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From: Greenwood, Lauren@Energy
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To: Energy - Docket Optical System
Cc: McKinney, Jim@Energy
Subject: 14-IEP-1B Lead Commissioner Workshop on Electric and Natural Gas Vehicles in California
Attachments: Slide 4 -Greater Focus Needed on Methane Leakage_Environmental Defense Fund_ PNAS-2012-Alvarez-6435-40.pdf; Slide 6 - Comparative Life-Cycle Air Emissions of Coal, Domestic Natural Gas, LNG, and SNG for Electricity Generation_Ex._80_-_Jaramillo_ 2007.pdf; 1 - University of Texas Austin_Published Study_Measurements of Methane Emissions at Natural Gas_PNAS-2013-Allen-17768-73.pdf; 1 - University of Texas Austin_FAQ.docx; 2 - NOAA-CIRES_A new look at methane and nonmethane hydrocarbon_Journal of Geophysical Research Atmospheres-2014-Pétron, Gabrielle, et al..pdf; 2 - NOAA-CIRES_FAQ.docx; 3 - Washington State University_Press Release_Local Distribution.docx; 8 - West Virginia University_Press Release_Transportation.docx; 11 - Colorado State University_Press Release_Transmission.docx; 13 - Colorado State University_Press Release_Gathering and Processing.docx; Methane Leaks from North American Natural Gas Systsems_ScienceMethane.02.14.14.pdf; A Multi-tower Measurement Network Estimate of California's Methane Emissions_Jeong.pdf

Hi Lauren,

Thanks for following up with us on information from Tim's presentation - we're excited to have these valuable studies formally on file at the Energy Commission. Below is an explanation providing context to the attachments. I've laid it out in similar form as your first email below.

---**Attachment 1** is the Alvarez et al study referenced on slide 4.
---**Attachment 2** is the Jaramillo et al. study referenced on slide 6.
---There were 16 additional studies referenced in Tim's presentation. Of those 16, only 2 have been published - therefore data and results are only available for those 2. **Attachments 3-6** include both of those published studies along with corresponding FAQs. Of the remaining 14 unpublished studies, there are 4 studies that have press releases. I've attached those press releases to provide additional context (**attachments 7-10**). Due to the stage of the research, we are unable to provide additional information on the remaining 10 unpublished studies (not published and without press releases). The summary slides Tim used in his presentation provide the most thorough information on those 10, currently active studies. The attachments I've discussed here are titled with a number that corresponds to their reference location in Tim's presentation. For example, the University of Texas study and FAQ (attachment 3 and 4) are titled starting with a 1 – this number matches the studies placement in the presentation.
--I've attached 2 additional studies **(attachments 11 and 12)** that I believe will prove useful for the Commission.

Please let me know if you have any question - I'm happy to clarify anything over the phone or email.

Best,
- Andy

Andy Wunder
Policy Associate, California Climate Initative

Environmental Defense Fund
123 Mission St, 28th Floor
San Francisco, CA 94105
T 415-293-6152

awunder@edf.org
edf.org

Timothy J. O'Connor
Senior Attorney / Director, California Climate Initiative
Environmental Defense Fund
Office: (415) 293 - 6132
Cell: (916) 549 - 8423
123 Mission St., 28th Floor, San Francisco, CA, 94105
toconnor@edactionfund.org

Greater focus needed on methane leakage from natural gas infrastructure

Ramón A. Alvarez[a,1], Stephen W. Pacala[b,1], James J. Winebrake[c], William L. Chameides[d], and Steven P. Hamburg[e]

[a]Environmental Defense Fund, 301 Congress Ave Suite 1300, Austin, TX 78701; [b]Department of Ecology and Evolutionary Biology, 106A Guyot Hall, Princeton University, Princeton, NJ 08544; [c]College of Liberal Arts, Rochester Institute of Technology, Rochester, NY 14623; [d]School of the Environment, Duke University, Durham, NC 27708; and [e]Environmental Defense Fund, 18 Tremont Street, Boston, MA 02108

Contributed by Stephen W. Pacala, February 13, 2012 (sent for review December 21, 2011)

Natural gas is seen by many as the future of American energy: a fuel that can provide energy independence and reduce greenhouse gas emissions in the process. However, there has also been confusion about the climate implications of increased use of natural gas for electric power and transportation. We propose and illustrate the use of technology warming potentials as a robust and transparent way to compare the cumulative radiative forcing created by alternative technologies fueled by natural gas and oil or coal by using the best available estimates of greenhouse gas emissions from each fuel cycle (i.e., production, transportation and use). We find that a shift to compressed natural gas vehicles from gasoline or diesel vehicles leads to greater radiative forcing of the climate for 80 or 280 yr, respectively, before beginning to produce benefits. Compressed natural gas vehicles could produce climate benefits on all time frames if the well-to-wheels CH_4 leakage were capped at a level 45–70% below current estimates. By contrast, using natural gas instead of coal for electric power plants can reduce radiative forcing immediately, and reducing CH_4 losses from the production and transportation of natural gas would produce even greater benefits. There is a need for the natural gas industry and science community to help obtain better emissions data and for increased efforts to reduce methane leakage in order to minimize the climate footprint of natural gas.

With growing pressure to produce more domestic energy and to reduce greenhouse gas (GHG) emissions, natural gas is increasingly seen as the fossil fuel of choice for the United States as it transitions to renewable sources. Recent reports in the scientific literature and popular press have produced confusion about the climate implications of natural gas (1–5). On the one hand, a shift to natural gas is promoted as climate mitigation because it has lower carbon per unit energy than coal or oil (6). On the other hand, methane (CH_4), the prime constituent of natural gas, is itself a more potent GHG than carbon dioxide (CO_2); CH_4 leakage from the production, transportation and use of natural gas can offset benefits from fuel-switching.

The climatic effect of replacing other fossil fuels with natural gas varies widely by sector (e.g., electricity generation or transportation) and by the fuel being replaced (e.g., coal, gasoline, or diesel fuel), distinctions that have been largely lacking in the policy debate. Estimates of the net climate implications of fuel-switching strategies should be based on complete fuel cycles (e.g., "well-to-wheels") and account for changes in emissions of relevant radiative forcing agents. Unfortunately, such analyses are weakened by the paucity of empirical data addressing CH_4 emissions through the natural gas supply network, hereafter referred to as CH_4 leakage.* The U.S. Environmental Protection Agency (EPA) recently doubled its previous estimate of CH_4 leakage from natural gas systems (6).

In this paper, we illustrate the importance of accounting for fuel-cycle CH_4 leakage when considering the climate impacts of fuel-technology combinations. Using EPA's estimated CH_4 emissions from the natural gas supply, we evaluated the radiative forcing implications of three U.S.-specific fuel-switching scenarios: from gasoline, diesel fuel, and coal to natural gas.

A shift to natural gas and away from other fossil fuels is increasingly plausible because advances in horizontal drilling and hydraulic fracturing technologies have greatly expanded the country's extractable natural gas resources particularly by accessing gas stored in shale deep underground (7). Contrary to previous estimates of CH_4 losses from the "upstream" portions of the natural gas fuel cycle (8, 9), a recent paper by Howarth et al. calculated upstream leakage rates for shale gas to be so large as to imply higher lifecycle GHG emissions from natural gas than from coal (1). (*SI Text*, discusses differences between our paper and Howarth et al.) Howarth et al. estimated CH_4 emissions as a percentage of CH_4 produced over the lifecycle of a well to be 3.6–7.9% for shale gas and 1.7–6.0% for conventional gas. The EPA's latest estimate of the amount of CH_4 released because of leaks and venting in the natural gas network between production wells and the local distribution network is about 570 billion cubic feet for 2009, which corresponds to 2.4% of gross U.S. natural gas production (1.9–3.1% at a 95% confidence level) (6).† EPA's reported uncertainty appears small considering that its current value is double the prior estimate, which was itself twice as high as the previously accepted amount (9).

Comparing the climate implications of CH_4 and CO_2 emissions is complicated because of the much shorter atmospheric lifetime of CH_4 relative to CO_2. On a molar basis, CH_4 produces 37 times more radiative forcing than CO_2.‡ However, because CH_4 is oxidized to CO_2 with an effective lifetime of 12 yr, the integrated, or cumulative, radiative forcings from equi-molar releases of CO_2 and CH_4 eventually converge toward the same value. Determining whether a unit emission of CH_4 is worse for the climate than a unit of CO_2 depends on the time frame considered. Because accelerated rates of warming mean ecosystems and humans have less time to adapt, increased CH_4 emissions due to substitution of natural gas for coal and oil may produce undesirable climate outcomes in the near-term.

The concept of global warming potential (GWP) is commonly used to compare the radiative forcing of different gases relative

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*Challenges also exist in the quantification of CH_4 emissions from the extraction of coal. We use the term "leakage" for simplicity and define it broadly to include all CH_4 emissions in the natural gas supply, both fugitive leaks as well as vented emissions.

†This represents an uncertainty range between −19% and +30% of natural gas system emissions. For CH_4 from petroleum systems (35% of which we assign to the natural gas supply) the uncertainty is −24% to +149%; however, this is only a minor effect because the portion of natural gas supply that comes from oil wells is less than 20%.

‡One-hundred-two times on a mass basis. This value accounts for methane's direct radiative forcing and a 40% enhancement because of the indirect forcing by ozone and stratospheric water vapor (10).

†To whom correspondence may be addressed. E-mail: pacala@princeton.edu or ralvarez@edf.org.

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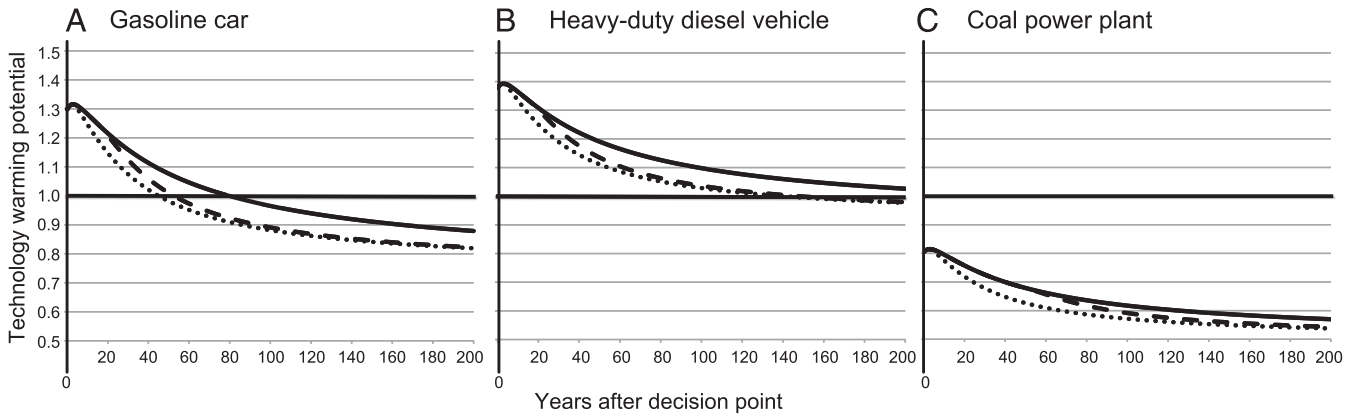

Fig. 1. Technology warming potential (TWP) for three sets of natural gas fuel-switching scenarios. (*A*) CNG light-duty cars vs. gasoline cars; (*B*) CNG heavy-duty vehicles vs. diesel vehicles; and (*C*) combined-cycle natural gas plants vs. supercritical coal plants using low-CH_4 coal. The three curves within each frame simulate real-world choices, including a single emissions pulse (dotted lines); emissions for the full service life of a vehicle or power plant (15 and 50 years, respectively, dashed lines); and emissions from a converted fleet continuing indefinitely (solid lines). For the pulse and service life analyses, our scenarios assume that the natural gas choice reverts back to the incumbent choice before the switch took place; for the fleet conversion analysis we assume that a natural gas vehicle or power plant is replaced by an identical unit at the end of its service life.

to CO_2 and represents the ratio of the cumulative radiative forcing t years after emission of a GHG to the cumulative radiative forcing from emission of an equivalent quantity of CO_2 (10). The Intergovernmental Panel on Climate Change (IPCC) typically uses 100 yr for the calculation of GWP. Howarth et al. (1) emphasized the 20-year GWP, which accentuates the large forcing in early years from CH_4 emissions, whereas Venkatesh et al. (2) adopted a 100-yr GWP and Burnham et al. (4) utilized both 20- and 100-yr GWPs.

GWPs were established to allow for comparisons among GHGs at one point in time after emission but only add confusion when evaluating environmental benefits or policy tradeoffs over time. Policy tradeoffs like the ones examined here often involve two or more GHGs with distinct atmospheric lifetimes. A second limitation of GWP-based comparisons is that they only consider the radiative forcing of single emission pulses, which do not capture the climatic consequences of real-world investment and policy decisions that are better simulated as emission streams.

To avoid confusion and enable straightforward comparisons of fuel-technology options, we suggest that plotting as a function of time the relative radiative forcing of the options being considered would be more useful for policy deliberations than GWPs. These technology warming potentials (TWP) require exactly the same inputs and radiative forcing formulas used for GWP but reveal time-dependent tradeoffs inherent in a choice between alternative technologies. We illustrate the value of our approach by applying it to emissions of CO_2 and CH_4 from vehicles fueled with CNG compared with gasoline or diesel vehicles and from power plants fueled with natural gas instead of coal.

Wigley also analyzed changes in the relative benefits over time of switching from coal to natural gas, but that was done in the context of additional complexities including specific assumptions about the global pace of technological substitution, emissions of sulfur dioxide and black carbon, and a specific model of global warming due to radiative forcing (5). We compare our results with Wigley's in the next section.

Results and Discussion

We focus on the TWPs of real-world choices faced by individuals, corporations, and policymakers about fuel-switching in the transport and power sectors. Each of the three curves within the panels of Fig. 1 represents a distinct choice and its associated emission duration: for example, whether to rent a CNG or a gasoline car for a day (Pulse TWP); whether to purchase and operate a CNG or gasoline car for a 15-yr service life (Service-Life TWP); and whether a nation should adopt a policy to convert the gasoline fleet of cars to CNG (Fleet Conversion TWP). In each of these cases, a TWP greater than 1 means that the cumulative radiative forcing from choosing natural gas today is higher than a current fuel option after t yr. Our results for pulse TWP at 20 and 100 yr are identical to fuel-cycle analyses using 20-year or 100-year GWPs for CH_4.

Given EPA's current estimates of CH_4 leakage from natural gas production and delivery infrastructure, in addition to a modest CH_4 contribution from the vehicle itself (for which few empirical data are available), CNG-fueled vehicles are not a viable mitigation strategy for climate change.[§] Converting a fleet of gasoline cars to CNG increases radiative forcing for 80 yr before any net climate benefits are achieved; the comparable cross-over point for heavy-duty diesel vehicles is nearly 300 yr.

Stated differently, converting a fleet of cars from gasoline to CNG would result in numerous decades of more rapid climate change because of greater radiative forcing in the early years after the conversion. This is eventually offset by a modest benefit. After 150 yr, a CNG fleet would have produced about 10% less cumulative radiative forcing than a gasoline fleet—a benefit equivalent to a fuel economy improvement of 3 mpg in a 30 mpg fleet. CNG vehicles fare even less favorably in comparison to heavy-duty diesel vehicles.

In contrast to the transportation cases, a fleet of new, combined-cycle natural gas power plants reduces radiative forcing on all time frames, relative to new coal plants burning low-CH_4 coal—assuming current estimates of leakage rates (Fig. 1*C*). The conclusions differ primarily because of coal's higher carbon content relative to petroleum fuels; however, fuel-cycle CH_4 leakage can also affect results. (As discussed elsewhere in this paper, our analysis considered only the emissions of CH_4 and CO_2. In *SI Text*, we examine the effect of different CH_4 leak rates in the coal and natural gas fuel cycles for the electric power scenario.)

To provide guidance to industry and policymakers, we also determined the maximum well-to-wheels or well-to-burner-tip leakage rate needed to ensure net climate benefits on all time frames after fuel-switching to natural gas (see Fig. 2). For example, if the well-to-wheels leakage was reduced to an effective leak rate of 1.6% of natural gas produced (approximately 45% below our estimate of current leakage of 3.0%), CNG cars would result

[§]The CH_4 from operation of a CNG automobile was estimated to be 20 times the value for gasoline vehicles (11), which is approximately 20% of the well-to-pump CH_4 leakage on a kg/mmBtu basis. This assumption deserves much further scrutiny.

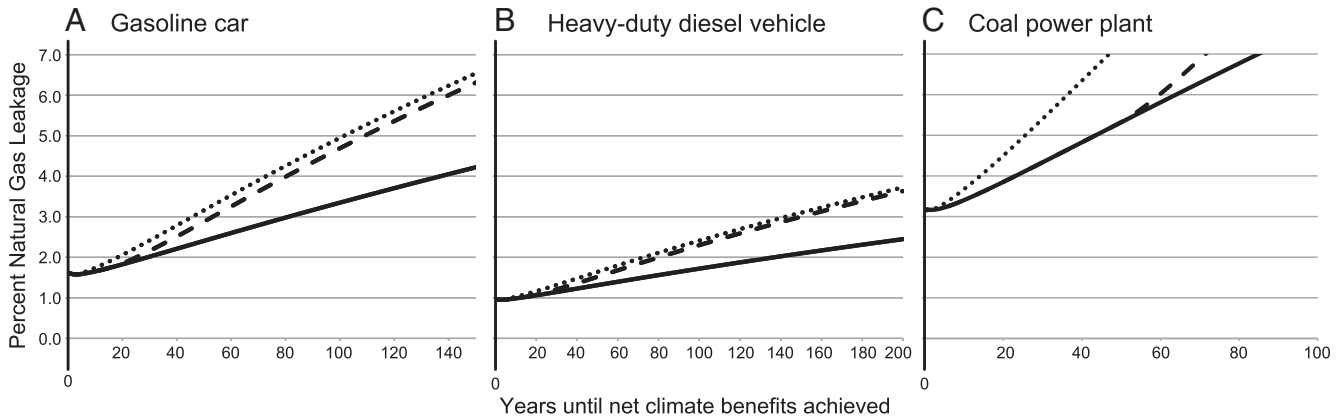

Fig. 2. Maximum "well-to-wheels" natural gas leak rate as a function of the number of years needed to achieve net climate benefits after choosing a CNG option in lieu of (*A*) gasoline cars; (*B*) heavy-duty diesel vehicles; and (*C*) coal power plants. For *A* and *B*, the maximum leakage is the sum of losses from the well through the distribution system plus losses from the CNG vehicle itself (well-to-wheels); for *C*, the maximum leakage is from the well through the transmission system where most power plants receive their fuel. When leak rates are less than the y-intercept, a fuel switch scenario would result in net climate benefits beginning immediately. The three curves within each frame follow the conventions outlined in Fig. 1 and represent: single emissions pulses (dotted lines); the service life of a vehicle or a power plant, 15 or 50 years, respectively (dashed lines); and a permanent fleet conversion (solid lines).

in climate benefits immediately and improve over time.[¶] For CNG to immediately reduce climate impacts from heavy-duty vehicles, well-to-wheels leakage must be reduced below 1%. Fig. 2*C* shows that new natural gas power plants produce net climate benefits relative to efficient, new coal plants using low-gassy coal on all time frames as long as leakage in the natural gas system is less than 3.2% from well through delivery at a power plant. Fig. 2 also shows, for a range of leakage rates, the number of years needed to reach the "cross-over point" when net climate benefits begin to occur after a fuel-technology choice is made.

We emphasize that our calculations assume an average leakage rate for the entire U.S. natural gas supply (as well for coal mining). Much work needs to be done to determine actual emissions with certainty and to accurately characterize the site-to-site variability in emissions. However, given limited current evidence, it is likely that leakage at individual natural gas well sites is high enough, when combined with leakage from downstream operations, to make the total leakage exceed the 3.2% threshold beyond which gas becomes worse for the climate than coal for at least some period of time.[‖] Our analysis of reported routine emissions for over 250 well sites with no compressor engines in Barnett Shale gas well sites in Fort Worth, Texas, in 2010 revealed a highly skewed distribution of emissions, with 10% of well sites accounting for nearly 70% of emissions (see *SI Text*).[**] Natural gas leak rates calculated based on operator-reported, daily gas production data at these well sites ranged from 0% to 5%, with six sites out of 203 showing leak rates of 2.6% or greater due to routine emissions alone.[††]

Our analysis of coal-to-natural gas fuel-switching does not consider potential changes in sulfate aerosols and black carbon, short-lived climate forcers previously shown to affect the climate implications of such fuel-switching scenarios (5, 13). Recently, Wigley concluded that coal-to-gas switching on a global scale would result in increased warming on a global scale in the short term, based on examining a set of scenarios with a climate model that included both the increased warming produced by CH_4 losses from the natural gas fuel cycle and the additional cooling that occurs due to SO_2 emissions and the sulfate aerosols they form as a result of burning coal (5). The applicability of Wigley's global conclusion to the United States or any other individual country is limited due to the reliance on global emissions scenarios. Analyses such as Wigley's, which model the climate impacts of all climate forcing emissions, are useful to evaluate specific fuel-switching scenarios; however, their ultimate relevance to policymakers and fleet owners will be determined by the fidelity with which they reflect actual emissions from all phases of each fuel cycle at the relevant geographic scale (e.g., national, continental, or global). The SO_2 emissions that Wigley assumed are much higher than those of the current fleet of coal electrical generation plants in the United States, where SO_2 emissions declined by more than 50% between 2000 and 2010.[‡‡] Moreover, due to state and federal pollution abatement requirements, U.S. SO_2 emissions are projected to continue declining, to roughly 30% of 2000 levels by 2014 (see *SI Text*). This means that by 2014 the projected sulfur emissions from the U.S. coal electrical generation plant fleet, 3 TgS/GtC, will approach the emission factor that Wigley assumed the global fleet would reach in 2060 (2 TgS/GtC), when he projected the climate benefits of fuel-switching might begin, and significantly lower than Wigley's estimated 2010 value of 12 TgS/GtC. Accounting for the lower SO_2 from U.S. coal plants in an integrated way will result in greater net climate impacts of using coal than reported by Wigley and in turn the net benefits of fuel-switching will occur much sooner than he projected.

Increasingly, this will also be the case globally. The production of sulfur aerosols as a result of coal combustion causes such negative impacts on human and ecosystem health that it is prudent to assume that policies will continue to be rapidly implemented in many, if not most, countries to reduce such emissions at a much faster pace than assumed by Wigley. Indeed, it has been reported that China has already installed SO_2 scrubbers on power plants accounting for over 70% of the nation's installed coal power capacity (14), such that SO_2 emissions from power plants in 2010 were 58% below 2004 levels (15). The SO_2 emissions factor from

[¶]Our estimate that current well-to-wheels leakage is 3.0% of gas produced assumes that 2.4% of gas produced is lost between the well and the local distribution system (based on EPA's 2011 GHG emission inventory) and that 0.6% is due to emissions during refueling and from the vehicle itself. For further discussion of the climatic implication of natural gas vehicles see (12).

[‖]EPA's GHG inventory suggests leakage from natural gas processing and transmission is 0.6% of gas produced, meaning production leakage must be greater than 2.6% for the total fuel cycle leakage of a power plant receiving fuel from a transmission pipeline to exceed 3.2%.

[**]Sites with compressor engines were excluded due to the contractor's assumption that all engines in the City were uncontrolled, which leads to erroneous emission estimates.

[††]Routine emissions do not include such occasional events as well completions and blowdowns. Only 203 of the 254 sites had data for gas production. An Excel spreadsheet containing the Fort Worth data and our calculations is provided in Dataset S1.

[‡‡]Emissions query performed on December 5, 2011, using the Data and Maps feature of the U.S. Environmental Protection Agency's Clean Air Markets Web page (http://camddataandmaps.epa.gov/gdm/).

Chinese coal plants in 2010 has been estimated to be 204 g/GJ, comparable to the 2010 value of 229 g/GJ (4.7 TgS/GtC) for U.S. coal plants (*SI Text*).

Little work appears to have been done to evaluate fuel-switching in on-road transportation with methods that consider the implications of all climate forcing emissions, including sulfur aerosols and black carbon, although the effect of short-lived climate forcers on individual transport sectors has been studied (16, 17). One study reports that the influence of negative radiative forcing due to emissions from on-road transport is much lower than for the power generation sector in both the United States and globally (18). This implies that our approach, which considers CO_2 and CH_4 emissions alone, provides a reasonable first-order estimate of changes in radiative forcing from fuel-switching scenarios for the on-road transport sector.

Conclusions

The TWP Approach Proposed Here Offers Policymakers Greater Insights than Conventional GWP Analyses. GWPs are a valuable tool to compare the radiative forcing of different gases but are not sufficient when thinking about fuel-switching scenarios. TWPs provide a transparent, policy-relevant analytical approach to examine the time-dependent climate influence of different fuel-technology choices.

Improved Science and Data Are Needed. Despite recent changes to EPA's methodology for estimating CH_4 leakage from natural gas systems, the actual magnitude remains uncertain and estimates could change as methods are refined. Ensuring a high degree of confidence in the climate benefits of natural gas fuel-switching pathways will require better data than are available today. EPA's rule requiring natural gas industry disclosure of GHG emissions should begin to produce data in 2012, though it is unlikely that most uncertainties will be resolved and possible systematic biases eliminated. Specific challenges include confirming the primary sources of emissions and determining drivers of variance in leakage rates. Greater direct involvement of the scientific community could help improve estimates of CH_4 leakage and identify approaches that enable independent validation of industry-reported emissions.

Reductions in CH_4 Leakage Are Needed to Maximize the Climate Benefits of Natural Gas. While CH_4 leakage from natural gas infrastructure and use remains uncertain, it appears that current leakage rates are higher than previously thought. Because CH_4 initially has a much higher effect on radiative forcing than CO_2, maintaining low rates of CH_4 leakage is critical to maximizing the climate benefits of natural gas fuel-technology pathways. Significant progress appears possible given the economic benefits of capturing and selling lost natural gas and the availability of proven technologies. (EPA's Natural Gas STAR program shows many examples: www.epa.gov/gasstar/tools/recommended.html.)

Table 2. Radiative efficiency (RE) values used in this paper

	Direct RE ($W\ m^{-2}\ ppb^{-1}$)	Relative direct + indirect RE (per ppb or molar basis)	Relative direct + indirect RE (per kg basis)*
CO_2	1.4×10^{-5}	1	1
CH_4	3.7×10^{-4}	37	102

*Obtained by multiplying the molar radiative efficiency by the ratio of molecular weights of CH_4 and CO_2.

Methods

Our approach of using TWPs to compare the cumulative radiative forcing of fuel-technology combinations is a straightforward extension of the calculation of GWP, which is given by Eq. **1** over a time horizon, TH, for a pulse emission of 1 kg of a generic GHG producing time-dependent radiative forcing given by $RF_{GHG}(t)$:

$$GWP = \frac{\int_0^{TH} RF_{GHG}(t)dt}{\int_0^{TH} RF_{CO_2}(t)dt}. \quad [1]$$

SI Text shows the analytical solution of Eq. **1** (i.e., GWP as a function of time horizon). Plotting the entire curve enables one to see the GWP values for all time horizons.

Our TWP approach extends the standard GWP calculation in two ways: by combining the effects of CH_4 and CO_2 emissions from technology-fuel combinations and by considering streams of emissions in addition to single pulses. Considering streams of emissions is more reflective of real-world scenarios that involve activities that occur over multiyear time frames.

Eq. **2** is our extension of the GWP formula Eq. **1** to calculate TWPs, with the following definitions. We label as Technology-1 the alternative that combusts natural gas and has CO_2 emissions E_{1,CO_2} and CH_4 emissions from the production, processing, storage, delivery, and use of the fuel: E_{1,CH_4}. If L_{REF} is the percent of gross natural gas produced that is currently emitted to the atmosphere over the relevant fuel cycle (e.g., electric power or transportation), then Technology-1's CH_4 emissions at leakage rate L would be: $(L/L_{REF})E_{1,CH_4}$. The calculations of TWP in this paper assume that the leakage rate L is at the national average value L_{REF} (and thus $L/L_{REF} = 1$). The scaling factor L/L_{REF} is included to allow calculations about changes in the national leakage rate or about individual wells and distribution networks that deviate from the national average. The values we used for L_{REF} are derived in *SI Text* using EPA's estimated emissions with one exception and are equal to 2.1% for a natural gas power plant and 3.0% for CNG vehicles. The exception to the last statement is that we estimated CH_4 from the operation of a CNG automobile to be 20 times that from a gasoline vehicle (11), which is approximately 20% of the well-to-pump CH_4 leakage on a kg/mmBtu basis. This assumption deserves much further scrutiny. Technology-2 combusts gasoline, diesel fuel, or coal and produces CO_2 emissions E_{2,CO_2} and methane emissions E_{2,CH_4}. Estimates of the Es for each of the technologies considered are reported in Table 1 and are explained in *SI Text*. The TWPs at each point in time can be obtained by substituting the total radiative forcing values, $TRF_{CH_4}(t)$ and $TRF_{CO_2}(t)$ for CH_4 and CO_2, respectively, and emission factors, $E_{n,GHG}$ from Table 1 into Eq. **2**:

Table 1. Emission factors used for TWP calculations in this paper

	Power Plants		Vehicles			
	Natural gas combined cycle* (kg/MW*h*)	Supercritical pulverized coal† (kg/MW*h*)	Light-duty CNG car (kg/mmBtuHHV)‡	Light-duty gasoline car (kg/mmBtuHHV)	Heavy-duty CNG truck (mg/ton-mile)	Heavy-duty diesel truck (mg/ton-mile)
Upstream CH_4	3.1	0.65	0.51	0.1	590	100
Upstream CO_2	36	7	9.4	15.9	10,000	15,000
In-Use CH_4	0	0	0.11	0.0056	15	0
In-Use CO_2	361	807	53.1	70.3	80,000	85,000
Fuel cycle CH_4	3.1	0.65	0.62	0.11	605	100
Fuel cycle CO_2	397	814	62.5	86.2	90,000	100,000

*Heat rate = 6,798 Btu/kWh.
†Heat rate = 8,687 Btu/kWh.
‡1 mmBtu = 10^6 Btu = 1.055 GJ.

Table 3. Total radiative forcing (TRF) functions for CH_4 and CO_2 used in calculation of TWP in Eq. 2 for three distinct emissions profiles

Case	$TRF_{CH_4}(t)$	$TRF_{CO_2}(t)$
Pulse TWP	$RE\{\tau_M(1-e^{-t/\tau_M})\}$	$a_0 t + \sum_{i=1}^{3} a_i\tau_i(1-e^{-t/\tau_i})$
Service Life TWP for $t \leq$ AMAX	$RE\{\tau_M t - \tau_M^2(1-e^{-t/\tau_M})\}$	$a_0\frac{t^2}{2} + \sum_{i=1}^{3} a_i(\tau_i t - \tau_i^2(1-e^{-t/\tau_i}))$
Service Life TWP for $t >$ AMAX	$RE\{\tau_M AMAX - \tau_M^2 e^{-t/\tau_M}(e^{AMAX/\tau_M}-1)\}$	$a_0[AMAX\, t - \frac{AMAX^2}{2}] + \sum_{i=1}^{3} a_i(\tau_i AMAX - \tau_i^2 e^{-t/\tau_i}(e^{AMAX/\tau_i}-1))$
Fleet Conversion TWP	$RE\{\tau_M t - \tau_M^2(1-e^{-t/\tau_M})\}$	$a_0\frac{t^2}{2} + \sum_{i=1}^{3} a_i(\tau_i t - \tau_i^2(1-e^{-t/\tau_i}))$

RE in these formulas is the radiative efficiency of CH_4 relative to CO_2 and equals 102.

$$TWP(t) = \frac{\frac{L}{L_{REF}} E_{1,CH_4} TRF_{CH_4}(t) + E_{1,CO_2} TRF_{CO_2}(t)}{E_{2,CH_4} TRF_{CH_4}(t) + E_{2,CO_2} TRF_{CO_2}(t)}. \quad [2]$$

The TRF values needed for Eq. **2** are derived as follows. Let $f(t, t_E)$ be the mass of a gas left in the atmosphere at time t if 1 kg of the gas was emitted at time t_E. The cumulative radiative forcing function, CRF(t) (in units of J m^{-2} kg^{-1}), at a later time t, due to emission of 1 kg of the gas at time t_E, is then:

$$CRF(t) \equiv \int_{t_E}^{t} RE\, f(x, t_E)dx, \quad [3]$$

where RE is the radiative efficiency of the gas. The integral in Eq. **3** sums radiative forcing for the $t - t_E$ years from the year in which the gas was emitted, $x = t_E$, to year $x = t$. For simplicity, we adopt units which make the RE of CO_2 equal to one, and so the RE of CH_4 is expressed as a multiple of the RE of CO_2. In these units, the RE of CH_4 is determined to be 102, using the values in Table 2 taken from the IPCC (10) and following the IPCC convention that methane's direct radiative efficiency be enhanced by 25% and 15% to account for indirect forcing due to ozone and stratospheric water, respectively.

Now suppose that instead of a single pulse, the gas is emitted continuously at a rate of 1 kg/yr from $t = 0$ until some maximum time t_{max}, as would occur, for example, if emissions were to continue over the service life of a vehicle, power plant, or fleet. For such cases we define the total radiative forcing (TRF) in year t to be:

$$TRF(t) \equiv \int_{0}^{t_{max}} \int_{t_E}^{t} RE\, f(x, t_E)dx\, dt_E. \quad [4]$$

In the special case of a single emission pulse, $TRF(t) = CRF(t)$. Our use of Eq. **4** assumes a constant, unit emission rate; a more general formulation could be employed to reflect potential technology improvements over time.

For CH_4, $f(t, t_E)$ is an exponential decay:

$$f(t, t_E) = e^{-\frac{t-t_E}{\tau_M}}, \quad [5]$$

where τ_M is 12 yr. For CO_2, we follow the IPCC and use the Bern carbon cycle model (10):

$$f(t, t_E) = a_0 + \sum_{i=1}^{3} a_i e^{-\frac{t-t_E}{\tau_i}} \quad [6]$$

where $\tau_1 = 172.9$, $\tau_2 = 18.51$, $\tau_3 = 1.186$, $a_0 = 0.217$, $a_1 = 0.259$, $a_2 = 0.338$, and $a_3 = 0.186$. Our calculations do not consider the CO_2 produced from the oxidation of CH_4, an approximation which introduces a small underestimation of the radiative forcing from a fuel cycle's CH_4 leakage.

If calculating the TWP for a single pulse of emissions (pulse TWP), then $t_E = 0$; $TRF_{CH_4}(t)$ is given by Eq. **3** with $f(t, t_E)$ given by Eq. **5**; and $TRF_{CO_2}(t)$ is given by Eq. **3** with $f(t, t_E)$ given by Eq. **6**. If calculating the TWP for a permanent fuel conversion of a fleet (fleet conversion TWP) then $TRF_{CH_4}(t)$ is given by Eq. **4** with $t_{max} = t$ and $f(t, t_E)$ given by Eq. **5**. Similarly, $TRF_{CO_2}(t)$ is given by Eq. **4** with $t_{max} = t$ and $f(t, t_E)$ given by Eq. **6**. If calculating the TWP for emissions over the service life of a vehicle or power plant (service life TWP) and $t \leq$ AMAX, where AMAX is the average age at which the asset ceases to emit, then $TRF_{CH_4}(t)$ and $TRF_{CO_2}(t)$ are the same as in the fleet conversion TWP calculations. However, if $t >$ AMAX, then $TRF_{CH_4}(t)$ is given by Eq. **4** with $t_{max} =$ AMAX and $f(t, t_E)$ given by Eq. **5**. Similarly, $TRF_{CO_2}(t)$ is given by Eq. **4** with $t_{max} =$ AMAX and $f(t, t_E)$ given by Eq. **6**. The solutions for all of these cases are in Table 3. We use AMAX = 15 yr for vehicles and AMAX = 50 yr for power plants.

By rearranging terms in Eq. **2** when TWP = 1 to bring L to the left hand side, we obtain an equation for the relationship between the cross-over time (t^*—the time at which the two technologies have equal cumulative radiative forcing) and the percent leakage that makes this happen (L^*):

$$L^* = L_{REF}\left\{\frac{E_{2,CH_4}}{E_{1,CH_4}} + \frac{E_{2,CO_2} - E_{1,CO_2}}{E_{1,CH_4}} \frac{TRF_{CO_2}(t^*)}{TRF_{CH_4}(t^*)}\right\}. \quad [7]$$

Taking the limit of L^* as the cross-over time t^* goes to zero, we obtain an expression for the critical leakage rate L_0, which serves as an approximation of the leakage rate below which the natural gas-burning technology causes less radiative forcing on all time frames.

$$L_0 = L_{REF}\left\{\frac{E_{2,CH_4}}{E_{1,CH_4}} + \frac{E_{2,CO_2} - E_{1,CO_2}}{RE\ E_{1,CH_4}}\right\} \quad [8]$$

where RE = 102. Eq. **8** must be viewed as an approximation because L^* is a nonmonotonic function of t^* for small values of t^* (see Fig. 2, which plots L^* as a function of cross-over time t^*). The small decrease in L^* for small t^* is caused by the fact that 18.6% of the emitted CO_2 decays faster than CH_4 in the Bern carbon cycle model (time scales of 1.186 vs. 12 yr). The large increase in L^* for $t_* > 3$ years is caused by the rapid decay of CH_4 relative to the remaining 81.4% of the CO_2. The decay curves for CO_2 and CH_4 are shown in *SI Text*. Calculated values of L_o using Eq. **8** are within 2–3% of the absolute minima for L^*. Calculations of TWP and L^* using Eq. **2** and Eq. **8** were performed with an Excel spreadsheet and are available in Dataset S1.

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1. Howarth RW, Santoro R, Ingraffea A (2011) Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim Change* 106:679–690.
2. Venkatesh A, Jaramillo P, Griffin WM, Matthews HS (2011) Uncertainty in life-cycle greenhouse gas emissions from United States natural gas end-uses and its effect on policy. *Environ Sci Technol* 45:8181–8189.
3. Cathles LM, Brown L, Taam M, Hunter A (2012) A commentary on "The greenhouse-gas footprint of natural gas in shale formations" by R. W. Howarth, R. Santoro, and Anthony Ingraffea. *Clim Change*, 10.1007/s10584-011-0333-0.
4. Burnham A, et al. (2012) Life-cycle greenhouse gas emissions of shale gas, natural gas, coal and petroleum. *Environ Sci Technol* 46:619–627.
5. Wigley TML (2011) Coal to gas: The influence of methane leakage. *Clim Change* 108:601–608.
6. U.S. Environmental Protection Agency (2011) Inventory of US Greenhouse Gas Emissions and Sinks: 1990-2009 (EPA Publication 430-R-11-005).
7. U.S. Energy Information Administration (2011) *Annual Energy Outlook 2011*, (www.eia.gov/forecasts/aeo/).
8. Jaramillo P, Griffin WM, Matthews HS (2007) Comparative life-cycle air emissions of coal, domestic natural gas, LNG, and SNG for Electricity Generation. *Environ Sci Technol* 41:6290–6296.
9. Kirchgessner DA, Lott RA, Cowgill RM, Harrison MR, Shires TM (1997) Estimate of methane emissions from the U.S. natural gas industry. *Chemosphere* 35:1365–1390.
10. Forster P, et al. (2007) Changes in Atmospheric Constituents and in Radiative Forcing. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, eds S Solomon et al. (Cambridge Univ Press, New York), pp 210–214.

