Methane emissions inventory verification in southern California

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A B S T R A C T

Methane (CH\textsubscript{4}) and carbon monoxide (CO) mixing ratios were measured at an air quality monitoring station near the Mt. Wilson (MW) Observatory in southern California starting in the spring of 2007. Diurnal variation and mixing ratio correlation (R\textsuperscript{2} = 0.81) were observed. The correlation results observed agree with previous aircraft measurements collected over the greater Los Angeles (LA) metropolitan area. The consistent agreement between CH\textsubscript{4} and CO indicates these gases are well-mixed before reaching the sampling site and the emission source contributions of both compounds are reasonably constant. Since CH\textsubscript{4} and CO are considered non-reactive on the time scale of dispersion within the LA urban area and their emission sources are likely to be similarly distributed (e.g., associated with human activities) they are subject to similar scales of atmospheric transport and dilution. This behavior allows the relationship of CH\textsubscript{4} and CO to be applied for estimation of CH\textsubscript{4} emissions using well-documented CO emissions. Applying this relationship a “top–down” CH\textsubscript{4} inventory was calculated for LA County based on the measurements observed at MW and compared with the California Air Resources Board (CARB) “bottom–up” CH\textsubscript{4} emissions inventory based on the Intergovernmental Panel on Climate Change recommended methodologies. The “top–down” CH\textsubscript{4} emissions inventory is approximately one-third greater than CARB’s “bottom–up” inventory for LA County. Considering the uncertainties in both methodologies, the different CH\textsubscript{4} emissions inventory approaches are in good agreement, although some under and/or uninventoried CH\textsubscript{4} sources may exist.

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1. Introduction

Methane (CH\textsubscript{4}) is emitted both naturally and through human activities. It is the greenhouse gas (GHG) second only to carbon dioxide in enhanced climate forcing from the pre-industrial era (1750) to the present (Simpson et al., 2006; Hofmann et al., 2006). The global mixing ratios of CH\textsubscript{4} in the atmosphere have more than doubled since the pre-industrial period, rising from around 750 parts per billion (ppb) in 1800 (Simpson et al., 2002; Dlugokencky et al., 2003) to the current level of around 1770 ppb (NOAA, 2008). The rate of increase slowed to 5–10 ppb year\textsuperscript{-1} by the late 1980s and continued to decline into the 1990s, though with considerable annual growth variation (Dlugokencky et al., 1994, 1998; Simpson et al., 2002). These unpredicted growth rate fluctuations have been linked primarily to non-cyclical events such as the eruption of Mt. Pinatubo in 1991, the Indonesian and boreal wildfires of 1997 and 1998, respectively, and anomalous wetland emissions in 1998 (Dlugokencky et al., 1996; Duncan et al., 2003; Prinn et al., 2005).

The California Global Warming Solutions Act of 2006 (Assembly Bill 32, AB 32, Núñez) requires the California Air Resources Board (CARB) to report and verify the statewide GHG emissions inventory (COLC, 2006). To support the AB 32 program, CARB developed a statewide GHG emissions inventory that provides estimates of the amount of GHG released to the atmosphere by human activities annually within California (CARB, 2008a). The CARB inventory was developed using the Intergovernmental Panel on Climate Change (IPCC) recommended methodologies and covers the years 1990–2004. These GHG emissions estimates rely primarily on state, regional or national data sources, rather than individual facility-specific emissions. CARB’s GHG inventory uses a “bottom–up” approach and is calculated based on emission factors (e.g., grams of CH\textsubscript{4} per gallon of gasoline combustion) multiplied by activity data (e.g., gallons of gasoline combusted). This inventory provided the basis for developing the 1990 statewide emissions level and 2020 emissions limit required under AB 32. CARB’s emission reduction program relies on accurate knowledge of the emissions to ensure that reductions are actually achieved.

In California, the main anthropogenic emission sources of CH\textsubscript{4} are ruminant livestock, landfills, wastewater treatment, losses
occurring during oil and gas extraction and transmission, combustion of fossil fuels and biomass, and rice cultivation (CARB, 2008a). Natural sources of CH₄ are dominated by wetlands. The primary sink for CH₄ is its destruction in the atmosphere by hydroxyl radicals (Prinn et al., 1995, 2001). Some CH₄ is also oxidized by microorganisms (called methanotrophs), which use CH₄ as a source of carbon and energy. Tropospheric CH₄ is eventually oxidized to carbon dioxide; its atmospheric lifetime is estimated to be 8–12 years (NOAA, 2000; Cunnold et al., 2002; IPCC, 2007).

