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**Quantifying Greenhouse Gas and Air Quality Pollutant
Emissions using Airborne Measurements**

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for the degree of
Doctor of Philosophy

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2023

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.



Jeffrey W. Peischl

Dedication

This Ph.D. would not be possible without the help of the following people and institutions, to whom I owe a great deal of gratitude and thanks: my mother Gertrude W. Peischl, the memory of my father Dr. Thomas M. Peischl, and my sister Terri L. Hall for their support, especially during my twenties when I was on a circuitous path to the field of science; Professor L. Gregory Huey and David J. Tanner at Georgia Tech who taught me much about instrumentation for the measurement of trace gases, electronics, and general laboratory work, and provided me with my first taste of field work in Summit, Greenland; Dr. Thomas B. Ryerson, who taught me much more about the measurement of trace gases and how to write for scientific journals; all my co-authors and colleagues, from whom I continue to learn new things; the University of Colorado's Cooperative Institute for Research in Environmental Sciences and the NOAA Chemical Sciences Laboratory, which provide me access to new and unique data that few others have; Dr. Albert A. Ruth and Dr. Steven S. Brown, for guiding me through what is likely the last but most important degree of my career.

Preface

In August 2005, I came to NOAA for the purpose of engineering a commercial carbon dioxide analyzer for use on aircraft for the NOAA Chemical Sciences Laboratory's airborne field studies. After successfully deploying the instrument for the Texas Air Quality Study 2006, I realized there was scientific analysis that could be done using the data I collected that none of my colleagues were interested in doing; therefore, I took it upon myself to do it. I analyzed emissions from numerous power plants in Texas and compared them with emissions data reported to the U.S. Environmental Protection Agency. I presented my results to the State of Texas' Commission on Environmental Quality with a poster that I later presented at the American Geophysical Union's Fall Meeting. This gave me my first taste of presenting the results of scientific analysis I had done, and I thoroughly enjoyed it. I then decided to write a paper, which resulted in my first peer-reviewed first-author publication in 2010.

Around this time, I was tasked with operating a new commercial instrument that measured carbon dioxide and methane for the California Nexus study. I was fortunate enough to deploy this instrument at a time when there were not many methane instruments installed on aircraft. This gave me the opportunity to critically evaluate the State of California's Air Resources Board's greenhouse gas inventory in a way that had never been done before. I published two more first-author papers using data from this project.

Finally, the 2010s were a period of rapid increase in the production of oil and natural gas in the United States due largely to the technological advancements of hydraulic fracturing and horizontal drilling. The scientific community quickly discovered large uncertainties regarding the methane emissions from regions of oil and natural gas production that affected the climate impact of using natural gas as a fuel. I took part in three airborne field projects from 2013–2015 with a goal of quantifying methane emissions from one or more of these regions. These projects led to a trilogy of first-author papers quantifying methane emissions from oil and gas producing regions in the U.S.

Abstract

The composition of the atmosphere affects the health and well-being of people around the world. Air quality is a leading risk factor for mortality in the world today, and climate change may have a similar impact in the future. Knowledge of the magnitude of trace gas emissions to the atmosphere is necessary for policy makers who wish to most effectively reduce emissions that lead to harmful air quality or climate change. This knowledge typically starts with an inventory, where activity data are multiplied by emission factors to arrive at total emissions. Inventories are often used by policy makers to determine what emissions are and how they may be effectively reduced. Inventories are also used by scientists to model the effects of greenhouse gases on climate and the effects of ozone or particulate matter production on air quality. Scientific advancement in these areas in turn informs policy. Therefore, verifying inventories is necessary so that policy makers can make the most informed decisions to mitigate the negative atmospheric impacts of human activities.

Here, I review multiple techniques used to verify inventories with measurements from trace gas analyzers installed aboard aircraft. The techniques are: (1) comparing an inventory emission ratio of two gases using atmospheric enhancement ratios; (2) comparing spatially broad airborne measurements to a local, in situ study using an atmospheric mixing model; (3) quantifying relative emissions using atmospheric enhancement ratios; and (4) directly quantifying emissions using airborne data. These techniques have been used to verify the accuracy of inventories and to reveal where improvements to inventories can be made.

Introduction

The composition of the atmosphere affects the lives of humans globally. Air quality is a leading risk factor for mortality globally (GBD 2019, 2020), while greenhouse gases (GHGs) are the main drivers of climate change, which may have an equally large impact on mortality in the future (Silva et al., 2017; Vicedo-Cabrera et al., 2021). The two most important GHGs that humans emit are carbon dioxide (CO_2) and methane (CH_4). Anthropogenic CO_2 is mainly emitted from combustion processes, especially the combustion of fossil fuels which converts carbon trapped underground as either oil, natural gas, or coal to CO_2 in the atmosphere. CH_4 is produced mainly through two processes: thermogenic and biogenic. Thermogenic sources include natural gas and coal emissions. Biogenic sources are microbial, and include CH_4 emitted from landfills, rice cultivation, and enteric fermentation – all places where oxygen is limited and the anaerobic microbes that produce CH_4 thrive. CH_4 in the atmosphere eventually reacts with either the hydroxyl radical (OH) or to a lesser extent atomic chlorine (Cl) and has an e-folding lifetime, i.e., the time it takes to reach $1/e$ of its previous concentration, of roughly a decade. The end result of the CH_4 oxidation process is typically CO_2 (Seinfeld & Pandis, 2006). During this process, CH_4 can form ozone (O_3) throughout the troposphere in regions with anthropogenic or lightning nitrogen oxide ($\text{NO}_x = \text{NO} + \text{NO}_2$) emissions (e.g., Fiore et al., 2002).

Ozone is a major component of smog, has adverse health effects on humans and agricultural crops, and is also a GHG. O_3 is formed in the lower part of the atmosphere through the chemical reactions of NO_x and volatile organic compounds (VOCs; Haagen-Smit, 1952; see Figure 0). Although O_3 is not directly emitted by humans, both NO_x and

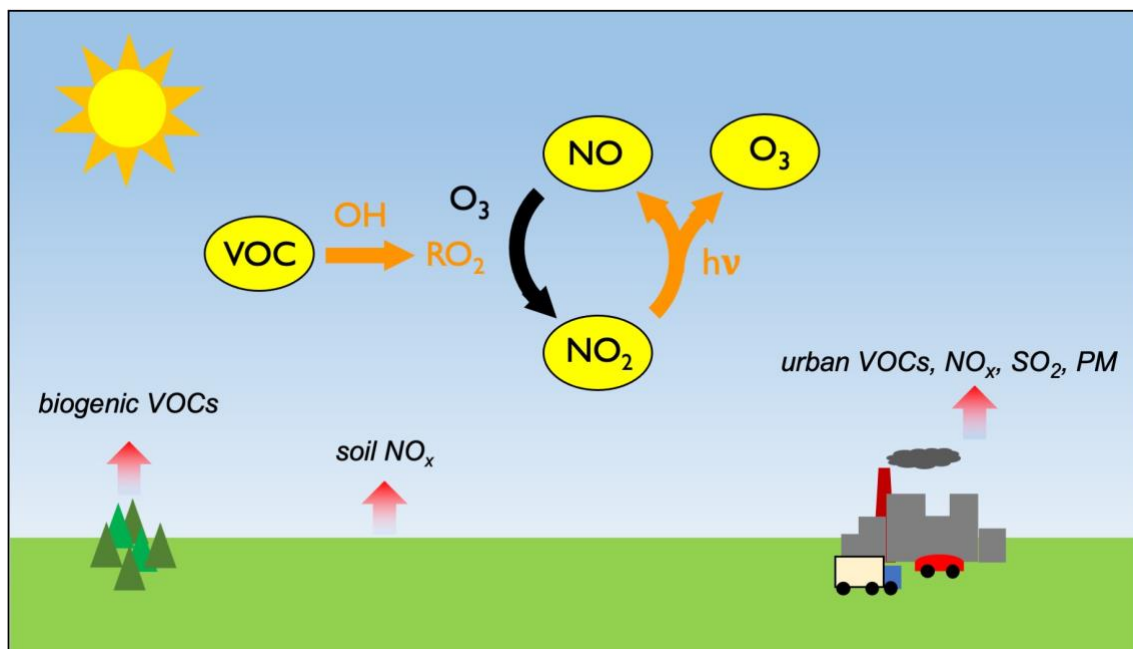


Figure 0. Simplified schematic showing the relevant VOC and NO_x photochemistry, illustrating O₃ formation. The arrows and text in orange require sunlight; the black arrow showing NO + O₃ forming NO₂ does not. Also shown are some of the major global natural and anthropogenic sources of VOCs, NO_x, SO₂, and particulate matter (PM).

VOCs are. NO_x is a byproduct of combustion processes, where either nitrogen in fuel is oxidized to NO or NO₂, or if hot enough, the O₂ in air thermally dissociates and initiates a chain reaction with N₂ to form NO (Zeldovich, 1946). VOC emissions come from fuels, solvents, and other chemicals that humans either produce or extract from the earth, as well as natural sources. Finally, particulate matter, which contributes to 6–7 million premature deaths per year globally (GBD 2019, 2020), is both directly emitted and formed from the atmospheric chemistry of sulfur dioxide (SO₂), NO_x, ammonia, and VOCs.

Mitigating the effects of these gases requires knowledge of their emission magnitude and how to most effectively regulate their emissions. For example, CH₄ is 81

times more potent per mass than CO₂ at trapping heat in its first 20 years from emission (Smith et al., 2021), and studies have shown that the most effective way to reduce the effects of climate change is through simultaneous CO₂ and CH₄ emissions controls (Shindell et al., 2012). However, anthropogenic emissions of CH₄ are not as well-known as they are for CO₂. Further, atmospheric chemical models use inventories to understand the chemical lifetimes of GHGs, including CH₄, which directly affect the global warming potentials of these gases. Atmospheric chemical models are also used to study the formation mechanisms of ozone and particulate matter. By adjusting emissions in these models, scientists learn how to best reduce the effects of species detrimental to climate and/or air quality. This science in turn informs policy for governments looking to reduce the impacts of air quality or climate change on their constituents. Also, when national or local governments commit to reducing their GHG emissions, they require inventories to determine whether their targets were hit. Therefore, it is important to verify the accuracy of inventories in order to improve the composition of the atmosphere and thereby the lives of humans throughout the world.

Inventories are typically created using “bottom-up” techniques, where an emission factor for some type of activity is multiplied by the frequency of that activity to determine a total emission. Errors in inventories arise when extrapolating from few tests that determine emission factors to large populations of that activity, or when certain types of emissions are completely excluded. Multiple bottom-up inventories for the same gas often disagree in either magnitude or the relative breakdown of sectoral emissions. For example, one recent study of CH₄ emissions from the northeastern U.S. (Plant et al., 2019) examined two CH₄ inventories, the Emission Database for Global

Atmospheric Research (EDGAR; Janssens-Maenhout et al., 2019) and a gridded U.S. Environmental Protection Agency (EPA) GHG inventory (Maasakkers et al., 2016). These two CH₄ inventories differed in both magnitude and in the dominant sources of CH₄ in the regions: EDGAR assigned most CH₄ emissions to urban regions, while the EPA inventory assigned more to oil and natural gas production and coal mining. Thus, there is a need to critically evaluate inventories in order to determine their accuracy.

The accuracy of inventories is often assessed using “top-down” methods. These methods use atmospheric measurements of a gas to determine emissions. For example, Plant et al. (2019) used the atmospheric enhancement ratio of CH₄ to carbon monoxide (CO) downwind of northeastern U.S. cities and multiplied this slope by CO inventories for these cities to arrive at an estimate of CH₄ emissions from the urban regions. This method assumes that all emissions from a given region have been equally well-mixed in the atmosphere before the measurement has been made, and that there has been no other significant enhancement or loss of the two species since emission. Plant et al. (2019) found that urban CH₄ emissions were nearly double that in the EPA GHG inventory, largely due to leaks from the natural gas distribution system that were not included in the inventory.

Another frequently used top-down method, inverse modeling (e.g., Thomson, 1987), uses an emission inventory, measurements of a trace gas, and a computer model of air transport to determine what trace gas concentrations would be at the measurement location. Inventory emissions are then either increased or decreased until the measurements match the model. However, this method requires modeling atmosphere dynamics correctly, and does not have a well-defined mechanism to estimate

uncertainty. Therefore, other top-down methods are often used that do not have these shortcomings.

This thesis presents different approaches of testing inventories using airborne instrumentation. Four techniques will be explained in detail, followed by a scientific analysis using the technique in a peer-reviewed publication. The techniques are: (1) comparing an inventory emission ratio of two gases using atmospheric enhancement ratios; (2) comparing spatially broad airborne measurements to a local, in situ study using an atmospheric mixing model; (3) quantifying relative emissions using atmospheric enhancement ratios; and (4) directly quantifying emissions using airborne data. All measurements presented here were made from trace gas analyzers installed on aircraft for targeted regional field campaigns in the U.S.

1. Comparing an inventory emission ratio of two gases using atmospheric enhancement ratios

1.a. Introduction to Publication I

In the 1990s, the Houston and Dallas metropolitan regions in Texas struggled to meet the U.S. EPA ambient air quality standards for ozone and particulate matter. At the time, these standards required the 4th-highest daily maximum 8-hour average daily (MDA8) O₃ concentration averaged over a 3-year period, also known as the O₃ design value, not to exceed 0.080 parts per million by volume (ppmv), or 80 parts per billion by volume (ppbv). When regions fail to comply with air quality standards, the EPA requires states to develop an implementation plan to improve air quality in these regions. One tactic employed by air quality managers in Texas was requiring power plants to install NO_x and SO₂ scrubbers to reduce emissions and thereby reduce regional O₃ and particulate matter concentrations. As part of the Acid Rain program, the U.S. EPA requires large power plants to report their emissions of CO₂, NO_x, and SO₂. This included numerous power plants in Texas, including several nearby Houston and Dallas. According to data reported by these power plants to the EPA, NO_x and SO₂ reductions had occurred in the early 2000s. However, one question that remained for regulators in Texas was whether these regulations were effective, i.e., could the self-reported measurements be trusted and were emissions of NO_x and SO₂ to the atmosphere reduced? To answer this question among others, NOAA was tasked with studying air quality in Texas with two field studies, the Texas Air Quality Study (TexAQS) 2000 in summer 2000 and a follow up TexAQS 2006 in summer 2006.

Typically, the CO₂ emissions from either coal- or natural gas-fired burners are believed to be accurate. The fuel sales are taxed and therefore tracked, so there is an accurate means to convert the mass of the fuel sold to a power plant to CO₂ emissions through the carbon content of the fuel. Therefore, the CO₂ emissions reported to the EPA are expected to be accurate. The NO_x and SO₂ emissions, however, are less well known. Emissions of both depend partly or wholly on the nitrogen and sulfur content of coal. NO_x is also produced at the high temperatures of the combustion process and the efficiency of individual processes may vary widely. Ultimately, emissions of both from the power plant stack rely on the efficacy of emissions controls, or scrubbers, in the power plant exhaust system. If the self-reported emission values for NO_x and SO₂ were accurately reported, they could then be used as inputs to air quality models to determine ozone or particulate matter production, and thereby determine if the regulations requiring scrubbers were effective.

Peischl et al. (2010) showed that the NO_x and SO₂ emissions from Texas power plants reported to the EPA were indeed accurate relative to the CO₂ emissions. CO₂, NO_x, and SO₂ were measured from aircraft which transected plumes downwind of power plants in 2000 and 2006. Between these years, many power plants installed NO_x and/or SO₂ scrubbers. Peischl et al. (2010) compared enhancement ratios of SO₂/CO₂ and NO_x/CO₂ measured in the atmosphere downwind of power plants and compared these to the self-reported emission inventories and found they were accurate to within the uncertainties required by law. They also found significant carbon monoxide (CO) emissions that were not always accounted for by inventories. CO is an indicator of

incomplete combustion, and thus power production inefficiency, and is also an O₃ precursor.

I. A top-down analysis of emissions from selected Texas power plants during TexAQS 2000 and 2006

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I. Abstract. Airborne measurements were taken downwind of eleven Texas power generation facilities in 2000 and 2006 as part of the two Texas Air Quality Study (TexAQS) campaigns. From these measurements, we determine emission ratios of NO_x (= NO + NO₂), SO₂, and CO to co-emitted CO₂ for each facility. These measurements provide an independent external assessment of reported emission ratios from continuous emission monitoring systems (CEMS). During the TexAQS study years, we find the SO₂/CO₂ and NO_x/CO₂ emission ratios derived from measurements aboard the aircraft agree quantitatively with inventory values from CEMS, with standard deviations of less than ±14%. We document significant decreases in atmospheric mixing ratios of NO_x as a result of emission reductions due to controls implemented at the W. A. Parish plant after TexAQS 2000. For several of the facilities, CO emissions appear relatively

constant in time. Derived CO/CO₂ emission ratios agree substantially better with Texas Commission on Environmental Quality inventories in 2006 than in 2000, which we attribute to better inventory data from three facilities that installed CO CEMS between the two study years, and not because of any significant change in CO emissions. Other plants appear to have varying CO emissions over time, complicating comparison to annual inventory values. Finally, we use two independent NO₂ measurements, along with measurements of O₃, NO₃, and N₂O₅, to quantify the fraction of NO_x directly emitted as NO₂ from the Oklaunion power plant, providing the first quantitative estimate of NO₂ emissions from a power generation facility using ambient data.

I.1. Introduction

Electric generation utility (EGU) power plants in the United States are required to report hourly-averaged emissions of nitrogen oxides (NO_x = NO + NO₂), sulfur dioxide (SO₂), and carbon dioxide (CO₂) as described in Title 42 of the United States Code section 7651k. These data are provided by continuous emission monitoring systems (CEMS), which determine mixing ratios of NO_x, SO₂, and CO₂ in the stack exhaust, installed at each plant. Combined with measured stack flow rates, an hourly emission flux is calculated, subjected to quality control procedures, and reported to the U.S. Environmental Protection Agency (EPA) every quarter. These data are subsequently posted to the EPA web site (<https://www.epa.gov/airmarkets/power-sector-emissions-data>). Accuracy is assessed by independent sampling of stack gases and flow rate, typically performed periodically by a variety of contractors on a plant-by-plant basis. CEMS systems are in compliance with the U.S. Code of Federal Regulations

(C.F.R.) if independent tests agree within $\pm 10\%$ for NO_x , SO_2 , and CO_2 concentrations with no low bias and within $\pm 10\%$ for stack flow (40 C.F.R. § 75). Assuming random errors are normally distributed, mass emission rates from EGUs equipped with CEMS should be accurate to better than $\pm 14\%$ (after summing the concentration and flow uncertainties in quadrature), and enhancement ratios (e.g., NO_x/CO_2) should also be accurate to better than $\pm 14\%$, assuming the stack flow rate uncertainties are the same for each trace gas measurement. Further, the State of Texas, through the Texas Commission on Environmental Quality (TCEQ), requires EGUs in the state to report annual emissions of NO_x , SO_2 , and carbon monoxide (CO), among others. The annual NO_x and SO_2 emissions reported to TCEQ typically differ by less than 1% of the emissions reported to the EPA.

The CEMS data are used to track regulatory performance of emission control measures, to calculate daily and annual emissions from EGU power plants, and as inputs to regulatory models. Assessment of CEMS mass emission rates and enhancement ratios using ambient measurements (Frost et al., 2006; Kim et al., 2006; Ryerson et al., 1998; Trainer et al., 1995) provides a valuable additional independent evaluation of emissions tabulations from a significant anthropogenic emission source sector.

To provide external assessment of CEMS performance, we report enhancement ratios in near-field transects of EGU power plant plumes measured from instrumented research aircraft downwind of several power plants during the two Texas Air Quality studies (TexAQS 2000 and 2006). We compare measured ratios to those calculated from the CEMS data inventory from these plants to evaluate CEMS accuracy for ratios of NO_x and SO_2 to co-emitted CO_2 , as well as for TCEQ inventories of CO. Further, we

compare measurements from the W. A. Parish plant over the two study years to assess the effectiveness of mandated NO_x emission reductions, and to evaluate the changes in atmospheric mixing ratios resulting from emission control measures.

I.2. Instrumentation

I.2.1. Nitrogen Oxides, O₃, SO₂, CO, Actinic Flux, and Wind Speed

NO was measured by NO/O₃ chemiluminescence (CL). NO₂ was measured by photolytic conversion to NO and subsequent detection of NO by chemiluminescence (P-CL), with ambient NO₂ calculated from the calibrated difference between these two NO measurements. NO_y (total reactive oxidized nitrogen) was measured by NO/O₃ chemiluminescence after catalytic conversion to NO on a 300 °C Au surface in the presence of 1.5% CO. Imprecision of the 1-Hz NO, NO₂, and NO_y data is determined by counting statistics and ranged from ±0.015 to ±0.4 parts per billion by volume (ppbv) for the plumes examined here (all uncertainties given herein are 1σ); inaccuracy is estimated to be: ±5% for NO measurements, ±9% for NO₂ measurements, and ±10% for NO_y measurements taken in 2000 and ±12% for 2006 (Ryerson et al., 1999; Ryerson et al., 2000). In 2006, an independent measurement of NO₂ was made by cavity ring-down absorption spectroscopy (CaRDS) (Osthoff et al., 2006). Imprecision of the 1-Hz CaRDS NO₂ data is ±0.1 ppbv; inaccuracy is estimated to be ±5%. Also measured with the CaRDS instrument were NO₃ and N₂O₅ (Dubé et al., 2006). Imprecision of the 1-Hz NO₃ data is ±1.5 parts per trillion by volume (pptv); inaccuracy is estimated to be ±20%. Imprecision of the 1-Hz N₂O₅ data is ±1 pptv; inaccuracy is estimated to be ±20%. O₃ was measured by NO/O₃ chemiluminescence (Ryerson et al., 1998). Imprecision of the

2006 1-Hz O₃ data is ± 0.050 ppbv; inaccuracy is estimated to be $\pm 3\%$. SO₂ was measured by pulsed UV fluorescence using a modified Thermo Environmental Instruments, Inc. model 43S (Ryerson et al., 1998). Imprecision of the 1-Hz SO₂ data is ± 0.3 ppbv; inaccuracy is estimated to be $\pm 12\%$ for 2000 and $\pm 10\%$ for 2006. CO was measured by vacuum UV resonance fluorescence (Holloway et al., 2000). Imprecision of the 1-Hz CO data is ± 1 ppbv; inaccuracy is estimated to be $\pm 5\%$ for both 2000 and 2006. Spectral solar actinic flux was measured by a spectroradiometer. Inaccuracy of $j(\text{NO}_2)$ derived from these measurements is estimated to be $\pm 15\%$ (Stark et al., 2007). The uncertainty of the wind speed measurements derived from various sensors aboard the aircraft is estimated to be ± 1 m/s for both 2000 and 2006.

I.2.2. CO₂ Instrument Description and Operation

For TexAQS 2000, CO₂ was measured by a pressure-controlled nondispersive infrared absorption (NDIR) instrument based on a LI-COR model 6262 analyzer (Nicks et al., 2003). Imprecision of the 1-Hz CO₂ data is stated as ± 0.08 parts per million by volume dry air mole fraction (ppmv) at 370 ppmv, and inaccuracy is estimated to be $\pm 3\%$ of the absolute difference in mixing ratio from 370 ppmv.

In 2005, an improved NDIR instrument, modeled closely on the National Aeronautics and Space Administration (NASA) ER-2 flight instrument developed at Harvard (Daube et al., 2002), was developed, tested, and fielded to make highly accurate, in situ measurements of CO₂ from the National Oceanic and Atmospheric Administration (NOAA) WP-3D Orion (P-3) aircraft; its first description is provided here. The NOAA CO₂ instrument was constructed using the optical bench from a LI-COR 6262 carbon dioxide and water vapor analyzer; a schematic of the instrument is

shown in Figure 1. The LI-COR 6262 optical bench uses two absorption cells, a sample cell and a reference cell, and outputs a CO₂ signal as the difference in absorption between the two cells. A reference gas (~380 ppmv) is continuously flowed through the reference cell during flight. Atmospheric air is sampled continuously aboard the NOAA P-3 through a rearward-facing, 0.95 cm (3/8") o.d. stainless steel inlet. The inlet flow is dried to a dew point temperature of -78°C after passage through a 50-strand Nafion dryer (Perma Pure, p/n PD-50T-24MPS) and a dry ice trap. The sample flow next passes through a 10- μm stainless steel disc frit (Upchurch Scientific, p/n C-413) filter, and a pressure controller (MKS model 640A) set to approximately 33.33 kPa and held to within ± 0.0093 kPa during flight (250 ± 0.07 Torr) before entering the sample absorption

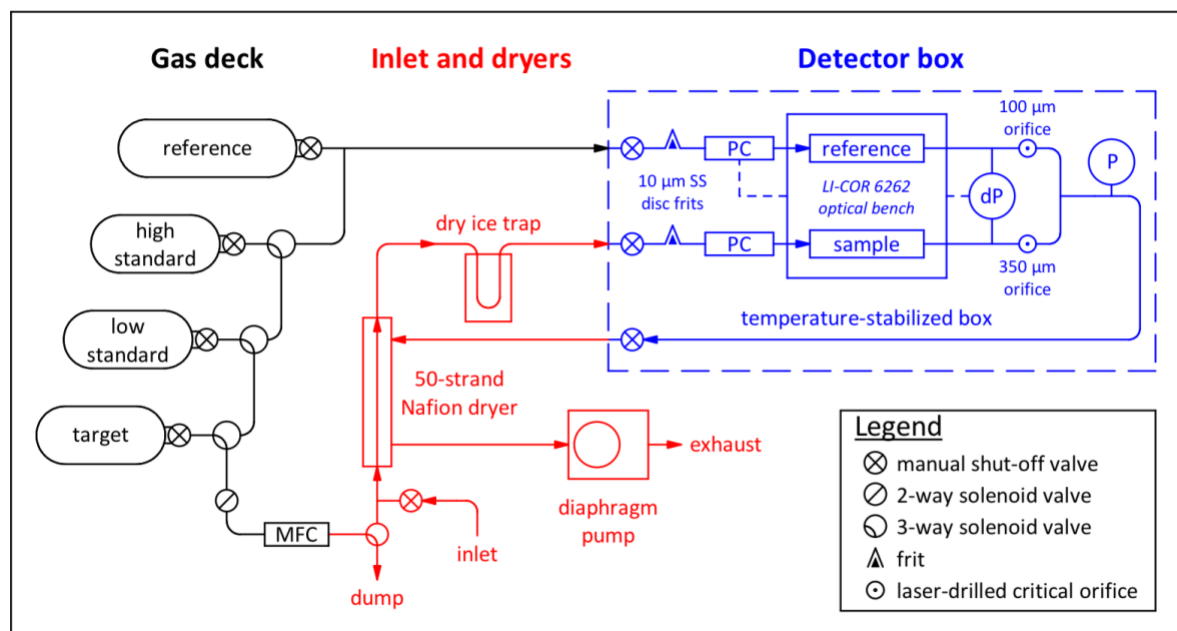


Figure 1. Plumbing diagram of P-3 CO₂ instrument in 2008. MFC: MKS 1179 mass flow controller; PC: MKS 640A pressure controller; dP: MKS 229B differential pressure transducer; P: MKS 750B pressure transducer. The pressure controller upstream of the reference cell is an MKS 640A-28156, a custom-made pressure controller without an internal pressure transducer.

cell of the optical bench. Downstream of the optical bench, inlet flow is restricted to ~400 standard cubic centimeters per minute (sccm) by a 350- μ m critical orifice. Pressure downstream of the orifice ranges from 80–100 Torr, depending on altitude. A differential pressure transducer (MKS model 223B) measures the difference in pressure between the sample and reference cells of the optical bench; the output signal controls a valve upstream of the reference cell such that the differential pressure between the two cells is ~0 Torr and held to within ± 0.02 Torr during flight. A 100- μ m critical orifice is used to restrict the reference flow to ~40 sccm. After passage through the instrument, the dried sample flow is used as the sheath flow for the Nafion dryer. The optical bench, pressure controllers, and critical orifices are mounted on wire-rope isolators in order to reduce the effects of airframe vibration and in-flight turbulence on vibration-sensitive components. The temperature of the absorption cells is controlled to ~38°C by a ThermOptics heater mounted directly to the optical bench. Finally, the optics, power, and flow control components are contained within a temperature-regulated enclosure to further minimize the dependence of the NDIR CO₂ measurement on cabin temperature variations.

Immediately inside the aircraft fuselage, three calibration gas standards were regularly delivered to the inlet line in flight to evaluate instrument zero (determined by introducing a ~380 ppmv reference standard into both absorption cells simultaneously) and instrument gain (evaluated from ~345 to ~480 ppmv, and including the ~380 ppmv reference gas as a known standard). While the exact standard tank values varied over the course of a field project, each was known to within ± 0.08 ppmv. The calibration gases were added at a rate sufficient to replace the ambient sample and overflow the inlet. No

change in water vapor between sampling ambient air and sampling the compressed standards was detected, suggesting essentially complete drying of ambient air. Quadratic fits of instrument responses to these calibration standards in flight were reproducible to within ± 0.08 ppmv for the full calibration range over the course of the six-week project. Flight CO₂ standard tanks were filled from tertiary standards and calibrated before and after flight against secondary standards on the ground. All secondary standards were calibrated against a set of five primary CO₂-in-air standards, spanning 346 to 496 ppmv, purchased from the Global Monitoring Division (GMD) of NOAA's Earth System Research Laboratory (ESRL) in Boulder, Colorado. After the TexAQS 2006 campaign, two additional GMD primary gas standards of 550.26 (± 0.07) and 642.87 (± 0.07) ppmv were used to evaluate measurement accuracy at mixing ratios higher than the in-flight calibration range, and this additional term is included in the uncertainty calculations described below.

Following Daube et al. (2002), we examine two separate methods of evaluating CO₂ uncertainty. First, the total uncertainty for each 1-second CO₂ datum between 345 and 480 ppmv was calculated by summing in quadrature the known sources of uncertainty, listed below with the general range of error attributed to each: instrument gain, including standard tank uncertainties: ± 0.07 to ± 0.20 ppmv; absolute value of the reference tank mixing ratio value: ± 0.02 ppmv; 1-second imprecision during smooth, level flight: ± 0.05 ppmv; and dependence on aircraft acceleration, attributed to displacement of the lamp filament in the optical bench during turbulence and aircraft acceleration: averaging ± 0.03 ppmv in level flight in the daytime boundary layer, and increasing to ± 0.20 to 0.40 ppmv during tight turns and light to moderate turbulence.

Estimated uncertainties in ambient data above the in-flight calibration range (above 480 ppmv) depend additionally on the mixing ratio, increasing linearly from 0.1 ppmv at 480 ppmv and reaching 0.75 ppmv at 643 ppmv. This first method of uncertainty assessment resulted in an average uncertainty of ± 0.11 ppmv for ambient CO₂ in the TexAQS 2006 data set.

Second, an additional gas standard tank, known as the ‘target’ (or ‘long-term surveillance’ by Daube et al., 2002), was regularly introduced at the inlet in flight but not used in determining instrument zero or gain parameters. The flight target tank value was calibrated according to the procedure for the flight calibration tanks described previously, and its mixing ratio of ~ 400 ppmv selected to approximate median ambient CO₂ values in the Houston summertime boundary layer. The introduction of the target standard was well-separated in time from the instrument zero and gain calibrations and done during all types of flight conditions (smooth, level flight; aircraft banks; turbulence; high and low altitudes; etc.). The target was treated as an unknown in the data reduction, and its mixing ratio retrieved to evaluate long-term instrument imprecision and inaccuracy. Over the course of the TexAQS 2006 campaign, all in-flight 1-second target data averaged 0.02 (± 0.11) ppmv higher than the ‘known’ tank mixing ratio, demonstrating essentially zero bias (and within the uncertainty of the ‘known’ target mixing ratio) and a total uncertainty in quantifying ambient CO₂ of ± 0.11 ppmv. During the 2008 Aerosol, Radiation, and Cloud Processes affecting Arctic Climate (ARCPAC) campaign, all in-flight 1-second target data averaged 0.00 (± 0.11) ppmv relative to the ‘known’ value. Therefore, this second method of uncertainty

assessment is in quantitative agreement with the uncertainty derived from the first method, above.

I.2.3. External Evaluation of Flight CO₂ Instrument Performance

Additional independent performance tests of the new P-3 flight CO₂ instrument were provided by blind comparisons against whole-air samples taken aboard the P-3 aircraft (Conway et al., 1994; Thoning et al., 1995), during wingtip comparisons with an NDIR CO₂ instrument aboard the NASA DC-8 instrumented research aircraft (Vay et al., 2003), and during close approaches to instrumented tall towers. The results of these comparisons are summarized in Table 1 and described in more detail below.

During the ARCPAC campaign in March and April 2008, whole air samples were taken aboard the P-3 and later analyzed with minor modifications to the method described in the work of Thoning et al. (1995) by NOAA GMD. A linear orthogonal distance regression (ODR) fit forced through zero resulted in a slope of 1.0004 and a standard deviation of the residuals of ± 0.14 ppmv. Further, and in conjunction with NASA's Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS), the NOAA P-3 flew a 'wingtip-to-wingtip' comparison with the NASA DC-8, instrumented with its own NDIR CO₂ instrument (see Figure 2). Figure 2A shows a comparison of preliminary field data during a vertical profile. We use the preliminary data to show instrument performance assessed using a blind data exchange; the final data comparison does not differ significantly, but does not afford a blind comparison. The average difference of the two 1-second data sets during the vertical profile ($n=1084$) in a blind data exchange is $-0.001 (\pm 0.187)$ ppmv. Figure 2B shows a scatter plot for all preliminary field 1-second data ($n=2901$), excluding a non-coincident

Table 1. Summary of comparisons between the P-3 CO₂ instrument and other CO₂ measurements

Event	Date	Instruments	CO ₂ (ppmv)	Average distance (km)
KWKT spiral	13 Sept. 2006	P-3	378.32 (±0.15) ^a	3.6 (±0.4)
		tall tower	378.30 ^b (±0.09)	
KWKT spiral	25 Sept. 2006	P-3	377.47 (±0.22) ^a	2.8 (±0.7)
		tall tower	377.50 ^b (±0.08)	
BAO spiral	1 April 2008	P-3	393.92 (±0.25) ^a	3.6 (±1.8)
		tall tower	393.93 ^b (±0.11)	
Slope				
ARCPAC project	29 March to 23 April 2008	P-3 vs. P-3 flask (n=89)	1.0004 (±0.0001) residual 1σ = ±0.11 ppmv	same aircraft
wingtip comparison	11 April 2008	P-3 vs. NASA DC-8	1.000 (±0.000) ^c residual 1σ = ±0.16 ppmv	0.25 (±0.10)

^a atmospheric variability of the measurement, not including instrument uncertainties. The uncertainty in the P-3 CO₂ measurements during spirals is approximately ± 0.20 ppmv.

^b Tall tower data from the highest inlet (457 m AGL at KWKT, 300 m AGL at BAO).

^c Blind comparison of preliminary field data. Data timing was matched for three different altitudes due to ambient pressure effects on flow rate.

pollution plume; the slope of the 1-second data with the ODR fit forced through zero was 1.000 (± 0.000) with a standard deviation of the orthogonal residuals of ± 0.125 ppmv. Finally, the P-3 flew close-approach spirals around the KWKT television tower near Moody, Texas during TexAQS 2006 and the Boulder Atmospheric Observatory (BAO) in Erie, Colorado during ARCPAC 2008. These towers are instrumented by NOAA GMD as part of their tall tower network for carbon tracking (Andrews et al.,

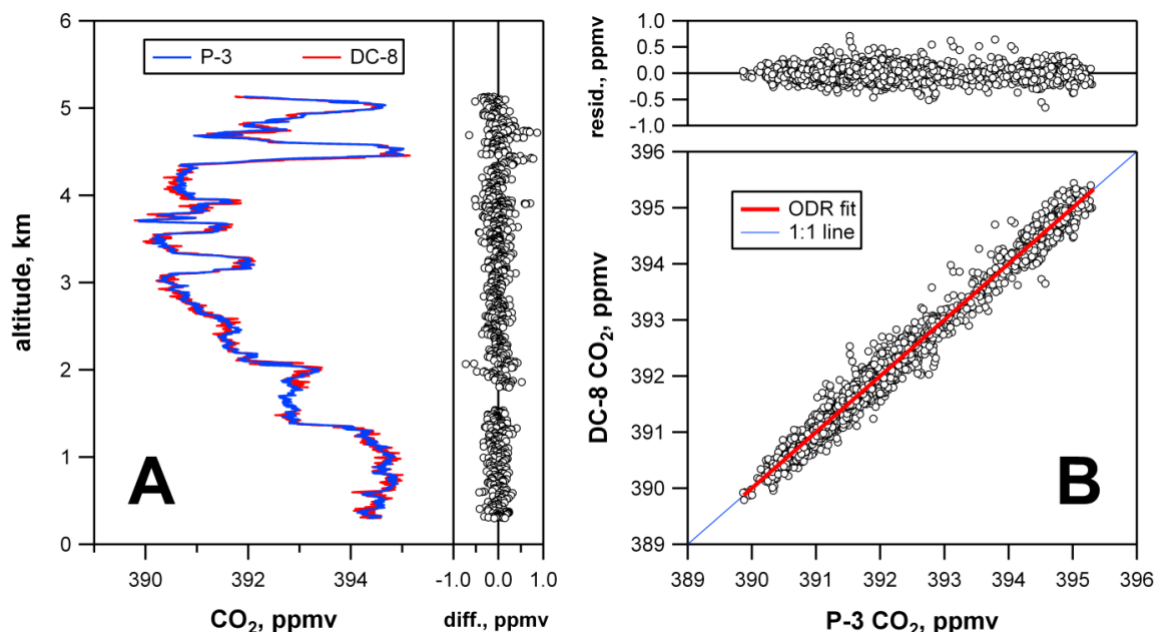


Figure 2. NOAA P-3 CO₂ comparison with NASA DC-8 during 12 April 2008 flight using 1-Hz preliminary field data with a blind data exchange. (A) Vertical profile during en route descent. The blue trace is CO₂ data from the NOAA P-3; the red trace is CO₂ data from the NASA DC-8. (B) Scatter plot of all preliminary field data excluding non-coincident pollution plume (not shown). The red trace is the ODR fit to the data. The blue trace is a 1:1 line. The residuals represent the orthogonal distance from the points to the linear fit.

2009). They report 30-second averages (beginning four and a half minutes after switching to a new inlet height) from three sampling heights. The highest sampling height at KWKT is 457 m above ground level (AGL), while the highest sampling height at BAO is 300 m AGL. An 8-minute travel time through the tower tubing is approximated using measured flow rates and subtracted from the reported time for KWKT measurements, and similarly a 5-minute travel time is approximated and subtracted from the reported time for BAO measurements. The P-3 spirals occurred within 5 minutes of the estimated sampling times at KWKT, and within 10 minutes of

the BAO sampling time. Only data from the highest sampling heights were used in the comparisons due to the slight spatial variability in boundary layer CO₂ mixing ratios, including possible CO₂ uptake near ground-level vegetation, and because the P-3 was always closest in altitude to these inlets. During the P-3's spiral descent around a tower, an average CO₂ mixing ratio was calculated for the well-mixed boundary layer from the aircraft data. In Table 1, only the atmospheric variability is given for these data. The uncertainty in the 1-second P-3 CO₂ measurements during spirals is approximately ± 0.15 to ± 0.20 ppmv. For all three tower spirals, the CO₂ comparisons agreed within the combined uncertainties.

Instrument performance assessed by the above blind evaluations suggest the resulting P-3 flight CO₂ data are directly traceable to the World Meteorological Organization scale (Zhao & Tans, 2006), with sufficiently small and quantified uncertainties to provide reference data from which to determine emissions ratios downwind of EGU power plants as described below.

I.3. Experiment

As part of TexAQS 2000 and 2006, NOAA-instrumented aircraft flew downwind of several Texas power plants, including W. A. Parish, Big Brown, Knox Lee, Lake Creek (TXU/Luminant), Limestone, Martin Lake, Monticello, Oklaunion, Tradinghouse, Twin Oaks, and Welsh power generation facilities (Figure 3). We analyze data from near-field plume transects downwind of EGU point sources (Figure 4). We determine the plumes are attributable to specific point sources by measuring the background trace gas levels upwind of the sources and noting the prevailing wind

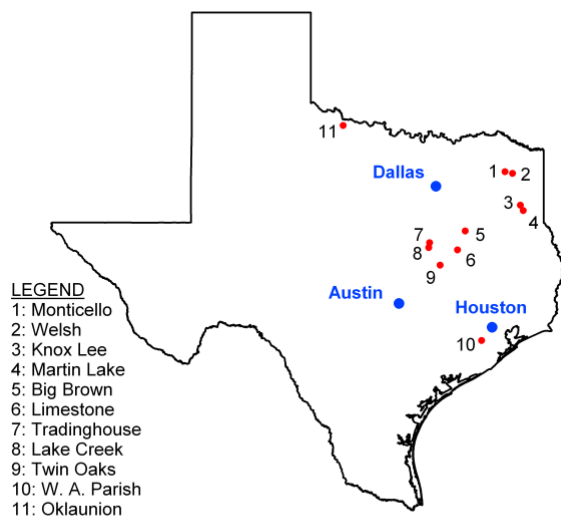


Figure 3. Map of Texas showing EGU power plants examined during TexAQS 2000 and 2006.

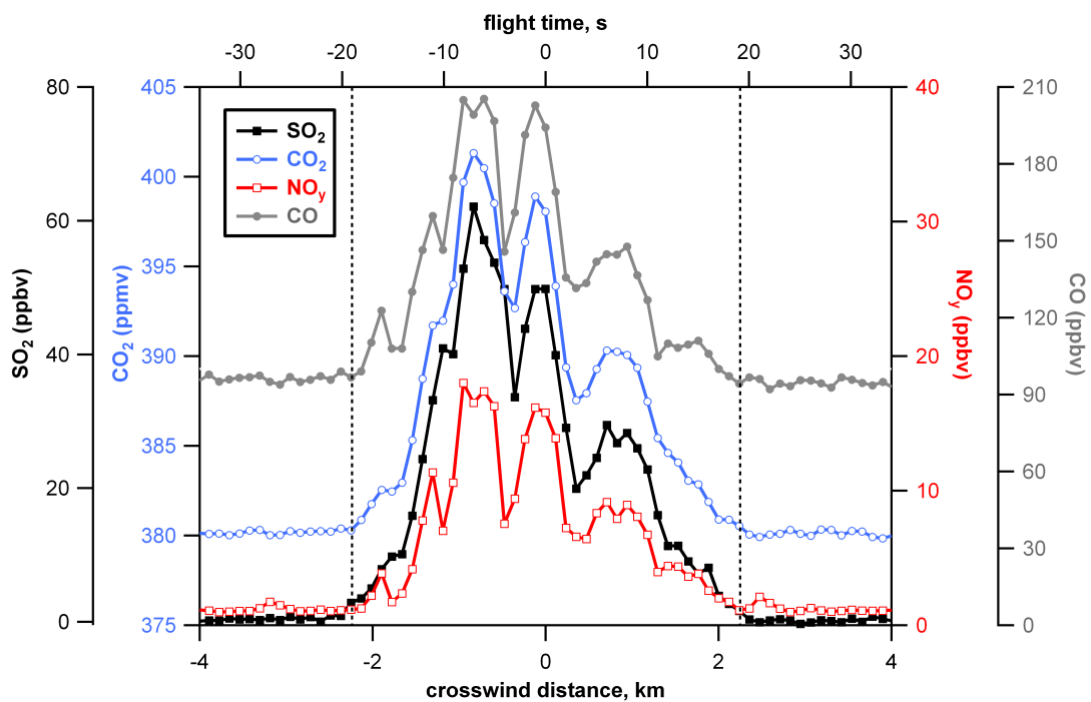


Figure 4. An example of one-second measurements during a P-3 transect 7.5 km downwind of Monticello power plant, 16 September 2006. The P-3 crossed the ~4 km wide plume in approximately 40 s. The data between the dotted lines are plotted in Figure 5.

direction downwind of the sources (Ryerson et al., 2003; White et al., 1976). We then plot the enhancements of a species of interest against CO_2 for each plume, adjust the measurements in time (by one or two seconds to accommodate instrument sampling time differences) such that the highest R^2 is achieved, and calculate bivariate, linear least-squares (ODR) regression fits to the data, weighted by each instrument's imprecision (Figure 5). The slope of the fitted line represents the emission ratio of the trace gas of interest to CO_2 from a given point source (Ryerson et al., 1998). The total uncertainty in the emission ratio derived from ambient measurements is determined by adding in quadrature the uncertainty in the fitted slope to the calibration uncertainties of the relevant trace gas measurements.

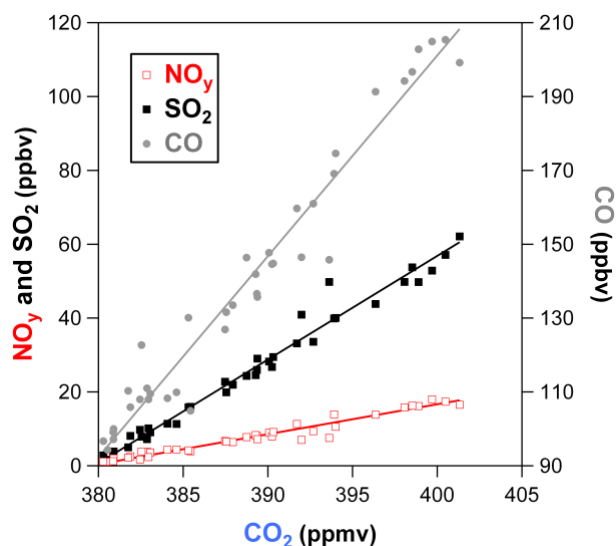


Figure 5. Enhancements in NO_y , SO_2 , and CO plotted against the enhancement in CO_2 for Monticello plume (data between dotted lines, Figure 4). Bivariate fits weighted by instrument imprecisions yield the following emission ratios, with uncertainties determined from fit and measurement uncertainties: $\Delta\text{NO}_y/\Delta\text{CO}_2 = 0.81 (\pm 0.10)$ ppbv/ppmv; $\Delta\text{SO}_2/\Delta\text{CO}_2 = 2.81 (\pm 0.28)$ ppbv/ppmv; $\Delta\text{CO}/\Delta\text{CO}_2 = 5.44 (\pm 0.27)$ ppbv/ppmv.