11. Lipman TE, Delucchi MA (2002) Emissions of nitrous oxide and methane from conventional and alternative fuel motor vehicles. *Clim Change* 53:477–516.
12. Victor DG (1992) Leaking methane from natural gas vehicles: implications for transportation policy in the greenhouse era. *Clim Change* 20:113–141.
13. Hayhoe K, Kheshgi HS, Jain AK, Wuebbles DJ (2002) Substitution of natural gas for coal: Climatic effects of utility sector emissions. *Clim Change* 54:107–139.
14. Xu Y (2011) Improvements in the operation of SO_2 scrubbers in China's coal power plants. *Environ Sci Technol* 45:380–385.
15. Lu Z, Zhang Q, Streets DG (2011) Sulfur dioxide and primary carbonaceous aerosol emissions in China and India, 1996-2010. *Atmos Chem Phys* 11:9839–9864.
16. Fuglestvedt J, Berntsen T, Myre G, Rypdal K, Skeie RB (2008) Climate forcing from the transport sectors. *Proc Natl Acad Sci USA* 105:454–458.
17. Skeie RB, et al. (2009) Global temperature change from the transport sectors: historical development and future scenarios. *Atmos Environ* 43:6260–6270.
18. Unger N, Shindell DT, Wang JS (2009) Climate forcing by the on-road transportation and power generation sectors. *Atmos Environ* 43:3077–3085.

FAQ About the University of Texas Methane Study

Frequently asked questions:

Why is the University of Texas (UT) study important?

Methane, the primary component of natural gas, is a powerful greenhouse gas — at least 84 times more potent than carbon dioxide over a 20-year time frame. The largest single source of U.S. methane emissions is the vast

network of infrastructure that supplies natural gas. These emissions, if not controlled, pose a significant risk to the climate. In the near term, the opportunity to maximize the lower carbon characteristics of natural gas compared to other fossil fuels rests on whether methane emissions are well understood and whether they can be sufficiently controlled.

This is important work and what seems like small changes in percentages can have a large impact. For example, EPA currently estimates methane escaping during development and delivery of natural gas to be 1.5 percent of total U.S. production, including associated gas from oil wells. Getting that number down to one percent — controlling just a third of the emissions — would have the same climate benefit over the next 20 years as retiring another 10 percent of U.S. coal generation. That's a big deal, and it's possible. A key takeaway of the UT study is that emission control technologies, such as so-called green completions (see below), are available and effective at reducing methane emissions.

How does the UT study advance what we know?

The UT study takes the first in a series of steps to gather the facts on methane emissions from the natural gas supply chain. It provides the most complete information in 20 years on methane emissions associated with unconventional natural gas extraction — specifically, some of the first ever direct measurements on shale gas wells that use hydraulic fracturing. Nine participating natural gas companies (Anadarko, BG Group, Chevron, Encana, Pioneer, Shell, Southwestern Energy, Talisman Energy and XTO Energy) provided access to their production equipment and facilities around the country, allowing UT to measure at the source of emissions.

Drilling practices have evolved rapidly in recent years, and a new set of EPA regulations governing air emissions from natural gas wells (known as New Source Performance Standards, or NSPS) is now coming into force. The intent of this study is to deepen our understanding of methane emissions associated with natural gas production employing the types of practices being used in the field today. Recently, there have been varying estimates on the rate of methane emissions from the natural gas system, with total emissions estimates for the supply chain (production, processing, distribution and delivery) ranging from 1% to 8%. These estimates have largely relied on data published in a 1996 EPA and Gas Research Institute methane report. While data on methane has improved over the last few years, UT's study presents the first scientifically reviewed dataset of methane emissions gathered directly at the source during some activities associated with hydraulically fractured wells.

What are the study's conclusions about methane emissions from natural gas production?

UT estimates the national methane leakage rate associated with the phase of natural gas extraction to be equivalent to 0.42% of total U.S. natural gas produced. This finding is in line with EPA's current emission inventory estimate for the production segment of the supply chain, though the study also found emissions from specific phases of production are likely to be higher or lower than EPA estimates. For example, emissions from well completions were lower than estimated in the EPA inventory, in large part because many of the wells studied used emission control technologies. Other sources UT studied turned out to be higher than EPA

estimates. This included emissions from pneumatics, equipment used to control routine operations at the well site, and equipment leaks. These findings point to activities where more can be done to contain overall production emissions. The study also found regional variations in the emission rates from pneumatic pumps and controllers — for example, emissions per pump in the Gulf Coast region were an order of magnitude higher than the Midcontinent region. Further study in the second phase of this project will focus on pneumatics and liquids unloading, in order to better determine the emissions profile of these specific components of the natural gas production sector.

What does the UT study tell us about EPA's NSPS regulations?

EPA's national emission standards that apply to new and refractured natural gas wells will take full effect in January 2015 and require use of Reduced Emissions Completions (RECs) practices, commonly known as green completions (an emissions control method that routes excess gas to sales). Since October 2012, operators are required under an early phase of EPA's NSPS to either flare (burn off) or capture these emissions with RECs. The majority of wells observed by UT used one of these capture and control methods. Eighteen wells used RECs or flares to reduce emissions during "flowback", the end of the hydraulic fracturing process when frac fluids and sands are drawn back up the well to make way for gas production. In the case of RECs, an approach some in industry claimed was not a viable option, this finding indicates the technology is available, it is effective and it is being implemented by some companies in the field. EPA was right to require green completions, and the agency's standards are beginning to achieve the desired effect.

As more producers move to comply with the EPA's REC requirements that go into effect in 2015, the study suggests, the greater use of RECs will reduce the emissions profile of the natural gas sector. No national survey of how many operators currently use RECs is available, but the data suggest that once this practice is required, emissions from this phase of the production process will decline, reflecting the well completion results seen in this study.

Overall, the story told by the well completions data is a positive one. It shows green completions are feasible and can effectively reduce emissions. The data provide a clear picture of what industry can achieve once this suite of technologies is universally deployed.

Do the UT results indicate no further regulation of the oil and gas industry is required?

No. Some emission sources in the UT study are shown to emit more methane than current EPA estimates and point to potential opportunities where EPA can strengthen NSPS and facilitate additional methane reductions. In the production sector this includes replacing higher emitting pneumatics with low-bleed devices (pressurized controllers used for routine functions at a well pad designed to emit the least methane); regularly inspecting for leaks at wellheads and other equipment used in production and quickly repairing those leaks; and using best available technologies and maintenance practices to minimize emissions from compressors and other equipment. For well completions, where regulations only apply to new hydraulically fractured wells, an

opportunity also exists to close the regulatory gaps to ensure producers control all well emissions, including those from oil wells and hybrid oil and gas wells.

Why do UT's production emissions estimates appear lower than those in the Howarth, et. al study?

Disparate research methods and underlying assumptions, in addition to geological differences, limit the ability to broadly compare one scientific study to another. One contrast likely to be made, but difficult to do, is between the new UT study (Allen et al.) and the April 2011 Howarth, et al. paper regarding methane emissions associated with U.S. natural gas production. Whereas the Allen, et al. paper includes new empirical data of actual methane emissions, the Howarth et al. study relies on pre-existing emissions estimates. Howarth et al. also uses different assumptions when calculating some emission sources. For well completions, for example, Howarth et al. assumed neither green completions nor flares were used to control emissions. While that may have been the case several years ago, it isn't the case now, as the evidence from the UT study suggests. Once EPA regulations are fully implemented, all new hydraulically fractured natural gas wells will be required to use green completion technologies. A similarity exists around equipment leaks and routine venting, in which, Howarth et al. assumes emissions are between 0.3% and 1.9% of production and the UT study supports the lower end of the range, suggesting the potential use of best available technology and practices at the well sites observed by UT.

How does UT's research method compare to the use of aircraft overflight measurements?

The two are different but complementary. On-the-ground data collection is essential to identifying the specific sources of emissions, but there is a limitation to bottom-up measurements in that it is difficult to canvas all potential sources of emissions at any particular site. This means some emissions can be missed. There are millions of potential methane emissions sources ranging from well pads to storage facilities to miles of pipelines across the country and it is not possible to measure every source using bottom-up techniques. Aircraft overflight readings are effective in measuring total methane fluxes in a given area, which promises the ability to capture methane emissions that an on-the-ground approach alone might miss, but this method also has its limitations. It is challenging to apportion overflight results between multiple sources (i.e. landfills, agriculture, oil and gas production, gathering systems, processing and pipelines). Together, these two methods can complement each other and provide greater insight and certainty than either method alone. EDF is working with a variety of academics and scientists to further explore how these two methods, deployed in concert, can further our understanding of the magnitude and sources of methane emissions across the natural gas supply chain.

What do the results suggest about the climate benefit of natural gas?

Whether natural gas can provide a climate benefit relative to other fossil fuels over the short to medium term depends on how much methane is lost, as gas moves from the well to our homes and businesses. Uncontrolled

venting and leaks across the natural gas supply chain can eliminate the potential climate benefits of substituting natural gas for coal or oil for some period of time. The UT study measured methane emissions for some key sources associated with the production of gas at the well pad, but not for the gathering, processing, storage, local delivery or transportation use of this fuel. Until emissions from the entire supply chain have been measured, no definitive conclusions can be drawn about the climate benefit of natural gas relative to other fossil fuels. We expect to be in a better position to answer this question when the entire scientific body of work that EDF and its partners have underway is finished — including studies that will go beyond the UT study to shed additional light on production sector emissions.

If forthcoming studies of other phases of the natural gas supply chain also bring results similar to EPA estimates, that would mean that the nation's methane leakage rate could amount to roughly 1.5% of total U.S. production, not including emissions from end uses including those in homes, businesses, and natural gas fueling stations and vehicles. According to a recent paper in the *Proceedings of the National Academy of Sciences*, a leak rate of 1.5% would mean that switching from coal to natural gas in the generation of electricity is immediately beneficial for the climate, but switching from diesel to natural gas fueled vehicles would produce climate damage for decades.
In the meantime, we know enough to say that methane emissions are an important issue worth the time and attention of government and industry. Methane emissions must be reduced wherever possible, as soon as possible. And while there are companies that are demonstrating practices can be improved, more needs to be done by all sectors of the industry to get this right. Given the dramatic impact methane emissions have on global warming in the near term, we can't afford to wait.

Does the UT study data impact EDF's target of minimizing methane emissions to 1% or less?

EDF's fundamental goal is reducing methane emissions system-wide to the lowest possible extent. In pursuit of this, our immediate objective is to reduce total methane emission to a rate of 1% or less of total U.S. natural gas production. This objective is based on a framework EDF and other scientists developed last year to begin to explain the climate impact of natural gas. One percent is a performance level, based on best available science that presents a critical threshold when fuel switching to natural gas from any other fossil fuels can be good for the climate across all points in time — a true win, not a mixed bag.

Does the UT study give a complete picture of methane emissions from the natural gas system?

No. Natural gas production is an important part of the natural gas system, but it is only one piece. The UT study was not intended to provide a complete picture of methane emissions from the supply chain or to be the definitive answer on production segment emissions. Rather it is intended to advance what is known about methane emissions from production and inform pre-existing estimates in this sector with hard data.

UT's study marks the first of sixteen methane studies in which EDF is participating, a groundbreaking series involving more than 90 partner universities, scientists, research facilities, and natural gas industry companies

that will quantify national methane leakage rates using diverse and scientifically rigorous methods. The effort is designed to better understand how much methane is released across the entire natural gas supply chain, as new technologies have unlocked a vast supply of U.S. natural gas. Together, these studies will provide a clearer national picture of methane emissions. The UT study is the first link in this chain. But science will continue to evolve, as it should, and this body of work needs to be furthered by others to ensure the U.S. and other countries get a handle on methane emissions.

How representative is the UT study data?

Nine natural gas companies, out of thousands of producers in the U.S., volunteered for this study. The UT study collected data that characterized the practices at particular sites operated by the participating companies, not industry at large. In 2011, the participants accounted for roughly 12% of all U.S. gas wells, 16% of gross gas production and almost half of all new well completions. In 2012, the 150 production sites UT visited include 478 wells, or about 0.1% of the national total of 446,745 gas wells. While this study reflects only a portion of what is happening in the field in 2012, in the absence of a statistically valid national survey, we are only able to use the data we collected as the basis to assess the national implications of the results. This is the way the 1990s EPA/GRI study presented its results, which served as the basis for much of EPA's current inventory. However, if the emissions profile of other producers or other regions differs significantly from the results of the UT study, then the national emission estimates in this study may change.

How do the study authors know that the nine companies are representative of all natural gas producers?

They don't. There are some 2,000 natural gas producers in the U.S., and incomplete data exist on how many of them are currently performing RECs, are using other activities designed to capture methane, or are employing leading operational practices.

How were the sites selected?

UT researchers identified production activities to be tested in various basins across the country. Participating companies gave access to their production operations based on the criteria given to them by UT, with particular attention to locations where well completions were scheduled to occur.

This study was conducted using standard scientific procedures for this kind of research and sites were selected as follows: For completions, the study team provided time windows when the measurement team would be available in certain regions and host companies identified completions that would begin as soon as possible after the study team arrived. Sites selected for unloading, workover and production site sampling were selected based on proximity to completion sampling. Typically, a list of candidate sites was provided by the host company. If the list was too long to be entirely sampled in the allotted time, the study team selected sites based on ability to sample as many as possible in the time available.

At the time field measurements took place, the market price for natural gas was low, which limited the number of new wells being completed. This suggests that operators had a fewer number of sites to make available; typically the study team would sample the only completion available during their field deployment in a region. However, participating companies have affirmed that all sites meeting study criteria were made available during the time UT conducted its field campaign.

Where were the measurements taken?

UT sampled 150 natural gas production sites with wells using hydraulic fracturing across the Gulf Coast, Mid-Continent, Rocky Mountain and Appalachian regions. Measurements were taken at well pads in gas producing basins around the country to ensure the results presented a good cross-section of what's happening in the U.S. Data is provided by regions, to show emissions at a regional and national scale.

Why not disclose emissions by company?

This study was not intended to provide a company-by-company inventory of total emissions. The purpose of this study was to improve our understanding of emissions from natural gas production in major natural gas producing regions around the country and to gather data that could be aggregated and analyzed on a regional or national scale. Even though emissions are not linked to the specific companies, all of the data collected are being released to the public, along with the study's methodology and results that were scientifically reviewed by independent experts prior to submission for publication and by reviewers selected by the *Proceedings of the National Academy of Sciences* as part of the process PNAS undertook to decide if the research warranted publication. These data provide benefit to the public, regulators, industry and the scientific community in that there is now, for the first time, publicly available data on directly measured emissions, in addition to formula-based estimates.

Were study participants involved in the preparation of the results?

No. The data was processed by the study team independent of the study participants. The study participants, however, were asked to review draft results, reports and communications materials and provided UT with comments. A Scientific Advisory Panel made up of six independent academic experts also reviewed the project plans before data collection began and preliminary findings during data collection. The Panel also reviewed the draft final report and co-authored the published manuscript. However, UT retained total control, and had ultimate authority, over the content of the PNAS paper, how the results would be reported, how to release the full dataset and communicate publically about the results.

When there was disagreement on how data should best be interpreted, it was noted in the study. For example, through discussions about the nine liquids unloading measurements it was determined that the data were insufficient to scale nationally, as described in the report. Open questions surrounding liquids unloading are largely why some participants agreed to a second phase of the UT study in order to transparently gather additional data to address areas of uncertainty.

Why was Dr. David Allen selected to lead this study?

Dr. Allen is a highly respected scientist in the field of air quality. Previously he was a lead investigator for one of the largest and most successful air quality studies: the Texas Air Quality Study. He was a long time member of the EPA's Science Advisory Board (SAB), on which he has served on since 2002 and has focused on issues of air quality modeling and cost-benefit analysis of the Clean Air Act. Since the start of the UT study, Dr. Allen has taken over the role of chair of the EPA's SAB.

How can we trust science funded in part by industry? How was rigor and scientific integrity assured?

One of the key elements of this study, and the rest of those supported by EDF, is an ability to verify its scientific integrity at every step of the process. Built into the research process of each industry sponsored study is an independent Scientific Advisory Panel. Scientific experts from academic and other institutions served as external advisors and reviewed the procedures, results and conclusions. These reviewers received standard government rate remuneration for their time. The study results and dataset then went through additional peer review as part of the evaluation by the external reviewers selected by the journal editor. The integrity of the UT study is reflected by acceptance for publication in the *Proceedings of National Academy of Sciences*, one of the nation's most prestigious scientific journals. Another critical aspect is that the data is being made public, allowing others to analyze it independently and critically examine the reported results.

Is this data more reliable than previous methane studies?

This study focused on making measurements of methane at the point of emissions. Recent attempts to estimate methane emissions from natural gas have been based on emission factors, which are estimates of the emissions coming from various types of equipment and processes rather than direct measurement. Data collected for the UT study were gathered at the site of production using multiple scientifically rigorous methods — independent measurements of methane emissions were made using different approaches and the results then compared. This inter-comparison using both bottom-up and top-down techniques provided strong evidence of the robustness of the data quality.

Will the participant companies take action on the higher emission source categories?

Only the individual companies can answer this question. But, based on some of the UT study findings, as well as what can be learned from other recent studies such as the one reporting high regional methane emissions in the Uintah Basin in Utah, there is more that can and should be done industry-wide to control emissions.

Why is EDF working with industry on these studies?

We know some don't like the idea of environmentalists working with industry to solve problems, but industry involvement and access to facilities is critical to advancing our understanding of the magnitude and source of emissions. This is because estimates of methane emissions from the natural gas supply chain have varied widely as a result of reports relying heavily on emissions factors derived from nearly 20 year-old data. Radical

changes in technology, such as the rapid rise of hydraulic fracturing combined with horizontal drilling, and industry practices have occurred since then — leaving a knowledge gap in what we know about from where and how much methane is lost today across the supply chain.

Industry also knows the natural gas system well, and their input in designing the protocols and scope of these studies have been invaluable to the researchers' ability to gather data accurately, effectively and safely.

EDF never accepts funding from energy companies or their corporate foundations. We never have and never will. What we require in exchange for our involvement in this collaborative research effort is the companies' steadfast commitment to terms that we can be collectively proud of: making all the results and data publicly available, peer-review throughout the study, release of the results through peer-reviewed publications, and control of the research by independent academic scientists.

Were there any production activities that the UT study did not measure?

Yes. No high-bleed pneumatics were observed at production sites UT sampled. These represent an additional source of production emissions; recent EPA data and a 2012 American Petroleum Institute and American Natural Gas Alliance report high-bleed pneumatics to account for 10% and 24%, respectively, of the total number of pneumatic devices used in the field.

While the study also includes some measurements of emissions from storage tanks at active production sites, these measurements did not capture all emissions and as a result, were not analyzed by UT.

Moreover, the study measured significant sources reported by EPA to represent roughly 55% of methane emissions in the production sector. However, the remaining portion, including sources such as dehydrator vents and engine exhaust were not measured. They were not prioritized since there are dozens of individual and relatively small sources comprising this 30% and because it is unclear if there are cost-effective avenues to reduce methane emissions.

Are there public health or local air quality implications of the emissions data that was collected?

The UT study did not include a health impacts assessment; the emissions measurements were not evaluated for purposes of assessing health and safety. The study quantified methane emissions rates from discrete sources at well sites. This study also did not assess the impacts of methane or other emissions on air quality. Methane is relatively slow to react in the atmosphere so its effects on air quality would occur on a large regional or global scale. Some papers have reported health benefits of global methane reductions due to resultant reductions in tropospheric ozone levels. The study did not quantify emissions of other constituents of natural gas, including hydrocarbons such as benzene and volatile organic compounds, which can contribute to more localized air

pollution. These, and other related air pollution issues associated with oil and gas production, deserve further study.

Why did the wells with no capture or control technology still have low emissions?

The nine wells surveyed that had no control technology were expected to have low initial gas production compared to the controlled wells. In other words, the wells with uncontrolled releases had much lower than average potential to emit. Uncontrolled well completions with higher potential to emit would be expected to have higher emissions.

Does this study show that EPA's estimates of completion emissions are flawed?

No. EPA's estimates predate the requirement that facilities perform green completions. Federal requirements didn't exist in 2011, the year of EPA's most recent estimates (released in 2013). The EPA's 2011 estimates only included emission reductions from green recompletions required by Colorado and Wyoming state regulations or voluntarily reported to EPA. EPA will revise future estimates to reflect green completions required by the NSPS.

That doesn't mean the work ends there. As industry evolves, so does the science and the need for policy reform. The study findings point to potential areas where additional mitigation strategies for equipment leaks or pneumatics could help reduce emissions.

What are the most important gaps in current regulation?

Considerable opportunities exist under the Clean Air Act to strengthen NSPS in order to further reduce methane emissions. Currently NSPS does not require emissions controls for equipment routinely found at oil and natural gas production sites, such as valves or connectors at the well pad or pressure relief valves on storage tanks. Nor are there federal requirements for the nearly half a million existing pneumatic devices at natural gas wells, controlling various mechanical operations, and for the thousands of existing compressors, pressurized motors used to move the gas from the wellhead through processing plants and pipelines before reaching end users. Similarly the NSPS do not contain requirements to reduce completion and production-related emissions from wells that produce both oil and natural gas (known as "co-producing wells."), which are becoming much more common as the price of oil remains high. Finally, robust leak detection and repair requirements are necessary to assure the equipment in the field is operated and maintained properly at all times. Many of the same cost-effective clean air measures that the NSPS deploys can be used to reduce emissions from these potentially significant sources. An additional opportunity for emissions reductions should be considered as further data unfolds around liquids unloading.

Which companies are involved in phase two and what does this project entail?

Anadarko, BG Group, Chevron, Conoco-Phillips, Encana, Pioneer, Shell, Southwestern Energy, Statoil and XTO Energy are all participating in the UT study phase two, already underway. The project is focused on collecting more data on methane emissions from liquids unloading and conducting further study of pneumatics devices in order to better explain regional variations in emissions rates observed by UT's initial work. This effort is expected to result in a paper submitted for scientific peer review in March 2014.

Why study pneumatics and liquids unloading further but not well completions?

Pneumatic controllers were the largest emission source observed in the first phase of UT's work and a better understanding of their emissions, particularly the regional variations, could lead to more effective mitigation options. Additionally, no high-bleed pneumatics were measured and more data is needed to accurately characterize emissions from pneumatics in the field. For liquids unloading, only nine measurements were made with large variability observed. EPA's estimates of liquids unloading have changed considerably over the last few years, pointing to the need for additional data to answer important questions about this potential emissions source. It is likely EPA and the UT study datasets for well completions will converge as EPA's NSPS requires broad adoption of green completions in January 2015.

Why is there so much disparity in published U.S. methane leakage rates?

Accurately calculating a methane leakage rate to explain total methane emissions is difficult because regional and site specific differences can be large. Things like the basin's geology (porosity and permeability of the rock), whether oil or gas dominates production and if the basin produces wet or dry gas, which is primarily made up of methane, whereas wet gas also includes ethane, butane, propane and pentane. Equipment and field performance, state regulation and other factors can play a role in the amount of methane leakage observed. Part of the confusion also stems from a lack of any standard set of metrics for what is being observed. For example, an oil basin with very little gas production could skew results if a methane leak rate was calculated, as typically done, by dividing the total methane emissions by the amount of gas produced. Such an approach could yield leakage rates in excess of 100% - a non-sensible scientific conclusion!

What can the data tell us about regional emissions?

The UT study observed regional differences for certain sources. For example, emissions from pneumatic controllers were lower in the Rockies than in the Appalachian, Gulf Coast or Mid-continent regions. Similarly, emissions from pneumatic pumps in the Gulf Coast were statistically higher than those in the Midcontinent. Regional differences were not as pronounced for equipment leaks. It is hard to characterize the causes of these differences without further study and a better understanding of regional variations in equipment and activities,

particularly those observed among liquids unloadings and pneumatics. Additional data is being collected as part of the second phase of the UT study to help answer these questions.

Does the UT study show methane is an urgent issue?

Absolutely yes. While this study shows lower than previously indicated emissions rates for certain production activities operated by some leading companies, there are other areas that were reported to be higher than EPA's current estimates. Without further improvements across the entire supply chain, natural gas will not be in a position to help the U.S. meet its climate goals.

Methane requires attention now.

For the natural gas industry, it's an issue to own in order to show it is serious about delivering on its environmental promises. Industry has unparalleled technological skill and can tackle big challenges — IF it's a priority. Better control of methane emissions improves operations, and in many cases delivers a financial payback.

For the climate, it's a make or break moment. This is because methane is much more potent than carbon dioxide — ounce for ounce methane is at least 84 times more powerful than CO2 over the first two decades after it is released. In other words, increasing methane emissions means higher temperatures, longer droughts and more extreme weather over the near to medium term.

Now it is critical for policymakers and industry to put the data collected to work. The additional data released over the next year will inform this important work, but we know enough to get started. There is no reason to wait.

Corrections

PERSPECTIVE

Correction for "Theory of mass-independent fractionation of isotopes, phase space accessibility, and a role of isotopic symmetry," by Rudolph A. Marcus, which appeared in issue 44, October 29, 2013, of *Proc Natl Acad Sci USA* (110:17703–17707; first published June 28, 2013; 10.1073/pnas.1213080110).

The author notes that, on page 1, middle column, lines 11–16 "Fewer accidental resonances mean less energy sharing and so less statistical behavior with a consequence that they are in equilibrium with the population of accessible states of O_3^* at low pressures, as discussed later." should instead appear as "Fewer accidental resonances mean less energy sharing and so less statistical behavior with a consequence of a shorter lifetime of O_3^* at low pressures, as discussed later."

On page 2, middle column, first full paragraph, lines 11–14 "This major difference in the pressure effect indicates a difference in the role of the collisions in these two distant phenomena." should instead appear as "This major difference in the pressure effect indicates a difference in the role of the collisions in these two distinct phenomena."

On page 3, middle column, first paragraph, lines 4–7 "The overall deviation from statistical theory for the recombination rate constant was (N. Ghaderi) perhaps a factor of 2." should instead appear as "The overall deviation from statistical theory for the recombination rate constant was (N. Ghaderi) less than a factor of 2."

On page 3, middle column, first full paragraph, lines 22–26 "Any chaos in the form of higher-order resonances within a volume element h^N would be coarse gained and so presumably contribute to quantum chaos." should instead appear as "Any chaos in the form of higher-order resonances within a volume element h^N would be coarse gained and so presumably not contribute to quantum chaos."

Both the online article and the print article have been corrected.

www.pnas.org/cgi/doi/10.1073/pnas.1315099110

ENVIRONMENTAL SCIENCES

Correction for "Measurements of methane emissions at natural gas production sites in the United States," by David T. Allen, Vincent M. Torres, James Thomas, David W. Sullivan, Matthew Harrison, Al Hendler, Scott C. Herndon, Charles E. Kolb, Matthew P. Fraser, A. Daniel Hill, Brian K. Lamb, Jennifer Miskimins, Robert F. Sawyer, and John H. Seinfeld, which appeared in issue 44, October 29, 2013, of *Proc Natl Acad Sci USA* (110:17768–17773; first published September 16, 2013; 10.1073/pnas.1304880110).

The authors note that upon publication their conflict of interest statement was not complete. The updated disclosure statement is as follows, "Jennifer Miskimins holds a joint appointment with Barree & Associates and the Colorado School of Mines. She has also served as an advisor to Nexen in 2012. David T. Allen served as a consultant for the Eastern Research Group and ExxonMobil in 2012, and is the current chair of the Science Advisory Board for the EPA. John H. Seinfeld has served as a consultant for Shell in 2012. David T. Allen, Matthew Harrison, Charles E. Kolb, and Robert F. Sawyer variously serve as members of scientific advisory panels for projects supported by Environmental Defense Fund and companies involved in the natural gas supply chain. These projects are led at Colorado State University (on natural gas gathering and processing), Washington State University (on local distribution of natural gas), and the University of West Virginia (on CNG fueling and use in heavy duty vehicles)."

Both the online article and print article have been corrected.

www.pnas.org/cgi/doi/10.1073/pnas.1318658110

Correction for "mitoBK$_{Ca}$ is encoded by the *Kcnma1* gene, and a splicing sequence defines its mitochondrial location," by Harpreet Singh, Rong Lu, Jean C. Bopassa, Andrea L. Meredith, Enrico Stefani, and Ligia Toro, which appeared in issue 26, June 25, 2013, of *Proc Natl Acad Sci USA* (110:10836–10841; first published June 10, 2013; 10.1073/pnas.1302028110).

PNAS notes that a conflict of interest statement was omitted during publication. PNAS declares that "The editor, Ramon Latorre, is a recent coauthor with the authors of this publication, having published a paper with them in 2012."

Additionally, the authors note:

"Although Figs. 1 and S1 display the same sequence template, the analyses of LC/MS/MS data were performed against the respective databases, rat for Fig. 1, and mouse for Fig. S1. Sequence alignment of rat (NCBI:Q62976.3; UniProtKB: Q62976-1 V.3, which differs by 3 amino acids near the N terminus with that of Figs. 1 and S1) and mouse (NCBI: NP_001240298.1) isoforms show 98.9% amino acid identity with differences circumscribed to the extreme N and C termini. Peptides identified by LC/MS/MS have the exact sequence in rat and mouse as shown in Figs.1 and S1."

"In published Fig. 7, panels *E* and *F* show slices of the same heart in each condition; to better display the infarcted vs. healthy portions, these images were scaled to approximately the same size. We noticed that some data points in panel *G* were slightly moved during figure preparation. The revised Fig. 7 now shows heart slices at their original magnification (*E* and *F*) and the correct panel *G*. The corrected figure and its legend appear below."

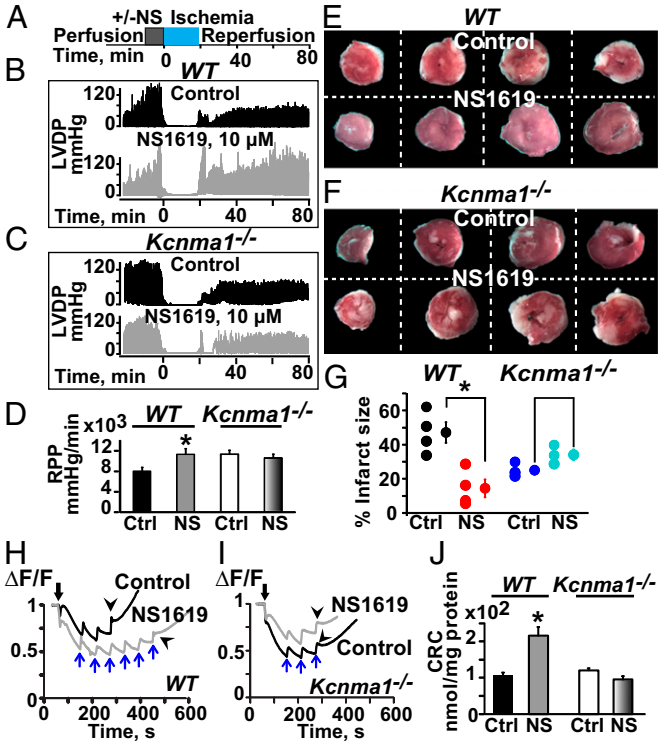

Fig. 7. BK$_{Ca}$ protects the heart from ischemic injury. (*A*) Ischemia/reperfusion protocol. (*B* and *C*) Function traces of hearts preconditioned with vehicle (DMSO, control) or with NS1619 (10 μM) in WT and *Kcnma1*$^{-/-}$ mice. (*D*) NS1619 significantly improved mean RPP in WT but not in *Kcnma1*$^{-/-}$ mice. (*E* and *G*) WT hearts preconditioned with NS1619 exhibited less infarct size (white) compared with the control. (*F* and *G*) In *Kcnma1*$^{-/-}$, infarct size was not reduced with NS1619. (*H–J*) Mitochondrial Ca^{2+} uptake. NS1619 preconditioning increased the amount of Ca^{2+} needed to induce a large Ca^{2+} release in WT but not in *Kcnma1*$^{-/-}$samples. Black arrows, addition of mitochondria. Blue arrows, 40 nmol Ca^{2+} pulses. Arrowheads, massive release of Ca^{2+}. *$P < 0.05$ vs. control (Ctrl); CRC, Ca^{2+} retention capacity.

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Measurements of methane emissions at natural gas production sites in the United States

David T. Allen[a,1], Vincent M. Torres[a], James Thomas[a], David W. Sullivan[a], Matthew Harrison[b], Al Hendler[b], Scott C. Herndon[c], Charles E. Kolb[c], Matthew P. Fraser[d], A. Daniel Hill[e], Brian K. Lamb[f], Jennifer Miskimins[g], Robert F. Sawyer[h], and John H. Seinfeld[i]

[a]Center for Energy and Environmental Resources, University of Texas, Austin, TX 78758; [b]URS Corporation, Austin, TX 78729; [c]Aerodyne Research, Inc., Billerica, MA 01821; [d]School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287; [e]Department of Petroleum Engineering, Texas A&M University, College Station, TX, 77843-3116; [f]Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164; [g]Department of Petroleum Engineering, Colorado School of Mines, Golden, CO 80401; [h]Department of Mechanical Engineering, University of California, Berkeley, CA 94720-1740; and [i]Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

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Engineering estimates of methane emissions from natural gas production have led to varied projections of national emissions. This work reports direct measurements of methane emissions at 190 onshore natural gas sites in the United States (150 production sites, 27 well completion flowbacks, 9 well unloadings, and 4 workovers). For well completion flowbacks, which clear fractured wells of liquid to allow gas production, methane emissions ranged from 0.01 Mg to 17 Mg (mean = 1.7 Mg; 95% confidence bounds of 0.67–3.3 Mg), compared with an average of 81 Mg per event in the 2011 EPA national emission inventory from April 2013. Emission factors for pneumatic pumps and controllers as well as equipment leaks were both comparable to and higher than estimates in the national inventory. Overall, if emission factors from this work for completion flowbacks, equipment leaks, and pneumatic pumps and controllers are assumed to be representative of national populations and are used to estimate national emissions, total annual emissions from these source categories are calculated to be 957 Gg of methane (with sampling and measurement uncertainties estimated at ±200 Gg). The estimate for comparable source categories in the EPA national inventory is ∼1,200 Gg. Additional measurements of unloadings and workovers are needed to produce national emission estimates for these source categories. The 957 Gg in emissions for completion flowbacks, pneumatics, and equipment leaks, coupled with EPA national inventory estimates for other categories, leads to an estimated 2,300 Gg of methane emissions from natural gas production (0.42% of gross gas production).

greenhouse gas emissions | hydraulic fracturing

Methane is the primary component of natural gas and is also a greenhouse gas (GHG). In the US national inventories of GHG emissions for 2011, released by the Environmental Protection Agency (EPA) in April 2013 (1), 2,545 Gg of CH_4 emissions have been attributed to natural gas production activities. These published estimates of CH_4 emissions from the US natural gas industry are primarily based on engineering estimates along with average emission factors developed in the early 1990s (2, 3). During the past two decades, however, natural gas production processes have changed significantly, so the emission factors from the 1990s may not reflect current practices. This work presents direct measurements of methane emissions from multiple sources at onshore natural gas production sites incorporating operational practices that have been adopted or become more prevalent since the 1990s.

Horizontal drilling and hydraulic fracturing are among the practices that have become more widely used over the past two decades. During hydraulic fracturing, materials that typically consist of water, sand and, additives, are injected at high pressure into low-permeability formations. The injection of the hydraulic fracturing fluids creates channels for flow in the formations (often shale formations), allowing methane and other hydrocarbon gases and liquids in the formation to migrate to the production well. The well and formation is partially cleared of liquids in a process referred to as a completion flowback, after which the well is placed into production. Production of natural gas from shale formations (shale gas) accounts for 30% of US natural gas production, and this percentage is projected to grow to more than 50% by 2040 (4).

Multiple analyses of the environmental implications of gas production using hydraulic fracturing have been performed, including assessments of water contamination (5–8), criteria air pollutant and air toxics releases (9–11), and greenhouse gas emissions (11–18). Greenhouse gas emission analyses have generally been based on either engineering estimates of emissions or measurements made 100 m to a kilometer downwind of the well site. This work reports direct on-site measurements of methane emissions from natural gas production in shale gas production regions.

Significance

This work reports direct measurements of methane emissions at 190 onshore natural gas sites in the United States. The measurements indicate that well completion emissions are lower than previously estimated; the data also show emissions from pneumatic controllers and equipment leaks are higher than Environmental Protection Agency (EPA) national emission projections. Estimates of total emissions are similar to the most recent EPA national inventory of methane emissions from natural gas production. These measurements will help inform policymakers, researchers, and industry, providing information about some of the sources of methane emissions from the production of natural gas, and will better inform and advance national and international scientific and policy discussions with respect to natural gas development and use.

Author contributions: D.T.A. and M.H. designed research; D.T.A., V.M.T., J.T., D.W.S., M.H., A.H., and S.C.H. performed research; C.E.K., M.P.F., A.D.H., B.K.L., J.M., R.F.S., and J.H.S. analyzed data; and D.T.A. wrote the paper.

Conflict of interest statement: J.M. holds a joint appointment with Barree & Associates and the Colorado School of Mines. She has also served as an advisor to Nexen in 2012. D.T.A. served as a consultant for the Eastern Research Group and ExxonMobil in 2012, and is the current chair of the Science Advisory Board for the EPA. J.H.S. has served as a consultant for Shell in 2012. D.T.A., M.H., C.E.K., and R.F.S. variously serve as members of scientific advisory panels for projects supported by Environmental Defense Fund and companies involved in the natural gas supply chain. These projects are led at Colorado State University (on natural gas gathering and processing), Washington State University (on local distribution of natural gas), and the University of West Virginia (on CNG fueling and use in heavy duty vehicles).

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[1]To whom correspondence should be addressed. E-mail: allen@che.utexas.edu.

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Methane emissions were measured directly at 190 natural gas production sites in the Gulf Coast, Midcontinent, Rocky Mountain, and Appalachian production regions of the United States. The sites included 150 production sites with 489 wells, all of which were hydraulically fractured. In addition to the 150 production sites, 27 well completion flowbacks, 9 well unloadings, and 4 well workovers were sampled; the sites were operated by nine different companies. The types of sources that were targeted for measurement account for approximately two-thirds of methane emissions from all onshore and offshore natural gas production, as estimated in the 2011 national greenhouse gas emission inventory (1). A summary of the scope of the study, along with a rationale for the inclusion or exclusion of sources for direct measurement efforts, is provided in *SI Appendix*. Sampling was conducted from May 2012 through December 2012 at sites throughout the United States (see *SI Appendix* for a map and for the number of sampling sites in each region). All nine companies that participated in the study provided sites for sampling, and at least three companies provided sites in each of the regions (*SI Appendix*).