The objectives of this study were to conduct a pilot program to measure atmospheric CH₄ mixing ratios, to estimate the CH₄ emissions inventory for Los Angeles (LA) County California using the resulting field measurements, and to assess CARB’s official CH₄ emissions inventory. This paper presents CH₄ and carbon monoxide (CO) mixing ratios measured at the Mt. Wilson (MW) monitoring station. A “top–down” emission inventory estimation methodology based on the correlation between CH₄ and CO observed at MW is described, and the estimated CH₄ inventory with level of uncertainty is presented. Finally, the comparison between the “top–down” inventory estimate and CARB’s “bottom–up” official CH₄ inventory for LA County is presented. Sources of uncertainty in both emission estimates are also discussed in this paper.

2. Experimental methods

An air quality monitoring station adjacent to the MW Observatory (34°13′21″N, 118°3′42″W, elevation 1735 m) was installed in April 2007 to study GHG emissions in the LA urban area. Mt. Wilson is one of the prominent peaks in the San Gabriel Mountains, in the Angeles National Forest, and located in northern LA County. The monitoring station is south-facing overlooking the LA metropolitan area from the top of the San Gabriel Fault scarp, making it an ideal site to collect comparative air samples from both the LA urban boundary layer and overlying free troposphere. The sampled air at the station is influenced by strong and rapid upslope flow of well-mixed air from the urban lowland during daylight hours (Fig. 1), with reversed subsidence flow replacing the urban air with air from the lower free troposphere (LFT) at night. This flow pattern is typical of the southern California climate and very persistent in all seasons; the upslope flow is driven by the regular sea breeze on the coastal plain pushing urban air toward the base of the scarp, lofting it to the monitoring site. The LFT air at MW generally arrives from the northwest, flowing off the eastern Pacific Ocean. Despite the site’s proximity to the 15 million inhabitants of southern California, nighttime air at MW is generally as clean or cleaner than air measured at the background station at Trinidad Head (NOAA, 2008) on the northern California coast (VanCuren, 2008). Note that LA County splits into the Mojave Desert Air Basin to the northeast and South Coast Air Basin (SoCAB) to the south (Fig. 2). As described above, the MW monitoring station samples the SoCAB portion of LA County urban area, due to its predominant south winds.

This study included continuous real-time monitoring of CH₄ and metrological conditions and intensive hourly canister sampling for comprehensive organic gases and CO in discrete seasonal campaigns. The four intensive sampling periods were April 28th–May 6th, 2007; September 8th–16th, 2007; November 10th–18th, 2007; and February 9th–17th, 2008. Methane was measured using two techniques: 1) cavity enhanced laser absorption spectroscopy using a tunable diode laser (TDL) analyzer (Los Gatos Research Model 908-0001) with 1 s intervals, 2) analysis of hourly-integrated canister samples with an Agilent 5890 gas chromatograph (GC) using flame ionization detection (FID). The same canister samples were also analyzed for CO using an Agilent 6890 GC-FID through packed column separation followed by catalytic conversion to CH₄. Meteorological conditions were monitored for wind speed (Met One 010C), wind direction (Met One 020C), temperature (Met One 060-1), and relative humidity (Vaisala HMP-45D). The TDL CH₄ analyzer was calibrated daily using zero air and CH₄ standard gas (3.950 parts per million, ppm) on site. Canister samples were quantified with GCs calibrated immediately before analysis. Comparison between the two different CH₄ measurement approaches reveals good agreement (linear regression slope = 1.00, $R^2 = 0.94$). The consistency between the measurements provides confidence in the results and strengthens the validity of their application in emission inventory calculations.

3. Results and discussion

3.1. Atmospheric CH₄ and CO mixing ratios

Nighttime inversion conditions followed by strong daytime mixing frequently occur at MW. These meteorological conditions
lead to characteristic diurnal mixing ratio variations of CH4 and CO emitted in LA County (Fig. 3). The quartile plots present frequency distributions of mixing ratios by hour of the day of the four intensive sampling periods, excluding mixing ratios measured on February 14, 2008 when winds were from the north. Exclusion of this date will be explained in the next section. Elevated mixing ratios of both compounds are observed during early afternoon hours. These higher mixing ratios are attributable to influence from emission sources in LA County during midday when inversion layer heights are above the MW monitoring site and strong onshore sea breezes are pushing urban air upslope of the scarp. The observed mixing ratios ranged from 1.76 to 2.16 ppm for CH4 and 0.055–0.725 ppm for CO, which are quite similar to the 2002 National Oceanic and Atmospheric Administration (NOAA) airborne measurements over LA (CH4: 1.73–2.06 ppm; CO: 0.084–0.67 ppm, Parrish, 2008). In addition, the lower CH4 and CO levels are slightly (approximately 10 ppb) below those measured via aircraft at 2000 m above sea level near Trinidad Head, California (NOAA, 2008). The results demonstrate that the MW site observes both urban boundary layer and overlying background troposphere air masses.

