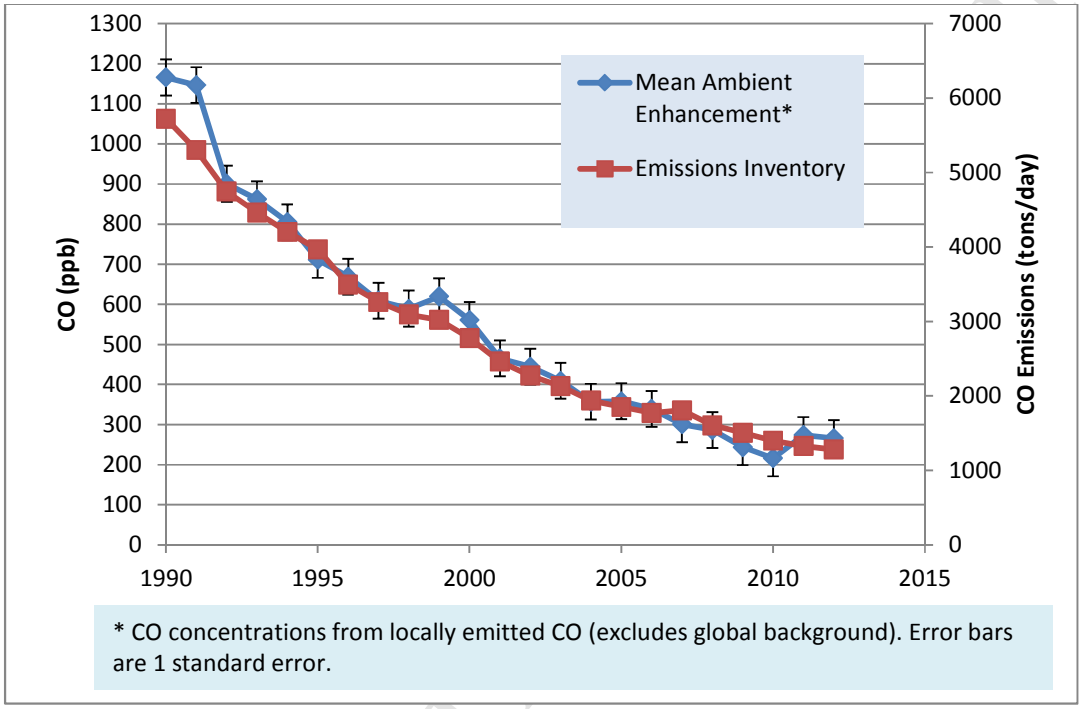


Figure 4. Trends in Bay Area ambient and inventory CO 1990-2012. Ambient trends are enhancements above background.

To estimate the uncertainty in total Bay Area-wide CO emissions, we assume that on-road CO emissions are accurate to a standard error of 20%, and each of the other major CO sources (including off-road gasoline, diesel, woodburning, natural gas) is accurate to a standard error of 50%. Assuming the sources of error are uncorrelated, then the variance of the total CO emissions equals the sum of the variances; the resulting uncertainty in total CO emissions has a standard error that is 19%.

Similarly, Bay Area-wide CH_4 emissions estimates were obtained from the District's GHG Inventory (BAAQMD 2014 (2)), which includes estimates ranging back to 1990. Figure 5 shows these emissions estimates along with estimated Bay Area enhancements to ambient CH_4. Because CH_4 is not regulated by the BAAQMD, we do not have an explicit prior uncertainty estimate for the CH_4 emissions.

Figure 2 above shows a pattern of a reduction in Bay Area mean total CH_4 concentrations in the early 1990s followed by an increasing trend. But it also shows that background CH_4 concentrations are increasing. Figure 5 shows the same pattern in the local CH_4 enhancements, indicating that the origins of this pattern are changes in local CH_4 emissions.

Also shown are error bars representing year-over-year variation in the mean enhancement. We believe that much of the annual variation derives from spatial inhomogeneity in emissions combined with local meteorology (including, wind direction, speed, mixing height) rather than annual variation in emissions. Thus, the changes in annual mean from 2005 to 2007 appear accountable from variation in meteorology rather than emissions.

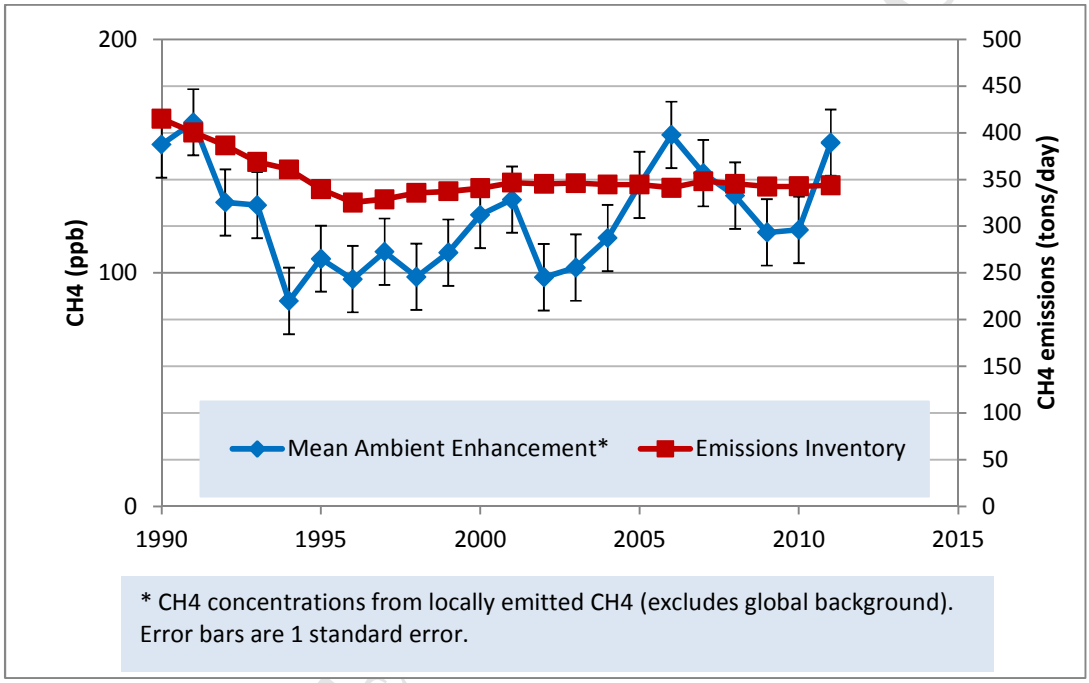


Figure 5. Trends in Bay Area ambient and inventory CH4 1990-2011. Ambient trends are enhancements above background.

2.5 Estimating local CH_4 emissions

For each sequ ence of 3-year periods, we computed linear regressions of background-subtracted CH_4 on background-subtracted CO for each site with sufficient data for that period. We then applied the formula to estimate annual CH_4 emissions:

$$E_{CH4}\text{ (metric tons/ year)} = CH_4\text{:CO slope} * (16/28) * E_{CO}\text{ (metric tons/ year)} \qquad (2)$$

where E_{CO} are the BAAQMD Emissions Inventory estimated CO emissions for that period, and the ratio of molecular weights for CH_4 (16) to CO (28) converts the slope from volumetric (ppb) units to mass ($\mu g/m^3$) units. Resulting CH_4 emissions are compared with bottom-up estimates of annual average emissions of CH_4 and CO reported by the BAAQMD. Because 1990 was chosen as the base year for California's AB-32 GHG reductions efforts, we used this year as the initial year for our analysis.

3. Results

3.1 Methane to Carbon Monoxide Enhancements

Over the period of study, methane enhancements have varied, but were similar in 2009-2011 to what they were in 1989-91 (Figure 3). In contrast, carbon monoxide enhancements have decreased by approximately 80% from 1990 to the present (Figure 2). We note that the decrease in observed CO enhancements are well-matched by decreases in the BAAQMD Emissions Inventory for CO, whereas the inventory shows a decrease in methane emissions of about 20%. Thus, the CH_4-CO relationship has changed over time and, to take this into account, separate regression relations were estimated for several different periods: 1989-91, 1993-95, 1996-98, 1999-01, 2002-04, 2005-07, and 2009-12. (The last period, 2009-12, encompassed 4 years to include sites with less than 3 years of data at the beginning or the end of the period.)

The slopes of CH_{4local} to CO_{local} were then computed using simple linear regression and are reported in Table 1. In this analysis we found that the residuals contained significant first order autocorrelations (>0.5). Hence, we applied the Cochran-Orcutt method (Cochrane and Orcutt 1949) to adjust for autocorrelation which, to more correctly estimate the uncertainty.

Table 1. Slopes(s.e.'s) of regressions of background adjusted CH4 on background adjusted CO.