Using the average wind speed during a plume transect and the distance from the plume center to the point source, we estimate the time that the sampled air mass was emitted. We compare the emission ratios calculated from airborne measurements to those calculated from the hourly CEMS data (Figure 6) and present our results here (Tables 2 and 3). Generally, the downwind transects were flown at times when plant operating outputs were relatively stable. Thus, the CEMS emission ratios tend to remain fairly constant for an hour or two before and after the estimated time of emission. When

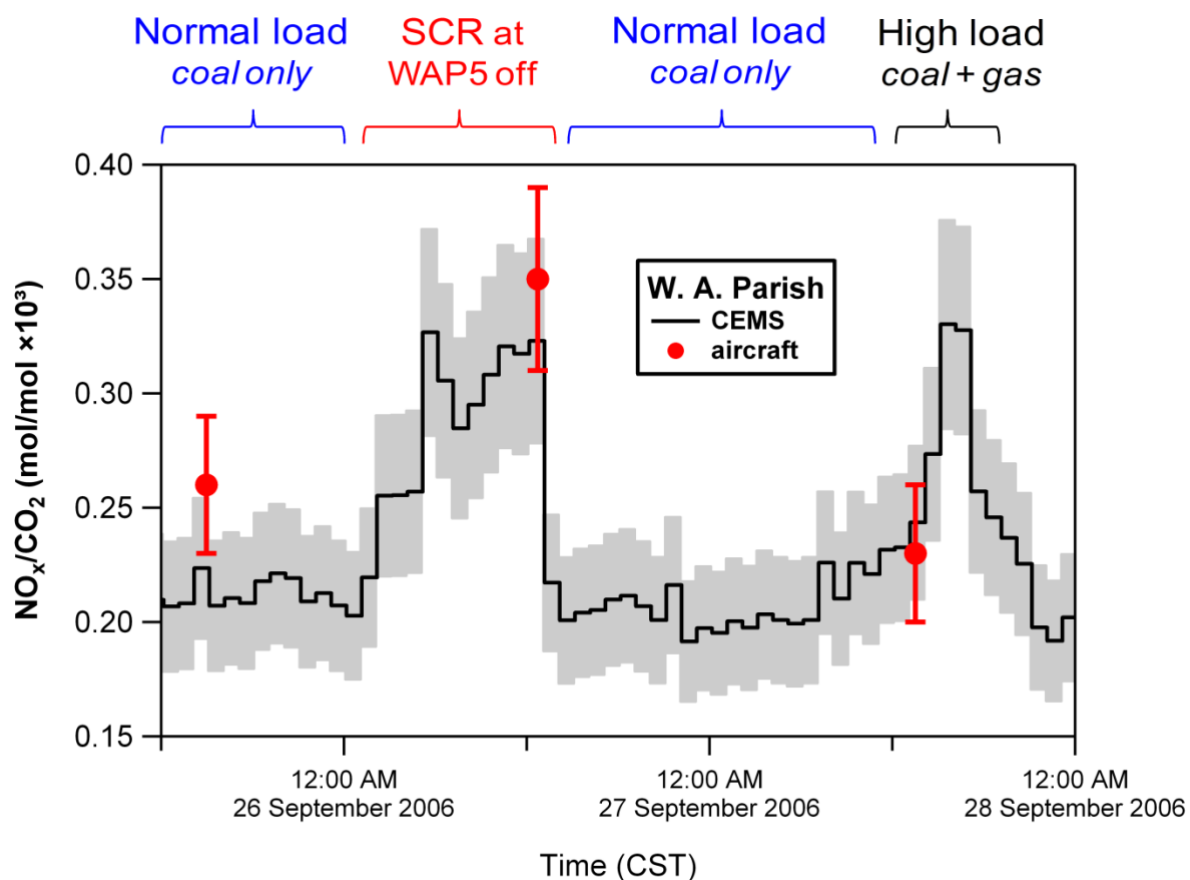


Figure 6. A sample of CEMS-derived NO_x/CO_2 emission ratios with ratios from three P-3 transects overlaid. CEMS emission ratios for each hour are in black, with error bars ($\pm 14\%$) in gray. Aircraft-derived emission ratios are red dots, with (1σ) error bars.

Table 2. Aircraft-derived and inventory-tabulated emission ratios from TexAQS 2000

Emission Ratios, ^a TexAQS 2000							
Date	EGU	SO ₂ /CO ₂		NO _x /CO ₂		CO/CO ₂	
		aircraft	CEMS	aircraft	CEMS	aircraft	inventory ^b
27 Aug.	W. A. Parish	–	1.88	0.88 (±0.09)	1.07	5.20 (±0.30)	0.45
30 Aug.	W. A. Parish	1.71 (±0.21)	1.79	–	1.32	1.47 (±0.09)	0.56
1 Sept.	W. A. Parish	1.80 (±0.22)	1.96	1.13 (±0.12)	1.16	0.54 (±0.04)	0.49
6 Sept.	W. A. Parish	2.19 (±0.27)	1.62	–	1.13	2.48 (±0.15)	0.48
10 Sept.	W. A. Parish	2.76 (±0.34)	2.15	1.19 (±0.12)	1.24	0.32 (±0.02)	0.52
10 Sept.	Big Brown	6.72 (±0.83)	5.07	1.36 (±0.14)	1.28	3.04 (±0.19)	0.12
7 Sept.	Lake Creek	0	0	4.17 (±0.44)	3.80	0.45 (±0.06)	1.39
10 Sept.	Lake Creek	0	0	3.61 (±0.38)	3.09	0.29 (±0.14)	1.13
7 Sept.	Limestone	1.51 (±0.19)	1.52	1.30 (±0.14)	1.33	0.28 (±0.04)	0.11
10 Sept.	Limestone	1.91 (±0.24)	1.96	1.24 (±0.13)	1.40	0.17 (±0.05)	0.12
3 Sept.	Martin Lake	3.03 (±0.38)	2.61	1.22 (±0.13)	1.27	4.53 (±0.27)	0.15
3 Sept.	Monticello	5.08 (±0.63)	5.18	–	1.30	5.60 (±0.33)	0.18
3 Sept.	Monticello	5.14 (±0.64)	5.18	1.14 (±0.12)	1.30	6.76 (±0.39)	0.18
7 Sept.	Tradinghouse	0	0	6.13 (±0.64)	5.69	0.46 (±0.08)	1.44
10 Sept.	Tradinghouse	0	0	4.97 (±0.52)	4.77	0.82 (±0.08)	1.21
10 Sept.	Twin Oaks	1.54 (±0.19)	1.45	0.70 (±0.07)	0.73	0	0.32
3 Sept.	Welsh	2.09 (±0.26)	2.42	–	1.48	0.83 (±0.05)	0.22
3 Sept.	Welsh	2.33 (±0.29)	2.45	1.43 (±0.15)	1.53	0.91 (±0.06)	0.23
3 Sept.	Welsh	2.45 (±0.30)	2.45	–	1.53	1.03 (±0.07)	0.23

^a All ratios given in units of ppbv/ppmv and rounded to two decimal places. A hyphen (–)

indicates missing aircraft data. A zero (0) indicates an emission statistically equal to zero using our analysis.

^b Estimates of inventory values are annual TCEQ CO/NO_x ratios multiplied by hourly CEMS NO_x/CO₂ ratios.

Table 3. Aircraft-derived and inventory-tabulated emission ratios from TexAQS 2006

Emission Ratios, ^a TexAQS 2006							
Date	EGU	SO ₂ /CO ₂		NO _x /CO ₂		CO/CO ₂	
		aircraft	CEMS	aircraft	CEMS	aircraft	inventory ^b
13 Sept.	W. A. Parish	1.61 (±0.16)	1.69	0.19 (±0.02)	0.20	0.37 (±0.02)	0.27
19 Sept.	W. A. Parish	2.28 (±0.23)	2.19	0.28 (±0.03)	0.23	0.41 (±0.03)	0.31
20 Sept.	W. A. Parish	2.06 (±0.21)	2.31	–	0.21	0.08 (±0.02)	0.28
20 Sept.	W. A. Parish	2.15 (±0.21)	2.31	–	0.21	0.45 (±0.03)	0.28
20 Sept.	W. A. Parish	1.79 (±0.18)	2.20	0.22 (±0.03)	0.20	0.21 (±0.02)	0.27
21 Sept.	W. A. Parish	1.75 (±0.18)	2.05	0.23 (±0.03)	0.21	0.15 (±0.02)	0.28
25 Sept.	W. A. Parish	1.96 (±0.20)	1.97	–	0.22	0.14 (±0.03)	0.29
26 Sept.	W. A. Parish	2.23 (±0.22)	2.16	0.35 (±0.04)	0.32	0.08 (±0.01)	0.43
27 Sept.	W. A. Parish	2.01 (±0.20)	1.83	0.23 (±0.03)	0.24	0.20 (±0.02)	0.32
6 Oct.	W. A. Parish	2.19 (±0.22)	1.90	0.27 (±0.03)	0.24	–	0.32
6 Oct.	W. A. Parish	2.31 (±0.23)	1.78	0.26 (±0.03)	0.29	0	0.39
8 Oct.	W. A. Parish	1.85 (±0.19)	1.56	0.23 (±0.03)	0.25	0.30 (±0.02)	0.33
11 Oct.	W. A. Parish	1.97 (±0.20)	1.86	0.23 (±0.03)	0.23	0.46 (±0.02)	0.31
11 Oct.	W. A. Parish	1.93 (±0.19)	1.82	0.21 (±0.03)	0.25	0.64 (±0.03)	0.33
25 Sept.	Big Brown	7.78 (±0.78)	7.07	–	0.54	6.81 (±0.36)	5.02
16 Sept.	Knox Lee	0	0	1.93 (±0.23)	1.69	0	0.14
16 Sept.	Martin Lake	2.98 (±0.30)	2.80	0.77 (±0.09)	0.76	6.05 (±0.30)	6.63
16 Sept.	Monticello	2.81 (±0.28)	2.78	0.81 (±0.10)	0.77	5.44 (±0.27)	6.01
10 Oct.	Oklaunion	0.45 (±0.04)	0.51	2.53 (±0.30)	2.08	0	0.11
10 Oct.	Oklaunion	0.52 (±0.05)	0.49	2.19 (±0.26)	2.16	0	0.12
10 Oct.	Oklaunion	0.49 (±0.05)	0.49	2.19 (±0.26)	2.16	0	0.12
10 Oct.	Oklaunion	0.48 (±0.05)	0.53	2.32 (±0.28)	2.00	0	0.11
10 Oct.	Oklaunion	0.46 (±0.05)	0.53	2.24 (±0.27)	2.00	0	0.11
25 Sept.	Twin Oaks	1.27 (±0.16)	1.45	–	0.67	0	0.34
16 Sept.	Welsh	1.50 (±0.15)	1.65	1.19 (±0.14)	1.04	1.68 (±0.11)	0.92

^a All ratios given in units of ppbv/ppmv and rounded to two decimal places. A hyphen (–) indicates missing aircraft data. A zero (0) indicates an emission statistically equal to zero using our analysis.

^b Estimates of inventory values are annual TCEQ CO/NO_x ratios multiplied by hourly CEMS NO_x/CO₂ ratios.

the CEMS emission ratio did change substantially (i.e., by more than 25% in an hour) within an hour of the estimated time of emission, in no case did the change result in better agreement with the emission ratio measured aboard the aircraft (e.g., see Figure 6). This observation suggests that the errors in estimating the time of emission did not play a significant role in our analysis. We selected data from near-field transects (2–40 km downwind of point sources, corresponding to transport times of 4–120 minutes), thereby minimizing differential losses of the directly emitted species. To this end, we further selected plume transects such that NO_x enhancements accounted for more than 90% of the NO_y enhancement in the plume. A 1- σ confidence interval of, e.g., 10–20%, is written as 15% ($\pm 5\%$) herein. For the transects studied here, NO_x averages 100% ($\pm 6\%$) of the NO_y enhancements in these plumes, which is within the combined uncertainties of the measurements, suggesting that oxidation and subsequent losses were minimal. NO_y measured from the aircraft and NO_x emitted by point sources are thus used interchangeably throughout this paper. We further assume dilution affects all trace gas species equally, so emission ratios are preserved during the short transport times prior to sampling by the aircraft. We interpret the measured plume enhancement ratios (e.g., $\Delta\text{NO}_y/\Delta\text{CO}_2$) as a direct measure of emission ratios from EGU power plants (e.g., NO_x/CO₂, Ryerson et al., 1998). Moreover, we assume emissions from different stacks

at a power plant to be mixed together downwind of the plant, such that the measured enhancement ratios represent those of the plant as a whole. This assumption, and its exceptions, is discussed in more detail below.

For the 2000 data, we account for the slower time response of the SO₂ instrument by calculating enhancement ratios from integrated plume areas rather than slopes (Figure 7). This method made no statistically significant difference to the $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios for 2000 due to similar time responses of the two instruments. By 2006, the time response of the SO₂ instrument was sufficiently fast to allow the use of linear least-squares regression slopes to accurately evaluate $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios.

Our calculated emission ratio serves as a 10-second to 2-minute ‘snapshot’ of emissions from a point source. We assume these emissions remain relatively constant

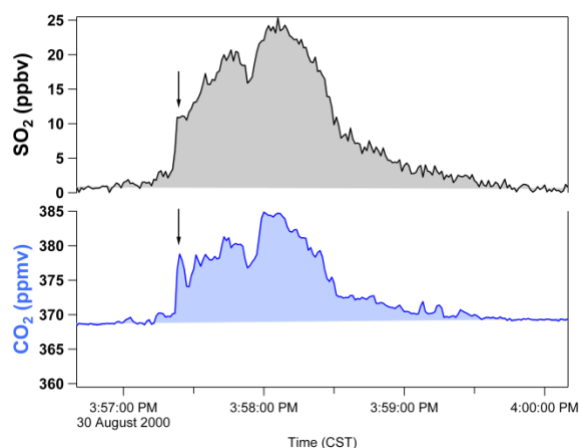


Figure 7. Example of 1-second measurements and integrated plume areas from W. A. Parish plume transect, 30 August 2000. The SO₂ trace is smoother than the CO₂ trace (see arrows) due to the SO₂ instrument's slightly slower time response that year. The gray area under the SO₂ trace equals 1439 (± 173) ppbv s; the light blue area under the CO₂ trace equals 839 (± 25) ppmv s. The resulting $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratio equals 1.71 (± 0.21) ppbv/ppmv. All TexAQS 2000 aircraft $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios (Table 2) were calculated in this manner.

during any given hour of operation. The ‘snapshot’ is compared to hourly CEMS data, and it is these hourly data that are aggregated to form annual emissions inventories. Therefore, comparison of hourly CEMS ratios with aircraft ratios allows an evaluation of the accuracy with which the facility is measuring and reporting its emissions.

I.4. Results and Discussion

Comparisons were made between the aircraft and CEMS emission ratios according to the equation:

$$\% \Delta = 100 \times \left(\frac{\text{CEMS emission ratio}}{\text{aircraft emission ratio}} - 1 \right) \quad (1)$$

where $\% \Delta$ is the percent difference between the CEMS and aircraft emission ratios relative to the emission ratio measured from the aircraft.

I.4.1. TexAQS 2000

For the 14 near-field plume transects in which SO_2 data were reported in 2000, the average difference between CEMS SO_2/CO_2 and aircraft $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios is -3.7% ($\pm 13.0\%$) (Figure 8) with a combined estimated uncertainty for each calculation of 19%. The geometric mean and standard deviation of a comparison of the ratios are 0.954 (or -4.6%) and 1.153, respectively, which suggests taking the arithmetic mean and standard deviation result in minimal bias.

For 14 transects in which NO_y data were reported in 2000, the average difference between CEMS NO_x/CO_2 and aircraft $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios equals 2.3% ($\pm 9.8\%$) (Figure 8), with a combined uncertainty of 18%. Using the same peak-integration method as used for $\Delta\text{SO}_2/\Delta\text{CO}_2$ results in an average difference of 10% ($\pm 14\%$), which suggests the two methods of determining an emission ratio are statistically identical as long as the

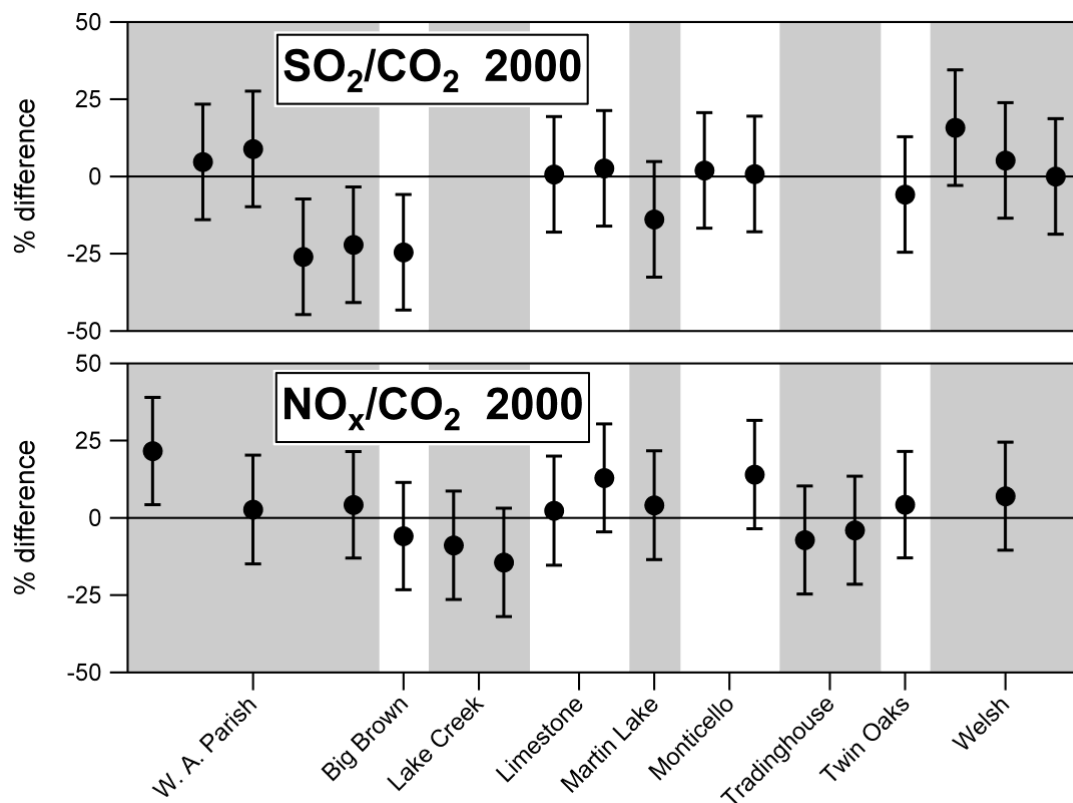


Figure 8. Percentage difference between CEMS and aircraft emission ratios relative to aircraft emission ratios for SO_2/CO_2 and NO_x/CO_2 during TexAQS 2000. Error bars are the combined (1σ) uncertainties of both measurements.

time responses of the instruments are similar. The geometric mean of the comparison is 1.9%.

I.4.2. TexAQS 2006

For 24 transects with SO_2 data in 2006, the average difference between CEMS SO_2/CO_2 and aircraft $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios is 1.1% ($\pm 11.6\%$) (see Figure 9), with a combined uncertainty of 17%. The geometric mean of the comparison is 0.5%. For 19 transects with NO_y data, the average percent difference between CEMS NO_x/CO_2 and aircraft

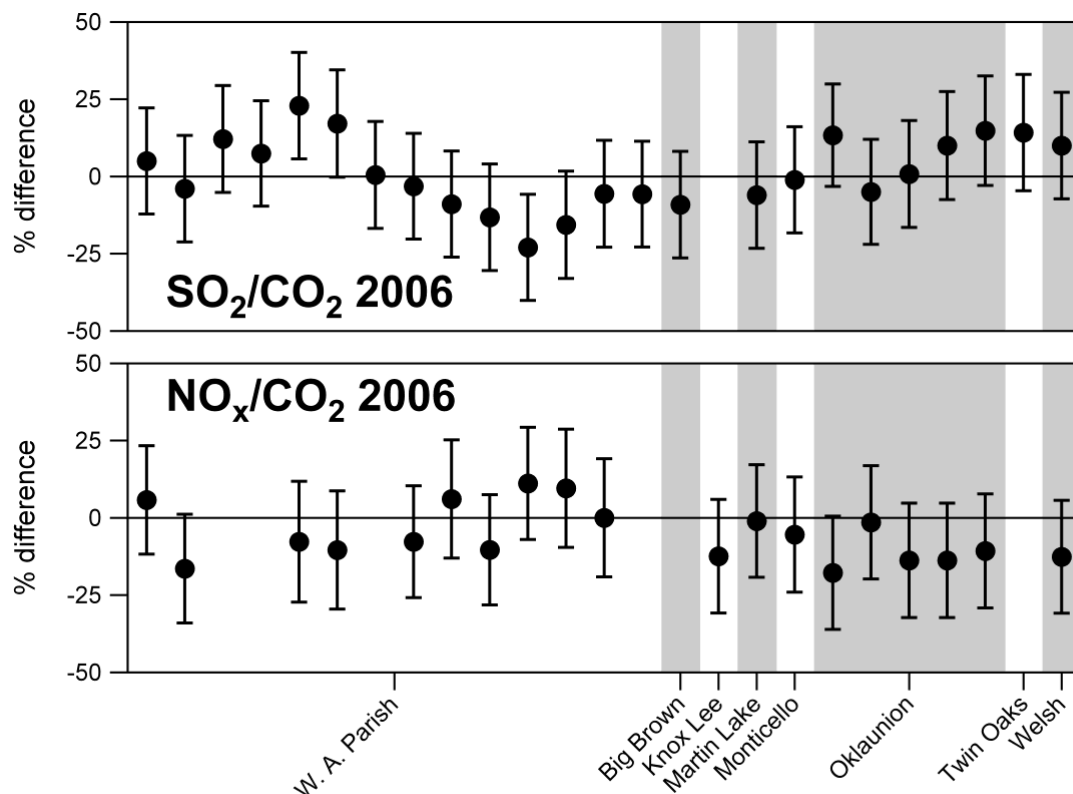


Figure 9. Percentage difference between CEMS and aircraft emission ratios relative to aircraft emission ratios for SO_2/CO_2 and NO_x/CO_2 during TexAQS 2006. Error bars are the combined (1σ) uncertainties of both measurements.

$\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios is -5.7% ($\pm 8.9\%$) (see Figure 9), with a combined uncertainty of 19%. The geometric mean of the comparison is -6.1% .

I.4.3. TexAQS 2000 and 2006 combined

The average percentage difference between all CEMS SO_2/CO_2 and aircraft $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios for 2000 and 2006 equals -0.7% ($\pm 12.1\%$); for NO_x/CO_2 and $\Delta\text{NO}_y/\Delta\text{CO}_2$ it is -0.9% ($\pm 10.4\%$). Assuming the standard deviation of the mean represents the estimated total uncertainty of the CEMS and aircraft measurements (i.e., $\sigma_{\text{total}} =$

$\sqrt{\sigma_{\text{CEMS}}^2 + \sigma_{\text{aircraft}}^2}$), we use this equation to estimate the uncertainty of the CEMS

measurements. The 1σ uncertainties for all aircraft measurements of $\Delta\text{SO}_2/\Delta\text{CO}_2$ and combining both study years average 11.2% and 11.4%, respectively, but these are conservative estimates. It is likely that the uncertainties of the $\Delta\text{NO}_y/\Delta\text{CO}_2$ NO_y measurements in this analysis are overstated because much of the NO_y uncertainty comes from uncertainties in the conversion of nitric acid, peroxyacyl nitrates (PANs), and other nitrogen-containing species to NO on the Au catalyst. Because we selected NO_y plumes when $\Delta\text{NO}_x/\Delta\text{NO}_y$ was greater than 90%, the NO_y measurement uncertainty for the plumes was likely on the order of 6% (summing in quadrature the 5% uncertainty for NO and a 3% uncertainty for NO_2 conversion in the NO_y converter). Assuming the CEMS and aircraft measurements contribute equally to the observed scatter, then for SO_2/CO_2 , $\sigma_{\text{CEMS}} = \sigma_{\text{aircraft}} = 8.6\%$; for NO_x/CO_2 , $\sigma_{\text{CEMS}} = \sigma_{\text{aircraft}} = 7.4\%$. If the errors from our experimental assumptions are small or are accounted for by the conservative measurement uncertainties, this suggests the (1σ) uncertainty for the CEMS ratios is on the order of 8%, which puts the uncertainty of the individual stack measurements of NO_x , SO_2 , and CO_2 at $\sim 6\%$, and significantly below the 10% required by statute.

I.4.4. Emission Differences between TexAQS 2000 and TexAQS 2006

I.4.4.1. NO_x/CO_2

The aircraft data provide an independent measure of the efficacy of the NO_x control strategy implemented by the State of Texas as a result of their State Implementation Plans (SIPs) between 2000 and 2006. These SIPs in part mandated NO_x reductions from many EGU power plants, including W. A. Parish, the only EGU power

plant sampled sufficiently often from the P-3 to provide a statistically meaningful comparison of NO_x/CO_2 ratios in both TexAQS 2000 and 2006.

In 2000, $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios from airborne data in near-field W. A. Parish plumes averaged $1.07 (\pm 0.16)$ ppbv/ppmv ($n = 3$). In 2006, W. A. Parish $\Delta\text{NO}_y/\Delta\text{CO}_2$ averaged $0.25 (\pm 0.04)$ ppbv/ppmv ($n = 11$). The aircraft measurements document a decrease in $\Delta\text{NO}_y/\Delta\text{CO}_2$ emissions from W. A. Parish of 77% between 2000 and 2006. The NO_x/CO_2 reduction according to annual CEMS data is 79% (1.14 in 2000; 0.24 in 2006). W. A. Parish reported a 72% decrease in NO_x mass emitted between the two study years, largely due to the installation of selective catalytic reduction (SCR) NO_x scrubbers after the first TexAQS field study took place. This reduction in NO_x is seen directly as a reduction in the atmospheric mixing ratio of NO_x (and NO_y) downwind of W. A. Parish (Figure 10). For a given level of CO_2 above background, NO_y levels were

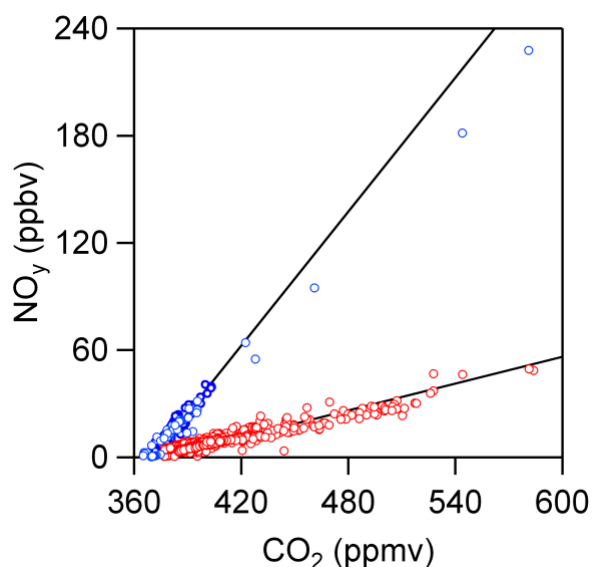


Figure 10. All W. A. Parish transect data from TexAQS 2000 (blue) and TexAQS 2006 (red). Lines with slopes 1.25 and 0.25 are shown for comparison.

consistently and significantly lower downwind of W. A. Parish in 2006 than they were in 2000. Therefore, the analysis using aircraft data confirms that W. A. Parish has substantially reduced their NO_x emissions, and that the ratios of emissions the plant reported via CEMS appear to be accurate. Further, because aircraft $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios from other power plants compare just as favorably to the CEMS NO_x/CO_2 ratios, this analysis confirms the use of CEMS data to verify EGU compliance with the mandated emissions reductions.

I.4.4.2. SO_2/CO_2

The $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratios calculated from the aircraft and CEMS data were also in quantitative agreement with no significant bias for either study year (see Figures 8 and 9). No general trend is detectable in the SO_2 emissions between 2000 and 2006 for these power plants. Data from EGUs which burn natural gas only (and do not emit significant amounts of SO_2 compared to coal-fired plants) are not shown; however, our analysis was carried out and in each instance a slope was generated that confirmed no detectable emission of SO_2 .

I.4.4.3. CO/CO_2

We examined $\Delta\text{CO}/\Delta\text{CO}_2$ ratios in plume transects less than 3 hours old (CO typically has an atmospheric lifetime of weeks or months) and less than 40 km from the point source. Because the EPA does not require point sources to report CO as part of the CEMS, we used 2000 and 2006 annual TCEQ CO/NO_x inventory ratios and multiplied these annual ratios by hourly CEMS NO_x/CO_2 ratios to approximate an expected hourly CO/CO_2 ratio for each EGU.

Nicks et al. (2003) suggested that 1999 inventories of CO emissions from Big Brown, Martin Lake, and Monticello underestimated CO emissions from these EGUs by more than a factor of 20, assuming the emissions measured from the aircraft during TexAQS 2000 were representative of normal operating conditions. Using 2000 TCEQ inventories not available at the time to Nicks et al. (2003; it typically takes a few years to finalize EPA and TCEQ emission inventories), we reach a similar result (see Table 4). By 2006, the CO emissions inventory was in substantially better agreement with aircraft measurements, and the CEMS estimated hourly CO/CO₂ emission ratios are

Table 4. Aircraft-derived and inventory-tabulated CO/CO₂ emission ratios

Source	2000 ^a	2000 ^b	2006 ^c
	Derived ÷ tabulated	Derived ÷ tabulated	Derived ÷ tabulated
Martin Lake	29	33	1.5
Monticello	34	32	0.81
Big Brown	22	26	1.3

^afrom Nicks et al. (2003) using 1999 inventories.

^bemissions obtained from EPA and TCEQ inventories for 2000.

^cemissions obtained from EPA and TCEQ inventories for 2006.

now at least within a factor of two of the ratios derived from airborne data (Figure 11). The most significant change between TexAQS 2000 and 2006 in this regard was that in the early part of the decade, TXU/Luminant plants (Big Brown, Monticello, and Martin Lake) began measuring CO in situ via CEMS monitors rather than using EPA AP-42 emissions factors to calculate CO emissions [Randy Hamilton, TCEQ; personal communication, 1 July 2009]. Therefore, we conclude the tabulated CO emissions from the 1999 and 2000 point source emissions inventories, calculated using

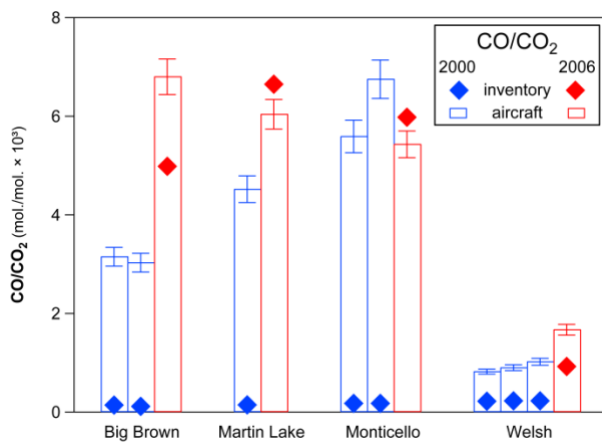


Figure 11. A comparison of CO/CO₂ ratios from both TexAQS study years. Each bar represents a separate plume transect. The inventory ratios represent annual CO/NO_x ratios reported to TCEQ multiplied by hourly NO_x/CO₂ CEMS ratios.

AP-42 emission factors, substantially under-represented actual CO emissions from the TXU/Luminant plants, consistent with the conclusions in the work of Nicks et al. (2003).

For Welsh and W. A. Parish power plants, annual inventory CO emissions appear to be relatively accurate. Welsh appears to be a consistent emitter of CO, and the inventory values typically disagree by a factor of two or three, but this could be explained by any error in our assumption that CO is co-emitted with NO_x at a constant rate. CO emissions from W. A. Parish may have been underreported in 2000, but because they were highly variable and our sample size was small, it is difficult to draw any quantitative conclusions. W. A. Parish CO emissions do appear to be lower in 2006, however. W. A. Parish has been omitted from Figure 11 because the discrepancies between aircraft measurements and the TCEQ inventory do not appear to be systematic.

I.4.5. Emissions from Separate Stacks

The EGUs studied here generally have one or two stacks within close proximity and at identical heights. The one exception is W. A. Parish, which has eight combustion units with eleven stacks at four different heights, ranging from 51 to 183 m AGL, separated by as much as one kilometer. One or two stacks serve a combustion unit burning either coal or natural gas, with distinct NO_x/CO_2 and SO_2/CO_2 emission ratios characteristic of each fuel type. Figure 6 shows the hourly total NO_x/CO_2 emission ratio from W. A. Parish. The first increase in this emission ratio during the night of 26 September is due to an increase from ~ 0.25 to ~ 0.60 ppbv/ppmv in NO_x/CO_2 from coal-burning unit 5 (referred to as WAP5 in the CEMS inventory), likely due to its SCR NO_x scrubber failing or having been turned off for maintenance. The second increase during 27 September is due to the operation of gas units (which were not in operation during 26 September, according to the CEMS inventory), characterized by a higher NO_x/CO_2 emission ratio than the coal units. In the following section, we exploit periods of limited vertical atmospheric mixing to assess CEMS accuracy for a subset of stacks at an EGU with multiple stacks.

On 5 October 2006, a cloudy day with broken cumulus clouds, the P-3 made two transects of the W. A. Parish plume: the first was 1.7 km (and approximately 8 min) downwind; the second was 2.8 km (and approximately 20 min) downwind. Both transects were evidently dominated by the gas unit emissions, because the $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratio was much higher (see Figure 12) and the $\Delta\text{SO}_2/\Delta\text{CO}_2$ ratio was much lower than observed on other days. According to the CEMS data for the second transect, unit 3 was the only unit with a NO_x/CO_2 emission ratio higher than that observed from the aircraft

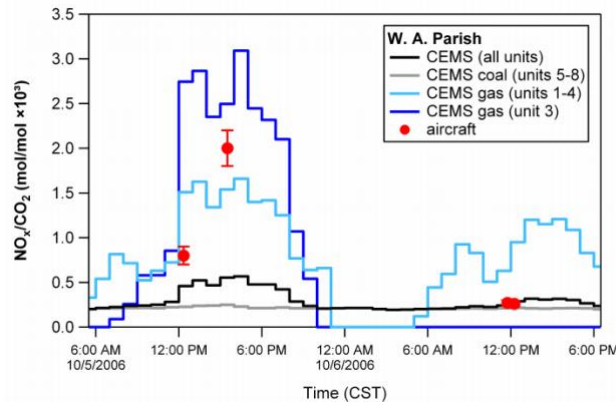


Figure 12. $\Delta\text{NO}_y/\Delta\text{CO}_2$ ratios from four P-3 transects of the W. A. Parish plume, all less than 3 km downwind of the power plant, plotted with hourly CEMS emission data.

data, which suggests the plume sampled by the aircraft was specifically dominated by emissions from unit 3. For comparison, two plume transects from 6 October, a day with few clouds, are also shown in Figure 12. The two 6 October transects were 1.9 km (and approximately 11 min) and 2.7 km (and approximately 13 min) downwind, respectively, with transect altitudes and wind speeds similar to that of 5 October. Therefore, it was likely that the clouds on 5 October, by limiting solar radiation-driven convection, prevented the W. A. Parish emissions from fully mixing in the vertical before the P-3 sampled the plume. Rather than estimating the degree to which the W. A. Parish plume had been mixed on this day, the two 5 October transects have been omitted from our overall analysis of emission ratios. However, for the second of the two 5 October transects, the $\Delta\text{CO}/\Delta\text{CO}_2$ emission ratio was $4.23 (\pm 0.21)$ ppbv/ppmv, by far the highest CO emission rate measured from W. A. Parish by the P-3 in 2006 (see Table 4 for comparison). This is further evidence the gas-fired units may be responsible for a large share of the CO emissions from W. A. Parish, as previously suggested by Nicks et al. (2003).

Similarly, during the 8 October 2006 flight, the first plume transect 12 km (35 min) downwind of W. A. Parish occurred just after sunset and suggested the emissions had not completely mixed (Figure 13). The first part of the plume (labeled ‘1’ in Fig. 13) showed an SO₂ enhancement with a relatively small NO_x enhancement; the second part (labeled ‘2’ in Fig. 13) showed a large NO_x enhancement and no detectable SO₂ enhancement. The two parts of the plume were analyzed separately, and the emission ratios suggest the first part of the plume was dominated by emission from the coal stacks and the second part was dominated by the gas stacks (Figure 14). Further, the plume locations are qualitatively consistent with the relative location of the stacks at W. A.

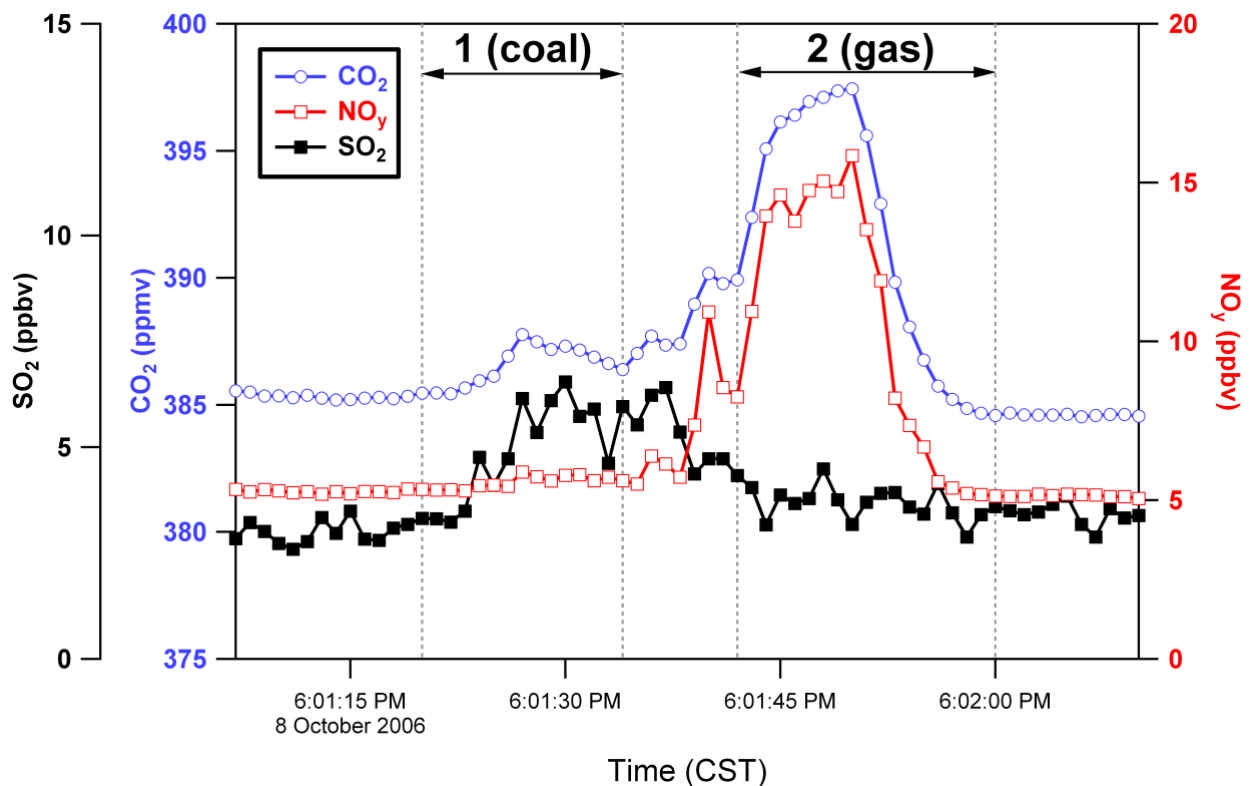


Figure 13. P-3 transect of W. A. Parish plume, 8 October 2006, showing physical separation of coal and gas unit emissions under conditions of reduced atmospheric mixing. The results of a separate analysis of each part of the plume, 1 and 2, are shown in Figure 14.

Parish. As the aircraft flew northwestward with winds from the northeast, it first encountered the emissions from the coal-burning stacks, which are located to the south of the gas-burning stacks. All ratios in Figure 14 agree to within the combined uncertainties of the aircraft and CEMS measurements. This suggests no bias in CEMS measurements from the gas vs. the coal stacks at W. A. Parish. While the qualitative analysis is compelling, rather than estimating which stack's emissions were sampled by the P-3, these transects were omitted from the overall quantitative analysis.

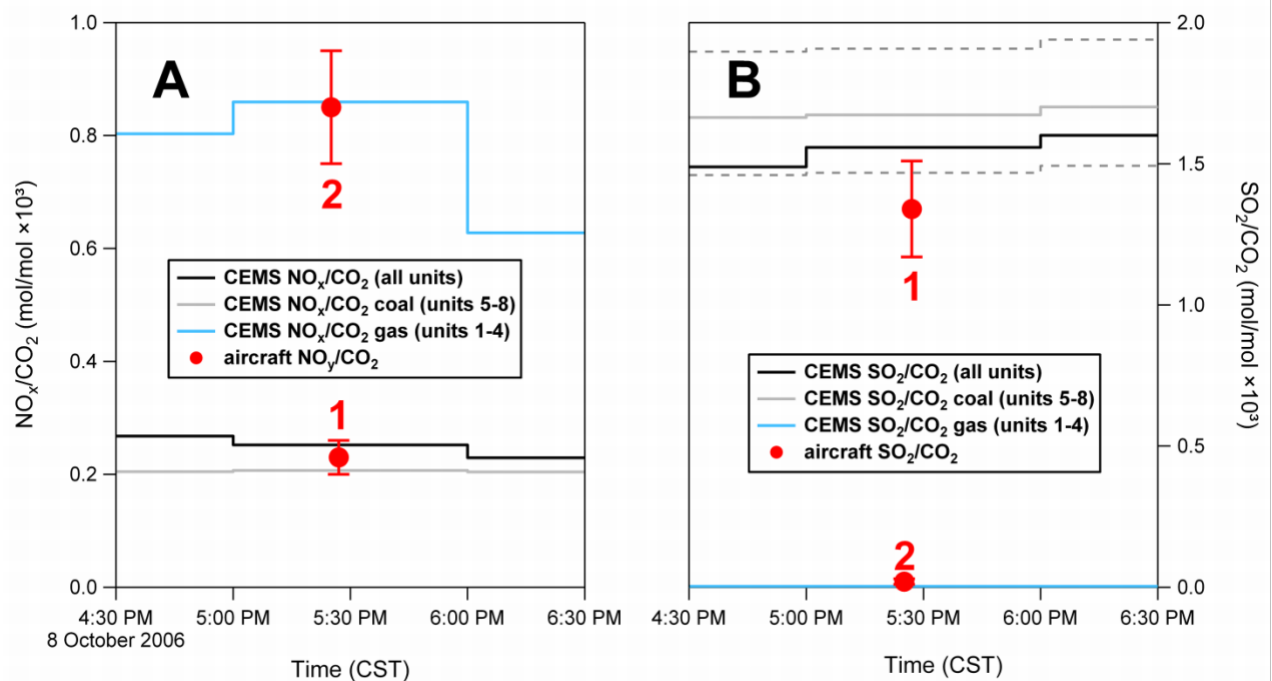


Figure 14. NO_x/CO_2 (A) and SO_2/CO_2 (B) emission ratios determined from separately analyzing the first and second parts of the plume data in Figure 13, compared with CEMS-derived emission ratios. The dotted lines in (B) represent a 14% uncertainty in the SO_2/CO_2 ratio for the combined W. A. Parish coal units.

I.4.6. Direct emissions of NO₂

NO_x emissions from an EGU are generally expected to be emitted primarily as NO, though there may be small direct emissions of NO₂. The ratio in which NO and NO₂ are emitted is important for understanding ozone production, because NO emissions titrate O₃ near the source and must be oxidized to NO₂ by a species other than O₃ (e.g., peroxy radicals derived from volatile organic compound oxidation) before net ozone production can occur. Direct emissions of NO₂, on the other hand, act as a direct source of ozone via photolysis. For this reason, many studies have been conducted to measure the NO₂/NO_x ratio from gasoline and diesel automobile engines (e.g., see Carslaw & Beevers, 2004. These studies typically ratio an enhancement in total oxidant, or odd oxygen (O_x = NO₂ + O₃), to an enhancement in NO_x, and are conducted during the daytime very near the NO_x source before ozone production or further NO_x oxidation can take place. These studies focus on the following set of reactions:



Thus, during the daytime, the odd oxygen atom emitted in NO₂ is later found in either NO₂ or O₃. However, when NO_x is emitted at night, we may ignore odd oxygen production via subsequent ozone photochemistry, which makes it simpler to quantify odd oxygen downwind of a NO_x-emitting point source. At night, NO_x may undergo the following additional reactions:





Thus, before N_2O_5 is lost to nitric acid (eq. 8), the nocturnal odd oxygen budget is:

$$\text{O}_x (\text{nocturnal}) = \text{O}_3 + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 \quad (9)$$

where the stoichiometric coefficients represent the number of odd oxygen atoms present in the molecule (Brown et al., 2006). Using this definition of nocturnal O_x , we attempt to quantify the NO_2 directly emitted from one EGU during a nighttime flight.