3.2. Relationship between CH4 and CO mixing ratios

The relationship between CH4 and CO mixing ratios measured between 11 am and 6 pm at the MW monitoring station during the four discrete seasonal campaigns is presented in Fig. 4 and Table 2. Good linear correlation was observed ($R^2 = 0.81$), indicating that both gases are well-mixed before reaching the MW site and source contributions of both compounds are reasonably consistent. Even though the correlation of CH4 and CO mixing ratios using all 24-h data gives a similar slope and correlation coefficient, we chose to use the data collected between 11 am and 6 pm for the correlation analysis as they represent both CH4 and CO emitted from LA County and observed at the MW site (see Fig. 3). This is supported by a simulated surface wind field in the SoCAB (Fig. 1) where typical onshore and inland winds move air parcels from the western coast to the north and east of the basin from the mid-morning to late-afternoon (Stolzenbach et al., 2001). During transit from the coast, air parcels receive pollutant emissions from the sources encountered on the particular trajectory of transit. Variations of wind speed and direction about the average conditions, and intermixing of air parcels within the basin ensures that the air sampled at MW represents a wide spectrum of emission sources within the basin.

Fig. 4 includes all measurements from all four seasonal campaigns, with the exception of the data collected on February 14, 2008 when the winds were from the north. Methane and CO mixing ratios measured on this day were not impacted by emissions from the LA urban area and do not show elevated mixing ratios during early afternoon hours (Fig. 5).
As a quality assurance measure, the CH₄ and CO correlation result was compared with the previous NOAA aircraft measurements collected within the mixing layer over the LA urban area during a single flight on May 13th, 2002. These aircraft measurements reveal a similar linear regression slope (0.46, Parrish, 2008) and correlation ($R^2 = 0.86$) to those collected at the MW site. Consistency between these two approaches indicates that the MW site is a representative location to evaluate the CH₄ emission inventory for LA County.

3.3. Estimate of LA County CH₄ emissions based on atmospheric mixing ratios

This section describes a "top–down" approach to calculate the total average CH₄ emission rate for LA County based on the CH₄ and CO relationship observed at MW and the CO emissions inventory. A scaling ratio (or enhancement factor) method using correlation of pollutant mixing ratios above the background to estimate trace gas emissions was utilized. This "top–down" approach relies on the fact that both CH₄ and CO are non-reactive on the time scale of dispersion. The atmospheric lifetime of CH₄ is estimated to be 8–12 years (NOAA, 2000; Cunnold et al., 2002; IPCC, 2007). Carbon monoxide is an excellent tracer for observing global transport in the troposphere (NCAR, 1999). Its lifetime of one to three months depending upon season is long enough for the gas to be tracked as it rises from the surface and journeys around the globe. Additionally, CO emission sources are mostly associated with human activities, primarily on-road and off-road vehicles in the LA Basin. The accuracy of this "top–down" approach relies both on the quality of the CARB CO inventory, which has been developed over decades using extensive monitoring programs with validation from ambient ratio studies, tunnel studies, fuel-based inventories, and remote sensing techniques (Singer and Harley, 2000; Marr et al., 2002; Wenzel, 2005; Wunch et al., 2008), and on the validity of the assumption that the approximately constant CH₄ to CO ratio observed at MW is representative of the total emission of the LA County area.

Sources of both CH₄ and CO are likely to be similarly distributed (e.g., with population) and subject to similar scales of atmospheric transport and dilution. Also, as discussed in the previous section, both gases are well-mixed before reaching the MW site and source contributions of both compounds are reasonably consistent. Thus, the slope of the regression line for concentrations of CH₄ and CO allows scaling the local CH₄ emissions to the local CO emissions. This methodology was applied by Warneke et al. (2007) to estimate emissions of volatile organic compounds (VOCs) for comparison with the United States Environmental Protection Agency (EPA) National Emissions Inventory (NEI) database. Other research groups using this methodology include scientists conducting the Advanced Global Atmospheric Gases Experiment (AGAGE), which has been measuring compositions of the global atmosphere continuously since 1978. Greally et al. (2007) and Reimann et al. (2005) of AGAGE used the trace gas to CO scaling ratio method to estimate emissions inventories for HFC-152a and methyl chloroform. Wiedinmyer and Friedli (2007) calculated emission factors for mercury (Hg) from fires using correlation of measured Hg and CO in a fire plume based on a similar scaling ratio approach. Additionally, this atmospheric concentration ratio analysis was presented by CARB as one of the three verification methods in the 1997 Senate Bill 2174 (Health and Safety Code section 39 607.3) staff report (CARB, 1997).