Site	1989-91	1993-95	1996-98	1999-01	2002-04	2005-07	2009-12
Napa	0.18(0.01)	0.23(0.01)	0.26(0.01)				
Fremont	0.23(0.01)	0.29(0.01)	0.34(0.01)	0.41(0.01)	0.51(0.02)	0.67(0.03)	1.14(0.05)
San Jose	0.22(0.01)	0.28(0.01)	0.33(0.01)	0.34(0.01)	0.48(0.01)	0.60(0.01)	0.80(0.02)
San Rafael	0.24(0.01)	0.28(0.01)					
Pittsburg	0.38(0.01)	0.49(0.01)					
Vallejo	0.35(0.01)	0.33(0.01)					
Richmond	0.25(0.01)	0.28(0.01)					
Concord	0.22(0.01)	0.27(0.01)	0.32(0.01)	0.37(0.01)	0.57(0.02)	0.80(0.03)	1.14(0.04)
Redwood City	0.34(0.01)	0.28(0.01)	0.35(0.01)	0.40(0.01)			
Santa Rosa	0.20(0.01)	0.23(0.01)	0.26(0.01)	0.32(0.05)			
Livermore	0.22(0.01)	0.34(0.01)	0.43(0.01)	0.49(0.01)	0.73(0.02)	1.14(0.03)	1.23(0.07)
San Francisco	0.26(0.01)	0.39(0.01)	0.43(0.01)	0.51(0.01)	0.54(0.01)	0.65(0.02)	0.58(0.02)
Berkeley							0.93(0.02)
Cupertino							0.63(0.03)

ACCEPTED MANUSCRIPT

3.2 . Comparison of CO-estimated methane with the Emissions Inventory values

Figure 6 shows the methane emissions implied for the SFBA for each time period as $\widehat{M}_{ij} = C_j\hat{\beta}_{ij}$, where i=site, j=period, C_j = the BAAQMD emissions inventory estimate of annual CO emissions in period j, and $\hat{\beta}_{ij}$ is the CH_4/CO slope from Table 1. The standard errors of the estimates range from 19% to 22% of the corresponding $\widehat{M}_{ij}$. As can be observed in the figure, there are large differences among the methane emissions estimates for different sites and over time. A number of these differences are statistically significant.

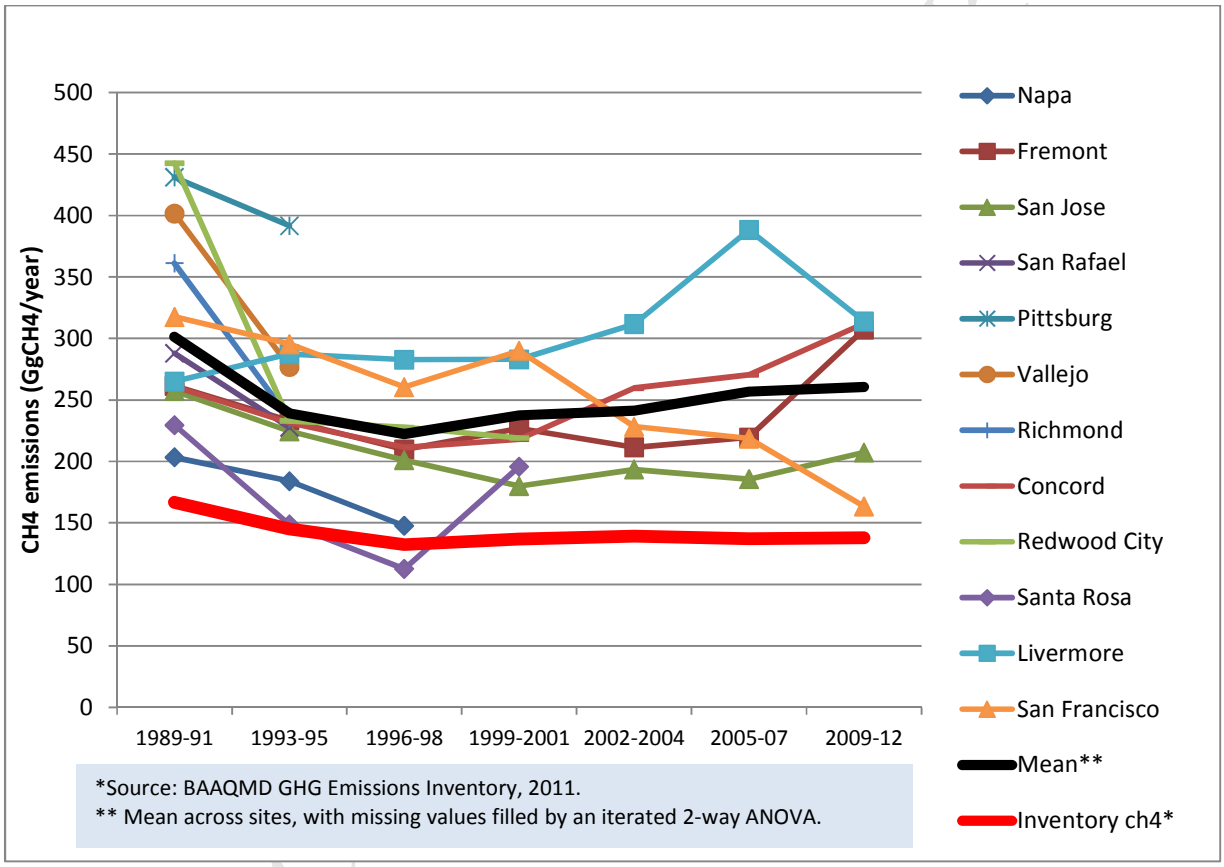


Figure 6. CH_4 emissions estimated for the SFBA over time. Emissions are estimated as the product of CH_4:CO slopes from individual sites and SFBA-wide CO emissions. Estimated standard errors range from 19% to 22% of the corresponding estimate.

To account for the variations across sites and time, we use the $\widehat{M}_{ij}$ as the unit of analysis, and compute the standard errors of the $\widehat{M}_{ij}$ for each period.

Figure 7 compares the mean estimated methane emissions with the emissions inventory values. The upper panel of Figure 7 parallels Figure 5, with the same emissions inventory estimates, but with top-down CH_4 emissions estimates rather than ambient CH_4 concentrations. The top-down

estimates follow the same general shape as the ambient concentrations, namely a reduction in the 1990s followed by a gradual increase to 2010. Bars for 95% confidence intervals for the mean show that the CO-estimated CH_4 emissions are consistently larger than the emissions inventory estimate for every period. The lower panel in Figure 7 shows the ratio of CO-estimated methane to EI methane, together with the uncertainty in mean ratio, where ratios are found to fall between 1.5 and 2.0.

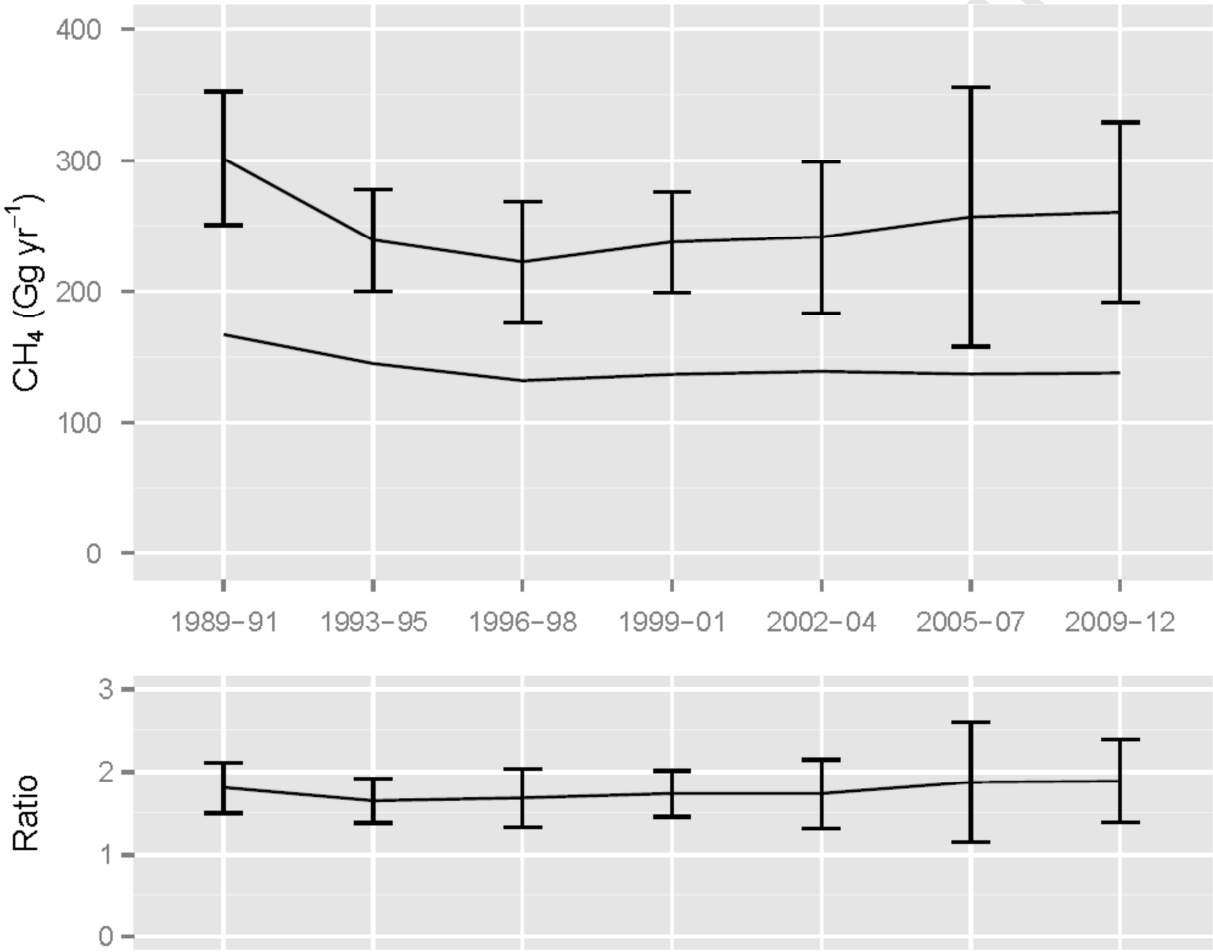


Figure 7. Upper figure shows mean CO-estimated methane, with error bars vs. emissions inventory estimates; lower figure shows their ratio (CO-estimated/EI). Bars represent 95% confidence intervals for the mean.