The data presented in this report represent hundreds of measurements of methane emissions from several types of onshore natural gas production activities; however, the sites sampled still represent a small fraction of the total number of sites nationwide (Table 1). This dataset is designed to be representative of the participating companies' activities and practices, but not necessarily all activities and practices. Multiple methods were used to minimize the potential for bias in the sample set, as described in *SI Appendix*.

Results

Emission measurements were performed for 27 well completion flowbacks, 9 liquids unloadings, 4 well workovers, and 150 production sites with 489 hydraulically fractured wells (Table 1 and *SI Appendix*). Data are summarized here for the well completion flowbacks, liquids unloading, and production site emissions. *SI Appendix* provides additional details. The data on well workovers, collected for workovers without hydraulic fracturing, are not presented because the data set was small and emission estimates for workovers without fracturing represent less than 0.1% of national emission estimates.

Well Completion Flowbacks. After a well is drilled, the well is "completed." Completion is the process of making a well ready for continuous production. Specifically, after drilling and fracturing, before natural gas production can begin, the well must be cleaned of sand and liquid of various types that had been injected into the well. The recovery of these liquids is referred to as a flowback, and gas, including methane, can be dissolved or entrained in the flowback liquids. Some of the methane in the liquids can be sent to sales or emission control devices, but some can be emitted.

Measurements were made of methane emissions during 27 completion flowback events. Emissions data for each of the 27 events is provided in *SI Appendix*. Five of the flowbacks were in the Appalachian region, seven in the Gulf Coast region, five in the Midcontinent region, and 10 in the Rocky Mountain region. The durations of the completions ranged from 5 to 339 h (2 wk). Measured methane emissions over an entire completion flowback event ranged from less than 0.01 Mg to more than 17 Mg, with an average value of 1.7 Mg and a 95% confidence interval of 0.67–3.3 Mg. Measurement and sampling uncertainty are included in the confidence interval; uncertainties due to a limited sample size dominate the overall uncertainty estimate. Methods for determining the confidence intervals are described in *SI Appendix*.

The completions with the lowest emissions were those in which the flowback from the well was sent immediately, at the start of the completion, to a separator, and all of the gases from the separator were sent to sales. The only emissions from these completions were from methane dissolved in liquids (mostly water) sent from the separator to a vented tank. The completion flowback with the highest total emissions, 17 Mg, was the longest in duration (339 h) and had initial flowback into a vented tank with very high methane concentrations. Some of the other relatively high emission completion flowbacks (~3 Mg to 6 Mg of methane) involved large amounts of flared gas (up to 130 Mg of methane to the flare, which was assumed to combust the methane at 98% efficiency, *SI Appendix*). Another completion with emissions of 4 Mg of methane was one in which all gases, for the entire event, were vented to the atmosphere. This type of venting for the entire duration of the completion was observed in 9 of the 27 completions. However, the nine completions of this type showed a wide range of emissions (4 Mg of methane for one completion and 0.5 Mg of methane for another completion of this type for an adjacent well).

These data provide extensive measurements on methane emissions from well completions that can be used in national emission estimates. Current national inventories of methane emissions have been assembled, based on simple engineering models of the completion process. In the most recent EPA national greenhouse gas emission inventory (2011 inventory, released April 2013) (1), 8,077 well completions with hydraulic fracturing are estimated to result in 654 Gg per year of emissions, for an average of 81 Mg of methane per completion flowback (compared with 1.7 Mg per flowback for the events reported here). To understand the reasons for the much lower emissions per event reported in this work, it is useful to define a potential emission for each flowback. The potential of a flowback to emit is defined here, and in the EPA national inventory (1), as the methane that would be emitted if all of the methane leaving the wellhead during the flowback were vented to the atmosphere. Potential emissions for the wells in this work ranged from 0.2 Mg to more than 1 Gg methane, with an average of 124 Mg. The average from the EPA national inventory is slightly higher at 151 Mg. Net emissions are calculated, in the EPA national inventory, by reducing potential emissions by estimates of methane captured or controlled

Table 1. Comparison of sample set size to emission source populations

Source	No. of events/locations sampled	Total no. of events/locations
Well completions	27	8,077*
Gas well unloading	9	35,828†
Well workovers	4	1782 (11,663)‡
Wells	489	446,745§

*Completions, with hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1).
†Wells without plunger lift that have unloading events (the type of event sampled in this work) reported in the 2011 National GHG Emission Inventory (1).
‡Workover events with (and without) hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1).
§Gas wells with and without hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1); 513,000 on-shore natural gas wells are reported by the Energy Information Administration (20); see *SI Appendix*.

because of regulatory or voluntary emission reductions. In the current national inventory, emission reductions are roughly one-half of potential emissions (*SI Appendix*). In this work, net or measured emissions for the total of all 27 completions are 98% less than potential emissions. This large difference between the net emissions measured in this work and the net emissions estimated in the national inventory is due to several factors. First, consistent with emerging regulatory requirements (21) and improved operating practices, 67% of the wells sent methane to sales or control devices. Second, for those wells with methane capture or control, 99% of the potential emissions were captured or controlled. Finally, the wells with uncontrolled releases had much lower than average potential to emit. Of the nine wells in this work that had uncontrolled venting of methane, the average potential to emit was 0.83 Mg, which is 0.55% of the average potential to emit in the national inventory. The relative importance of these factors is discussed in *SI Appendix*.

Unloadings. Gas wells often produce liquid hydrocarbons and water along with natural gas. In most new wells, the velocity of natural gas up the production tubing of the well is sufficient to lift any produced water out of the well with the gas. As gas production declines, the velocity may no longer be sufficient to lift the liquids, which begin to accumulate in the wellbore and eventually restrict gas flow from the producing formation. Liquids accumulation therefore needs to be removed to allow the well to continue to produce gas at optimal rates.

There are multiple methods of unloading a gas well, some of which do not result in emissions. In this work, sampling was performed for unloadings in which an operator manually bypasses the well's separator. Unlike automated plunger lift methods, these manual unloading events could be scheduled, allowing the study team adequate time to install measurement equipment. As the flow to the separator, which typically operates at pressures of multiple atmospheres, is bypassed, flow is diverted to an atmospheric pressure tank. This diversion allows the well to flow to a lower pressure destination (the atmospheric pressure tank, rather than the pressurized separator). This lower pressure end point allows more gas to flow, increasing velocity in the production tubing and lifting the liquids out of the well. Gas is discharged from the tanks through the tank vent, unless the tanks have an emissions control system such as a combustor.

The nine unloading events reported in this work were varied in their characteristics. Methane emissions ranged from less than 0.02 Mg to 3.7 Mg. Some unloadings lasted 2 h (or more) and had relatively uninterrupted flow. Other unloadings were as short as 10–15 min with uninterrupted flow, and still others had intermittent flow for short periods and periods of no flow for much of the unloading period. Some of the wells sampled only unloaded once over the current life of the well, whereas others were unloaded monthly. The average emission per unloading event was 1.1 Mg of methane (95% confidence limits of 0.32–2.0 Mg). If the emissions per event for each well are multiplied by the event frequency (events per year) reported by the well operators, the average emission per well per year was 5.8 Mg (an average of 5.9 events per unloaded well per year). The sampled population reflected a wide range of emission rates, with a population of high emitting wells and a population of low emitting wells. When emissions are averaged per event, emissions from four of the nine events contribute more than 95% of the total emissions. *SI Appendix* provides more information about individual unloading events.

Because the characteristics of the unloading events sampled in this work are highly variable, and because the number of events sampled is small, extrapolating the results to larger populations should be done with caution. One source of data on larger populations of wells with unloadings, to which the population sampled in this work can be compared, is a survey reported by the American Petroleum Institute and America's Natural Gas Alliance (API/ANGA) (22). In this survey, more than 20 companies provided data and well characteristics for 40,000–60,000 wells (with the number in the sample depending on the type of emission event). These API/ANGA data were used by the EPA to arrive at 2011 national inventory emission estimates for 35,828 wells without plunger lift and 22,866 with plunger lift, which vent for unloading. Unloading emissions for the wells in the API/ANGA survey were estimated based on well characteristics such as well bore volume, well pressure, venting time, and gas production rate (3). For the unloading events without plunger lift, 100 of the 2,901 wells (3%) in the survey account for 50% of the estimated emissions. Ninety percent of the estimated emissions in the API/ANGA survey are due to one-half of the wells. Because a small population of wells (3%) accounts for one-half of the emissions, if this relatively small population of high emitting wells is not adequately sampled, it is not possible to accurately estimate national emissions. The wells sampled in this work unloaded relatively infrequently. In contrast, some wells in the API/ANGA survey, including some of the highest emitting wells, unload with a daily or weekly frequency. An average frequency of unloading for the wells in the API/ANGA survey is 32.57 events per year, compared with an average observed in this work of 5.9.

Because a small number of unloading events accounts for a large fraction of emissions in the API/ANGA survey (22), and because some of these wells had frequencies of unloading higher than any of the events observed in this work, the sample set of nine events reported in this work is not sufficient for accurately estimating emissions from unloading at a national scale. Nevertheless, the data reported here provide valuable insights for the design of future sampling campaigns.

One important result from the measurements reported here is that current EPA estimation methods overpredict measured emissions. If the emission estimation method (3) used in the API/ANGA survey is applied to the events sampled in this work, estimates are 5 times higher than measured emissions. Estimates of the emissions for the nine events are 5.2 Mg per event versus measured emissions of 1.1 Mg per event. Emissions were overestimated for every event. The percentage by which emissions are overestimated increases as emissions per event decrease (*SI Appendix*). Possible causes of the overestimate include the assumptions in the estimation method that the entire well bore volume is released in an unloading and that the gas flow during an unloading is continuous.

Overall, the implication of all of these issues is a large uncertainty bound in the national emissions from gas well unloading. If the per well annual emissions from this work are used, a national emission estimate based on counts of wells that undergo unloading is in reasonable agreement with emissions in the EPA national inventory (1). In contrast, another estimate of unloading emissions, based on the per event emissions observed in this work and an estimate of national unloading events (22), would lead to a national estimate five times the estimate based on well counts. This estimate is not supported by the available data, given that the national event count is dominated by high frequency unloading events and the wells observed here unloaded far less frequently with much higher emission estimates per event. A lower estimate of unloading emissions could be suggested based on national well counts, emission estimates, and the finding that emission estimation methods, used in many EPA inventory estimates, overestimate observations made in this work by a factor of 5. All of these methods, however, assume a single scalar value represents a wide range of unloadings; the data presented in this work and in the API/ANGA survey (22) suggest that refined emission estimation methods, taking into account well and unloading characteristics, will be required. Additional measurements of unloading emissions are needed, both to resolve the

Table 2. National emission estimates for the natural gas production sector, based on this work and the 2011 national inventory

Category	2011 EPA GHG inventory net emissions,* Gg of methane/yr	Emission estimates from this report,† Gg of methane/yr	Comments
Sources with emissions measurements from this work used to generate national emission estimates			
Completion flowbacks from wells with hydraulic fracturing	654*	18‡ (5–27)§	Decrease in national emission estimate
Chemical pumps	34*	68 (35–100)§	Increase in national emission estimate
Pneumatic controllers	355*	580‡ (518–826)§	Increase in national emission estimate; if national emission factors derived from this work are used, this estimate becomes 790 Gg (*SI Appendix*)
Equipment leaks	172–211*,¶	291‡ (186–396)§	Increase in national emission estimate; this comparison is based on equivalent categories of equipment, not all equipment leaks¶ (*SI Appendix*)
Subtotal, national emissions, estimated based on this work	1215–1254†#	957 ± 200 #	Decrease of ~250 Gg for national emission estimate
Sources with limited measurements; national emissions not estimated			
Unloadings (nonplunger lift)	149* (EPA inventory)		Highly diverse events; small data set collected in this work; preliminary national emission estimates have a broad range of values (25–206 Gg; see text)
Workovers (without hydraulic fracturing)	0.3* (EPA inventory)		Measurements in this work included only one recompletion and three swabbing events (see text)
Other sources, not measured in this work			
Unloadings (plunger lift)	108* (EPA inventory)		No measurements made in this work
Workovers (with hydraulic fracturing)	143* (EPA inventory)		No measurements made in this work; equipment configurations are similar to completion flowbacks for wells with hydraulic fracturing; if emissions per event are comparable to completion flowbacks, current inventories may overestimate emissions
Other sources, not measured in this work	891–930*,¶ (EPA inventory)		Includes potential emissions of sources not measured less prorated regulatory and voluntary emission reductions*
Total methane, Gg	2,545	2,300	Decrease of ~250 Gg for estimate
Methane emissions,*,** % [percent of gross gas production]	0.47% [0.59%]	0.42% [0.53%]	Brackets: gross gas emitted/gross gas produced (assuming produced gas is 78.8% methane)

*Emissions from EPA national inventory are based on reported potential emissions less reductions; when reductions are reported for combined source categories, identical percentage reductions of potential emissions are assumed to apply across source categories (*SI Appendix*, section S5).
†Emission factors used to estimate national inventories are designed to be representative of the participating companies' activities and practices, but not necessarily all activities and practices.
‡National emissions based on a regionally weighted average (*SI Appendix*, section S5).
§Ranges are based on 95% confidence bounds of emission factors; activity factors are identical to those used in EPA inventory. Uncertainties in activity factors (e.g., device counts) are not included. Uncertainties associated with whether regional or national averaging is performed are included in the uncertainty estimate (*SI Appendix*, section S5.4).
¶Sampling in this work included compressors on well sites, but not all gathering compressors. Well site and gathering compressors are combined in the national inventory. Range reported for national inventory for equipment leaks and "other" sources reflect uncertainty in attributing compressor emissions from national inventory to a specific source category.
#Uncertainty bound assumes uncertainties for completion flowbacks, pneumatic pumps and controllers and leaks are independent, and consequently, the combined uncertainty is the square root of the sum of the squares of the individual uncertainties.
**US total gross gas production (oil and coal bed, gas, and shale, onshore and offshore): 547,000 Gg.

differences between estimates and measurements and to better characterize the population of wells with unloading emissions.

Finally, it is also clear from the data that properly accounting for unloading emissions will be important in reconciling emission inventories with regional ambient measurements. Average methane emission rates for a single unloading ranged from roughly 100 g/min to in excess of 30,000 g/min. These rates are much larger than emission rates for production sites (typically tens of grams of methane per minute per well) or from completions (typically a few hundred grams per event per minute). At these emission rates, a single unloading event could, during the short period that it is occurring, result in emissions that are the equivalent of just a few wells in routine production to the equivalent of up to several thousand wells in routine production. Therefore, reconciliation between instantaneous ambient measurements and emission inventories will need to carefully represent the emissions from unloadings.

Well Sites in Routine Production. A well site contains one or more wellheads and may contain separators, pneumatic controllers, water tanks, hydrocarbon tanks (oil or condensate), and possibly other devices such as dehydrators, compressors, and flares. In this work, measurements were made from pneumatic controllers and pumps, because these devices release methane as part of their routine operation, and from equipment leaks detected by using an infrared camera (*SI Appendix*) at well sites.

Emissions for equipment on well sites, in routine production, that were targeted for measurements had much narrower uncertainty bounds than well completion flowbacks or well unloadings. Emissions from pneumatic chemical injection pumps measured in this work averaged 3.7 ± 1.6 g of methane per minute per pump, 9% lower than the EPA emission factor (*SI Appendix*, section S2). Intermittent and low bleed pneumatic devices measured in this work averaged 5.9 ± 2.4 and 1.7 ± 1.0 g

Table 3. Measurement methods used in the study

Source	Direct measurement methods	Mobile downwind sampling
Well completions	Measurements from flowback tanks made by using enclosures and temporary stacks with measurements of flow rate and composition	Downwind tracer ratio methods: Metered release of C_2H_2 and N_2O on site and downwind measurements of methane to C_2H_2 and methane to N_2O concentration ratios
Gas well unloading	Temporary stack with measurements of flow rate and composition	
Well workovers	Measurements from flowback tanks made by using enclosures and temporary stacks with measurements of flow rate and composition	
Production sites	Infrared (FLIR) camera surveys of sites and flow rate measurements using a HiFlow device	Metered release of C_2H_2 and N_2O on site and downwind measurements of methane to C_2H_2 and methane to N_2O concentration ratios

of natural gas per device per minute, 29% and 270% higher than EPA emission factors, respectively (*SI Appendix*, section S2). No high bleed pneumatic devices were identified at the sampling sites, and the average emission rate for the population of pneumatic controllers sampled in this work was 3.36 ± 0.65 g of methane per min (3.8 ± 0.69 g of natural gas per min). Equipment leaks measured in this work averaged 1.23 ± 0.44 g of methane per minute per well, which can be compared with an EPA estimate of potential emissions (no regulatory or voluntary emission reductions) of 1.37–1.67, derived from EPA's inventory for similar equipment types (wellheads, separators, heaters, meters/piping, and dehydrator fugitives), with the range reflecting whether small compressors are added to the comparison (*SI Appendix*, section S5). Comparing to net emissions is challenging because EPA does not assign emission reductions to specific equipment categories. Additional information is provided in *SI Appendix*.

There was significant geographical variability in the emissions rates from pneumatic pumps and controllers, but these regional differences were not as pronounced for equipment leaks. Emissions per pump from the Gulf Coast are statistically significantly different and roughly an order of magnitude higher than from pumps in the Midcontinent. Emissions per controller from the Gulf Coast are highest and are statistically significantly different from controller emissions in the Rocky Mountain and Appalachian regions. Emissions per controller in the Rocky Mountain region are lowest and an order of magnitude less than the national average (*SI Appendix*).

Implications for National Emission Estimates. If the average emissions reported in this work for well completion flowbacks, pneumatic devices, and equipment leaks are assumed to be representative of national populations and are applied to national counts of completions, pneumatic devices, and wells in EPA's national inventory, emissions from these source categories would be calculated as 957 Gg (with sampling and measurement uncertainties estimated at ±200 Gg), compared with 1,211–1,250 Gg methane per year in the 2011 EPA national inventory (1) for the same source categories. A large emissions decrease associated with completion flowbacks is partially offset by emission increases from pneumatic controllers and equipment leaks. Reasons for these differences are described in *SI Appendix*.

The estimated uncertainty in the national emission estimates based on this work is ~20% (200 Gg). The sources of uncertainty include measurement uncertainty, uncertainty introduced by the selection of sites, and uncertainty due to choices in performing regional or national averaging of equipment counts and emission factors. These components of the quantified uncertainty are described in *SI Appendix*. The uncertainty estimate does not include factors such as uncertainty in national counts of wells or equipment and the issue of whether the companies that provided sampling sites are representative of the national population.

The 957 ± 200 Gg in emissions for completion flowbacks, pneumatics, and equipment leaks, coupled with national inventory estimates for other categories, leads to an estimated 2,300 Gg of methane emissions from natural gas production (0.42% of gross gas production). A summary is provided in Table 2, and details of the calculations are available in *SI Appendix*.

Total emissions estimated based on measurements in this work (2,300 Gg) are comparable with the most recent EPA national GHG inventory (2,545 Gg in the 2011 inventory, released in April 2013) (1). Table 2 also compares emissions in specific source categories, estimated based on the measurements made in this work, to EPA estimates of the same categories in the national inventory (1). For some emission categories, such as completion flowbacks and pneumatic controllers, conclusions can be drawn from the comparisons. Specifically, measured emissions from completion flowbacks are roughly 600 Gg lower than the completion flowback emissions in the current inventory; measured emissions from pneumatic controllers are 150–500 Gg higher than in the current inventory. For other emission categories, such as equipment leaks and pneumatic pumps, however, drawing conclusions is more difficult. For these source categories, the national inventory reports potential emissions for each category, but aggregates emission reductions, creating uncertainty in the net emissions in these categories (see *SI Appendix*, section S5.5 for more details).

It should also be noted that the national inventory has changed in recent years based on evolving regulations (21) and understanding of emission sources. In this work, comparisons are made to the most recent release of the inventory (2011 final version, released in April 2013) and back casts to previous years by using consistent calculation methodologies. Emissions were estimated as 2,545 Gg in 2011, compared with 2,948 Gg in 2009 and 2,724 Gg in 2010. The work presented here suggests practices such as combusting or capturing emissions from completion flowbacks, as required by New Source Performance Standards subpart OOOO and the revised National Emission Standards for Hazardous Air Pollutants subpart HH (21), are resulting in reduced methane emissions. Other source categories require more data to produce national emission estimates, and adjustments in the inventory may emerge as more emission measurements are performed. Emission estimates may be adjusted downward if workovers with hydraulic fracturing are found to have emissions per event that are similar to completion flowbacks and may be adjusted either upward or downward as more emissions data are collected for liquids unloading or pneumatic devices.

Finally, an emissions intensity of 0.42% is reported in Table 2. The intensity expresses a methane emission per unit of gross gas production. This intensity should be interpreted with caution, because it includes only production operations and implicitly attributes all methane emissions from natural gas wells to natural gas production, although natural gas wells produce substantial amounts of natural gas liquids and oil. The intensity is reported here because it facilitates comparisons with other analyses that have appeared in the literature (23).

Methods

Multiple independent and complementary techniques were used to measure methane emissions. The primary procedures involved direct measurements of CH_4 emissions at their source. A variety of different procedures were used for direct source measurements, depending on the type of source being sampled and the type of natural gas production equipment being used. Table 3 summarizes the direct source methods used in the study; detailed descriptions of the methods are provided in *SI Appendix*.

In addition to direct source measurements, tracer ratio measurements, designed to estimate the total methane emissions from a site, were made at 20% of the well completion flowbacks and 13% of the production sites. The tracer release method was developed in the 1990s to quantify methane emissions from a wide range of natural gas system components (24, 25). Sites for tracer releases were selected for their steady, moderate winds and downwind access. Measurements for sites without downwind access could not be made. Table 3 also summarizes these measurement methods, which are described in detail in *SI Appendix*. In brief, tracer compounds were released at a known rate on-site; downwind measurements of methane (minus background) and the tracer (minus background) were assumed to be equal to the ratio of emission rates, allowing methane emissions to be estimated. These measurements were performed for a subset of the sampling locations that had relatively open terrain and steady winds, producing well-defined emission plumes downwind of the sites. The tracer studies allowed for an independent measurement of emissions that were also measured by using direct source methods. For completion flowbacks, emission estimates based on the downwind measurements were generally within a factor of 2 of the direct source measurements, supporting the conclusion that emissions from completion flowbacks are roughly 97% below the most recent national estimates and that emissions from completion flowbacks without methane control or recovery equipment, observed in this work, are well below the average potential emissions in current national inventories (1). For the production sites, emissions estimated based on the downwind measurements were also comparable to total on-site measurements; however, because the total on-site emissions were determined by using a combination of measurements and estimation methods, it is difficult to use downwind measurements to confirm the direct source measurements. Tracer study results are summarized in *SI Appendix*.

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1. US Environmental Protection Agency (EPA) (2013) *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2011* (Environ Protect Agency, Washington, DC). EPA 430-R-13-001.
2. Harrison MR, Shires, TM, Wessels JK, Cowgill RM (1996) *Methane Emissions from the Natural Gas Industry, Volumes 1–15,* Final Report. (Gas Res Inst and Environ Protec Agency, Washington, DC) GRI-94/0257 and EPA-600/R-96-080, Appendix B-1.
3. Code of Federal Regulations, Title 40 Section 98.233, Calculating GHG Emissions, 75 FR 74488, November 30, 2010, as amended at 76 FR 80575, December 23, 2011.
4. Energy Information Administration (2013) Annual energy outlook, early release. Available at www.eia.gov/forecasts/aeo/er/index.cfm. Accessed January 31, 2013.
5. U.S. Environmental Protection Agency (2011) Plan to study the potential impacts of hydraulic fracturing on drinking water resources (Environ Protect Agency, Washington, DC). Available at www2.epa.gov/hfstudy/plan-study-potential-impacts-hydraulic-fracturing-drinking-water-resources-epa600r-11122. Accessed August 27, 2013.
6. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108(20):8172–8176.
7. Vidic RD, Brantley SL, Vandenbossche JM, Yoxtheimer D, Abad JD (2013) Impact of shale gas development on regional water quality. *Science* 340(6134):1235009.
8. Rahm B, Riha S (2012) Toward strategic management of shale gas development: Regional, collective impacts on water resources. *Environ Sci Policy* 17:12–23.
9. McKenzie LM, Witter RZ, Newman LS, Adgate JL (2012) Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci Total Environ* 424:79–87.
10. Litovitz A, Curtright A, Abramzon S, Burger N, Samaras C (2013) Estimation of regional air quality damages from Marcellus Shale natural gas extraction in Pennsylvania. *Environ Res Lett* 8:014017.
11. Pacsi AP, Alhajeri NS, Zavala-Araiza D, Webster MD, Allen DT (2013) Regional air quality impacts of increased natural gas production and use in Texas. *Environ Sci Technol* 47(7):3521–3527.
12. Hayhoe K, Kheshgi HS, Jain AK, Wuebbles DJ (2002) Substitution of natural gas for coal: Climatic effects of utility sector emissions. *Clim Change* 54:107–139.
13. Lelieveld J, et al. (2005) Greenhouse gases: Low methane leakage from gas pipelines. *Nature* 434(7035):841–842.
14. Wigley TML (2011) Coal to gas: The influence of methane leakage. *Clim Change* 108: 601–608.
15. Howarth RW, Santoro R, Ingraffea A (2011) Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim Change* 106:679–690.
16. Kargbo DM, Wilhelm RG, Campbell DJ (2010) Natural gas plays in the Marcellus Shale: Challenges and potential opportunities. *Environ Sci Technol* 44(15):5679–5684.
17. Kerr RA (2010) Energy. Natural gas from shale bursts onto the scene. *Science* 328(5986):1624–1626.
18. Laurenzi IJ, Jersey GR (2013) Life cycle greenhouse gas emissions and freshwater consumption of Marcellus shale gas. *Environ Sci Technol* 47(9):4896–4903.
19. International Energy Agency (2012) Golden rules for a golden age of gas. Available at www.worldenergyoutlook.org/media/weowebsite/2012/goldenrules/WEO2012_GoldenRulesReport.pdf. Accessed August 15, 2012.
20. Energy Information Administration (2012) Summary statistics for natural gas in the United States, 2007-2011. Available at www.eia.gov/naturalgas/data.cfm#production. Accessed January 31, 2013.
21. Code of Federal Regulations 40, Part 60 Subpart OOOO and NESHAP 40, CFR 63 Subpart HH, 77 FR 49490, August 16, 2012.
22. American Petroleum Institute and America's Natural Gas Alliance (API/ANGA) (2012) Characterizing pivotal sources of methane emissions from natural gas production summary and analyses of API and ANGA survey responses, final report, updated September 2012. Available at www.api.org/news-and-media/news/newsitems/2012/oct-2012/~/media/Files/News/2012/12-October/API-ANGA-Survey-Report.pdf. Accessed February 28, 2013.
23. Alvarez RA, Pacala SW, Winebrake JJ, Chameides WL, Hamburg SP (2012) Greater focus needed on methane leakage from natural gas infrastructure. *Proc Natl Acad Sci USA* 109(17):6435–6440.
24. Lamb BK, et al. (1995) Development of atmospheric tracer methods to measure methane emissions from natural gas facilities and urban areas. *Environ Sci Technol* 29(6):1468–1479.
25. Shorter JH, et al. (1997) Collection of leakage statistics in the natural gas system by tracer methods. *Environ Sci Technol* 31:2012–2019.

Colorado State University Researchers Measuring Methane Emissions from Natural Gas Transmission

Bryan Willson, professor of mechanical engineering, Colorado State University.

Note to Reporters: A photo of Bryan Willson is available with this release at news@colostate.edu

FORT COLLINS - Colorado State University's Engines and Energy Conversion Lab is leading a nationwide field study to quantify methane emissions associated with the transmission and storage of natural gas through the nation's interstate natural gas pipeline system and storage facilities. This month, a team led by Bryan Willson, CSU mechanical engineering professor, and researcher Dan Zimmerle will begin collecting data from potential methane sources in natural gas transmission, including compressor stations and underground storage facilities.

"The primary component of natural gas, methane, is a greenhouse gas many times more potent than carbon dioxide when released into the atmosphere uncombusted," Willson said. "So, understanding how much methane leaks at various points along the supply chain, including the transmission and storage segment, is critical to discerning the potential of natural gas to offer climate benefits in various fuel-switching scenarios."

In the U.S. Greenhouse Gas Emissions Inventory Report, the Environmental Protection Agency estimates that the natural gas industry accounts for 25 percent of U.S. methane emissions, with transmission and storage accounting for 30 percent of this quantity (i.e., 7.5 percent of the U.S. total).

"This study will provide an additional, independent assessment for the transmission and storage sector that can be linked to other studies to allow an accurate, impartial, peer-reviewed and scientifically published estimate of leakage throughout the entire 'well-to-burner tip' supply chain," Willson said.

Results are expected to be released the first half of 2014 and will help better define a national methane emissions rate for U.S. transmission and storage systems. The CSU Engines and Energy Conversion Lab is one of the largest independent engine testing laboratories of its kind in the world. Carnegie Mellon University's Allen Robinson is leading the testing teams with URS and Aerodyne Research. Sponsors include Environmental Defense Fund, CenterPoint Energy Gas Transmission, Dow Chemical, Dominion, The Interstate Natural Gas Association of America, Kinder Morgan, TransCanada and Williams. The pipeline operators -- CenterPoint Energy Gas Transmission, Dominion, Kinder Morgan, TransCanada, and Williams -- are providing access to their gas facilities and equipment for tests in different regions throughout the country.

The CSU study is part of a two-year effort in which the Environmental Defense Fund and the natural gas industry are funding more independent academic research with a stated mission of more fully characterizing methane emissions from the production, transmission and storage, gathering and processing, local distribution, and end-use of natural gas.

To quantify how much methane is released into the atmosphere from transmission and storage facilities, the study will evaluate existing data and take additional measurements throughout the summer and fall of 2013.

Measurements taken by the research team will be primarily focused on compressor stations and underground storage facilities, and will consist of downwind tracer gas measurements paired with simultaneous source-by-source measurements.

Companies will also provide emissions and operating data from previous methane measurements. The total data set, including the measurements from the CSU team, will then be used in a model to estimate transmission and storage methane emissions in the United States.

A scientific advisory panel composed of professors and experts in the fields relevant to the study will serve as independent advisors reviewing the appropriateness of the methodologies, the model, statistical methods, and study results.

To see Bryan Willson's bio, go to www.eecl.colostate.edu/staff/Bryan_Willson

Colorado State University Researchers Measuring Methane Emissions from Natural Gas Gathering and Processing Facilities

Colorado State University Energy Institute researchers Daniel Zimmerle, left, and Anthony Marchese at a natural gas facility.

Note to Reporters: A photo of CSU researchers at a gathering and processing plant is available with this release at news.colostate.edu

FORT COLLINS - Colorado State University is leading a groundbreaking field study to quantify methane emissions associated with natural gas gathering and processing.

This month, a team led by Anthony Marchese, mechanical engineering professor and new director of the CSU Engines and Energy Conversion Laboratory, will begin collecting data from potential methane sources associated with natural gas midstream facilities, between the wellhead and long-distance transmission pipelines.

Methane is a potent greenhouse gas, and natural gas and petroleum systems are the largest single source of man-made methane emissions in the United States, according to the Environmental Protection Agency. This study will concentrate on the second stage in the natural gas supply chain – gathering and processing – where the gas is collected from the well, then compressed and processed to remove water, hydrogen sulfide, carbon dioxide and heavier hydrocarbons before entering the transmission system.

“Although some data exist on the larger processing plants, there is very little existing data on the methane emissions from other components of the gathering system,” Marchese said. “Our study will provide additional independent assessment of emissions from the gathering and processing sector of the on-shore natural gas industry, and our measurements will create the baseline for future studies.”

While larger gas processing facilities are required to report methane emissions to the EPA, Marchese said that the methods used in the CSU study are intended to help ensure that other midstream emissions sources are accounted for. The research team will be taking downwind tracer gas measurements to capture the total facility level methane emissions from each measured site. The results of this study will be linked to other studies already underway to allow an accurate, impartial, peer-reviewed and journal-published estimate of methane leakage throughout the entire natural gas supply chain.

“The companies participating in the study want to know where there are leaks in the system, because that’s where they are losing their product,” Marchese explained. “Understanding this creates opportunities for the companies to improve their environmental performance and ensures they are maximizing the economics of their activity.”
Carnegie Mellon University professor Allen Robinson will perform the tracer gas measurements along with Aerodyne Research. Over the next six months, measurements will be made at more than 100 different sites in 12 states.

Sponsors of the $1.9 million study include the Environmental Defense Fund (EDF); Access Midstream; Anadarko Petroleum Corp.; Hess Corp.; Southwestern Energy Co.; and Williams. Operators are providing access to their gas facilities and equipment for tests in different regions throughout the country. While not a financial sponsor, DCP Midstream is also allowing the study team access to its sites. Hess Corp. is participating only in the development of methodologies.
In addition, participating companies will provide emissions and operating data from previous methane measurements.

“It’s important that we have access not only to the gathering and processing sites, but to the operators’ records to determine the conditions of the facilities as we take our measurements and compare our findings to past results,” Marchese said.
The total data set, including the measurements from the CSU team, will then be used in a model to estimate methane emissions from the natural gas gathering and processing sector in the United States. Daniel Zimmerle, a senior researcher with CSU’s Energy Institute, will be leading the data analysis and modeling efforts.

“The diversity of the types of gathering and processing systems in the U.S. makes the modeling and scaling process extremely challenging,” Zimmerle said. “We are confident, though, that our data analysis approach will result in an accurate evaluation of methane emissions from this sector.”
A panel of professors and experts in the fields relevant to the study will serve as independent advisors reviewing the appropriateness of the methodologies, the model, statistical methods, and study results.

Results are expected to be submitted for publication in summer 2014 and will help better define a national methane emissions rate for the U.S. natural gas infrastructure.

The CSU study is part of a two-year comprehensive methane research effort involving more than 90 academic, research and industry partners organized by EDF. The stated mission of the large research effort is to collect and evaluate data to more fully characterize methane emissions across the natural gas supply chain.

This is the second methane emissions study undertaken by CSU this year. Researchers from the University’s Energy Institute, including Zimmerle and director Bryan Willson, are leading a study of methane emissions from natural gas transmission and storage facilities, also part of the multi-phase infrastructure study organized by EDF.
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AGU PUBLICATIONS

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Journal of Geophysical Research: Atmospheres

RESEARCH ARTICLE
10.1002/2013JD021272

Key Points:
- Emissions from an oil and gas basin are estimated using airborne measurements
- Inventories underestimate hydrocarbon emissions by a factor of 2 or more

Supporting Information:
- Readme
- Supplemental Text S1, Tables S1 and S2, and Figures S1–S5

Correspondence to:
G. Pétron,
Gabrielle.Petron@noaa.gov

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A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin

Gabrielle Pétron[1,2], Anna Karion[1,2], Colm Sweeney[1,2], Benjamin R. Miller[1,2], Stephen A. Montzka[2], Gregory J. Frost[1,2], Michael Trainer[2], Pieter Tans[2], Arlyn Andrews[2], Jonathan Kofler[1,2], Detlev Helmig[3], Douglas Guenther[1,2], Ed Dlugokencky[2], Patricia Lang[2], Tim Newberger[1,2], Sonja Wolter[1,2], Bradley Hall[2], Paul Novelli[2], Alan Brewer[2], Stephen Conley[4], Mike Hardesty[1], Robert Banta[2], Allen White[2], David Noone[1,5], Dan Wolfe[1], and Russ Schnell[2]

[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA, [2]NOAA Earth System Research Laboratory, Boulder, Colorado, USA, [3]Institute for Arctic and Alpine Research, University of Colorado Boulder, Boulder, Colorado, USA, [4]Department of Land, Air and Water Resources, University of California, Davis, California, USA, [5]Department of Atmospheric and Oceanic Sciences, University of Colorado Boulder, Boulder, Colorado, USA

Abstract Emissions of methane (CH_4) from oil and natural gas (O&G) operations in the most densely drilled area of the Denver-Julesburg Basin in Weld County located in northeastern Colorado are estimated for 2 days in May 2012 using aircraft-based CH_4 observations and planetary boundary layer height and ground-based wind profile measurements. Total top-down CH_4 emission estimates are 25.8 ± 8.4 and 26.2 ± 10.7 t CH_4/h for the 29 and 31 May flights, respectively. Using inventory data, we estimate the total emissions of CH_4 from non-O&G gas-related sources at 7.1 ± 1.7 and 6.3 ± 1.0 t CH_4/h for these 2 days. The difference in emissions is attributed to O&G sources in the study region, and their total emission is on average 19.3 ± 6.9 t/h, close to 3 times higher than an hourly emission estimate based on Environmental Protection Agency's Greenhouse Gas Reporting Program data for 2012. We derive top-down emissions estimates for propane, *n*-butane, *i*-pentane, *n*-pentane, and benzene from our total top-down CH_4 emission estimate and the relative hydrocarbon abundances in aircraft-based discrete air samples. Emissions for these five nonmethane hydrocarbons alone total 25.4 ± 8.2 t/h. Assuming that these emissions are solely originating from O&G-related activities in the study region, our results show that the state inventory for total volatile organic compounds emitted by O&G activities is at least a factor of 2 too low for May 2012. Our top-down emission estimate of benzene emissions from O&G operations is 173 ± 64 kg/h, or 7 times larger than in the state inventory.

1. Introduction

As a result of its unique geology, the state of Colorado has had a long history of natural resources extraction [*Scamehorn*, 2002]. More recently, Colorado has experienced an unconventional fossil fuel production boom in coal bed methane, tight sand and shale natural gas, shale oil, and associated gas. Tar sands and shale oil development could be next (http://ostseis.anl.gov/eis/index.cfm). The Denver-Julesburg (D-J) Basin in NE Colorado produces both oil and natural gas (O&G) from mostly tight sand and shale formations. The formation extends eastward from the Rocky Mountains to western Nebraska and Kansas and northward from Denver, Colorado, to southern Wyoming. It has been actively explored and drilled since the 1970s. The most densely drilled region of the D-J Basin is located in Weld County, between Denver and Greeley (Figure 1).

With higher natural gas prices between 2004 and 2009 and, more recently, the discovery of crude oil in the Niobrara Shale [*Colorado Department of Natural Resources*, 2011], Weld County has been experiencing a drilling surge, with the addition of close to 10,000 new wells since 2005 [*Colorado Oil and Gas Conservation Commission* (*COGCC*), 2014] (see supporting information Figure S1). In 2012, Weld County was home to 24,000 active oil and gas wells that accounted for 74% of the oil (5.8 million m3 out of 7.8 million m3 or 36.5 out of 49 million barrels) and 13% of the natural gas (7.7 billion m3 out of 59.5 billion m3 or 272 billion cubic feet out of 2.1 trillion cubic feet) produced in Colorado [*COGCC*, 2014]. Garfield County (19.8 billion m3 or 700 Bcf) in the Piceance Basin in western Colorado and La Plata (11.1 billion m3 or 393 Bcf) and Montezuma (10.5 billion m3 or 370 Bcf) Counties in the San Juan Basin in southwestern Colorado were the top three natural gas producers in 2012 [*COGCC*, 2014].