On the night of 10 October 2006, several transects were flown downwind of Oklaunion power plant, a coal-burning EGU with one stack. All plume transects occurred after dark, and most of the emissions encountered were transported downwind at times when j -values were essentially zero. To ensure minimal O_x loss via NO_3 and N_2O_5 loss in the presence of aerosols (Dentener & Crutzen, 1993), we examine six transects which had both a significant (>15 ppbv) NO enhancement and a NO_x/NO_y ratio greater than 90%. The presence of NO in these plumes limits the further, nighttime oxidation of NO_x by rapidly converting NO_3 back to NO_x (equation 7). These transects range from 18 to 60 km downwind of Oklaunion, with transport times ranging from 36 (± 5) min to 2.0 (± 0.25) h. The ratio of NO_2 to NO_x at the stack is deduced from the aircraft measurements as an enhancement in O_x :

$$\left(\frac{\text{NO}_2}{\text{NO}_x}\right)_{\text{stack}} = \frac{\Delta\text{O}_x}{\Delta\text{NO}_x} = \left(\frac{\Delta\text{O}_3 + \Delta\text{NO}_2 + 2\Delta\text{NO}_3 + 3\Delta\text{N}_2\text{O}_5}{\Delta\text{NO} + \Delta\text{NO}_2 + \Delta\text{NO}_3 + 2\Delta\text{N}_2\text{O}_5}\right)_{\text{aircraft}} \quad (10)$$

where the numerator of the aircraft ratio represents the sum of odd oxygen species and the denominator represents the sum of NO_x and its nocturnal oxidation products. The aircraft ratio accounts for the nighttime conversion of NO to NO_2 by reaction with O_3 during transport, the conversion of NO and NO_2 to NO_3 and N_2O_5 , and the conversion of

NO₃ and N₂O₅ to NO₂ in a high-NO environment. In the near-field plume transects we examined, the presence of NO in the plume prevented NO₃ from rising significantly above background levels and prevented N₂O₅ from rising above 0.5 ppbv on the fringes of the plume. This in turn delayed the heterogeneous production of HNO₃, previously shown to have been a slow process during TexAQS 2006 (Brown et al., 2009) and confirmed by HNO₃ measurements in these plumes. Also, measurements of PANs show these species did not play significant roles in the odd oxygen budget for near-field nighttime data, so these species have been omitted from our analysis. Again due to different instrument time responses, integrated plume areas were used to calculate the emission ratio. The results are presented in Figure 15. NO₂/NO_x ratios calculated using NO₂ data from the P-CL NO₂ instrument average 6.1% (±3.9%). Ratios calculated using NO₂ data from the CaRDS NO₂ instrument average 6.7% (±2.7%). For comparison, an ODR slope calculation of $[\Delta\text{O}_3 + \Delta\text{NO}_2 (\text{CaRDS})]/\Delta\text{NO}_y$ yielded an average ratio of 6.8% (±3.8%). The blue trace in Figure 15 shows $j(\text{NO}_2)$, a measure of potential daytime odd oxygen formation, estimated at Oklaunion power plant's location based on clear-sky $j(\text{NO}_2)$ data measured from the P-3 at sunset during TexAQS 2006. The time-integrated $j(\text{NO}_2)$, equivalent to less than 2 minutes of noontime insolation, suggests odd oxygen formation in these plumes was minimal for the two transects that had been emitted before full sunset.

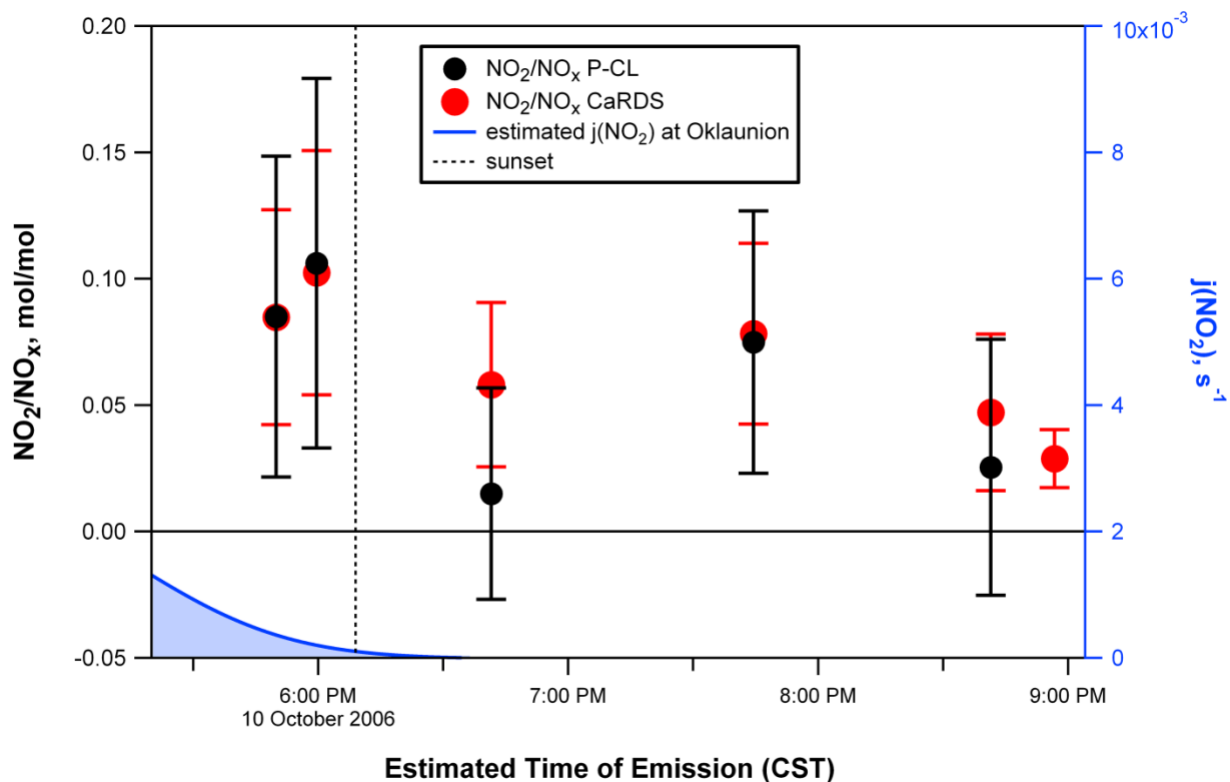


Figure 15. NO₂/NO_x ratios (calculated as $\frac{\Delta O_3 + \Delta NO_2 + 2\Delta NO_3 + 3\Delta N_2O_5}{\Delta NO + \Delta NO_2 + \Delta NO_3 + 2\Delta N_2O_5}$ from the aircraft data) for six plumes downwind of Oklaunion power plant on the night of 10 October 2006, with (1 σ) error bars. The blue trace is j(NO₂) as a function of time estimated for the Oklaunion power plant location.

I.5. Conclusions

Measurements of $\Delta NO_y/\Delta CO_2$ and $\Delta SO_2/\Delta CO_2$ emission ratios made aboard aircraft agree quantitatively with data from EGU power plant CEMS for both 2000 and 2006 TexAQS study years. NO_x/CO₂ ratios agree to within $\pm 11\%$; SO₂/CO₂ ratios agreed to within $\pm 12\%$. This is an independent confirmation using a top-down approach that emissions ratio data provided through CEMS are accurate to within their specified accuracy of $\pm 14\%$.

Further, from the aircraft data we confirm that W. A. Parish has decreased its NO_x emissions by about 80% in accordance with the CEMS emission inventory data between 2000 and 2006 as a result of installing SCR scrubbers after 2000. Aircraft data also suggest that the current TCEQ inventories of CO emissions are more accurate than inventories of CO emissions from 1999 and 2000 for the point sources studied here, a direct result of implementing CO CEMS measurements rather than using calculations based on AP-42 estimates of CO emissions factors.

Finally, we have shown using two separate NO₂ measurement techniques that NO₂/NO_x emission ratios from Oklaunion EGU sampled on one night were approximately 6%. We plan to continue to evaluate NO₂ direct emissions in future field missions using recently improved NO₂ measurements (Fuchs et al., 2009; Pollack et al., 2011).

1.b. Conclusions of Publication I

The work of Peischl et al. (2010) showed the Texas Commission on Environmental Quality that the regulations on power plant emissions had their intended effect: between 2000 and 2006, both SO₂ and NO_x emissions had decreased relative to CO₂ emissions. In addition, air quality regulators implemented controls on emissions of VOCs from the petrochemical industry, and automobiles continued to emit less NO_x and VOCs. Soleimanian et al. (2022) showed that not only have NO_x emissions decreased in the Houston region, citing the work of Peischl et al. (2010), but the yearly mean MDA8 O₃ in Houston had decreased from 2000 to 2020. For the 2019–2021 time period, the O₃ design values for Houston and Dallas are 0.077 and 0.076 ppmv, respectively

(<https://www.epa.gov/ground-level-ozone-pollution/timeline-ozone-national-ambient-air-quality-standards-naaqs>, downloaded August 2022). Thus, it would appear air

quality managers in Texas achieved their goals of reducing O₃ pollution. However, both cities remain in nonattainment of the EPA's air quality standards because the standard was reduced to 0.075 ppmv in 2008, and then to 0.070 ppmv in 2015. This underscores the need for continually verifying emissions inventories that affect air quality.

The work of Peischl et al. (2010) has also been cited by the broader scientific community for numerous reasons. For example, recent work has cited this paper for: evidence for the reduction in NO_x emissions from power plants (Wren et al., 2020); evidence of CO emissions from power plants (DiGangi et al., 2023); the reliability of the accuracy of the Continuous Emissions Monitoring Systems (Lindenmaier et al., 2014; Day et al., 2019; Angevine et al., 2020; Anderson et al., 2021); Continuous Emissions Monitoring Systems uncertainties (Keppel-Aleks & Washenfelder, 2016; Salmon et al., 2018; Hajny et al., 2019); the technique used to measure primary NO₂ emissions (Wild et al., 2017); and the measured mix of NO and NO₂ in NO_x emissions from power plants (Fry et al., 2018; Meidan et al., 2019), which directly impacts O₃ production in the plume downwind. Thus, the impacts that power plants have on air quality and climate ensure that the work of Peischl et al. (2010) will continue to be cited in the coming years.

2. Comparing spatially broad airborne measurements to a local, in situ study using an atmospheric mixing model

2.a. Introduction to Publication II

In 2006, California was one of the first U.S. states to enact climate legislation with a goal to decrease GHG emissions to 1990 levels by 2020. This required compiling GHG inventories for 1990 and for each year beginning in 2005. In 2010, NOAA led the California Nexus (CalNex) field campaign, one of the goals of which was to assess California's GHG inventory (Ryerson et al., 2013).

One significant emission sector in their CH₄ inventory was rice cultivation, which is grown mainly in the Sacramento Valley in northern California in an area roughly a third of the size of County Cork, Ireland. Prior to the CalNex campaign, McMillan et al. (2007) made measurements at a rice paddy for two years and reported temporal fluxes of CH₄ and CO₂ through parts of three growing seasons. One question scientists had was whether these results held for only one rice paddy, or if they could be extrapolated to the entire rice growing region in the Sacramento Valley.

Peischl et al. (2012) discovered that the results from one rice paddy did apply to the entire rice growing region. Peischl et al. (2012) used atmospheric data from one flight during the peak of the rice growing season in a mixing model to determine the relative fluxes of CO₂ and CH₄ from this region of California, which were within the range of emissions reported by McMillan et al. (2007).

II. Airborne Observations of Methane Emissions from Rice Cultivation in the Sacramento Valley of California

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II. Abstract. Airborne measurements of methane (CH₄) and carbon dioxide (CO₂) were taken over the rice growing region of California's Sacramento Valley in the late spring of 2010 and 2011. From these and ancillary measurements, we show that CH₄ mixing ratios were higher in the planetary boundary layer above the Sacramento Valley during the rice growing season than they were before it, which we attribute to emissions from rice paddies. We derive daytime emission fluxes of CH₄ between 0.6 and 2.0% of the CO₂ taken up by photosynthesis on a per carbon, or mole to mole, basis. We also use a mixing model to determine an average CH₄/CO₂ flux ratio of -0.6% for one day early in the growing season of 2010. We conclude the CH₄/CO₂ flux ratio estimates from a single rice field in a previous study are representative of rice fields in the Sacramento Valley. If generally true, the California Air Resources Board (CARB) greenhouse gas inventory emission rate of 2.7×10^{10} g CH₄/yr is approximately three times lower than the range of probable CH₄ emissions ($7.8 - 9.3 \times 10^{10}$ g CH₄/yr) from rice cultivation derived in this study. We attribute this difference to decreased burning of the residual rice crop since 1991, which leads to an increase in CH₄ emissions from rice paddies in succeeding years, but which is not accounted for in the CARB inventory.

II.1. Introduction

Methane (CH₄) is a potent greenhouse gas whose emissions in California are regulated under Assembly Bill 32, signed into law as the Global Warming Solutions Act of 2006, which requires statewide greenhouse gas emissions not to exceed 1990 levels

by the year 2020. Effective regulation requires accurate knowledge of the distribution and relative contributions of CH₄ sources within California, which include livestock, landfills, wastewater treatment, oil and gas drilling and distribution, and rice cultivation. An inventory of annually-averaged greenhouse gas emissions for California was developed by the California Air Resources Board (CARB) in order to quantify these emissions.

In CARB's CH₄ inventory, rice cultivation accounts for approximately 1.8% of California's annually-averaged anthropogenic CH₄ emissions (<http://www.arb.ca.gov/cc/inventory/data/data.htm>, accessed August 2012). However, the majority of these rice emissions occur during the growing season, which typically runs from mid-May to the end of August (McMillan et al., 2007). Therefore, during the growing season, rice cultivation should account for approximately 6–7% of California's anthropogenic methane emissions, which is similar in magnitude to the emissions from oil and gas extraction (approximately 8%), making it one of the larger non-livestock methane emission sectors during this time of year.

Several previous works have examined CH₄ fluxes from California rice paddies (e.g., Cicerone et al., 1992; Lauren et al., 1994; Bossio et al., 1999; Fitzgerald et al., 2000; Redeker et al., 2000; McMillan et al., 2007). Here we focus on the work of McMillan et al. (2007) because they additionally measured carbon dioxide (CO₂) fluxes, which, in combination with CH₄ fluxes, provide a more complete greenhouse gas picture and a basis for a flux ratio comparison. McMillan et al. (2007) measured fluxes at one rice paddy (39.28°N latitude, 122.18°W longitude) located in the Sacramento Valley of California. This was a multi-year project that included three growing seasons

from 2000 to 2002. They showed that during the growing season, CH₄ and CO₂ emissions were negatively correlated during the daytime (i.e., CH₄ was emitted while CO₂ was taken up by the rice crop during photosynthesis), and positively correlated at nighttime (i.e., CH₄ was emitted while CO₂ was respired). They determined stoichiometric flux ratios of CH₄ to CO₂ throughout the project. Although CH₄ is produced by microbes in the soil, the main pathway for this CH₄ to reach the atmosphere during the growing season is through the rice plants (Cicerone & Shetter, 1981; Le Mer & Roger, 2001), while other pathways, such as ebullition and diffusion, are co-located with the rice plants. As a result, correlations of CH₄ emissions with CO₂ uptake reported by McMillan et al. (2007) are high ($r^2 > 0.98$), and it is this signal, once vertical mixing has occurred, that we determine from samples taken aboard an instrumented research aircraft. Specific to the analysis below, McMillan et al. (2007) determined daytime CH₄/CO₂ flux ratios of −0.6% (per carbon, or mole to mole) during the seedling stage (0–23 days after planting) and −2.7% during the mid-vegetative stage (24–47 days after planting) of rice growth. However, that study was necessarily confined to one rice paddy and dependent on the farming practices of one rice farmer. This paper complements the work of McMillan et al. (2007) by expanding the spatial domain to the entire rice growing region of the Sacramento River Valley for three days: two in the Spring of 2010 and one in the Spring of 2011.

We use data from two flights of a chemically-instrumented National Oceanic and Atmospheric Administration (NOAA) P-3 research aircraft over the rice-growing region of the Sacramento Valley, where the majority of rice paddies in California are located (e.g., see https://www.nass.usda.gov/Charts_and_Maps/Crops_County/), to examine the

possible sources of CH₄ emissions during the flights. The two flights occurred on 11 May (before the growing season) and 14 June (during the growing season) 2010, during the California Research at the Nexus of Air Quality and Climate Change (CalNex) field study. For the 14 June flight, we use ancillary measurements of black carbon (BC) to separate biomass burning emissions of CH₄ and CO₂ from the expected emissions of CH₄ and uptake of CO₂ from the rice paddies. We also use correlations with carbon monoxide (CO) to discriminate between urban and rice paddy emissions of CH₄. Next, we show that CH₄ and CO₂ data over rice paddies are consistent with the findings of McMillan et al. (2007), and use a mathematical model to determine that the ratios of CH₄ and CO₂ fluxes measured by McMillan et al. (2007) from one rice paddy in 2000–2002 are representative of an area-wide survey of the majority of California’s rice paddies for one day in 2010.

Additionally, we use data from a flight of an instrumented Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter on 15 June 2011, during the California Airborne Biogenic Volatile Organic Compound Emission Research in Natural Ecosystem Transects (CABERNET) field campaign, which support the CH₄/CO₂ flux ratio determined by measurements from the NOAA P-3 in 2010 and the work of McMillan et al. (2007).

II.2. Instrumentation

II.2.1. CO₂ and CH₄ Instrumentation and Description

CO₂ and CH₄ were measured aboard both aircraft using a modified commercial wavelength-scanned cavity ring-down analyzer (Picarro 1301-m) (Crosson, 2008).

Though sold as a CO₂/CH₄/H₂O analyzer, we included a drier in the sample flow and did not measure H₂O to increase the sampling frequency for both CO₂ and CH₄ to 1 Hz.

Atmospheric air was sampled through a 0.95 cm (3/8 in.) OD stainless steel rearward facing inlet on the NOAA P-3 and from the main inlet on the CIRPAS Twin Otter (Hegg et al., 2005), and dried to a dew point temperature of -78°C by passage through a 200-strand Nafion dryer (p/n PD-200T-24MPS) and a dry ice trap (Peischl et al., 2010). The absorption cell pressure was controlled at 140 Torr (± 0.2 Torr during smooth flight, and ± 0.5 Torr during typical boundary layer flight conditions; all stated uncertainties are $\pm 1\sigma$). Absorption cell pressure instability led to decreased precision in the turbulent daytime boundary layer, as discussed in more detail below.

Immediately inside the fuselage, two CO₂ and CH₄ calibration gas standards were regularly delivered to the inlet line during flight to evaluate instrument sensitivity. The calibration standards bracketed the expected ambient range of each gas and were known to within ± 0.07 ppmv CO₂ and ± 1 ppbv CH₄ (all CO₂ and CH₄ mixing ratios are reported as dry air mole fractions). The calibration gases were added at a flow rate sufficient to displace ambient air and overflow the inlet. These flight standard tanks, or secondary standards, were calibrated before and after the field project using primary CO₂/CH₄ standard tanks tied to the WMO standard from the Global Monitoring Division (GMD) at the NOAA Earth System Research Laboratory (ESRL; Dlugokencky et al., 2005; Zhao & Tans, 2006). A third calibration standard (referred to here as a “target”; Daube et al., 2002; Peischl et al., 2010) was regularly introduced to the inlet between calibrations and treated as an unknown to evaluate long-term instrument performance (Figure 16). The accuracy of the 20-second averaged target retrievals did

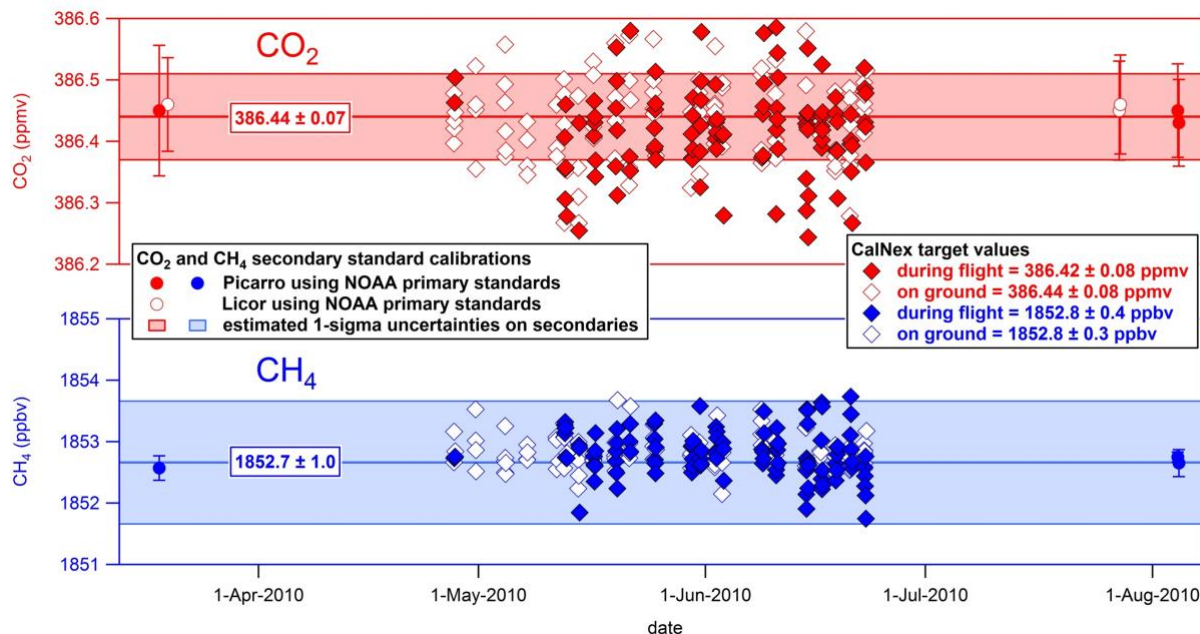


Figure 16. In-flight target retrievals from CalNex data set (red and blue diamonds). Pre-flight target retrievals are included for comparison (white diamonds). Calibrated in the lab with primary standards from NOAA ESRL GMD before and after CalNex, the CO₂ target tank averaged 386.44 ppmv and the CH₄ target tank averaged 1852.7 ppbv, with no significant drift in either. These numbers are represented by the solid horizontal lines in the graphs. In-flight CO₂ target retrievals averaged 386.42 (± 0.08) ppmv; pre-flight target retrievals while the aircraft was on the ground averaged 386.44 (± 0.08) ppmv. In-flight CH₄ target retrievals averaged 1852.8 (± 0.4) ppbv; pre-flight target retrievals averaged 1852.8 (± 0.3) ppbv. The $\pm 1\sigma$ limits are represented by the shaded area in the graph. Due to a leak in the calibration system, in-flight calibrations from 30 April – 11 May are not included.

not depend on flight conditions, as the pre-flight target retrievals are statistically equal to the in-flight retrievals. Isotopic corrections for ¹³C and ¹⁸O were made to calibration and ambient CO₂ data following the work of Chen et al. (2010), and assumptions of isotopic abundance in California air between May and June were based on long term measurements at Trinidad Head and Pt. Arena, California (White & Vaughn, 2009). To

check these isotopic corrections, the flight standard tanks were additionally calibrated for CO₂ with a different set of GMD primary tanks using a modified LI-COR 6262 CO₂ analyzer (Peischl et al., 2010). These analyses yielded the same calibrated CO₂ mixing ratio value as those performed with the aircraft instrument (Figure 16). The uncertainties of the flight standards, shown as the shaded areas in Figure 16, are dominated by the uncertainties in the primary standards.

Independent of the target retrievals, we estimate a total uncertainty in the measurements by summing in quadrature the known sources of uncertainties. We derive combined inaccuracy in CO₂ of ± 0.10 ppmv and in CH₄ of ± 1.2 ppbv, with the error attributed to each individual term as follows (given for CO₂, CH₄): primary standard uncertainty (± 0.07 ppmv, ± 1.0 ppbv), additional secondary standard uncertainty (± 0.02 ppmv, ± 0.1 ppbv), calibration uncertainty (± 0.06 ppmv, ± 0.6 ppbv), and isotope correction uncertainty (± 0.015 ppmv, negligible). One-second imprecision of the CO₂ measurement was ± 0.10 ppmv during smooth flight and ± 0.15 ppmv during turbulent flight. One-second imprecision of the CH₄ measurement was ± 1.5 ppbv during smooth flight and ± 2.0 ppbv during turbulent flight. The estimated uncertainties were similar for the installation on the CIRPAS Twin Otter.

A separate instrument aboard the NOAA P-3 measured CO₂ and CH₄, along with CO and nitrous oxide (N₂O), by quantum cascade laser direct absorption spectroscopy (QCLS; Kort et al., 2011). The mean differences between all 10-s averaged QCLS and Picarro CalNex measurements were 0.01 (± 0.53) ppmv CO₂ and 4.4 (± 3.4) ppbv CH₄. The mean CO₂ differences were larger for flights in which the aircraft cabin temperature

approached 40°C; the comparison therefore does not include data from these flights (30 April, 4 May, and 7 May).

II.2.2. Carbon Monoxide, Black Carbon, Ethane, Propane, and Nitrogen Oxides on the NOAA P-3

CO was measured by vacuum ultraviolet fluorescence spectroscopy (Holloway et al., 2000). Imprecision of the 1-s CO data is ± 1 ppbv; inaccuracy is estimated to be $\pm 5\%$. During CalNex, the mean difference between all 10-s averaged CO measurements for this and the QCLS instrument was 1.2 (± 3.3) ppbv. Black carbon aerosol was measured using a Single Particle Soot Photometer (Schwarz et al., 2008). Imprecision of the 1-s BC mass mixing ratio data averaged $\pm 20\%$ for the data used here; inaccuracy is estimated to be $\pm 30\%$. Ethane and propane were measured from whole air samples (WAS) (Colman et al., 2001). For both measurements, the detection level is 3 pptv and imprecision is $\pm 2\%$; inaccuracy is estimated to be $\pm 10\%$. Nitric oxide (NO) was measured by ozone-induced chemiluminescence (CL; Ryerson et al., 2000). Imprecision of the NO measurement is ± 0.01 ppbv for the 1-s data used here; inaccuracy is estimated to be $\pm 3\%$. Nitrogen dioxide (NO₂) was measured by photolysis-CL (Pollack et al., 2011). Imprecision of the NO₂ measurement is ± 0.03 ppbv for the 1-s data used here; inaccuracy is estimated to be $\pm 4\%$. All data reported are 1-s, except for comparisons with WAS, in which 1-s data were averaged over the sample fill time (typically 4–10 s).

II.2.3. Acetaldehyde on the CIRPAS Twin Otter

Acetaldehyde was measured by proton transfer reaction mass spectrometry (PTRMS) for 100 ms approximately every 0.8 s. Imprecision of the 10-Hz acetaldehyde data is ± 0.27 ppbv; inaccuracy is estimated to be $\pm 15\%$ (Karl et al., 2007).

II.3. Experiment

The NOAA P-3 twice flew over the rice-growing region of the Sacramento Valley (Figure 17) in order to assess changing CH₄ emissions from rice paddies. The first flight on 11 May 2010 occurred just prior to the growing season while many fields were being flooded; the second flight on 14 June 2010 took place early in the growing season. The map in Figure 17a shows the distribution of potential sources of CH₄ in this region, including rice paddies, natural gas wells, dairies (Salas et al., 2008), wetlands, point sources, known biomass burning events, and urban areas in the Sacramento Valley. The rice and wetland data are from the United States Department of Agriculture - National Agricultural Statistics Service (<http://nassgeodata.gmu.edu/CropScape/>).

The rice paddy studied by McMillan et al. (2007; yellow square, Figure 17a) was planted in mid- to late-May in 2001–2002, approximately one week after flooding. We assume rice farmers throughout the Sacramento Valley followed a similar schedule in 2010–2011, which is qualitatively confirmed by examination of Aeronet MODIS Rapid Response satellite images (NASA/GSFC, Rapid Response, Terra Bands 7-2-1, http://lance-modis.eosdis.nasa.gov/imagery/subsets/?subset=AERONET_Fresno). The 11 May 2010 Aeronet MODIS image (Figure 17b) shows relatively few flooded paddies (black) compared to the image from 29 May, which shows more extensive flooding of the rice paddies (Figure 17c). The Aeronet MODIS image from 14 June shows the paddies turning green as rice shoots appear above the water surface of the flooded paddies (Figure 17d).

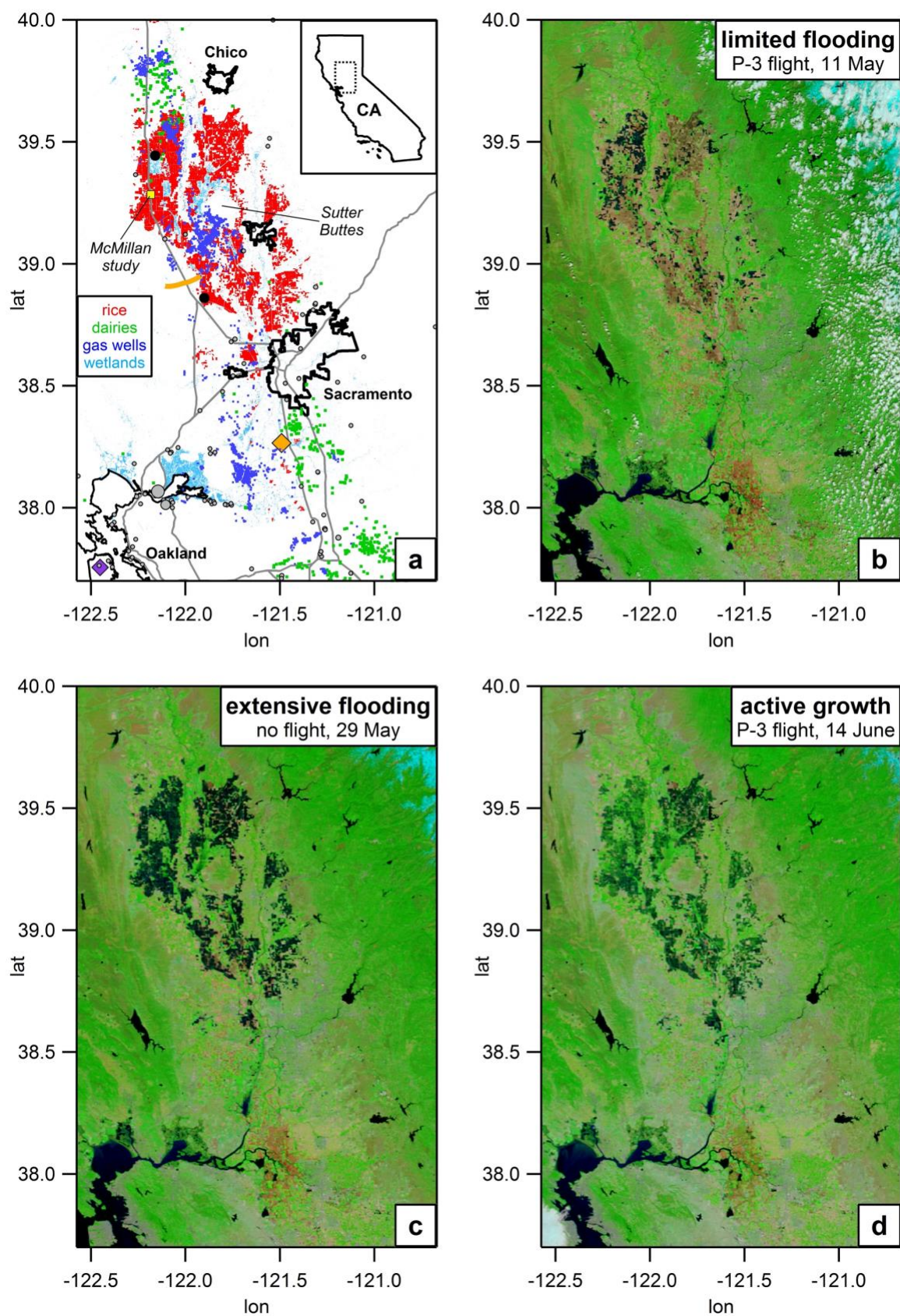


Figure 17. a) Map of region of study, including possible CH₄ sources in the Sacramento Valley: rice paddies (red); active natural gas wells (blue dots); dairies (green dots); wetlands (light blue); CH₄ point sources (filled gray circles sized by CH₄ emissions), of which the two largest are the Shell Oil Company and Valero refineries, located along the Carquinez Strait; two biomass burning locations on 14 June 2010 (filled black circles); interstate highways (gray lines); and urban areas (outlined by black). The paddy studied by McMillan et al. (2007) is located at the yellow square. The Walnut Grove tower is located at the orange diamond; the Sutro tower is located at the purple diamond on the San Francisco Peninsula. The descent into the Sacramento Valley by the CIRPAS Twin Otter is shown with a thick orange line. **b–d)** Aeronet MODIS Terra 7-2-1 images on three days in 2010. Panel (b) is the image from 11 May, when few paddies were flooded, assumed to be before the growing season for the majority of rice paddies. Panel (c) shows 29 May; although there was no P-3 flight, the image shows that by this day, nearly all of the rice paddies had been flooded. The black, flooded rice paddies are nearly identical to the red trace in Panel (a). Panel (d) shows 14 June; by this day, most paddies should have been planted, and the green shoots of rice plants can be seen above the surface of the water in many paddies.

II.3.1. Flight before rice growing season

On 11 May, the winds in the Sacramento Valley were predominantly from the northwest. The NOAA P-3 entered the northern Sacramento Valley at approximately 11:45 am (all times given in Pacific Standard Time, PST) and flew crosswind transects successively downwind, from northwest to southeast, with periodic vertical profiles. A map of the flight track, colored and sized by CH₄ mixing ratio when in the Sacramento Valley planetary boundary layer (PBL), is provided in Figure 18a. The P-3 flew over Sacramento at 3 pm and proceeded to fly crosswind transects down

the Sacramento-San Joaquin River Delta before exiting the boundary layer near San Francisco at 3:50 pm PST.

II.3.2. Flights during rice growing season

On 14 June, the NOAA P-3 aircraft flew a similar pattern as before, entered the Sacramento Valley at approximately 12:15 pm PST, passed over Sacramento at 3 pm, and exited the boundary layer near San Francisco at 3:45 pm. A map of this flight track, colored and sized by CH₄ mixing ratio when in the Sacramento Valley PBL, is provided in Figure 18b. The color and size scales are the same for Figures 18a and 18b. On this day, winds in the Sacramento Valley were predominantly from the southeast, while winds in the Sacramento-San Joaquin River Delta region were predominantly from the west-southwest.

On 15 June 2011, the CIRPAS Twin Otter flight plan focused on the western coastal mountain ranges between Monterey and Mendocino, California. However, the aircraft briefly descended into an area downwind of a rice growing region in the Sacramento Valley, southeast of Arbuckle, California. The wind direction on this day was from the northwest. Examination of the Aeronet MODIS image from this day shows evidence of green rice shoots above the surface of rice paddies, which indicates that this day was also in the rice growing season. Data from this flight segment, the thick orange line in Figure 17a, are discussed in Section 4.3.

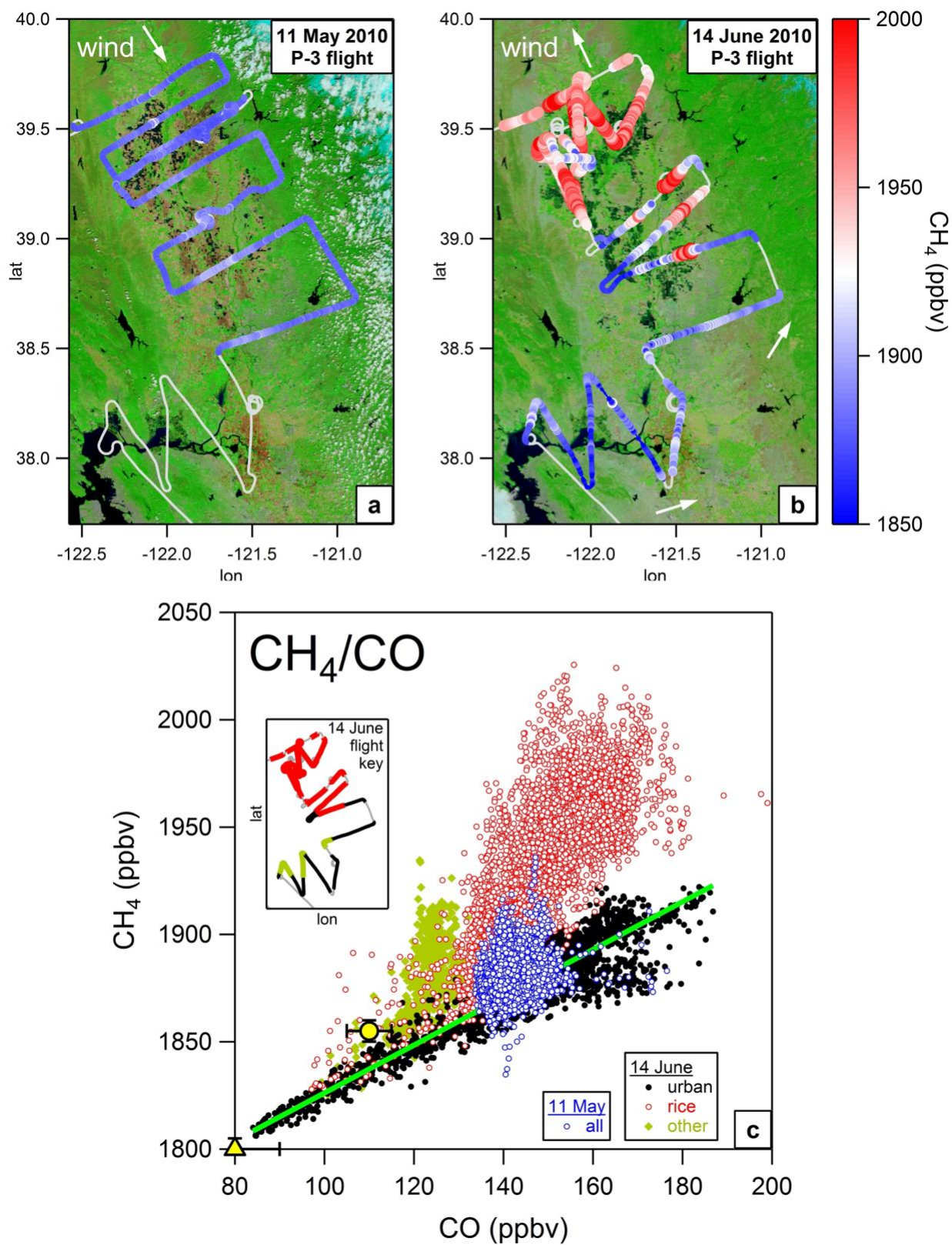


Figure 18. a) Aeronet MODIS image from 11 May 2010 with prevailing wind direction shown by white arrow, and the P-3 flight track shown in light gray. Measurements of CH₄ in the planetary boundary layer of the Sacramento Valley are colored according to the legend at right. **b)** As in (a), but for 14 June 2010; wind directions varied during the flight and are given by the three white arrows. CH₄ data through the Sacramento-San Joaquin River Delta are included to determine the influence of upwind CH₄ sources on the Sacramento Valley. **c)** CH₄ data from (a) and (b) are plotted against measured CO. For 11 May (blue circles), no clear correlation exists between CH₄ and CO, and 1- σ variability in CH₄ is ± 8 ppbv, which we attribute to the other CH₄ sources in the area (Figure 17a). For 14 June, a significant enhancement in CH₄ occurs over and downwind of the rice paddies (open red circles) compared to upwind regions on this day and to the 11 May flight. Using location and enhancement ratios with CO, we separate the urban CH₄ emission (filled black circles), located along and to the south of the Sacramento-San Joaquin River Delta and over Sacramento, from other CH₄ emissions (filled olive green diamonds), located to the north of the delta where wetlands predominate (Figure 17a). The map inset in (c) shows the location of these measurements along the 14 June flight track using the same color scheme. The slope of a weighted ODR fit to the urban CH₄/CO enhancement (green line) is 1.11 (± 0.06) ppb CH₄/ppb CO. Also shown are the approximate background levels of CH₄ and CO measured at NOAA ESRL GMD baseline observatories Mauna Loa (yellow triangle) and along the coast of California at Trinidad Head (yellow circle). The error bars for the GMD markers represent the approximate 1- σ seasonal variability.

II.4. Discussion

In the following sections, we consider different potential sources for CH₄ found in the Sacramento Valley. We extract the contributions from fresh biomass burning emissions from the CH₄ enhancements observed, and define an urban contribution to the remaining enhancements. We then examine CH₄ and CO₂ fluxes from a region with minimal interference from these other potential sources. Finally, we reincorporate all the

data from the Sacramento Valley PBL into a mixing model to calculate the estimated contribution of rice cultivation to the CH₄ and CO₂ measured in the entire region.

II.4.1. Biomass Burning

Biomass burning is a known source of CH₄, CO, and CO₂ to the atmosphere (Andreae & Merlet, 2001). The NOAA P-3 encountered several small biomass burning events on 14 June 2010. The largest was a prescribed burn of grass/wetland in the Sacramento National Wildlife Refuge (SNWR) (see Figure 17a, the light blue patch to the north of the McMillan et al. (2007) study site with the filled black circle). Because this burn was located in an area surrounded by wetlands and rice paddies, it is difficult to determine whether the CH₄ measured in the plume came from the combustion process or from the surrounding air entrained into the fire plume. We assume that CH₄ mixing ratios are highest near the surface of the rice paddy, and it is this air that is most likely entrained into the fire. A buoyant combustion plume would loft air with higher levels of CH₄ directly to altitudes observable by the NOAA P-3. Therefore, we cannot assume that all CH₄ enhancements measured in these biomass burning plumes were a direct result of the combustion process.

A time series of CH₄ measured during a spiral descent into the SNWR biomass burning plume is shown in Figure 19. BC increased by 5000 ng/kg, CO increased by 1000 ppbv, and CO₂ increased by 15 ppmv in this plume. CH₄ increased by 100 ppbv, which was about twice the variability in CH₄ outside the plume. This variability contributes to the low correlation between CH₄ and CO in this plume ($r^2 = 0.02$), and complicates comparisons to emission factors. For example, the Environmental Protection Agency (EPA) AP-42 emission factor for the open burning of unspecified

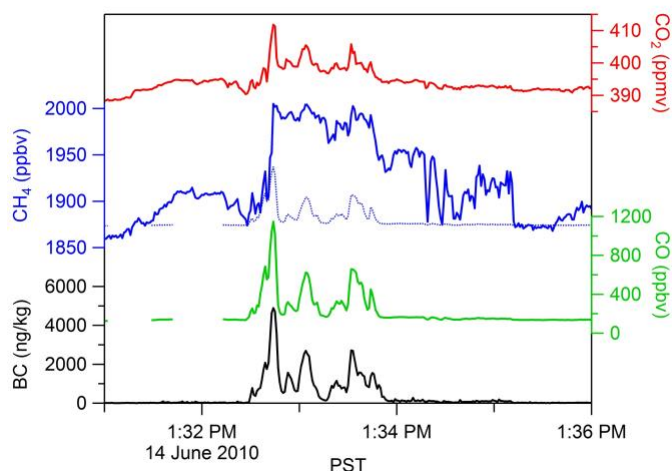


Figure 19. Time series of CO₂ (red), CH₄ (blue), CO (green), and BC (black) during spiral descent into SNWR biomass burning plume. The plume transect resulted in enhancements of up to 1000 ppbv in CO, up to 5000 ng/kg in BC, and 15 ppmv in CO₂. The enhancement in CH₄ based on CO and an AP-42 emission factor for unspecified weeds would appear as the dotted blue trace on the CH₄ axis.

weeds is 0.062 mol CH₄/mol CO (Chapter 2, U.S. EPA, 1995). Assuming background levels of 1875 ppbv for CH₄ and 150 ppbv for CO, CH₄ from the biomass burning would appear as the dotted blue trace in Figure 19. Assuming this emission factor were correct, this emission would be hidden by the surrounding CH₄ variability. Other biomass burning plumes encountered during this flight resulted in BC enhancements of 1000–2000 ng/kg, CO enhancements of 50–200 ppbv, and CO₂ enhancements of up to 5 ppmv, but any CH₄ enhancement in these plumes was poorly correlated and likely masked by the variability of the surrounding air, as in Figure 19. Outside of these biomass burning plumes, BC and CO vary at most by 500 ng/kg and 100 ppbv, respectively. Scaling from the largest burning plume, we conclude that biomass burning

had a small impact ($\ll 20$ ppbv) on the CH_4 mixing ratios outside of the freshest biomass burning plumes in the Sacramento Valley on this day.

However, because the biomass burning plumes encountered by the aircraft show significant enhancements in CO and CO_2 , we exclude data from plumes with BC enhancements greater than 500 ng/kg for the correlation plots of CH_4/CO and CH_4/CO_2 below, which removes the freshest plumes from these plots. It does not, however, remove any diluted CO and CO_2 biomass burning emissions, which are a source of possible interference in the analysis presented below. For example, as these biomass burning emissions traveled downwind, they may have mixed with CH_4 emissions from the rice paddies. Therefore, after mixing, it would appear that CH_4 and CO were positively correlated. Further, if the CO_2 emissions from biomass burning were greater than the uptake by rice paddies, CH_4 from rice may appear to be positively correlated with CO_2 . Ultimately, however, all biomass burning data are used as inputs to the mixing model described later.

II.4.2. Urban Emissions

On 14 June 2010, southeasterly winds brought urban emissions from Sacramento and the Sacramento-San Joaquin Delta region into the Sacramento Valley. In order to define this urban emission signature, we examine correlations of CH_4 with CO for both flights.

II.4.2.1. CH_4/CO before rice growing season

The 11 May CH_4 data shown in Figure 18a are plotted against CO in Figure 18c (blue circles). With relatively clean background air coming from the northwest (Redding, the largest California city north of 40°N latitude, is approximately 100 km

upwind of the northernmost NOAA P-3 transect), the CH₄ mixing ratio in the boundary layer averaged 1880 (± 8) ppbv, and was not correlated with CO. We attribute the small residual variability in CH₄ to the other non-rice CH₄ sources in the region, including dairies, natural gas production, and wetlands along the Sacramento River and its tributaries (see Figure 17a). The P-3 did not sample any large sources of CO during this part of the flight.