The supporting materials (S3) present another approach using the standard errors of the slopes. This approach shows that most of the variation in the $\widehat{M}_{ij}$ comes from systematic differences between sites; there is little systematic difference by period, with most of the remaining variation explained by site-period interactions.

3.3 Pooled estimate of the top-down/bottom-up ratio

To evaluate the variation by site and time period, we performed a two-way ANOVA of the ratios on site and time period, but found time period was not statistically significant. If we consider the sites as representing a random sample of Bay Area locations, we can estimate the uncertainty in the pooled ratio estimate using a random effects model, namely, the ratio R_{sy} for site s, period y would be:

$$R_{sy} = \mu + \delta_s + \varepsilon_{sy}$$

for s = 1 to number of sites, and y = 1 to 7 (number of periods), where μ is the pooled ratio, δ_s are random site effects with mean 0 and variance σ_δ^2, and ε_{sy} are random errors with mean 0 and variance σ_e^2, all terms statistically independent.

To estimate the average CH_4 over multiple time periods, we created a pooled estimate of the top-down/bottom-up ratio, the arithmetic mean $\bar{R} = \frac{1}{n}\sum_{sy} R_{sy}$, where n = 56 = total site-periods. This simple estimate is 1.74, with variance

$$\sigma_{\bar{R}}^2 = Var(\bar{R}) = \frac{\sum_s n_s^2}{n^2}\sigma_\delta^2 + \frac{\sigma_e^2}{n}$$

Using a method of moments approach, we estimate $\hat{\sigma}_\delta^2 = .12325 \; and \; \hat{\sigma}_\varepsilon^2 = .08622$. This yields an estimate, $\hat{\sigma}_{\bar{R}} = .116$. An approximate 95% confidence interval is 1.74 ± 2*0.12 = 1.50 to 1.98. We note that estimating the pooled ratio in other ways yields similar results: The mean of the 14 site means is 1.75. An average weighted inversely to the variances of the slopes yields an estimate of 1.62.

4. Discussion

This analysis applied a "top-down" approach to estimate methane emissions via the more established CO emissions and the relationship of ambient CH_4 to CO. The top-down estimates are almost uniformly greater than the corresponding bottom up estimates from the emissions inventory. For the most recent period, the analysis suggests that CH_4 emissions are as much as double the BAAQMD inventory estimates, similar to or greater than results obtained previously for other periods and areas of California (Wennberg *et al*. 2009, Hsu et al. 2010, Singh *et al.* 2010, Jeong *et al*. 2013, Peischl *et al*. 2013).

Here we note that while estimated methane emissions differ across sites, the differences are within a factor of two for 90% of the site pairs . Also, the rank order of the emissions is fairly constant, such that a site with an above average slope in one period is likely to have an above average slope in other periods and vice versa. Taken together, the analysis shows that if the sites

ACCEPTED MANUSCRIPT

are treated as a random sample of Bay Area locations, these top-down estimates exceeded the corresponding Emissions Inventory estimates by 50% to 100% with approximately 95% confidence.

The above observations are consistent with the sites differing in the relative intensities of CH_4 to CO emissions sampled by the different sites and suggest the need for caution in interpreting the above estimates as an upper limit on total Bay Area methane emissions. Because most of the BAAQMD monitoring sites are located in urban or suburban areas, it is likely that local CO emissions are at least as high, on average as at a randomly selected Bay Area location, whereas CH_4 emissions are equal to or lower, because the Bay Area's two largest CH_4 sources (landfills and livestock) are located in rural areas. Thus, we expect that the slopes may underestimate the ratio of CH_4:CO and hence estimated CH_4 emissions. This suggests the need for additional measurements in rural areas.

The general outline of both the CH_4 enhancements (Figure 5) and top-down CH_4 emissions estimates (Figure 7) is down in the early 1990s followed by an upswing since then. The early 1990s reduction is likely due to California regulation of landfills, and parallels the reduction in the EI. The gradual increase since then matches an increase in Bay Area population, suggesting a factor proportional to population such as waste water, natural gas use, or waste added to landfills.

Further work is also needed to identify the sources of CH_4 within the Bay Area. Measurement of covariate gas species could be useful in this regard (e.g., ethane for natural gas, alcohols for livestock, and perhaps $^{13}C/^{12}C$ ratio of methane). Another avenue of research is atmospheric inverse model analysis linking measured methane concentrations with emissions from different areas and sources to aid with spatial attribution. The outcome of such work would help in identifying opportunities for mitigation of methane emissions from the mixture of urban, suburban, and rural activities.

Acknowledgements

We thank Eric Stevenson and the monitoring section at the BAAQMD, who maintained the high quality CO and CH_4 measurements across the SFBA monitoring sites, Phil Martien and his staff who provided inventory estimates of CO and CH_4 emissions, David Holstius for graphics help, and Saffet Tanrikulu for useful comments that improved the manuscript. We also gratefully acknowledge Arlyn Andrews, and Edward Dlugokencky and the Carbon Cycle Group at NOAA for flask sampling at Mount Sutro and the larger NOAA network sampling and analysis of CH_4 and CO. MLF was supported by a grant from the California Energy Commission's Natural Gas Research Program to the Lawrence Berkeley National Laboratory under contract DE-AC02-05CH11231.

ACCEPTED MANUSCRIPT

References

40 CFR 53. Code of Federal Regulations, Title 40, Chapter 53, Subchapter C Air Programs, Part 53 Ambient Air Monitoring Reference and Equivalent Methods.

AB-32 (2006). California Global Warming Solutions Act of 2006.

BAAQMD (2014 (1)). *Bay Area Emissions Inventory Summary Report: Criteria Air Pollutants Base Year 2011*. Planning Division, Bay Area Air Quality Management District, San Francisco, CA. Updated May, 2014.

BAAQMD (2014 (2)). *Bay Area Greenhouse Gas Emissions Inventory: 2011*. Planning Division, Bay Area Air Quality Management District, San Francisco, CA.

Brandt, AR, *et al*. (2014). "Methane Leaks from North American Natural Gas Systems." *Science* 14 February 2014: 343.

Cochrane, D, and GH Orcutt (1949). "Application of least squares regression to relationships containing autocorrelated error terms." *J. Amer. Stat. Assoc.* ***44***, 32-61.

Hsu, YK, *et al*. (2010). "Methane inventory verification in southern California." *Atmospheric Environment*, 44, 1-7.

IPCC (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Jeong, S, YK Hsu, AE Andrews, L Bianco, P Vaca, JM Wilczak, and ML Fischer (2013). "A multitower measurement network estimate of California's methane emissions." *J. Geophys. Res. Atmos*., 118(19):11339–11351. DOI:10.1002/jgrd.50854.

McDonald, B, and R Harley. *EMFAC 2011 Model Evaluation – Draft Final Report*. Prepared for California Air Resources Board, July 2013.

Miller, SM, *et al.* (2013). "Anthropogenic emissions of methane in the United States." *Proceedings of the National Academy of Sciences*, 110(50):20018–20022.

NOAA (2014). Global Monitoring System Observatory Operations, Earth System Research Laboratory, National Oceanic and Atmospheric Administration. http://www.esrl.noaa.gov/gmd/obop/

ACCEPTED MANUSCRIPT

Peischl, J, *et al. (*2013*),* "Quantifying sources of methane using light alkanes in the Los Angeles basin, California*." J. Geophys. Res. Atmos.*, 118, 4974–4990. doi: 10.1002/jgrd.50413.

Singh, HB, *et al.* (2010), Pollution influences on atmospheric composition and chemistry at high northern latitudes: Boreal and California forest fire emissions. *Atmospheric Environment*. 44, 4553-4564.

US-EPA (2014), *Improvements Needed in EPA Efforts to Address Methane Emissions From Natural Gas Distribution Pipelines*. Report No. 14-P-0324.

Wennberg, PO*, et al.* (2012), "On the Sources of Methane to the Los Angeles Atmosphere." *Environ. Sci. Technol.*, 2012, 46 (17), pp 9282–9289 DOI: 10.1021/es301138y.

WRI (2014) "Climate Analysis Indicators Tool (CAIT) Version 2.0. (Washington, DC: World Resources Institute, 2014)." World Resources Institute. Retrieved 2014-06-27. Accessed 2014-09-25.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Supporting Materials

S1. Estimation of Bay Area background methane concentrations

Local measurements appropriate for estimating background methane have been available from Sutro Tower 232 m agl in San Francisco. These are grab samples that have been collected once or twice daily since 2007. Background measurements have also been made at Trinidad Head, a site on the California coast approximately 400 km north of the Bay Area. These have been collected hourly since mid-1995. Additionally, methane samples were collected on a weekly basis on Mauna Loa in the range of 1900-2100 hours UTC since mid-1983.