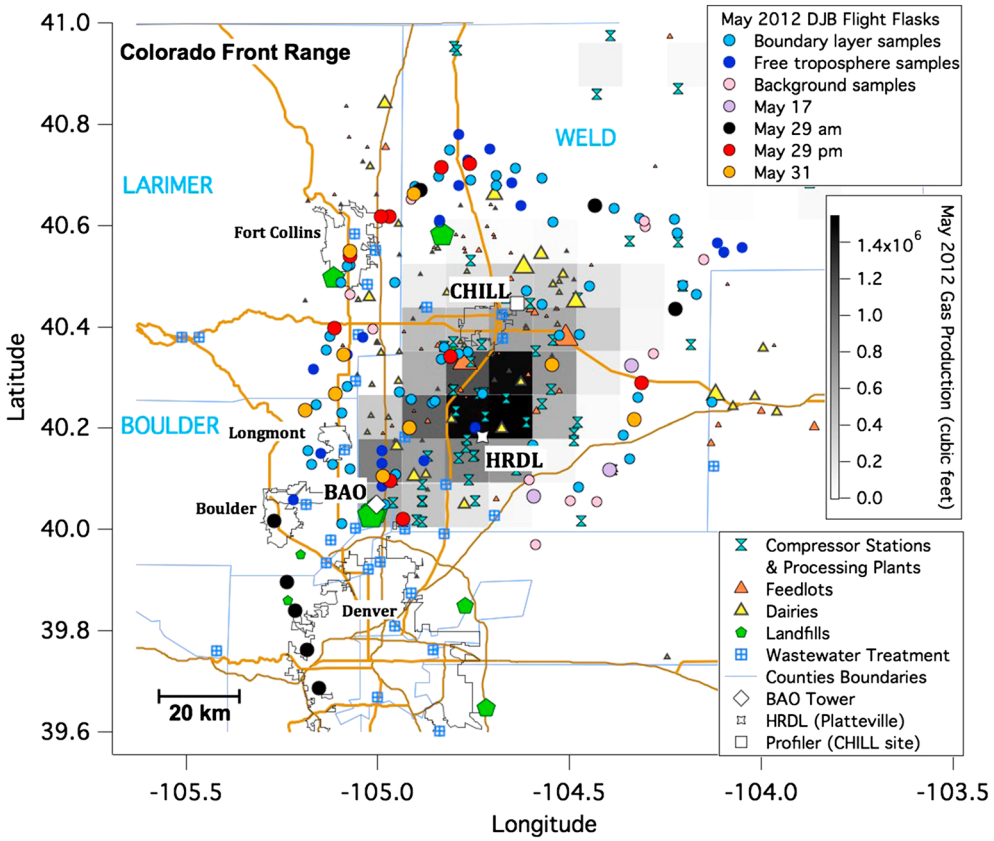

Figure 1. Map of Colorado's northern Front Range. Locations of ground-based meteorological measurements HRDL and CHILL and the BAO tower are shown in white symbols. The locations of the aircraft discrete air samples collected in May 2012 are shown with colored circles: light blue for boundary layer samples, dark blue for free troposphere samples, light pink for background samples, light purple, red, and orange for flights on three different days (17, 29, and 31 May 2012). Natural gas production in May 2012 (binned by township 6×6 km^2) is shown on a gray scale in the background. Compressor stations and processing plants are shown with blue hourglass symbols, feedlots with orange triangles, dairy farms with yellow triangles, landfills with green pentagons, and wastewater treatment plants with blue crossed squares. The size of the symbols for animal operations reflect their permitted capacity, and the size of the symbols for the landfills reflect the 2012 facility-level CH_4 emission estimates reported to the Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP).

In 2007, a large region encompassing the Denver metropolitan area and most of the northern Front Range of Colorado was officially declared a nonattainment area (NAA) for the national ambient air quality standard for 8 h average ground-level ozone (O_3) (www.colorado.gov/cdphe/attainment). The urban corridor in the Front Range lies between the Rocky Mountains and the D-J Basin's O&G operations. Under stagnant and hot summer conditions, O_3 precursors (volatile organic compounds (VOCs) and nitrogen oxides) emitted by various sources accumulate and react, leading to elevated O_3 levels. Previous analysis found that O&G operations were responsible for 40% of the total mass of anthropogenic VOCs emitted in the NAA [*Colorado Department of Public Health and the Environment* (*CDPHE*), 2008]. As a result, since 2007 the Colorado Department of Public Health and the Environment (CDPHE) has implemented stricter VOC emission regulations for O&G sources in the Colorado Front Range NAA.

Atmospheric chemical measurements conducted throughout the northern Colorado Front Range between 2007 and 2010 showed elevated levels of several hydrocarbons found in natural gas and oil, including CH_4 and other light alkanes (ethane (C_2H_6), propane (C_3H_8), *i*-butane (iC_4H_{10}), *n*-butane (nC_4H_{10}), *i*-pentane (iC_5H_{12}), and *n*-pentane (nC_5H_{12})), and sometimes aromatics including the carcinogen benzene (C_6H_6) [*Eisele et al.*, 2009; *Pétron et al.*, 2012; *Lafranchi et al.*, 2013]. These measurements showed similar relative enhancements of nonmethane hydrocarbons (NMHCs) as those observed in the early 1990s by *Goldan et al.* [1995] [see *Pétron et al.*, 2012].

In February 2011, *Gilman et al*. [2013] and *Swarthout et al*. [2013] participated in a 3 week intensive measurement campaign at the National Oceanic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory (BAO) tower, on the southwest edge of the D-J Basin. They measured an extensive suite of VOCs in situ and in flasks near the surface and confirmed the likely large role played by O&G operations emissions in the Front Range summertime O_3 problem. *Gilman et al*. [2013] showed that effluents from O&G operations in the region during the campaign contributed over half of the total VOC reactivity with OH, the first step in the chemical oxidation chain leading to near-surface O_3 formation.

Pétron et al. [2012] and *Swarthout et al*. [2013] both attempted to constrain emissions of CH_4 and several NMHCs from O&G operations in Weld County. *Pétron et al*. [2012] used hydrocarbon dry air mole fractions measured in air samples collected daily (between fall 2007 and April 2010) at midday from a 300 m agl (meters above ground level) inlet at the NOAA BAO tower and bottom-up information (raw natural gas mean composition and flashing (degassing) emissions from oil storage tanks estimates provided by the State). *Pétron et al*. [2012] estimated that in 2008 fugitive emissions of raw natural gas were underestimated by a factor of 2. The likely leakage range fell within 2.3% to 7.7% of production (average 4%), compared to an estimated 1.6% based on inventory data [*Bar-Ilan et al*., 2008; *Pétron et al*., 2012]. *Pétron et al*. [2012] estimated that CH_4 and C_3H_8 annual emissions from O&G operations in Weld County in 2008 likely ranged between 71 and 252 Gg/yr (8–29 t/h) and 21 and 65 Gg/yr (2.4–7.4 t/h), respectively.

Swarthout et al. [2013] calculated emission rates for several alkanes and C_6H_6 based on the increase in NMHCs mixing ratios in air samples collected from a 22 m agl inlet at the NOAA BAO tower site in the nocturnal boundary layer during five nights with low surface winds in February 2011, assuming no vertical mixing and no chemical destruction. They extrapolated their BAO flux results to the Wattenberg Field and to Weld County (two different but largely overlapping subregions of the D-J Basin that both lie within the Colorado Front Range NAA), assuming emissions were homogeneous in space and could be scaled with surface area. Their extrapolated C_3H_8 emission estimates were 13 ± 3 Gg/yr (1.5 ± 0.3 t/h) using the Wattenberg Field surface area and 40 ± 4 Gg/yr (4.6 ± 0.5 t/h) using the larger surface area of Weld County. February 2011 oil and natural gas production statistics for the Wattenberg Field were 19% and 7% lower than production statistics for Weld County, while the *Swarthout et al*. [2013] surface area-based emission estimates for these two regions differed by a factor of 3. It is important to note that large areas in Weld County have no oil and gas operations (Figure 1), so it is not appropriate to simply scale the BAO results with surface area.

The emission estimates reported in *Pétron et al*. [2012] and *Swarthout et al*. [2013] relied in part on simple emission models with unverifiable assumptions [*Levi*, 2012; *Pétron et al*., 2013] and, in the case of *Swarthout et al*. [2013], on measurements with likely limited spatial representativeness. In this paper, we present results from an alternative top-down approach to estimate the total emissions of CH_4 and five NMHCs in Weld County on 2 days in May 2012.

The rest of the paper is organized as follows. In section 2 we describe the study region and the measurements during the intensive airborne campaign. Top-down regional emission estimates for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are presented in section 3. In section 4, we compare these results with inventories. In section 5, we conclude with a summary of the measurement-based results and their significance.

2. Experiment

2.1. Region of Study

The D-J Basin is a prolific fossil fuel reserve, with a stack of multiple sedimentary rocks in the form of sandstone and shale deposited in the Western Interior Basin of North America during the Cretaceous and now buried thousands of feet below the surface. Several of these rock formations contained deposits rich in marine organic matter [*Sonnenberg*, 2012]. The organic matter trapped in buried rocks underwent thermogenic decomposition in the deeper part close to the north/south axis of the D-J Basin and biogenic decomposition in some of the shallower parts on the eastern flank [*Fishman et al*., 2005; *Higley and Cox*, 2007; *Sonnenberg*, 2012].

Our study focuses on a 70 km × 85 km region in northeastern Colorado encompassing the highest density of the O&G production activities in the D-J Basin, mostly located in Weld County, north of Denver and east of Boulder and Larimer Counties (Figure 1). Most wells in the region produce what is referred to as wet or

associated gas, which means natural gas coproduced with oil. Oil wells contribute close to 50% of the total natural gas produced in the region [*Pétron et al*., 2013]. In addition to over 24,000 producing wells in 2012, Weld County was also home to more than 6000 oil or liquid condensate storage tanks (the vast majority located on well pads), 27 gathering compressor stations, 11 processing plants (CDPHE, personal communication, 2013), and over 1000 miles of natural gas transmission pipelines.

Every year, between several hundred and a few thousand new wells are drilled and completed (with hydraulic fracturing) in Weld County [*COGCC*, 2014]. Existing wells are sometimes refractured to target new natural gas and oil-bearing formations or to restimulate production from previously targeted zones. The American Petroleum Institute reports that the D-J Basin has the highest refracturing rate in the nation, 14%, versus 1% for the national average [*API/ANGA*, 2012].

Over 100 different oil- and gas-producing companies operate in the D-J Basin. A team of nine O&G inspectors at CDPHE is in charge of checking compliance for O&G permitted facilities. They typically inspect a subset of operations from larger companies every 3 years on average and from smaller companies every 5 years on average (CDPHE, personal communication, 2013).

There are other CH_4 sources in the region. Beef and dairy production is a major economic activity in Weld County, with over half a million head of cattle [*USDA*, 2012]. Enteric fermentation in ruminants and manure management facilities are known sources of CH_4 [*Johnson and Johnson*, 1995; *U.S. Environmental Protection Agency* (*EPA*), 2013a]. CH_4 is also emitted from a few large landfills and several wastewater treatment plants servicing the over 2 million people living in the northern Colorado Front Range.

2.2. Methods

The ground and airborne-based measurements conducted in the D-J Basin in May 2012 were similar to those carried out in the Uinta Basin of northeastern Utah in February 2012 and described in *Karion et al*. [2013]. Airborne measurements of CH_4 with a Cavity Ring Down Spectroscopic gas analyzer (Picarro Model # G2401-m) were conducted on 11 different days (12 flights) between 4 and 31 May 2012. Each flight lasted between 3 and 4 h. In-flight measurement repeatability of the CH_4 dry air mole fraction was ± 0.5 ppb (defined as the standard deviation of measurements of a standard gas at the measurement frequency of ~0.5 Hz), and total uncertainty of the measurements was ± 2 ppb (see section S1 in Text S1). The single-engine Mooney TLS aircraft was stationed at Boulder Municipal Airport, located in the southwest corner of the study region, which was the starting and ending point of each flight. A total of 118 discrete air samples (up to 12 on each individual flight) were collected on those flights and analyzed at the National Oceanic and Atmospheric Administration Earth System Research Laboratory Global Monitoring Division (NOAA ESRL GMD) in Boulder for 49 trace gases, including carbon monoxide (CO) and the following seven hydrocarbons: CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6H_6, and acetylene (C_2H_2).

In May 2012, NOAA ESRL also deployed a boundary layer wind profiler and a high-resolution Doppler lidar (HRDL) at two different locations in the basin; both provided vertically resolved measurements of horizontal wind speed and direction and boundary layer height at 20 to 30 min resolution [*Grund et al*., 2001]. Meteorological measurements (surface temperature and turbulent heat flux) conducted by the University of Colorado near the NOAA BAO tower outside Erie, Colorado, were used to assess the surface energy budget and the resulting vertical mixing within the planetary boundary layer (PBL) on the 2 days retained for a mass-balance flux calculation. All measurements are described in further detail in Text S1.

To put the intensive aircraft campaign results into a broader context, we compare the airborne flask measurements with long-term measurements of flask air samples collected daily from the 300 m agl inlet of the NOAA BAO tower since fall 2007. To filter the BAO data by wind sector, we use 30 s wind speed and direction measurements collected by the NOAA ESRL Physical Sciences Division at the tower 300 m agl level (www.esrl.noaa.gov/psd/technology/bao).

The aircraft and BAO discrete air samples discussed here were all analyzed by NOAA ESRL GMD for CH_4 using a gas chromatography GC-flame ionization detector [*Dlugokencky et al*., 1997], for CO using resonance fluorescence at ~150 nm with a repeatability of ± 0.4 ppb [*Novelli et al*., 1998] and for 43 other compounds including the six nonmethane hydrocarbons mentioned above using a GC-mass spectrometry (MS) [*Montzka et al*., 1993; *Pétron et al*., 2012; *Lafranchi et al*., 2013]. The GMD analyses of NMHCs in aircraft and BAO samples are reported on the same calibration scale: C_6H_6 on NOAA-2006 and all other hydrocarbons (besides CH_4) on

NOAA-2008. See also section S2 in Text S1 for more information on the NOAA CH_4 calibration scale and results from a NMHC interlaboratory measurement comparison, which GMD participated in.

3. Results and Discussion

3.1. Total CH_4 Emission Mass-Balance Estimates

In the mass-balance approach used here, airborne measurements of CH_4 dry air mole fraction (moles of CH_4 per mole of dry air) are combined with ground-based wind speed and direction measurements to estimate total CH_4 mass fluxes in and out of a region of the atmosphere surrounding O&G producing wells in the D-J Basin (Figure 1). The resulting top-down CH_4 flux reflects an aggregate emission from all CH_4 sources within the region for several hours on the days of the measurements (see section S6 in Text S1 for more details). Given the short transit time between the emission sources and our measurements ($<$ 0.5 day) and a global CH_4 lifetime close to 9 years, atmospheric chemical losses of CH_4 are insignificant and are not considered here. In the rest of this section, we describe the main atmospheric measurements used to derive the total top-down CH_4 flux estimates on 29 and 31 May 2012.

A first estimate of CH_4 emissions from the D-J Basin is made using two separate downwind transects at two different altitudes 150 m apart on 29 May (Figure 2, Table S1, and section S6 in Text S1). On that day the average winds in the planetary boundary layer (PBL) are from the SE at 3.7 ± 0.9 m/s, and the downwind transects on the western side of the region show a 90 km long CH_4 plume with enhancements spanning 10 to 35 ppb over background (1881 ± 4 ppb). The highest enhancements in CH_4 ($>$20 ppb above background) occur downwind of the most active oil and natural gas production area in the basin (centered around Platteville, Colorado; Figure 1). The top of the PBL during the downwind transect on 29 May is located at 3600 m above sea level (m asl, ~2100 ± 230 m agl).

On 31 May, the airplane first sampled clockwise the outer perimeter of the part of the O&G basin with the densest distribution of wells and then conducted transects in the middle of the region (Figure 3). The upwind CH_4 level in the PBL on that day is 1870 ± 4 ppb (Figure 3c). CH_4 enhancements measured in the downwind plume range from 10 to 100 ppb above the upwind background level (Figure 3c). Winds in the PBL on 31 May are from the NE as indicated by the 6 h back trajectory of the air mass derived from the HRDL wind measurements, averaged with height within the PBL (black line and diamonds, Figure 3a). On that day, the average wind speed in the PBL during the 6 h prior to the downwind plume measurement is 3.1 ± 1.1 m/s.

The top of the convective boundary layer during the downwind transect on 31 May is located at 3000 m asl (~1500 ± 230 m agl), as defined by the altitude of the sharp gradient in both the trace gas mole fractions and potential temperature measured during an aircraft vertical profiling spiral from 19:15 to 19:39 GMT on the western (downwind) side of the D-J Basin, north of Longmont, Colorado (Figure 3b). Variability in the CH_4 mole fraction visible in this downwind vertical profile is caused by horizontal variability in CH_4 mole fraction from local sources over the 4–6 km wide spiral that the aircraft conducted as it performed a vertical profile (Figure S3).

The total CH_4 emission for the area encircled by each flight is estimated using the mass-balance approach and the chemical and physical measurements described above and in Text S1. The mass-balance calculation yields 25.8 ± 8.4 t h^{-1} on 29 May (this value represents an average of the two downwind flight segments at two aircraft altitudes) and 26.2 ± 10.7 t h^{-1} on 31 May (Table 1). We have propagated the measured variability of the various parameters in the mass-balance equation to quantify the 1σ uncertainty on the total CH_4 emissions estimate on each day (section 6 in Text S1 and Tables S1 and S2). Because the estimates on these two different days are independent, the 1σ uncertainty on the average top-down CH_4 flux (26.0 t/h) for the 2 days is 6.8 t h^{-1}, or close to 26% of the total flux, which is lower than the uncertainties of 33–41% derived on each day.

3.2. CH_4 Source Attribution

The top-down CH_4 fluxes derived above encompass all CH_4 sources in the area located between the downwind and upwind transects for each flight. We do not have enough information to quantitatively partition the emissions between the various CH_4 sources based on the airborne measurements alone. Here we estimate CH_4 emissions from agricultural operations, landfills, and wastewater treatment plants located within our mass-balance region based on available bottom-up information. We use emission factors from the

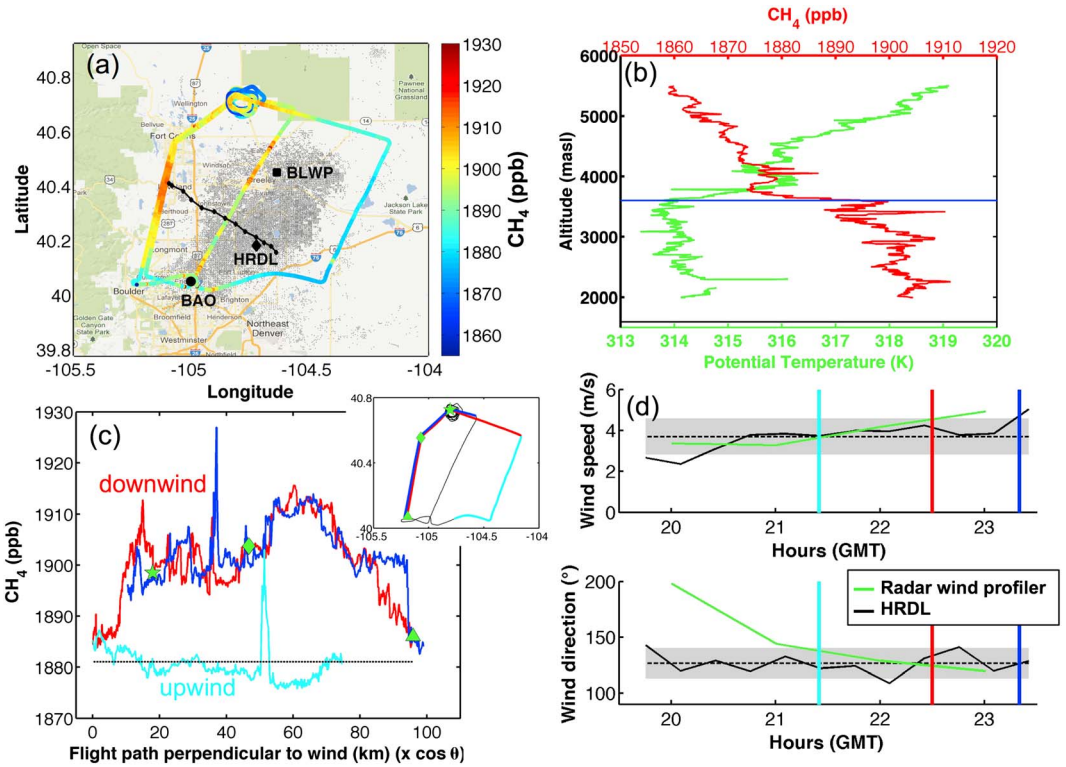

Figure 2. Measurements used on 29 May 2012 CH_4 flux calculation. (a) Map of flight track color-coded with CH_4 mole fraction, 4 h back trajectory of the downwind air mass (from HRDL winds, black line and dots), and the locations of oil and gas wells (gray dots). (b) Vertical profiles of CH_4 mole fraction (red, top axis) and potential temperature (green, bottom axis) measured during a spiral at the northernmost point of the flight track, during the red-colored downwind segment (indicated by green star in inset of Figure 2c); blue line indicates the top of the planetary boundary layer (PBL), and the black line at the bottom shows the mean ground level for the region. (c) CH_4 mole fraction as a function of distance along the flight track perpendicular to the mean wind direction. The average upwind mole fraction (1881 ± 4 ppb CH_4, black dashed line) derived from the upwind measurements (light blue line) is subtracted from the two downwind segments (dark blue, flown at ~2000 m asl (~400 m agl), and red, before they are integrated along the flight path perpendicular to the wind direction; the downwind segments were flown at ~2150 m asl (~550 m agl)) along the western and northern sides of the flight track; the upwind measurements (light blue) were made in the southeast and eastern portions of the track (inset) at 2000 m asl (400–600 m agl depending on ground elevation). A narrow large CH_4 plume was sampled in the upwind leg, most likely from a local point source given its narrow width. Green symbols in the figure correspond to locations indicated with same symbols in inset map. (d) Wind (top) speed and (bottom) direction from HRDL, averaged through the PBL (black, with dashed line indicating the average used in the calculation and gray bar indicating the uncertainty derived in section S6 in Text S1); green line indicates the same measurement from the radar wind profiler near Greeley. Light blue, red, and dark blue vertical lines indicate the average times of the upwind and two downwind legs, corresponding to the same colors in Figure 2c. Local (daylight savings) time was GMT 6 h.

literature, activity or inventory data compiled by the state of Colorado, and annual facility-level emission estimates reported to the Environmental Protection Agency (EPA) Greenhouse Gas Reporting Program (GHGRP) for 2012 [*EPA*, 2013b].

Cattle feeding and dairy and egg production are major economic activities in the NE Front Range. Enteric fermentation in ruminants is the largest agricultural source of CH_4 in the region. Our study region encompasses more than 100 animal feeding and dairy permitted operations in Weld County, 11 operations in Larimer County, and 2 small operations in Boulder County. We derive CH_4 emission estimates for these operations using 2012 cattle head count statistics provided by the state of Colorado [*NASS*, 2014] and the 2007 Agricultural Census statistics for sheep and poultry [*USDA*, 2012]. More than 97% and 100% of beef and dairy permitted capacities in Weld County are within the study region, respectively, and so we choose to round the percent number for beef cattle up to 100% and use total beef and dairy head counts in Weld County. For Larimer County, 5.5% and 52% of beef and dairy permitted capacities are within the study region. These fractions are used to prorate the total Larimer County cattle statistics.

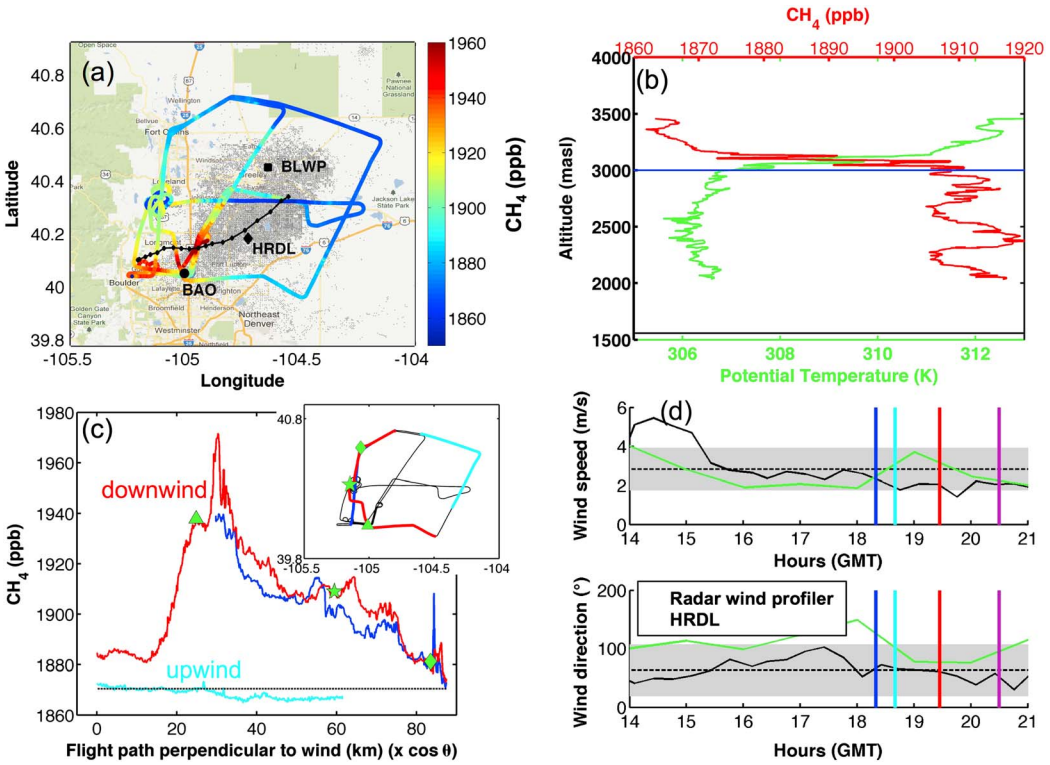

Figure 3. Same as Figure 2 but for measurements used in 31 May 2012 CH_4 flux calculation. (c) One downwind segment (red, flown at 2020 m asl (~500 m agl)) was integrated for the flux calculation after the background mole fraction (1870 ± 4 ppb CH_4, black dashed line) was subtracted. The upwind measurements (light blue), sampled in the northeastern portion of the track (inset) at 2000 m asl (~400 magl), were used to define the background condition for the flux calculation. The dark blue line shows the mole fraction along the earlier downwind segment at the same altitude that captured only part of the plume. (d) The purple line indicates the average time of a second descending profile, shown in Figure S4.

In 2012, according to the state of Colorado Agricultural Statistics, Weld (Larimer) County was home to 50,000 (12,000) beef cows and 70,000 (12,000) dairy cows, and the total number of cattle and calves was 565,000 (51,000). Between 2008 and 2013, the interannual variability in these statistics is ≤12%. We assume that a total of 51,000 beef cows and 76,000 dairy cows were in our study region in May 2012.

We assume that 80% of the beef cows in Weld and Larimer Counties had calved by the time we conducted our campaign in May [*EPA*, 2014, Table A-179, Annex 3], and we use the US national statistics on cattle population [*EPA*, 2014, Table A-178, Annex 3] to derive head counts for calves and replacement heifers in dairy farms. We use the ratios of bulls to cows reported for Colorado in 2012 (5.6%) and the total number of cows in

Table 1. CH_4 Emission Estimates for Weld County for 29 and 31 May 2012

CH_4 Emissions (t/h)		29 May[a]	31 May	Average[b]
Total measurement-based estimates		25.8 ± 8.4 (33%)	26.2 ± 10.7 (41%)	26.0 ± 6.8 (26%)
Non-O&G sources—inventory-based	Animals	3.9 ± 0.7	3.9 ± 0.7	
estimates (see text and Tables 2 and 3 for details)	Animals waste	0.7 ± 0.2	0.7 ± 0.2	
	Landfills	1.5 ± 1.5	0.7 ± 0.7	
	Municipal wastewater plants	0.5 ± 0.15	0.5 ± 0.15	
	Industrial wastewater plant	0.5 ± 0.15	0.5 ± 0.15	
	Total nonoil and gas sources	7.1 ± 1.7	6.3 ± 1.0	
Remaining balance: O&G sources		18.7 ± 8.6	19.9 ± 10.7	19.3 ± 6.9

[a]The value from 29 May is the average of calculations from two separate downwind legs.
[b]The variance of the average flux is calculated as the sum of the individual day variances divided by 4.

Table 2. Bottom-Up Information and CH_4 Emission Estimates (t/h) From Livestock Operations, Enteric Fermentation in Ruminants (E1), and Manure Management (E2 and E3) in the Region Encompassed by the 29 and 31 May 2012 Flights[a]

Source	Enteric Fermentation					Manure			
Livestock	Head Count[b] (×1000)	EF1[c]	SD[c]	E1 (t/h)	SD[d]	EF2[e]	E2 (t/h)	EF3[f]	E3 (t/h)
Cattle in feedlots	308	4.3	1.4	1.32	0.51	0.23	0.07	0.97	0.30
Beef cows	51	7.8	1.6	0.40	0.11	0.23	0.01	0.97	0.05
Beef cows calves	41	1.0	0.2	0.04	0.01	0.23	0.01	0.97	0.04
Beef stockers	10	5.7	1.2	0.06	0.02	0.23	<0.01	0.97	0.01
Beef heifers	10	7.1	1.4	0.07	0.02	0.23	<0.01	0.97	0.01
Bulls	7	10.0	2.0	0.07	0.02	0.23	<0.01	0.97	<0.01
Dairy cows	76	18.3	3.7	1.39	0.36	6.16	0.47	2.74	0.21
Dairy cows calves	38	3.2	0.7	0.12	0.03	0.23	0.01	1.76	0.07
Replacement heifers 7–11 months	11	5.6	1.1	0.06	0.02	0.23	<0.01	1.76	0.02
Replacement heifers 12–23 months	27	7.9	1.6	0.21	0.06	0.23	<0.01	1.76	0.04
Sheep	200	0.9[e]	0.2	0.18	0.05	0.003	<0.01	0.066	0.01
Poultry (mostly egg layers)	3,000	na	na	-	-	0.014	0.04	0.025	0.08
Total	-	-	-	3.9	0.7	-	0.6	-	0.8

[a]Units for the emissions factors EF1, EF2, and EF3 are g/head/h (10^6 g = 1 t). The derivation of the head count for each animal category is provided in the main text.
[b]Estimated based on 2012 Colorado Agricultural Statistics for county-level total numbers of beef cows, dairy cows, and other cattle and calves, rounded 2007 Agricultural Census statistics for poultry and sheep totals and calves production and cattle replacement statistics from US EPA 2013.
[c]Cattle emission factors (EF1) based on *Johnson and Johnson* [1995, Table 2]. Standard deviation (SD) on EF1 is set to 20% except for feedlot cattle including stockers, where it is 33%.
[d]The emission estimate standard deviation takes into account the prescribed standard deviation of emission factor EF1 and 20% uncertainty in head count for each animal category.
[e]Source for EF2 emission factors used to derive emission estimates E2 [*IPCC*, 2000].
[f]Source for EF3 emission factors used to derive emission estimates E3 [*CDPHE*, 2002].

our study region to estimate the total number of bulls (~7000). We use these estimates and the constraint on the total cattle head counts to estimate the total number of feedlot cattle in the study region at 308,000 head.

These figures for total beef and dairy cattle agree to within 10% with the total permitted capacity for dairy cattle (167,000 heads) and beef cattle (405,000 heads in large feedlots with > 1000 heads each; and 6000 heads in <1000-head operations) in the study region (CDPHE, personal communication). We assume a 20% uncertainty on the total head count for all animal categories and a 20% uncertainty on the emission factors for all categories except for feedlot cattle (33%) (see details in Table 2).

For each animal category, we use an average emission factor from *Johnson and Johnson* [1995], which is still one of the most exhaustive references for US cattle. The emission factors we use are similar to values reported or used in more recent publications on North American cattle (see *EPA* [2013a, Table A-182], *Stackhouse et al.* [2011], *Kebreab et al.* [2008], and *Westberg et al.* [2001], for example). The total bottom-up emission estimate from enteric fermentation in cattle in Weld County in May 2012 amounts to an average of 3.8 ± 0.7 t/h (Table 2).

Another source of agricultural CH_4 from animal husbandry comes from animal manure disposal systems. Emissions from livestock manure depend in large part on how animal solid waste is managed [*Lodman et al.*, 1993; *Steed and Hashimoto*, 1994]. Dry aerobic management systems result in lower conversion of organic matter in the manure to CH_4, while the diversion of waste with water into anaerobic lagoons can result in very efficient conversion to CH_4 [*EPA*, 1999, 2009]. In Colorado's arid climate, animals are kept in dry lots for many feedlot and dairy operations [*Sharvelle and Loetscher*, 2011] and manure is removed mechanically and composted nearby.

EPA [2013a] uses a detailed emission model to derive CH_4 manure emissions for US operations, which we cannot downscale as we do not have detailed information on waste management practices for the facilities in the region of interest. Instead, we use emission factors from two reports, *IPCC* [2000] and *CDPHE* [2002]. The two reports have very different emission factors for dairy farms and beef operations (EF2 and EF3 in Table 2), and the final total CH_4 emissions for all animal operations are 0.6 and 0.8 t/h, respectively. It is possible that *CDPHE* [2002] emission factors reflect Colorado's practices better. In Colorado, a small percentage of total dairy farm waste is managed with anaerobic lagoons, a more common practice in the US Midwest. *EPA*

Table 3. Hourly CH_4 Emission Estimates for the Five Major Landfills Operating in the Region Encompassed by the Flights Based on Annual Estimates Reported for 2012 [*EPA*, 2013b]

Facility	Latitude	Longitude	2012 Emissions (t/h)
North Weld Sanitary Landfill	40.585°	−104.826°	0.50
Central Weld Sanitary Landfill (closed)	40.349°	−104.806°	0.16
Denver Regional Landfill (closed) [a]	40.022°	−105.028°	0.51[b]
Denver Regional North Landfill (closed)[a]	40.031°	−105.032°	0.02[b]
Front Range Landfill	40.022°	−105.009°	0.25[b]
Total Upwind on 29 May 2012			1.44
Total Upwind on 31 May 2012			0.66

[a]These two closed (no longer in operation) landfills have recovery systems.
[b]The last three landfills were beyond the downwind transect for the 31 May flight.

[2013a] reports a 2σ relative uncertainty of −18% to +20% on manure management CH_4 emissions from all cattle in the US inventory for 2011. We assume that the uncertainty is larger at the regional scale than for the national scale. We use the average of the two inventory-based estimates (0.7 t/h) with a 1σ uncertainty 0.2 t/h.

The flux region encompassed by the 29 May 2012 flight has two active landfills and three closed landfills, two of which have a CH_4 recovery system (see Figure 1 and Table 3). Only the two landfills in the northern half of Weld County are within the flux region of the 31 May flight: the three southernmost landfills are south (downwind) of the flight "downwind" transects. Based on annual facility-level emissions reported to the EPA GHGRP for 2012 [*EPA*, 2013b], we calculate hourly average emission estimates for these five landfills (Table 3) and assume that these emission magnitudes are representative of both days in May 2012. The bottom-up estimates for CH_4 emissions from landfills total 1.7 t/h on 29 May and 0.7 t/h on 31 May. There are no uncertainty estimates reported in the EPA GHGRP, but field measurements around landfills have shown how emission rates depend on the soil microclimate and surface meteorological conditions including surface pressure [*Czepiel et al*., 1996; *Mosher et al*., 1999; *Czepiel et al*., 2003; *Bogner et al*., 2011]. For landfill emissions of CH_4 in the national inventory, EPA reports a 2σ relative uncertainty of −54% to +46% [*EPA*, 2013a]. Much of this uncertainty is due to the lack of measurements to assess the efficiency of installed methane recovery and/or flaring systems. Given the lack of validation for this estimate, a 1σ uncertainty of 100% for both days is used in our analysis.

Another smaller source of CH_4 in the region is from anaerobic digestion of sludge by bacteria at municipal and industrial wastewater treatment facilities. There are 11 municipal facilities in the region sampled by the May 2012 flights: 5 in Larimer County (out of 6), 5 in Weld County (out of 9), and 1 in Boulder County (in Longmont). To estimate the CH_4 emissions from these facilities, we use the projected state-level estimate for 2010 (3.59 t/h) derived by *Strait et al*. [2007] and scale it by the fraction of the state population residing in Weld County, Larimer County and the city of Longmont, which is 12.7% in 2010. We then use the relative increase in population from 2010 to 2012 (4%) to scale the 2010 estimate and obtain an estimate for total CH_4 emissions in 2012 for these 11 facilities of 0.47 t/h. The methodology followed by *Strait et al*. [2007] is based on the EPA State GHG Inventory Tool, which is very similar to the method used by EPA for the national-level greenhouse gas (GHG) inventory [*EPA*, 2013a]. There is also a large industrial wastewater facility associated with the JBS Swift slaughterhouse in Greeley. The facility processes close to 400 head of cattle into beef per hour, and its reported CH_4 emissions from its wastewater treatment in 2011 equal 0.47 t/h [*EPA*, 2013b]. The industrial wastewater plant did not report emissions to the GHGRP for 2012 even though it was still in operation; therefore, we use the reported emissions for 2011 assuming operations did not change. The 2σ uncertainty reported by *EPA* [2013a] for national CH_4 emissions from wastewater treatment facilities ranges between −29% and +28%. We use 29% as the 1σ relative uncertainty (or 0.14 t/h) in the regional scale emission estimates for both municipal and industrial wastewater plants.

A few additional processes in the region contribute a small amount to the total CH_4 flux. Based on flux measurements in the D-J Basin reported by *Klusman and Jakel* [1998], we calculate that the natural flux of CH_4 from natural microseepage in the region likely amounts to less than 0.1 t/h. The Fort St. Vrain 969-MW natural-gas-fired power plant near Platteville was found by our airborne measurements to have no detectable CH_4 emissions. Two aircraft transects passing ~2 km to the west of the power plant on 31 May

2012 include distinct CO_2 plumes (not shown) downwind of the power plant with no coincident detectable CH_4 enhancements. Abandoned coal mines are another possible source of CH_4 in the area. Over 200 small coal mines were exploited in the Front Range in the Boulder-Weld coal field in an arc extending from Marshall south of Boulder toward Frederick north of Denver [*Roberts et al.*, 2001]. Coal mines in this area have been closed since at least 1978 and, unlike those in the Piceance Basin in Western Colorado, are not categorized by the EPA as being in a gassy coal basin [*EPA*, 2004]. Some of our flight transects through the region sampled downwind of some of these mines locations, and our in situ CH_4 analyzer did not detect any noticeable CH_4 enhancement. We surmise that emissions from these mines are likely to be insignificant, because they are covered mines and have not been previously noted as major sources. They are not included in our analysis.