II.4.2.2. CH₄/CO during rice growing season

CH₄ mixing ratios measured from the aircraft showed greater variability and were substantially enhanced on 14 June compared to 11 May (Figure 18). Mixing ratios of CH₄ greater than 1950 ppbv were observed over and downwind of rice paddies, which we attribute to rice paddy emissions. The potential sources of CH₄ in the Sacramento Valley other than rice paddies are assumed to have been similar in magnitude on both flight days, although the air temperature in the boundary layer did increase from 14°C on 11 May to 26°C on 14 June. This assumption is based on the three following reasons. First, CH₄ emissions from wetlands and rice scale with biomass (Whiting & Chanton, 1993; McMillan et al., 2007), and because wetlands in the Sacramento Valley were green in satellite images both before and during the rice growing season (Figure 17), and they account for only 15% of modeled CH₄ emissions from the Sacramento Valley (Jeong et al., 2012), we conclude that wetlands accounted for less than 15% of possible CH₄ enhancements. Second, ethane and propane correlated better with CO than with CH₄ for both flights. Since ethane and propane are significant natural gas components, this provides evidence that natural gas production in the Sacramento Valley did not account for the increase in CH₄ mixing ratios. Further, the

correlations appear to be due to industrial and urban sources from along the Sacramento-San Joaquin River Delta; over the rice growing region of the Sacramento Valley, CH₄ is not well correlated with either ethane or propane ($r^2 = 0.32$ and 0.13 , respectively).

Third, according to the CARB greenhouse gas inventory, CH₄ emissions from manure management are not dependent on temperature. We therefore estimate the uncertainty in attributing the CH₄ increase solely to rice cultivation at less than 15%.

As stated above, an additional factor complicates the analysis of the 14 June data: the winds on this day were from the southeast, which brought urban emissions of CO and CH₄ into the Sacramento Valley. This urban CH₄/CO emission signature is apparent upwind of the rice-growing region (Figure 18c). We define an urban CH₄ emission enhancement based on location of sampling and correlations with CO, which are plotted as black filled circles, and sampled from the parts of the flight path along and to the south of the Sacramento-San Joaquin River Delta and over Sacramento (Figure 18c, inset). The remaining data points, sampled from regions to the north of the Delta and plotted as filled olive green diamonds in Figure 18c, show a different correlation with CO than the urban emissions, and are possibly influenced by wetlands north of the San Francisco Bay and the Sacramento-San Joaquin River Delta (see Figure 17a).

Also plotted in Figure 18c are CH₄ and CO mixing ratios, with estimated 1- σ error bars accounting for seasonal variability, measured at the NOAA ESRL GMD Mauna Loa, Hawaii (yellow triangle) and Trinidad Head, California (yellow circle) baseline monitoring observatories for early June, 2010. On 14 June 2010, it appears an air mass more typical of the average Mauna Loa background values in early June influenced the Sacramento-San Joaquin River Delta. We interpret the enhancement ratio

in CH₄/CO as urban emissions into this background air mass, because the observed mixing ratios and enhancements are less consistent with the typical Trinidad Head background for early June.

From the defined urban emissions, we attribute CH₄ measurements of greater than 1950 ppbv to strong contributions from rice cultivation emissions. This was the approximate maximum CH₄ mixing ratio measured in air upwind of the rice growing region, from either urban or unknown sources.

II.4.2.3. Quantifying urban and Sacramento-San Joaquin Delta emissions

A linear orthogonal distance regression (ODR; Boggs et al., 1989) fit to the urban enhancement, weighted by the imprecision of each measurement (weighted ODR), resulted in a slope of 1.11 (± 0.06) ppbv CH₄/ppbv CO and is plotted as a green line (Figure 18c). This slope is similar to the daytime enhancement ratio measured from the Walnut Grove tower (38.2650° N latitude, 121.4911° W longitude, orange diamond in Figure 17a) in a collaboration between the California Greenhouse Gases Emission Measurement (CALGEM) project (Zhao et al., 2009) and the NOAA ESRL Tall Tower network (Andrews et al., 2009). Figure 20 shows all hourly-averaged CH₄ and CO data (red circles) sampled from the 483-m above ground level (AGL) Walnut Grove tower inlet between 12 pm and 4 pm PST for the months of May and June, 2010 (n=183). A weighted ODR fit to these data resulted in a slope of 1.09 (± 0.04) mol CH₄/mol CO. The data identified with an urban signature defined in Figure 18 are plotted as gray circles in Figure 20 for comparison.

Also plotted in Figure 20 (blue circles) are data from afternoon measurements (n=43) between 12 May and 30 June 2010, at 232 m AGL on a communications tower

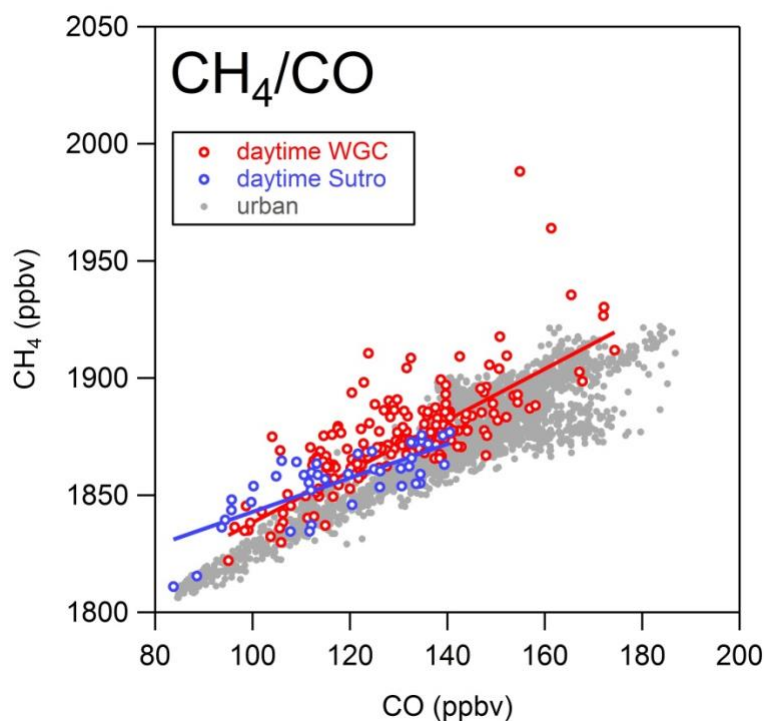


Figure 20. Data for the months of May and June, 2010, between 12 pm and 4 pm PST from the Walnut Grove tower (WGC), located at the orange diamond in Figure 17a, are plotted as red circles. Data from this same time period from the Sutro tower in San Francisco, located at the purple diamond in Figure 17a, are plotted as blue circles. Weighted ODR fits to these data sets result in CH_4/CO slopes of $1.09 (\pm 0.04)$ mol/mol at WGC, and $0.72 (\pm 0.10)$ mol/mol at Sutro tower. Data from urban emissions in Figure 18 are plotted in gray for reference.

located on Mt. Sutro (37.7553° N latitude, 122.4517° W longitude, purple diamond in Figure 17a) in San Francisco, California. These tower measurements are also operated by the CALGEM project in collaboration with the NOAA ESRL Tall Tower network. Flask samples at this site were typically taken twice per day: once at night, and once at approximately 2 pm PST. A weighted ODR fit to the daytime Sutro tower data resulted in a slope of $0.72 (\pm 0.10)$ mol CH_4 /mol CO. With typical daytime winds in the Sacramento-San Joaquin Delta from the west (Bao et al., 2008), the CH_4/CO emissions

ratio increases from west to east from the Sutro tower to the Walnut Grove tower. This increase in CH₄ emissions relative to CO is likely in part due to the wetlands and refineries located along the Sacramento-San Joaquin Delta (which likely account for the CH₄ emissions not correlated with CO, labeled “other”, in Figure 18c), including the two largest inventoried CH₄ point sources in California, the Shell Oil and Valero refineries, which are the largest two gray circles shown in Figure 17a. Using the data from the Sutro and Walnut Grove towers, we conclude that the urban emissions that influenced the air in the Sacramento Valley on 14 June 2010 were typical of this area during May and June, 2010.

II.4.3. Rice paddy emissions

As stated above, in addition to CH₄ and CO, biomass burning and urban emissions also contain CO₂, which complicates CH₄/CO₂ emission ratio calculations for the rice paddies. In the Sacramento Valley, the urban areas are located along the eastern side, while the two largest known biomass burning events on 14 June 2010 were along the western side of the valley (Figure 17a). Therefore, we closely examine one portion of the flight track in the middle of the valley that was over or downwind of rice paddies, but not immediately downwind of urban areas or known biomass burning, in order to discern the clearest signal of rice paddy CH₄ emissions and CO₂ uptake on this day (Figure 21).

The NOAA P-3 flew three vertically stacked north-south transects immediately downwind of several rice paddies that were among the earliest flooded in the 2010 season (Figure 21a–d). Portions of these transects were selected by latitude (between 39.47° N and 39.565° N latitude) because Aeronet MODIS images show several rice

paddies immediately upwind had been flooded by 2 May (Figure 21c) and had started to turn green by 29 May (Figure 21d). The northern latitude limit is upwind of nearby dairies (green dots in Figure 21b). The portion from the lowest altitude transect, flown at approximately 350 m AGL, is denoted by the left red trace in Figure 21b; the portion from the following transect, flown at approximately 450 m AGL, is denoted by the right red trace in Figure 21b. The portion from the highest transect, flown at approximately 575 m AGL, resulted in no correlation between CH₄ and CO₂ ($r^2 = 0.02$), and is therefore not shown in detail. We attribute this lack of correlation to the altitude of the transect; the vertical mixing of this plume had not reached 575 m AGL.

Figure 21e shows a time series of CO₂ and CH₄ data from the portion along the flight track shown as a thick black trace in Figure 21b. The black diamond in Figure 21e shows the same point in time along the flight track in Figure 21b. The red portions of the flight track in Figure 21b are also represented by the red traces in Figure 21e atop the altitude trace.

The lowest two transects showed anti-correlation between CH₄ and CO₂, especially outside the larger plumes of CH₄ (i.e., where CH₄ < 1970 ppbv). The larger CH₄ enhancements, shown in more detail in Figures 21f and 21h, had different correlations with CO₂ (open circles in Figures 21g and 21i), possibly because they were lofted by a combustion process, or because of a greater CH₄ emission per mole of CO₂ taken up by the growing rice. The plumes labeled 1 and 2 in Figure 21e were correlated with enhancements of up to 0.7 ppbv of NO_x (= NO + NO₂), which is emitted primarily from combustion sources. Plume 2 also had an enhancement in CO of 10 ppbv. However, no significant enhancements in NO_x or CO were measured in Plumes 3 or 4.

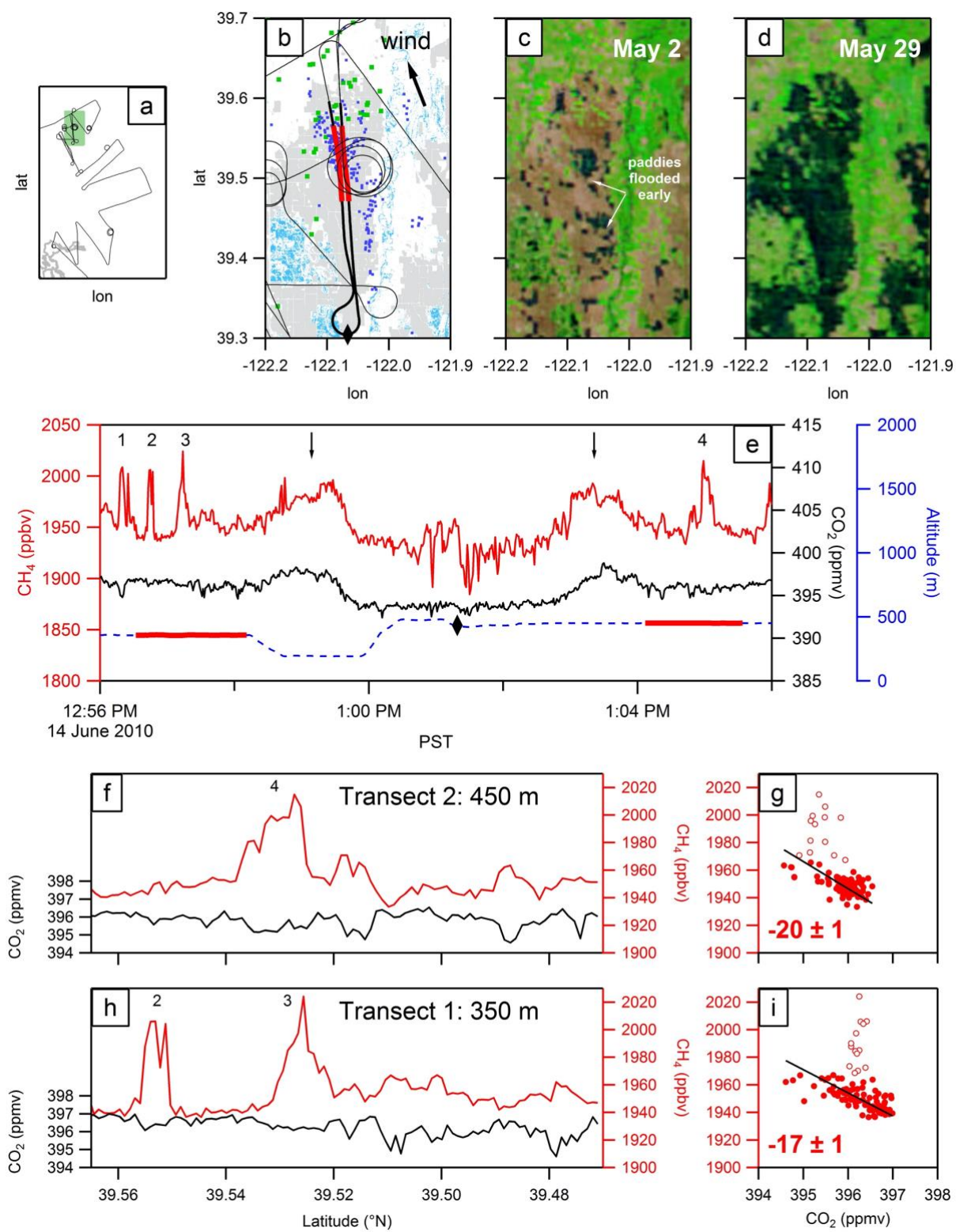


Figure 21. **(a)** Inset of California from Figure 17 showing 14 June 2010 flight track (black trace) and inset (green rectangle) for panels (b–d). **(b)** Portion of flight track (black line) over rice paddies (gray). As in Figure 17b, dairies are plotted as green dots, active natural gas wells are plotted as dark blue dots, and wetlands regions are light blue. The left red trace shows a level flight leg at approximately 350 m altitude. The right red trace shows a level flight leg at approximately 450 m altitude. The thin black line is the entire flight track; the thick black line is the portion of the flight track shown in (e). **(c)** Aeronet MODIS image from 2 May 2010 showing some of the earlier flooded paddies. **(d)** Aeronet MODIS image from 29 May 2010 showing these paddies were also among the first to turn green. The red portions of the flight track in (b) are downwind of these paddies. **(e)** Time series of CH₄ (red), CO₂ (black), and aircraft altitude (dashed blue). The red portions of the altitude trace correspond in time to the latitude-longitude coordinates in (b). **(f)** Time series of portion of flight track at the 450-m leg in (b) and (e). **(g)** Scatter plot of CH₄ vs. CO₂ at the 450-m leg in (b) and (e). The open red circles represent data with CH₄ > 1970 ppbv. **(h)** As in (f), but for the 350-m leg in panels (b) and (e). The CH₄ enhancements in (f) and (h) have different CH₄/CO₂ correlation fit slopes to each other and the surrounding air. **(i)** As in (g), but for the 350-m leg.

For data with less than 1970 ppbv CH₄, weighted ODR fits from the 350-m flight leg resulted in a slope of $-17 (\pm 1)$ ppbv CH₄/ppmv CO₂ ($r^2 = 0.48$), or -1.7% mol/mol, and from the 450-m flight leg resulted in a slope of $-20 (\pm 1)$ ppbv CH₄/ppmv CO₂ ($r^2 = 0.37$), or -2.0% mol/mol. These ratios are within the range of CH₄/CO₂ flux ratios measured by McMillan et al. (2007) during the early stages of rice growth (-0.6% to -2.7%). For CH₄ measurements greater than 1970 ppbv, a negative correlation with CO₂ exists, but at higher ratios of CH₄ emission to CO₂ uptake than measured by McMillan et al. (2007).

A positive correlation between CH₄ and CO₂ appears in Figure 21e, indicated by arrows. These features, sampled to the south of the red traces in Figure 21b, are not correlated with NO_x or BC, but correlated with CO between the arrows, and are well above background levels of CH₄ and CO₂ found above the PBL. This is possibly a residual signature of CH₄ and CO₂ emissions from Sacramento and/or the rice paddies during the nighttime or early morning hours. A calculation based on average wind speed would place this air mass over the rice paddies just to the north of Sacramento at 8 am. This is evidence that on broader time scales, the CH₄/CO₂ analysis is influenced by what could be aged urban or nighttime agricultural emissions. This limits our analysis of CO₂ to the high-frequency variability on top of these lower frequency, positively-correlated features.

On 15 June 2011, winds were from the northwest, and the chemically-instrumented CIRPAS Twin Otter briefly descended into an area downwind of a rice-growing region of the Sacramento Valley, southeast of Arbuckle, California (thick orange line in Figure 17a). With favorable winds compared to the 14 June 2010 flight, this region was not downwind of any large urban area. However, biomass burning was still a potentially complicating factor. During the descent, CH₄ and CO₂ were anti-correlated within the PBL (Figures 22a and 22b). At the bottom of the descent, the aircraft encountered a plume in which mixing ratios of CO₂, CH₄, and acetaldehyde exceeded 415 ppmv, 2000 ppbv, and 40 ppbv, respectively, which, after examination of onboard video, was visibly identified as a biomass burning plume. The plume was located directly above an irrigation canal, denoted as Main Canal on Colusa County, California maps (<https://www.countyofcolusa.org/DocumentCenter/View/543/Colusa->

[County-Road-Map?bidId=](#)). This was the same irrigation canal along which burning took place on the 14 June 2010 NOAA P-3 flight. The width of the plume corresponded spatially to approximately the width of the canal, indicating the Twin Otter transected the plume before much mixing and broadening of the plume occurred. After encountering this plume, the aircraft turned southeast and flew downwind for several minutes before turning west again and ascending out of the Sacramento Valley. Along this downwind portion of the flight track prior to ascent, the Twin Otter encountered several smaller plumes in which measurements of CH₄, CO₂, and acetaldehyde were positively correlated, which we interpret as influence from biomass burning. Vertical gradients in chemical species measured by PTRMS on the ascent indicate the well-mixed PBL height was approximately 1000 m. Due to the biomass burning plume, we

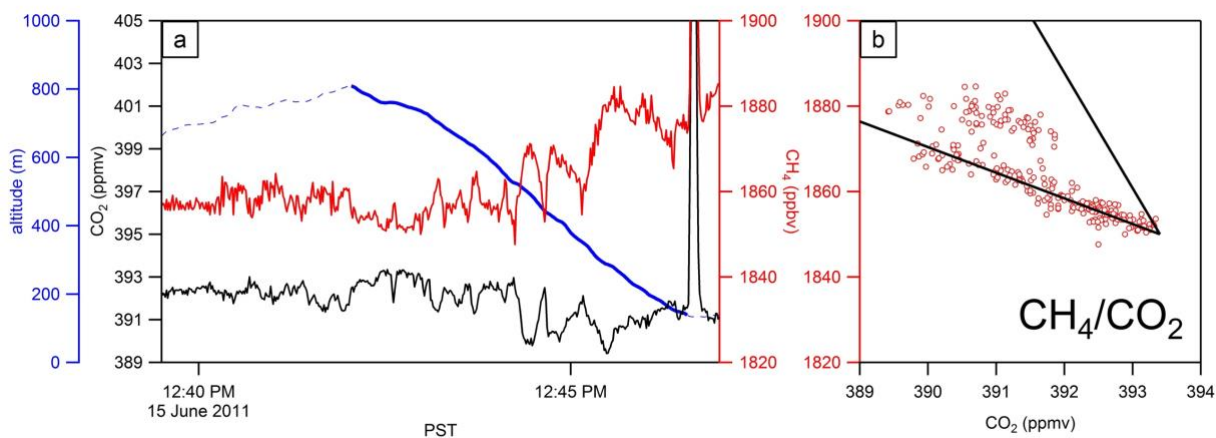


Figure 22. a) Timeline of CIRPAS Twin Otter descent into Sacramento Valley on 15 June 2011.

The top of the descent down to 138 m is plotted as a thick blue line atop the dashed blue altitude trace. b) Scatter plot of CH₄ vs. CO₂ for the descent. The black lines represent the mol/mol flux ratios reported by McMillan et al. (2007) for the seedling (−0.6%, lower bound) and mid-vegetative (−2.7%, upper bound) stages of rice growth, with an arbitrary background.

interpret data only from the descent, upwind of most interference from the plume.

Figure 22b plots CH₄ vs. CO₂ from the top of the descent at 808 m down to 138 m, just before the biomass burning plume. Also plotted are lines representing the expected CH₄/CO₂ flux ratios as reported by McMillan et al. (2007) for the seedling and mid-vegetative stages of rice growth. An arbitrary background value was chosen close to the lowest mixing ratios of CH₄ and CO₂ observed during the descent. Data above approximately 300 m fall along the line representing a -0.6% mol/mol flux ratio. Data below this altitude are also negatively correlated and have a similar slope, but with ~ 10 ppbv more CH₄. We interpret these data as consistent with the flux ratio reported by McMillan et al. (2007) for the seedling stage of rice growth.

As stated above, the high frequency anti-correlation of CH₄ and CO₂ is not consistently observed throughout the 14 June 2010 P-3 flight. Using the same urban and rice definitions as in Figure 20, we plot CH₄ vs. CO₂ from the 14 June flight in Figure 23. CH₄ and CO₂ are generally positively correlated ($r^2 = 0.41$) above the rice-growing region, likely in part due to biomass burning and urban emissions of CO₂ overwhelming the signal of CO₂ taken up during rice photosynthesis, and in part due to residual, positively-correlated emissions of CH₄ and CO₂ from the rice paddies during the night and early morning. According to McMillan et al. (2007), during this stage of the growing season, we expect daytime CH₄ emissions to equal approximately 0.6–2.7% of the CO₂ uptake. Given the enhancement of approximately 100 ppbv in CH₄ above the urban emissions in Figure 20, we would expect to see a CO₂ uptake of approximately 4–16 ppmv. However, because the variability of CO₂ from the urban emissions alone spans 15 ppmv, and the diluted emissions from biomass burning add additional CO₂ positively

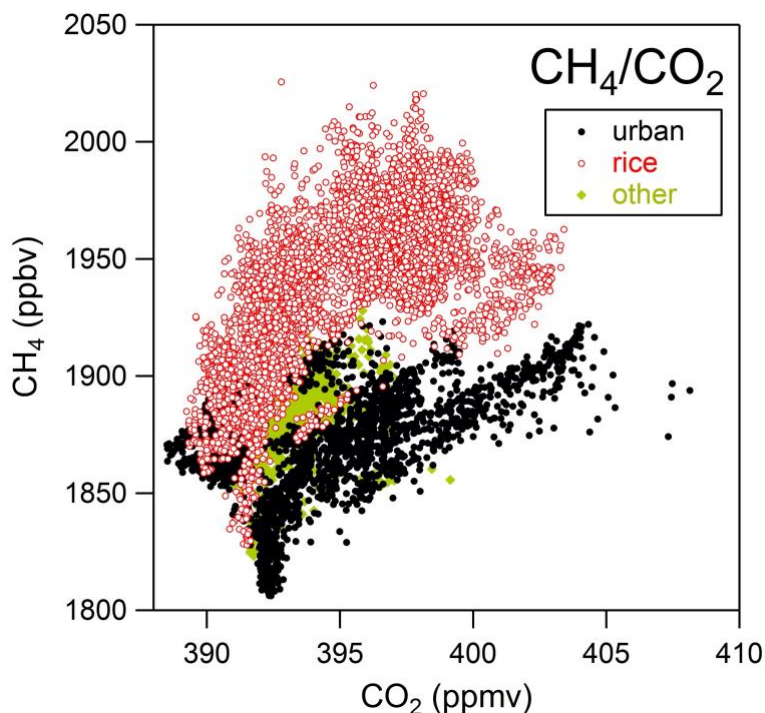


Figure 23. CH₄ vs. CO₂ for 14 June 2010, with the same color definitions as Figure 18c.

Photosynthetic uptake of CO₂ correlated with CH₄ emissions is difficult to discern within the variability of urban and other CO₂ emissions.

correlated with CH₄ to the area, this rice uptake signal is almost certainly lost in the variability from mixing of other source signatures.

II.4.4. Mixing Model

Extracting emissions information from observed bivariate relationships (e.g., Figs. 18c and 23) is complicated by atmospheric mixing of emissions from multiple sources. We interpret bivariate enhancement ratios as emission ratios only where emission from a single source dominates the relationship (e.g., Figs. 21g, 21i, and 22b). Here, we use a multivariate linear regression to derive emission ratios from individual sources based upon the complete data set within the boundary layer in the Sacramento Valley and Sacramento-San Joaquin River Delta from the 14 June 2010 flight (Figs. 18c

and 23), comprising over 2.5 hr of 1-second data (> 9000 1-s data points). The multivariate linear regression is formulated as a mixing model (Nowak et al., 2004), which here assumes each 1-second average datum represents a background air parcel with a linear combination of added emissions from urban, biomass burning, and daytime agriculture, each providing enhancements of CH₄, CO₂, CO, and BC with specific and distinct ratios. Initial estimates of enhancement ratios characteristic of each source type are based on measurements made during the flight, and provide initial input to the model. The daytime agricultural CO₂ “emission” is set to be negative, consistent with its uptake in photosynthetic plants. A multivariate, linear least-squares fitting routine was applied to all of the data collected in the boundary layer over the Sacramento Valley. In the fit, each measurement is weighted by 1/precision², where the precision is the estimated 1-σ variability in a measurement due to variability in the sources’ emission of CH₄, CO₂, CO or BC relative to the emissions of the other three or due to other, unaccounted sources of the measured species. The mixing model solves the following system of equations, in the form $Ax = b$:

$$\begin{bmatrix} \text{CH}_{4_{bkgd}} & \text{CH}_{4_{urb}} & \text{CH}_{4_{agr}} & \text{CH}_{4_{bb}} \\ \text{CO}_{2_{bkgd}} & \text{CO}_{2_{urb}} & \text{CO}_{2_{agr}} & \text{CO}_{2_{bb}} \\ \text{CO}_{bkgd} & \text{CO}_{urb} & \text{CO}_{agr} & \text{CO}_{bb} \\ \text{BC}_{bkgd} & \text{BC}_{urb} & \text{BC}_{agr} & \text{BC}_{bb} \end{bmatrix} \begin{bmatrix} 1 \\ f_{urb\ i} \\ f_{agr\ i} \\ f_{bb\ i} \end{bmatrix} = \begin{bmatrix} \text{CH}_{4_i} \\ \text{CO}_{2_i} \\ \text{CO}_i \\ \text{BC}_i \end{bmatrix} \quad (11)$$

where X_i is the mixing ratio for $X = \text{CH}_4, \text{CO}_2, \text{CO},$ and BC for each i^{th} 1-second average datum observed from the P-3 aircraft; *bkgd* represents the assumed background mixing ratio; *urb*, *agr*, and *bb* represent the characteristic relative enhancements in X for urban, daytime agriculture, and biomass burning sources, respectively; and f represents

the fraction each source contributes to the observed i^{th} mixing ratios. The mixing model minimizes the quantity χ^2 :

$$\chi^2 = \sum_X \sum_i \left(X_i - (f_{urb_i} \times X_{urb} + f_{agr_i} \times X_{agr} + f_{bb_i} \times X_{bb}) \right)^2 \times \frac{1}{\sigma_X^2} \quad (2)$$

which is summed over all i data points and over the four gas species, X . The X_{urb} , X_{agr} , and X_{bb} parameters in the matrix A of equation (11) are iteratively changed until χ^2 converges to a minimum.

The mixing model achieved a minimum χ^2 with negative correlation between agricultural CH_4 and CO_2 at a slope of $-6 (\pm 2)$ ppb CH_4 /ppm CO_2 . Uncertainty on this slope is estimated as the change in the slope of the daytime agriculture air mass that would increase the overall χ^2 by 1, similar to the error estimation set forth by Bevington (1969). The derived uncertainty is robust to the addition in quadrature of a 15% uncertainty due to other CH_4 emission sources in the region. Therefore, this slope is assumed to be the average flux ratio for agricultural emissions in the Sacramento Valley, which is dominated by rice paddies. This slope is consistent with that derived using a bivariate approach in Figure 22b, and is further consistent with the seedling stage of rice growth measured by McMillan et al. (2007), which, at the time of the 14 June flight, would include all rice planted after 22 May 2010.

II.4.5. Comparison of CH_4 emissions from rice cultivation to the CARB greenhouse gas inventory and recent studies

The CARB greenhouse gas inventory specifies an annual emission of 122 kg of CH_4 per hectare of rice crop (Franco, 2002). This value was determined by averaging flux results from a variety of farming practices and conditions based on experiments performed in the 1980s and 1990s by Cicerone et al. (1992), Bossio et al. (1999),

Fitzgerald et al. (2000), and Redeker et al. (2000). Notably, each of these studies reported at least a factor of 2 increase in CH₄ emissions when rice straw or other organic material was incorporated into the soil before the growing season.

Additionally in the 1990s, with the passage of the Connelly-Areias-Chandler Rice Straw Burning Reduction Act of 1991 and Senate Bill 318, the State of California phased down, then banned, most residual rice crop burning in the Sacramento Valley by the year 2001 in an effort to improve air quality in that region. This was significant, because according to the 1990 CARB greenhouse gas inventory (<https://ww2.arb.ca.gov/ghg-1990-to-2004>), 99% by area of fields with rice crop residue were burned; in the 2009 inventory, this number had fallen to 11%. This is reflected in the inventory by a decrease in CO₂ emissions from rice crop burning from 1.1 Tg in 1990 to 0.2 Tg in 2009. Presumably, this decrease in burning led to an increase in the incorporation and/or rolling of the rice crop residue into the soil, which, as shown by previous studies, should lead to increased CH₄ emissions in subsequent years. Yet the 122 kg/ha annual CH₄ emission rate has remained unchanged in the CARB greenhouse gas inventory since 1990.

Because only a small percentage of the rice acreage in the Sacramento Valley is burned, the CH₄ fluxes reported by McMillan et al. (2007) for a farm that incorporated residual rice crop into the soil are likely representative of the majority of the Sacramento Valley rice crop in the present day, which is confirmed by our analysis above. For simplicity, we assume the annual CH₄ flux of 348–413 kg/ha reported by McMillan et al. (2007; calculated by $26.1\text{--}31.0 \text{ g CH}_4\text{-C/m}^2 \times 16 \text{ g CH}_4/12 \text{ g CH}_4\text{-C} \times 10^{-3} \text{ kg/g} \times 10^4 \text{ m}^2/\text{ha}$) represents the annual emission rate for the entire Sacramento Valley rice

crop. Under this assumption, annual CH₄ emissions from rice cultivation should be increased from 2.7×10^{10} g to $7.8 - 9.3 \times 10^{10}$ g in the 2009 inventory, or an increase by a factor of 2.9–3.4, to properly account for changes in rice straw incorporation practices. CH₄ emission from rice cultivation would then represent 5.0–5.8% of inventoried annual California anthropogenic CH₄ emissions.

The CH₄ emissions from rice cultivation in the Sacramento Valley derived here ($7.8-9.3 \times 10^{10}$ g) are also consistent with results from recent studies. Salas et al. (2006) estimated CH₄ emissions from rice cultivation in the Sacramento Valley at 6.7×10^{10} g during a warm, dry spring (modeled after the 1997 growing season) and 7.6×10^{10} g during a cool, wet spring (modeled after the 1983 growing season). Jeong et al. (2012) reported CH₄ emissions 55 (±24)% higher than their California-specific inventory, which included the 1983-level CH₄ rice emissions from the study by Salas et al. (2006). Jeong et al. (2012) noted a seasonal pattern in modeled CH₄ emissions from the Sacramento Valley, consistent with the rice growing season, and concluded that emissions from rice and wetlands were larger than predicted by Salas et al. (2006). The range of CH₄ emissions derived here are 3–22% greater than the 1983-level emissions estimated by Salas et al. (2006), suggesting rice cultivation contributes significantly to the excess CH₄ measured by Jeong et al. (2012). Finally, a parallel work by Santoni et al. (2013) uses P-3 data from CalNex and an inverse modeling approach to estimate CH₄ rice emissions in the Sacramento Valley that are consistent with our analysis.

II.5. Conclusions

Analysis of data from two flights of the NOAA P-3 over the Sacramento Valley shows that during the early stages of the rice growing season, emissions from rice cultivation dominate CH₄ emissions in this region. Spatial coverage provided by the NOAA P-3 complements the temporal coverage of the ground-based study by McMillan et al. (2007) in determining flux ratios of CH₄/CO₂ from the rice paddies in this region. Analysis of high-frequency anti-correlation between CH₄ and CO₂ data above one region of the Sacramento Valley found emission fluxes of CH₄ corresponding to between 1.7 and 2.0% of the CO₂ taken up by photosynthesis on a per carbon, or mole to mole, basis for growing rice plants. However, meteorology, biomass burning, and urban emissions of CO and CO₂ complicate this type of analysis. Additional analysis with a mixing model that incorporated these biomass burning and urban emissions resulted in a smaller average agricultural CH₄ flux of 0.6% mol/mol CO₂ taken up, valid for the entire Sacramento Valley on 14 June 2010. Data from one flight of the CIRPAS Twin Otter on 15 June 2011 show a similar flux of CH₄ relative to photosynthetic CO₂ uptake. Our analysis is consistent with fluxes measured during the seedling (0–23 days after planting) and mid-vegetative (24–47 days after planting) stages of rice growth reported by McMillan et al. (2007) of 0.6% and 2.7% CH₄/CO₂ taken up, respectively.

In all, the ratios presented here suggest the findings of McMillan et al. (2007) are representative of the entire rice growing region in the Sacramento Valley of California. The annual CH₄ flux reported by McMillan et al. (2007) ranges from 348 to 413 kg/ha, which is approximately three times the CARB greenhouse gas inventory annual emission rate of 122 kg/ha. We attribute this difference to a mandated decrease of rice

crop residue burning and the resulting increase in the incorporation and/or rolling of the residue back into the soil, which increases CH₄ emissions the following year by a factor of 2 to 10 (Cicerone et al., 1992; Bossio et al., 1999; Fitzgerald et al., 2000; Redeker et al., 2000). The emission rate of 122 kg/ha in the CARB inventory was determined from a time when the majority of rice crop residue in California was burned. For simplicity, if we attribute the flux reported by McMillan et al. (2007) to the entire California rice crop, then CH₄ emissions from rice cultivation would be a factor of 2.9–3.4 greater than the current CARB greenhouse gas inventory, and would account for 5.0–5.8% of statewide anthropogenic CH₄ emissions.

We note that the increase in CH₄ emissions, which accompanies the decrease in rice crop residue burning, worsens the climate change impact of rice cultivation as predicted by Cicerone et al. (1992). It is an unintended consequence of a policy implemented to improve air quality, and thus provides an example of the difficulties of simultaneously addressing both climate change and air quality through public policy.

2.b. Conclusions of Publication II

After the publication by Peischl et al. (2012), one other study was performed using the CalNex data set and an inverse model (Santoni, 2013). Santoni (2013) determined that rice emissions were a factor of 3.2 greater than the CARB GHG inventory. However, this study was only published as part of a Ph.D. dissertation and was not peer reviewed.

Within two years of the publication by Peischl et al. (2012), the CARB GHG inventory increased emissions of CH₄ from rice by more than a factor of 1.6 between

2010 and 2012 despite the area of rice planted in California increasing by less than 1% (<https://ww2.arb.ca.gov/ghg-inventory-archive> and <http://quickstats.nass.usda.gov/>, accessed August 2022). Later modeling studies found good agreement between the emission determined by Peischl et al. (2012) and inverse models. These studies were: Wecht et al. (2014), whose modeled emissions of 80 Gg CH₄ per year were within the range reported by Peischl et al. (2012) of 78–93 Gg CH₄ per year; Jeong et al. (2016), who modeled emissions of 70 ± 16 Gg CH₄ per year; and Cui et al. (2019), who determined that emissions from the Sacramento Valley, the majority of which came from rice cultivation, were a factor of 1.0 to 1.5 higher than a different California CH₄ inventory for 2014–2016. By 2018, area emissions from rice cultivation in the CARB GHG inventory were higher than in the 2010 inventory when the work of Peischl et al. (2012) was written, but lower than the area emission used for the 2012 inventory. This shows that CARB’s GHG inventory is constantly being modified, which underscores the necessity of verifying these changes using top-down methods. Although rice agriculture is not a large source of CH₄ emissions in the United States, it is the primary food crop for half of the world’s population. Therefore, understanding CH₄ emissions from this source sector will be important as the world tries to reduce its greenhouse gas emissions in the future.

3. Quantifying relative emissions using atmospheric enhancement ratios

3.a. Introduction to Publication III

Another goal of CalNex was to determine why CH₄ emissions in the Los Angeles urban area were higher than population-apportioned assessments of the CARB GHG inventory reported by previous studies (Wunch et al., 2009; Hsu et al., 2010). These studies compared urban enhancements of CH₄/CO with a ratio of the CH₄ and CO inventories for Los Angeles and found more CH₄ in the atmosphere relative to CO than expected. CARB's inventory for CO was trusted more than the recently developed CH₄ inventory, as it had been compiled and revised for decades prior for air quality purposes. However, these studies were unable to determine where the “missing” source of CH₄ came from. Wennberg et al. (2012) analyzed the CalNex dataset and suggested that natural gas distribution could account for all of the inventory shortfall, but they neglected to consider landfill emissions in the region. Peischl et al. (2013) attributed CH₄ to various sources in the Los Angeles Basin by using the enhancement ratios of multiple light alkanes to CO in order to constrain the various emission sectors for these gases. They found the missing CH₄ came from a combination of natural gas distributed in pipelines and natural gas from the local oil and gas industry.

III. Quantifying sources of methane using light alkanes in the Los Angeles Basin, California

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III. Abstract. Methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and C_2 – C_5 alkanes were measured throughout the Los Angeles (L.A.) area in May and June 2010. We use these data to show that the emission ratios of CH_4/CO and CH_4/CO_2 in the L.A. Basin are larger than expected from bottom-up state inventories, consistent with previously published work. We use experimentally determined CH_4/CO and CH_4/CO_2 emission ratios in combination with annual State of California CO and CO_2 inventories to derive a yearly emission rate of CH_4 to the L.A. Basin. We further use the airborne measurements to directly derive CH_4 emission rates from dairy operations in Chino, and from the two largest landfills in the L.A. Basin, and show these sources are accurately represented in the California Air Resources Board greenhouse gas inventory for CH_4 . We then use measurements of C_2 – C_5 alkanes to quantify the relative contribution of other CH_4 sources in the L.A. Basin, with results differing from those of previous studies. The atmospheric data are consistent with the majority of CH_4 emissions in the region coming from fugitive losses from natural gas in pipelines and urban distribution systems and/or geologic seeps, as well as landfills and dairies. The local oil and gas industry also provides a significant source of CH_4 in the area. The addition of CH_4 emissions from natural gas pipelines and urban distribution systems and/or geologic seeps and from the local oil and gas industry is sufficient to account for the differences between the top-down and bottom-up CH_4 inventories identified in previously published work.

III.1. Introduction

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

Several recent works have estimated CH_4 emissions to the South Coast Air Basin (SoCAB; Fig. 24a), which are summarized in Table 5. Wunch et al. (2009) used a Fourier transform spectrometer at the Jet Propulsion Laboratory (JPL) in Pasadena, California to measure vertically-integrated total column enhancement ratios of CH_4 relative to CO and to CO_2 . The observed column enhancement emission ratios, multiplied by CARB inventory values of CO for 2008 and an average of 2006 CARB GHG inventory and 2005 Emission Database for Global Atmospheric Research (EDGAR) for CO_2 , were used to derive a lower limit to CH_4 emissions of 400 ± 100 Gg CH_4/yr (based on CO) or 600 ± 100 Gg CH_4/yr (based on CO_2) for the SoCAB. One reason for the discrepancy in their top-down analysis was that their observed CO/ CO_2 enhancement ratio of 11 ± 2 ppb CO/ppm CO_2 was greater than the ratio of the CO to CO_2 inventories of 8.6 ppb CO/ppm CO_2 . Wunch et al. (2009) contrasted these top-down assessments to a bottom-up estimate of 260 Gg CH_4/yr using the 2006 CARB

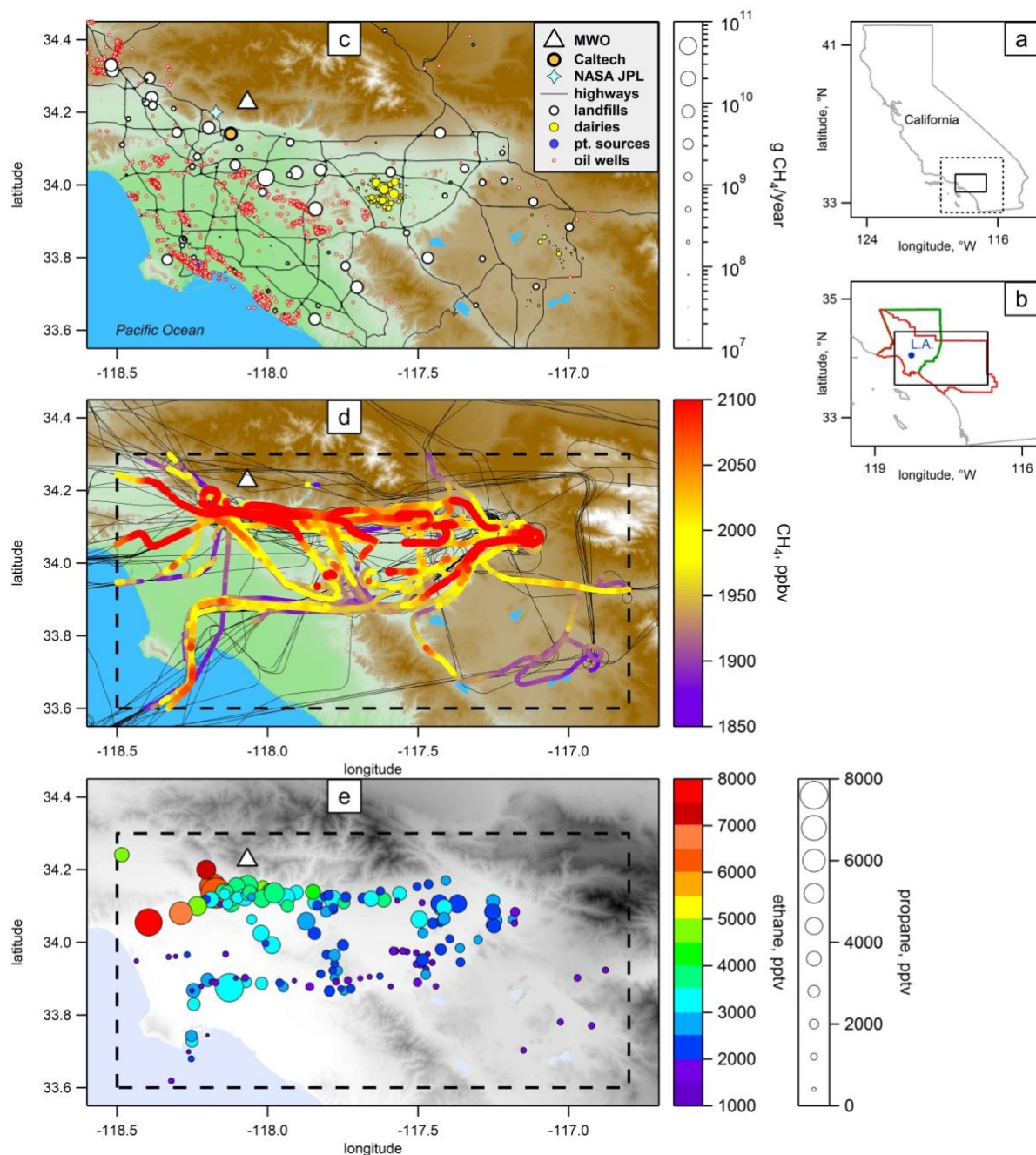


Figure 24. **a)** Map of California. The dashed box shows the inset for panel (b), the solid box shows the extent of the map boundaries for panels (c)–(e). **b)** Map of southern California showing the location of downtown L.A. (blue dot), the limits of Los Angeles County (green), the South Coast Air Basin (red), and the extent of the map boundaries for panels (c)–(e) (black box). **c)** Map of the L.A. region showing possible sources of CH_4 in the L.A. Basin. The white triangle shows the location of the Mt. Wilson Observatory, where ground-based measurements

of CH₄ and CO were made by Hsu et al. (2010) and in this study. The light blue star shows the location of the Jet Propulsion Laboratory, where Wunch et al. (2009) made their measurements. The CalNex Pasadena ground site was located on the California Institute of Technology (Caltech) campus, located at the orange filled circle. Landfills (white circles) and CH₄ point sources (filled blue circles) are sized by emissions in the 2008 CARB greenhouse gas inventory. Dairies (filled yellow circles) are sized by the estimated emissions from the number of cows from Salas et al. (2008) multiplied by the 2009 CARB GHG inventory annual CH₄ emission per cow from enteric fermentation. **d)** Same map of the Los Angeles region as in (c), with flight tracks from 16 daytime flights of the NOAA P-3 (thin black lines). CH₄ measurements from the daytime boundary layer are color-coded atop these tracks according to the legend to the right. **e)** Locations of whole air samples in the L.A. Basin, colored by ethane mixing ratio and sized by propane mixing ratio as indicated in the legends to the right.

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

Hsu et al. (2010) took a similar top-down approach and used observed atmospheric enhancement ratios of CH₄ to CO from in situ whole air samples taken at Mt. Wilson (34.22°N, 118.06°W, 1770 masl), scaled by the projected CARB CO inventory for 2008, to derive CH₄ emissions of 200 ±10 Gg CH₄/yr for the L.A. County (Figure 24b) portion of the SoCAB (L.A. County ∩ SoCAB). They used methods prescribed by the Intergovernmental Panel on Climate Change (IPCC) to create the CARB GHG inventory to construct a bottom-up inventory estimate of 140 Gg CH₄/yr, or 60 Gg less than their top-down calculation for the L.A. County portion of the SoCAB. Hsu et al. (2010) used higher spatial resolution emissions data from CARB to

Table 5. Summary of past studies investigating CH₄ emissions in the L.A. Basin.