We also use wind data from Fort Funston, a meteorological site within half a kilometer of the Pacific Ocean on the west side of San Francisco.

S1.1 Approach and methods

The goal of this analysis is to provide a good estimate of daily oceanic background methane concentrations adjacent to the SF Bay Area from 1990 through 2010. We focus on the Trinidad Head measurements because they are both extensive and collected relatively near to the Bay Area. We first compare Trinidad Head and Sutro Tower methane concentrations. We then consider the seasonal variations and trends at Trinidad Head, establishing a regression relation as a function of year and season, the latter modeled with sine/cosine terms in Julian day. Finally, we estimate the relation between annual mean methane at Trinidad Head and Mauna Loa to provide estimates of background methane prior to 1995.

ACCEPTED MANUSCRIPT

S1.2 Comparison of Trinidad Head and Sutro Tower methane

Figure S1 shows methane measured at Sutro Tower and Trinidad Head matched by hour and day. The points are divided according to whether the winds had had a westerly component. Specifically, the red squares are days/hours for which the average u-component of the Fort Funston wind over the previous 5 hours was greater than 2 m/s. Note that with the exception of one outlier, the observations collected when the winds were westerly cluster around the line y = x.

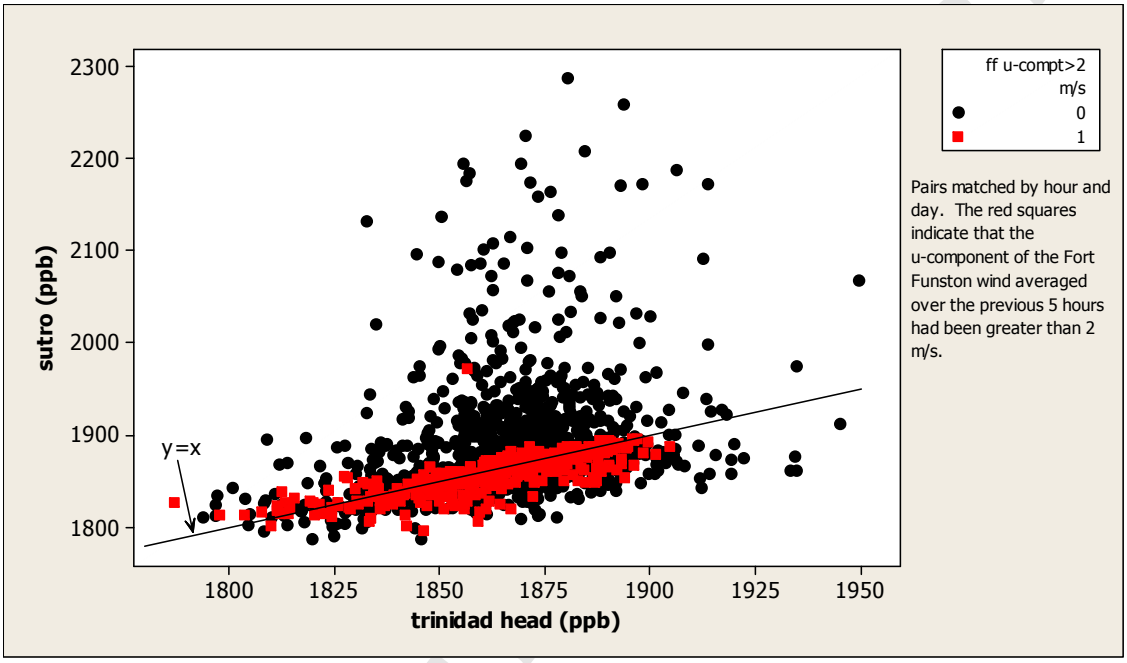


Figure S1. Sutro Tower vs. Trinidad Head CH_4.

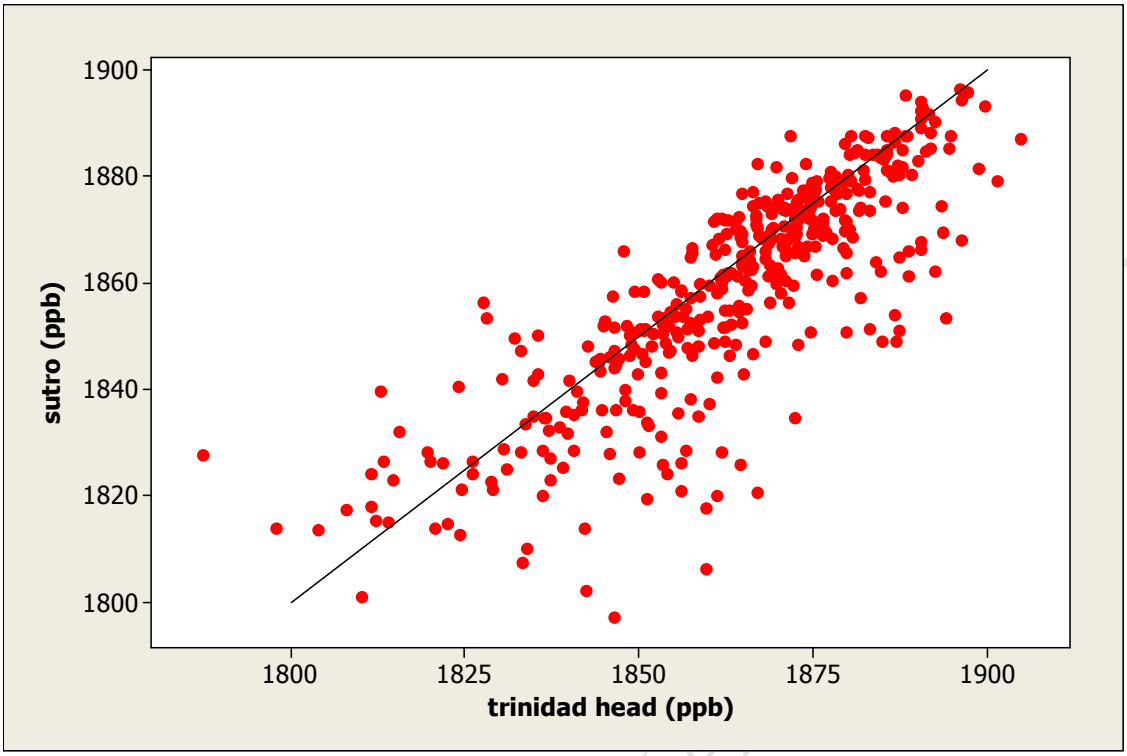


Figure S2. Sutro vs. Trinidad CH4 for hours when previous 5-hour average winds at Fort Funston had a westerly component > 2 m/s.

Figure 2 shows the subset of observations with westerly winds and the outlier removed. It shows a relatively even spread around the y=x line, with Trinidad Head perhaps predominating somewhat. A Wilcoxon signed rank test was applied to the pairwise differences between Sutro Tower and Trinidad Head methane. Trinidad Head does indeed predominate, by a small amount. A 95% Wilcoxon confidence interval was -0.45 to -0.25 for the median Sutro-Trinidad difference.

Given the small difference, and factoring in the uncertainty in comparing the surface-level ocean air experienced by District monitoring sites with the air sampled on Sutro Tower that is 232 AGL with a base that is 260 m ASL, we conclude that Trinidad Head measurements provide a reasonable basis for estimating the oceanic background methane that affects the San Francisco Bay Area.

In the remainder of the analysis, we consider daily average Trinidad Head methane measurements as the unit of analysis.

S1.3 Temporal modeling of Trinidad Head methane

Figure S3 shows the time series of daily mean Trinidad Head methane. A seasonal pattern is clearly present with a dip in the middle of each year. There also appears to be an uptrend, though not a totally linear one.