The total bottom-up hourly average CH_4 flux for non-O&G sources in the study region is estimated to be 7.1 ± 1.7 t CH_4/h on 29 May and 6.3 ± 1.0 t CH_4/h on 31 May (Table 1). The uncertainties on the non-O&G emission estimates are added in quadrature to obtain the 1σ uncertainty for the total non-O&G emissions. When we subtract these fluxes from the top-down estimates of the total CH_4 flux in the region on 29 and 31 May 2012, we are left with an average flux of 19.3 ± 6.9 t CH_4/h (1σ uncertainty) attributable to O&G operations, or 75% of the total top-down regional CH_4 emission estimate (Table 1).

3.3. Light Alkanes and Benzene Correlations

Dry air mole fractions for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6H_6, C_2H_2, and CO were measured by NOAA ESRL GMD in 118 discrete air samples collected in flasks on the 12 flights conducted in the D-J Basin in May 2012 (Figures 1 and 4). Air samples were typically acquired to ascertain hydrocarbon mole fractions in upwind legs, in the free troposphere above the PBL, and downwind of (and within) the D-J Basin.

Mole fractions of all the light alkanes in flask air samples collected directly downwind of O&G operations in the D-J Basin are elevated above background levels measured in upwind legs and in the free troposphere. The 97 air samples collected by the airplane in the PBL (below 3000 m asl) have an average mole fraction and 1σ mole fraction variability of 1891 ± 24 ppb for CH_4 and 4.3 ± 3.2 ppb for C_3H_8, compared to 1854 ± 10 ppb for CH_4 and 0.46 ± 0.58 ppb for C_3H_8 in the 21 air samples collected by the airplane above 3000 m asl.

In Figure 4, we show correlation plots for the hydrocarbons' dry air mole fractions measured in the aircraft flasks. Correlation slopes for the 97 PBL air samples are derived using an orthogonal distance regression (ODR) with a 2 ppb uncertainty for the CH_4 measurements, a 5% uncertainty for the NMHC measurements, and no constraint on the y intercept. The slopes, the attached 1σ uncertainties, and R^2 are reported in Table 4. Below, we discuss CH_4 and C_3H_8 mixing ratios correlation in the aircraft samples. Then we describe another strong feature of this data set, which relates to the very tight correlations between the C_{3-5} alkane mixing ratios. We also report on the analysis of C_6H_6 mixing ratios correlations with C_3H_8 and C_2H_2 mixing ratios. Finally, the May 2012 flight results are compared with other measurements conducted at the NOAA BAO facility.

CH_4 and C_3H_8 in the aircraft PBL air samples are correlated, with an R^2 of 0.66 and a CH_4-to-C_3H_8 correlation slope of 6.2 ppb/ppb (Figure 4). From flight to flight, CH_4 "background" mole fractions in the upwind aircraft flasks range between 1846 and 1876 ppb, while the enhancements above background in downwind flasks ranged between 1 and 104 ppb. The flight-to-flight variability in the upwind CH_4 mole fraction can be as high as on e third of the downwind enhancement signals we want to interpret. C_3H_8 mole fractions in upwind aircraft flasks range between 0.16 and 1.80 ppb, while the enhancements in all other PBL flasks range between 0.09 and 15 ppb (Figure 4).

To remove the influence of the varying background (upwind) mole fractions from flight to flight, we derive enhancements of CH_4 and C_3H_8 above background for each flask air samples collected below 3000 m asl on 11 different flights. For each flight, we define the measured CH_4 and C_3H_8 background mole fractions as the level measured in one flask air sample collected in the PBL upwind of the O&G operations out of a maximum of 12 flasks collected during each flight. For one flight, we do not have a background air flask sample. The correlation slope of CH_4 and C_3H_8 enhancements for the 76 remaining PBL aircraft samples (using the same assumptions as above) is 6.1 ± 0.4 ppb CH_4/ppb C_3H_8. The higher R^2 (0.80) compared to the correlation of absolute CH_4 and C_3H_8 mole fractions is an indication that removing the flight-to-flight varying background is important when interpreting CH_4 and C_3H_8 mixing ratios measurements from multiple days. We consider this latter slope of 6.1 ± 0.4 ppb/ppb to reflect the overall ratio of CH_4 to C_3H_8 total emissions in the study region in May 2012.

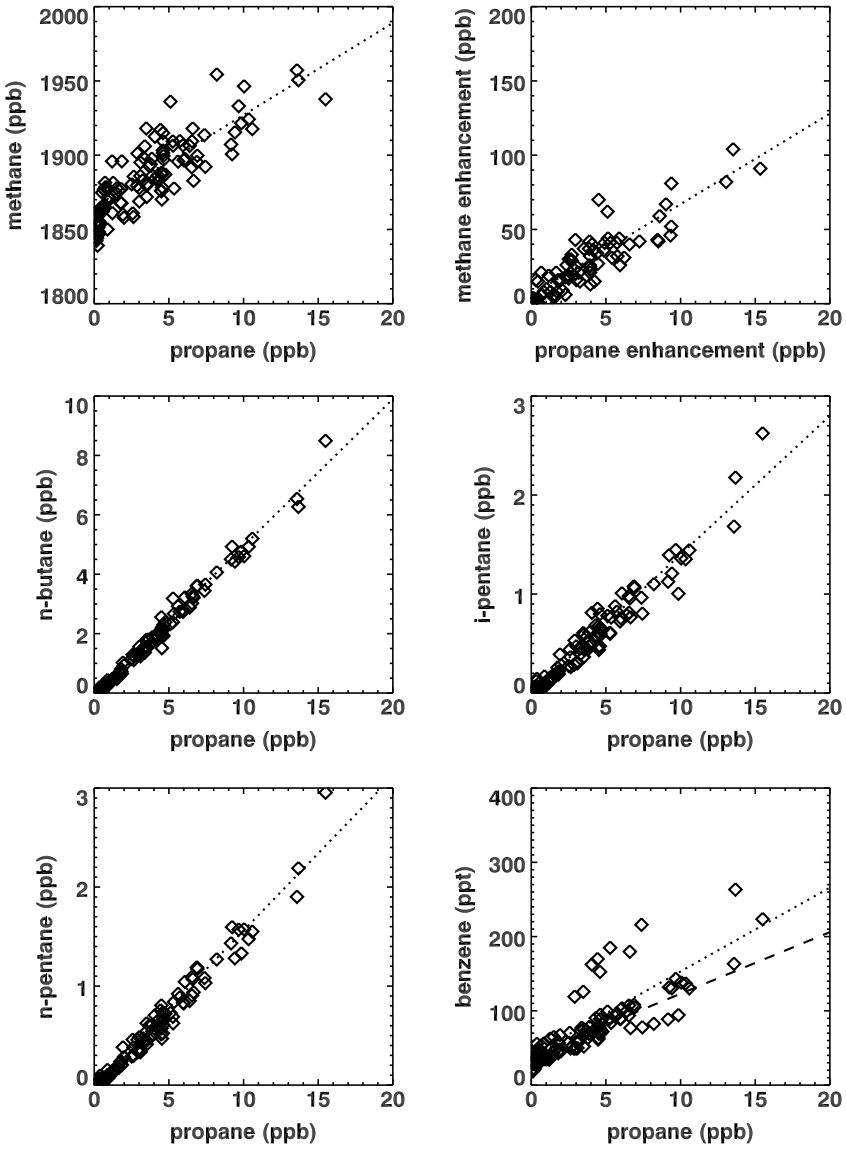

Figure 4. Correlation plots for different hydrocarbon versus propane mixing ratios (or enhancements above background as noted) in flasks sampled by aircraft in the boundary layer. The dotted lines show the correlation slopes of the single regression as reported in Table 4. The dashed line in the benzene to propane figure shows the multiregression slope also reported in Table 4. All the data come from the NOAA GMD multiple species analysis by GC-MS of discrete air samples collected with the aircraft on different days in the Denver-Julesburg Basin in May 2012.

The tight correlations between the C_{3-5} alkane mixing ratios for all samples collected in the PBL by the airplane ($R^2 \geq 0.99$) with the same slopes for all flight data suggest that these gases are emitted by the same sources located in the study region and at a fairly constant ratio, as concluded by *Pétron et al.* [2012]. None of the nonmethane light alkanes measured correlates with either CO or C_2H_2 ($R^2 < 0.2$), which shows that these gases are emitted by noncombustion processes.

For all 97 aircraft PBL flask samples, C_6H_6 correlates well with both C_3H_8 (O&G source) and C_2H_2 (mobile combustion source) ($R^2 = 0.65$ in both cases) (Figures 4 and S5). Using a multilinear regression to explain C_6H_6 variability, we find that the regression coefficients a_{C3H8} (8.3 ± 0.4 ppt/ppb) and a_{C2H2} (0.39 ± 0.02 ppt/ppt) are lower than the single regression correlation slopes we report in Table 4. The R^2 values for the correlation of aircraft ($[C_6H_6] - a_{C2H2}*[C_2H_2]$)-to-$C_3H_8$ and ($[C_6H_6] - a_{C3H8}*[C_3H_8]$)-to-$C_2H_2$ are 0.85 and 0.88, respectively. This increase in the R^2 compared to the single regression correlation coefficient suggests that the variability in the C_6H_6 enhancements is mostly due to these two different sources.

Table 4. Summary of Correlation Slopes (ppb/ppb) Between Various Hydrocarbons' Dry Air Mole Fractions Measured in Air Samples Collected With the Aircraft in May 2012[a]

	This Study—Boundary Layer Samples Only			BAO 2008–2012 NE Sector May–June (85 Samples)			BAO 2007–2012 NE Sector November–April (919–988 Samples[b])			G13 BAO Feb 2011 Multiregression			S13 BAO Feb 2011		
Data Sets Species	Slope	SD	R^2	Slope	SD	R^2	Slope	SD	R^2	Slope	SD	R^2	Slope	SD	R^2
CH_4 to C_3H_8 enhancements	6.1	0.3	0.81	-	-	-	-	-	-	-	-	-	-	-	-
CH_4 to C_3H_8	6.2	0.5	0.66	8.1	0.8	0.56	8.9 ± 0	0.2	0.89	-	-	-	-	-	-
nC_4H_{10} to C_3H_8	0.495	0.007	1.00	0.475	0.007	1.00	0.438	0.003	1.00	0.563	0.004	0.96	0.46	0.01	0.96
iC_5H_{12} to C_3H_8	0.140	0.004	0.99	0.131	0.005	0.93	0.131	0.002	0.99	0.168	0.002	0.91	0.13	0.005	0.91
nC_5H_{12} to C_3H_8	0.156	0.003	0.99	0.146	0.005	0.94	0.137	0.002	0.99	0.190	0.002	0.92	0.13	0.005	0.92
C_6H_6 to C_3H_8	11.3×10^{-3}	0.9×10^{-3}	0.65	8.7×10^{-3}	0.8×10^{-3}	0.62	8.7×10^{-3}	0.3×10^{-3}	0.79	-	-	-	6.3×10^{-3}	0.4×10^{-3}	0.79
C_6H_6 to C_2H_2	0.54	0.04	0.65	0.35	0.06	0.33	0.38	0.01	0.82	-	-	-	0.39	0.01	0.94
C_6H_6 to C_3H_8 (multiregression)	8.3×10^{-3}	0.4×10^{-3}	0.85[c]	7.5×10^{-3}	0.7×10^{-3}	0.66	5.3×10^{-3}	0.2×10^{-3}	0.91	4.3×10^{-3}	0.1×10^{-3}		-	-	-
C_6H_6 to C_2H_2 (multiregression)	0.39	0.02	0.88[c]	0.23	0.04	0.35	0.222	0.007	0.88	0.166	0.005		-	-	-

[a]These slopes are compared with results from a similar analysis by GMD of midday samples collected from the NOAA BAO tower 300 m level (2007–2012) for the NE wind sector. The last two columns provide emission ratios reported by *Gilman et al.* [2013] (abbreviated G13) and *Swarthout et al.* [2013] (abbreviated S13) for VOC measurements at 22 m at BAO during a 3-week intensive campaign in February 2011.
[b]The number of valid BAO samples for each pair of trace gases varied and was within the range provided in the column header.
[c]R^2 for the residuals.

The hydrocarbon correlation slopes for the aircraft samples are now compared with results from three different BAO data sets. In Table 4, we report correlation slopes for the GMD long-term midday flask samples collected at the 300 m agl level of the BAO tower (calculated using the same ODR technique). The last two columns in Table 4 also show results presented in *Gilman et al.* [2013] and *Swarthout et al.* [2013] on VOC measurements collected during a 3 week intensive campaign at BAO in February 2011. We filter the GMD BAO data set to keep air samples coming from the NE only (flasks with prior 30 min mean wind from a direction of 0–140° and a mean wind speed $>$ 2.5 m/s). The BAO NE data are also filtered by time of year: data from May and June 2008–2012 are compared with the May 2012 aircraft data, and data from November to April 2007–2012 are compared with the wintertime results reported by *Gilman et al.* [2013] and *Swarthout et al.* [2013] (denoted G13 and S13, respectively, in Table 4). *Gilman et al.* [2013] and *Swarthout et al.* [2013] report their VOC measurements on different calibration scales than GMD. They also sampled day and night closer to the surface, which may make some of their measurements less representative of a large area because the highest mole fraction enhancements tend to occur at night when winds are lower.

For the GMD data sets, nC_4H_{10}-to-C_3H_8, iC_5H_{12} -to-C_3H_8 and nC_5H_{12}-to-C_3H_8 correlation slopes for the aircraft PBL samples are 4–7% higher than the BAO NE May and June samples slopes. Conversely, the CH_4-to-C_3H_8 enhancements slope for the airplane PBL samples is 23% lower that the BAO NE May and June samples slope. The overall mix of hydrocarbon sources located within the footprints of the airplane and BAO samples have different chemical compositions, especially in terms of CH_4 relative to other light alkanes. This difference may reflect a higher contribution of hydrocarbon emissions related to oil and liquid condensate production (enriched in NMHCs relative to CH_4) in

Table 5. Emission Estimates for Methane and Five Nonmethane Hydrocarbons in Weld County Based on Aircraft Measurements in May 2012

Compound	Total Emissions (t/h) 2 Days in May 2012	Method
CH_4	26.0 ± 6.8	Mass-balance estimate
C_3H_8	11.8 ± 3.8	Based on CH_4 to C_3H_8 mixing ratios enhancements slope
nC_4H_{10}	7.7 ± 2.6	Based on C_3H_8 total emissions estimate and nC_4H_{10} to C_3H_8 mixing ratios slope
iC_5H_{12}	2.7 ± 0.9	Based on C_3H_8 emissions estimate and iC_5H_{12} to C_3H_8 mixing ratios slope
nC_5H_{12}	3.0 ± 1.0	Based on C_3H_8 emissions estimate and nC_5H_{12} to C_3H_8 mixing ratios slope
C_6H_6	0.17 ± 0.06	Based on C_3H_8 emissions estimate and C_6H_6 to C_3H_8 multiregression coefficient
Total for measured NMHC	25.4 ± 8.2	Sum of C_3H_8, nC_4H_{10}, iC_5H_{12} , nC_5H_{12} and C_6H_6 emissions

the air masses sampled with the aircraft. The C_{3-5} alkane correlation slopes we report for BAO NE winter samples are closer to the slopes reported by *Swarthout et al.* [2013] and 22–28% lower than the slopes reported by *Gilman et al.* [2013]. At this time, it is not clear if the different calibration scales and sampling procedures between the three groups may explain some of the differences in correlation slopes observed.

The C_6H_6-to-C_3H_8 multivariate slopes for the May 2012 aircraft flasks and the BAO NE May–June flasks agree within their calculated 1 sigma: 8.3 ± 0.4 ppt/ppb and 7.5 ± 0.7 ppt/ppb, respectively. The multiregression slope we report for the BAO NE winter samples (5.3 ± 0.2 ppt/ppb) is 29% lower than the BAO NE May–June slope. It is in between the multiregression slope reported by *Gilman et al.* [2013] (4.3 ± 0.1 ppt/ppb) and the emission ratio reported by *Swarthout et al.* [2013] (6.3 ± 0.4ppt/ppb) for February 2011. These different measurements suggest that the relative strength of the C_6H_6 and C_3H_8 emissions from O&G sources in the region site may vary over time and space.

3.4. Light Alkanes and Benzene Measurement-Based Regional Emission Estimates

In this section we derive top-down estimates of light alkane and C_6H_6 emissions. We first scale the average CH_4 regional total top-down emission estimate (26.0 ± 6.8 t/h) obtained with the mass-balance approach with the inverse of the CH_4-to-C_3H_8 enhancements slope obtained for the aircraft flask samples. The total relative uncertainty in the C_3H_8 emission estimate is the sum of the relative uncertainty in the total CH_4 emission estimate and the relative uncertainty in the CH_4-to-C_3H_8 slope. The resulting total C_3H_8 mean hourly emission estimate for May 2012 is 11.8 ± 3.8 t/h.

Top-down emission estimates for *n*-C_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are calculated by scaling the C_3H_8 top-down emission estimate with the NMHC-to-C_3H_8 slopes reported in Table 4 for the aircraft flask samples. Uncertainty estimates again reflect the uncertainty in the C_3H_8 top-down emission estimate and the slopes. The resulting nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 mean hourly emission estimates for May 2012 are 7.7 ± 2.6 t/h, 2.7 ± 0.9 t/h, 3.0 ± 1.0 t/h, and 173 ± 64 kg/h (1 kg = 0.001 t), respectively.

Gilman et al. [2013] attributed 100% of the light alkane (C_{3-5}) mixing ratio enhancements above background they observed at BAO in February 2011 to O&G operations emissions. We too assume that the emission estimates we derived above for these nonmethane light alkanes can be entirely attributed to O&G sources in the study region. For C_6H_6, we use the slope from the multiple regression analysis to isolate the contribution from O&G sources alone (see previous section). The top-down emission estimates for C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 are summarized in Table 5 and add up to 25.4 ± 8.2 t/h.

This small suite of NMHCs measured by GMD in the aircraft flasks represent a subset of the nonmethane and nonethane hydrocarbons emitted by O&G sources. C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 represent on average 77% of the total NMHC mass in raw natural gas from the Wattenberg field and between 68% and 88% of the total NMHC mass in flashing emissions from oil and liquid condensate storage tanks [see also *Pétron et al.*, 2012, supporting information Figure S4; CDPHE, personal communication]. In the CDPHE inventory, as in other air quality emission inventories, ethane is not included in sum of the NMHC due to its low reactivity and low impact on local air quality.

Other NMHC reported in composition profiles for raw natural gas and flashing emissions from storage tanks, which GMD did not measure in the aircraft samples, are *i*-butane (iC_4H_{10}), alkanes with six carbons or more (C_{6+}), toluene, ethylbenzene, and xylenes [*Pétron et al.* 2012, supporting information]. GMD is currently developing a new GC-MS system to measure several of these gases in future discrete air samples. In order to estimate

emissions for the NMHCs not analyzed by GMD, one could use the *Gilman et al.* [2013] and *Swarthout et al.* [2013] BAO VOC measurements, assuming they are representative of the mean emission ratios in Weld County.

4. Comparison With Inventory-Based Emissions Estimates

4.1. Nonmethane Hydrocarbons

CDPHE has developed bottom-up methods to track VOC emissions from O&G sources, which rely on both permit data and empirical equations. Flashing emissions of volatile compounds occur every time "new" oil or liquid condensate is dumped from the on-site separator into a storage tank. In the CDPHE inventory these emissions are treated as an area source proportional to oil and liquid condensate production. We use the May 2012 total oil and liquid condensate production volume for Weld County and an empirical equation described in *Wells* [2012] and *Bar-Ilan and Morris* [2012] to estimate the flashing emissions from storage tanks in Weld County. The empirical equation developed by CDPHE uses an emission factor of 13.7 lb VOC per barrel of oil or liquid condensate produced and assumes an overall emission reduction factor of 53% from the mandatory use of flares or vapor recovery units in the NAA [*Wells*, 2012]. Hourly emissions from oil and liquid condensate storage tanks in Weld County in May 2012 are estimated at 11.8 t/h. Other sources, including compressor engines, truck liquid loading, produced water storage tanks, etc., add 1.14 t/h (D. Wells, personal communication, 2014), while drill rigs, completion, and recompletion add another estimated 0.12 t/h (projected from WestJump (2008) [*Bar-Ilan and Morris*, 2012] to May 2012). In Weld County, according to the state inventory, the bulk of total O&G VOC emissions come from uncaptured or unburned flashing emissions at oil and liquid condensate storage tanks. The bottom-up total VOC emission estimates from O&G sources add up to 13.1 t/h. No uncertainties are available for this estimate. The bottom-up total is about half of the top-down total emission we derive for C_3H_8, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6H_6 in May 2012 (25.4 ± 8.2 t/h) alone.

In the CDPHE inventory of C_6H_6 sources, highway and nonroad vehicles are responsible for close to 90% of the total C_6H_6 emissions in the Front Range ozone nonattainment area, or 139 kg/h in 2011 (the 2012 estimate is not available yet). The CDPHE inventory estimate of C_6H_6 emissions from O&G operations in Weld County in 2012 amounts to 25.2 kg/h: 17.9 kg/h from oil and liquid condensate storage tanks and 7.3 kg/h from other O&G sources, including produced water tanks, crude oil and condensate loading and transportation, natural gas dehydration and processing operations, flares, and compressor engines. This official estimate is 7 times lower than our average top-down estimate (173 ± 64 kg/h). Taking into account the 1 sigma uncertainty in our estimate, there is 68% chance that the inventory underestimates these emissions by a factor of 4 to 9. Our results indicate that C_6H_6 emissions from O&G operations in Weld County may be as large or even larger than vehicle emissions. This finding stresses the need for further work to better understand and track the substantial "missing" sources of C_6H_6 (and potentially other hazardous air pollutants) in O&G production and processing operations [*Pétron et al.*, 2012].

4.2. Methane

To date, neither the state of Colorado nor EPA provides complete, up-to-date, and spatially resolved (county or smaller scale) inventories of CH_4 sources. The most detailed and regionally relevant information source for CH_4 emissions from O&G sources is the EPA Greenhouse Gas Reporting Program (GHGRP), which collects emissions data from the largest sources of GHG in the US under the Consolidated Appropriations Act of 2008 [*EPA*, 2013b].

The GHGRP Subpart W covers almost all segments of petroleum and natural gas systems from production, processing, transmission compression, storage, and distribution besides emissions from stationary fuel combustion covered by Subpart C (http://www.epa.gov/ghgreporting/documents/pdf/infosheets/OnshorePetroleumNaturalGasSystems.pdf). Owners of O&G facilities emitting more than 25,000 t CO_2 equivalent/yr (from single point sources or as an aggregate for operations over an O&G basin) are required to report annual GHG emissions data to the EPA following specified methods to promote consistency across operators. Smaller operators and a few source categories do not report emissions data to the GHGRP Subpart W. For example, natural gas gathering compressors do not report to the program at this time. Despite these obvious limitations, it is currently the most detailed and basin-specific inventory of GHG emissions. In November 2013, the GHGRP made public the second year of emissions data reported to Subpart W for operations during 2012.

Twelve large oil and gas producers in the D-J Basin (out of 269 operators) report basin-level CH_4 emissions for their area distributed operations to the GHGRP. Their reported CH_4 emissions total 6.7 t/h for an average

day in 2012. The two largest sources categories are pneumatic devices and pumps (3.8 t/h) and other equipment leaks from well pads (2.1 t/h). Reported emissions from other operations at well pads including liquid unloading, oil and liquid condensate storage tanks, and completions and workovers total 0.55, 0.15 and 0.14 t/h, respectively [*EPA*, 2013b]. Eleven facilities (large natural gas processing plants and transmission compressor stations) in Weld County also report facility-level GHG emissions to the GHGRP, and their aggregated CH_4 emission estimate for an average day in 2012 is 0.2 t/h.

Weld County is the largest O&G producing county by far in the D-J Basin. Here we use the assumption that the GHGRP area source emission estimates reported for the D-J Basin can be scaled by O&G production (expressed in Btu) to derive estimates of emissions for all O&G operators in Weld County in 2012, and we use heat contents for natural gas of 1.021 million Btu per thousand cubic feet and for oil of 5.871 million Btu per barrel of oil. In 2012, the 12 operators in D-J Basin reporting emissions to the GHGRP produced an equivalent of 5.07×1014 Btu, while all operators in Weld County produced an equivalent of 5.01×1014 Btu. We scale the GHGRP reported D-J Basin emissions total by 0.989 ($= 5.01 \times 1014/5.07 \times 1014$) and derive an estimated total emissions of 6.6 t CH_4/h for all O&G area sources in Weld County on an average day in 2012.

To account for all sources, emissions from large point sources (compressors and processing plants) not reporting to the GHGRP should also be added. It is not clear, however, how to scale the 0.2 t/h reported for a subset of 11 such facilities. With a simple scaling of 30/11, we get an estimate of 0.5 t CH_4/h for the identified 30 large O&G point sources in the study region (out of 38 total facilities in the state inventory for Weld County).

Overall there is a large gap between the CH_4 emissions we estimate based on the GHGRP data for O&G operations in Weld County for an average day in 2012 (7.1 t/h) and the 19.3 ± 6.9 t/h average top-down estimate we derive for 2 days in May 2012.

Following CDPHE bottom-up calculations for VOCs flashing emissions from storage tanks, hourly average CH_4 flashing emission estimates in Weld County in May 2012 range between 0.9 and 5.9 t/h based on 16 different flashing emissions composition profiles, with an average of 2.8 t/h. The GHGRP reported CH_4 emissions from oil and liquid condensate storage tanks in the D-J Basin in 2012 total 0.15 t/h and may be underestimated.

One clear limitation of this comparison has to do with the different temporal coverage of the top-down (daytime for 2 days) and bottom-up (annual) emission estimates. It is beyond the scope of this paper to derive an emission inventory for the same time period represented by our measurements, i.e., a midday snapshot on 2 days in May 2012. Further coordinated work to reconcile CH_4 and NMHC emissions estimates based on inventory models and atmospheric measurements studies at different spatial and temporal scales is needed to better characterize how O&G sources impact air quality and climate.

Several studies have expressed CH_4 emissions from O&G systems in terms of the fraction of produced CH_4 (or natural gas) lost to the atmosphere [*U.S. Environmental Protection Agency/Global Reporting Initiative* (*EPA/GRI*), 1996; *Shorter et al*., 1997; *Pétron et al*., 2012; *Peischl et al*., 2013; *Karion et al*., 2013; *Allen et al*., 2013]. We estimate that the fraction of gross natural gas production from oil and gas wells lost to the atmosphere in Weld County in May 2012 is 4.1 ± 1.5 %. This number is close to the middle scenario (4%) reported by *Pétron et al*. [2012] for 2008 for the same region. Our current measurements do not allow us to separate the emissions contributions from oil production versus natural gas production. Our total loss rate is substantially lower than the 8.9 ± 2.8 % (1σ) loss rate reported by *Karion et al*. [2013] for the Uinta Basin gas field in northeastern Utah for one mass-balance flight conducted in February 2012.

5. Conclusions

This study presents estimates of total emissions of methane (CH_4), propane (C_3H_8), *n*-butane (nC_4H_{10}), *i*- and *n*-pentane (iC_5H_{12} and nC_5H_{12}), and the carcinogen benzene (C_6H_6) from the most densely drilled region of the Denver-Julesburg oil and natural gas basin in Weld County in May 2012. Our estimation approach is based on aircraft in situ continuous (CH_4) and discrete (CH_4, NMHCs) chemical measurements and ground-based wind profilers.

Our top-down total hourly average emission rates for CH_4, C_3H_8, nC_4H_{10}, iC_5H_{12}, and nC_5H_{12} are 26.0 ± 6.8, 11.8 ± 3.8, 7.7 ± 2.6, 2.7 ± 0.9, and 3.0 ± 1.0 t/h, respectively. Based on the lack of correlation we observe between these alkanes and combustion tracers (CO, C_2H_2) in the airborne flask samples along with previous

analysis of NMHC observations in the Basin [*Gilman et al*., 2013], we attribute 100% of these nonmethane emissions to oil and natural gas operations. We also derive a top-down average emission estimate for C_6H_6 emissions from oil and natural gas operations of 173 ± 64 kg/h.

Inventory estimates for nonoil and gas CH_4 sources in the region suggest that 7.1 ± 1.7 t/h on 29 May and 6.3 ± 1.0 t/h on 31 May were emitted by nonoil and natural gas sources. On average, we estimate that 75% (19.3 ± 6.9 t/h) of the total CH_4 emissions we detected are attributable to O&G operations in the study region.

Overall, our top-down emission estimates for CH_4 and NMHCs from oil and natural gas sources are at least twice as large as available bottom-up emission estimates. Accurate estimates of emissions from oil and natural gas operations at the regional and national levels are still needed to quantify (and minimize) their impacts on climate forcing and air quality. Research studies like this one, relying on recent technical developments in atmospheric measurements, are a necessary component for the evaluation of emissions inventories and emissions reduction programs. Further efforts are underway to overcome some of the limitations of the regional mass-balance approach. Specifically, the use of a dense network of CH_4, $\delta^{13}CH_4$, and hydrocarbon observations to attribute the total CH_4 emissions between different sources is under investigation. Longer-term monitoring observations ingested into inverse models (such as *Miller et al*. [2013]) can also provide a valuable approach to extend the temporal coverage of top-down emission estimates. More top-down studies are needed to evaluate (1) hydrocarbons emission inventories for dry gas/wet gas/oil production regions and (2) the actual impacts of emission mitigation regulations and best management practices including Leak Detection and Repair programs. Future research should also include the investigation of the apparent gap between bottom-up and top-down hydrocarbon emission estimates at the regional and national scales to track down which sources are either missing or underestimated and to quantify the contribution of anomalously large emitters, as suggested by *Brandt et al*. [2014].

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References

Allen, D. T., et al. (2013), Measurements of methane emissions at natural gas production sites in the United States, *Proc. Natl. Acad. Sci. U. S. A.*, doi:10.1073/pnas.1304880110.

API/ANGA (2012), Characterizing pivotal sources of methane emissions from natural gas production, 57 pp.

Bar-Ilan, A., and R. Morris (2012), 2008 O&G emissions for Colorado Basins (Denver-Julesburg, Piceance, and North San Juan), final emissions technical memorandum 4a.

Bar-Ilan, A., et al. (2008), Development of baseline 2006 emissions from oil and gas activity in the Denver-Julesburg Basin, WRAP Phase III report, 34 pp., Western Reg. Air Partnership, Fort Collins, Colo. [Available at http://www.wrapair.org/forums/ogwg/documents/2008-04_06_Baseline_Emissions_D-J_Basin_Technical_Memo_(04-30).]

Bogner, J., K. Spokas, and J. Chanton (2011), Seasonal greenhouse gas emissions (methane, carbon dioxide, nitrous oxide) from engineered landfills: Daily, intermediate, and final California landfill cover soils, *J. Environ. Qual.*, *40*, 1010–1020.

Brandt, A. R., et al. (2014), Methane leaks from North American natural gas systems, *Science*, *343*(6172), 733–735, doi:10.1126/science.1247045.

Colorado Department of Public Health and the Environment (CDPHE) (2002), Colorado greenhouse gas emissions inventory & forecast: 1990 to 2015, 74 pp.

Colorado Department of Public Health and the Environment (CDPHE) (2008), Denver metropolitan area and north Front Range 8-hour ozone state implementation plan, Technical Support Document For Proposed Pneumatic Controller Regulation. [Available at http://www.colorado.gov/airquality/documents/deno308/Pneumatic_Controller_TSD_DRAFT.pdf.]

Colorado Department of Natural Resources (2011), Colorado new oil boom: The Niobrara, Rock Talk, vol 13(1). [Available at http://geosurvey.state.co.us/pubs/Documents/rtv13n1%204-15-11%20B.pdf.]

Colorado Oil and Gas Conservation Commission (COGCC) (2014), County level production data available in the "DataBase" section. [Available at http://cogcc.state.co.us/.]

Czepiel, P. M., B. Mosher, R. C. Harriss, J. H. Shorter, J. B. McManus, C. E. Kolb, E. Allwine, and B. K. Lamb (1996), Landfill methane emissions measured by enclosure and atmospheric tracer methods, *J. Geophys. Res.*, *101*(D11), 16,711–16,719, doi:10.1029/96JD00864.

Czepiel, P. M., J. H. Shorter, B. Mosher, E. Allwine, J. B. McManus, R. C. Harriss, C. E. Kolb, and B. K. Lamb (2003), The influence of atmospheric pressure on landfill methane emissions, *Waste Manage.*, *23*(7), 593–598.

Dlugokencky, E. J., K. A. Masarie, P. P. Tans, T. J. Conway, and X. Xiong (1997), Is the amplitude of the methane seasonal cycle changing?, *Atmos. Environ.*, *31*(1), 21–26, doi:10.1016/s1352-2310(96)00174-4.

Eisele, A., M. Hannigan, J. Milford, D. Helmig, and P. Milmoe (2009), Understanding air toxics and carbonyl pollutant sources in Boulder County, Colorado, prepared for Environmental Protection Agency Region 8, 145 pp. [Available at http://www.epa.gov/ttnamti1/files/20052006csatam/BCPHAirToxicsReportEPA.pdf.]

Fishman, N. S., et al. (2005), *Energy Resource Studies, Northern Front Range, Colorado*, *U. S. Geol. Surv. Prof. Pap., 1698*. [Available at http://pubs.usgs.gov/pp/2005/1698/pdf/P1698.pdf.]

Gilman, J. B., B. M. Lerner, W. C. Kuster, and J. de Gouw (2013), Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado, *Environ. Sci. Technol.*, doi:10.1021/es304119a.

Goldan, P. D., M. Trainer, W. C. Kuster, D. D. Parrish, J. Carpenter, J. M. Roberts, J. E. Yee, and F. C. Fehsenfeld (1995), Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado: Implications for emission inventories, *J. Geophys. Res.*, *100*(D11), 22,771–22,783, doi:10.1029/95JD01369.

Grund, C. J., et al. (2001), High-resolution Doppler lidar for boundary layer and cloud research, *J. Atmos. Oceanic Technol.*, *18*(3), 376–393.

Higley, D., and D. Cox (2007), Oil and gas exploration and development along the front range in the Denver Basin of Colorado, Nebraska, and Wyoming, in Higley, D.K., compiler, Petroleum systems and assessment of undiscovered oil and gas in the Denver Basin Province, Colorado, Kansas, Nebraska, South Dakota, and Wyoming—USGS Province 39: U.S. Geo. Surv. Digital Data Ser. DDS–69–P, ch. 2, 41 pp.

IPCC (2000), Background papers IPCC expert meetings on good practice guidance and uncertainty management in national greenhouse gas inventories, CH_4 and N_2O emissions from livestock manure, pp. 321–338. [Available at http://www.ipcc-nggip.iges.or.jp/public/gp/gpg-bgp.html.]

Johnson, K. A., and D. E. Johnson (1995), Methane emissions from cattle, *J. Anim. Sci.*, *73*(8), 2483–92.

Karion, A., et al. (2013), Methane emissions estimates from airborne measurements over a western United States natural gas field, *Geophys. Res. Lett.*, *40*, 4393–4397, doi:10.1002/grl.50811.

Kebreab, E., K. A. Johnson, S. L. Archibeque, D. Pape, and T. Wirth (2008), Model for estimating enteric methane emissions from United States dairy and feedlot cattle, *J. Anim. Sci.*, *86*, 2738–2748, doi:10.2527/jas.2008-0960.

Klusman, R., and M. Jakel (1998), Natural microseepage of methane to the atmosphere from the Denver-Julesburg basin, Colorado, *J. Geophys. Res.*, *103*(D21), 28,041–28,045, doi:10.1029/98JD02399.

LaFranchi, B. W., et al. (2013), Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$, *Atmos. Chem. Phys.*, *13*, 11,101–11,120, doi:10.5194/acp-13-11101-2013.

Levi, M. A. (2012), Comment on "Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study" by Gabrielle Pétron et al., *J. Geophys. Res.*, *117*, D21203, doi:10.1029/2012JD017686.

Lodman, D. W., M. E. Branine, B. R. Carmean, P. Zimmerman, G. M. Ward, and D. E. Johnson (1993), Estimates of methane emissions from manure of U.S. cattle, *Chemosphere*, *26*(1–4), 189–199.

Miller, S. M., et al. (2013), Anthropogenic emissions of methane in the United States, *Proc. Natl. Acad. Sci. U.S.A.*, doi:10.1073/pnas.1314392110.

Montzka, S. A., R. C. Myers, J. H. Butler, J. W. Elkins, and S. O. Cummings (1993), Global tropospheric distribution and calibration scale of HCFC-22, *Geophys. Res. Lett.*, *20*(8), 703–706, doi:10.1029/93GL00573.

Mosher, B. W., P. Czepiel, R. Harriss, J. Shorter, C. Kolb, J. B. McManus, E. Allwine, and B. Lamb (1999), CH_4 emissions at nine landfill sites in the northeastern United States, *Environ. Sci. Technol.*, *33*, 2088–2094.

NASS (2014), Colorado agricultural statistics 2013. [Available at http://www.nass.usda.gov/Statistics_by_State/Colorado/Publications/Annual_Statistical_Bulletin/Final%202013.pdf.]

Novelli, P. C., et al. (1998), An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements, *J. Geophys. Res.*, *103*, 19,285–19,293, doi:10.1029/97JD00031.

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

Pétron, G., et al. (2012), Hydrocarbon emissions characterization in the Colorado Front Range—A pilot study, *J. Geophys. Res.*, *117*, D04304, doi:10.1029/2011JD016360.

Pétron, G., G. J. Frost, M. K. Trainer, B. R. Miller, E. J. Dlugokencky, and P. Tans (2013), Reply to comment on "Hydrocarbon emissions characterization in the Colorado Front Range—A pilot study" by Michael A. Levi, *J. Geophys. Res. Atmos.*, *118*, 236–242, doi:10.1029/2012JD018487.

Roberts, S. B., J. L. Hynes, and C. L. Woodward (2001), Map showing the extent of mining, locations of mine shafts, adits, air shafts, and bedrock faults, and thickness of overburden above abandoned coal mines in the Boulder-Weld Coal Field, Boulder, Weld, and Adams Counties, Colorado. [Available at: http://pubs.usgs.gov/imap/i-2735/.]

Scamehorn, L. (2002), High altitude energy: A history of fossil fuels in Colorado. Boulder: University Press of Colorado, 2002. xvi +232 pp. ISBN 0-87081-661-6.

Sharvelle, S., and L. Loetscher (2011), Anaerobic digestion of animal wastes in Colorado, Livestock Series - Management, Fact Sheet, 1.227, 3 pp. [Available at http://www.ext.colostate.edu/pubs/livestk/01227.pdf.]

Shorter, J. H., et al. (1997), Collection of leakage statistics in the natural gas system by tracer methods, *Environ. Sci. Technol.*, *31*, 2012–2019.

Sonnenberg, S. (2012), *The Niobrara Petroleum System, Rocky Mountain Region, Search and Discovery Article #80206*. [Available at: http://www.searchanddiscovery.com/documents/2012/80206sonnenberg/ndx_sonnenberg.pdf.]