The scaling ratio approach typically utilizes the linear regression slope of the two compounds under consideration as provided in Fig. 4 (Warneke et al., 2006, 2007). Using this relationship, the MW scaling ratio ($\Delta$CH₄ = slope × ∆CO) combined with the total CO emissions from the CARB inventory (CARB, 2005) gives the CH₄ emissions for LA County. Fig. 4 provides the CH₄ and CO mixing ratios regression trend line slope (0.52) and its uncertainty (±0.015) from all four seasonal sampling campaigns, with the exception of the data collected on February 14, 2008 when the winds were from the north. The regression trend line intercept (i.e., 1.76) in the scatter plot (Fig. 4) is the result of both CH₄ and CO background mixing ratios measured at the MW site. The estimated CH₄ inventory is calculated using Equation (1), which includes the respective compound molecular weights to convert from volume concentration to mass units.

$$\text{CH}_4 \text{ metric tons} = (\text{CO metric tons}) (0.52 \pm 0.015) / (16 / 28) \quad (1)$$

The 2007 SoCAB portion of LA County CO emissions (1800 metric tons day⁻¹) is available from CARB’s Emission Forecasting System (CARB, 2008b). The CO inventory includes anthropogenic emissions only (i.e., not including wildfires emissions), since there were no known wildfires near the MW monitoring station during the period of study. This CO inventory is incorporated into Equation (2) which calculates annual CH₄ emissions for LA County.
CH$_4$ metric tons year$^{-1}$

\[
= (1800 \text{ metric tons day}^{-1}) \times (0.52 \pm 0.015) \\
\times (16/28) \times 365 (\text{day year}^{-1}) \\
= 200,000 \pm 5600 \text{ metric tons of CH}_4 \text{ year}^{-1} \\
= 4.2 \pm 0.12 \text{ MMT CO}_2 \text{ E year}^{-1}
\] (2)

The unit of MMT – million metric tons or teragrams (Tg) – CO$_2$ E accounts for the greater Global Warming Potential (GWP) of CH$_4$, which is 21 times the GWP of CO$_2$ (for consistency with CARB’s GHG inventory methodology). Note that the estimated CH$_4$ emissions uncertainty reflects only the error in the slope determination from the regression between CH$_4$ and CO mixing ratios. Additional uncertainty due to LA County CO emissions should be considered (see Equation (2)); however, this value is currently not available.

3.4. Statewide and LA County CH$_4$ emissions – based on IPCC methods

In order to evaluate the accuracy of CARB’s “bottom-up” CH$_4$ inventory, via comparison with the “top-down” inventory based on the observations at MW, it must be disaggregated to LA County for the same geographic scale. The majority (93%) of the CH$_4$ statewide inventory was originally calculated using data with spatial information. For example, livestock populations and locations are available from California Department of Food and Agriculture (California Department of Food and Agriculture, 2008). There are no known livestock activities in the study area, which is the SoCAB (California Department of Food and Agriculture, 2008). These activities include rice cultivation or dairy activities in LA County. Using these data, individual livestock sectors were assigned to LA County, and a carbon conversion factor was applied to the amount of feed consumed by those animals. The resulting emissions were obtained by calculating the emissions for each sector and then summing them to obtain the total emissions for the study area. The emissions for each sector were calculated using the following equations:

\[
\text{CH}_4 \text{ emissions} = \text{livestock population} \times \text{emission factor} \\
\text{CO emissions} = \text{vehicle miles traveled} \times \text{emission factor}
\]