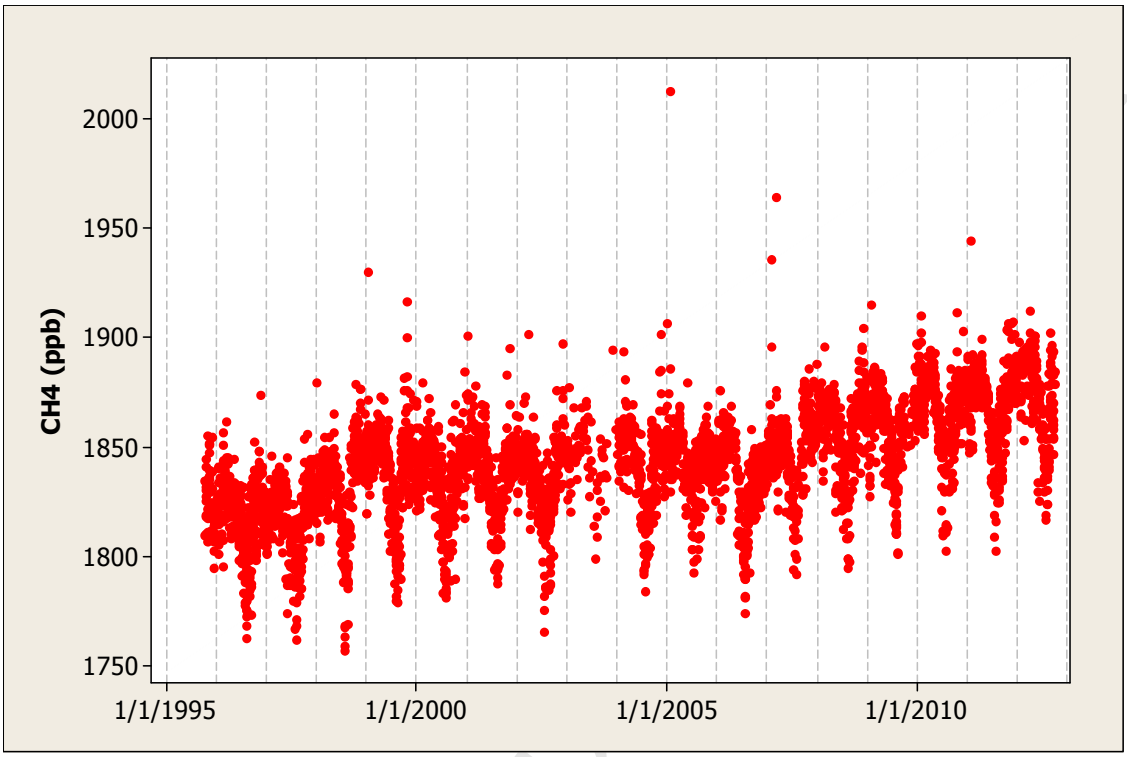


Figure S3. Trinidad Head methane – daily means.

We modeled the time series with sine and cosine terms representing season along with annual means. Specifically we fit the model:

$$y_{it} = \mu_i + \sum_{k=1}^{6} \alpha_k \sin(\frac{2\pi kt}{365.25}) + \beta_k \cos(\frac{2\pi kt}{365.25})$$

for i = 1995 to 2012, and t = 1 to length of year i. The model terms have the advantage of being mutually orthogonal. Six sine and cosine terms were found statistically significant; further terms were not significant.

Fitting this model with least squares resulted in a regression s = 12.6 ppb, and an adjusted R^2 of 72%.[1] The residuals appeared homoscedastic, but there was a substantial autocorrelation, 0.54, so that the significance of individual terms will be overestimated somewhat using the standard methodology.

[1] The R^2 value compares the regression SSE with the sum of squared deviations from the grand mean (SST).

Figure S4 shows the fits in four arbitrarily selected years. The seasonal patterns appear relatively consistent from year to year, and match the seasonal curve reasonably well.

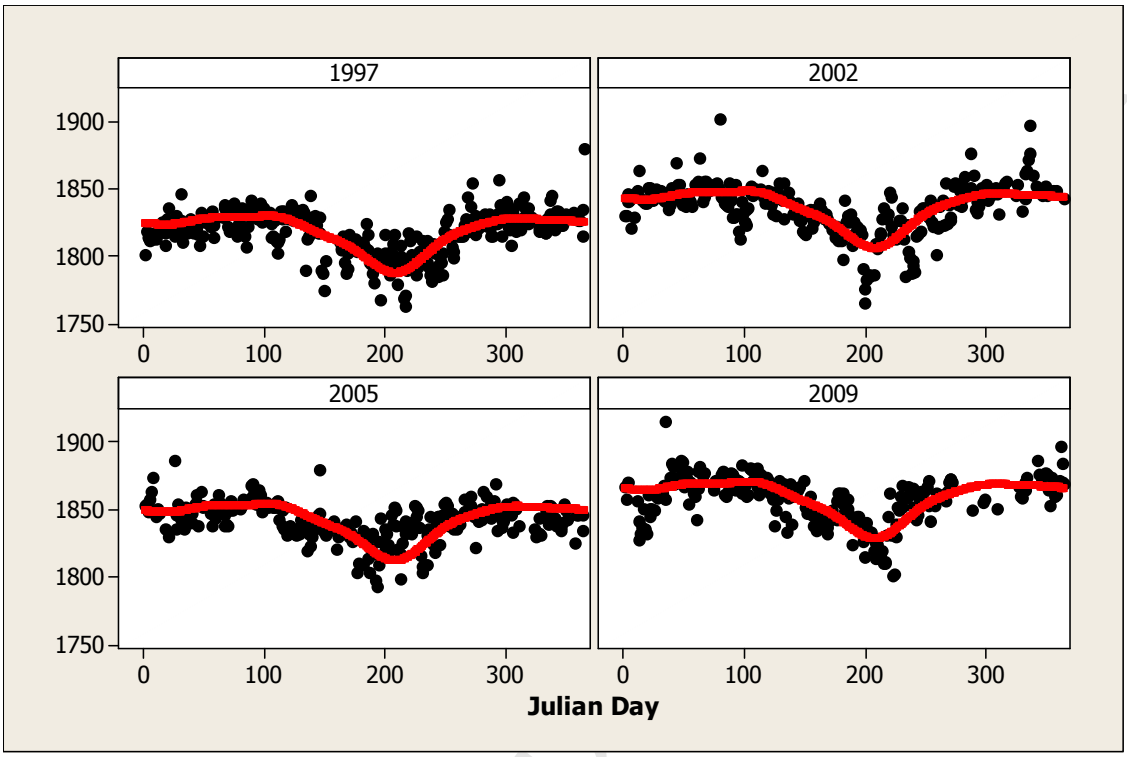


Figure S4. Trinidad Head methane observations and fitted curves (ppb) for selected years.

S1.4 Comparison with Mauna Loa methane

In order to estimate background we compare the Trinidad Head annual means estimated with the regressions in relation to methane measured at Mauna Loa. Figure S5 shows that the two sites share very similar trends. The difference in means falls between 51 ppb and 56 ppb with two exceptions.

ACCEPTED

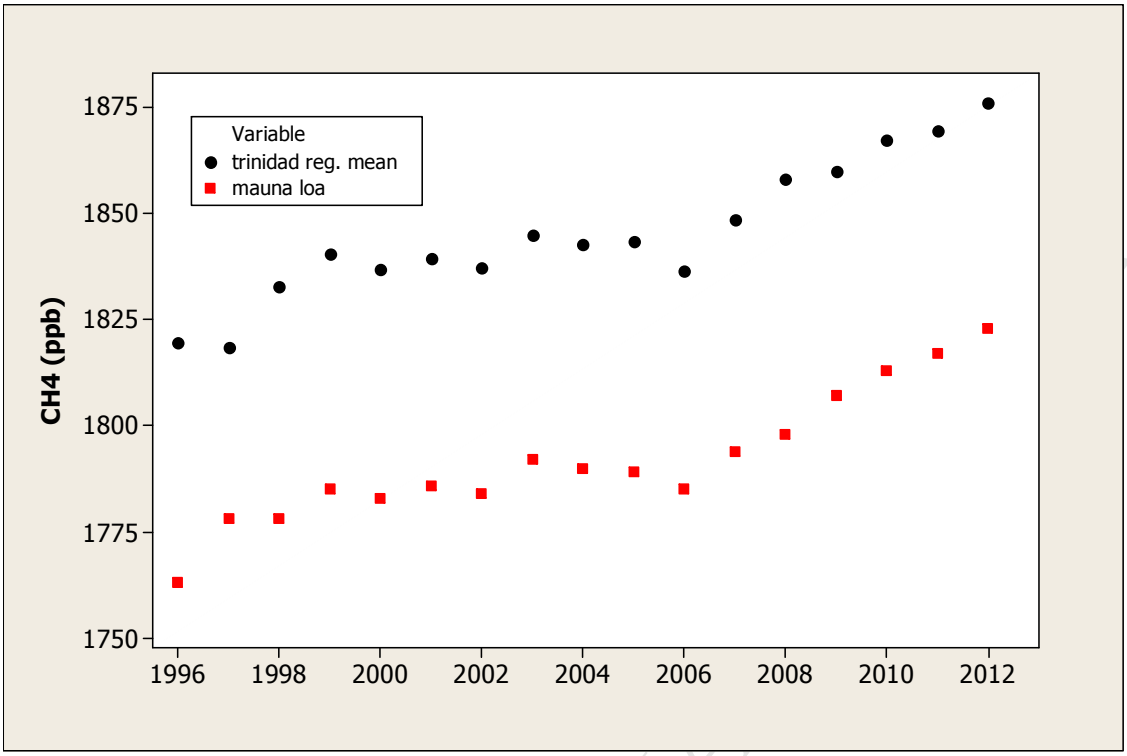


Figure S5. Mauna Loa annual mean and Trinidad Head modeled mean.

The median difference was 53 ppb. Thus, we used Mauna Loa mean methane + 53 to estimate Trinidad mean values for 1990-1995.

S2. Estimation of background carbon monoxide concentrations

S2.1 Data

The Sutro Tower, Trinidad Head and Mauna Loa sites all collected carbon monoxide. However, whereas at Sutro Tower and Mauna Loa, CO was collected simultaneously with methane on most days, Trinidad Head CO measurements were limited to roughly 50 a year, and date back only to 2002.