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

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

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

construct their bottom-up inventory, and therefore did not have to rely on population apportionment methods used by Wunch et al. (2009).

The difference between the top-down CH₄ emissions reported by Wunch et al. (2009) and by Hsu et al. (2010; 400 Gg and 200 Gg, respectively, both based on the CARB CO inventory) are in part due to the different geographic areas for which they calculate CH₄ emissions, and in part due to differences in observed CH₄/CO enhancements between these two studies: 0.66 ±0.12 mol/mol for Wunch et al. (2009; Wennberg et al., 2012) and 0.52 ±0.02 mol/mol for Hsu et al. (2010). Both works

suggested that fugitive losses of natural gas (NG) could be the source of the CH₄ missing from the bottom-up inventories.

More recently, Townsend-Small et al. (2012) analyzed stable CH₄ isotope ratios in atmospheric samples taken at Mt. Wilson and elsewhere in the western L.A. Basin and showed they were consistent with isotope ratios in natural gas sources. Wennberg et al. (2012) used the different atmospheric ethane/CH₄ enhancement ratios observed from research aircraft during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) field project in 2008 and the California Research at the Nexus of Air Quality and Climate Change (CalNex) field project (Ryerson et al., 2013) in 2010 to estimate an upper limit of 400 Gg CH₄/yr from natural gas leakage in the SoCAB. Further, their top-down analysis resulted in a calculated emission of 440 Gg CH₄/yr in the SoCAB. Wennberg et al. (2012) also re-calculated the data used by Hsu et al. (2010) to derive CH₄ emissions for the entire SoCAB, and calculated a SoCAB CH₄ emission from 2008 using data from ARCTAS. The results are summarized in Table 5.

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

SoCAB, and use them in a system of linear equations to further quantify the source apportionment of CH₄ in the L.A. Basin.

III.2. Measurements

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

were derived from various sensors aboard the NOAA P-3; the uncertainty of the wind speed is estimated to be ± 1 m/s. Sensors aboard the NOAA P-3 also measure relative humidity, ambient temperature, and potential temperature with an estimated uncertainty of $\pm 0.5^\circ\text{C}$, $\pm 0.5^\circ\text{C}$, and $\pm 0.5\text{K}$, respectively.

At the CalNex Pasadena ground site, located on the California Institute of Technology (Caltech) campus, measurements of $\text{C}_2\text{--C}_5$ alkanes were made by a gas chromatograph mass spectrometer (GC-MS) on 5-minute integrated samples taken every half hour (Gilman et al., 2010). Imprecision of these measurements are $\pm 8\%$ for ethane and $\pm 6\%$ for propane; inaccuracy is estimated at $\pm 15\%$ for each. Data from the ground site were taken between 15 May and 15 June, 2010. CH_4 was not measured at the Pasadena ground site.

Additionally, whole-air flask samples were taken twice daily at the Mount Wilson Observatory (MWO) for most days during May and June 2010, and analyzed for a variety of trace gas species, including CH_4 , CO_2 , CO , and hydrocarbons (Dlugokencky et al., 2011; Conway, et al., 2011; Novelli & Masarie, 2010). Imprecision of the CH_4 measurement is ± 1 ppb; imprecision of the CO_2 measurement is ± 0.1 ppm; imprecision of the CO measurement is ± 1 ppbv, and inaccuracy of the CO measurement is estimated to be $\pm 5\%$.

We also analyze alkane data from whole air samples taken in the L.A. Basin prior to 2010. Ethane and propane were measured in whole air samples taken on four flights in L.A. aboard an instrumented National Aeronautics and Space Administration (NASA) DC-8 research aircraft during ARCTAS in June 2008 (Simpson et al., 2010). Ethane and propane were also measured on one flight in L.A. aboard the NOAA P-3

during the Intercontinental Transport and Chemical Transformation (ITCT) study in May 2002 (Schauffler et al., 1999).

III.3. Methods

To ensure sampling from the L.A. Basin, we consider aircraft data collected between 33.6 and 34.3°N latitude and 118.5 and 116.8°W longitude (Figure 24d, dashed box) in the following analysis. Aircraft data were further limited to samples taken between 1000 and 1700 PST, between 200 and 800 m above ground, and below 1400 m above sea level, to ensure daytime sampling in the well-mixed boundary layer, which averaged 1000 ± 300 m above ground level for the daytime L.A. flights (Neuman et al., 2012). Ground-based measurements at Pasadena were retained between 1000 and 1700 PST to ensure sampling of a well-mixed daytime boundary layer. For MWO measurements, afternoon samples, which typically occurred between 1400 and 1500 PST, were retained to capture upslope transportation from the L.A. Basin (Hsu et al., 2010). Linear fits to the data presented below are orthogonal distance regressions (Boggs et al., 1989) weighted by instrument imprecision (weighted orthogonal distance regression, ODR). The total uncertainty in the fitted slope is calculated by quadrature addition of the fit uncertainty and the measurement uncertainties (i.e., calibration uncertainties).

For flux determinations, crosswind transects were flown downwind of known point sources. Enhancements of CH₄ above background levels were integrated along the flight track, and a flux was calculated using the following equation:

$$flux = v \cos(\alpha) \int_{z_0}^{z_1} n(z) dz \int_{-y}^y X_m(y) dy \quad (12)$$

where $v \cos(\alpha)$ is the component of the average wind velocity normal to the flight track, n is the number density of the atmosphere, z_0 is the ground level, z_1 is the estimated boundary layer height, and X_m is the measured mixing ratio enhancement above the local background along the flight track (White et al., 1976; Trainer et al., 1995; Ryerson et al., 1998; Nowak et al., 2012). Boundary layer heights are estimated from vertical profiles of relative humidity, ambient temperature, and potential temperature made prior to and after the crosswind transects. We assume the plume is well-mixed vertically and the wind velocity is constant between emission and measurement. We estimate the uncertainty in these assumptions, combined with the uncertainties of the wind speed, wind direction, temperature, and integrated gas species, to be $\pm 50\%$ (Nowak et al., 2012). Weighted averages of the fluxes are calculated following Taylor (1997). When calculating the CH_4 flux from dairies, CH_4 variability immediately upwind of the dairies is sufficiently large to complicate interpolation from the downwind local background. To account for this, we take the weighted ODR slope of CH_4/CO immediately upwind, multiply this ratio by the measured CO downwind of the dairies, and integrate the CH_4 enhancement above CH_4 calculated from CO ($\text{CO} \times [\text{CH}_4/\text{CO}]_{\text{upwind}}$), similar to the integrations performed by Nowak et al. (2012). This assumes the dairies emit a negligible amount of CO . Fluxes are calculated for P-3 transects that are mid-way between the ground and the top of the well-mixed layer of the atmosphere.

As with previously published works (Wunch et al., 2009; Hsu et al., 2010; Wennberg et al., 2012), we estimate total CH_4 emissions in the SoCAB by multiplying enhancement ratios of CH_4 to CO and CO_2 by inventory estimates of CO and CO_2 for that region:

$$E_{CH_4} = \left(\frac{CH_4}{X} \right)_{ODR\ slope} \times \left(\frac{MW_{CH_4}}{MW_X} \right) \times E_X \quad (13)$$

where E_{CH_4} is the emission of CH_4 , X is either CO or CO_2 , MW is the molecular weight, and E_X is the inventory emission value of either CO or CO_2 . Although not necessarily emitted from the same sources, we assume emissions of CH_4 , CO, and CO_2 are well-mixed by the time they are sampled from the NOAA P-3. We also do not estimate an uncertainty for the inventory value of either CO or CO_2 .

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

CARB projects the total 2010 annually averaged CO emissions in the SoCAB at 979 Gg CO/yr (Table 6). We use the CARB inventory which excludes biomass burning CO emissions because no known biomass burning events occurred during CalNex. This estimate is 4% less than the summertime CO inventory without biomass burning emissions, and approximately 6% less than the annually averaged CO inventory

Table 6. Inventories used in current analysis

Emission	Inventory	Year	Geographic Area
180 Tg CO_2 /yr	CARB GHG ^a	2009	SoCAB ^c
979 Gg CO/yr	CARB ^b	2010	SoCAB
301 Gg CH_4 /yr	CARB GHG ^a	2009	SoCAB ^c

^a 2009 CARB CO_2 and CH_4 emissions (<http://www.arb.ca.gov/cc/inventory/data/data.htm>)

^b projected 2010 CARB CO emissions

(<http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php>)

^c statewide inventory apportioned by SoCAB population

including biomass burning emissions used by Wennberg et al. (2012). To estimate 2010 CH₄ emissions in the SoCAB using the 2009 CARB GHG inventory, we follow the method used by Wunch et al. (2009), and take the total statewide emission of 1525 Gg CH₄/yr, less agricultural and forestry CH₄ emissions of 898 Gg CH₄/yr, then apportion the remainder by population. Scaling by population results in some additional inventory uncertainty, since not all CH₄ emissions will scale with population; however, we do not attempt to quantify the uncertainty in the CARB GHG inventory. In 2010, the SoCAB comprised 43% of California's population

(http://www.arb.ca.gov/app/emsinv/trends/ems_trends.php). However, unlike Wunch et al. (2009), we add back an agricultural emission of 31.6 Gg CH₄/yr, calculated in section 4.3 below, from SoCAB dairy operations. Therefore, we attribute 301 Gg CH₄/yr to the SoCAB from the 2009 CARB GHG inventory (Table 6).

According to CARB's mobile source emission inventory for the Los Angeles County portion of the SoCAB, mobile source CO₂ emissions remained essentially unchanged (39.94 to 39.95 Tg CO₂/yr) in 2009 and 2010. Additionally, the statewide CARB GHG inventory for CO₂, with out-of-state electricity generation emissions removed, decreased by less than 2% between 2008 and 2009. Therefore, we assume errors due to sampling year are negligible in examining the CO₂ emission inventories in the SoCAB from 2009–2010. To estimate 2010 CO₂ emissions in the SoCAB using the 2009 CARB GHG inventory, we take the total statewide emission of 465.7 Tg CO₂/yr, less out-of-state electricity generation of 47.9 Tg CO₂/yr, then apportion the remainder by population. We therefore attribute 180 Tg CO₂/yr to the SoCAB using the 2009

CARB GHG inventory. We do not compare to the Vulcan CO₂ inventory (Gurney et al., 2009) because it is only available for the 2002 reporting year.

III.4. Results and Discussion

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

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

Figure 24c shows known stationary sources of CH₄ in the L.A. area, which include landfills, dairies, wastewater treatment facilities, and oil fields, as well as the location of measurement sites used in this study. Dairy sources are sized by estimated CH₄ emissions from enteric fermentation, as explained in section 4.3. Landfills are sized by CH₄ emissions from the 2008 CARB GHG inventory (L. Hunsaker, personal communication, 2011). Point sources are sized by 2009 CARB individual facility CH₄ emissions, but do not stand out in the map due to their low CH₄ emissions relative to the landfills and dairies. Figure 24d shows the locations of daytime boundary-layer CH₄ data from the P-3, colored by observed mixing ratio, that were retained for the analysis as described previously. The largest concentrations of CH₄ were typically encountered along the mountains at the north edge of the L.A. Basin, likely driven by transport of air within the basin, as typical daytime winds in the L.A. Basin were from the west and southwest during May and June 2010 (Washenfelter et al., 2011). CalNex CH₄ data are

plotted against observed CO in Figure 25a. Weighted ODR fits to these data resulted in derived enhancement ratios of 0.74 ± 0.04 and 0.68 ± 0.03 ppbv CH₄/ppbv CO from the NOAA P-3 and MWO, respectively. The ratio of the CARB inventories from Table 6 is 0.54 ppb CH₄/ppb CO, and is displayed for comparison. We note that the same CH₄/CO enhancement ratio of 0.74 ± 0.03 was reported by Wennberg et al. (2012) using the CalNex P-3 data with different selection criteria. We include box and whisker plots in Figure 25a to show that the linear fit to the data is not heavily influenced by the relatively few data points of higher CH₄.

CalNex CH₄ data are plotted against observed CO₂ in Figure 25b. The slope from a weighted ODR of P-3 data is 6.70 ± 0.01 ppb CH₄/ppm CO₂ and of MWO data is 6.60 ± 0.04 ppb CH₄/ppm CO₂. The ratio of the CARB inventories from Table 6 is 4.64 ppb CH₄/ppm CO₂, and is displayed for comparison. In this case, because CH₄ and CO₂ are measured with high precision and accuracy, the largest uncertainties in interpreting the slope as an emissions ratio are likely determined by the extent of mixing of emissions from different sources within the Los Angeles air shed. Similarly, Figure 25c shows a correlation plot of CO against CO₂. The slope from a weighted ODR of P-3 data is 9.4 ± 0.5 ppb CO/ppm CO₂ and of MWO data is 10.4 ± 0.5 ppb CO/ppm CO₂. The ratio of the CARB inventories from Table 6 is 8.5 ppb CO/ppm CO₂, and is plotted for comparison. Quantitative agreement between emission ratios derived from P-3 and MWO data (Figures 25a–c) is likely due to the fact that the transport within the basin was driven by the land-sea breeze, meaning typical daytime winds in the Pasadena area near Mt. Wilson were from the southwest (Washenfelter et al., 2011). This transport, and the highest values of CH₄ and CO₂ in the P-3 data that are not seen at MWO

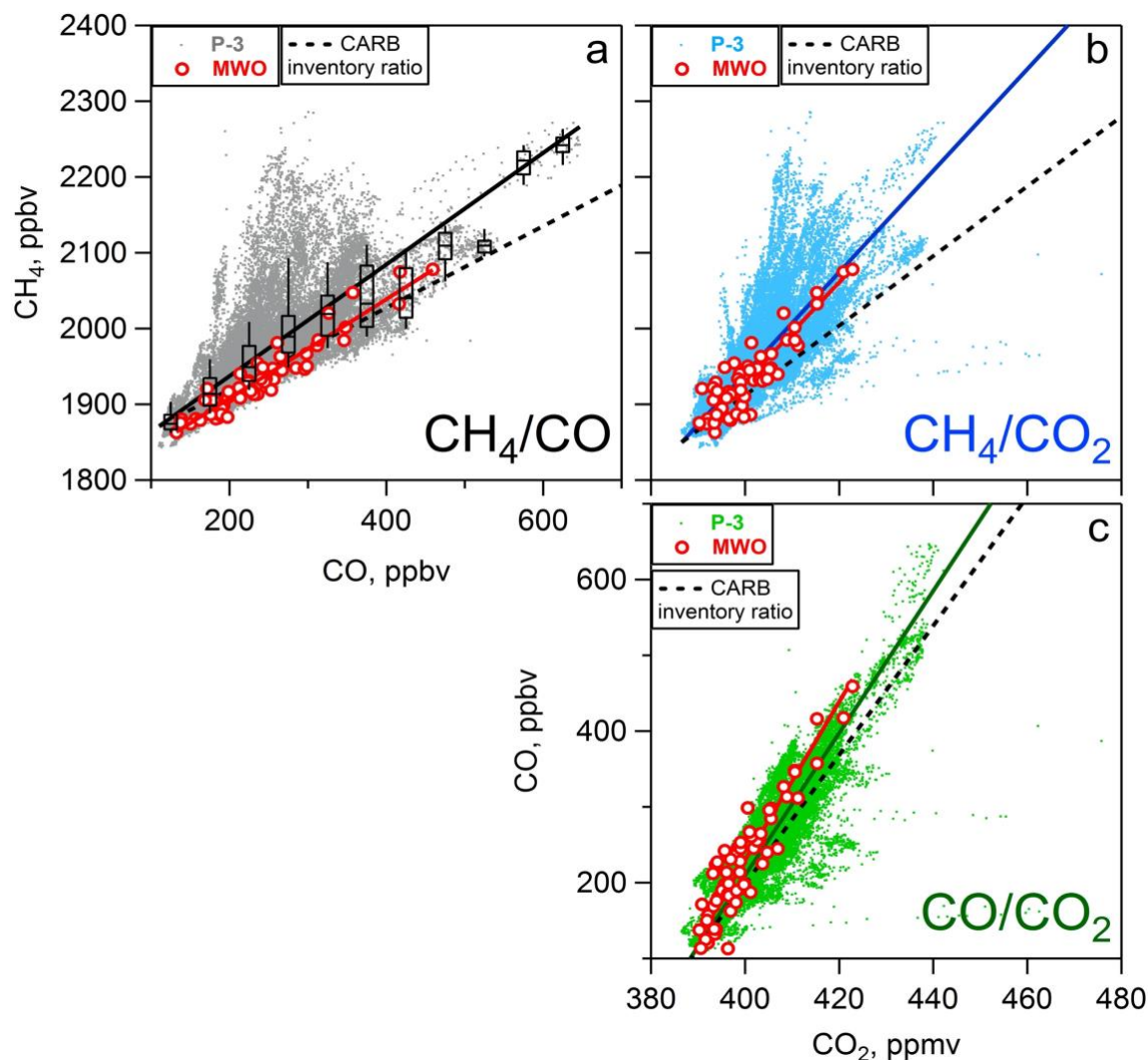


Figure 25. Correlation plots of CH₄, CO₂, and CO from all 1-second data points along flight track highlighted in Figure 24. Dots are from the NOAA P-3, while red circles are from NOAA GMD flask samples taken at the Mt. Wilson Observatory during CalNex. Weighted ODRs (solid lines) result in slopes of **(a)** 0.74 ± 0.04 and 0.68 ± 0.04 ppb CH₄/ppb CO; **(b)** 6.70 ± 0.01 and 6.60 ± 0.04 ppb CH₄/ppm CO₂; and **(c)** 9.4 ± 0.5 and 10.4 ± 0.5 ppb CO/ppm CO₂ from the NOAA P-3 and Mt. Wilson Observatory, respectively. The black dotted lines represent molar ratios of the CARB inventories listed in Table 6: CH₄:CO = 0.54, CH₄:CO₂ = 4.64×10^{-3} , and CO:CO₂ = 8.5×10^{-3} , where the background values used are the same as those determined from the fitted slopes. Also plotted in Figure 25a are boxes (25–75%), whiskers (10–90%), and the median (horizontal line) for distributions of CH₄ data from the NOAA P-3 in bins 50 ppbv CO wide.

(Figures 25a and b), also suggests that MWO preferentially samples the western part of the L.A. Basin (Hsu et al., 2010). We therefore use enhancement ratios determined from the NOAA P-3 data to derive CH₄ emissions from the entire basin.

We note that the ratio of the latest CARB CO and CO₂ inventories (Table 6) are in better agreement with our measurements than was the case for Wunch et al. (2009). This is likely due to either improved CARB inventories, the present use of a basin-wide data set to determine basin-wide emission ratios, or both.

With the slopes and inventory values quantified, we next derive a CH₄ emission using equation (13). Using the NOAA P-3 CH₄/CO slope and the projected 2010 CARB annually-averaged CO emission inventory in equation (13) yields an estimated SoCAB emission of 410 ± 20 Gg CH₄/yr. The stated uncertainty neglects uncertainty in the CARB CO inventory and is determined solely from measurement uncertainty and errors on the slope of the ODR fit to P-3 data. We note our derived emission of 410 ± 20 Gg CH₄/yr is similar to that derived from the P-3 data by Wennberg et al. (2012), which was 440 ± 100 Gg CH₄/yr using different selection criteria. It is further consistent with the emission derived by Wunch et al. (2009) of 400 ± 100 Gg CH₄/yr, which included a CARB CO inventory uncertainty of 15%. Including a 15% CO inventory uncertainty would result in an estimated emission of 410 ± 70 Gg CH₄/yr, which brings the absolute uncertainty closer in line with those of Wunch et al. (2009) and Wennberg et al. (2012). We also determine CH₄ emissions using estimates of CO₂ emissions in the SoCAB. P-3 measurements of the CH₄/CO₂ enhancement ratio observed during CalNex and SoCAB CO₂ emissions inferred from the 2009 CARB GHG inventory result in an emission rate of 440 Gg CH₄/yr, with very small uncertainties, as discussed above. This value is

therefore likely consistent with that derived using P-3 measurements and the CO inventory.

The derived top-down SoCAB CH₄ emission of 410 and 440 Gg CH₄/yr using either CARB CO or CO₂ inventories, respectively, are in much better agreement with one another than in 2008 (Wunch et al., 2009), and are a factor of 1.35 to 1.45 greater than the modified population-apportioned 2009 CARB GHG inventory value of 301 Gg CH₄/yr (Table 6). For consistency with published works (Wunch et al., 2009; Hsu et al., 2010; Wennberg et al., 2012), we choose the top-down CH₄ emission derived from the CARB CO inventory (410 ±20 Gg CH₄/yr) for the remainder of our analysis. Finally, calculated CO emissions based on the CO/CO₂ enhancement ratio observed during CalNex, and multiplied by SoCAB CO₂ emissions inferred from the 2009 CARB GHG inventory, of 1070 Gg CO/yr are within 10% of the projected 2010 CARB CO inventory.

III.4.2. Methane emissions from L.A. Basin landfills

Landfills are the largest non-fossil fuel CH₄ emission source in bottom-up inventories compiled by Hsu et al. (2010) and by Wennberg et al. (2012), but these two studies disagree on the magnitude of this source. Hsu et al. (2010) estimated annual emissions from landfills totaled 90 Gg CH₄/yr from the Los Angeles County portion of the South Coast Air Basin. Wennberg et al. (2012) estimated landfill emissions at 86 Gg CH₄/yr from the entire South Coast Air Basin. However, we believe that number is applicable to just the L.A. County portion of the SoCAB, and therefore in close agreement with that reported by Hsu et al. (2010) [P. Wennberg, personal communication, 2012].

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

The first landfill we examine is the Olinda Alpha landfill (33.934°N, 117.841°W) in Brea, Orange County, California. The NOAA P-3 flew four daytime boundary-layer transects on four different days downwind of this landfill (Figure 26),

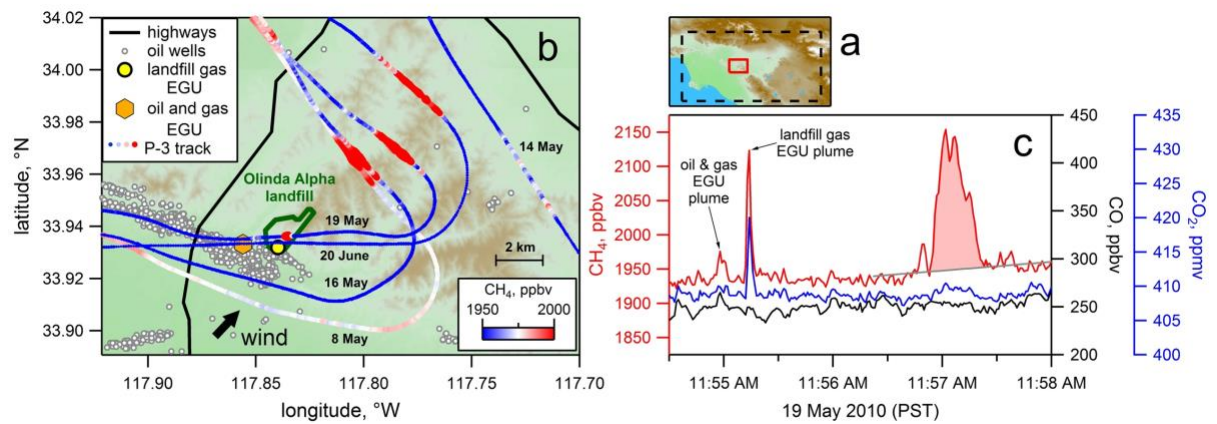


Figure 26. **a)** The map from Figure 24c–e shows the inset for part (b) in red. **b)** Four downwind transects, sized and colored by CH₄ mixing ratio, showing enhancements in CH₄ downwind of the Olinda Alpha landfill (green outline). Winds were from the southwest, except on 14 May, when they were out of the west-southwest. **c)** Example of integration of the CH₄ plume from the 19 May flight. The filled pink area is integrated above the surrounding background (gray line). The upwind transect on this day passed downwind of two power plant (Electric Generating Unit (EGU)) plumes.

and a CH₄ emission flux was determined for each transect using equation (12). The results are summarized in Table 7. For the three transects when both the WS-CRDS and QCLS CH₄ instruments were sampling ambient air, flux determinations using these independent CH₄ measurements agreed within 3%. In these cases, the flux was averaged and reported in Table 7. Three nearby CH₄ point sources are identified in the 2009 CARB GHG inventory: an oil and gas field power plant, which burns natural gas for fuel; the landfill power plant at Olinda Alpha, which burns landfill gas for fuel; and general stationary combustion from the landfill operations. Inventory data suggest that these three sources together emit between 0.0004 and 0.0015 Gg CH₄/yr, a negligible amount relative to CH₄ emitted directly from the landfill. On 19 May, the NOAA P-3 sampled plumes from the nearby oil and gas power plant and the landfill's power plant, both of which burn natural gas as fuel (Figure 26c). A large spike in CO₂ was

Table 7. Landfill emission fluxes determined aboard the NOAA P-3 in 2010 from downwind plume transects.

Landfill	Transect Date	Flux, 10 ²⁵ molecules/s	Flux, Gg/yr	2008 CARB GHG inventory, ^a Gg/yr
Olinda Alpha	14 May	1.45	12.2	11.0
	16 May	1.74	14.6	
	19 May	1.61	13.5	
	20 June	2.90	24.3	
	average^b	1.70 ±0.44	14.3 ±3.7	
Puente Hills	8 May	4.29	36.0	38.8
	19 May	3.62	30.4	
	20 June	4.48	37.6	
	average^b	4.06 ±1.18	34.0 ±9.9	

^a data from CARB (L. Hunsaker, personal communication, June 2011)

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

encountered in the landfill power plant plume, as well as CH₄ and perhaps a small amount of CO. However, downwind of the landfill in the large plume of CH₄, the CO₂ enhancement does not stand out significantly above the background variability.

Therefore, our analysis of P-3 data supports the conclusion from the inventory that landfill CH₄ emissions dominate the observed plume enhancements downwind of Olinda Alpha landfill. Using NOAA P-3 CH₄ data from all four transects, we directly calculate a weighted average CH₄ emission flux via equation (12) of $1.70 \pm 0.44 \times 10^{25}$ molecules/s, equal to 14.3 ± 3.7 Gg CH₄/yr assuming a constant emission, where the weights are the 50% uncertainty of each determination. For comparison, the CARB GHG inventory emission estimate from the Olinda Alpha landfill is 11.0 Gg/yr for 2008, showing agreement within the errors of the direct estimate using P-3 airborne data.

The second landfill we examine in depth is the Puente Hills landfill (34.020°N, 118.006°W) in City of Industry, Los Angeles County, California. Of all California landfills, Puente Hills is the largest emitter of CH₄ in the 2008 CARB GHG inventory. Nearby sources of CH₄ in the 2008 CARB GHG inventory include the Puente Hills power plant (0.00045 Gg CH₄/yr) and the Savage Hills Canyon landfill (1.1 Gg CH₄/yr), both of which are small relative to the CARB GHG inventory of 39 Gg CH₄/yr emission rate for Puente Hills. From NOAA P-3 data over three daytime boundary layer plume transects, we determine an average emission flux of $4.06 \pm 1.18 \times 10^{25}$ molecules/s, which extrapolates to 34.0 ± 9.9 Gg CH₄/yr assuming a constant emission (Table 7). Similar to the findings for Olinda Alpha, the CARB GHG inventory of 39 Gg CH₄/yr

for the Puente Hills landfill is in agreement within the errors of the direct estimate using P-3 airborne data.

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

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

III.4.3. Methane emissions from L.A. Basin dairies

Salas et al. (2008) published dairy locations in California for the year 2005, with an estimate of dairy cow population for each. The locations are plotted as filled yellow circles in Figure 24c, and sized by the expected CH₄ emission from enteric fermentation according to the 2009 CARB GHG inventory (144 kg CH₄/yr per cow). According to Salas et al. (2008), all dairies in San Bernardino and Riverside counties were also located in the SoCAB, and 87% of the 199,995 dairy cows in the SoCAB were located in the Chino area (the large grouping of dairies in Figure 24c). The Chino-area dairy operations, which at one time were distributed across the Riverside-San Bernardino

county line in satellite images, now appear to be located mainly in San Bernardino County as the Riverside dairies have been converted to residential neighborhoods (e.g., see Google Earth historical imagery since 2000). This declining number of dairies is confirmed by the United States Department of Agriculture (USDA)

([https://www.nass.usda.gov/Statistics by State/California/Publications/County Estimates/](https://www.nass.usda.gov/Statistics_by_State/California/Publications/County_Estimates/)), which reports a decrease in dairy cows in San Bernardino and Riverside Counties from 200,000 head in 2005 to 137,500 head in 2010. In addition to dairy cows, dairies also stock immature heifers. Further, there are beef operations in the SoCAB, but these are negligible compared to the San Bernardino and Riverside dairy populations. According to the USDA, there were a total of 431,000 cattle in San Bernardino and Riverside counties in 2005, and 295,000 cattle in 2010. For both years, dairy cows represented approximately 46.5% of the cattle population in the SoCAB. From these dairy and cattle populations, we construct a bottom-up emissions inventory for the SoCAB using the same emission factors as the CARB GHG inventory.

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

In addition to enteric fermentation, manure management practices have a substantial effect on CH₄ emissions from livestock operations. In the L.A. Basin, dairies typically practice solid storage (<http://www.aqmd.gov/docs/default-source/rule->

[book/support-documents/rule-1127/final-staff-report.pdf](#)), which emits relatively low levels of CH₄ (17 kg/yr per cow) according to the 2009 CARB GHG inventory. The tradeoff for this practice is that it emits larger amounts of NH₃ than other types of manure management (<https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-fifth-edition-volume-i-chapter-9-food-and-0>). Therefore, if we attribute dry manure management emissions to the SoCAB dairy cow population, and the dry lot emission rate of 2.1 kg CH₄/yr for the remaining heifers, we get an additional 2.7 Gg CH₄/yr from dairy operation manure management in the SoCAB. This results in a total of 31.6 Gg CH₄/yr from enteric fermentation and manure management for the SoCAB dairy operations. This is the emission from agriculture and forestry that we add back into the population-apportioned CARB CH₄ inventory above (Table 6).

Our estimate of 31.6 Gg CH₄/yr, based on inventory data, is less than half of the 76 Gg CH₄/yr estimated by Wennberg et al. (2012). We attribute this difference in bottom-up inventories to the different assumptions of manure management practices. Wennberg et al. (2012) scaled total California CH₄ emissions by livestock population, which also assumes the manure management practices from the San Joaquin Valley apply to the L.A. Basin. For example, the anaerobic lagoons more commonly used in the San Joaquin Valley emit 325 kg CH₄/yr per cow according to the 2009 CARB GHG inventory, significantly higher than 17 kg CH₄/yr per cow from dry manure management practices typical of the L.A. Basin.

Nowak et al. (2012) used P-3 data from CalNex to derive emissions of ammonia (NH₃) from dairy farms in the Chino area. From NOAA P-3 measurements, we determine a CH₄ flux from the Chino-area dairies for the same three downwind transects

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

III.4.4. Spatial distribution of methane sources

Townsend-Small et al. (2012) concluded that the CH₄ emissions in the L.A. region had a stable isotope ratio similar to that of fossil-fuel CH₄. This conclusion was based on measurements made at the Mt. Wilson Observatory. A back-trajectory (White et al., 2006; <http://www.esrl.noaa.gov/psd/programs/2010/calnex/traj/>) from MWO for 5 August 2009, the specific day that Townsend-Small et al. (2012) used to determine the excess CH₄ stable isotopic ratio, the prevailing winds to MWO were from the southwest, or from downtown L.A. and the coast west of downtown L.A. The trajectory tool also shows winds from the eastern basin on the previous day, which was excluded by Townsend-Small et al. (2012) due to lower correlation between the excess CH₄ and

$\delta^{13}\text{C}$. Using the trajectory tool, we conclude that the MWO data interpreted by Townsend-Small et al. (2012) were dominated by emissions from the western basin only, and were not influenced by emissions from either the largest landfills (Puente Hills and Olinda Alpha), or from the dairies in the eastern part of the L.A. Basin. This spatially-biased sampling is consistent with their conclusion that landfills do not contribute significantly to the total atmospheric CH_4 burden in L.A.

Evidence for the heterogeneous spatial distribution of CH_4 sources in the SoCAB can be seen in the NOAA P-3 data. Figure 27 shows that the correlation of ethane with CH_4 is dependent on the sample location in the L.A. Basin. Also shown in Figure 27 is the slope used by Wennberg et al. (2012) to represent the ethane/ CH_4 ratio (16.5 ± 2.5 ppt ethane/ppb CH_4) in pipeline-quality dry natural gas from the Southern California Gas Company (SoCalGas), the major provider of natural gas to the SoCAB, for 2010. The chemical data in Figure 27 reflect the known source types shown on the map in Figure 24c: the large CH_4 sources in the eastern L.A. Basin, primarily landfills and dairies, are not significant sources of ethane relative to CH_4 .

We can reconcile the conclusions of Townsend-Small et al. (2012) and Wennberg et al. (2012) with the CARB GHG inventory by noting that fossil fuel CH_4 emissions predominate in the western basin, and that landfill and livestock CH_4 emissions predominate in the eastern basin. However, in contrast to the findings of Wennberg et al. (2012), we find that natural gas leaks from the SoCalGas and in-home pipelines are not the only possible source of fossil fuel CH_4 to the western basin, as described below.

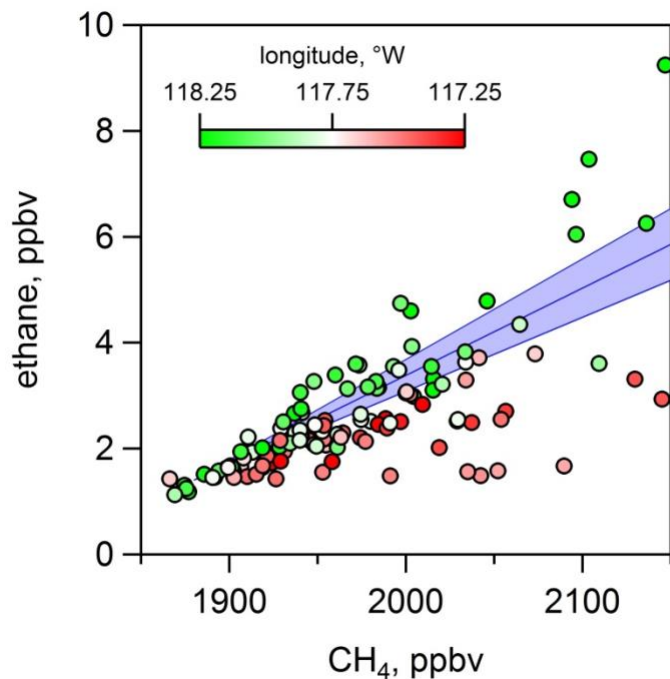


Figure 27. Correlation plot of ethane vs. CH₄ from the NOAA P-3 in the L.A. Basin. Data points are colored by longitude to show the different correlations of ethane to CH₄ in the western part of the basin (green) and the eastern part (red). The blue line represents the slope of 1.65 ± 0.25 % used by Wennberg et al. (2012) to represent the estimated ethane/CH₄ ratio of pipeline-quality dry natural gas from the Southern California Gas Company's pipelines.

III.4.5. Light alkane emissions from local natural gas production

Los Angeles was only one of three out of 28 cities characterized by propane and ethane levels within 10% of one another in the atmosphere, despite the shorter atmospheric lifetime of propane (Baker et al., 2008). Figure 28 shows correlations of propane vs. ethane in whole-air samples from various aircraft projects in the Los Angeles region (ITCT 2002, ARCTAS 2008, and CalNex 2010), as well as measurements from the CalNex Pasadena ground site in 2010. Also plotted are lines

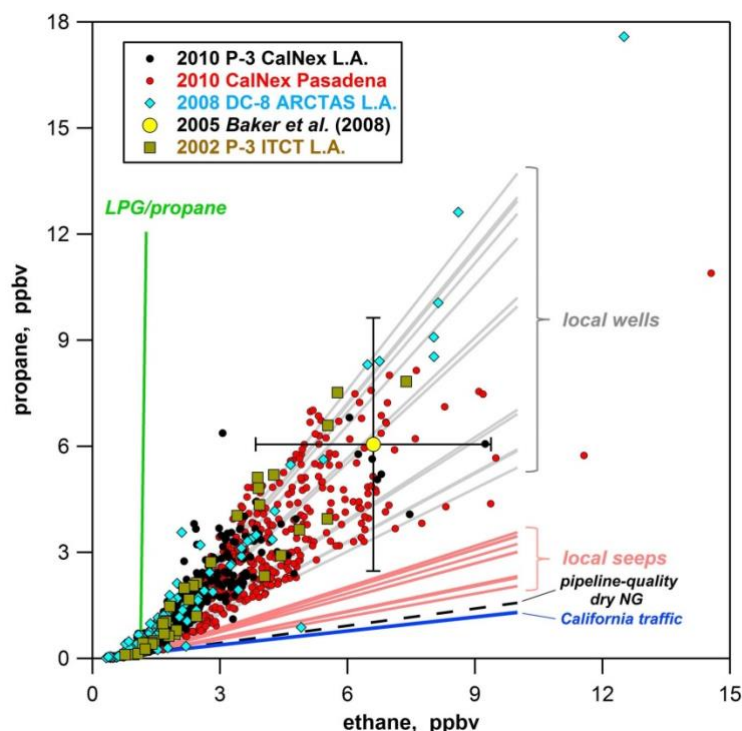


Figure 28. Correlation plot of propane vs. ethane from four Los Angeles datasets. Also plotted are composition ratios of local wells (gray lines) and local seeps (salmon lines) reported by Jeffrey et al. (1991), the composition ratio of pipeline-quality dry natural gas (black dashed line), the propane/ethane emission ratio from a San Francisco Bay-area tunnel study reported by Kirchstetter et al. (1996), and the average composition ratio of liquefied petroleum gas (LPG), or propane (green line).

representing the composition ratios of other possible sources of ethane and propane in Los Angeles.

The L.A. Basin is home to oil and gas operations (see Figure 24c); the composition ratios depicting possible emissions from local natural gas (gray lines) and local geologic seeps (salmon lines) in Figure 28 are those reported by Jeffrey et al. (1991). The lower propane content relative to ethane seen in the seeps (e.g., the La Brea tar pits) compared to the local natural gas is attributed to near-surface microorganisms

breaking down larger alkanes into smaller alkanes (Jeffrey et al., 1991) during the time the natural gas migrates toward the surface. The average propane/ethane ratio for processed gas in SoCalGas pipelines (Wennberg et al., 2012) is plotted as a dashed black line. Pipeline-quality dry natural gas has a low propane/ethane ratio because the natural gas has been processed (i.e., the higher alkanes have been removed from the natural gas for use elsewhere) before distribution. The SoCalGas ratio is representative of natural gas piped in from out of state (e.g., from Texas, Wyoming, and Canada); approximately 90% of natural gas used in California is imported (http://www.socalgas.com/regulatory/documents/cgr/2010_CGR.pdf). The on-road emissions are taken from a San Francisco Bay-area tunnel study by Kirchstetter et al. (1996), who reported a vehicular emission ratio of 0.13 mol propane/mol ethane roughly similar to those by Fraser et al. (1998; 0.27 mol propane/mol ethane) and by Lough et al. (2005; 0.06–0.18 mol propane/mol ethane). Vehicle engine exhaust typically contains small, decreasing amounts of CH₄, ethane, and propane due to incomplete combustion, as gasoline and diesel fuel do not contain significant amounts of these light alkanes. The on-road emissions, local geologic seeps, and the pipeline-quality dry natural gas from SoCalGas contain 3–5 times more ethane than propane, and therefore cannot alone explain the ambient ratios measured in the L.A. Basin. The propane and ethane composition of unprocessed natural gas from local wells, on the other hand, closely matches the SoCAB ambient measurements from three aircraft campaigns, the CalNex ground site measurements, and the Baker et al. study (2008). Propane and ethane were also typically enhanced at the same time, with the exception of one measurement with elevated propane near the Long Beach area (Figure 24e).

The data in Figure 28 are suggestive that local oil and gas wells contribute significantly to the atmospheric propane burden in the SoCAB. However, Wennberg et al. (2012) suggested a large source of propane from fugitive losses from the liquefied petroleum gas (LPG) industry (i.e., propane tanks) may exist in addition to leaks from the pipeline-quality dry natural gas distribution system in the L.A. Basin. This would be consistent with the findings of past works that have found significant fugitive losses of propane in other cities, such as Mexico City (Blake & Rowland, 1995). We therefore extend our analysis to simultaneously incorporate ethane, propane, and C₄ (*n*- and *i*-butane) and C₅ (*n*- and *i*-pentane) isomers to better attribute and quantify the sources of light alkanes and CH₄ to the SoCAB atmosphere. Light alkanes are plotted in Figure 29, with lines depicting the composition of natural gas in SoCalGas pipelines (Wennberg et al., 2012) and of on-road emissions (Kirchstetter et al., 1996). We assume any daytime chemical processing of these alkanes is negligible as there are no obvious differences between daytime and nighttime correlations of these alkanes with CO, similar to what Borbon et al. (2013) found for *n*-butane and CO at the CalNex Pasadena ground site. Atmospheric enhancement ratios of propane, *n*-butane, and *i*-butane (Figures 29b–d) relative to ethane are consistent with the compositions of local natural gas (Jeffrey et al., 1991). On-road emissions do not appear to contribute significantly to the CH₄, ethane, and propane in the L.A. atmosphere, and pipeline-quality dry natural gas and/or local geologic seeps do not appear to contribute significantly to the propane and *n*-butane relative to ethane in the L.A. atmosphere. Because the C₂–C₄ alkane composition signatures of local natural gas reflect the observations, we conclude that the local natural gas industry has a significant impact on atmospheric C₂–C₄ alkanes, including propane,

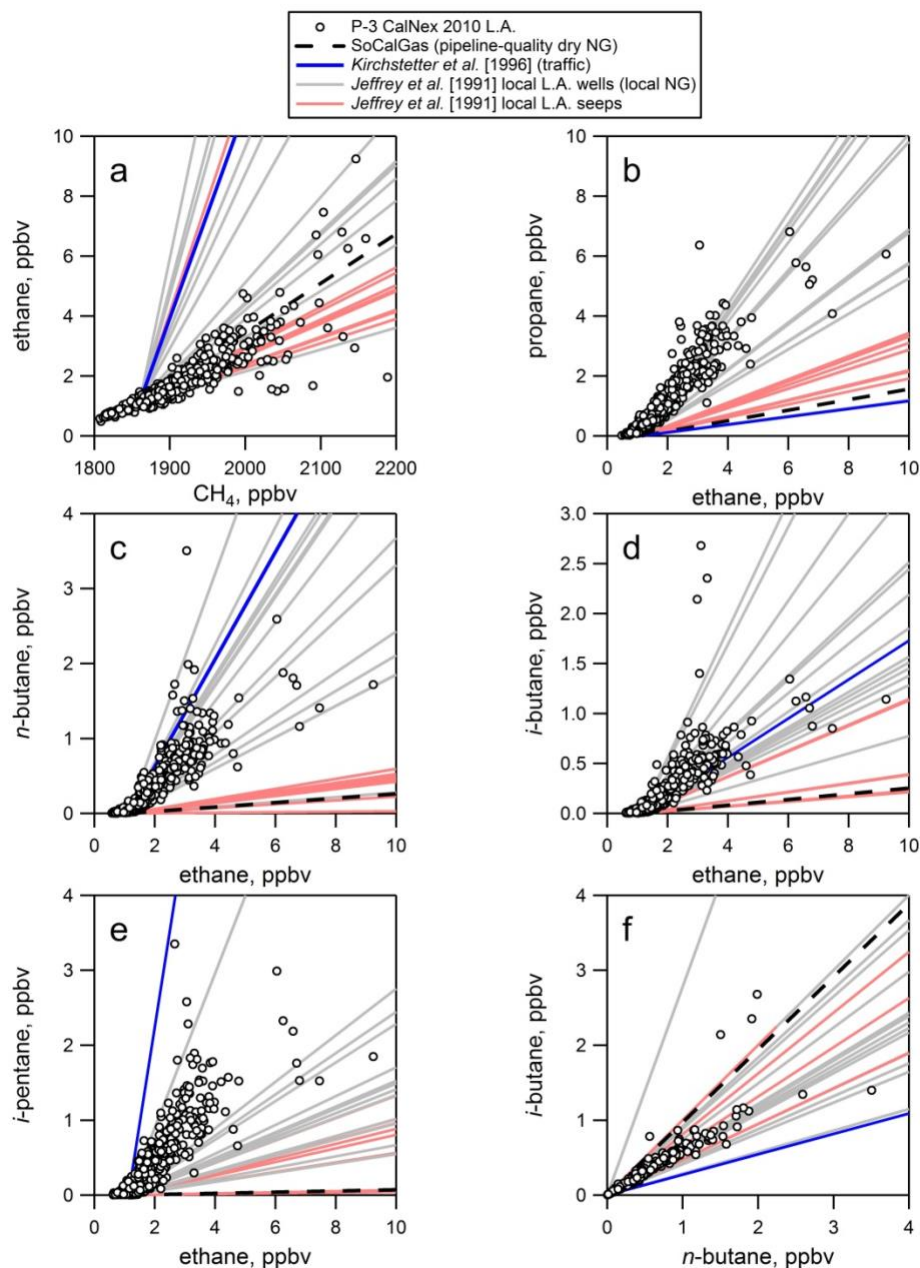


Figure 29. Plots of CH_4 and $\text{C}_2\text{--C}_5$ alkanes from the NOAA P-3 CalNex data set, selected for L.A. (black circles). Nighttime and high-altitude data are included. Also included for reference are the emission ratios of mobile sources from Kirchstetter et al. (1996; blue line), composition ratios measured by Jeffrey et al. (1991) for local natural gas (gray lines) and local geologic seeps (salmon lines), and composition ratios from pipeline-quality dry natural gas (NG) delivered by SoCalGas (dashed black line). These ratios were plotted from daytime background levels.

in the L.A. Basin. We infer CH₄ emissions from the local natural gas industry are non-negligible as well, as discussed below.