3.5. Uncertainties in inventory sectors

This section describes several uncertainties identified in the current study. First, the “top-down” inventory was estimated based on the ambient atmospheric measurements observed in 2007 and 2008, while the CARB “bottom-up” statewide CH$_4$ emissions were only available for up to 2004. Using the same increasing growth trend (Fig. 6), the CH$_4$ inventory discrepancies could be smaller than they are shown in Table 3. Secondly, there might be natural CH$_4$ emissions contributing to the MW site which could lead to an overestimate of CH$_4$ emissions, e.g., CH$_4$ from seeps on the ocean floor near Santa Barbara (UCSB, 2007). However, according to Mau et al. (2007), the emitted CH$_4$ from the Santa Barbara Channel is on the order of 0.006 MMT CO$_2$ E year$^{-1}$, which is insignificant as compared to the emissions shown in Table 1. Wetlands are another natural CH$_4$ emission source. According to Potter et al. (2006), biogenic CH$_4$ emissions from wetlands in LA County are negligible. It is therefore fair to neglect natural CH$_4$ emissions in LA County. Finally, an important source of uncertainty is the CO inventory, which is obtained from the National Emissions Inventory Program (NEI). In the literature, Marr et al. (2002) reported the fuel-based CO emissions inventory was 10–50% lower than the one estimated by CARB’s motor vehicle emission factor model (EMFAC). However, a recent study estimated 2004 CO emissions inventory in the SoCAB using a remote sensing technique and EMFAC model with statewide fuel sales data, and both methods yield identical results (Wenzel, 2005).

Table 1

| Sector                      | Statewide emissions$^a$ | SoCAB portion of LA County emissions$^b$ | Major sources               |
|-----------------------------|------------------------|----------------------------------------|-----------------------------|
| Agriculture & forestry      | 0.81                   | 0.06                                   | Rice cultivation$^b$        |
| Fuel combustion             | 1.0                    | 0.21                                   | Transportation              |
| Fugitive emissions          | 2.6                    | 0.01                                   | Natural gas pipelines      |
| Wastewater treatment        | 2.8                    | 0.77                                   |                             |
| Landfills                   | 5.6                    | 1.9                                    |                             |
| Livestock                   | 13                     | 0                                      | Dairy and beef cows$^b$     |
| Total                       | 26                     | 3.0                                    |                             |

Data Source – California Greenhouse Gas Emissions Inventory (CARB, 2008a).

$^a$ MMT CO$_2$ E year$^{-1}$.

$^b$ There is no known rice cultivation or dairy activities in LA County.
In addition, there are known uncertainties in GHG inventory methods. For example, there are concerns about the default landfill gas collection efficiency and landfill gas emissions models (CARB, 2008a). Based on the default landfill inventory method, 75% of CH4 generated from landfills is assumed to be removed with collection systems and the remaining 25% of CH4 generated is either oxidized (approximately 10% of the total) by microorganisms in cover soil or emitted to the atmosphere. Some landfill operators in SoCAB have questioned the appropriateness of the default 75% collection efficiency and claim to have higher collection efficiencies (Hunsaker, 2008). Methane emissions from landfills have been estimated by the First Order Decay method. This method assumes that the degradable organic component in waste decays slowly throughout a few decades, during which CH4 and CO2 are formed. If conditions are constant, the rate of CH4 production depends solely on the amount of carbon remaining in the waste. As a result, emissions of CH4 from waste deposited in a disposal site are highest in the first few years after deposition, and then gradually decline as the degradable carbon in the waste is consumed by the bacteria responsible for the decay.

Another source of possible error is the fugitive CH4 emissions from the natural gas distribution systems. Despite the fact that the SoCAB portion of LA County has 27% of the statewide population, the CARB CH4 inventory only attributes 0.4% of the statewide fugitive CH4 emissions from natural gas systems to LA County (Table 1). Since natural gas consumption and distribution systems are likely associated with population, fugitive CH4 emissions from this sector should be reviewed.

Other sources of uncertainty include emissions from interstate (e.g., aircraft and trains) and international (e.g., ocean-going ships) transport which are not well accounted for in the CARB “official” statewide GHG inventory. However, aircraft and ocean-going vessels burn jet fuel and diesel, and consequently emit very little CH4 (EPA, 2008).

4. Conclusions and next steps

The comparison of estimated anthropogenic CH4 inventories for the SoCAB portion of LA County is presented in Table 3. It is estimated that the “top–down” CH4 inventory based on the mixing ratios measured at MW is approximately one-third greater than the CARB “official” statewide inventory when it is allocated to LA County. Considering the many possible uncertainties described above, the two estimates are in reasonable agreement, but this difference may still suggest under- and/or un inventoried sources of CH4 in LA County. More work is required to better quantify the CH4 emissions from each of the large source sectors listed in Table 1, with perhaps special focus on CH4 fugitive emissions.

Finally, the data and analysis presented here demonstrate that the MW site is a very useful location for applying the scaling factor method to develop a “top–down” CH4 inventory for the SoCAB portion of LA County. The CH4 and CO correlation results from the present study agree well with the NOAA WP-3 aircraft study in the mixing layer over the LA urban area in 2002. We plan to apply this scaling factor method to other GHGs and in other air basins, in order to evaluate emissions inventories and to investigate whether there are un inventoried GHG sources in California.

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