The hours of collection varied, raising the question of how much this factor mattered. An ANOVA on hour and month for Trinidad Head found hour statistically insignificant with 520 observations (adjusted $R^2 = 0$), whereas month was highly significant with an adjusted R^2 of 44.5%. For Sutro Tower, an ANOVA yielded a statistically significant result, although the adjusted R^2 was only 2.7% whereas it was 55.6% for month. Thus, it was decided to ignore hour as an independent factor.

Figure S6a shows Sutro and Trinidad seasonal patterns with 2007-2012 data pooled. The two sets of data show a similar seasonal pattern. Figure S6b shows that the two sites exhibit a pattern of increasing mean CO until about julian hour 2000 (late March), then decreasing until about julian hour 5000 (late July), then increasing to the end of the year, with a blip around julian day 6000 (early September).

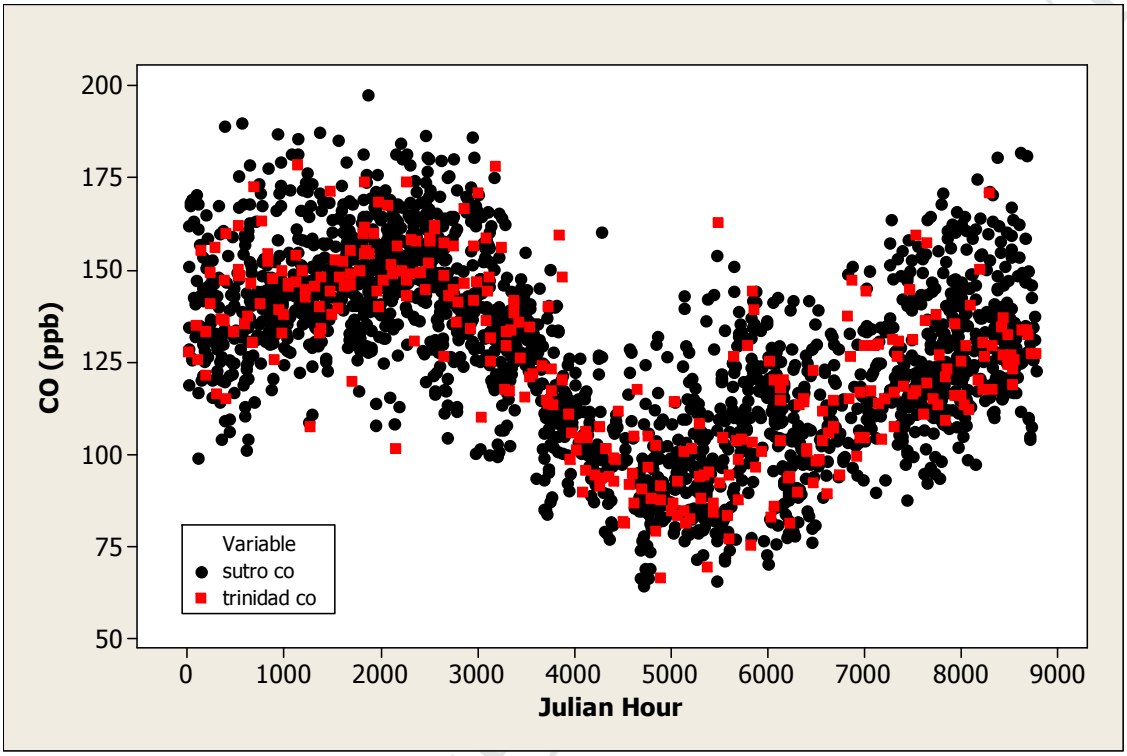


Figure S6a. Seasonality of Sutro Tower and Trinidad Head CO.

ACCEPTED MANUSCRIPT

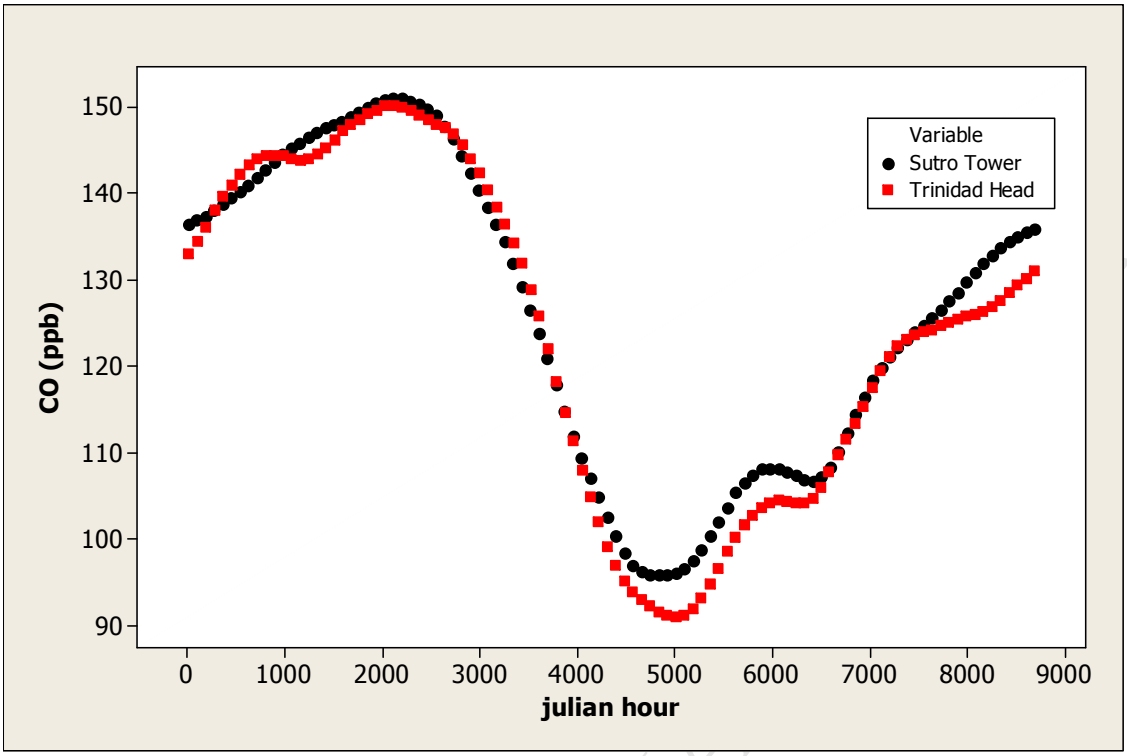


Figure S6b. Fitted seasonal curves for the CO season.

S2.2 Annual trend

Since neither Sutro Tower nor Trinidad Head has CO data before 2002, Mauna Loa was used to adjust earlier years. Figure S7 shows that the seasonal pattern for Mauna Loa was similar, but not identical to Trinidad Head, and that the mean value is substantially less.

ACCEPTED MANUSCRIPT

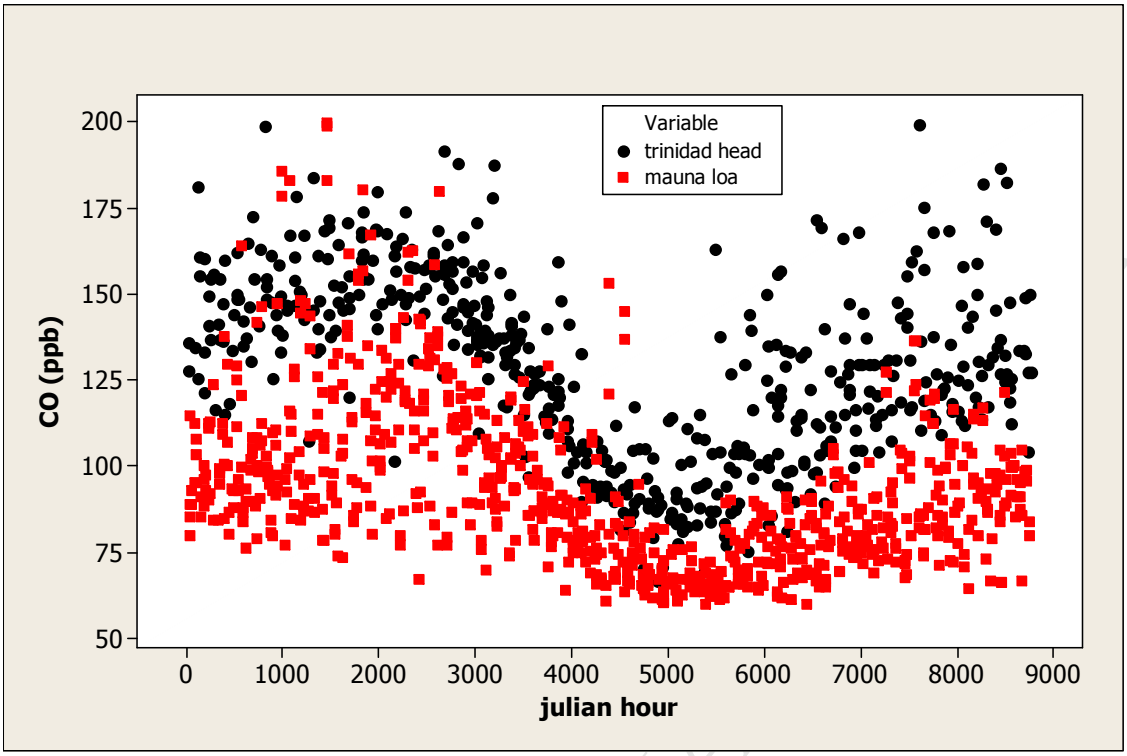


Figure 7. Seasonal CO – Trinidad Head and Mauna Loa 2002-2012

To compare the mean values and how these have changed over time, seasonal curves were fitted for TH and ML and shown in Figure S6b, using all the available data from 2002-2012. In order to account for partial sampling during some years, each individual measurement was adjusted by subtracting off the smooth for that hour and adding back in the annual mean of the smooth. Then annual averages were computed.