III.4.6. Source Attribution

Here we quantify total emissions of C₂–C₅ alkanes in the L.A. Basin based on their observed enhancement ratios to CO, as for CH₄ above. Figure 30 shows C₂–C₅ alkanes plotted versus CO with their respective ODR fits. The slopes from these fits are used in equation (13) along with the projected 2010 CARB CO inventory to calculate annual alkane emissions in the SoCAB. We assume the slopes represent a direct emission with no chemical aging. These emissions are listed in the right-most column of Table 8. Also listed in Table 8 are the estimated contributions from mobile sources in the SoCAB, using modified C₁–C₅ to CO emission ratios from Kirchstetter et al. (1996; discussed below) and CO emissions from the mobile sources category in the projected 2010 CARB CO inventory, equal to 925 Gg CO/yr, in equation (13).

Wennberg et al. (2012) attribute the inventory CH₄ shortfall (Wunch et al., 2009; Hsu et al., 2010) by ascribing much of the CH₄ and ethane enhancements to fugitive losses of processed pipeline-quality dry natural gas. They further suggest the majority of atmospheric propane is due to LPG industry/propane tank fugitive losses. Here, we consider other possible explanations of the sources of CH₄ and light alkanes in the L.A. Basin for the following two reasons. First, the source attribution by Wennberg et al. (2012) leaves little room for CH₄ emissions from landfills, wastewater treatment plants, and dairies in the L.A. Basin. This solution seems unlikely based on direct emissions flux estimates using the P-3 data downwind of landfills and dairies in the SoCAB, as described above. Second, the attribution by Wennberg et al. (2012) would leave a

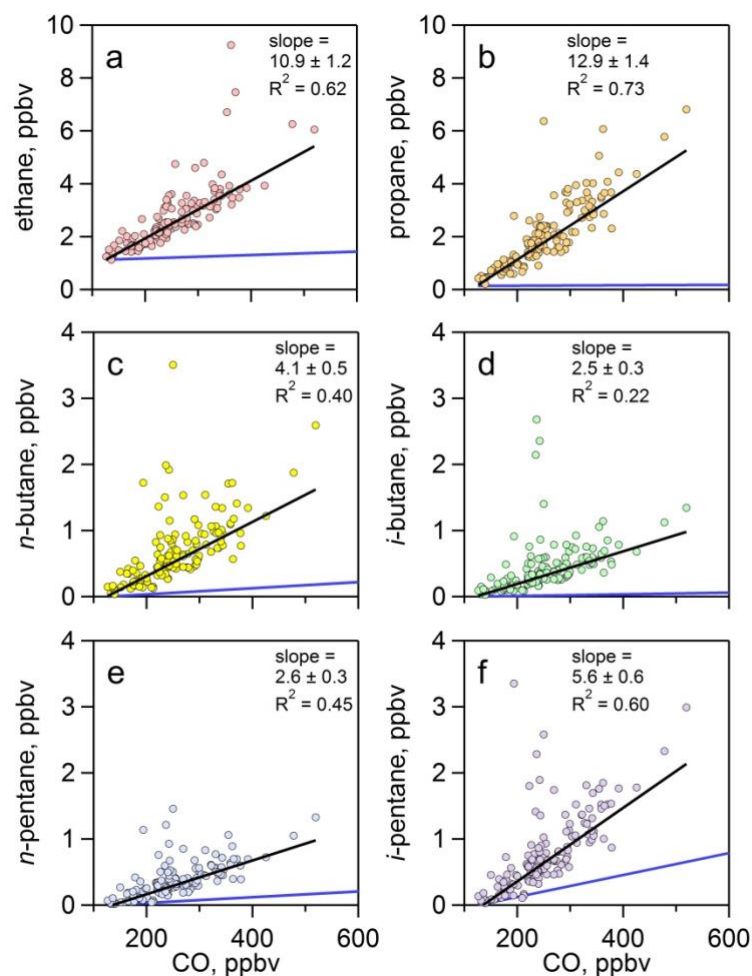


Figure 30. a–f) Daytime measurements of alkanes vs. CO from the NOAA P-3 in the L.A. Basin during CalNex are plotted as filled circles. For comparison, the alkane/CO emission ratios from a San Francisco Bay-area tunnel study (Kirchstetter et al., 1996) are plotted as a solid blue line, which extends to the right axis. The slope from a weighted ODR (given as ppt alkane/ppb CO), total slope uncertainty, and R^2 are given in each panel.

shortfall in both *n*- and *i*-butane emissions that cannot be explained by gasoline evaporation or emissions from mobile sources. We use a multivariate approach based on a linear combination of the CH_4 and light alkane compositions from known sources in order to attribute and quantify total CH_4 and $\text{C}_2\text{--C}_5$ alkane emissions in the South Coast Air Basin.

Table 8. Derived emissions in the South Coast Air Basin (in Gg/yr) for 2010 from each source sector used in linear analysis.

	Pipeline-quality dry NG/ local seeps	CH ₄ -dominant (landfills, dairies, etc.)	Local NG	LPG/propane	Evaporated gasoline	Mobile sources	CARB other	Summed source totals	Estimated SoCAB total
CH ₄	192 ±54	182 ±54	32 ±7	---	---	4.9 ±1.3	1.2 ±0.3	411 ±77	411 ^a ±21
ethane	5.9 ±1.7	---	4.5 ±1.0	0.05 ±0.02	0.0 ±0.0	0.6 ±0.1	0.3 ±0.1	11.4 ±1.9	11.4 ^a ±1.3
propane	1.5 ±0.4	---	9.9 ±2.0	6.6 ±2.9	0.006 ±0.001	0.1 ±0.0	1.6 ±0.4	19.8 ±3.6	19.8 ±2.2
<i>n</i> -butane	0.3 ±0.1	---	5.9 ±1.2	0.02 ±0.01	0.5 ±0.1	0.3 ±0.1	1.4 ±0.4	8.5 ±1.3	8.3 ±1.0
<i>i</i> -butane	0.3 ±0.1	---	2.2 ±0.5	0.13 ±0.06	0.08 ±0.02	0.04 ±0.01	1.8 ± 0.5	4.6 ±0.6	5.1 ±0.6
<i>n</i> -pentane	0.07 ±0.02	---	2.2 ±0.5	---	2.6 ±0.4	1.0 ±0.1	0.3 ±0.1	6.6 ±0.6	6.5 ±0.8
<i>i</i> -pentane	0.11 ±0.03	---	2.4 ±0.5	0.003 ±0.001	7.6 ±1.0	3.9 ±0.5	0.03 ±0.01	14.1 ±1.2	14.1 ±1.5

^a Wennberg et al. (2012) estimate emissions to the SoCAB of 440 ±100 Gg CH₄/yr and 12.9 ±0.9 Gg ethane/yr

We include seven different source types (sectors) with distinct and known CH₄ and C₂–C₅ alkane compositions in the following analysis: (1) Leaks of processed dry natural gas from pipelines, and/or emissions from local geologic seeps (this approach cannot distinguish between pipeline-quality dry natural gas and local seeps); (2) CH₄-dominated emissions, such as from landfills, wastewater treatment plants, and dairies; (3) Leaks of unprocessed, local natural gas; (4) Leaks of liquefied petroleum gas from propane tanks; (5) On-road combustion emissions from mobile sources; (6) Emissions

of CH₄ and C₂–C₅ alkanes in the SoCAB from other source sectors; and (7) Evaporative emissions from gasoline. These are described briefly below.

1. The South Coast Air Basin contains 14.8 million people, and SoCalGas delivers approximately 11 Tg/yr of natural gas to the Los Angeles area. Additionally, the Earth's natural degassing is a known source of CH₄, ethane, and propane to the atmosphere (Etiope et al., 2008; Etiope & Ciccioli, 2009), and the L.A. Basin contains abundant geologic hydrocarbon reserves (Jeffrey et al., 1991). We group fugitive losses from processed pipeline-quality dry natural gas with the emissions from local geologic seeps because the C₁–C₄ emissions from these sources are not orthogonal enough to be treated separately in our linear combination analysis (see the similarity in ratios of the salmon lines and dashed black line in Figure 29). Both pipeline-quality dry natural gas and local seep emissions contain similar amounts of CH₄ and ethane relative to one another, and have less C₃–C₅ alkanes relative to ethane than local, unprocessed natural gas. For pipeline-quality dry natural gas, most C₃₊ alkanes are removed during the processing stage, which is typically done close to the source, which for ~90% of the natural gas used in California is in Canada, Wyoming, and/or Texas. For local seeps, most C₃₊ alkanes are either preferentially adsorbed compared to CH₄ in shallow sediments, or biodegraded by microbes in the earth's crust during the seepage of local natural gas to the surface (Jeffrey et al., 1991). We use SoCalGas samples of pipeline-quality natural gas from 2010 (Wennberg et

al., 2012) to represent this source, and estimate the uncertainty of the composition at 15%.

2. CH₄-dominant emission sources, which for this analysis include landfills, wastewater treatment plants, and livestock, emit CH₄ but no significant amounts of C₂–C₅ alkanes. This is represented in our analysis as a unit vector containing only CH₄.
3. From 2007–2009, the oil and gas industry in the L.A. Basin typically produced 12–13 billion cubic feet of natural gas per year, mostly associated gas from oil wells (https://www.conservation.ca.gov/calgem/pubs_stats/annual_reports/Pages/annual_reports.aspx). We use an average of the samples reported by Jeffrey et al. (1991) weighted by 2009 gross natural gas production per field, and estimate the uncertainty of this composition at 25%.
4. Two types of LPG are sold in the Los Angeles area: one is almost completely composed of propane, the other has traces of *n*- and *i*-butane (http://www.arb.ca.gov/research/apr/past/98-338_1.pdf). We use the ratios reported by Blake & Rowland (1995) from direct analysis of LPG in Los Angeles, which is consistent with an average of the two types of LPG sold in L.A, and estimate the uncertainty of the composition at 10%.
5. On-road combustion emissions are taken from the work of Kirchstetter et al. (1996) by multiplying emission ratios of alkanes to CO by the 925 Gg CO/yr from on-road sources in the projected 2010 CARB CO inventory. The C₄–C₅ emissions represent unburned fuel and are typically proportional to the fuel

composition; the C₁–C₃ emissions typically represent incomplete combustion products. To account for differing fuel compositions since the time of the Kirchstetter et al. (1996) study, the *i*- and *n*-butane emissions calculated for mobile sources in the SoCAB (Table 8) have been scaled to the *i*-pentane emissions based on their relative abundance in gasoline (Gentner et al., 2012).

6. The use of aerosol spray cans, solvents, etc. are additional sources of light alkanes in the SoCAB. We use the 2010 CARB speciated inventory for total organic gases (<https://ww2.arb.ca.gov/speciation-profiles-used-carb-modeling>) and projected 2010 total organic gas emissions (<http://www.arb.ca.gov/app/emsmv/fcemssumcat2009.php>) for the SoCAB to estimate emissions of light alkanes not specified in other source sectors. These include emissions from aerosol spray cans and other consumer products, coatings and solvents, adhesives and sealants, and fiberglass and plastics manufacturing. For example, propane, *n*- and *i*-butane are commonly used as propellants in aerosol spray cans, having replaced CFCs in the United States in the 1970s (e.g., CARB estimates 0.6 Gg of aerosol antiperspirant were emitted to the SoCAB in 2010, of which 0.14 Gg, 0.03 Gg, and 0.15 Gg were propane, *n*-, and *i*-butane, respectively). These emissions are summed and listed in the “CARB other” column in Table 8. Emissions from natural gas leaks, petroleum refining, petroleum marketing (gas stations), landfills and composting, and mobile sources are not included

in these totals, because they are accounted for elsewhere in other source sectors. We estimate a 25% uncertainty in the “CARB other” inventory.

7. Emissions ratios from evaporated gasoline were calculated from ten gasoline samples from five Pasadena gas stations in the summer of 2010, weighted by estimated sales of 80% regular and 20% premium (Gentner et al., 2012).

Uncertainties are those reported by Gentner et al. (2012).

First, we start with estimated annual C_1 – C_5 emissions in the SoCAB (right-most column of Table 8), then subtract modified on-road emissions (Kirchstetter et al., 1996) and projected emissions of C_1 – C_5 alkanes from other sources (source sector 6, above). Next, we place the remaining source sector characteristics into a matrix and solve for the fraction each source contributes to the remaining alkane observations for the L.A. Basin based on each source’s relative abundances of various light alkanes. The matrix has five columns representing the five remaining source sectors, and seven rows containing C_1 – C_5 alkanes. We solve the equation (e.g., see §4.2 of Kim et al., 2011)

$$\mathbf{A}_{i,j} \mathbf{x}_j = \mathbf{b}_i \quad (14)$$

where $\mathbf{A}_{i,j}$ is a matrix of the C_1 – C_5 alkane composition, i , for the source sectors, j , defined above; $\mathbf{x}_j$ is the fraction each source contributes to the total observed emissions, and $\mathbf{b}_i$ is the total observed emission of alkane i minus the contributions from the mobile and “other” source sectors (Table 8). The columns of the matrix $\mathbf{A}$ are proportional to the first five columns of Table 8. We solve for the unique linear least squares solution that minimizes $(\mathbf{Ax} - \mathbf{b})$. Uncertainties in the derived x_j are estimated by a sensitivity study, where we run the solution 1,000,000 times by randomly varying $\mathbf{A}_{i,j}$ and $\mathbf{b}_i$ according to their estimated uncertainties, then use the standard deviation of the

1,000,000 $\times_j$ determinations to estimate the uncertainty in the source attribution fraction. The source attribution fractions and their uncertainties are multiplied by the total estimated SoCAB emission for each alkane, then summed with the uncertainties added in quadrature. CH₄ and C₂–C₅ alkane emissions totals, their uncertainties, and the contributions from each source type are given in Table 8. The source attribution solution solves the observed SoCAB alkane emission to within each alkane’s emission uncertainty.

The modeled source attribution presents an alternative to the alkane source distribution in the L.A. Basin atmosphere as set forth by Wennberg et al. (2012). From a total calculated source of 411 ± 21 Gg CH₄/yr in the SoCAB, our analysis determines that 47% comes from leaks of processed pipeline-quality dry natural gas and/or from local geologic seeps; 44% of the CH₄ comes from the sum of landfill, wastewater treatment, and dairy emissions; 8% from the leaks of unprocessed natural gas from production in the western L.A. Basin; and 1% from mobile sources. The attribution is presented graphically in Figure 31. Figure 31a displays the total SoCAB emissions as a black horizontal line in each panel, with contributions from the different source sectors filled below the line. Figure 31b shows the proportion each source sector contributes to the emissions of each alkane using pie charts.

Our analysis attributes CH₄ emissions of 192 ± 54 Gg CH₄/yr to leaks of pipeline-quality dry processed natural gas and/or leaks from local geologic seeps, but does not distinguish further between these two different sources. The population-apportioned 2009 CARB GHG emissions inventory estimates 40 Gg CH₄/yr lost from natural gas pipelines in the SoCAB. Our estimate of 192 Gg CH₄/yr (a) is less than the

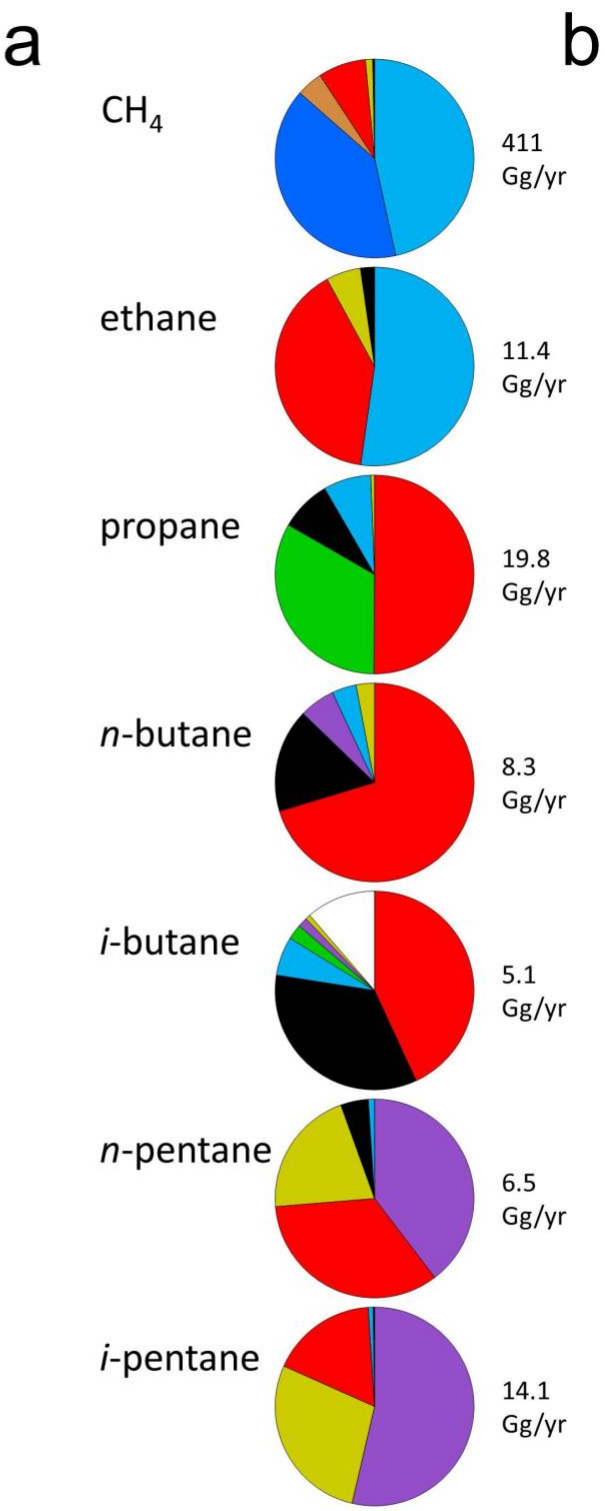
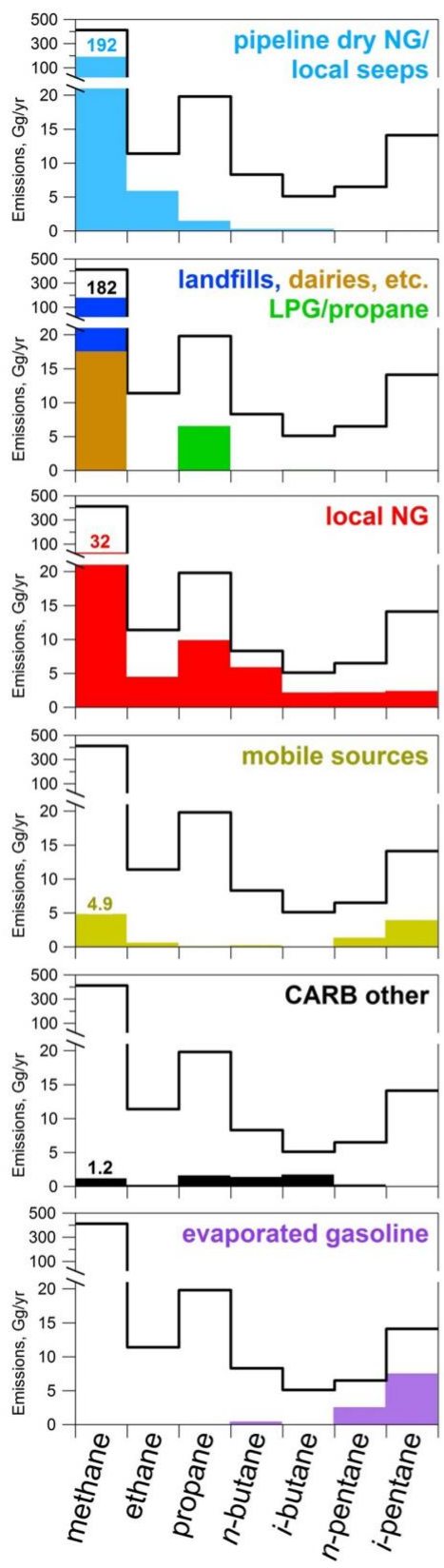


Figure 31. a) Results from a linear least squares solution to a combination of six sources and seven trace gas species in the SoCAB. The thick black line represents the estimated total annual emission to the SoCAB for seven alkanes (CH_4 and $\text{C}_2\text{--C}_5$). The colored bars represent the fraction of the total contributed by each of the six source sectors used in the linear analysis. CH_4 emissions are written above the bar. **b)** Pie charts for the same data in (a) showing the relative contributions from each source for each of seven alkanes, colored as in part (a). The white region in the *i*-butane pie chart represents the shortfall between our source attribution and our estimated emission to the SoCAB. The total emission of the alkane to the SoCAB is given to the right of each pie chart.

maximum emission of 400 ± 150 Gg CH_4/yr estimated by Wennberg et al. (2012), and (b) would represent approximately 2% of the natural gas delivered to customers in the SoCAB and, including storage and deliveries to customers outside the SoCAB, 1% of the gas flowing into the basin (Wennberg et al., 2012). These percentages would decrease linearly with any CH_4 emissions attributed to local geologic seeps. Farrell et al. (2013) estimate up to 55 Gg CH_4/yr are emitted from the La Brea Tar Pits in western L.A. County alone; if accurate, this would imply pipeline leaks of only 0.7% of the gas flowing into the basin, or a factor of at least two lower than the 2% proposed by Wennberg et al. (2012).

Our analysis attributes 182 ± 54 Gg CH_4/yr in the SoCAB to emissions from landfills, wastewater treatment, and dairies. SoCAB landfills account for 164 Gg CH_4/yr in the 2008 CARB GHG inventory, a value supported by our analysis in section 4.2. In section 4.3, we estimated in a bottom-up inventory that SoCAB dairies emitted 31.6 Gg CH_4/yr . Wennberg et al. (2012) estimated an emission of 20 Gg CH_4/yr from wastewater

treatment. These independent estimates sum to 216 Gg CH₄/yr and are consistent with our source apportionment using NOAA P-3 data.

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

(https://www.conservation.ca.gov/calgem/pubs_stats/annual_reports/Pages/annual_reports.aspx). This number assumes a CH₄ composition of 72.5% by volume for natural gas produced in the South Coast Air Basin, which is calculated as an average from the samples reported by Jeffrey et al. (1991) weighted by 2009 production. Although 17% of local production seems unrealistically high, it may be supported by a new bottom-up estimate commissioned by CARB.

A new bottom-up inventory survey, conducted by CARB for the calendar year 2007 but not yet incorporated into the official GHG inventory, indicates that 109 Gg CH₄/yr, since revised to 95.5 Gg CH₄/yr (S. Detwiler, personal communication, October 2012), were emitted throughout California by the oil and gas industry via combustion, venting, and fugitive losses (Table 3-1, <https://ww2.arb.ca.gov/sites/default/files/2018-06/FinalReportRevised.pdf>). This updated value is a factor of 2.5 larger than the current CARB GHG inventory tabulation of 38 Gg CH₄/yr from oil and gas extraction for 2007 in California. CH₄-specific emissions for the South Coast Air Quality Management District in the new CARB survey report show 24.6 Gg CH₄/yr were emitted in the SoCAB (S. Detwiler, personal communication, October 2012). According to the survey, emissions in the SoCAB accounted for 26% of the revised statewide total oil and gas operations CH₄ emission in 2007, despite accounting for only 4.4% of statewide natural

gas production in the basin that year. Our attribution of CH₄ emissions from local natural gas for 2010 based on P-3 data from CalNex is within a factor of 1.5 of the CARB bottom-up inventory in the 2007 survey. According to the survey, the other oil and gas producing regions in California do not have nearly as large CH₄ loss rates as attributed to the SoCAB. For instance, statewide losses of CH₄ represent approximately 2.1% of statewide production, and CH₄ losses from the San Joaquin Air Quality District represent approximately 1.4% of production (from Oil and Gas Districts 4 and 5). This indicates that losses from natural gas production in the L.A. Basin are unique in the State of California.

A propane emission of 6.6 ± 2.9 Gg/yr from LPG/propane tanks would represent approximately 1% of sales (<http://www.aqmd.gov/docs/default-source/ceqa/documents/aqmd-projects/2012/final-environmental-assessment-for-proposed-rule-1177.pdf>), which is less than the ~4% calculated by Wennberg et al. (2012), and closer to the 0.6% estimated from the document cited.

Finally, the analysis above suggests a resolution to the discrepancies noted between previous top-down assessments and the bottom-up inventory calculations for CH₄ in the SoCAB (e.g., Wunch et al., 2009; Hsu et al., 2010; Townsend-Small et al., 2012; Wennberg et al., 2012). We conclude the most probable source for the excess atmospheric CH₄ is likely due to a combination of primarily leaks, not accurately represented in the current CARB GHG inventory, from natural gas pipelines and urban distribution systems and/or from local geologic seeps, and secondarily leaks of unprocessed natural gas from local oil and gas production centered in the western L.A. Basin. This finding is based on the spatial information provided by P-3 measurements

during CalNex, as well as the characteristic enhancement ratios of CH₄ and the various C₂–C₅ alkanes consistently observed in the L.A. atmosphere. Also, the updated values for oil and gas industry emissions in the recent GHG survey commissioned by CARB, when incorporated fully into the official CARB GHG record, will likely help to reduce this long-standing discrepancy between top-down assessments and bottom-up inventories.

III.5. Conclusions

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

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

compiled by Salas et al. (2008) and with previous inventory estimates (Wennberg et al., 2012).

Finally, we present a top-down assessment of C₂–C₅ alkane sources in the L.A. Basin, then apportion CH₄ and the C₂–C₅ alkanes to specific source sectors in the region. Using this source apportionment approach, we estimate that 32 ±7 Gg of CH₄/yr, or 8% of the total CH₄ enhancement observed in the SoCAB during CalNex, came from the local oil and gas industry. This number represents approximately 17% of the natural gas produced in the region, which is a factor of 1.5 greater than the 12% calculated from a recent CARB bottom-up inventory survey. We estimate 182 ±54 Gg CH₄/yr are emitted by landfills, dairies, and wastewater treatment, which is consistent with bottom-up inventories, and 192 ±54 Gg CH₄/yr are emitted of processed pipeline-quality dry natural gas and/or from geologic seeps in the region. We further conclude that leaks of processed pipeline-quality dry natural gas and/or local geologic seeps, and unprocessed natural gas from local oil and gas production are the most likely major contributors to the previously noted discrepancy between CH₄ observations and State of California inventory values for the South Coast Air Basin. To further distinguish and elucidate the sources of CH₄ in the L.A. Basin, more studies from mobile instrumented laboratories, similar to Farrell et al. (2013), should be done that target natural gas pipelines and urban distribution systems, geologic seeps and local oil and gas industry production sites.

3.b. Conclusions of Publication III

After publication of the Wennberg et al. (2012) and Peischl et al. (2013) studies, the CARB GHG inventory increased fugitive emissions from the distribution of natural

gas in the state such that the population-apportioned emissions from the Los Angeles Basin region now closely match the results of Peischl et al. (2013; <https://ww2.arb.ca.gov/ghg-inventory-archive>, accessed August 2022).

In 2016, CARB announced that California had met its climate goals by reducing its GHG emissions to 1990 levels four years ahead of schedule. What's more, they did so despite increasing inventory CH₄ emissions from the rice and fugitive natural gas sectors. California now has executive orders to reduce GHG emissions to 40% below 1990 levels by 2030, and to achieve carbon neutrality by 2045 (<https://ww2.arb.ca.gov/resources/fact-sheets/ab-32-global-warming-solutions-act-2006>, accessed August 2022). Therefore, additional top-down studies will be required in the future to determine if California meets these goals.

Furthermore, Los Angeles is one of 97 cities around the world that have joined the C40 cities initiative (www.c40.org) with the goal of developing and implementing climate action plans to reduce their greenhouse gas emissions consistent with the Paris Agreement of 2016. This may be especially important in the future if the climate goals of some of the world's largest cities conflict with the intentions of their country's governments. The techniques used by Peischl et al. (2013) are therefore important for attributing CH₄ emissions to sources in complex urban environments.

Numerous studies have cited the work by Peischl et al. (2013) since it was published, including many that noted a growing trend of underreported CH₄ inventories in the scientific literature. Other studies cited this work for the following: quantifying the CH₄ emissions from Los Angeles (Wong et al., 2016; Yadav et al., 2023); quantifying the CH₄ emissions from feedlots (Viatte et al., 2017); quantifying CH₄

emissions from landfills (Mønster et al., 2019; Yesiller et al., 2022); VOC sources from oil and gas leading to SOA production (Gentner et al., 2017); the emissions from the natural gas distribution system (Weger et al., 2017; Sargent et al., 2021); the VOC source signature of petroleum sources (Kuwayama et al., 2019; Meyer et al., 2022); the mix of CH₄ and other VOCs from fossil fuels (Verhulst et al., 2017); and the variability of VOCs in different source fingerprints (Ramsden et al., 2022; Etiope et al., 2017).

Thus, due to the scientific interest in quantifying CH₄ emissions from Los Angeles, the techniques set forth by Peischl et al. (2013) will be used by the scientific community for the foreseeable future.

4. Directly quantifying emissions using airborne data

4.a. Introduction to Publication IV

Power generation in the U.S. was dominated by coal-fired power plants for most of the industrial era. In 2001, coal-fired power plants generated 51% of all electric power in the U.S. compared to 17% for natural gas-fired power plants, with nuclear and hydroelectric accounting for most of the remainder. By 2020, coal-fired plants generated 22% of power versus 38% for natural gas (www.eia.gov). This was partly due to the advent of hydraulic fracturing and horizontal drilling techniques that increased natural gas production to an all-time high and lowered the price of natural gas in the U.S. during that time. At first glance, this trend seemed beneficial to the climate because emissions of CO₂ from combined-cycle natural gas-fired power plants are half those of coal for the same electrical output. However, to understand the full impact on climate, the CH₄ emissions from coal mining and natural gas extraction also had to be accounted for. Alvarez et al. (2012) calculated the climate benefits of switching to a natural gas-powered economy and determined a natural gas loss rate to the atmosphere below 3.2% had immediate climate benefits for power generation. At the time, little was known about how much natural gas was emitted to the atmosphere during production or transportation, but the U.S. EPA GHG inventory estimated approximately a 1% emission rate from natural gas production. The first two studies of oil and natural gas producing regions by Pétron et al. (2012) and Karion et al. (2013) determined emission rates to the atmosphere of approximately 4% and 9% from areas of Colorado and Utah, respectively. However, Peischl et al. (2015) showed that not all regions' emissions were that high.

IV. Quantifying atmospheric methane emissions from the Haynesville, Fayetteville, and northeastern Marcellus shale gas production regions

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IV. Abstract. We present measurements of methane (CH₄) taken aboard a NOAA WP-3D research aircraft in 2013 over the Haynesville shale region in eastern Texas/northwestern Louisiana, the Fayetteville shale region in Arkansas, and the northeastern Pennsylvania portion of the Marcellus shale region, which accounted for the majority of Marcellus shale gas production that year. We calculate emission rates from the horizontal CH₄ flux in the planetary boundary layer downwind of each region after subtracting the CH₄ flux entering the region upwind. We find one-day CH₄ emissions of $(8.0 \pm 2.7) \times 10^7$ g/hr from the Haynesville region, $(3.9 \pm 1.8) \times 10^7$ g/hr from the Fayetteville region, and $(1.5 \pm 0.6) \times 10^7$ g/hr from the Marcellus region in northeastern Pennsylvania. Finally, we compare the CH₄ emissions to the total volume of natural gas extracted from each region to derive a loss rate from production

operations of 1.0–2.1% from the Haynesville region, 1.0–2.8% from the Fayetteville region, and 0.18–0.41% from the Marcellus region in northeastern Pennsylvania. The climate impact of CH₄ loss from shale gas production depends upon the total leakage from all production regions. The regions investigated in this work represented over half of the U.S. shale gas production in 2013, and we find generally lower loss rates than those reported in earlier studies of regions that made smaller contributions to total production. Hence, the national average CH₄ loss rate from shale gas production may be lower than values extrapolated from the earlier studies.

IV.1. Introduction

Natural gas accounted for 30% of the energy produced in the United States (U.S.) in 2013 (U.S. Energy Information Administration (EIA), www.eia.gov). So-called unconventional shale gas extraction, using directional drilling and hydraulic fracturing, has become a major source of natural gas in recent years (Figure 32); as of June 2013, unconventional natural gas extracted from shale formations accounted for 40% of the nation's total natural gas extraction. Current EIA estimates place the total recoverable shale gas in the world at over 2×10^{14} m³ (7 quadrillion cubic feet, <http://www.eia.gov/todayinenergy/detail.cfm?id=11611>), which at 2013 natural gas consumption rates would take the U.S. approximately 260 years to consume, making shale gas a significant source of energy for the future.

Natural gas is a mixture primarily composed of methane (CH₄) with C₂–C₅ alkanes, nitrogen (N₂), and carbon dioxide (CO₂) typically making up the balance. The

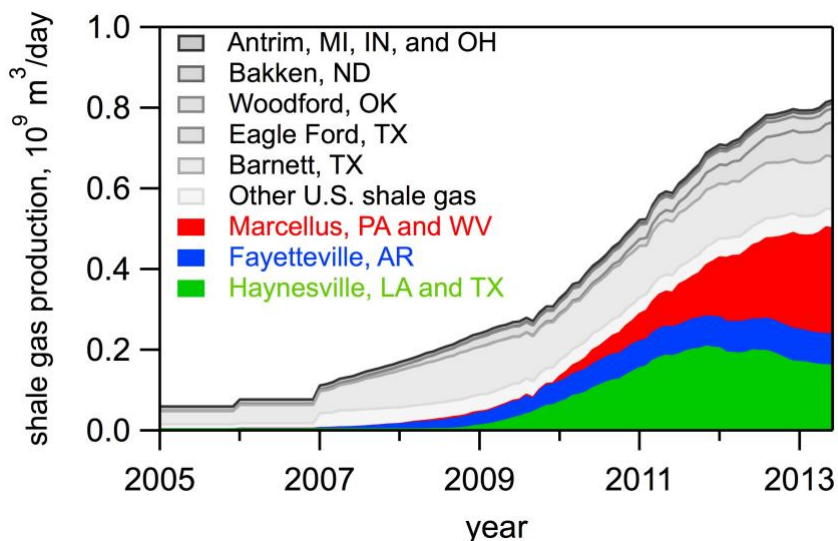


Figure 32. Unconventional shale gas production from various shale plays through June 2013.

Source: U.S. Energy Information Administration (downloaded December 2013)

relative abundances of these alkanes depend on the geologic formation from which it was extracted; natural gas associated with oil deposits is typically wetter, i.e., has more C₂–C₅ alkanes relative to CH₄ than natural gas not associated with oil deposits. Most natural gas, once extracted from the ground, requires additional processing before it is ready to be used as a fuel. This processing includes removing any water (H₂O) from the gas, and removing the C₂–C₅ alkanes for their use separately as fuel and chemical feedstocks. The result of this processing is called dry natural gas, which is composed mainly of CH₄, with C₂+ alkanes typically making up less than 5% of the gas by volume. Dry natural gas is then compressed and transported through pipelines for use downstream in residential, commercial, electrical, and industrial applications. Here, we use the term “production” in an operational sense to refer to upstream natural gas extraction, processing, and compression operations within specific geographic areas sampled by our atmospheric measurements.

Natural gas is a more efficient fuel for power plants than coal, resulting in a lower CO₂ emission per unit of energy produced (e.g., see de Gouw et al., 2014). However, CH₄ is 28 times more potent a greenhouse gas than CO₂ on a 100-year time horizon (Myhre et al., 2013). Therefore, the amount of natural gas, and thus CH₄, that is emitted to the atmosphere before it is burned as a fuel has a significant effect on the net climate impact of using natural gas for energy production. Many published works have analyzed the climate impacts of CH₄ emissions from natural gas production by comparing the net effects on the radiative forcing of the atmosphere between a coal- versus natural gas-based energy supply (e.g., Hayhoe et al., 2002). Here, we summarize recent work published since the boom in shale gas production in the late 2000s. Howarth et al. (2011) estimated that a total loss rate, from extraction through end use, above 2–3% would offset the climate benefits of using natural gas as a fuel instead of oil or coal. Howarth et al. (2011) further summed bottom-up estimates of loss rates for various stages of shale gas production, and estimated that 3.6–7.9% of the natural gas extracted from shale is lost to the atmosphere over the lifetime of a shale gas well. They estimated that 1.9% of the natural gas is lost during the well completion stage, and 0.3–1.9% is lost during routine operations of a well. However, Cathles et al. (2012) argued that the loss rates used by Howarth et al. (2011) for some stages of the natural gas production were too high by up to a factor of 10, and concluded that the net climate impact of natural gas is a factor of 2–3 less than that of coal. Wigley (2011) examined different scenarios of switching from coal to natural gas as a power plant fuel, and concluded that a total natural gas loss rate below 2% would reduce the net CH₄ emissions to the atmosphere, but that loss rates as high as 10% would still prove

beneficial after many years because of the increased efficiency of, and decreased black carbon emissions from, natural gas-fired power plants when compared to coal-fired power plants throughout the world. Alvarez et al. (2012) concluded that a total natural gas loss rate below 3.2% represented an immediate climate benefit if natural gas were to replace coal as fuel for power plants. Ultimately, the total end-to-end loss rates from natural gas production and consumption have implications for future fuel choices and climate change mitigation, and top-down estimates of CH₄ emissions from natural gas production regions are critically needed to verify bottom-up emissions estimates upon which climate policy decisions are based.

Studies using atmospheric measurements have only recently constrained CH₄ emissions to the atmosphere from natural gas production in source regions. Several of these studies have estimated CH₄ emissions using ambient measurements and calculated a loss rate by dividing these CH₄ emissions by the total CH₄ from natural gas produced in the region. Pétron et al. (2012) estimated natural gas losses to the atmosphere in 2008 equal to 3.1–5.3% of production from the Denver-Julesburg Basin in northeastern Colorado, a region that accounted for approximately 0.9% of U.S. natural gas production in 2008. Pétron et al. (2014) revisited the Denver-Julesburg Basin in 2012 and, using a different approach, again concluded that $(4.1 \pm 1.5)\%$ of the natural gas produced in the region was emitted to the atmosphere. Karion et al. (2013) estimated a 6.2–11.7% loss from natural gas production in the Uinta Basin in northeastern Utah, a region that accounted for approximately 1.0% of U.S. natural gas production in February 2012. Peischl et al. (2013) estimated a $(17 \pm 5)\%$ loss from natural gas production in the Los Angeles basin in California, a region of very low production

(approximately 0.05% of U.S. natural gas production in 2010). Caulton et al. (2014), found loss rates of 2.8–17.3% for two June 2012 flights in the southwestern Pennsylvania region of the Marcellus shale at a time when that region accounted for approximately 2.7% of U.S. natural gas production. Each of these loss rate determinations was significantly greater than the U.S. Environmental Protection Agency (EPA) estimates for the loss rate from production in 2008, which ranged from 0.16% to 1.47% (Karion et al., 2013). In contrast, Allen et al. (2013) measured CH₄ emissions from different stages of natural gas production from hundreds of wells across the U.S., and found that the losses from production operations, 0.42%, were similar to the EPA estimate of 0.47% in 2011. The wide range of natural gas loss estimates indicates further investigation of this issue is necessary. These studies provide key top-down information on CH₄ losses from production, processing, and distribution in source regions, to which CH₄ losses from downstream natural gas distribution and use must be added before comparing total climate impacts to coal.

Here, we derive atmospheric CH₄ emission rates from three natural gas production regions, which together accounted for over 50% of the unconventional shale gas produced in the U.S. and approximately 20% of the entire U.S. natural gas production in June 2013. The first region we examine is the Haynesville shale play located in eastern Texas and northwestern Louisiana. Unconventional natural gas production from the Haynesville shale increased steadily from late 2008 until late 2011, when it reached $2.1 \times 10^8 \text{ m}^3$ (7 billion cubic feet) per day (EIA) (Figure 32). At that time, the field was the largest producer of unconventional shale gas in the U.S. Since the end of 2011, production decreased to approximately $1.6 \times 10^8 \text{ m}^3$ (5.6 billion cubic feet)

per day by June 2013, when it accounted for 6.9% of U.S. natural gas production and 19.5% of U.S. unconventional shale gas production. This region accounted for 8.5% of June 2013 U.S. natural gas production when production from formations in the region other than the Haynesville shale is included. The second region we examine is the Fayetteville shale play located in central Arkansas. Unconventional natural gas production from the Fayetteville shale began in 2007, peaked in late 2012, and was $7.6 \times 10^7 \text{ m}^3$ (2.7 billion cubic feet) per day in June 2013, when it accounted for 3.4% of U.S. natural gas production and 9.5% of U.S. unconventional shale gas production. The third region we examine is a portion of the Marcellus shale play located in northeastern Pennsylvania where unconventional drilling predominates. Natural gas production from the Marcellus shale has increased steadily since early 2010. By June 2013, production from the entire Marcellus shale formation was over $2.6 \times 10^8 \text{ m}^3$ (9.2 billion cubic feet) per day, which made it the largest shale gas producing play in the U.S. The northeastern Pennsylvania portion of the Marcellus shale play accounted for approximately 70% of the total Marcellus production, as discussed in more detail below. In June 2013, the northeastern Pennsylvania portion of the Marcellus shale play accounted for approximately 8.0% of U.S. natural gas production and 22.5% of U.S. unconventional shale gas production.

We estimate the total CH_4 emission to the atmosphere from these regions using measurements taken aboard the chemically-instrumented National Oceanic and Atmospheric Administration (NOAA) WP-3D (P-3) aircraft in the summer of 2013 during the Southeast Nexus (SENEX) field campaign, based out of Smyrna, TN (Figure 34). Using a mass balance approach, we calculate the horizontal flux of CH_4 through the

planetary boundary layer (PBL) downwind of the Haynesville, Fayetteville, and a portion of the Marcellus shale regions. In cases with full upwind transects, we calculate the CH_4 flux flowing into the region, and the difference between the upwind and downwind fluxes provides an estimate of the CH_4 emissions from the region. Otherwise, we use the downwind transect only with an increased uncertainty in the upwind background CH_4 mixing ratio to derive an emissions estimate. We then divide this emission by the natural gas production to derive a loss rate from natural gas production in each region.

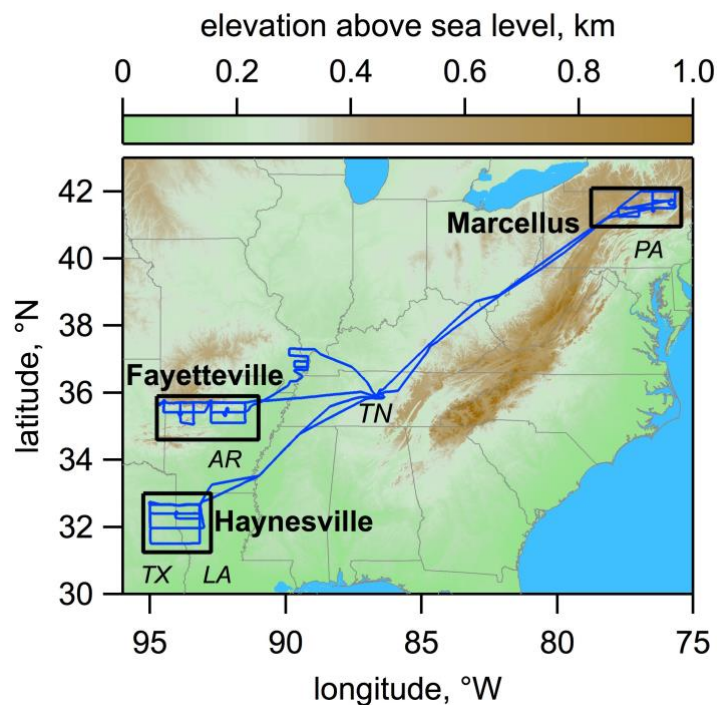


Figure 34. Map of the three study areas. The black rectangles show the insets for the maps of the Haynesville, Fayetteville, and Marcellus shale regions shown in Figures 34, 38, and 40, respectively. The blue traces show three of the flight tracks of the NOAA P-3 during SENEX.

IV.2. Instrumentation

CH₄, C₂–C₅ alkanes, ammonia (NH₃), carbon monoxide (CO), and meteorological measurements, among many others, were made aboard an instrumented NOAA P-3 research aircraft during June and July 2013 for the SENEX field campaign. CH₄ was measured with a Picarro 1301-m once per second with an estimated accuracy of ± 1.2 ppb (all uncertainties herein are 1- σ); 1-second precision was ± 1.5 ppb (Peischl et al., 2012). All CH₄ units herein are dry air mole fractions of nanomole/mole, or ppb. Ethane was measured with an estimated accuracy of $\pm 19\%$ in whole air sample canisters (Coleman et al., 2001), which typically took about 10 seconds to fill. In addition to ethane, hydrocarbons such as propane, *n*- and *i*-butane, and *n*- and *i*-pentane were measured in the whole air samples, as well as aromatics such as benzene and toluene. NH₃ was measured by chemical ionization mass spectrometry with an estimated accuracy of $\pm(25\% + 80$ parts per trillion by volume (pptv)) and a 1-second precision of ± 30 pptv (Nowak et al., 2007). CO was measured by vacuum ultraviolet resonance fluorescence with an estimated accuracy of $\pm 5\%$ and a 1-second precision of ± 1 parts per billion by volume (ppbv) (Holloway et al., 2000). Meteorological and navigational data were measured once per second by various sensors aboard the NOAA P-3. We estimate the uncertainties for these measurements as follows: wind speed (± 1 m/s), wind direction ($\pm 5^\circ$), ambient temperature (± 0.5 °C), potential temperature (θ , ± 0.5 K), dew point (± 0.5 °C), heading ($\pm 0.5^\circ$), radar altitude (± 15 m), GPS altitude (± 16 m), H₂O ($\pm 5\%$ in units of g/kg), and ground speed (± 3.4 m/s). We additionally derive the virtual potential temperature ($\theta_v = \theta \times [1 + 0.61 \times \text{H}_2\text{O}/1000]$) for use during vertical profiles to help define the depth of the planetary boundary layer (PBL), and the terrain height

directly below the P-3 (= GPS altitude – radar altitude). 1-sigma estimates of the uncertainty in wind speed and direction along a P-3 transect are calculated using the method of Yamartino (1984).