Stackhouse, K. R., Y. Pan, Y. Zhao, and F. M. Mitloehner (2011), Greenhouse gas and alcohol emissions from feedlot steers and calves, *J. Environ. Qual.*, *40*, 899–906, doi:10.2134/jeq2010.0354.

Steed, J., Jr., and A. G. Hashimoto (1994), Methane emissions from typical manure management systems, *Bioresour. Technol.*, *50*(2), 123–130.

Strait, R., S. Roe, A. Bailie, H. Lindquist, and A. Jamison (2007), Colorado greenhouse gas inventory and reference case projections 1990–2020, report, 99 pp., CDPHE, Denver, Colo. [Available at http://www.cdphe. state.co.us/ap/studiesreports.html.]

Swarthout, R. F., R. S. Russo, Y. Zhou, A. H. Hart, and B. C. Sive (2013), Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources, *J. Geophys. Res. Atmos.*, *118*, 10,614–10,637, doi:10.1002/jgrd.50722.

USDA (2012), 2007 census of agriculture, County Level Data accessible via the USDA National Agricultural Statistical Services quick stat. [Available at http://quickstats.nass.usda.gov/.]

U.S. Environmental Protection Agency/Global Reporting Initiative (EPA/GRI) (1996), Methane emissions from the natural gas industry, Volume 2: *Tech. Rep.*, EPA-600/R-96-080b, 152pp.

U.S. Environmental Protection Agency (EPA) (1999), U.S. methane emissions 1990–2020: Inventories, projections, and opportunities for reductions, Appendix V: Livestock Manure Management, 26 pp. [Available at http://www.epa.gov/outreach/reports/05-manure.pdf.]

U.S. Environmental Protection Agency (EPA) (2004), Methane emissions from abandoned coal mines in the United States: Emission inventory methodology and 1990–2002 emissions estimates, 90 pp. [Available at http://www.epa.gov/cmop/docs/amm_final_report.pdf.]

U.S. Environmental Protection Agency (EPA) (2009), Technical support document for manure management systems: Proposed rule for mandatory reporting of greenhouse gases, 20 pp. [Available at: http://www.epa.gov/ghgreporting/documents/pdf/archived/tsd/TSD%20manure_020409.pdf.]

U.S. Environmental Protection Agency (EPA) (2013a), Inventory of U.S. greenhouse gas emissions and sinks: 1990–2011. [Available at http://www.epa.gov/climatechange/ghgemissions/usinventoryreport/archive.html.]

U.S. Environmental Protection Agency (EPA) (2013b), 2012 greenhouse gas emissions from large facilities. [Available at http://ghgdata.epa.gov/ghgp/main.do.]

U.S. Environmental Protection Agency (EPA) (2014), Draft inventory of U.S. greenhouse gas emissions and sinks: 1990–2012. [Available at http://www.epa.gov/climatechange/ghgemissions/usinventoryreport.html.]

Wells, D. (2012), Condensate tanks emissions, Extended abstract to EPA 2012 International Emission Inventory Conference "Emission Inventories - Meeting the Challenges Posed by Emerging Global, National, Regional and Local Air Quality Issues", 12 pp. [Available at http://www.epa.gov/ttnchie1/conference/ei20/.]

Westberg, H., B. Lamb, K. A. Johnson, and M. Huyler (2001), Inventory of methane emissions from U.S. cattle, *J. Geophys. Res.*, *106*, 12,633–12,642, doi:10.1029/2000JD900808.

FAQ About the NOAA-CIRES Colorado Methane Study

Frequently asked questions:

What are the main takeaways of this study?

Methane emissions from the oil and gas industry are a problem that requires action now. The NOAA-CIRES study, part of the larger methane research series funded by EDF, is another important contribution to the mounting scientific evidence that underscores oil and gas methane emissions are too high.

The study gives a basin-wide snapshot of emissions over two days in Colorado's most active oil and gas region, which contains infrastructure ranging from production to distribution. The data shows that state inventories underestimate hydrocarbon emissions in the basin by a factor of 2 or more. Estimated methane emissions are reported to be almost three times higher than those derived from estimates using EPA's 2012 greenhouse gas reporting data. The authors also suggest this corresponds to a 2.6 – 5.6% leak rate of total natural gas production from oil and gas wells. Emissions of smog-forming VOCs are twice as high as state estimates and seven times higher for emissions of benzene, a known carcinogen.

This study also confirms a trend we have seen in many recent academic studies – that methane emissions are higher than they should be, and there are clear and cost-effective paths to reducing these emissions.

What is the methodology of the NOAA-CIRES study?

The NOAA-CIRES team flew 12 flights around and through the Denver Julesburg Basin. During these flights they collected real-time methane data and up to 12 flask samples of whole air which were analyzed in the lab for hydrocarbons. By flying a box around the basin to quantify methane concentrations at the upwind and downwind edges of the box, the scientists were able to determine how much methane was emitted within the box flown.

To determine how much of the total methane flux was due to oil and gas sources, the scientists subtracted from the total their best estimates of emissions from all the non-oil and gas sources. No direct bottom-up

measurements were made for this study, so they had to use several assumptions and data sets to determine how much each source type contributed to the overall methane levels measured in the study.

Is this study a complete picture of methane emissions from the natural gas system across the country?

No. The NOAA-CIRES study fills in another important data point in our ever-increasing knowledge of methane emissions from oil and gas operations, but it is not meant to be a stand-alone, particularly because measurements were made in one only basin.

What are the differences between the NOAA-CIRES study and the UT study released last September?

The two studies are not an apple-to-apple comparison and are not meant to be. The NOAA-CIRES study is measuring all methane emissions within the Denver Julesburg Basin and then subtracting out the non-oil and gas emissions. What's left is the emissions from oil and gas from all segments, production, gathering, transmission and distribution. The UT study only studied production, specifically hydraulically fractured well sites. The NOAA-CIRES study used aircraft overflight measurements while the UT study used on-the-ground data collection – two distinct methods.

EDF has undertaken an overall series of studies for this very reason – because the natural gas supply chain is diverse and cannot be measured by any one method or in any one study.

What are the differences between aircraft overflight measurements and on-the-ground data collection?

The two methods are complementary. On-the-ground measurements, also known as "bottom-up", are essential to identifying specific sources of emissions, but there is a limitation in that this form of measurement is difficult to canvas all potential sources at any particular site. This means some emission sources can be missed. There are millions of potential sources of methane emissions ranging from well pads to storage facilities to miles of pipelines across the country and it is not possible to measure every source directly. This inherent challenge could lead to bottom-up techniques missing the "fat tail" or the small percentage of sources that are responsible for the largest percentage of emissions. Some recent studies have suggested bottom-up measurements may be underrepresenting emissions for this reason but additional work is needed to better understand this.

Conversely, aircraft overflight readings (or "top-down" studies) are effective in measuring total methane fluxes in a given area, which promises the ability to capture methane emissions that an on-the-ground approach alone might miss, but this method also has its limitations. Assumptions are required to apportion overflight results between multiple sources (i.e. landfills, agriculture, oil and gas production, gathering systems, processing and

pipelines). If the assumptions about non-oil and gas sources are wrong, that may lead to over reporting of emissions with this methodology.

Together, these two methods can complement each other and provide greater insight and certainty than either method alone. EDF is working with a variety of academics and scientists in its methane research series to further explore how these two methods, deployed in concert, can further our understanding of the magnitude and sources of methane emissions across the natural gas supply chain.

Why is there so much disparity in published U.S. methane leakage rates?

No one study is the answer to methane emissions. Each one adds new insights. Regional and site specific differences can be also large. Things like the basin's geology (porosity and permeability of the rock), whether oil or gas dominates production and if the basin produces wet or dry gas, which is primarily made up of methane, whereas wet gas also includes ethane, butane, propane and pentane.

That doesn’t mean that we don’t know anything. We know plenty – methane rates are too high and can and should be reduced. But it’s important that we further our understanding to improve our accuracy in pinpointing emissions to keep up with evolving field practices and ensure that we are truly effective in fixing this problem.

Does this study show that EPA estimates are three times too low?

No. The authors developed an inventory of oil and gas emissions derived from data reported to EPA as part of the Greenhouse Gas reporting rule. This is not data from the US EPA Greenhouse Gas Inventory nor is it a national estimate. Rather it is a list of sources reporting their data to EPA and suggests that emissions estimates derived from that reporting may be underestimating emissions in Colorado.

Natural gas methane emissions focus of new study

April 10, 2013

PULLMAN, Wash. – Washington State University's Laboratory for Atmospheric Research is leading a nationwide field study to better understand methane emissions associated with the distribution of natural gas.

Beginning this month, a WSU research team led by Regents Professor Brian Lamb will quantify methane emissions throughout local gas systems (from city border to customer meter) and use the data to estimate a national methane emissions rate for U.S. natural gas distribution systems.

"This work is important and the study is unique,'' said Lamb. "It is critical to do these careful measurements along the entire natural gas industry supply chain, so that we have a clear understanding of the impact of the industry's greenhouse gas emissions. These are critical questions as our nation faces the challenges of energy, sustainability and climate change.''

The work will be conducted with coordination and support from major natural gas utilities, the Environmental Defense Fund (EDF) and Conestoga-Rovers and Associates, an engineering and environmental consulting firm.

Potent greenhouse gas

Large amounts of natural gas are domestically available because of dramatic advancements in technology, creating significant economic and energy security benefits for the nation. Composed mostly of methane, natural gas is a cleaner fossil fuel that, when burned, produces less carbon dioxide and fewer greenhouse gas emissions than any other fossil fuel.

However, uncombusted natural gas is a potent greenhouse gas. When it is released into the atmosphere at various points along the supply chain, it has a higher warming potential than carbon dioxide, the principal contributor of manmade climate change. Greenhouse gas emissions from human activity are believed to be impacting the earth's climate.

Obtaining direct, carefully measured data under real-world conditions is essential to determine the scope of methane emissions from natural gas operations, including local distribution systems. The U.S. Environmental Protection Agency's (EPA) most recent assessment indicates methane emissions from natural gas operations are lower than previous reports, with data based on emissions estimates. A greater understanding of the total methane loss throughout natural gas operations can play a key role in development of sound energy policies and management practices.

Detailed, accurate measurements

The researchers will make direct emission measurements component by component at company gas facilities and for individual underground pipeline leaks.

The American Gas Association (AGA), EDF, National Grid, Pacific Gas and Electric Company (PG&E)and Southern California Gas Company (SoCalGas) commissioned this study to measure methane emissions when gas is routed through local service and distribution main pipelines, as well as gas metering and regulating stations.

The WSU study is part of a two-year research series on which EDF is collaborating with the natural gas industry and universities to more accurately characterize and understand methane emissions across the value chain. National Grid, PG&E and SoCalGas are providing access to their gas facilities and equipment for tests in different regions throughout the country. Several companies are participating through AGA and are also providing access to their gas facilities for testing, including CenterPoint Energy, Citizens Energy Group, NW Natural, Piedmont Natural Gas, Questar Gas and Xcel Energy.

Work begins this month

“Brian Lamb and WSU’s Laboratory for Atmospheric Research were instrumental in the first national natural gas emissions study issued by the EPA in the early 1990s,’’said Mark Brownstein, associate vice president and chief counsel, EDF’s U.S. Energy and Climate Program. “His expertise is valuable in both designing the right scientific approach to gather data and then extrapolating those results nationally.

“We expect this study to continue to advance the discussion around methane leakage and, to the extent necessary, provide a business case for public utility commissions to better monitor and reduce leaks that lead to methane emissions,” he said.

Field work will begin this month in multiple U.S. cities in coordination with local utilities and distribution service companies. The research team is carefully selecting numerous sites in various regions around the country that meet specific criteria in order to ensure that the dataset will be as comprehensive and representative for national scaling as possible. Results are expected to be released in a peer-reviewed journal in early 2014.

A scientific advisory panel comprised of professors and experts in the fields relevant to the study will serve as independent advisors, charged with reviewing the appropriateness of the methodologies, results and statistical methods.

All Posts

New collaborative study at WVU will measure methane emissions associated with natural gas vehicles and fueling stations

March 4th, 2013

The Center for Alternative Fuels, Engines and Emissions at West Virginia Universityannounced a new study that aims to determine fugitive emissions of methane, a powerful greenhouse gas, associated with routine operation of natural gas fleet vehicles fueled by compressed or liquefied natural gas.

Natural gas powered vehicles are expected to play an increasing role in meeting future transportation needs. This study will measure methane leaks that occur at various stages in the refueling and operations of heavy-duty natural gas vehicles to provide scientific insights given the projections of industry growth.

Natural gas is a cleaner-burning fossil fuel that consists mostly of methane. Natural gas vehicles have the potential to produce fewer greenhouse emissions than diesel – if methane leaks are kept low. Uncombusted natural gas, when released into the atmosphere, can accelerate climate change due to the potency of methane.

Environmental Defense Fund is collaborating with academic and industry stakeholders on numerous scientific studies to characterize methane emissions from the production and delivery of natural gas to end users. This comprehensive research series will provide empirical methane data collected at various points across the natural gas supply chain. Results of the first study focused on production will be released in the coming months.

EDF, along with industry and research organizations, is sponsoring this new project led by CAFEE to better understand methane leakage associated with natural gas vehicles and fueling stations. Other sponsors include: the American Gas Association, International Council on Clean Transportation, PepsiCo, Shell, Volvo Group, Waste Management, Cummins Westport and Westport Innovations. Sponsors are providing access to vehicles or facilities, and a number of other industry participants are contributing equipment for testing.

The study will directly measure methane emissions at CNG and LNG refueling sites and maintenance facilities, and that result during the operation of natural gas powered heavy-duty vehicles. Final results are expected to be released in a peer-reviewed journal late 2013 or early 2014 and to assist industry in developing improvements to fueling operations and identifying best practices for minimizing leakage.

“CAFEE has a 24-year history of advanced energy research with rapid delivery of data and research products,” said Nigel Clark, George Berry Chair of Engineering at WVUand principal investigator on the project. “This is right in CAFEE’s wheelhouse. Our faculty, students and research staff have conducted numerous prior studies involving natural gas engines and vehicles, heavy-duty emissions inventory and modeling in the environmental and transportation sectors.”

Vehicles to be tested include transit buses, tractor-trailers, and vocational vehicle fleets with access to private and public fueling sites. Measurements gathered during evaluations associated with this

program will be combined with available vehicle exhaust emissions data to provide a statistically valid view of a modern natural gas fleet.

CAFEE researchers will also gather data on methane emissions from fueling stations and maintenance facilities through a combination of leak detections, leak measurements, operational and maintenance procedure review, and equipment audits, which will all be used to develop a consolidated database and model. To assist them in their methane quantification efforts, the researchers constructed a mobile dilution sampling system. A Scientific Advisory Panel comprised of professors and experts in the fields relevant to the study will also serve as independent advisors, charged with reviewing the appropriateness of the methodologies, results and their statistical methods.
- See more at: http://wvutoday.wvu.edu/n/2013/03/04/scemr-release#sthash.wQAcij0x.dpuf

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Author:
Jeong, Seongeun

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A Multi-tower Measurement Network Estimate of California's Methane Emissions

Seongeun Jeong[1], Ying-Kuang Hsu[2], Arlyn E. Andrews[3], Laura Bianco[3,4], Patrick Vaca[2], James M. Wilczak[3], Marc L. Fischer[1]

[1]Environmental Energy Technologies Division, Lawrence Berkeley National Lab, Berkeley, CA, USA

[2]California Air Resources Board, 1001 "I" Street, Sacramento, CA, USA

[3]Earth System Research Laboratory, NOAA, Boulder, CO, USA

[4]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA

Corresponding author:

Seongeun Jeong

MS 90R2002

1 Cyclotron Rd.

Berkeley, CA 94720 USA

phone: 510-486-7216

email: sjeong@lbl.gov

Key Points:

- Multi-site observations constrain Central Valley CH_4 emissions
- California total emissions are likely 1.3 -1.8 times the state inventory
- Additional measurements will help guide CH_4 mitigation activities

Abstract

We present an analysis of methane (CH_4) emissions using atmospheric observations from five sites in California's Central Valley across different seasons (September 2010 to June 2011). CH_4 emissions for spatial regions and source sectors are estimated by comparing measured CH_4 mixing ratios with transport model (WRF-STILT) predictions based on two 0.1 degree CH_4 (seasonally varying "California-specific" (CALGEM) and a static global (EDGAR42)) prior emission models. Region-specific Bayesian analyses indicate that for California's Central Valley the CALGEM- and EDGAR42-based inversions provide consistent annual total CH_4 emissions (32.87±2.09 vs. 31.60±2.17 Tg CO_2eq yr^{-1}; 68% C.I., assuming uncorrelated errors between regions). Summing across all regions of California, optimized CH_4 emissions are only marginally consistent between CALGEM- and EDGAR42-based inversions (48.35±6.47 vs. 64.97±11.85 Tg CO_2eq), because emissions from coastal urban regions (where landfill and natural gas emissions are much higher in EDGAR than CALGEM) are not strongly constrained by the measurements. Combining our results with those from a recent study of the South Coast air basin narrows the range of estimates to 43 – 57 Tg CO_2eq yr^{-1} (1.3 - 1.8 times higher than the current state inventory). These results suggest that the combination of rural and urban measurements will be necessary to verify future changes in California's total CH_4 emissions.

Keywords: methane, greenhouse gas, emission inventory, atmospheric transport, inverse model

Index Terms: 0365, 0345, 0368

1. Introduction

Methane (CH_4) is the second highest contributor to climate change among greenhouse gases (GHGs) behind carbon dioxide (CO_2), based on its concentration changes in the atmosphere since the start of the industrial revolution, the long residence time of CH_4 and its ability to absorb infrared radiation. Atmospheric CH_4 levels have increased by about 150% since 1750 accounting for ~ 25% of the global total radiative forcing from all long-lived and globally mixed GHGs [Hofman et al., 2006; Montzka et al., 2011]. Given the significance of CH_4 as a GHG it is

important to be able to quantify changes in emissions. However, bottom-up emission inventory models are highly uncertain due to lack of driver data and incomplete understanding of emission processes. Atmospheric inverse modeling, which uses observed concentration changes in CH_4 to infer sources, potentially provides an effective tool for understanding CH_4 emissions [Houweling et al., 1999; Gimson and Uliasz, 2003; Kort et al., 2008; Zhao et al., 2009; Jeong et al., 2012a].

California currently emits approximately 500 Tg of CO_2eq GHGs, with CH_4 estimated to contribute ~6% of the total [California Air Resources Board (CARB), 2011]. Because California has committed to an ambitious plan to reduce GHG emissions to 1990 levels by 2020 through Assembly Bill 32 (AB-32), planning effective mitigation efforts and verifying future emission reductions require accurate accounting of CH_4 emissions.

This paper quantifies regional CH_4 emissions from California within a Bayesian inverse modeling framework, representing the first analysis of CH_4 emissions in California using atmospheric observations from multiple sites across different seasons (September 2010 – June 2011). The work expands on studies by Zhao et al. [2009] and Jeong et al. [2012a] that quantified CH_4 emissions from central California using a single tower near Walnut Grove, California (WGC) by combining measurements from the additional sites in the Central Valley and including published emission estimates from the Los Angeles metropolitan area to capture emissions from California's urban regions. In Section 2, we describe the methods we employed, including atmospheric measurements, *a priori* CH_4 emissions inventories, meteorology and trajectory transport modeling, and the Bayesian inverse method. Section 3 presents results, including seasonal variation in footprints, and the inferred surface emissions of CH_4 from California for different regions and sources. Section 4 further discusses the results and presents conclusions for CH_4 emissions in California.

2. Data and Models

2.1. CH_4 Measurements and Boundary Conditions

CH_4 measurements were made at the collaborative five-site GHG network in California's Central Valley during September 2010 – June 2011: Arvin (35.24°N, 118.79°W; ARV), Madera (36.87°N, 120.01°W; MAD), Tranquility (36.63°N, 120.38°W; TRA), Sutter Buttes (39.21°N, 121.82°W; STB), and WGC (38.27°N, 121.49°W) (STB measurements are available only for May – June 2011). CH_4 measurements at WGC were made at 91 and 483 m above ground level on a tall tower, beginning in September 2007 [Andrews et al., 2013]. CH_4 measurements at 91 m were used for inverse modeling, and additional information about these measurements is provided by Zhao et al. [2009] and Jeong et al. [2012a]. All other stations measured CH_4 at ~10 m above the ground using Picarro model 2301 analyzers that were calibrated with standard gases from NOAA every six months and programmed to measure a standard gas every 11 hours in order to check the precision. After examining precision checks and removing special events (e.g., changing filters), raw data collected every few seconds are averaged into 3-hourly measurements for inverse modeling. We apply data filtering based on vertical mixing to data from WGC where vertical CH_4 profiles are available. As in Jeong et al. [2012a], data were selected such that the CH_4 mixing ratio difference ($C_{91} - C_{483}$) between 91 and 483 m fell within the range -1 sd $< (C_{91} - C_{483}) < 3$ sd, where sd is the standard deviation of the difference of the mean diurnal cycle between 1200 and 1700 local standard time (LST). For other sites, we use afternoon data (1200 – 1700 LST) when boundary layers are reasonably well developed in the Central Valley [Bianco et al., 2011]. As will be described in Section 3.1, for winter we use data during 1100 – 1600 LST due to earlier collapse of the boundary layer in simulations than in measurements. In Section 3.1, we also report results of a sensitivity test to periods with potentially low simulated boundary

layers that suggests our posterior emissions estimates are not significantly affected by inadequate mixing.

CH_4 boundary values were estimated using data from the NOAA Earth System Research Laboratory's Global Monitoring Division (ESRL/GMD) using an approach similar to the one used in Jeong et al. [2012b]. Marine boundary layer data from the Cooperative Air Sampling Network (http://www.esrl.noaa.gov/gmd/ccgg/flask.html) and vertical profile data from aircraft (http://www.esrl.noaa.gov/gmd/ccgg/aircraft/) were used to create a smoothed three-dimensional (3-D) curtain representing the Pacific boundary and varying with latitude, height and time. The NOAA aircraft data are primarily collected over North America and along the Pacific Coast. Since data along the coasts are sparse and the impact of surface fluxes on free tropospheric data is small, we have used all available aircraft data in our estimate. We ran back trajectories for all aircraft observations using the National Centers for Environmental Prediction (NCEP) reanalysis wind fields (global) and removed any observations for which the trajectories drop below 3 km above ground level. We defined a domain following the coast of North America and identified the latitude and altitude when the trajectory exits the domain. We also used aircraft data from Hawaii, which is outside the North American domain, and in that case the actual latitude and altitude of the observation were used. Data are binned according to the latitude and altitude where they exit the domain (10° latitude resolution over 20° - 70°, 1000 m vertical resolution, 3000 - 7000 m.a.s.l.). We then fit smooth curves to the binned data using the method of Thoning et al. [1989] (see also http://www.esrl.noaa.gov/gmd/ccgg/mbl/crvfit/crvfit.html). For altitudes below 1000 m.a.s.l., we use a Pacific version of the NOAA Greenhouse Gas Marine Boundary Layer Reference (http://www.esrl.noaa.gov/gmd/ccgg/mbl/) that is based on surface observations from the Cooperative Air Sampling Network and which varies with latitude and time. In the

range 1000 - 3000 m.a.s.l., values are interpolated between the Pacific Marine Boundary Layer Reference and the free-tropospheric curtain derived from the aircraft data. Time-varying uncertainty in the boundary curtain is estimated using the seasonal cycle of the root mean square of the residuals from the smoothed-curves. Average background values are computed for each footprint simulation by sampling the curtain at each of the 500 particle trajectory endpoints (near the domain boundary at 130°W) and calculating the average values. Uncertainty in the estimated background values is discussed in Section 2.5.

2.2. *A priori* CH_4 Emission Models

This work adopts the California Greenhouse Gas Emission Measurements (CALGEM) project *a priori* CH_4 emission model (henceforth CALGEM model) described by Jeong et al. [2012a], which is provided at a high spatial resolution ($0.1^o \times 0.1^o$) for California and has seasonal components for wetlands and crop agriculture [CALGEM, 2013]. Table 1 provides CALGEM emissions used in this study by source and region, which include emissions from rice agriculture and wetlands (see Figure 1 for regions). Here the high-resolution emissions were scaled to match the CARB inventory for 2008 by sector (summing to a total of 28 Tg CO_2eq for California) [CARB, 2010]. The EDGAR42 (European Commission Joint Research Centre (JRC) and Netherlands Environmental Assessment Agency, Emission Database for Global Atmospheric Research (EDGAR), release version 4.2, 2011, http://edgar.jrc.ec.europa.eu) CH_4 emission model (annual total = 38 Tg CO_2eq or 1.4 times CALGEM total) also provides high-resolution ($0.1^o \times 0.1^o$) emission maps. Table 2 shows all 16 emission source sectors from the EDGAR42 prior emission model by region, which can be compared with the CALGEM model shown in

Table 1. Bayesian inversions adjust region sums (region analysis) or source sums (source analysis) shown in Tables 1 and 2 to yield optimized (posterior) emissions.

Figure 1 shows the annual total emission maps for the CALGEM and EDGAR42 prior models along with the sub-region classification for inverse modeling. Compared with the California-specific CALGEM model, EDGAR42 generally shows a similar spatial distribution of CH_4 emissions. The CALGEM model estimates higher total emissions for the Central Valley (Regions 6, 8 and 12) than EDGAR42, mainly due to the higher estimates of dairy emissions. As shown in Tables 1 and 2, for Regions 7 and 10, which include the San Francisco Bay Area and the Southern California region, respectively, the EDGAR42 model estimates significantly higher CH_4 emissions than the CALGEM model.

Because there is no specific emission estimate for wetlands from CARB, wetland CH_4 emissions (not included in EDGAR42) for the CALGEM prior emission model were taken from monthly averages of the Carnegie-Ames-Stanford-Approach CH_4 (CASA-CH_4) model from Potter et al. [2006]. Also, seasonally varying (monthly) CH_4 emissions for crop agriculture were taken from the DeNitrification-DeComposition (DNDC) model output (assuming the 1983, high irrigation case) described by Salas et al. [2006]. The crop agriculture sector was scaled to the CARB 2008 inventory (0.54 Tg CO_2eq yr^{-1}) using the seasonal pattern from DNDC. As shown in Table 2, EDGAR42 provides an emission sector for agriculture (i.e., agricultural soils).

2.3. Atmospheric Transport Modeling

We use the coupled WRF-STILT (Weather Research and Forecasting and Stochastic Time-Inverted Lagrangian Transport) model for particle trajectory simulations [Lin et al., 2003; Skamarock et al., 2008; Nehrkorn et al., 2010]. The WRF-STILT model has been used to

constrain GHG emissions in many studies including airborne measurement-based (e.g., Gerbig et al., 2003; Kort et al., 2008) and tower measurement-based (e.g., Zhao et al., 2009; Jeong et al., 2012a; Jeong et al., 2012b) inversions. An ensemble of 500 STILT particles are run backwards in time for 7 days driven with meteorology from the WRF model (version 3.2.1) [Skamarock et al., 2008]. Hourly predicted mixing ratios based on WRF-STILT are aggregated into 3-hourly averages for inverse modeling.

The WRF model simulations closely follow those described in Jeong et al. [2012a, 2012b] with some modifications, which are summarized here. We use version 3.2.1 of the WRF model [Skamarock et al., 2008] instead of WRF2.2. Five domains (d01 – d05) of 36, 12, 4, and two 1.3 km resolutions were used in the WRF simulations. The 4-km domain (i.e., d03) was configured to represent most of California with the two 1.3-km nested domains (d04 and d05) that cover the San Francisco Bay Area and the metropolitan area of Los Angeles, respectively. In this study, we used the WRF meteorology within the d01, d02 and d03 domains to drive the STILT model because the GHG measurement sites are located in the Central Valley. The WRF model was run with two-way nesting instead of one-way nesting used in Jeong et al. [2012a, 2012b]. As in Jeong et al. [2012a, 2012b], 50 vertical levels were employed to resolve planetary boundary layer (PBL) heights over complex terrain features of California. Initial and boundary meteorological conditions were provided by the North American Regional Reanalysis (NARR) dataset [Mesinger et al., 2006]. All simulation durations were 30 hours including 6 hours of model spin up. The model also incorporated 3-D analysis nudging every three hours in the 36-km domain.

As an extension beyond the previous work, we ran the WRF model multiple times to evaluate different combinations of surface model and boundary layer schemes. The specific

combination of land surface models (LSMs) and PBL schemes that yielded the best comparison with PBL heights retrieved from the wind profilers [Bianco and Wilczak, 2002; Bianco et al., 2008] in the Central Valley varied with season and location. Here, we evaluated the WRF meteorology using data for the Sacramento (SAC), Chowchilla (CCL), Chico (CCO) and Lost Hills (LHS) sites shown in Figure 2 (see Section 2.5 for details on evaluation). For late spring through early fall, the combination of the five-layer thermal diffusion LSM (5-L LSM hereafter) and the Mellor-Yamada-Janjic (MYJ) PBL scheme [Mellor and Yamada, 1982; Janjić, 1990] performed best. For example, for the summer month of June 2010 (due to profiler data availability, 2010 data are used for some sites and months), the 5-L LSM and MYJ combination (root mean square (RMS) errors = 280 - 290 m) performed better than the Noah LSM and MYJ combination (RMS errors = 400 - 450 m) for the SAC and CCL sites. This is likely due to the fact that the 5-L LSM actively manages soil moisture as a function of season and land cover types that include irrigated soils. Thus, we use the 5-L LSM during the months of April – September that were identified as the period of the year with strong evapotranspiration (California Irrigation Management Information System, http://wwwcimis.water.ca.gov/cimis/data.jsp). The 5-L LSM scheme uses a fixed season-dependent value for the irrigated soil (i.e., irrigated cropland and pasture category) to generate an accurate boundary condition for soil moisture and hence energy balance. The one exception is that of the LHS site during late spring - early fall where the 5-L LSM and Yonsei University (YSU) PBL scheme combination performed better than the 5-L LSM and MYJ combination. For example, for June 2010, the RMS error for the 5-L LSM and MYJ combination (526 m) was significantly larger than that of the 5-L LSM and YSU combination (359 m). We speculate that the 5-L LSM may overestimate soil moisture at the LHS site, reducing PBL height in a manner

that is compensated for by the overestimation of PBL height by the YSU scheme. However, we lack the data to test this hypothesis at this time. For late fall through early spring, the Noah LSM and MYJ combination performed well because the more complicated Noah LSM handles the energy balance better when precipitation is the dominant source of moisture.

2.4. Bayesian Inverse Model

The inversion approach expands on earlier efforts by Zhao et al. [2009] and Jeong et al. [2012a; 2012b], and we express the model-measurement relation through a linear model:

$$\mathbf{c} = \mathbf{K}\boldsymbol{\lambda} + \mathbf{v}, \qquad (1)$$

where $\mathbf{c}$ is the measurement vector ($n \times 1$, n = number of measurements), which represents 3-hour mean, background-subtracted CH_4 mixing ratios, $\mathbf{K} = \mathbf{FE}$ (an $n \times k$ matrix, k is the number of regions or sources), $\mathbf{F}$ is the footprint ($n \times m$, m is the number of grid cells of 0.1° × 0.1°), $\mathbf{E}$ is emissions ($m \times k$), $\boldsymbol{\lambda}$ is a $k \times 1$ state vector for scaling factors, and $\mathbf{v}$ is a vector representing the model-data mismatch with a covariance matrix $\mathbf{R}$ ($n \times n$), i.e., $\mathbf{v} \sim N(\mathbf{0}, \mathbf{R})$ where N denotes the normal distribution. We model $\mathbf{R}$ as a diagonal matrix to represent the total variance associated with all error sources following Gerbig et al. [2003], Zhao et al. [2009], Göckede et al. [2010], and Jeong et al. [2012a; 2012b]. The uncertainty analysis, which constructs the $\mathbf{R}$ matrix, is presented in detail in the following section. Depending on the month and measurement site, we estimated the errors to be 20 - 233 ppb (~30 – 60% of the background-subtracted mean mixing ratio) to fill the diagonal elements of $\mathbf{R}$. Following the Gaussian assumptions, the posterior estimate for $\boldsymbol{\lambda}$ is

$$\boldsymbol{\lambda}_{post} = \left(\mathbf{K}^T\mathbf{R}^{-1}\mathbf{K} + \mathbf{Q}_{\lambda}^{-1}\right)^{-1}\left(\mathbf{K}^T\mathbf{R}^{-1}\mathbf{c} + \mathbf{Q}_{\lambda}^{-1}\boldsymbol{\lambda}_{prior}\right) \qquad (2)$$

where $\boldsymbol{\lambda}_{prior}$ is the *a priori* estimate for $\boldsymbol{\lambda}$ (initially set to one for all elements), and $\mathbf{Q}_{\lambda}$ is the error covariance matrix ($k \times k$) for $\boldsymbol{\lambda}$. The corresponding posterior covariance for $\boldsymbol{\lambda}$ is

$$\mathbf{V}_{post} = \left(\mathbf{K}^T \mathbf{R}^{-1} \mathbf{K} + \mathbf{Q}_{\lambda}^{-1}\right)^{-1}.$$

We apply the inversion method at a monthly temporal scale solving for $\boldsymbol{\lambda}_{post}$ for each month. We relax our assumption on prior uncertainty to 70% from the 50% uncertainty used in Jeong et al. [2012a]. We use this relaxed prior uncertainty because this analysis estimates CH_4 emissions for a much larger region with a higher uncertainty than that (i.e., central California) of Jeong et al. [2012a]. The inverse modeling approach is applied in two phases as in Bergamaschi et al. [2005] and Jeong et al. [2012a; 2012b]. After a first inversion, the second (final) inversion uses data points that are accepted by applying the selection criteria $|\mathbf{c}_i - (\mathbf{K}\boldsymbol{\lambda})_i|^2 < \alpha \mathbf{R}_i$, where α is a fixed value ($\alpha = 3$). The outlier removal rates are 4.7 – 5.1% of a total of 1659 (i.e., total size of n) observations depending on the inverse analysis. As in the first inversion, the final inversion is performed using the original *a priori* emission maps, and therefore the first inversion is used as a data selection tool for the atmospheric observations.

2.5. Uncertainty Analysis

The uncertainty in the model-measurement differences controls the relative weighting of the prior flux estimates and the measured data in the inversion, adjusting posterior CH_4 emissions relative to *a priori* emissions. Following Gerbig et al. [2003], Zhao et al. [2009], Göckede et al. [2010], and Jeong et al. [2012a], the model-measurement mismatch matrix, $\mathbf{R}$ (an $n \times n$ matrix), is represented as the linear sum of uncertainties from several sources and modeled as a diagonal matrix:

$$\mathbf{R}_i = \mathbf{S}_{part} + \mathbf{S}_{aggr} + \mathbf{S}_{bkgd} + \mathbf{S}_{transPBL} + \mathbf{S}_{transWIND},$$

where the particle number error (S_{part}) is due to the finite number of released particles at the receptor location while the aggregation error (S_{aggr}) arises from aggregating heterogeneous fluxes within a grid cell into a single average flux. The background error (S_{bkgd}) is due to the uncertainty in estimating the background contribution to the CH_4 measurements at the receptor. $\mathbf{S}_{transWIND}$ and $\mathbf{S}_{transPBL}$ represent the uncertainty in CH_4 mixing ratios caused by the errors in wind speeds and directions, and the errors in PBL heights, respectively. For the aggregation error ($\mathbf{S}_{aggr}$), we adopt the result from Jeong et al. [2012a] and use 11% of the background-subtracted mean mixing ratio. The background error ($\mathbf{S}_{bkgd}$) is estimated by combining (in quadrature) the RMS error in the estimation of the 3-D curtain (similar to that used in Jeong et al. [2012b]) and the standard error of 500 WRF-STILT background samples. Average values for S_{bkgd} were calculated for each month during September 2010 – June 2011. Recall that for each simulation time, 500 particles are released from the measurement location and tracked backwards in time for 7 days, and each particle is associated with a background value at its final location. Each background value also has an uncertainty estimate that is the time-, height-, and latitude-dependent RMS error of the residuals of the data that were used to construct the background curtain. We compute the mean RMS error over the 500 particles for each observation. The background errors were estimated to be 17 – 25 ppb depending on the season and measurement site. Only observation time points for which more than 80% of the particles reached the western boundary of the domain (130°W) were included in the study (an average of ~85% retained after the filtering with summer having the highest of >95%).

To estimate the uncertainty in predicted CH_4 mixing ratios due to errors from modeled PBL heights ($\mathbf{S}_{transPBL}$) and winds ($\mathbf{S}_{transWIND}$), we evaluated WRF model errors in winds and PBL

heights and then calculated the RMS difference in CH_4 mixing ratios obtained from simulations with and without input of an additional stochastic component of wind and PBL errors in STILT. As described previously, we evaluated PBL heights (*Zi*) and winds at four profiler sites (Figure 2): CCO, SAC, CCL, and LHS. The radar wind profiler can retrieve data in two different modes (high and low resolutions) with vertical resolutions of 60 m and 105 m, respectively. PBL heights used in this study were estimated from sub-hourly vertical velocity and returned signal strength (signal-to-noise ratio) data using the algorithms and qualitative analysis following Wyngaard and LeMone [1980], Bianco and Wilczak [2002], and Bianco et al. [2008]. The wind profiler can detect PBL heights from about 150 m to 4000 m with an accuracy of ±200 m [Dye et al., 1995]. Hourly wind (0000 – 2300 LST) and *Zi* (0800 – 1700 LST, available only during daytime) measurements from the closest profiler to the GHG measurement site were used to evaluate WRF simulations. For example, most relevant to the ARV GHG measurement site, we compared *Zi* from WRF with measurements from the LHS profiler. For the MAD and TRA GHG sites, we used wind profiler data from the CCL site. As in Zhao et al. [2009] and Jeong et al. [2012a, 2012b], we assume that the RMS scatter in predicted versus measured *Zi* can be represented as the sum of squares of measurement uncertainty (~ 200 m, Dye et al. [1995]) and WRF model uncertainty. In other words, the model uncertainty is estimated by computing the model-data RMS scatter using hourly data and subtracting an estimated measurement error (~200 m) in quadrature. When the model-data RMS error is less than 200 m, we use the calculated RMS error value for the model uncertainty. For comparison between WRF and profiler measurements, we used data for May 2010, June 2010, October 2010, and January 2011 to represent spring, summer, fall, and winter seasons, respectively. Due to data availability we used 2010 data for spring and summer except for the CCO site for which May and June 2011 data

were used. For the LHS site, we used September 2010 data for fall because the LHS profiler data were not available after September 2010. Thus, we used the result from the CCL site for the LHS site after September 2010. Based on 2008 data at the Sacramento profiler used for Jeong et al. [2012a, 2012b], we note that the RMS values in PBL depth comparison (predicted vs. measured) are high (310 to 415 m) during winter and relatively low (160 – 220 m) during summer, showing seasonal variation. The error analysis obtained in the current study exhibits similar seasonal variation (i.e., high winter error vs. low summer error) in the PBL error, suggesting posterior emission estimates likely capture variations in seasonal emissions and annual total emissions, though it is possible that transport uncertainties over the three-month seasonal periods may vary somewhat from those determined from the individual months.