Figure 8 shows the results. There is a statistically significant downtrend at both sites. Although the Trinidad Head trend appears steeper, the trend in the differences in annual means (TR – ML) is not statistically significant. The mean difference in means is 40 ppb.

Thus, our estimate for background CO for a given julian hour, j, in a given year y is smooth(j) – smean + a(y), where smooth(j) is the value of the Trinidad Head curve in Figure 6b, smean is the mean over j of smooth(j), and a(y) is the adjusted annual Trinidad Head mean for Trinidad Head for y = 2002 through 2012, and the adjusted Mauna Loa CO + 40 ppb, for y = 1990 through 2001.

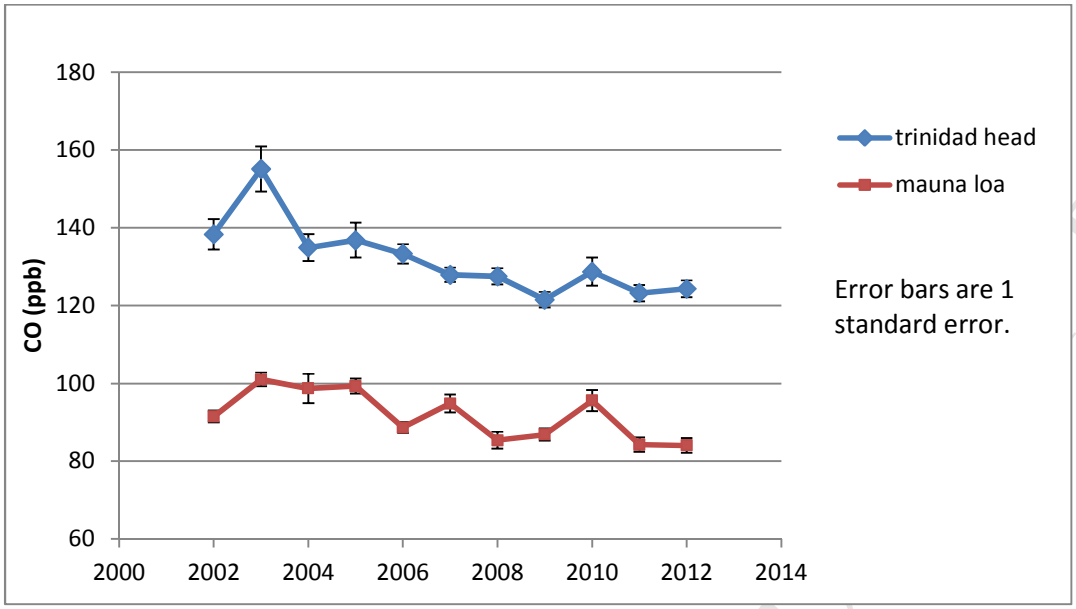


Figure S8. Annual means adjusted for season.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

S3. Analysis of variance of methane emissions estimate using individual observations as the units of analysis

Rather than using the site-year methane emissions estimates, $\widehat{M}_{ij}$, as the unit of analysis, we can consider these as statistics from the underlying regressions. The slopes of these regressions have corresponding uncertainties. We can estimate uncertainty in the $\widehat{M}_{ij}$ from the regression slope uncertainties only as, $C_j\hat{\tau}_{ij}$ where $\hat{\tau}_{ij}$ is the standard error of the slope. Let's assume that the regression standard errors are all equal independent of i and j, that is, $\tau_{ij} = k_{ij}\sigma$, where $k_{ij} = \sqrt{1/\sum_k (x_{ijk} - \bar{x}_{ij})^2}$. Define weights $w_{ij} = 1/(C_j\hat{\tau}_{ij})^2$, and the weighted mean of the $\widehat{M}_{ij}$, $\widehat{M} = \sum_{ij} w_{ij}\widehat{M}_{ij} / \sum_{ij} w_{ij}$, where the sums are taken over all n=56 i,j pairs with slopes in Table 1. Define the "total sum of squares" as SST = $\sum_{ij} w_{ij}(\widehat{M}_{ij} - \widehat{M})^2 / \sum_{ij} w_{ij}$, and the mean sum of squares total ≡ MST = SST/(n-1). If the expected values of the $\widehat{M}_{ij}$ were all equal, then SST would have an approximately Chi-square distribution with n-1 degrees of freedom, so that E(MST) = 1. The computed value was MST = 56.5, so that approximately (56.5 – 1)/56.5 = 0.98, or 98% of the variation, derives from site-period differences in the actual M_{ij}. We can roughly decompose SST into effects for site, period and site-period interactions by performing a weighted regression with indicator variables for site and period. Depending on the order of entry, we get a range of values shown in Table S2.

Table S2. Rough breakdown into components of variance

	Site	Period	Site-Period Interaction	Total
% of total variation	≤54%	≤13%	≥34%	98%

The table shows that as much as 2/3 of the variation in the $\widehat{M}_{ij}$ can be explained by site and period, with roughly half of the variation explainable by site to site differences. There may be some systematic difference by period, but the main differences between periods are site-period interactions. This analysis shows that from period to period, the site-specific CH_4/CO relationship shifts,

S4. Comparison of slopes of drift-corrected CO

As noted above, we examine the effect of subtracting drifts in measured CO using periodic zero-check measurements. Figure 4 shows the relationship between background-adjusted methane and zero-adjusted, and background-subtracted CO. Table S3 provides a comparison of the CH4/CO regressions with and without adjustment for zero values. For all sites without a trace-level monitor, the fit improved or stayed the same. For six of the seven sites, the slope increased. We

note that because the slopes and their standard errors are derived from the Cochrane-Orcutt method, they differ slightly from the slopes shown in Figure S9. Because none of the changes were large enough to change the mean CH_4 emission estimates for the 2009-2012 period substantially, and were unavailable for the earlier periods, we used the results uncorrected for drift in our analysis.

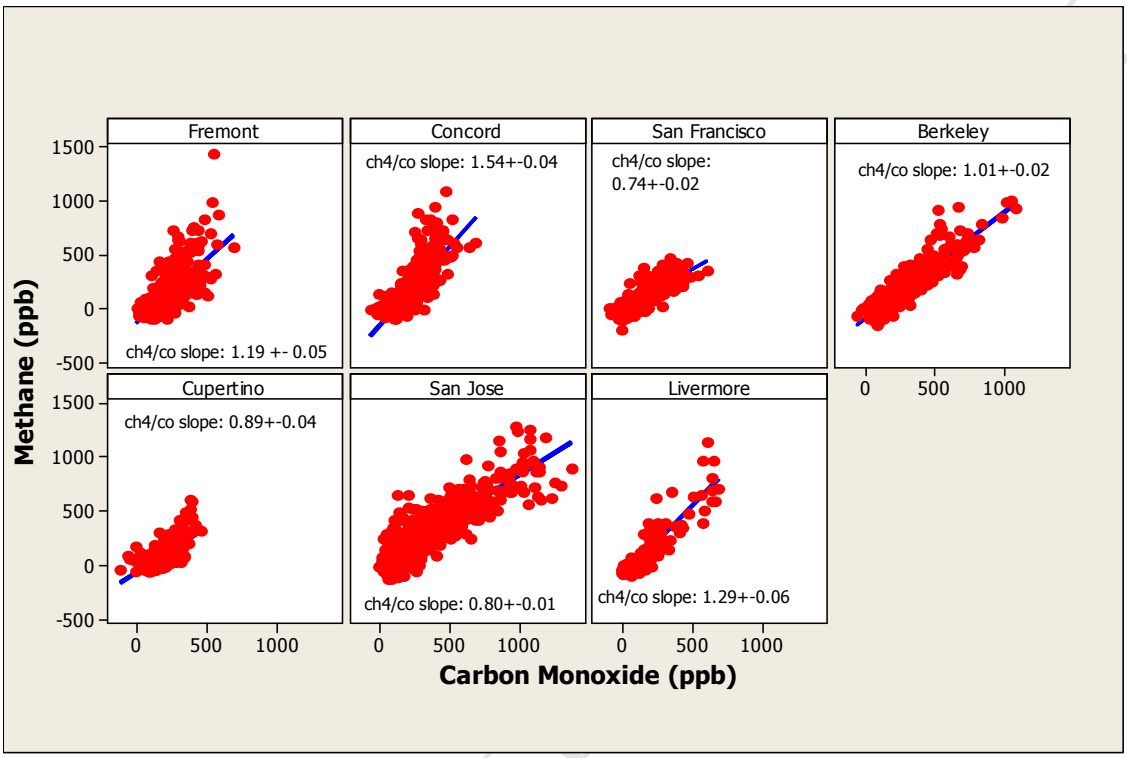


Figure S4. Scatter plots of CH_4 vs. drift corrected CO for the 2009-2012 period. Methane and CO background adjusted. CO also zero-adjusted.