IV.3. Other Data

Louisiana well locations were obtained from the Louisiana Department of Natural Resources website (<http://dnr.louisiana.gov/index.cfm?md=pagebuilder&tmp=home&pid=442>, accessed November 2013). Louisiana well production data were obtained from the State of Louisiana Department of Natural Resources Strategic Online Natural Resources Information System database (<http://sonris.com/>, accessed March 2014). Texas well locations and natural gas production data were obtained from the Railroad Commission of Texas (RRC) website (<http://webapps2.rrc.state.tx.us/EWA/ewaPdqMain.do>, accessed November 2013). Arkansas well locations and natural gas production data were obtained from the State of Arkansas Oil and Gas Commission (<https://www.aogc.state.ar.us/>, accessed March 2014). Pennsylvania well locations and natural gas production data were obtained from the Pennsylvania Department of Environmental Protection (<https://www.dep.pa.gov/DataandTools/Reports/Oil%20and%20Gas%20Reports/pages/default.aspx>, accessed March 2014).

Locations of known point sources of CH₄ were obtained from the 2012 EPA greenhouse gas (GHG) inventory website (<http://ghgdata.epa.gov/ghgp/main.do>, accessed November 2013). Some latitude-longitude coordinates in the 2012 EPA GHG

inventory dataset have been modified to match the locations determined using Google Earth imagery. Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model back-trajectories (Draxler & Rolph, 2013; <https://www.ready.noaa.gov/HYSPLIT.php>) are used to check spatial and temporal uniformity of wind fields, and are run with the following settings: Meteorology, North American Mesoscale Forecast System (NAM) 12 km; Vertical motion, model vertical velocity. As discussed above and in Figure 32, shale gas production data were obtained from the EIA website. The average natural gas chemical composition from each region is determined from a 2009 U.S. Geological Survey (USGS) database (<http://energy.cr.usgs.gov/prov/og/index.htm>) for wells that lie within the study regions. County-level cattle and calf populations were obtained from the U.S. Department of Agriculture (USDA) National Agriculture Statistics Service (NASS) (<http://www.nass.usda.gov>). Assuming the same cattle population distribution as the EPA GHG inventory, we estimate an average emission of 67.8 kg CH₄/yr per head from enteric fermentation. In cases where the NOAA P-3 flight track transects a county or parish, an apportionment based on geographical area is used to determine how many livestock are within the study region by scaling linearly the number of cattle and calves as a function of the county area. County-level manure emissions estimates were obtained from the National Renewable Energy Laboratory (NREL) website (<http://maps.nrel.gov/biomass>), and were based on 2002 USDA data. We apportion the manure emissions geographically the same as for enteric fermentation.

IV.4. Mass Balance Approach

The mass balance approach is used to estimate CH₄ fluxes (White et al., 1976). This technique uses the fact that emissions mix and disperse vertically and horizontally through the atmosphere as they are carried downwind. The flux of the integrated emissions of a conserved tracer through a plane normal to the wind velocity should be constant as the plume moves downwind, so long as the wind field remains constant. We assume, and verify with measurements, that these CH₄ emission plumes mix downwind until they uniformly fill the depth of the PBL, at which point they continue to dilute horizontally with minimal detrainment into the overlying free troposphere. In this experiment, the NOAA P-3 aircraft characterized the upwind methane concentrations and transected emission plumes downwind of a targeted region to estimate CH₄ emissions from that region. We calculate the flux of a species X through a plane defined by an aircraft transect:

$$flux = v \cos(\alpha) \int_{z_0}^{z_1} \int_{-y}^y (X - X_{bg}) dy dz \quad (15)$$

where $v \cos(\alpha)$ is the magnitude of the component of the wind velocity normal to the flight track, z_0 is the ground level, z_1 is the adjusted mixing height discussed in detail below, $(X - X_{bg})$ is the enhancement of CH₄ above the tropospheric background, and y is the crosswind distance (White et al., 1976).

This method of determining emission fluxes was found to be in good agreement with an EPA emission inventory of nitrogen oxide emissions from Birmingham, Alabama (Trainer et al., 1993), with EPA continuous emissions monitoring measurements for nitrogen oxide emissions from power plants (Ryerson et al., 1998), and with the California Air Resource Board's GHG inventory for CH₄ emissions from

landfills (Peischl et al., 2013). This method is similar to the method used by Mays et al. (2009) to determine greenhouse gas emissions from Indianapolis, IN, and by Caulton et al. (2014) to determine CH₄ emissions from oil and gas operations and coal mining in southwestern Pennsylvania. The mass balance technique was also used to determine CH₄ emissions from oil and natural gas operations in the Uinta Basin (Karion et al., 2013) in Utah and the Denver-Julesburg Basin (Pétron et al., 2014) in Colorado.

We assume that the CH₄ emitted from a region is well mixed through the depth of the PBL by the time it is measured aboard the NOAA P-3. This assumption is tested with frequent vertical profiles, usually once or twice per hour, which also serve to assess the PBL depth. We further assume that the wind fields were constant between emission and measurement aboard the P-3; this assumption is verified using HYSPLIT back-trajectories.

Determining Background CH₄ Mixing Ratios. We define the PBL background CH₄ mixing ratio, X_{bg} in Equation 15, as the lowest mixing ratios encountered in the PBL during the upwind portions of the flights. Uncertainty in the background is defined as the atmospheric variability in the upwind values that are not immediately influenced by known upwind sources. As the PBL grows over the course of a flight, entrainment occurs between the free troposphere and the PBL, which mixes free tropospheric air into the PBL, and vice versa. We define the entrainment height, z_e , as the altitude above the PBL to which this mixing occurs, based on examination of vertical profiles, and define the entrainment zone as the portion of the atmosphere located between the top of the PBL and the entrainment height. We assume the free tropospheric background level of CH₄ mixes with the PBL background proportional to the increase in the PBL depth,

weighted by the number density of the atmosphere. We test this assumption by integrating the estimated background CH_4 from ground level to the maximum entrainment height noted on each flight, similar to Figure 33 of the work of Sasakawa et al. (2013), for each vertical profile. We linearly interpolate between the PBL CH_4 background to the free tropospheric CH_4 background through the entrainment zone for this vertical integration calculation. We refer to this interpolation as the entrainment zone CH_4 background. As the PBL grows during the course of a flight, the PBL CH_4 background is adjusted so that the vertically integrated CH_4 background remains constant to within 0.5 ppb.

Determining Planetary Boundary Layer Depth and Adjusted Mixing Height. We define the top of the PBL as the altitude of maximum virtual potential temperature gradient, and corroborate this by examining gradients in CO, ambient temperature, wind speed and direction, and dew point temperature observed in vertical profiles. We further assume a constant mixing height above ground, and estimate a ± 200 m uncertainty for the assigned PBL depth.

CH_4 enhancements may be transported vertically through the top of the PBL from shear-induced mixing, transport through clouds, or from PBL depth changes over time. We account for this by defining the adjusted mixing height, z_1 in Equation 15, such that $z_1 > z_{\text{PBL}}$. As with the entrainment zone CH_4 background, we assume constant linear mixing in the entrainment zone, and therefore interpolate between the CH_4 enhancement in the PBL and the tropospheric background CH_4 . The CH_4 enhancement over background in the PBL during a vertical profile is represented as the area of a rectangle, with a width of $(X - X_{bg})$ and a height of $(z_{\text{PBL}} - z_0)$. Likewise, the CH_4

enhancement over background in the entrainment zone is represented as the area of a triangle, with a base of $(X - X_{bg})$ and a height of $(z_e - z_{PBL})$. We therefore define the adjusted mixing height by increasing z_{PBL} by the additional fraction of one-half the area of the triangle divided by the area of the rectangle:

$$z_1 = z_{PBL} \times \{1 + [(z_e - z_{PBL})(X - X_{bg})/4]/[(z_{PBL} - z_0)(X - X_{bg})]\} \quad (16)$$

The $(X - X_{bg})$ terms in Equation 16 cancel, and $z_0 = 0$ as defined in units of meters above ground level (m.a.g.l.). Therefore, Equation 16 simplifies to:

$$z_1 = (3z_{PBL} + z_e)/4 \quad (17)$$

where the z terms are also defined in units of m.a.g.l. We estimate the uncertainty of z_1 by summing in quadrature $(z_1 - z_{PBL})$ and 200 m. The result is an adjusted mixing height with uncertainties that encompass both z_{PBL} and the height of a rectangle with an area that represents the PBL CH_4 enhancements lost to detrainment.

Next, we fit a line to the adjusted mixing heights calculated for each vertical profile, weighted by the uncertainty in the adjusted mixing height. For each mass balance transect, z_1 in Equation 15 is found by taking the mean of the fit during the time of the transect. In each instance, the 1- σ confidence bar for the fit was $< \pm 200$ m. However, here we use a more conservative uncertainty estimate of ± 300 m, which encompasses all the adjusted mixing heights used in the fit.

We estimate uncertainties in the flux determination by quadrature addition of the uncertainties of each of the variables in Equation 15. In the cases where the NOAA P-3 did not fly a complete upwind transect, we increase the estimated uncertainty of the background CH_4 mixing ratio to include the upwind variability of CH_4 in areas not immediately downwind of known point sources.

IV.5. Results and Discussion

Five SENEX flights were conducted in regions with extensive unconventional shale gas production, with transects performed upwind, over, and downwind of these regions. Figure 33 shows three flight tracks of the NOAA P-3 to the regions of the Haynesville, Fayetteville, and the Marcellus shale plays in June and July 2013. Although the Marcellus shale formation is large, extending from New York through Pennsylvania and Ohio and into West Virginia, in 2013 the majority of unconventional natural gas production from the shale play was located in northeastern Pennsylvania. Using Equation 15, we determine the CH₄ emission fluxes from these three regions. We then determine the natural gas loss rate from oil and gas operations in these regions by converting the CH₄ emission to a natural gas emission, then dividing this calculated natural gas emission by the total natural gas production in that region.

IV.5.1. CH₄ Emissions to the Atmosphere from the Haynesville, Fayetteville, and Marcellus Study Regions

IV.5.1.1. Haynesville. The NOAA P-3 aircraft flew to the Haynesville region on 10 June and 25 June 2013. For the 10 June flight, the wind field was not uniform throughout the Haynesville region; we therefore apply the mass balance technique only to data from the 25 June flight. On the 25 June flight, the winds measured aboard the P-3 were consistently from the south-southwest over the range of the study area, which agree with both HYSPLIT back-trajectories and the location of plumes transected downwind of known point sources, such as the Martin Lake power plant.

A map of the 25 June flight shows the box pattern flown by the NOAA P-3 encompassed the majority of the wells in the Haynesville region (Figure 34). The blue

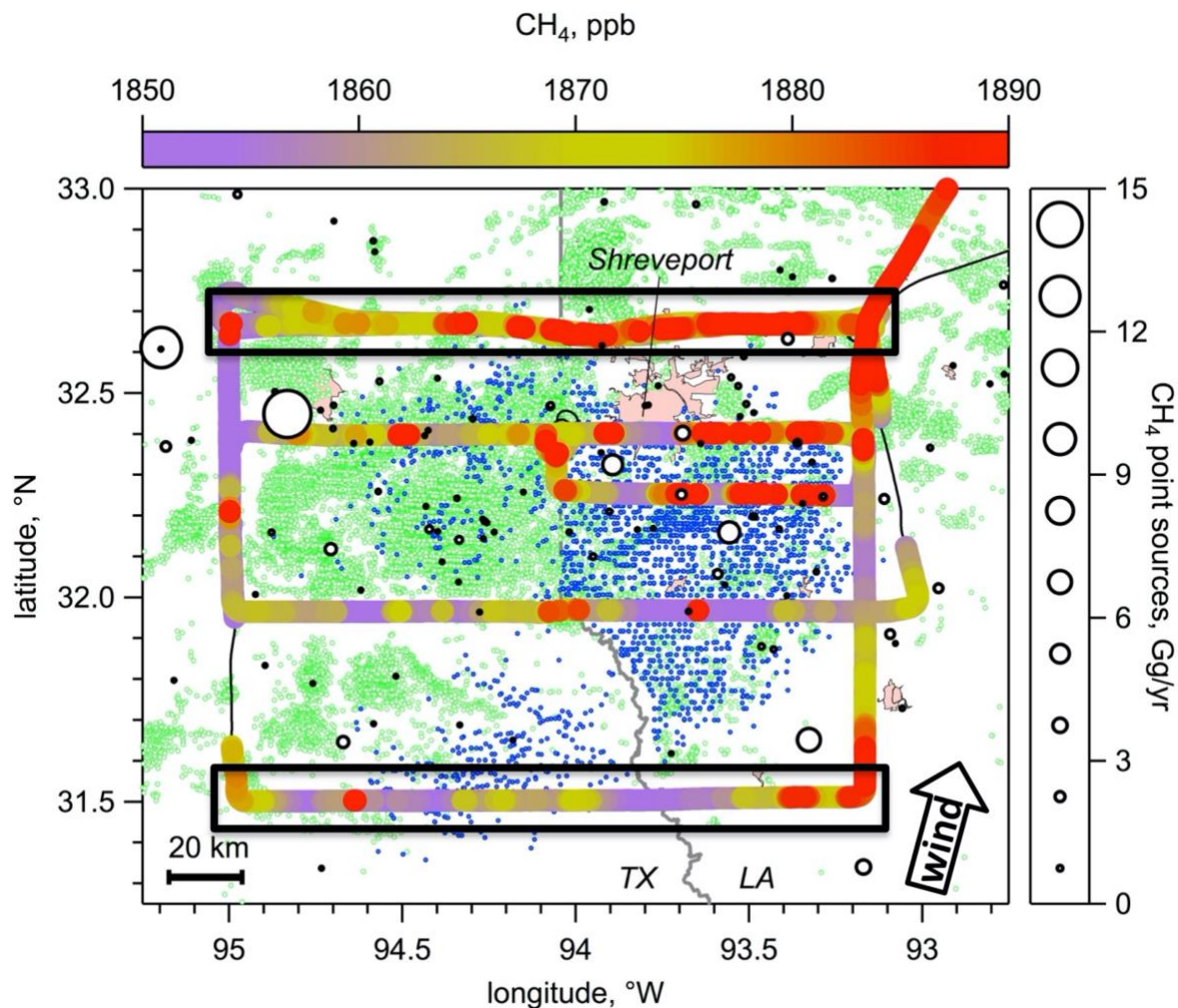


Figure 34. Map of the Haynesville shale region. The NOAA P-3 flight track from 25 June (black line) is colored by observed CH₄ mixing ratios in the boundary layer. Active unconventional gas wells drilled into the higher production Haynesville shale formation are shown as blue circles. All other active gas wells are shown as green circles. Point sources from the 2012 EPA GHG inventory are shown as open black circles sized by inventory CH₄ emissions. Urban areas, including Longview, TX, and Shreveport, LA, are shaded pink. The black rectangles highlight the locations of the upwind transect along 31.5°N latitude, and the three downwind transects along 32.7°N latitude.

circles in Figure 34 show the locations of unconventional wells drilled into the Haynesville shale formation. The green circles show the locations of both conventional and unconventional active natural gas wells drilled into other geologic formations. Also shown in Figure 34 are CH₄ point sources in the EPA GHG inventory sized by their respective CH₄ emission. The flight track in Figure 34 is colored by the CH₄ mixing ratio measured within the PBL aboard the P-3 aircraft. These measurements show a general increase in CH₄ mixing ratios as the number of wells upwind increases. Black rectangles highlight the upwind transect at approximately 31.5°N latitude, and the three downwind transects located at approximately 32.7°N latitude.

Figure 35 shows the time series of CH₄ and aircraft altitude for the one upwind and three downwind transects highlighted in Figure 34. Also plotted in Figure 35 is the estimate of the background CH₄ mixing ratio, which was adjusted to maintain a constant vertically integrated background as the PBL grew during the flight. We estimate an initial CH₄ background of 1847 ± 3 ppb for the upwind transect, 1846 ± 3 ppb for the first downwind transect, and 1844 ± 3 ppb for the final two downwind transects. Examples of the PBL depth estimates, determined using virtual potential temperature, ambient temperature, and dew point profiles, are shown for four vertical profiles in Figure 36. Figures 36a, b, c, and d show the vertical profiles immediately after the upwind transect, after the first downwind transect, after the second downwind transect, and before the third downwind transect, respectively. Figure 36a shows an example of how the adjusted mixing height is formulated for a vertical profile that indicates significant vertical CH₄ mixing above the PBL, possibly due to cumulus cloud formation. The dotted line in Figure 36a represents the estimated background CH₄ mixing ratio (i) in the

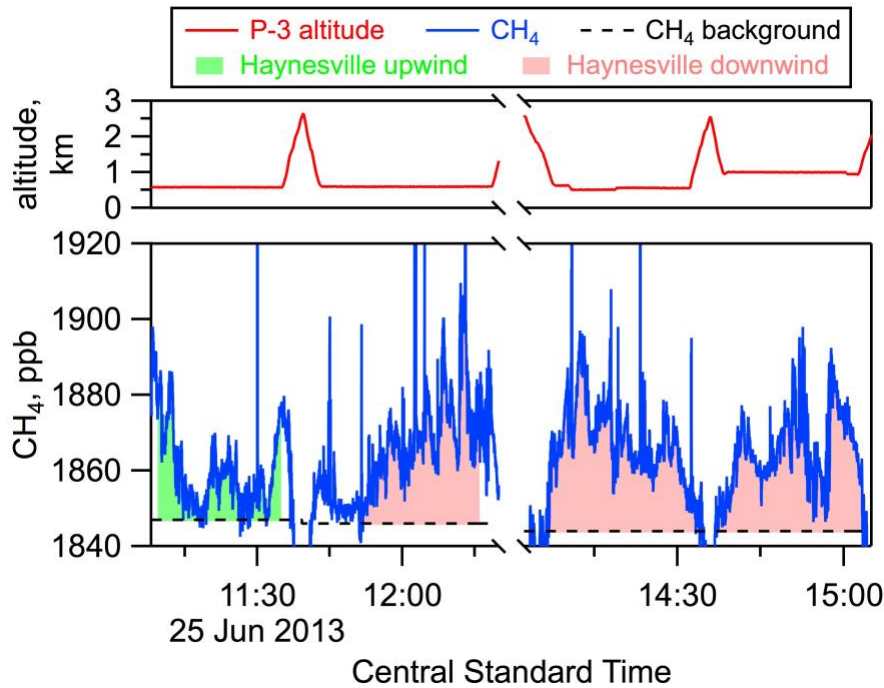


Figure 35. Time series of CH_4 measurements (blue) from the 25 June NOAA P-3 flight over the Haynesville study region. The red trace shows the P-3 altitude. The dashed black line indicates the background CH_4 mixing ratio, estimated at 1847 ppb for the upwind transect, 1846 ppb for the first downwind transect, and 1844 ppb for the final two downwind transects. The shaded areas show the CH_4 enhancement over background along the transect(s): upwind of the Haynesville region (green) and downwind of the Haynesville region (pink).

PBL (dashed line), below 1334 m.a.g.l., (ii) in the entrainment zone, between 1334 and 1926 m.a.g.l., and (iii) in the free troposphere, above 1926 m.a.g.l. The area between the CH_4 trace and the dotted line in the entrainment zone is approximately 22% of the area between the CH_4 trace and the dotted line in the PBL, assuming the average CH_4 mixing ratio in the PBL extends to the ground level, located at 77 m in this case. We therefore increase our estimated PBL depth, 1334 ± 200 m.a.g.l., by approximately $(11 \pm 11)\%$ to obtain the adjusted mixing height, 1482 ± 259 m.a.g.l., for this vertical profile, which is

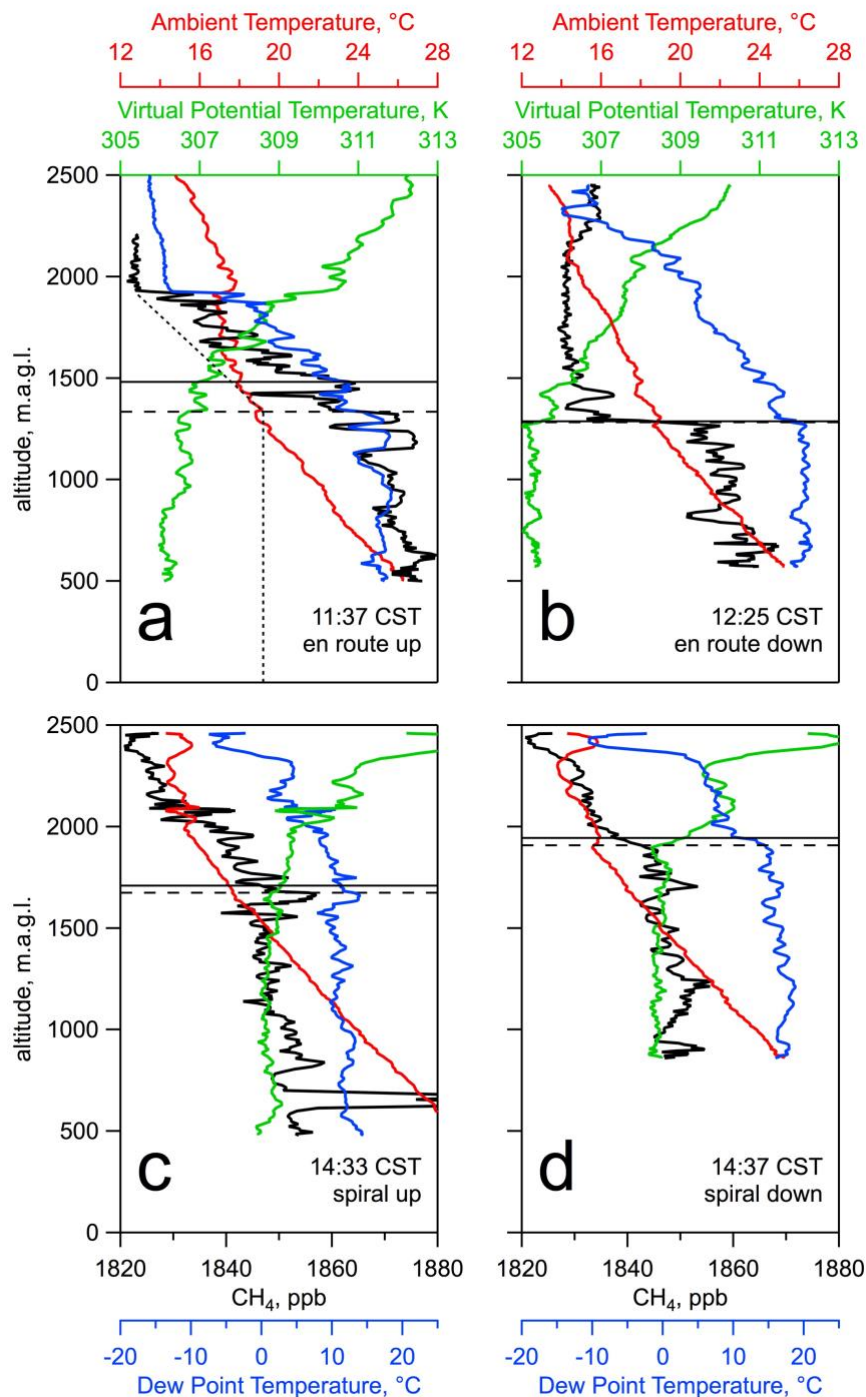


Figure 36. Four vertical profiles during the 25 June flight over the Haynesville study region. Dashed lines indicate estimates of the well-mixed PBL depth. Solid lines indicate the adjusted mixing height, z_1 . The dotted line in (a) represents the background CH₄ mixing ratio throughout the vertical profile: the PBL background below the dashed line, the free tropospheric background above approximately 2.0 km, and a linear interpolation in the entrainment zone.

indicated by the solid horizontal line in Figure 36a. We next fit a line to the adjusted mixing heights calculated for each vertical profile in order to estimate z_1 for the transects between vertical profiles. This results in adjusted mixing heights of 1471 ± 300 m.a.g.l. for the upwind transect immediately before the profile shown in Figure 36a, and 1541 ± 300 m.a.g.l. for the upwind transect shortly after the profile (Table 9). In Figure 36c, a plume of CH_4 was encountered at approximately 700 m during a spiral ascent. However, the P-3 was at or above the PBL when the aircraft would have encountered the plume farther downwind, so we cannot determine if the plume was well mixed vertically.

Table 9 lists the variables and their uncertainties used in Equation 15 to calculate the CH_4 flux for each transect. For this flight, the largest drivers of the flux uncertainty were the wind speed, $\pm 25\%$, and the mixing height, $\pm 20\%$, whereas the ± 3 ppb background uncertainty introduces only a $\pm 6\%$ flux uncertainty due to the fact that the upwind fluxes are subtracted from the downwind fluxes. The CH_4 fluxes calculated from the three downwind transects are $(9.1 \pm 3.1) \times 10^7$, $(11.0 \pm 3.7) \times 10^7$, and $(10.5 \pm 3.5) \times 10^7$ g CH_4/hr , with a $1/\sigma^2$ -weighted average of $(10.1 \pm 2.0) \times 10^7$ g CH_4/hr . In addition, CH_4 was enhanced above background along the eastern transect at 93.2°W longitude in Figure 34. The CH_4 flux calculated from this transect was $(2.4 \pm 0.9) \times 10^7$ g CH_4/hr (Table 9). The P-3 intercepted a small biomass burning plume along this transect, which constitutes a possible source of CH_4 unrelated to oil and gas operations. We account for this possible interference by assuming a CH_4/CO ratio of 2% in the biomass burning plume (Andreae & Merlet, 2001), and subtracting this CH_4 enhancement due to the biomass burning from the CH_4 measurement. The biomass

Table 9. Example of data used in Equation 15 from the 25 June 2013 flight to the Haynesville shale region.

Side of box	Terrain Height, m.a.s.l. ^a	Adjusted Mixing height, m.a.g.l.	Wind dir., °	Wind spd., m/s	Estimated CH ₄ background, ppb	CH ₄ flux (10 ²⁶ molec./s)	CH ₄ flux (10 ⁷ g/hr) ^b
North, Downwind #1	68 ±21	1560 ±300	204 ±9	7.0 ±1.8	1846 ±3	9.5 ±3.2	9.1 ±3.1
North, Downwind #2	75 ±22	1791 ±300	178 ±11	6.5 ±1.8	1844 ±3	11.5 ±3.9	11.0 ±3.7
North, Downwind #3	57 ±23	1840 ±300	190 ±11	6.8 ±1.8	1844 ±3	11.0 ±3.7	10.5 ±3.5
East, Downwind	44 ±19	1429 ±300	211 ±10	5.4 ±1.4	1847 ±3	2.5 ±0.9	2.4 ±0.9
South, Upwind	77 ±22	1471 ±300	192 ±10	6.0 ±1.6	1847 ±3	−4.1 ±1.6	−3.9 ±1.6
West, Upwind #1	92 ±33	1541 ±300	195 ±7	8.4 ±1.8	1846 ±3	−0.3 ±0.2	−0.3 ±0.1
West, Upwind #2	132 ±23	1636 ±300	182 ±9	6.8 ±1.8	1845 ±3	−0.2 ±0.1	−0.2 ±0.1

^a meters above sea level^b a negative flux indicates an upwind transect, where the flux is into the region

burning plume contributed little to the CH₄ enhancement during this transect, accounting for less than 1% of the calculated CH₄ flux through the eastern transect.

There were, however, significant CH₄ enhancements above background upwind of the Haynesville region. We estimate the flux of CH₄ along the upwind portion of the flight track (Figures 34 and 35) to be -4.1×10^7 g CH₄/hr, where the negative sign indicates excess CH₄ above background flowing into the region. Additionally, we estimate the flux of excess CH₄ along the western portion of the box to be -0.5×10^7 g CH₄/hr. This number is the sum of the fluxes calculated from the western transect (West, Upwind #1 in Table 9) plus a small portion of the transect along 32.0°N latitude between 94.93°W and 94.98°W longitude (West, Upwind #2 in Table 9) to account for when the P-3 was not in the boundary layer during a vertical profile. Although this is not a Lagrangian

study, in which the air mass we measure upwind is the same as the one we measure downwind, the upwind transects provide the best estimate of CH₄ enhancements above background flowing into the Haynesville region. Figure 37 shows data from the upwind transect and the first downwind transect of the Haynesville region. Histograms of these data are provided to the right of Figure 37, along with box and whisker plots of the CH₄ mixing ratio distribution along the two transects. The distributions show a significant increase in the CH₄ mixing ratio downwind of the Haynesville region. Figure 37 also illustrates our reason for including the sides of the box in the flux calculation. The upwind CH₄ enhancements located between 140 and 160 km (Figure 37) enter, then

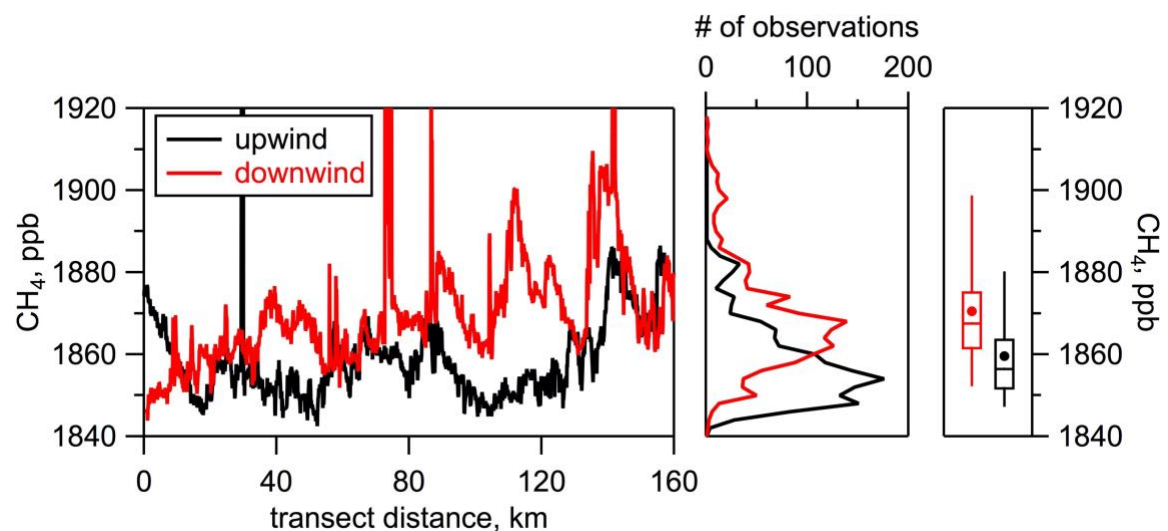


Figure 37. CH₄ measurements upwind (black) and downwind (red) of the Haynesville study region are shown in the left panel. The downwind data shown are from the first of three downwind transects at 32.75°N latitude. The middle panel shows histograms for the data presented to the left. The right panel shows box and whisker plots of the data, where the top and bottom of the box are the 75th and 25th percentiles, respectively, and the tips of the whiskers represent the 95th and 5th percentiles. The closed circles represent the means.

immediately exit, the study region in the southeast corner of the flight track (Figure 34), thereby negating these upwind emissions. Therefore, accounting for all sides of the box pattern flown by the P-3, we estimate the total CH₄ emission from within the box as $(8.0 \pm 2.7) \times 10^7$ g CH₄/hr, which is the value included in Table 10.

Table 10. Summary of CH₄ emissions from study regions.

Region	Haynesville	Western Arkoma	Fayetteville	Marcellus
CH ₄ flux (10 ⁷ g/hr)	8.0 ±2.7	3.3 ±1.5	3.9 ±1.8	1.5 ±0.6
CH ₄ from livestock and non-oil-and-gas point sources (10 ⁷ g/hr)	0.6	0.7	0.4	0.2
Natural gas production in June 2013 (10 ⁷ m ³ /day)	20 ±3	0.9	7.6	18 ±1
CH ₄ in natural gas	(90 ±7)%	(95 ±5)%	(94 ±5)%	(96 ±3)%
Natural gas loss rate	1.0–2.1%	6–20%	1.0–2.8%	0.18–0.41%

IV.5.1.2. Fayetteville and Western Arkoma. The NOAA P-3 aircraft flew to the Fayetteville region on 26 June and 8 July 2013. Due to active atmospheric mixing over mountainous terrain and a thunderstorm that forced the P-3 to leave the region prematurely, we do not interpret data from the 26 June flight. We apply the mass balance technique only to data from the Fayetteville region for the 8 July flight only (Figure 38). During the 8 July 2013 flight, the winds measured aboard the P-3 were consistently out of the south-southwest in this region, which is supported by HYSPLIT back-trajectories. The area of study on 8 July can be split into two regions, roughly east and west of 92.8°W longitude. Although both regions are geologically part of the

Arkoma Basin, there are different drilling strategies in these two regions. The Fayetteville shale play is represented by the large cluster of wells to the east (open blue circles in Figure 38), where the majority of unconventional drilling has occurred since 2010. The wells to the west are mostly conventional wells (green circles in Figure 38), and drilling in this region began in the early 1900s. Here, we refer to the eastern part of the Arkoma Basin in Arkansas as the Western Arkoma region. As in Figure 34, point

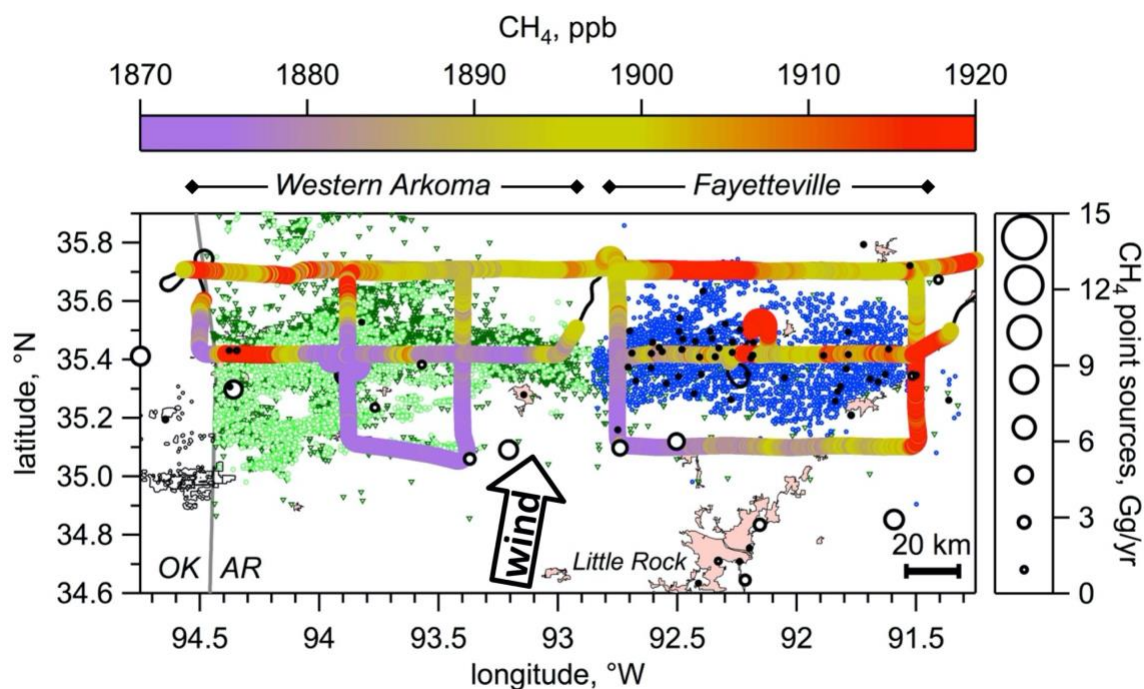


Figure 38. Map of the Fayetteville and Western Arkoma study regions. The NOAA P-3 flight track from 8 July (black line) is colored by observed CH₄ mixing ratios in the boundary layer. Active unconventional gas wells drilled into the Fayetteville shale formation are shown as blue circles. All other active gas wells are shown as green circles. Point sources from the 2012 EPA GHG inventory are shown as open black circles sized by inventory CH₄ emissions. Urban areas, including Little Rock, AR, are shaded pink. Plugged gas wells are shown as dark green triangles. Coal bed methane fields are shown with thin black lines along the Arkansas-Oklahoma border.

sources from the 2012 EPA GHG inventory are shown as open black circles sized by their respective CH₄ emission in Figure 38, and the P-3 flight track is colored by CH₄ mixing ratio in the PBL.

The P-3 flew two transects downwind of the Fayetteville region along 35.7°N latitude, and one upwind transect along 35.1°N latitude, between approximately 91.5° and 92.8°W longitude (Figure 38). We estimate the PBL CH₄ background mixing ratio, X_{bg} , at 1874 ppb for the initial downwind transect and at 1872 ppb for the later transects of the Fayetteville region. Although the CH₄ mixing ratios above the PBL on this flight were highly variable, ranging from 1850 to 1900 ppb, the adjustments to the PBL CH₄ background necessary to maintain a consistent vertically integrated CH₄ background were less than 1 ppb after 11 am Central Standard Time, so we treat the effect of the entrained variability as negligible. We estimate a PBL background uncertainty of ± 3 ppb for the Fayetteville region. On this flight, the largest sources of uncertainty were the wind speed, $\pm 35\%$, and the mixing height, $\pm 25\%$. The CH₄ fluxes calculated from the two downwind transects are $(5.7 \pm 2.4) \times 10^7$ and $(4.6 \pm 2.0) \times 10^7$ g CH₄/hr (Figure 39). The weighted average flux is $(5.0 \pm 1.5) \times 10^7$ g CH₄/hr. However, the upwind transect shows some CH₄ enhancements, above the assigned CH₄ background, flowing into the region from the Little Rock urban area (Figure 39). Accounting for fluxes through all four sides of the box yields $(3.9 \pm 1.8) \times 10^7$ g CH₄/hr emitted from the Fayetteville region on 8 July (Figure 39 and Table 10).

We also calculate the CH₄ flux downwind of the Western Arkoma region using the downwind transect along 35.7°N latitude, between 92.8° and 94.5°W longitude (Figure 39). In this region, the P-3 did not fly a complete transect upwind of the active

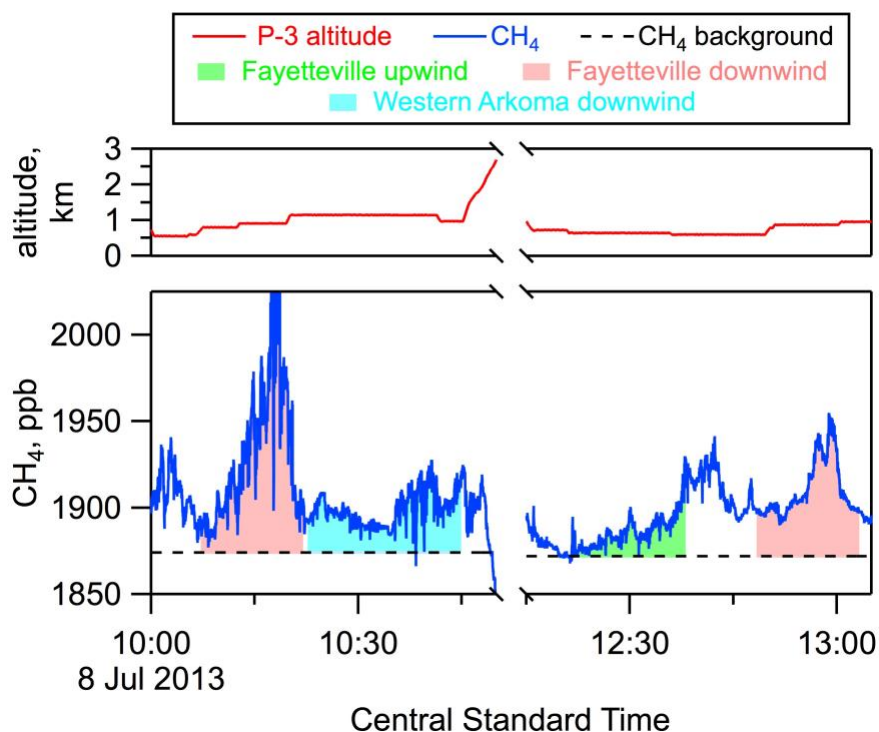


Figure 39. Time series of CH_4 measurements (blue) from the 8 July NOAA P-3 flight over the Fayetteville and Western Arkoma study regions. As in Figure 34, the red trace shows the P-3 altitude. The dashed black line indicates the background CH_4 mixing ratio, estimated at 1874 ppb for the first two downwind transects, and 1872 ppb for the remaining transects. The shaded areas below the CH_4 trace show the CH_4 enhancement over background along the transect(s): upwind of the Fayetteville region (green), downwind of the Fayetteville region (pink), and downwind of the Western Arkoma region (light blue).

gas wells (Figure 38). As with the first transect downwind of the Fayetteville shale region, we estimate the background CH_4 mixing ratio at 1874 ppb. We account for unknown upwind CH_4 sources by increasing the uncertainty of the background to ± 5 ppb. The largest uncertainties for this transect were the wind speed, $\sim 30\%$, mixing height, $\sim 25\%$, and the background uncertainty, in this case with no upwind transects,

$\pm 20\%$. The CH_4 emission derived from the downwind transect is $(3.3 \pm 1.5) \times 10^7$ g CH_4/hr (Table 10).

IV.5.1.3. Marcellus. The NOAA P-3 aircraft flew once to the Marcellus shale region in northeastern Pennsylvania on 6 July 2013 (Figure 40). Winds measured aboard the P-3 were consistently out of the west-southwest in this region for most of the flight in the boundary layer up until the last half hour of the flight, when they shifted to the southwest. The blue circles in Figure 40 show the locations of wells drilled into the Marcellus shale formation. The green open circles show the locations of conventional active natural gas wells. As in Figures 34 and 38, CH_4 point sources in the 2012 EPA GHG inventory are shown as open black circles sized by their respective CH_4 emission, and the flight track is colored by the CH_4 mixing ratio measured within the PBL.

The P-3 flew two sets of downwind transects on this day. The first was along 75.7°W longitude and then along 42°N latitude between 75.7° and 76.5°W longitude when the winds were from the south-southwest. The second was along 75.7°W longitude and then along 42°N latitude between 75.7° and 77.0°W longitude when the winds had shifted to the southwest. These sets of transects were downwind of nearly all the unconventional shale gas wells in this region. As with the Western Arkoma region, the P-3 did not fly a complete upwind transect on this day. Therefore, we assume a background CH_4 mixing ratio of 1862 ± 5 ppb for the first downwind transect, based on the lowest mixing ratios encountered in the PBL, and 1861 ± 5 ppb for the second downwind transect, estimated to maintain a constant vertically integrated CH_4 background (Figure 41). We then derive an upper limit to the CH_4 emissions from the region by applying the mass balance technique to the two sets of downwind transects.

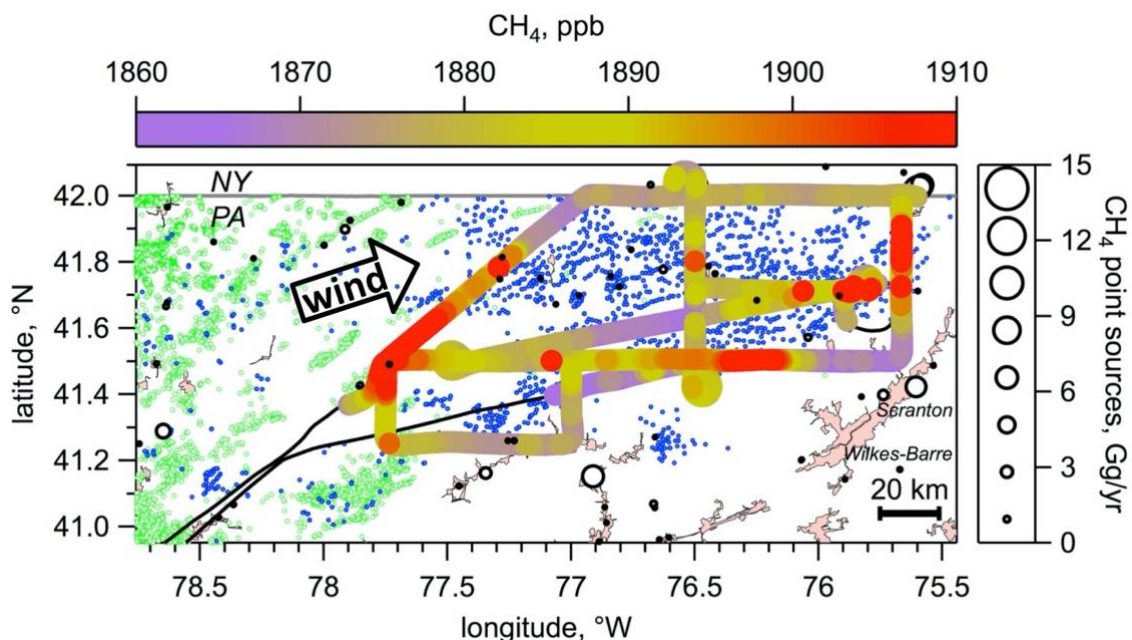


Figure 40. Map of the Marcellus study region in northeastern Pennsylvania. The NOAA P-3 flight track from 6 July (black line) is colored by observed CH₄ mixing ratios in the boundary layer. Active gas wells drilled into the Marcellus shale formation are shown as blue circles. All other active wells are shown as green circles. Point sources from the 2012 EPA GHG inventory are shown as open black circles sized by inventory CH₄ emissions. Urban areas are shaded pink.

The largest sources of uncertainty on this flight were the wind speed, $\pm 35\%$, the mixing height, $\pm 20\%$, and the background, $\pm 40\%$. The flux through the first set of downwind transects was $(1.3 \pm 0.7) \times 10^7$ g CH₄/hr. The flux through the second set of downwind transects, after the winds had shifted slightly more to the southwest, was $(1.9 \pm 1.0) \times 10^7$ g CH₄/hr. The weighted average of these two fluxes is $(1.5 \pm 0.6) \times 10^7$ g CH₄/hr (Table 10).