The WRF simulated *Zi* was generally consistent with the measured *Zi* based on the best fit slopes (~ unity) of predicted (WRF) vs. measured (wind profiler) *Zi*. For some cases, there were slight biases based on the regression analysis of predicted vs. measured *Zi*. During June, the CCO site showed a slightly higher best-fit slope of 1.29±0.13 than unity, while the LHS site yielded a slightly lower slope of 0.8±0.04 than unity. However, when we compared the mean diurnal cycles of predicted and measured *Zi*, we found no obvious bias at the two sites. Furthermore, we calculated the difference (predicted – measured) between the predicted and measured *Zi* means which were -64±86 m (95% C.I., due to a large enough sample size (>150) uncertainty estimation based on both t and normal distributions yielded the same C.I.) and 4±60 m for the LHS and CCO sites, respectively. This indicates that the mean biases are only ~5% and ~1% of the measurement means (1222 m and 539 m) for LHS and CCO, respectively and are well within the expected measurement accuracy (~200 m) of the wind profiler [Dye et al., 1995]. Also, the result in a t test for two means showed that the difference between predicted and

measured *Zi* for both sites was not significant: t(df = 358) = 1.47 with p-value = 0.14 and t(df = 295) = -0.14 with p-value = 0.89 for LHS and CCO, respectively. Based on this analysis we are reasonably confident in assuming that random errors dominate in the following analysis.

Following Jeong et al. [2012a, 2012b], we computed CH_4 mixing ratios (C_{CH4}) based on the perturbation in *Zi* (20% decrease) to estimate the sensitivity of C_{CH4} to *Zi* (i.e., dC_{CH4}/dZi) as a first order approximation. By reducing original *Zi* from the WRF model by 20%, we obtained perturbed CH_4 mixing ratios, which are compared with the original (normal) CH_4 mixing ratio to compute dC_{CH4}. Similarly, we computed *dZi* by comparing the perturbed *Zi* and normal *Zi*. Then, we calculated the monthly mean dC_{CH4}/dZi (in units of ppb/m), which represents the gradient of CH_4 mixing ratios with respect to *Zi*. Finally, we applied the inferred RMS errors (in units of m) in the WRF-STILT model to dC_{CH4}/dZi to estimate errors (in ppb) associated with *Zi* for each season and each site. Within a given season, monthly PBL uncertainty was obtained by scaling the uncertainty value for each representative month (a total of four months) in proportion to the background-subtracted mean mixing ratio. The estimated uncertainties ranged from ~5 ppb to over 200 ppb depending on the season and site, yielding large errors during winter and relatively small errors during summer. For instance, the ARV and MAD sites with the mean background-subtracted mixing ratio of ~500 ppb in January showed large errors associated with *Zi* (~200 ppb). In June, the uncertainties due to *Zi* errors in the ARV and MAD sites were relatively small (56 and 35 ppb, respectively) although the mean mixing ratios were also low (125 and 105 ppb).

Uncertainty in modeled CH_4 mixing ratios due to errors in modeled winds was estimated by comparing WRF-simulated winds and measured winds from the four wind profiler sites (Figure 2) for a total of four selected months as in the case of *Zi*. Following Jeong et al. [2012a] and Newman et al. [2013], when we compared WRF-simulated winds with profiler-measured winds

at the available levels of profilers near the surface (~200 m above mean sea level), the RMS errors in the wind U and V components varied depending on the season and measurement location. For the SAC profiler site (most relevant to WGC), the RMS errors for the wind U/V components were 3.42 (best-fit slope of predicted vs. measured with standard error = 1.00±0.03) / 2.95 (1.13±0.02), 2.89 (1.39±0.11) / 4.96 (1.41±0.11), 3.37 (1.04±0.04) / 3.11 (1.15±0.02), and 2.87 (0.98±0.03) / 2.88(1.05±0.03) m s^{-1} for October, January, May and June, respectively. For the CCL site (most relevant to MAD and TRA), we used data for October and January only because profiler data were not available for spring and summer 2011. The RMS errors for the U/V components were 3.77 (fit slope = 0.96±0.03) / 3.48 (fit slope = 1.04±0.03) and 2.76 (1.01±0.04) /2.91 (1.32±0.05) m s^{-1} for October and January (later we used the SAC site results for the other months to perform STILT ensemble runs). We evaluated winds at the CCO site for the months of May and June 2011 when CH_4 measurements were made at the STB site near the CCO site. The wind U/V RMS errors were 4.22 (fit slope = 1.03±0.04) / 5.99 (fit slope = 1.14±0.03) and 3.17 (0.95±0.03) / 4.45 (1.06±0.03) m s^{-1} for May and June, respectively. Since profiler wind data for the LHS site were not available after early September 2010, we used results from either SAC or CCL sites to run the STILT model for error quantification. For January when WRF overestimated wind speeds relative to profiler winds, we removed outliers (data points corresponding to > 2 standard deviation of hourly measured wind speed for the month) to avoid biases in inverse analyses. To estimate the effect of uncertainty in CH_4 mixing ratios due to winds ($\mathbf{S}_{transWIND}$) and particle number ($\mathbf{S}_{part}$), we ran the STILT model 10 times and computed ensemble predicted mixing ratios for a given site and month (a total of four selected months as in the *Zi* case). Based on 10 ensemble runs, we estimated the RMS difference about the mean of the ensemble mixing ratios for each model time step and use the monthly average

RMS as the combined uncertainty due to wind and particle number errors. Following the method in Zhao et al. [2009], Jeong et al. [2012a; 2012b] and Lin and Gerbig [2005] we propagated a stochastic component due to the wind velocity error, which was estimated from the model-data wind comparison, through STILT. As in Jeong et al. [2012a, 2012b], we adopted the set-up from Lin and Gerbig [2005] where they used 240 min, 120 km, and 900 m for correlation time scale (i.e., time scale for the temporal correlation to decay to zero), horizontal correlation scale and vertical correlation scale, respectively. This approach yielded a mixing ratio variation of 1 – 15 ppb depending on the season and site. As with the *Zi* case, the errors due to winds were higher during winter (8 – 15 ppb) than during summer (~ 2 ppb).

Following Zhao et al. [2009] and Jeong et al. [2012a; 2012b], we assumed that all of the errors are independent. The errors were combined in quadrature to yield a total expected model-data mismatch error, and the total error for each site is summarized in Table 3. Depending on the month and measurement location, the errors ranged from 20 to 233 ppb, which are approximately 30 – 60% of the background-subtracted mean mixing ratio. The total error was particularly large (100 – 233 ppb) during winter in the ARV and MAD sites where the background-subtracted mean mixing ratio was also high (220 - 520 ppb).

3. Results

3.1. CH_4 Mixing Ratios

Figure 3 shows the 3-hourly measured mixing ratio, background mixing ratio and predicted (before inversion) mixing ratio using the CALGEM prior model for the five network sites. Predicted mixing ratios are shown only for the data points used in the final inversion during the well-mixed periods (noon – afternoon). For inverse analyses, we use data during 12 – 17 hours

(LST) except for winter (11 – 16 LST) during which we found that PBL tends to collapse earlier in WRF simulations than in wind profiler measurements. Based on a sensitivity test to the outlier removal, we find that there is no significant difference in the posterior emissions for the Central Valley between the first and final inversions based on the CALGEM prior (33.01±1.97 vs. 32.87±2.09 Tg CO_2eq yr^{-1}). This suggests that the small amount of data (~ 5%) that were removed do not significantly affect the posterior emissions.

Overall, the predicted mixing ratios at all sites show underestimation of CH_4 compared to the measurements although the prediction captures the synoptic variation of the measured mixing ratios (Figure 3). The minimum measured mixing ratios approximate the predicted background CH_4 well, suggesting that the estimated background mixing ratios are reasonable and there is no significant bias in the measured mixing ratios. In order to examine systematic biases in background values, we also computed the intercept from the linear regression (predicted vs. measured) for each month after subtracting background values from measured CH_4 mixing ratios. We found no significant bias in this comparison except for January, March and April, which showed intercepts (in regression coefficients) of −28.65±19.39 (= standard error), −4.78±2.92, and −4.75±2.17, respectively. These values are small compared to the background-subtracted mean mixing ratio for the corresponding month, and did not affect inversion results significantly. The result also shows that there is a clear seasonal variation in CH_4 mixing ratios with high variability, particularly in winter while ARV and MAD show high variability throughout the seasons. The comparison result in STB indicates that the prior emissions from rice agriculture during late spring and early summer are significantly lower than actual emissions. The CALGEM prior estimate for crop agriculture based on the DNDC model suggests that CH_4 emissions from rice agriculture in Region 6 become strong starting in June with an

emission sum of 3.4 Tg CO_2eq yr^{-1} and peaking in August with emissions equating to 4.6 Tg CO_2eq yr^{-1}. We discuss more on rice emissions later in Section 3.3. For WGC, the predicted mixing ratios are significantly lower than the measurements, showing similar results to those shown in Jeong et al. [2012a].

3.2. Footprints

We present the first analysis of footprints that constrain most of California's Central Valley and its surrounding areas across different seasons. When footprints for all five sites are combined, the sensitivity of the measurement sites to surface emissions is significantly improved, as compared to the result with one site only. Figure 4 shows the average footprint from the multiple sites during September 2010 – June 2011, including the average footprint (May – June 2011) using a single site (i.e., WGC) for comparison. The significance of the multi-site network is clear in the figure where the averaged footprint from a single tower shows limited sensitivity while the footprint from the multiple sites shows strong sensitivity in the entire Central Valley. Although the measurement network significantly expands the area that is constrained, the network in the Central Valley shows limited ability to constrain CH_4 emissions in the Southern California region due to weak sensitivity.

Because measurements at STB were available only during May – June 2011, STB footprints were not simulated for other seasons. There is a clear seasonal pattern for the distribution of footprints, which is important to attribute mixing ratios to different emission sources for each season. Overall, the seasonal footprints are strong in the north-south direction in the Central Valley although footprints are strong in the west-east direction near the WGC site for some seasons. Depending on the season, footprints allow for constraining important urban emissions (e.g., South Coast Air Basin).

3.3. Bayesian Inverse Analysis

Bayesian inverse analysis was conducted using two independent prior emission models: CALGEM and EDGAR42 emission models. Using each emission model, we performed Bayesian inversion to estimate optimized emissions for 1) the 14 regions defined in Figure 1 (region analysis) and 2) individual emission source sectors (source analysis). For the region analysis, we solve for a total of 14 scaling factors (i.e., dimension of $\boldsymbol{\lambda} = 14 \times 1$) for each month including the region outside California for both emission models. The dimensions of $\boldsymbol{\lambda}$ for the source analysis (for each month) are 9×1 (i.e., 8 sectors and outside California) and 17×1 (16 EDGAR sectors and outside California) for the CALGEM and EDGAR42 cases, respectively.

Table 4 summarizes the chi-square linear analysis results where we show the best-fit slopes (with standard error) of predicted vs. measured CH_4 mixing ratios before (prior) and after (posterior) Bayesian region inversion [Press et al., 1992]. The best-fit slopes were obtained using the data from all sites for a given month, reflecting the aggregate regression of predicted vs. measured mixing ratios. The posterior results in Table 4 were obtained by applying Equations 1 and 2 in Section 2.4. Predicted CH_4 mixing ratios using the CALGEM emission model are typically 30 – 50% of measurements before inversion while EDGAR42-based prior mixing ratios are 20 – 40% of measurements. After inversion, the posterior CH_4 mixing ratios based on the CALGEM emission model are consistent with the measurements for most of the months, while the posterior mixing ratios from EDGAR42 are still lower than the measurements. To further examine the low best-fit slopes of posterior predictions vs. measurements based on EDGAR42, we conducted an inversion using 100% uncertainty in the prior. We find that the inversion still yields best-fit slopes of posterior predictions vs. measurements that are lower than unity (0.80–0.94) although the best-fit slopes based on the 100% uncertainty assumption are slightly higher

than those of the 70% assumption in the prior uncertainty. This suggests that the spatial distribution of CH_4 emissions in California is not well represented by EDGAR42. The counterpart source analysis showed a similar result where EDGAR-based mixing ratios are lower than those of the CALGEM case.

Inversions are performed at the monthly temporal scale, and inferred CH_4 emissions are reported by season (five bi-monthly seasons during September 2010 – June 2011) for the regions and source sectors where the total emissions are significant and footprints show sensitivity (Figure 5). Figure 5(a) shows the Bayesian region analysis result (solving $\boldsymbol{\lambda}$ for each region) using the CALGEM prior emission model. Overall, the inversion results show that actual CH_4 emissions are higher than the prior emissions for most of the regions. In particular, the posterior (optimized) emissions are significantly higher than the prior in the Central Valley (Regions 6, 8, and 12) where measurements are made and thus the emissions are well constrained. For Region 10 (Southern California region), the posterior uncertainties are only slightly reduced, suggesting that the measurements in the Central Valley weakly constrain the emissions in Region 10 (see Table 5 for details). The significantly higher posterior emissions in the San Joaquin Valley (Regions 8 and 12) suggest that emissions from the livestock source sector are significantly higher than the prior. Note that livestock emissions from the CALGEM emission model account for 87% (4.33 Tg CO_2eq) and 84% (6.77 Tg CO_2eq) of the total emissions in Regions 8 and 12, respectively. The results also show that there is a clear seasonal variation in CH_4 emissions. For example, in Region 6 where high emissions are expected from rice agriculture, the posterior emissions are high during the early fall and late spring - early summer seasons. We discuss more on rice emissions later in the section.

We also performed Bayesian region analysis based on the EDGAR42 emission model (Figure 5(b)) and compare the result with the CALGEM case (shown in Figure 5(a)). In Table 5, we summarized annual CH_4 emissions from the Bayesian region analyses based on the CALGEM and EDGAR42 prior emission models, including the aggregated uncertainty for the entire state as well as that of each region. For the uncertainty in state total emissions, we report the uncertainty using two error assumptions: uncorrelated (only including diagonal elements of the posterior error covariance matrix) and correlated (also including off-diagonal elements) errors among the regions. As shown in Table 5, the correlated error assumption yields slightly smaller aggregated uncertainty than that of the uncorrelated assumption. This is because there are anti-correlations (i.e., negative correlation coefficients, Tarantola [1987]) between some of the regions as reported by Jeong et al. [2012a] and Bergamaschi et al. [2005]. Bergamaschi et al. [2005] showed slightly smaller aggregated uncertainty in the correlated error estimation than in the uncorrelated error estimation. Hereafter, we only report more conservative uncertainty estimates (i.e., based on the uncorrelated error assumption) to consider potential uncertainties (e.g., uncaptured transport uncertainty) that we may not have identified although some of the regions may have correlated errors. Also, we note that we have not defined the correlations between regions to construct the prior error covariance for $\boldsymbol{\lambda}$. This might affect posterior uncertainty estimation and needs to be investigated further in future studies.

The region analysis results in Table 5 (also in Figures 5(a) and 5(b)) show that the current measurement network estimates annual average CH_4 emissions for the Central Valley (i.e., Regions 6, 8 and 12) to be 32.87±2.09 (prior = 15.09) Tg CO_2eq and 31.60±2.17 (prior = 10.79) Tg CO_2eq based on the CALGEM and EDGAR42 prior emission models respectively, assuming uncorrelated errors between regions. This suggests that the measurement network constrains

emissions in the Central Valley, independent of *a priori* emission models. However, the posterior emission estimates based on the EDGAR42 and CALGEM prior models are only marginally consistent in the predominantly urban regions (7 and 10) where the EDGAR42 model yields higher CH_4 emissions than those estimated with the CALGEM model: 29.11±11.59 vs. 12.92±6.08 Tg CO_2eq yr^{-1}. This is because the EDGAR42 emissions are significantly higher than the CALGEM emissions in Regions 7 and 10 (23.7 vs. 10.5 Tg CO_2eq yr^{-1}, see Tables 1 and 2), and our measurement sites in the Central Valley have relatively weak sensitivity to the urban regions. Although the results using multiple emission models help to characterize the uncertainty associated with estimating emissions at the sub-regional scale, these results demonstrate that additional measurements are required in the San Francisco Bay and Southern California areas in order to strongly constrain emissions from those urban regions.

We also estimate CH_4 emissions by inferring state-wide scaling factors for each emission source instead of each sub-region. Figure 5(c) shows the source analysis results using the CALGEM emission model. These results are consistent with those of the counterpart inverse analysis for regional emissions. For example, the source inversion suggests that actual emissions from livestock are much higher than the prior. Recall that the region analysis result showed higher posterior emissions in Regions 8 and 12 where livestock emissions are dominant (~90% of annual CH_4 emissions). Figure 5(c) indicates that CH_4 emissions from natural gas sources are generally higher than the prior. However, more measurements are required to effectively constrain natural gas emissions from the large urban areas (Regions 7 and 10), which account for 64% of the total natural gas emissions in the CALGEM model (urban ratio for natural gas in EDGAR42 = 76%).

The source analysis result also indicates that the posterior emissions for crop agriculture are higher during early fall and late spring-summer seasons than the prior, which are consistent with the region analysis (higher emissions in Region 6). Our result is similar to that of a recent study based on aircraft CH_4 measurements during the California Research at the Nexus of Air Quality and Climate Change (CalNex) period in summer 2010 [Peischl et al., 2012]. Peischl et al. [2012] estimated annual CH_4 emissions from rice cultivation to be 1.64 – 1.95 Tg CO_2eq, which is 3.0 – 3.6 times larger than the CARB 2008 inventory for rice CH_4 emissions (0.54 Tg CO_2eq yr^{-1}). This estimate by Peischl et al. [2012] is based on the rice emission study in a commercial rice field by McMillan et al. [2007] where they estimated annual CH_4 emissions of 26.1 – 31.0 g CH_4-C m^{-2} during October 2001 – October 2002. Assuming posterior emissions for July and August (not available in our study) are proportional to the prior and scaling (available) June posterior emissions according to the prior ratios of July and August to June (3.26 Tg CO_2eq / 3.59 Tg CO_2eq and 5.10 / 3.59, respectively), we find that the annual rice emission total is 1.43±0.19 Tg CO_2eq (original DNDC prior for rice = 1.34 Tg CO_2eq), which is very similar to that of Peischl et al. [2012]. The slight difference between the estimate by Peischl et al. [2012] and our estimate is possibly due to the difference in emissions during late fall and winter. CH_4 emissions during late fall and winter from McMillan et al. [2007] are not negligible while our *a priori* rice emissions based on the DNDC model described by Salas et al. [2006] are insignificant and often negative.

The source analysis results based on EDGAR42 are shown in Figure 5(d), where eight major sources (~95% of total emissions) out of a total of 16 sources are compared. While posterior emissions from livestock for the entire state are similar between the CALGEM (32.23±2.92 Tg CO_2eq) and EDGAR42 (33.60±3.72 Tg CO_2eq) models, the source analysis based on EDGAR42

shows different posterior emissions for some of the source sectors, compared to the CALGEM case. In particular, the state-wide annual CH_4 emission for solid waste (equivalent to landfill of the CALGEM model) based on the EDGAR42 prior model is 23.38±6.47 Tg CO_2eq, which is only marginally consistent with that (14.43±3.92) estimated using the CALGEM model. This is likely due to the fact that ~70% of landfill emissions are concentrated in the urban regions (Regions 7 and 10), and these urban regions are only weakly constrained by the measurements in the Central Valley.

4. Discussion and Conclusions

The current GHG network constrains annual CH_4 emissions from California's Central Valley to be 32.87±2.09 Tg CO_2eq and 31.60±2.17 Tg CO_2eq based on the CALGEM and EDGAR42 prior models respectively, showing consistency between the two independent prior emission models. However, as noted above, our region analysis estimates state total annual CH_4 emissions to be 1.51±0.20 times and 2.03±0.37 times (Table 5) the current CARB inventory (32 Tg CO_2eq; CARB, 2011) using the CALGEM and EDGAR42 priors, respectively. This suggests that uncertainty in the state total emission estimates are dominated by uncertainty in emissions from the urban regions.

To address the uncertainty in state total emissions by constraining urban emissions based on published work, we consider a range of emission estimates for the larger Los Angeles metropolitan area (hereafter SoCAB). All relevant studies in SoCAB use correlations of CH_4 to CO enhancements and CO emission inventories to estimate CH_4 emissions [Hsu et al., 2010; Wennberg et al., 2012; Peischl et al., 2013]. Here, we apply the results from Wennberg et al. [2012], which provide a more conservative estimate (0.44±0.15 Tg CH_4 yr^{-1}) for SoCAB than

those of Hsu et al. [2010] (0.38±0.10 Tg CH_4 yr^{-1}, recalculated by Wennberg et al. [2012]) and Peischl et al. [2013] (0.41±0.04 Tg CH_4 yr^{-1}). This estimate of urban emissions is 0.91 to 1.84 times the CALGEM prior for SoCAB but a factor of 0.45 to 0.91 times SoCAB emissions in EDGAR42, which taken together with results from the Central Valley suggest that CALGEM provides a superior representation of California CH_4 emissions. Here, we estimate state total CH_4 emissions as the sum of our posterior emission estimates for the Central Valley and other non-urban regions (33.24 – 37.63 Tg CO_2eq yr^{-1}) and the CALGEM prior emissions for major urban regions (10.45 Tg CO_2eq yr^{-1}) scaled by a factor ranging from 0.91 to 1.84 from the above comparison with Wennberg et al [2012]. This yields annual state total emissions of 42.75 Tg CO_2eq yr^{-1} (= 33.24 + 10.45 × 0.91) to 56.86Tg CO_2eq yr^{-1} (= 37.63 + 10.45 × 1.84), suggesting that California total emissions are 1.34 to 1.78 times the current CARB CH_4 inventory.

We also note that the primary source of uncertainty is due to under-sampling of urban regions, not temporal coverage. For example, when we compare the 10-month case (without July and August) with the full year case based on the results from Jeong et al. [2012a] that analyzed a full year of data from the Central Valley, we do not find a significant difference (13.0±2.0 vs. 14.1±2.2 Tg CO_2eq yr^{-1}) for the regions (Regions 6, 7 and 8) near the WGC tower.

In conclusion, our measurements constrain annual mean CH_4 emissions from California's Central Valley and state total emissions when combined with independent estimates from urban regions. In the future, we expect that additional tower measurements in the San Francisco Bay and Southern California areas will be effective in constraining urban emissions and that measurements of source specific tracers (e.g., CO, VOCs, and potentially CH_4 isotopes) will help separate different sources of CH_4 [Townsend-Small et al., 2012; Peischl et al., 2013].

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References

Andrews, A. E., J. D. Kofler, M. E. Trudeau, J. C. Williams, D. H. Neff, K. A. Masarie, D. Y. Chao, D. R. Kitzis, P. C. Novelli, C. L. Zhao, E. J. Dlugokencky, P. M. Lang, M. J. Crotwell, M. L. Fischer, J. T. Lee, D. D. Baumann, A. R. Desai, C. O. Stanier, S. F. J. de Wekker, D. E. Wolfe, J. W. Munger, M. J. Parker, and P. P. Tans (2013), CO_2, CO and CH_4 measurements from the NOAA Earth System Research Laboratory's tall tower greenhouse gas observing network: instrumentation, uncertainty analysis and recommendations for future high-accuracy greenhouse gas monitoring efforts, Atmospheric Measurement Techniques Discussions, 6, 1461–1553.

Bergamaschi, P., M. Krol, F. Dentener, A. Vermeulen, F. Meinhardt, R. Graul, M. Ramonet, W. Peters, and E. J. Dlugokencky (2005), Inverse modelling of national and European CH_4 emissions using the atmospheric zoom model TM5. Atmos. Chem. Phys., 5, 2431–2460.

Bianco, L., and J. Wilczak (2002), Convective boundary-layer depth: improved measurement by Doppler radar wind profile using fuzzy logic methods. J. Atmos. Oceanic Tech., 19, 1745-1758.

Bianco, L., J. Wilczak, and A. White (2008), Convective boundary layer depth estimation from wind profilers: statistical comparison between an automated algorithm and expert estimations. J. of Atmos. and Oceanic Tech., 25, 1397–1413, DOI: 10.1175/2008JTECHA981.1

Bianco, L., I. V. Djalalova, C. W. King, and J. M. Wilczak (2011), Diurnal evolution and annual variability of boundary-layer height and its correlation to other meteorological variables in California's Central Valley, Boundary-Layer Meteorology, 140, 491-511, DOI 10.1007/s10546-011-9622-4, 1-21.

CALGEM (2013), California Greenhouse Gas Emissions Measurement Project emissions maps (http://calgem.lbl.gov/prior_emission.html, document: CA-CH4-CALGEM-v2.1-20121221.zip).

CARB (2010), California Greenhouse Gas Emissions Inventory. California Air Resources Board Staff Report (personal communication, document: ghg_inventory_by_sector_00-08_2010-05-12.xls).

CARB (2011), California Greenhouse Gas Emissions Inventory. California Air Resources Board Staff Report (http://www.arb.ca.gov/cc/inventory/inventory.htm, document: ghg_inventory_by_ipcc_00-09_2011-10-26.xls).

Dye, T.S., C. G. Lindsey, and J. A. Anderson (1995), Estimates of mixing depth from "boundary layer" radar profilers. Preprints from the 9th Symposium on Meteorological Observations and Instrumentation, Charlotte, NC, March 27-31, 156-160 (STI-94212-1451).

Gerbig, C, J. Lin, S. Wofsy, B. Daube, A. E. Andrews, B. Stephens, P. S. Bakwin and C. Grainger (2003), Toward constraining regional-scale fluxes of CO_2 with atmospheric observations over a continent: 2. Analysis of COBRA data using a receptor-oriented framework. J. Geophys. Res., 108(D24), doi:10.1029/2003JD003770.

Gimson, N. R. and Uliasz, M. (2003), The determination of agricultural methane emissions in New Zealand using receptor-oriented modeling techniques. Atmos. Environ., 37, 3903-3912.

Göckede, M., A. M. Michalak, D. Vickers, D. P. Turner, and B. E. Law (2010), Atmospheric inverse modeling to constrain regional-scale CO_2 budgets at high spatial and temporal resolution. J. Geophys. Res., 115, D15113, doi:10.1029/2009JD012257.

Hofman, D. J., J. H. Butler, E. J. Dlugokencky, J. W. Elkins, K. Masarie, S. A. Montzka, and P. Tans (2006), The role of carbon dioxide in climate forcing from 1979 - 2004: Introduction of the Annual Greenhouse Gas Index. Tellus B, 58B, 614-619.

Houweling, S., T. Kaminski, F. Dentener, J. Lelieveld, and M. Heimann (1999), Inverse modeling of methane sources and sinks using the adjoint of a global transport model. J. Geophys. Res., 104(D21), 26137-26160.

Hsu, Y.-K., T. VanCuren, S. Park, C. Jakober, J. Herner, M. FitzGibbon, D. R. Blake, and D. D. Parrish (2010), Methane emissions inventory verification in southern California, Atmos. Environ., 44, 1 – 7, doi:10.1016/j.atmosenv.2009.10.002.

IPCC (1995), IPCC Second Assessment Report (SAR), “Climate Change 1995”.

Janjic, Z. I. (1990), The step-mountain coordinate: physical package. Mon. Weather Rev., 118, 1429–1443.

Jeong, S., C. Zhao, A. E. Andrews, L. Bianco, J. M. Wilczak, and M. L. Fischer (2012a), Seasonal variation of CH_4 emissions from central California. J. Geophys. Res., 117, D11306, doi:10.1029/2011JD016896.

Jeong, S., C. Zhao, A. E. Andrews, E. J. Dlugokencky, C. Sweeney, L. Bianco, J. M. Wilczak, and M. L. Fischer (2012b), Seasonal variations in N_2O emissions from central California. Geophys. Res. Lett., 39, L16805, doi:10.1029/2012GL052307.

Kort, E. A., J. Eluszkiewicz, B. B. Stephens, J. B. Miller, C. Gerbig, T. Nehrkorn, B. C. Daube, J. O. Kaplan, S. Houweling, and S. C. Wofsy (2008), Emissions of CH_4 and N_2O over the United States and Canada based on a receptor-oriented modeling framework and COBRA-NA atmospheric observations. Geophy. Res. Lett., 35, L18808, doi:10.1029/2008GL034031.

Lin, J. C., and C. Gerbig (2005), Accounting for the effect of transport errors on tracer inversions, Geophys. Res. Lett., 32, L01802, doi:10.1029/2004GL021127.

Lin, J. C., C. Gerbig, S. C. Wofsy, A. E. Andrews, B. C. Daube, K. J. Davis, and C. A. Grainger (2003), A near-field tool for simulating the upstream influence of atmospheric observations: The Stochastic Time-Inverted Lagrangian Transport (STILT) model. J. Geophys. Res., 108(D16), 4493, doi:10.1029/2002JD003161.

McMillan, A. M. S., M. L. Goulden, and S. C. Tyler (2007), Stoichiometry of CH_4 and CO_2 flux in a California rice paddy, J. Geophys. Res., 112, G01008, doi:10.1029/2006JG000198.

Mellor G. L. and T. Yamada (1982), Development of a turbulence closure model for geophysical fluid problems. Rev. Geophys. Space Phys. 20, 851–875.

Mesinger, F., G. DiMego, E. Kalnay, K. Mitchell, P. C. Shafran, W. Ebisuzaki, D. Jovic, J. Woollen, E. Rogers, E. H. Berbery, M. B. Ek, Y. Fan, R. Grumbine, W. Higgins, H. Li, Y. Lin, G. Manikin, D. Parrish, and W. Shi (2006), North American Regional Reanalysis. Bull. Amer. Meteor. Soc., 87 (3), 343-360.

Montzka, S. A., E. J. Dlugokencky1, and J. H. Butler (2011) Non-CO_2 greenhouse gases and climate change. Nature, 476, 43-50.

Nehrkorn, T., J. Eluszkiewicz, S. C. Wofsy, J. C. Lin, C. Gerbig, M. Longo, and S. Freitas (2010), Coupled weather research and forecasting - stochastic time-inverted lagrangian transport (WRF-STILT) model. Meteor. Atmos. Phys., 107 (1), 51-64, doi:10.1007/s00703-010-0068-x.

Newman, S., S. Jeong, M. L. Fischer, X. Xu, C. L. Haman, B. Lefer, S. Alvarez, B. Rappenglueck, E. A. Kort, A. E. Andrews, J. Peischl, K. R. Gurney, C. E. Miller, and Y. L. Yung (2013), Diurnal tracking of anthropogenic CO_2 emissions in the Los Angeles basin megacity during spring 2010, Atmos. Chem. Phys., 13, 4359–4372, doi:10.5194/acp-13-4359-2013.

Peischl, J., et al. (2012), Airborne observations of methane emissions from rice cultivation in the Sacramento Valley of California, J. Geophys. Res., 117, D00V25, doi:10.1029/2012JD017994.

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

Potter, C., S. Klooster, S. Hiatt, M. Fladeland, V. Genovese and P. Gross (2006), Methane Emissions from Natural Wetlands in the United States: Satellite-Derived Estimation Based on Ecosystem Carbon Cycling. Earth Interactions, 10, 1–12.

Press, W. H., S. A.Teukolsky, W. T. Vetterling, and B.P. Flannery (1992), Numerical Recipes in C, 2nd edition. Cambridge: Cambridge University Press.

Salas, W., P. Green, S. Frolking, C. Li and S. Boles (2006), Estimating Irrigation Water Use for California Agriculture: 1950s to Present. California Energy Commission, PIER Energy-Related Environmental Research. CEC-500-2006-057.

Skamarock, W.C., J. B. Klemp, J. Dudhia, D.O. Gill, D. M. Barker, X. Z. Huang, W. Wang, and J. G. Powers (2008), A description of the advanced research WRF version 3. Technical Note 475+STR. Mesoscale and Microscale Meteorology Division, NCAR, Boulder, Colorado.

Tarantola, A. (1987), Inverse Problem Theory Methods for Data Fitting and Model Parameter Estimation, 613 pp., Elsevier, New York.

Thoning, K.W., P. P. Tans, and W. D. Komhyr (1989), Atmospheric carbon dioxide at Mauna Loa Observatory, 2. Analysis of the NOAA/GMCC data, 1974 - 1985, J. Geophys. Res., 94, 8549 - 8565.

Townsend-Small, A., S. C. Tyler, D. E. Pataki, X. Xu, and L. E. Christensen (2012), Isotopic measurements of atmospheric methane in Los Angeles, California, USA: Influence of "fugitive" fossil fuel emissions, J. Geophys. Res., 117, D07308, doi:10.1029/2011JD016826.

Wennberg, P. O., W. Mui, D Wunch, E. A. Kort, D. R. Blake, E. L. Atlas, G. W. Santoni, S. C. Wofsy, G. S. Diskin, S. Jeong, and M. L. Fischer (2012), On the Sources of Methane to the Los Angeles Atmosphere. Environ. Sci. Technol., 46 (17), 9282 - 9289, doi:10.1021/es301138y.

Wyngaard, J. C., and M. A. LeMone (1980), Behavior of the refractive index structure parameter in the entraining convective boundary layer, J. Atmos. Sci., 37, 1573–1585.

Zhao, C., A. E. Andrews, L. Bianco, J. Eluszkiewicz, A. Hirsch, C. MacDonald, T. Nehrkorn, and M. L. Fischer (2009), Atmospheric inverse estimates of methane emissions from Central California. J. Geophys. Res., 114, D16302, doi:10.1029/2008JD011671.

Tables

Table 1. Annual CALGEM CH_4 Emissions by Region and Sector (Tg CO_2eq)[a]

Sector	Region													Sector Total
	R01	**R02**	**R03**	**R04**	**R05**	**R06**	**R07**	**R08**	**R09**	**R10**	**R11**	**R12**	**R13**	
Crop agriculture	0.00	0.00	0.00	0.01	0.00	0.50	0.00	0.01	0.00	0.00	0.01	0.00	0.02	**0.54**
Landfill	0.02	0.04	0.11	0.08	0.03	0.46	0.87	0.19	0.34	4.00	0.10	0.29	0.06	**6.60**
Dairy livestock	0.00	0.00	0.01	0.10	0.01	0.36	0.08	3.79	0.02	1.71	0.03	5.77	0.01	**11.90**
Non-dairy livestock	0.03	0.10	0.11	0.06	0.17	0.19	0.12	0.54	0.11	0.64	0.07	1.00	0.03	**3.17**
Natural gas	0.00	0.01	0.04	0.02	0.01	0.33	0.33	0.10	0.05	0.91	0.02	0.11	0.03	**1.95**
Petroleum	0.00	0.00	0.05	0.00	0.00	0.03	0.05	0.02	0.07	0.19	0.00	0.71	0.00	**1.13**
Wastewater	0.00	0.09	0.02	0.01	0.00	0.03	0.17	0.08	0.06	1.33	0.01	0.11	0.01	**1.92**
Wetland	0.01	0.00	0.00	0.00	0.22	0.18	0.03	0.27	0.01	0.03	0.01	0.02	0.01	**0.79**
Region Total	**0.06**	**0.24**	**0.34**	**0.28**	**0.44**	**2.08**	**1.65**	**5.00**	**0.66**	**8.81**	**0.25**	**8.01**	**0.17**	**28.00**

[a]Assumed a global warming potential of 21 g CO_2eq/g CH_4 [IPCC, 1995].

Table 2. Annual EDGAR42 CH_4 Emissions by Region and Sector (Tg CO_2eq)

Sector	Region													Sector Total
	R01	**R02**	**R03**	**R04**	**R05**	**R06**	**R07**	**R08**	**R09**	**R10**	**R11**	**R12**	**R13**	
Agricultural waste and burning	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	**0.02**
Energy manufacturing transportation	0.00	0.00	0.01	0.00	0.00	0.03	0.08	0.01	0.01	0.26	0.00	0.03	0.01	**0.44**
Enteric fermentation	0.05	0.24	0.24	0.14	0.35	0.37	0.31	1.38	0.27	1.18	0.15	2.44	0.09	**7.22**
Fugitive from solid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Gas production and distribution	0.01	0.02	0.11	0.04	0.02	0.86	2.05	0.29	0.29	5.90	0.04	0.74	0.13	**10.50**
Industrial process and product use	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.06	0.00	0.00	0.00	**0.10**
Manure management	0.02	0.03	0.02	0.02	0.04	0.04	0.10	0.71	0.04	0.92	0.02	0.38	0.01	**2.34**
Oil production and refineries	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.03	0.15	0.00	0.12	0.00	**0.45**
Residential	0.00	0.01	0.02	0.01	0.00	0.04	0.08	0.03	0.03	0.24	0.01	0.05	0.02	**0.54**
Road transportation	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.01	0.00	0.18	0.00	0.01	0.00	**0.29**
Solid waste disposal	0.02	0.06	0.23	0.12	0.05	0.88	2.24	0.49	0.34	6.92	0.08	0.81	0.16	**12.39**
Wastewater	0.00	0.00	0.03	0.01	0.00	0.19	0.63	0.09	0.08	2.14	0.01	0.13	0.03	**3.34**
Agricultural soils	0.00	0.01	0.01	0.00	0.01	0.17	0.02	0.15	0.00	0.02	0.00	0.28	0.01	**0.68**
Non-road transportation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Fossil fuel fires	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Large scale biomass burning	0.00	0.00	0.02	0.02	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	**0.10**
Region Total	**0.10**	**0.37**	**0.68**	**0.34**	**0.47**	**2.62**	**5.73**	**3.16**	**1.11**	**17.99**	**0.31**	**5.01**	**0.46**	**38.34**

Table 3. Summary of Estimated Model-Data Mismatch Uncertainty by Site (ppb)

Site	Month									
	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
ARV	61	48	53	144	218	112	111	76	46	61
MAD	61	64	98	150	233	100	77	53	34	41
TRA	58	57	100	110	148	73	44	35	30	32
STB	NA	NA	NA	NA	NA	NA	NA	NA	21	29
WGC	25	27	29	86	128	53	31	22	20	22

Table 4. Linear Regression Analysis (Predicted vs. Measured CH_4 Mixing Ratios) Results Before and After Bayesian Region Inversion

		Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Before Inversion (prior)[e]											
CA[a]	Slope[c]	0.47±0.02	0.56±0.04	0.49±0.03	0.51±0.04	0.38±0.04	0.33±0.03	0.37±0.02	0.43±0.02	0.45±0.02	0.53±0.04
	RMSE[d]	70	70	117	153	283	126	102	78	52	52
ED42[b]	Slope	0.28±0.03	0.43±0.05	0.31±0.02	0.35±0.04	0.26±0.03	0.29±0.03	0.24±0.02	0.26±0.01	0.31±0.02	0.42±0.04
	RMSE	90	73	137	168	312	133	114	90	61	54
After Inversion (posterior)											
CA	Slope	0.97±0.04	0.98±0.07	0.95±0.05	0.98±0.08	0.99±0.1	0.81±0.07	0.96±0.05	0.99±0.04	1.01±0.04	0.96±0.05
	RMSE	35	51	78	118	164	86	63	44	30	32
ED42	Slope	0.83±0.05	0.88±0.07	0.83±0.04	0.89±0.08	0.85±0.08	0.73±0.06	0.82±0.05	0.87±0.03	0.92±0.04	0.85±0.07
	RMSE	45	46	74	121	168	88	69	44	34	37

[a]CALGEM prior emission model

[b]EDGAR42 prior emission model

[c]Best-fit slope of predicted vs. measured mixing ratios with standard error

[d]Root mean square error in units of ppb

[e]Results after outlier removal

Table 5. Comparison of Annual Posterior CH_4 Emissions (Tg CO_2eq) between CALGEM-based and EDGAR42-based Bayesian Region Analysis

Prior Model	Emission	Region													Total
		R01	R02	R03	R04	R05	R06	R07	R08	R09	R10	R11	R12	R13	
CALGEM	Prior Emissions	0.06	0.24	0.34	0.28	0.44	2.08	1.65	5.00	0.66	8.81	0.25	8.01	0.17	**28.00**
	Prior Uncertainty[a]	0.04	0.17	0.24	0.20	0.31	1.46	1.15	3.50	0.46	6.17	0.18	5.61	0.12	**9.26**[b]
	Posterior Emissions	0.06	0.24	0.39	0.29	0.44	4.53	3.01	8.57	0.70	9.90	0.29	19.78	0.16	**48.35**
	Posterior Uncertainty[c]	0.04	0.17	0.24	0.20	0.29	0.63	1.00	1.27	0.46	6.00	0.17	1.54	0.11	**6.47**[d] **(6.27)**[e]
EDGAR42	Prior Emissions	0.10	0.37	0.68	0.34	0.47	2.62	5.73	3.16	1.11	17.99	0.31	5.01	0.46	**38.34**
	Prior Uncertainty[a]	0.07	0.26	0.48	0.24	0.33	1.83	4.01	2.21	0.78	12.59	0.22	3.51	0.32	**14.02**[b]
	Posterior Emissions	0.10	0.39	0.78	0.36	0.51	5.72	8.52	7.99	1.23	20.59	0.38	17.89	0.51	**64.97**
	Posterior Uncertainty[c]	0.07	0.26	0.47	0.24	0.33	0.96	1.97	1.20	0.77	11.43	0.21	1.53	0.32	**11.85**[d] **(11.57)**[e]

[a]70% uncertainty in priors

[b]Square root of sum of squares of prior uncertainty for each region

[c]Posterior uncertainty = 1σ

[d]This uncertainty is calculated based on the uncorrelated error assumption between the regions.