Table S3. Comparison of regressions of CH4 on adjusted and unadjusted CO.

	Adjusted* Regressions			Unadjusted* Regressions		
	Slope	Slope sd	adj R^2	Slope	Slope sd	adj R^2
Fremont	1.194	0.046	55.1	1.192	0.046	54.9
San Jose	0.807	0.014	76.2	0.804	0.014	76.3
Concord	1.538	0.036	68.2	1.210	0.035	57.6
Livermore	1.293	0.063	77.9	1.218	0.059	77.9
San Francisco	0.744	0.021	75.9	0.634	0.021	69.8
Berkeley	1.006	0.017	83.2	1.069	0.019	82.2
Cupertino	0.888	0.036	49.6	0.543	0.033	30.4

* Adjusted or unadjusted for zero values. These regressions didn't use the Cochran-Orcutt method.

ACCEPTED MANUSCRIPT

S5. Computing standard errors from second differences

This is a technique for estimating standard errors in trend data that eliminates the effect of any linear trend. Consider the sequence:

$$X_t = a + bt + e_t \qquad \text{(S5.1)}$$

where a and be are constants, t = time (e.g. year), t=1,2…,n, and the sequence e_1, e_2, …e_n, is a sequence of independent random variables with mean 0 and standard deviation σ. Let

$$D_t = X_{t+2} + X_t - 2X_{t+1}$$

(Note that D_t is the difference of 1st differences:$D_t = (X_{t+2} - X_{t+1}) - (X_{t+1} - X_t)$.

Substituting the right-hand side of (S5.1):

$$\begin{aligned} D_t &= a + b(t+2) + e_{t+2} + a + bt + e_t - 2a - 2b(t+1) - 2e_{t+1} \\ &= e_{t+2} + e_t - 2e_{t+1}. \end{aligned}$$

We have mean of $D_t = 0$, and Variance of Dt = $\mathrm{Var}(e_{t+2} + e_t - 2e_{t+1}) = \sigma^2 + \sigma^2 + 4\sigma^2 = 6\sigma^2$. Then

$$\hat{\sigma}^2 = \frac{1}{6(n-2)} \sum_1^{n-2} D_t^2$$

is an unbiased estimator of σ^2. To the extent that the trend is non-linear, $E(D_t^2)$ will exceed σ^2.

ACCEPTED MANUSCRIPT

S5. Auxiliary Tables

Auxiliary Table 1A. # of methane observations by year and site

Site:	np	fr	sj	sr	pt	va	ri	cc	rc	st	li	sf	bk	cu	trin	ma loa
1980	242	238	244	239	212	220	246	218	239	0	0	0	0	0	0	0
1981	354	360	365	359	345	333	324	337	353	207	0	0	0	0	0	0
1982	358	351	359	352	354	348	350	348	360	351	338	0	0	0	0	0
1983	350	352	358	361	355	348	360	363	358	357	324	0	0	0	0	33
1984	363	341	363	354	354	360	355	350	347	357	340	0	0	0	0	49
1985	359	358	361	358	355	361	361	363	349	353	350	0	0	0	0	47
1986	356	354	357	358	352	349	360	336	354	351	336	24	0	0	0	49
1987	343	357	358	352	362	341	365	355	353	356	343	352	0	0	0	51
1988	356	325	366	366	351	354	366	359	348	345	172	361	0	0	0	48
1989	362	349	356	319	362	355	360	365	365	329	299	292	0	0	0	49
1990	354	340	351	358	349	358	352	361	363	362	344	211	0	0	0	46
1991	359	361	345	360	360	355	353	355	358	361	353	347	0	0	0	52
1992	347	363	360	340	302	361	329	357	363	362	359	345	0	0	0	49
1993	357	336	357	338	355	355	344	362	365	307	360	362	0	0	0	51
1994	361	313	356	341	357	348	365	364	352	352	356	334	0	0	0	52
1995	362	357	347	197	267	250	264	351	353	288	363	303	0	0	81	50
1996	319	354	356	0	0	0	0	357	357	327	365	328	0	0	340	48
1997	349	355	358	0	0	0	0	360	356	336	361	358	0	0	331	50
1998	350	344	337	0	0	0	0	365	363	337	360	349	0	0	332	53
1999	34	362	339	0	0	0	0	354	359	33	357	356	0	0	348	51
2000	0	359	345	0	0	0	0	349	355	0	337	352	0	0	330	47
2001	0	312	331	0	0	0	0	329	323	0	353	356	0	0	316	51
2002	0	263	61	0	0	0	0	268	0	0	266	264	0	0	281	50
2003	0	344	326	0	0	0	0	343	0	0	358	345	0	0	69	56
2004	0	321	356	0	0	0	0	338	0	0	353	361	0	0	256	52
2005	0	360	339	0	0	0	0	345	0	0	360	354	0	0	274	52
2006	0	345	281	0	0	0	0	349	0	0	353	340	0	0	279	52
2007	0	342	354	0	0	0	0	270	0	0	347	352	19	0	280	52
2008	0	359	359	0	0	0	0	361	0	0	358	361	271	0	317	52
2009	0	355	335	0	0	0	0	353	0	0	357	352	353	0	255	53
2010	0	206	346	0	0	0	0	356	0	0	348	238	342	0	323	51
2011	0	0	353	0	0	0	0	149	0	0	363	0	0	270	275	52
2012	0	0	2	0	0	0	0	0	0	0	353	0	0	366	228	52
All	6635	10436	10781	5352	5392	5396	5454	10790	7693	6071	10586	7997	985	636	4915	1500

ACCEPTED MANUSCRIPT

Auxiliary Table 1B. # of carbon monoxide observations by year and site

	np_co N	fr_co N	sj_co N	sr_co N	pt_co N	va_co N	ri_co N	cc_co N	rc_co N	st_co N	li_co N	sf_co N	bk_co N	cu_co N	tr_co N	ml_co N
1980	362	359	366	363	355	366	366	356	0	363	344	364	0	0	0	0
1981	364	363	363	365	365	365	344	365	365	356	326	362	0	0	0	0
1982	357	365	365	357	364	363	365	365	365	363	363	362	0	0	0	0
1983	360	361	365	364	360	358	365	365	363	364	350	364	0	0	0	0
1984	363	366	365	366	365	366	364	366	364	360	358	366	0	0	0	0
1985	364	362	362	359	362	365	364	364	365	358	356	362	0	0	0	0
1986	365	362	361	356	364	364	359	360	363	365	351	361	0	0	0	0
1987	364	362	353	362	362	357	362	363	358	360	350	361	0	0	0	0
1988	362	362	366	364	361	363	365	366	366	358	357	363	0	0	0	0
1989	361	364	365	365	360	365	365	365	364	335	360	362	0	0	0	23
1990	355	362	365	365	362	365	361	365	358	360	363	363	0	0	0	47
1991	361	365	325	365	363	365	364	362	364	361	363	365	0	0	0	51
1992	360	366	364	348	358	366	359	366	363	363	365	366	0	0	0	48
1993	361	364	353	362	358	365	365	362	365	364	365	365	0	0	0	51
1994	358	362	361	364	362	365	359	365	362	365	360	357	0	0	0	52
1995	360	363	356	365	363	365	365	363	365	365	365	365	0	0	0	50
1996	363	366	362	361	366	366	366	366	364	351	365	365	0	0	0	49
1997	363	365	365	363	365	358	362	365	365	365	361	365	0	0	0	48
1998	364	362	358	365	365	365	365	365	359	350	362	364	0	0	0	53
1999	362	365	362	365	365	364	365	365	365	356	332	365	0	0	0	51
2000	365	366	366	366	361	366	366	366	361	366	361	362	0	0	0	48
2001	358	365	56	359	364	357	359	362	361	359	363	365	0	0	0	51
2002	362	347	61	364	365	365	336	365	362	364	363	358	0	0	27	51
2003	364	365	365	365	351	365	363	362	362	361	364	365	0	0	14	56
2004	359	364	365	358	366	365	0	348	363	366	358	365	0	0	63	53
2005	364	362	365	365	364	345	0	364	365	359	362	365	0	0	43	52
2006	365	365	340	365	365	365	0	365	365	365	362	364	0	0	50	52
2007	365	362	365	365	365	365	0	365	364	365	363	365	23	0	52	52
2008	362	362	359	357	362	358	0	363	363	362	365	363	360	0	52	52
2009	354	358	354	360	0	361	0	360	362	360	122	360	363	0	50	53
2010	359	298	356	361	0	349	0	361	355	360	0	362	356	89	52	52
2011	360	0	337	363	0	360	0	360	349	360	0	362	0	327	53	52
2012	361	0	352	364	0	358	0	361	361	360	0	356	0	366	51	52

ACCEPTED MANUSCRIPT

Highlights

- Top-down methane emissions estimate used to evaluate a bottom-up emissions inventory
- Estimates combine a two decades of CH4:CO enhancement ratios at 14 sites with CO emission inventory
- Resulting CH4 emissions 1.5 - 2 times greater than bottom-up inventory

ACCEPTED MANUSCRIPT