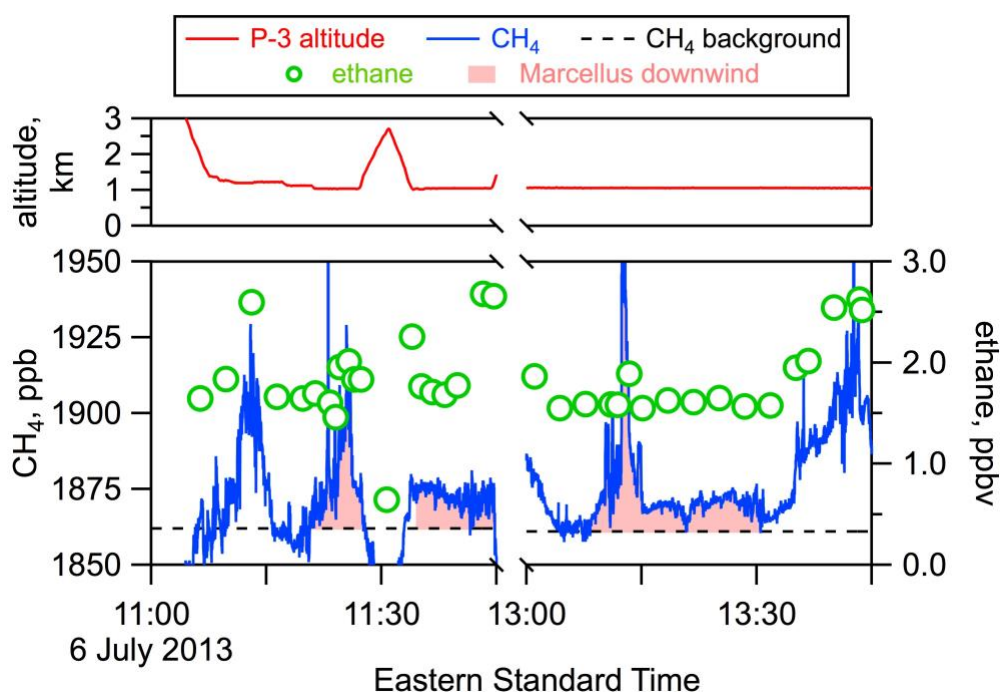


Figure 41. Time series of CH₄ measurements (blue) from the 6 July NOAA P-3 flight over the Marcellus shale region. As in Figures 34 and 38, the red trace shows the P-3 altitude. The dashed black line indicates the background CH₄ mixing ratio, estimated at 1862 ppb for the first set of downwind transects, and 1861 ppb for the second. The shaded areas show the CH₄ enhancement over background along the transects downwind of the Marcellus region (pink). Observed ethane mixing ratios are plotted as open green circles.

IV.5.2. Natural Gas Production in the Haynesville, Fayetteville, and Marcellus Study Regions

Monthly natural gas production in each of these three regions is estimated for the months of June and July from EIA data. Where possible, these production numbers are confirmed using state production data. We assume that daily natural gas production from these regions is equivalent to the monthly production divided by the number of days in the month of production. For ease of comparison between regions, we report all daily natural gas production figures in units of 10^7 m^3 .

IV.5.2.1. Haynesville. The average Haynesville shale gas production for the month of June 2013 was $16 \times 10^7 \text{ m}^3$ (5.6 billion cubic feet) per day according to the EIA (Figure 32). We confirm the EIA production number using state production data. Production from the Louisiana portion of the Haynesville shale (fields with lease/unit/well name beginning with “HA” in the SONRIS database) was $3.5 \times 10^9 \text{ m}^3$ (123.8 billion cubic feet) for the month of June 2013, which averages to $12 \times 10^7 \text{ m}^3/\text{day}$. Production from wells drilled into the Texas portion of the Haynesville shale (the Carthage shale play, which is how the State of Texas refers to the Haynesville shale) for the month of June 2013 was $9.3 \times 10^8 \text{ m}^3$ (32.9 billion cubic feet), which averages to $3.1 \times 10^7 \text{ m}^3$ per day. Combined, these total $15.1 \times 10^7 \text{ m}^3/\text{day}$, which is within 6% of the EIA production data.

However, natural gas production from geologic formations other than the Haynesville shale occurs in this region. We account for this additional production by using the state production data. In Louisiana, natural gas is extracted from other formations such as Cotton Valley and Hosston. In the 8-parish region encompassing the Haynesville shale play, total natural gas production was $4.2 \times 10^9 \text{ m}^3$ (148.1 billion cubic feet) in June 2013, which averages to $14 \times 10^7 \text{ m}^3/\text{day}$. Thus, the Haynesville shale accounted for 83% of the natural gas produced in the Louisiana portion of the Haynesville region. Similarly, in Texas, the total production from Gregg, Harrison, Nacogdoches, Panola, Rusk, and Shelby Counties, which were mostly covered by the P-3 flight track, was $1.9 \times 10^9 \text{ m}^3$ (68.6 billion cubic feet) in June 2013, or $6.5 \times 10^7 \text{ m}^3/\text{day}$. Thus, the Haynesville shale accounted for approximately 48% of the natural gas produced in the Texas portion of the Haynesville region. The box bounded by the P-3

flight track in Figure 34 encompasses approximately 88% of the active Texas wells in the Texas RRC Oil and Gas Division District 6 (https://www.rrc.texas.gov/media/3bkhbut0/districts_color_8x11.pdf). Based on this apportioning, we assume $5.7 \times 10^7 \text{ m}^3$ natural gas per day was produced from the Texas portion of the Haynesville shale region. Combining the EIA, Louisiana, and Texas data, we estimate natural gas production of $(20 \pm 3) \times 10^7 \text{ m}^3/\text{day}$ from within the area bounded by the P-3 flight track on 25 June 2013 (Table 10).

IV.5.2.2. Fayetteville and Western Arkoma. The average daily natural gas production from the Fayetteville shale play was $7.6 \times 10^7 \text{ m}^3$ (2.7 billion cubic feet) per day in July 2013 according to the EIA (Figure 32). In State of Arkansas reports, the Fayetteville shale play is referred to as field B-43. According to the 2012 Annual Report of Production by the Arkansas Oil and Gas Commissioner, the B-43 field produced 1.0×10^9 thousands of cubic feet (MCF) of natural gas in 2012, or $2.8 \times 10^{10} \text{ m}^3$, which averages to $8.0 \times 10^7 \text{ m}^3/\text{day}$, the same number the EIA provides for the Fayetteville shale play in 2012. The B-44 field, located in the Western Arkoma region, produced $6.4 \times 10^7 \text{ MCF}$, or $1.8 \times 10^9 \text{ m}^3$, of natural gas according to the 2012 Annual Report, which averages to $0.5 \times 10^7 \text{ m}^3/\text{day}$. Combined, these two fields produced 96% of the natural gas in northern Arkansas in 2012. This means the wells represented by the green circles in Figure 38, which include those in the B-44 field in the Western Arkoma region and remaining wells not part of either the B-43 or B-44 fields, produced at most $0.9 \times 10^7 \text{ m}^3$ of natural gas per day on average in 2012. We therefore estimate a daily natural gas production rate of $7.6 \times 10^7 \text{ m}^3/\text{day}$ from the Fayetteville shale region using EIA data,

and $0.9 \times 10^7 \text{ m}^3/\text{day}$ from the Western Arkoma region using EIA and State of Arkansas data (Table 10).

IV.5.2.3. Marcellus. The Marcellus shale play produced $26 \times 10^7 \text{ m}^3$ (9.3 billion cubic feet) of natural gas per day in July 2013 according to the EIA (Figure 32).

According to State of Pennsylvania data, unconventional gas wells produced an average of $21 \times 10^7 \text{ m}^3/\text{day}$ from January to June 2013, and an average of $26 \times 10^7 \text{ m}^3/\text{day}$ from July to December 2013. If we assume an average of these two numbers best represents the production for 6 July, when the NOAA P-3 flew to the area, then Marcellus shale gas production in Pennsylvania was approximately $24 \times 10^7 \text{ m}^3/\text{day}$, which is within a factor of 0.9 of the EIA production data. In contrast, production from conventional wells in Pennsylvania amounted to $1.6 \times 10^7 \text{ m}^3/\text{day}$ in 2013, or 7% that of the unconventional wells. The northern Pennsylvania portion accounted for about 73% of the Marcellus shale gas extracted in Pennsylvania in July 2013

(<http://www.eia.gov/todayinenergy/detail.cfm?id=12671>), although this northern Pennsylvania portion includes some areas of drilling outside the northeastern Pennsylvania study region for the 6 July flight. In 2012, the study region produced approximately 69% of the unconventional gas in Pennsylvania according to the Pennsylvania Department of Environmental Protection website. We therefore assume production from the northeastern Pennsylvania study region of (69 ± 3) percent of the total Marcellus shale gas production, which amounts to $(18 \pm 1) \times 10^7 \text{ m}^3$ of natural gas per day (Table 10).

IV.5.3. Source Apportionment of CH₄ Emissions in the Haynesville, Fayetteville, and Marcellus Study Regions

Several arguments indicate that the oil and gas industry is the dominant source of CH₄ to the atmosphere of the Haynesville, Fayetteville, and Marcellus study regions. CH₄ enhancements were measured downwind of activity related to the oil and gas industry on scales ranging from individual point sources to the aggregate of wells on every flight to the Haynesville, Fayetteville, and Marcellus regions. Additionally, atmospheric ethane to CH₄ enhancement ratios measured by instruments aboard the P-3 aircraft in the PBL of each region are similar to the composition ratios in natural gas from that region (Figure 42), which indicates natural gas is a dominant source of both alkanes to the atmosphere. Moreover, enhancement ratios of ethane, *n*-, and *i*-butane to propane in the PBL of the Haynesville and Fayetteville regions are similar to ratios in western oil and natural gas producing regions (e.g., Gilman et al., 2013), while those in the PBL of the Marcellus region of northeastern Pennsylvania are similar to those reported by Caulton et al. (2014) for the Marcellus region of southwestern Pennsylvania. Although natural gas emissions are believed to be the dominant source of CH₄ in these regions, other smaller contributing sources of CH₄ include agricultural emissions from livestock enteric fermentation and manure management, point source emissions from landfills and wastewater treatment facilities, and other emissions from coal mines and leaks from natural gas distribution systems and end use. In the following sections, we compare inventory-based (or bottom-up) estimates of CH₄ emissions from point sources and livestock to the region-wide CH₄ emissions derived in Section 5.1 to show that these source sectors are minor contributors to the overall CH₄ emissions. Additionally,

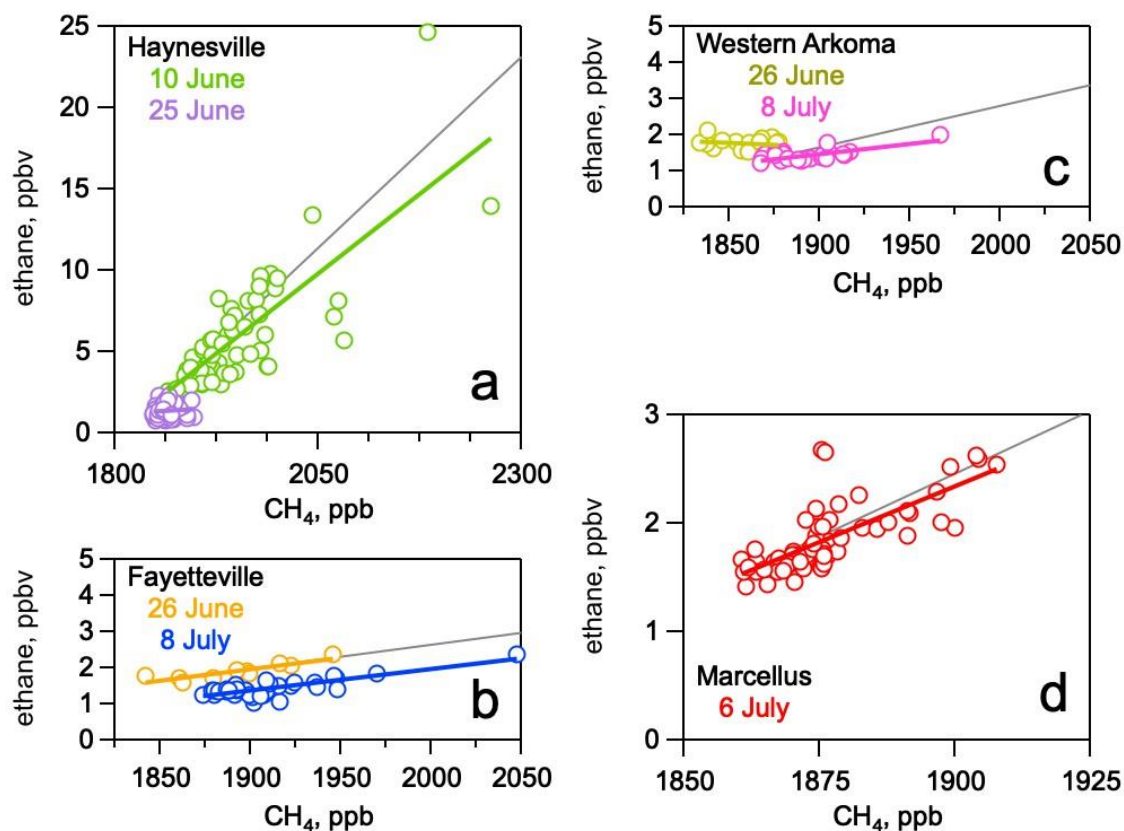


Figure 42. Scatter plots of ethane vs. CH₄ in the boundary layer for the (a) Haynesville, (b) Fayetteville, (c) Western Arkoma, and (d) Marcellus study areas. The colored lines are linear regression fits to the data. The gray lines represent the mean ratio of ethane to CH₄ in natural gas samples listed in the USGS database for each region. The shapes of the graphs maintain the same aspect ratio in the three panels, so that a direct comparison of the slopes can be made.

we use NH₃ measurements aboard the P-3 to verify that enteric fermentation and manure management are not large sources of CH₄ in the three regions. Since NH₃ is co-emitted with CH₄ from livestock, low NH₃ enhancements would indicate a minor livestock source of CH₄ to the regions studied here. Ultimately, because we cannot unambiguously attribute and quantify the agricultural emissions and the non-oil-and-gas

point source emissions in the EPA GHG inventory using the measurements aboard the P-3, we instead treat these emissions as additional lower-bound uncertainty in our analysis in section 5.4.

IV.5.3.1. Haynesville. We attribute the largest CH₄ enhancements from the 25 June flight to emissions from the oil and gas industry. The CH₄ enhancements over background increase along the crosswind P-3 transects as the number of wells upwind increases (Figure 34). Further, the wells with the highest production of natural gas in the Haynesville region are located in an area to the south and southeast of Shreveport, LA between approximately 32.1° and 32.5°N latitude, and the highest sustained measurements of CH₄ on 25 June were measured over and downwind of this same area (Figure 34). Additionally, CH₄ enhancements were measured immediately downwind of numerous point sources related to the oil and gas industry, such as gas plants and compressor stations. Finally, the boundary layer enhancement ratios of ethane to CH₄ determined from the slope of a one-sided regression fit, 0.039 ± 0.009 and 0.003 ± 0.004 ppbv ethane/ppb CH₄ on June 10 and 25, respectively, agree within uncertainties with the highly variable ethane/CH₄ composition ratio in natural gas from the region in the USGS database, 0.047 ± 0.053 (Figure 42a).

Agricultural emissions. We estimate that the 25 June P-3 flight track in the Haynesville region encompassed 245,000 cattle and calves, based on a geographical apportionment of USDA NASS county and parish data. These livestock emit an estimated 1.9×10^6 g CH₄/hr from enteric fermentation. CH₄ emissions from manure in this region are estimated at 0.6×10^6 g CH₄/hr (<http://maps.nrel.gov/biomass>). We therefore estimate a total livestock emission of 2.5×10^6 g CH₄/hr, or only 3% of the

total CH₄ emission of 8.0×10^7 g CH₄/hr from the region calculated for this day. Mean NH₃ mixing ratio enhancements along the upwind and three downwind transects of this region were statistically no different from zero, and 1-Hz NH₃ measurements did not exceed 0.26 ppbv for the entire flight.

Point source emissions. The total CH₄ emission from point sources in the 2012 EPA GHG inventory not related to oil and natural gas processing in the Haynesville region is 38.4 Gg CH₄/yr, which scales to 4.4×10^6 g CH₄/hr, or 5.5% of the CH₄ emission from this region assuming an average value applied to the 25 June flight. CH₄ was enhanced by approximately 10 ppb downwind of the largest point source, the Pinehill landfill located at 32.45°N latitude, 94.83°W longitude (Figure 34). However, these 1-minute-wide plumes, sampled at 11:55, 14:30, and 14:41 EST (Figure 35), did not stand out significantly from the surrounding CH₄ variability.

Other emissions. There are approximately 10 active surface coal mines in the Haynesville region, in addition to underground and abandoned mines. CH₄ was enhanced by up to 30 ppb directly downwind of several active coal mines surrounding the coal-fired Martin Lake power plant at 32.26°N latitude, 94.57°W longitude (Figure 34). However, by the furthest downwind transects, these emissions did not stand out above the CH₄ variability, and thus did not contribute significantly to the derived flux ascribed to the Haynesville oil and gas operations. Additionally, there are two cities in the study region with metropolitan area populations greater than 200,000: Longview, TX and Shreveport, LA (Figure 34). Possible CH₄ sources from these urban areas include the distribution of natural gas to homes and hydrocarbon refining operations in Shreveport. Although we cannot quantify these emissions using P-3 data, we treat them

as an additional lower-bound uncertainty for our analysis in section 5.4. We combine the point source and other emissions uncertainty and estimate an additional 10% uncertainty for the lower bound of the loss rate from the Haynesville region in section 5.4.

IV.5.3.2. Fayetteville and Western Arkoma. We attribute the largest CH₄ enhancements on the 8 July flight to the oil and gas industry in the Fayetteville region. As with the Haynesville region, the CH₄ enhancements increase as the crosswind P-3 transects move successively downwind of the Fayetteville wells (Figure 38). Additionally, the wells with the highest production of natural gas in the Fayetteville region are located in an area between 92.1°W longitude and 92.6°W longitude, and the highest sustained measurements of CH₄ on 8 July were located downwind of these wells (Figure 38). Finally, the boundary layer enhancement ratios of ethane to CH₄, 0.006 ± 0.002 ppbv ethane/ppb CH₄ for both flights, agree within uncertainties with the ethane/CH₄ composition ratio in natural gas from the region in the USGS database, 0.007 ± 0.003 (Figure 42b).

Agricultural emissions. We estimate that the 8 July flight track in the Fayetteville shale region encompassed 170,000 cattle and calves. This results in an estimated emission from enteric fermentation of 1.3×10^6 g CH₄/hr. CH₄ emissions from manure in this region are estimated at 1.1×10^6 g CH₄/hr (<http://maps.nrel.gov/biomass>). We therefore estimate a total livestock emission of 2.4×10^6 g CH₄/hr, or only 6% of the total CH₄ emission of 3.9×10^7 g CH₄/hr from the Fayetteville region calculated for this day. As with the Haynesville region, mean NH₃ mixing ratio enhancements along the upwind and two downwind transects of this region

were statistically no different from zero, and 1-Hz NH₃ measurements averaged 0.1 ppbv over the Fayetteville region.

Point source emissions. The total CH₄ emission from point sources in the 2012 EPA GHG inventory not related to the oil and gas industry in the Fayetteville shale region is 8.0 Gg CH₄/yr, which scales to 0.9×10^6 g CH₄/hr, or 2.3% of the CH₄ emission from this region. Emissions from two facilities, a paper manufacturing facility and a landfill, dominate the 2012 EPA GHG point source inventory and were both located along the southwestern edge of the 8 July flight path over the Fayetteville region (Figure 38). However, the emission plumes from these two point sources were lost in the CH₄ variability by the time the P-3 sampled them along the transect at 35.4°N latitude (Figure 38), suggesting a negligible contribution to the total CH₄ emission ascribed to Fayetteville oil and gas production.

Other emissions. There is no known coal mining activity in the Fayetteville region. Additionally, the flight track of 8 July did not encompass any large urban areas. We therefore treat these emissions as negligible for our analysis in section 5.4.

CH₄ enhancements also increase as the crosswind P-3 transects move successively downwind of the Western Arkoma wells (Figure 38). In addition to the approximately 4200 active gas wells, there are over 2500 plugged and abandoned gas wells in the Western Arkoma region. However, the largest sustained enhancements of CH₄ are located downwind of Ft. Smith, AR, located near 35.4°N latitude, 94.4°W longitude, and are attributed to emissions from a landfill and an unknown source, as discussed in more detail below.

Agricultural emissions. We estimate that the 8 July flight track encompassed 224,000 cattle and calves in the Western Arkoma region. This results in an estimated emission from enteric fermentation of 1.7×10^6 g CH₄/hr. CH₄ emissions from manure in this region are estimated at 3.0×10^6 g CH₄/hr. We therefore estimate a total livestock emission of 4.7×10^6 g CH₄/hr, or 14.5% of the total CH₄ emission of 3.3×10^7 g CH₄/hr from the region calculated for this day. Livestock in the Western Arkoma region therefore account for the largest percentage of non-oil and gas CH₄ emissions from any of the oil and gas regions studied, which is further apparent from NH₃ measurements aboard the P-3. Mean NH₃ mixing ratio enhancements upwind of the Western Arkoma region were negligible, but 1-Hz NH₃ measurements were as high as 0.6 ppbv along the downwind transect, and at times over 1 ppbv elsewhere in the region.

Point source emissions. The total CH₄ emission from point sources in the 2012 EPA GHG inventory not related to the oil and gas industry is 13.9 Gg CH₄/yr, which scales to 1.6×10^6 g CH₄/hr, or only 4.9% of the CH₄ emission from the Western Arkoma region. The largest of these point sources is the Ft. Smith Sanitary Landfill, located at 35.30°N latitude, 94.36°W longitude (Figure 38). According to the inventory, this landfill emits 5.0 Gg CH₄/yr, or an average of 5.7×10^5 g CH₄/hr. The combined point source and livestock emissions, 5.9×10^6 g CH₄/hr, comprise 19% of the total CH₄ emission from the region, the highest percentage for the oil and gas regions studied.

Other emissions. The NOAA P-3 sampled a CH₄ plume downwind of Ft. Smith during both flights to the Western Arkoma region; a weighted average of the CH₄ flux derived from these two transects is $(5.1 \pm 1.7) \times 10^6$ g CH₄/hr, or a factor of approximately 10 greater than the 2012 EPA GHG inventory for the landfill. The

crosswind extent (width) of the Ft. Smith CH₄ plumes indicates either an area source larger than the landfill itself, or an additional point source further upwind of the landfill. Other possible sources contributing to the Ft. Smith CH₄ plumes include active and plugged natural gas wells, active and abandoned coal mines, and coal bed methane production fields in Oklahoma (Figure 38). No whole air samples were taken in this particular plume on either flight day, so without corresponding ethane and propane data we cannot further identify the source of this CH₄ plume. However, it does account for 16% of the CH₄ emission calculated from this region. In addition to the plume downwind of Ft. Smith, active coal mines are found throughout the Western Arkoma region (<https://www.geology.arkansas.gov/>), but their contribution to the total CH₄ flux is not known. Finally, we do not estimate losses from natural gas distribution in Ft. Smith, which has a metropolitan area population of nearly 300,000. We combine the livestock, point source, and other emissions to estimate an additional 35% uncertainty for the lower bound of the loss rate from the Western Arkoma region in section 5.4.

IV.5.3.3. Marcellus. We attribute the largest CH₄ enhancements on the 6 July flight to the oil and gas industry. Although the P-3 did not fly a full upwind transect perpendicular to the prevailing wind direction, CH₄ enhancements were measured immediately downwind of numerous point sources related to the oil and gas industry, including compression stations and transmission stations. Additionally, the CH₄ enhancements measured during the flight were generally accompanied by ethane enhancements (Figures 41), indicating natural gas as the source of the majority of CH₄ emissions. Further, the boundary layer enhancement ratio of ethane to CH₄, 0.020 ±0.005 ppbv ethane/ppb CH₄, agrees within uncertainties with the ethane/CH₄

composition ratio of natural gas from the region in the USGS database, 0.023 ± 0.003 (Figure 42d). The highest levels of CH₄ and ethane were measured near 41.5°N latitude, 77.7°W longitude (Figure 40) at approximately 13:40 Eastern Standard Time (Figure 41). Three point sources related to either underground natural gas storage or natural gas transmission/compression in the EPA GHG inventory are located directly upwind of this location. However, due to their location in the midst of conventional gas wells, this emission may not be associated with natural gas production from the Marcellus shale, but rather from a conventional geologic formation.

Agricultural emissions. We estimate that the 6 July flight track in the Marcellus region encompassed 133,000 cattle and calves. This results in an estimated emission from enteric fermentation of 1.0×10^6 g CH₄/hr (Johnson & Johnson, 1995). CH₄ emissions from manure in this region are estimated at 0.1×10^6 g CH₄/hr. We therefore estimate a total livestock emission of 1.1×10^6 g CH₄/hr, or 8% of the total CH₄ emission of 1.5×10^7 g CH₄/hr from the region calculated for this day. These emissions are consistent with minimal (< 0.5 ppbv) enhancements in NH₃ measured aboard the aircraft in the region.

Point source emissions. The total CH₄ emission from point sources in the 2012 EPA GHG inventory not related to the oil and gas industry is 3.2 Gg CH₄/yr, which scales to 0.4×10^6 g CH₄/hr, or only 2.5% of the total CH₄ emission calculated from this region. One point source upwind of the study area is the Veolia landfill located at 41.29°N latitude, 78.65°W longitude (Figure 40). However, we assume emissions from it and the wells surrounding it contributed to the background level of CH₄ found over

the Marcellus unconventional shale wells (blue circles in Figure 40), thereby minimizing the effects of these emissions on our CH₄ flux calculations.

Other emissions. Although there are no large metropolitan areas in this region, there are coal mines in northeastern Pennsylvania which could contribute significantly to CH₄ emissions in the region. CH₄ enhancements were measured immediately downwind of one cluster of coal mines located at 41.5°N latitude, 76.4°W longitude (Figure 40). However, when the P-3 transected this area again later in the flight when the wind direction had shifted slightly to the southwest, CH₄ was enhanced upwind of the coal mines as well as downwind. We therefore attribute this CH₄ enhancement to the wells directly upwind of this area, and neglect emissions from coal mines for our analysis in section 5.4.

IV.5.4. Loss Rates to the Atmosphere from Natural Gas Production in the Haynesville, Fayetteville, and Marcellus Study Regions

Loss rates from natural gas operations in the three study regions are estimated by taking the derived CH₄ emission from a region, converting the mass emission to a volume of natural gas, and dividing by the volume of natural gas produced in the region. The natural gas composition from each region is determined from the USGS database. The mean CH₄ abundance in these samples is shown in Table 10. These analyses are consistent with published works that provide composition analysis. For example, Zumberge et al. (2012) found CH₄ accounted for 93–99% of all 101 natural gas samples taken from the Fayetteville shale, which compares well with the USGS database in which CH₄ averages (94 ± 5)% in natural gas from the Fayetteville shale region. Jackson et al. (2013) found ethane to CH₄ ratios of less than 3%, and propane to CH₄ ratios less

than 1%, in every sample from 81 drinking water wells near the Marcellus shale formation, which suggests CH₄ dominates the mix of alkanes similar to the USGS dataset for northeastern Pennsylvania, where CH₄ accounts for (96 ±3)% of the natural gas. Because we use the EIA estimate for natural gas production, we therefore use the EIA standard 23.69 mol/L of natural gas in the conversion from mass to volume.

The natural gas loss rates from the Haynesville, Fayetteville, Western Arkoma, and Marcellus regions are shown in Table 10. Howarth et al. (2011) estimate that routine venting and equipment leaks lead to a loss of 0.3–1.9% of the CH₄ produced over the lifecycles of both conventional and shale wells. The 1.0–2.1% and the 1.0–2.8% we report as loss rates from the Haynesville and Fayetteville study regions, respectively, are at the upper end of this range. The loss rate from the Marcellus study region, 0.18–0.41%, is at the lower end of this range. Howarth et al. (2011) estimated additional CH₄ emissions from well completions, liquid unloading, gas processing, and transport, storage, and distribution, however we do not attempt to compare emissions from these activities at this time.

The CH₄ loss rate calculated for the Western Arkoma region, 6–20%, is most likely an overestimate. Emissions from livestock, point sources not related to the oil and gas industry, and a plume of unknown origin may account for one third of the CH₄ emissions in this region, which interferes with our assumption that all CH₄ emissions in a region come from the oil and gas industry. However, the high calculated loss rate does indicate that CH₄ emissions from inactive wells may be a significant source of CH₄ in this region.

The loss rate calculated for the Fayetteville region is similar to a study in an Arkansas Department of Environmental Quality report. This study estimated a CH₄ emission from natural gas operations in the Fayetteville region in 2008 of 1.0×10^{11} g (112877 tons). Using 2008 EIA production data (7.5×10^9 m³), this results in a loss rate of 2.0%, which is nearly identical to the loss rate we derive from a single flight in July 2013.

The production-weighted loss rate from the Haynesville, Fayetteville, and Marcellus study regions is 1.1%, which is similar to a loss rate calculated using the 2012 EPA GHG inventory and 2012 EIA natural gas production data. For this calculation, we assume half the transmission and storage emissions from natural gas systems in the EPA GHG inventory occur in production regions, and half occur in distribution regions. Therefore, CH₄ emissions from the production side of natural gas systems in the 2012 EPA GHG inventory sum to 3920 Gg CH₄/yr. According to the EIA, natural gas production from gas, shale gas, and coalbed wells totaled 7.0×10^{11} m³ in 2012. Assuming an 80% abundance of CH₄ in natural gas, the 2012 EPA emission/EIA production loss rate equals 1.0%.

The CH₄ emissions derived here are comparable in magnitude to CH₄ emissions from the Denver-Julesburg and Uinta basins (Figure 43) (Pétron et al., 2012; Pétron et al., 2014; Karion et al., 2013). However, due to the significantly larger natural gas production, the loss rates derived from the Haynesville, Fayetteville, and Marcellus study regions are significantly lower than those studies. One reason for this may be the composition of the fossil fuel extracted. There is less oil relative to natural gas produced from the Haynesville, Fayetteville, and Marcellus shale plays than there are from the

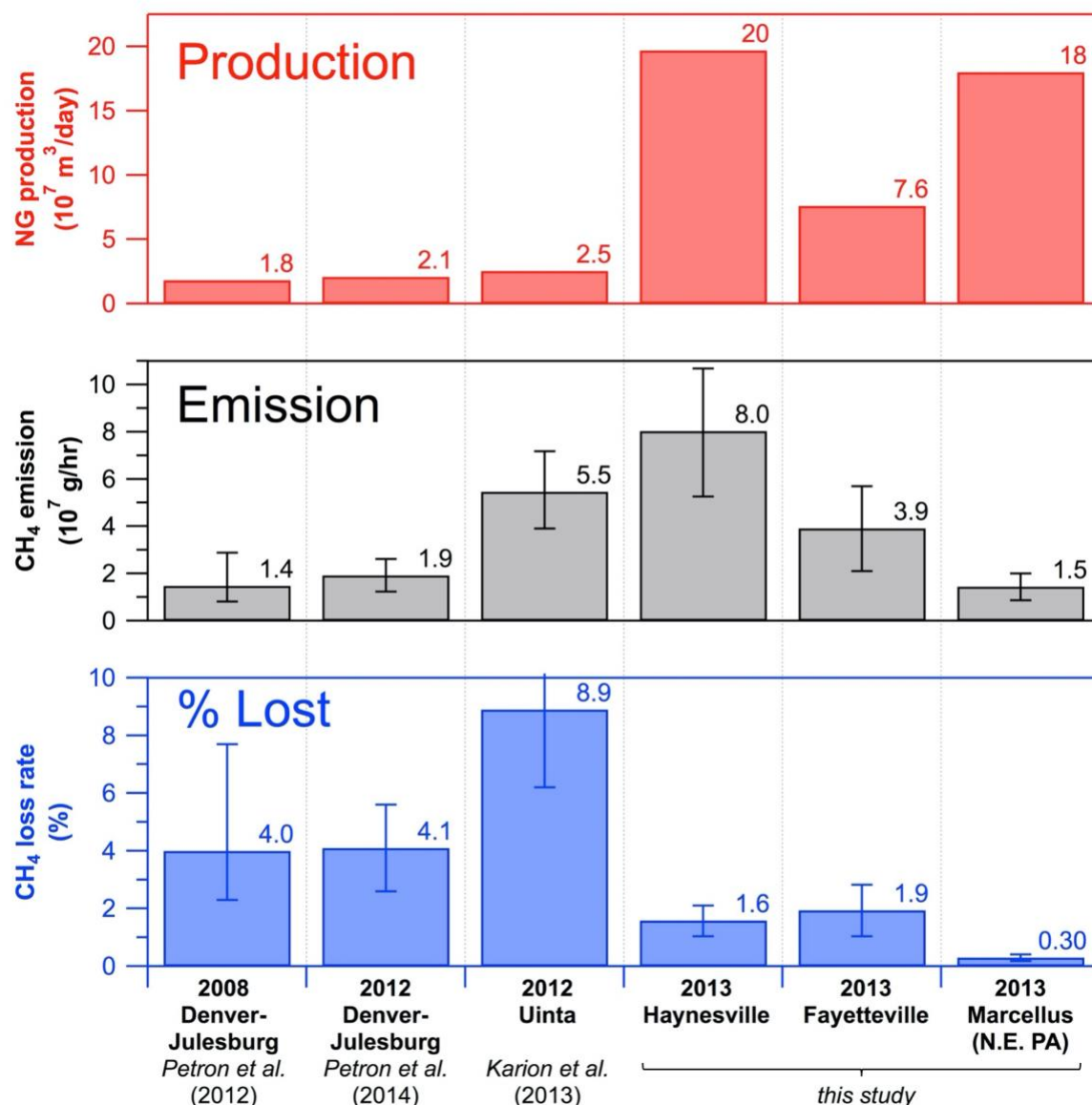


Figure 43. Summary of natural gas (NG) production, CH_4 emissions, and loss rates from oil and natural gas producing regions.

Denver-Julesburg and Uinta Basins. Further, the new-well gas production rate per drill rig has steadily increased since the late 2000s. Both improved technology and the exploration of new regions may play a role in this increased production efficiency. For example, the new-well gas production per rig was approximately a factor of 1.75 greater in the Marcellus region than in the Haynesville region for June and July 2013

(<http://www.eia.gov/petroleum/drilling/>), which may partly explain the lower loss rate found in the northeastern Pennsylvania portion of the Marcellus region.

IV.6. Conclusions

We calculate one-day CH₄ fluxes from three regions of unconventional shale gas production for early summer 2013, and find CH₄ emissions to the atmosphere of $(8.0 \pm 2.7) \times 10^7$ g/hr from the Haynesville shale region in Louisiana and Texas, $(3.9 \pm 1.8) \times 10^7$ g/hr from the Fayetteville shale region in Arkansas, and $(1.5 \pm 0.6) \times 10^7$ g/hr from the Marcellus shale region in northeastern Pennsylvania. We derive loss rates as a percentage of natural gas production in the ranges of 1.0–2.1% from the Haynesville study region, 1.0–2.8% from the Fayetteville study region, and 0.18–0.41% from the Marcellus study region in northeastern Pennsylvania. Airborne measurements of NH₃ and a bottom-up inventory both indicate that livestock are not a large source of CH₄ to the atmosphere in these regions, nor are landfills and other CH₄ point sources not related to the oil and gas industry in the 2012 EPA GHG inventory. Combined, livestock and these point sources account for approximately 10% of the total CH₄ emissions in the each of the Haynesville, Fayetteville, and Marcellus study regions.

The natural gas loss rates from the Haynesville, Fayetteville, and Marcellus study regions are within the range of emissions estimated by Howarth et al. (2011) from the routine venting and equipment leaks of shale gas wells of 0.3–1.9%, which would represent the minimum day-to-day emission from a production region. In addition, the loss rates are lower than the threshold set by Alvarez et al. (2013) of 3.2%, below which the climate impact of using natural gas as a fuel in power plants would be less than that

of coal. However, losses during the transmission and end-use stages will determine whether natural gas from these regions ultimately fall below the Alvarez et al. (2013) threshold. Yet, to our knowledge, this is the first airborne mass balance study in which CH₄ emissions from natural gas producing regions are below 3.2%. Further, the Haynesville, Fayetteville, and northeastern Pennsylvania Marcellus regions accounted for approximately 20% of U.S. natural gas production, and over 50% of unconventional shale gas production, at the time of the study. The production-weighted loss rate from the three regions is 1.1%. This rate is similar to a 1.0% loss rate derived from the 2012 EPA GHG emissions inventory for natural gas systems and 2012 EIA natural gas production numbers.

Finally, the magnitude of CH₄ emissions from the Haynesville, Fayetteville, and northeastern Pennsylvania Marcellus regions are comparable to those calculated from the Denver-Julesburg Basin in Colorado and the Uinta Basin in Utah, despite greater natural gas production from the former regions. Repeated measurements will be necessary to determine whether the one-day CH₄ emission rates for the regions studied here are fully representative for those regions, to determine whether the CH₄ emission rates change over the full life-cycle of fossil fuel production from each formation, and to understand the drivers behind regional differences in loss rates, of a factor of 20, now reported in the literature for different oil and gas producing regions.

4.b. Conclusions of Publication IV and Subsequent Oil and Gas Emissions Work

The work of Peischl et al. (2015) was highlighted in the scientific journal *Nature* by Tollefson (2015) due to the notable results that some regions' emissions were below

the EPA average emission rate of approximately 1%. After this work, Karion et al. (2015) quantified CH₄ emissions from the Barnett shale region of Texas, and Peischl et al. (2016) quantified emissions from the Bakken oil shale region of North Dakota. Both studies found emissions significantly greater than expected from the EPA average emission.

In a collaborative effort, Lyon et al. (2015) published a new bottom-up inventory from the Environmental Defense Fund (EDF) that Zavala-Araiza et al. (2015) reconciled with emissions determined using the top-down methods of Karion et al. (2015). What distinguished the EDF inventory from previous inventories was the addition of a “fat-tailed” distribution of sources, which included a relatively small number of sources that accounted for a relatively large percentage of the total emission. This fat-tailed distribution had been reported by numerous studies that inspected emissions from various components of natural gas production, including compressor stations, processing plants, and production sites (see Lyon et al., 2015, for more detail).

The EDF inventory was then applied to the entire country and compared with all the top-down emission estimates that had been published to date by Alvarez et al. (2018). This study found that CH₄ emissions were a factor of 1.6 greater than CH₄ emissions in the U.S. EPA GHG inventory. Of the nine basins studied by Alvarez et al. (2018), five came from my work (Peischl et al., 2015; Peischl et al. 2016). This is considered to be the definitive study of CH₄ emissions from oil and gas production in the U.S. to date.

However, work in this area is ongoing. One month after the work of Alvarez et al. (2018) was published, Peischl et al. (2018) published the first CH₄ emissions

estimates from the Eagle Ford region of Texas, along with emissions from previously-studied regions. An updated version of Figure 43 was also presented, shown here as Figure 44. More recently, CH₄ emissions from the largest oil and natural gas producing region in the U.S., the Permian Basin, were published using satellite data and an inverse model (Zhang et al., 2020). The cumulative work in this area over the past decade has provided scientists and policy-makers the first scientifically-based estimate for oil and gas CH₄ emissions in the U.S., and thus better knowledge of the impact of using natural gas as a fuel on climate.

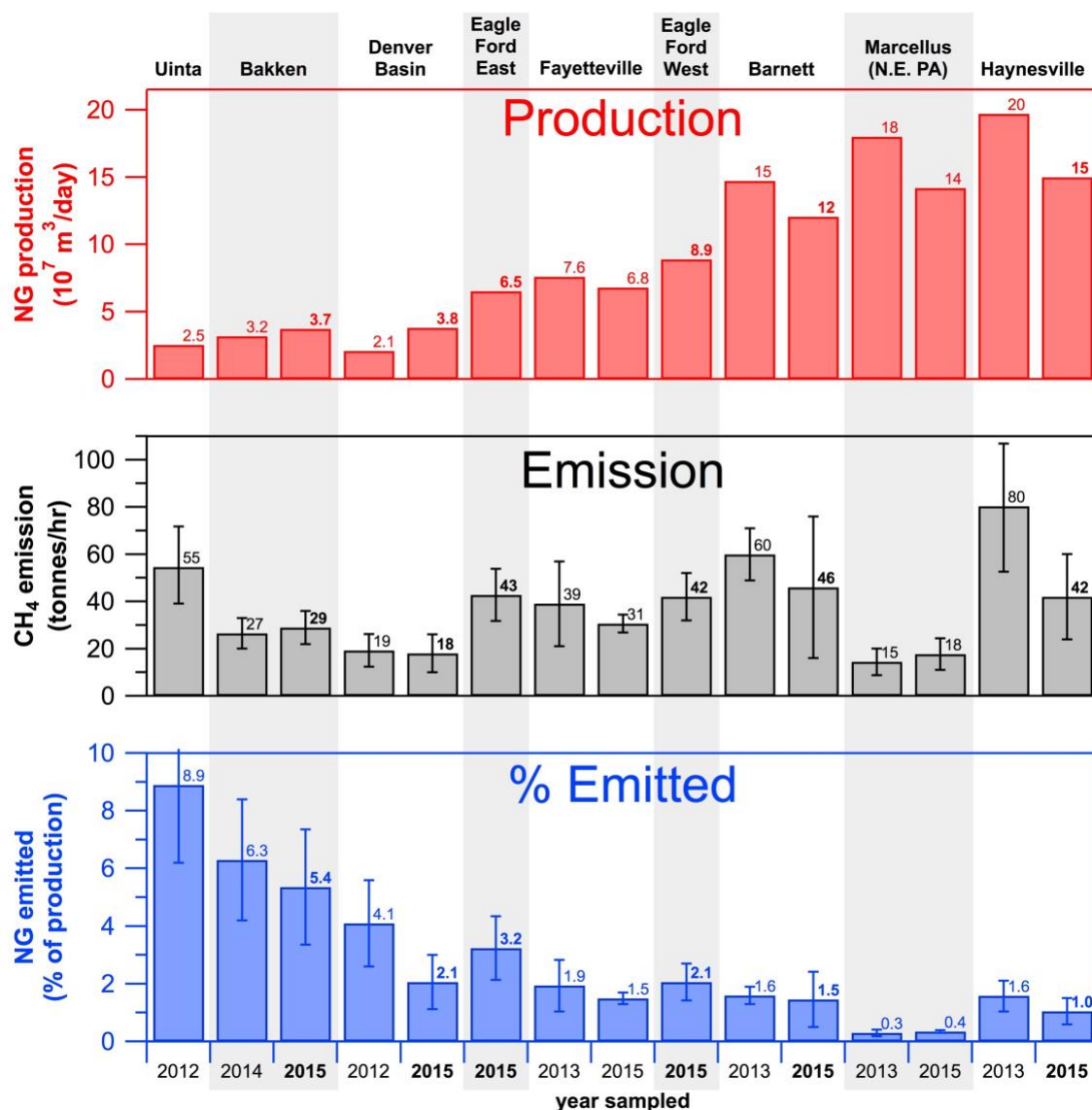


Figure 44. Summary of natural gas (NG) production, CH_4 emissions from oil and gas activity, and natural gas emitted as a percentage of natural gas produced in their respective regions. Numbers in boldface represent estimates presented by Peischl et al. (2018). Data from past studies are shown for comparison purposes (Karion et al., 2013; Peischl et al., 2016; Pétron et al., 2014; Peischl et al., 2015; Schwietzke et al., 2017; Karion et al., 2015; Peischl et al., 2015; Barkley et al., 2017; and Peischl et al., 2015). Gray shading is used to help the eye separate different regions down the columns of the three bar graphs.

5. Conclusions

This thesis presents multiple techniques to determine emissions of trace gases that impact both air quality and climate. In most cases, the emissions quantified here had never been evaluated beyond an initial bottom-up inventory. Therefore, these works often provided policy-makers and scientists alike with the first quantified estimates with uncertainties of these emissions. The analysis also notified industry that evidence of their emissions to the atmosphere could be determined by anyone with the right equipment at any time, thereby holding them accountable for their emissions.

The work determining NO_x and SO₂ emissions from power plants showed that regulations requiring emissions controls on power plants are effective. These regulations continue to this day, and the added expenses of scrubbers are one of the reasons for the shift away from coal-fired power to natural gas-fueled and renewable power.

The work determining CH₄ emissions from various sectors of California's GHG inventory will continue. According to the CARB GHG inventory, California's GHG emissions dropped below 1990 levels four years ahead of schedule in 2016. The state has passed additional measures requiring GHG emissions to be 40% below 1990 levels by 2030 and requiring carbon neutrality by 2045. Analysis of emissions in their GHG inventory will continue with future NOAA airborne field projects planned for 2023 and beyond.

The work presented above determining CH₄ emissions from oil and natural gas production, along with the work of the scientific community as a whole, has led states and the federal government to enact legislation with the purpose of limiting emissions from this sector. Further, it has led to the formation of numerous companies that

specialize in leak detection and repair in oil and gas fields (e.g., Schwietzke et al., 2018; Alden et al. 2019; Johnson et al., 2021) to help industry capture gains from a commodity lost to the atmosphere. To date, the latest, state-of-the-art satellite-based measurements have only quantified the largest emissions of CH₄ from point sources and regions. Therefore, studies similar to that presented above will be both relevant and necessary in the future to determine if regulations have had the intended effects of reducing CH₄ emissions.

However, satellite measurements of many trace gas species continue to improve. For example, the TROPospheric Monitoring Instrument (TROPOMI) aboard the Sentinel-5 satellite makes daily daytime measurements of CH₄, CO, CO₂, NO, NO₂, and O₃; the TEMPO instrument scheduled to launch in 2023 will make hourly daytime measurements of O₃ and NO₂; and the Geostationary Carbon Cycle Observatory (GeoCarb) currently scheduled to launch in 2025 will measure CO₂, CH₄, and CO throughout the daytime over North and South America. These satellite-based measurements will provide the scientific community with unprecedented temporal and spatial observations of gases that affect climate and air quality in the United States. In situ measurements will therefore be necessary to validate these satellite measurements.

Thus, future work will use similar techniques employed herein to determine emissions of gases that affect both air quality and climate. This type of work will be important and relevant for many years to come.

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IV. Data are publicly available at <https://csl.noaa.gov/groups/csl7/measurements/2013senex/P3/DataDownload/index.php?page=/groups/csl7/measurements/2013senex/P3/DataDownload/>. J.B.G. and B.M.L. thank NOAA Hollings Scholar M. Dumas and Hendrix College for partially funding A.

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