[e]This uncertainty in parentheses is calculated based on the propagation of correlated errors using the posterior error covariance matrix as:

$\sigma_e^2 = \sum_i^n (e_i \sigma_i)^2 + \sum_i^n \sum_{j(j \neq i)}^n e_i e_j \rho_{ij} \sigma_i \sigma_j$ where σ_e is the aggregated emission uncertainty, n is the number of regions (i.e., n = 13), e_i (or e_j) is the prior emission for each region, σ_i (or σ_j) is the posterior scaling factor uncertainty for each region from the posterior error covariance matrix, and ρ_{ij} is the correlation coefficient ($-1 \leq \rho_{ij} \leq 1$) between regions i and j.

Figures

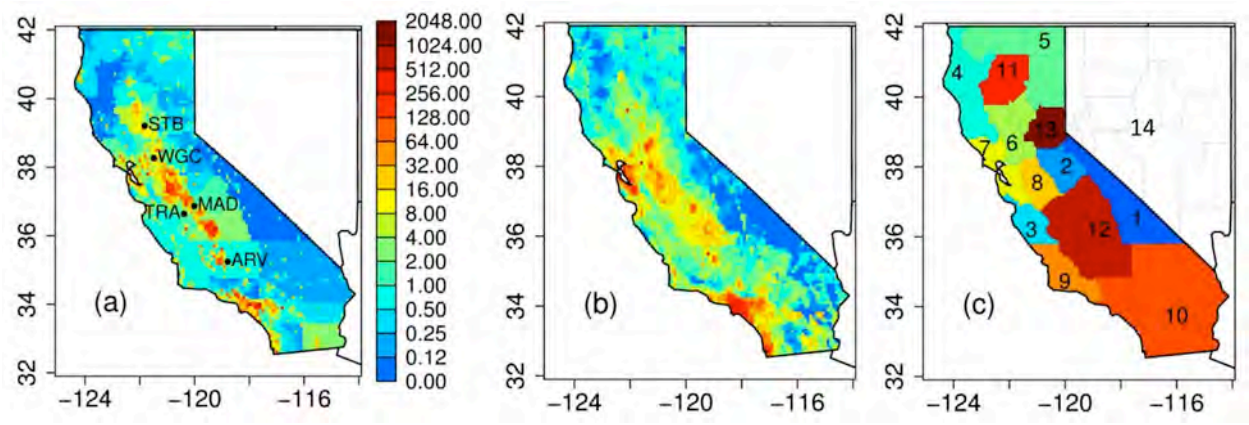


Figure 1. (a) CALGEM total CH_4 emissions (nmol m^{-2} s^{-1}) with network measurement locations (black dots), (b) EDGAR42 total CH_4 emissions (nmol m^{-2} s^{-1}), and (c) 14 sub-region classification for inverse modeling including the region outside California (Region 14).

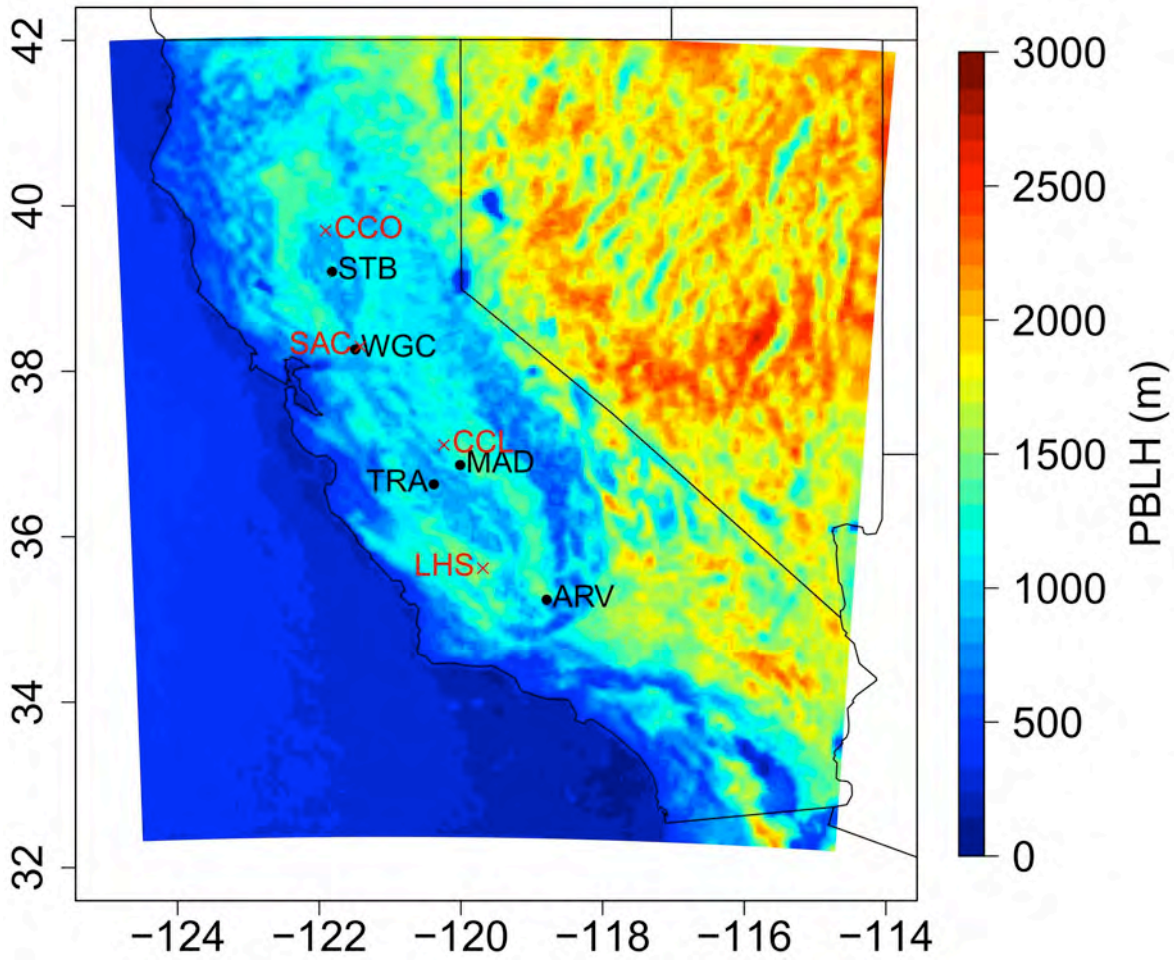


Figure 2. Location of GHG measurement sites (black) and wind profiler sites (red) in the Central Valley with predicted monthly mean PBL heights (m) for June 2011, 14:00 LST shown in color.

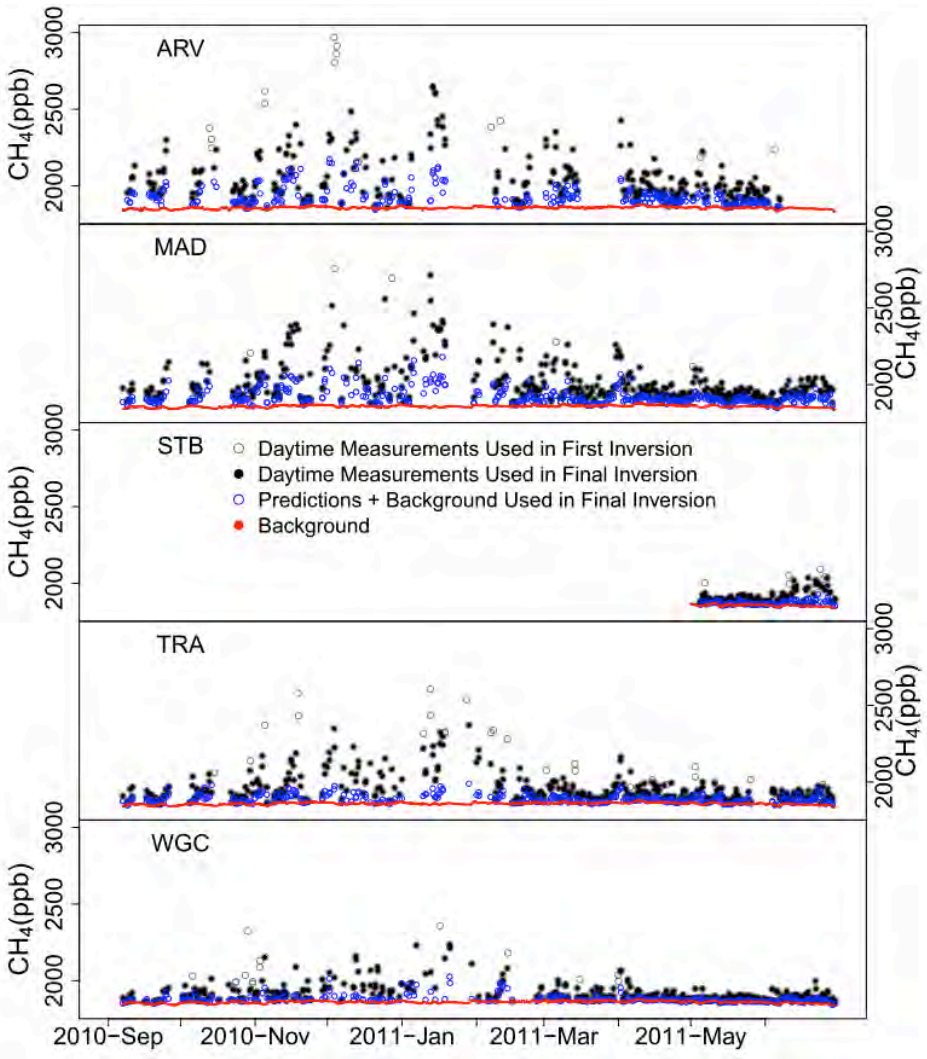


Figure 3. 3-hour mean CH_4 mixing ratio comparison: measured CH_4 mixing ratio during noon - afternoon hours used in the first inversion (gray open circle), measured CH_4 mixing ratio used in the final inversion (black filled circle), WRF-STILT predicted (before inversion) CH_4 mixing ratio using the CALGEM prior model + WRF-STILT predicted CH_4 background mixing ratio during noon – afternoon hours used for the final inversion (blue open circle), and WRF-STILT predicted CH_4 background mixing ratio using the 3-D curtain (red dots). Outliers were removed after the first inversion based on the data selection criteria described in Section 2.4.

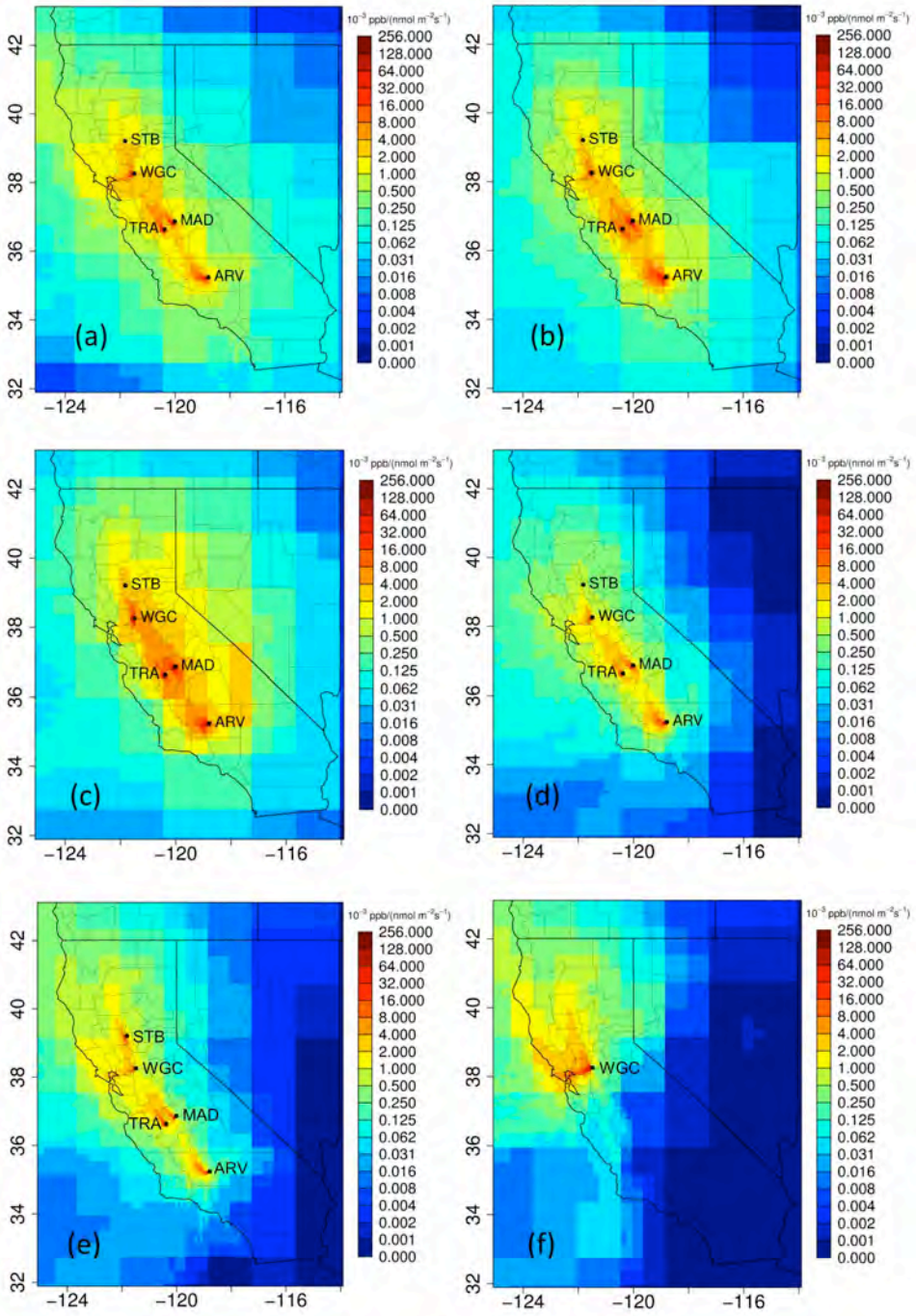


Figure 4. Seasonal mean footprints during the noon-afternoon hours for (a) September – October 2010, (b) November – December 2010, (c) January – February 2011, (d) March – April 2011, (e) May – June 2011 from all five sites, and (f) May – June 2011 from the WGC site only.

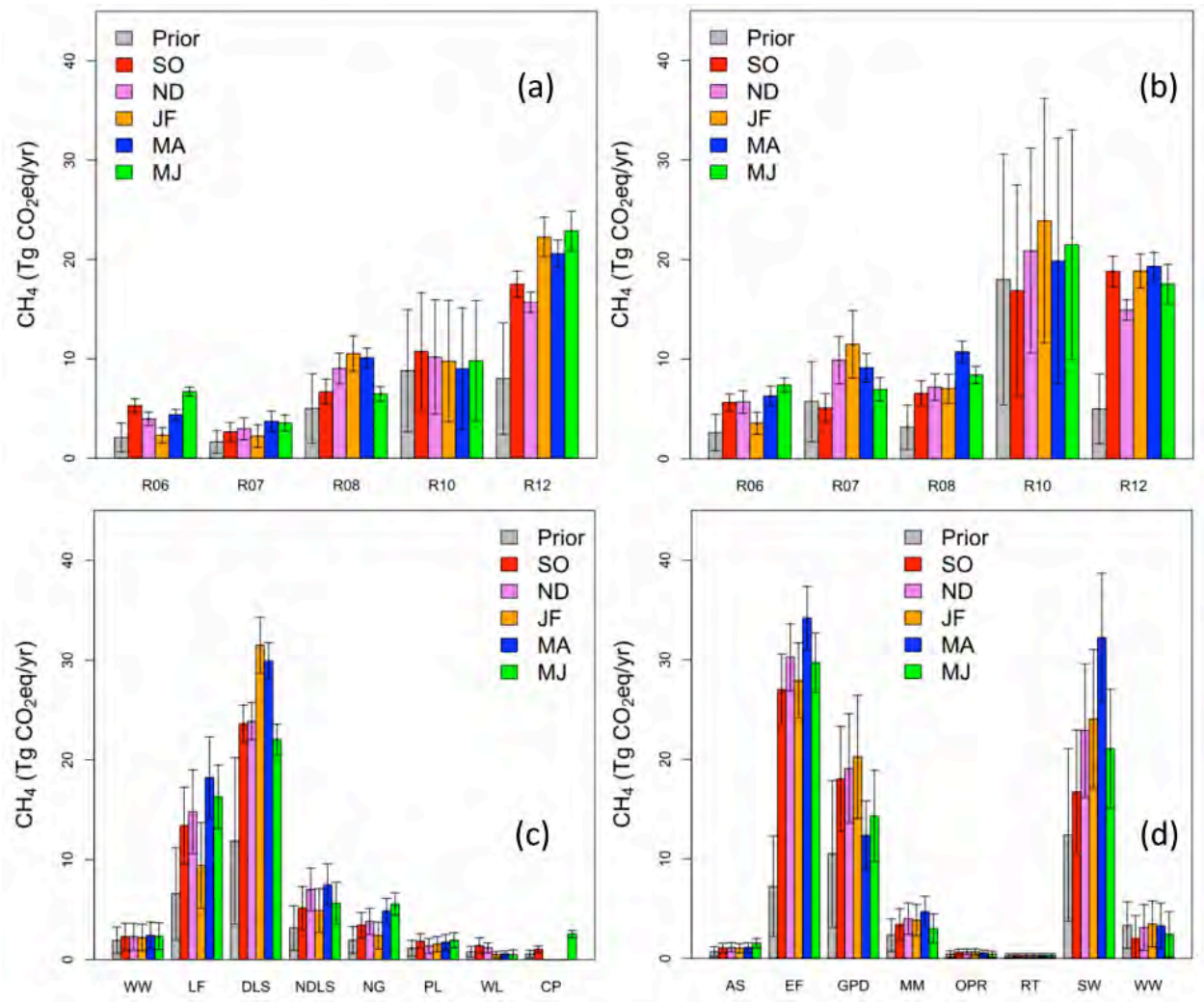


Figure 5. Estimates of posterior CH_4 emissions (Tg CO_2eq yr^{-1}) by season: (a) region analysis based on the CALGEM emission model, (b) region analysis based on EDGAR42, (c) source analysis based on the CALGEM emission model, and (d) source analysis based on EDGAR42. Only regions with significant emissions are shown. The annual mean prior (gray bar) is compared with posterior seasonal emissions (color bars). WW, LF, DLS, NDLS, NG, PL, WL and CP represent wastewater, landfill, dairy livestock, non-dairy livestock, natural gas, petroleum, wetland, and crop agriculture sources, respectively. AS, EF, GPD, MM, OPR, RT, SW, and WW represent agricultural soils, enteric fermentation, gas production and distribution, manure management, oil production and refineries, road transportation, solid waste, and wastewater, respectively.

DISCLAIMER

ENERGY AND ENVIRONMENT

Methane Leaks from North American Natural Gas Systems

Methane emissions from U.S. and Canadian natural gas systems appear larger than official estimates.

A. R. Brandt,[1]*‡ G. A. Heath,[2] E. A. Kort,[3] F. O'Sullivan,[4] G. Pétron,[5,6] S. M. Jordaan,[7] P. Tans,[5] J. Wilcox,[1] A. M. Gopstein,[8]† D. Arent,[2,9] S. Wofsy,[10] N. J. Brown,[11] R. Bradley,[12] G. D. Stucky,[13] D. Eardley,[13] R. Harriss[14]

Natural gas (NG) is a potential "bridge fuel" during transition to a decarbonized energy system: It emits less carbon dioxide during combustion than other fossil fuels and can be used in many industries. However, because of the high global warming potential of methane (CH_4, the major component of NG), climate benefits from NG use depend on system leakage rates. Some recent estimates of leakage have challenged the benefits of switching from coal to NG, a large near-term greenhouse gas (GHG) reduction opportunity (*1*–*3*). Also, global atmospheric CH_4 concentrations are on the rise, with the causes still poorly understood (*4*).

To improve understanding of leakage rates for policy-makers, investors, and other decision-makers, we review 20 years of technical literature on NG emissions in the United States and Canada [see supplementary materials (SM) for details]. We find (i) measurements at all scales show that official inventories consistently underestimate actual CH_4 emissions, with the NG and oil sectors as important contributors; (ii) many independent experiments suggest that a small number of "superemitters" could be responsible for a large fraction of leakage; (iii) recent regional atmospheric studies with very high emissions rates are unlikely to be representative of typical NG system leakage rates; and (iv) assessments using 100-year impact indicators show system-wide leakage is unlikely to be large enough to negate climate benefits of coal-to-NG substitution.

[1]Stanford University, Stanford, CA. [2]National Renewable Energy Laboratory, Golden, CO. [3]University of Michigan, Ann Arbor, MI. [4]Massachusetts Institute of Technology, Cambridge, MA. [5]National Oceanic and Atmospheric Administration, Boulder, CO. [6]University of Colorado, Boulder, CO. [7]University of Calgary, Calgary, Canada. [8]U.S. Department of State, Washington, DC. [9]Joint Institute for Strategic Energy Analysis, Golden, CO. [10]Harvard University, Cambridge, MA. [11]Lawrence Berkeley National Laboratory, Berkeley, CA. [12]Independent consultant, Gaithersburg, MD. [13]University of California, Santa Barbara, Santa Barbara, CA. [14]Environmental Defense Fund, Boulder, CO.

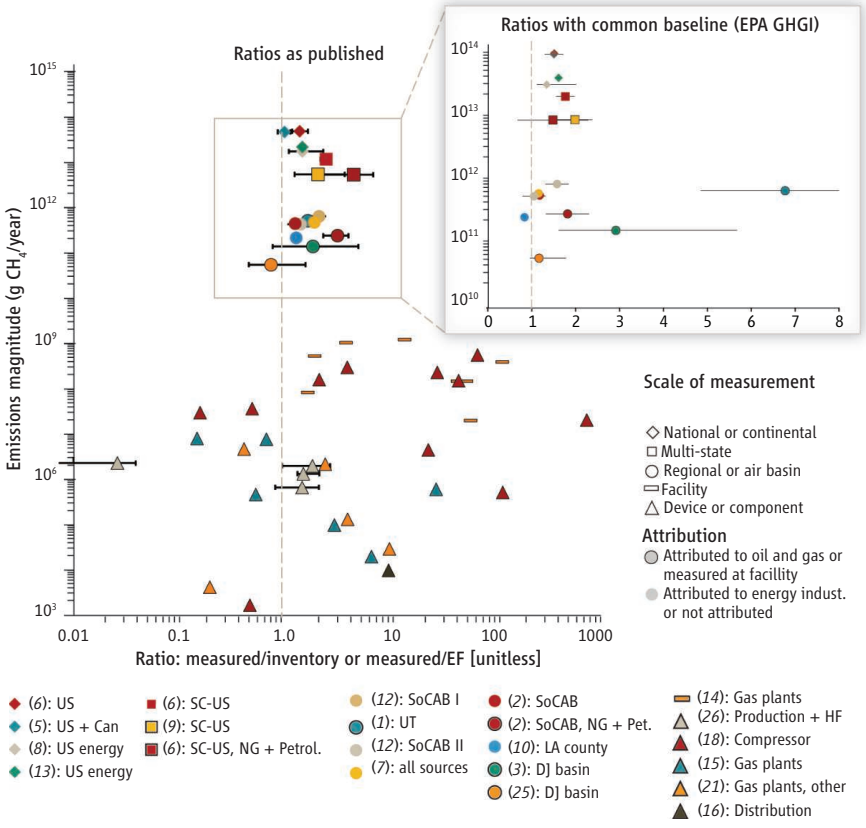
*Full affiliations for all authors are included in the supplementary materials. †Views expressed in this article are those of the author and do not necessarily reflect those of the U.S. Department of State or the U.S. Government. ‡Corresponding author. abrandt@stanford.edu

Underestimation—Device to Continent

This study presents a first effort to systematically compare published CH_4 emissions estimates at scales ranging from device-level (>10^3 g/year) to continental-scale atmospheric studies (>10^{13} g/year). Studies known to us that (i) report measurement-based emissions estimates and (ii) compare those estimates with inventories or established emission factors (EFs) are shown in the first chart.

Studies that measure emissions directly from devices or facilities ("bottom-up" studies) typically compare results to emissions factors (EFs; e.g., emissions per device). Large-scale inventories are created by multiplying EFs by activity factors (e.g., number of devices).

Studies that estimate emissions after atmospheric mixing occurs ("atmospheric" studies) typically compare measurements to emissions inventories, such as the U.S. Envi-



Inventories and emissions factors consistently underestimate actual measured CH_4 emissions across scales. Ratios >1 indicate measured emissions are larger than expected from EFs or inventory. Main graph compares results to the EF or inventory estimate chosen by each study author. Inset compares results to regionally scaled common denominator (*17*), scaled to region of study and (in some cases) the sector under examination. Multiple points for each study correspond to different device classes or different cases measured in a single study. Definitions of error bar bounds vary between studies. (US, United States; Can, Canada; SC, South Central; Petrol. and Pet., petroleum; SoCAB, South Coast Air Basin; LA, Los Angeles; DJ, Denver-Julesberg; UT, Utah; HF, hydraulic fracturing). See SM for figure construction details.

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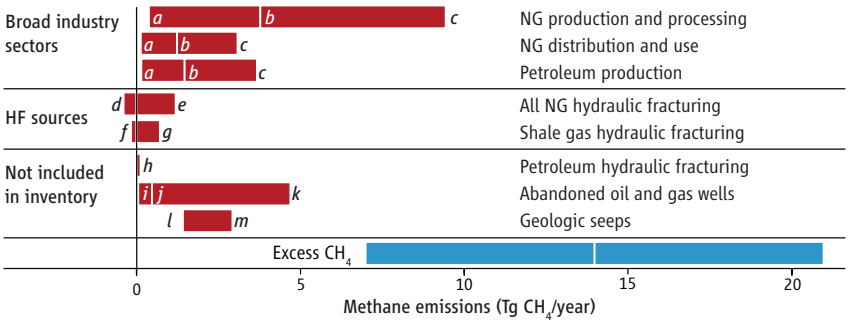
ronmental Protection Agency (EPA) national GHG inventory (GHGI). Atmospheric studies use aircraft (*1*, *5*–*8*), tower (*3*, *6*), and ground (*3*, *7*–*10*) sampling, as well as remote sensing (*7*, *11*, *12*). All such studies observe atmospheric concentrations and must infer fluxes by accounting for atmospheric transport. The various inference methods have strengths and weaknesses (see SM). The greatest challenge for atmospheric studies is attributing observed CH_4 concentrations to multiple potential sources (both anthropogenic and natural).

Results from bottom-up studies (generally $<10^9$ g CH_4/year) and atmospheric CH_4 studies at regional scale and larger (above 10^{10} g CH_4/year) are shown in the first chart. We also include studies that do not focus on NG systems, in order to place NG emissions in context with other CH_4 sources. Across years, scales, and methods, atmospheric studies systematically find larger CH_4 emissions than predicted by inventories. EFs were also found to underestimate bottom-up measured emissions, yet emissions ratios for bottom-up studies are more scattered than those observed in atmospheric studies (*13*–*16*).

Regional and multistate studies focusing on NG-producing (*1*–*3*, *9*) and NG-consuming regions (*2*, *7*, *10*–*12*) find larger excess CH_4 emissions than national-scale studies. This may be due to averaging effects of continental-scale atmospheric processes, to regional atmospheric studies focusing on areas with other air quality problems (*1*, *3*), or simply to methodological variation. Atmospheric measurements are constrained in spatial and temporal density: Regional studies cover 0.5 to 5% of NG production or consumption with dense measurements, although often limited to short-duration sampling "campaigns" (*3*, *7*); national studies cover wide areas with limited sample density (*6*) (table S5).

To facilitate comparison, the inset in the first chart normalizes atmospheric studies ($>10^{10}$ g CH_4/year) to baselines computed from the most recent (2011) EPA GHGI estimates for the year and region in which study measurements were made (*17*). After normalization, the largest (e.g., national-scale) atmospheric studies ($>10^{12}$ g CH_4/year) suggest typical measured emissions ~1.5 times those in the GHGI (*5*, *6*, *8*, *9*).

Why might emissions inventories be underpredicting what is observed in the atmosphere? Current inventory methods rely on key assumptions that are not generally satisfied. First, devices sampled are not likely to be representative of current technologies and practices (*18*). Production techniques are being applied at scale (e.g., hydraulic fracturing and horizontal drilling) that were not widely used during sampling in the early 1990s, which underlies EPA EFs (*18*).



Potential contributions to total U.S. CH_4 emissions above EPA estimates. EPA estimate in blue, based on central estimate and uncertainty range from large-scale studies from the inset in the first chart. Both NG sources and possible confounding sectors are included. NG production, petroleum production, and NG distribution emissions are based on regional empirical studies (*1*, *2*, *6*), which estimate emissions rates from high-emitting sources but do not estimate prevalence. Scenarios (*a*) to (*c*) correspond to 1, 10, and 25% of gas production or consumption from such high-emitting sources. Ranges (*d*) to (*g*) correspond to estimates for flowback emissions rates during hydraulic fracturing (HF) of all gas wells and shale gas wells, relative to EPA estimates. Ranges (*h*) to (*m*) reflect sources not included in EPA CH_4 inventories but which could be mistaken for NG emissions by chemical or isotopic composition. See SM for details.

Second, measurements for generating EFs are expensive, which limits sample sizes and representativeness. Many EPA EFs have wide confidence intervals (*19*, *20*). And there are reasons to suspect sampling bias in EFs, as sampling has occurred at self-selected cooperating facilities.

Third, if emissions distributions have "heavy tails" (e.g., more high-emissions sources than would be expected in a normal distribution), small sample sizes are likely to underrepresent high-consequence emissions sources. Studies suggest that emissions are dominated by a small fraction of "superemitter" sources at well sites, gas-processing plants, coproduced liquids storage tanks, transmission compressor stations, and distribution systems (see table S6 and fig. S2). For example, one study measured ~75,000 components and found that 58% of emissions came from 0.06% of possible sources (*21*).

Last, activity and device counts used in inventories are contradictory, incomplete, and of unknown representativeness (*17*, *22*). Data should improve with increased reporting requirements enacted by EPA (*23*, *24*).

Source Attribution in Atmospheric Studies

Does evidence suggest possible sources of excess CH_4 emissions relative to official estimates within the NG sector? A key challenge is attribution of atmospheric observations to sources. Isotopic ratios (*7*, *11*) and prevalence signatures of non-CH_4 hydrocarbons (*3*, *6*–*8*) can be used to attribute emissions to fossil sources rather than biogenic sources. Evidence from regional studies suggests that CH_4 emissions with fossil signatures are larger than expected (*3*, *6*, *7*, *9*, *11*), whereas national-scale evidence suggests a mix of biogenic and fossil sources (*6*). Atmospheric studies that control for biogenic CH_4 sources (*1*, *2*, *7*) are dependent on biogenic source estimation methods that also have high uncertainties (*6*). Natural geologic seeps could confound attribution (see the second chart and SM).

Studies can attribute emissions to liquid petroleum and NG sources rather than coal by sampling in places with little coal-sector activity (*2*, *3*, *6*, *7*, *9*). Attributing leakage to the NG system, as defined by EPA industry sector classifications, is more challenging. Alkane fingerprints may allow attribution to oil-associated NG (*9*), although NG processing changes gas composition, which may complicate efforts to pinpoint leakage sources. Geographic colocation of facilities and sampling, along with geographically isolating wind directions (*2*, *3*, *7*), can allow attribution of emissions to NG subsectors. Without spatial isolation, sector attribution can require assumptions about gas composition that introduce significant uncertainty (*2*, *3*, *25*).

We plotted results of a thought experiment (see the second chart) in which we estimated emissions ranges of selected possible sources within the NG sector, as well as sources that could be mistaken for NG emissions owing to chemical and isotopic signatures. Although such an analysis is speculative given current knowledge, it illustrates ranges of possible source magnitudes.

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We include in the second chart a range of excess CH_4 from all sources (7 to 21 × 10^{12} g or Tg/year) based on normalized national-scale atmospheric studies from the inset in the first chart. This excess is conservatively defined as 1.25 to 1.75 times EPA GHGI estimates. This estimate is derived from national-scale atmospheric studies and includes all sources of CH_4 emissions: It should not be expected that NG sources are responsible for all excess CH_4.

The scenarios in the second chart for NG production and/or processing, distribution, and petroleum system emissions apply observed leakage rates from the literature that are higher than EPA GHGI estimates (*1*, *2*, *7*). The frequency of such high-emitting practices is unknown, so illustrative prevalence scenarios are plotted: 1, 10, or 25% of activity is represented by high-emitters; the remaining facilities emit at EPA GHGI rates. This evidence suggests that high leakage rates found in recent studies (*1*, *2*, *7*) are unlikely to be representative of the entire NG industry; if this were the case, associated emissions would exceed observed total excess atmospheric CH_4 from all sources.

In general, the wide ranges in the second chart suggest a poor understanding of sources of excess CH_4 and point to areas where improved science would reduce uncertainty. However, hydraulic fracturing for NG is unlikely to be a dominant contributor to total emissions (*26*). Also, some sources not included in the GHGI may contribute to measured excess CH_4, e.g., abandoned oil and gas wells and geologic seeps (see SM).

Policy Challenges and Opportunities

Leakage scenarios in the second chart have implications for decision-making and policy. A key tool for environmental decision-making is life-cycle assessment (LCA), which compares impacts associated with varying methods of supplying a useful product (e.g., kWh of electricity). A key challenge in LCA studies is attribution of emissions from systems that produce two products, such as "gas" wells that also produce hydrocarbon liquids, or "oil" wells that also produce NG. This challenge is complicated by incongruence between LCA methodology and EPA sector definitions (see SM).

Recent LCAs have estimated GHG emissions from NG use in power generation and transport (see SM). LCA studies generally agree that replacing coal with NG has climate benefits (*27*). However, LCAs have relied heavily on EPA GHGI results. Updating these assessments with uncertainty ranges from the second chart (see SM) still supports robust climate benefits from NG substitution for coal in the power sector over the typical 100-year assessment period. However, climate benefits from vehicle fuel substitution are uncertain (gasoline, light-duty) or improbable (diesel, heavy-duty) (*28*). These conclusions may undercount benefits of NG, as both EPA GHGI methods and many regionally focused top-down studies attribute CH_4 emissions from coproducing NG systems to the NG sector, rather than to a mixture of oil and NG sources.

How can management and policy help address the leakage problem? Opportunities abound: Many solutions are economically profitable at moderate NG prices, with some technologies already being adopted or to be required in regulation (*23*, *26*) (e.g., reduced emissions completions). Facility studies using existing technology have found leakage detection and repair programs to be profitable (*21*).

The heavy-tailed distribution of observed emissions rates presents an opportunity for large mitigation benefits if scientists and engineers can develop reliable (possibly remote) methods to rapidly identify and fix the small fraction of high-emitting sources.

However, this heterogeneity also creates challenges in formulating statistical distributions for use in inventories. Approaches that assume "typical" emissions rates for this industry are inherently challenged. Inventories can be improved through efforts to better characterize distributions and by incorporating flexibility to adapt to new knowledge.

Improved science would aid in generating cost-effective policy responses. Given the cost of direct measurements, emissions inventories will remain useful for tracking trends, highlighting sources with large potential for reductions, and making policy decisions. However, improved inventory validation is crucial to ensure that supplied information is timely and accurate. Device-level measurements can be performed at facilities of a variety of designs, vintages, and management practices to find low-cost mitigation options. These studies must be paired with additional atmospheric science to close the gap between top-down and bottom-up studies. One such large study is under way (*29*), but more work is required.

If natural gas is to be a "bridge" to a more sustainable energy future, it is a bridge that must be traversed carefully: Diligence will be required to ensure that leakage rates are low enough to achieve sustainability goals.

References and Notes

1. A. Karion *et al.*, *Geophys. Res. Lett.* **40**, 4393 (2013).
2. J. Peischl *et al.*, *J. Geophys. Res.* **118**, 4974 (2013).
3. G. Pétron *et al.*, *J. Geophys. Res.* **117**, (D4), D04304 (2012).
4. E. G. Nisbet *et al.*, *Science* **343**, 493 (2014).
5. E. A. Kort *et al.*, *Geophys. Res. Lett.* **35**, L18808 (2008).
6. S. M. Miller *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 20018 (2013).
7. P. O. Wennberg *et al.*, *Environ. Sci. Technol.* **46**, 9282 (2012).
8. Y. Xiao *et al.*, *J. Geophys. Res.* **113**, (D21), D21306 (2008).
9. A. S. Katzenstein *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 11975 (2003).
10. Y.-K. Hsu *et al.*, *Atmos. Environ.* **44**, 1 (2010).
11. A. Townsend-Small *et al.*, *J. Geophys. Res.* **117**, (D7), D07308 (2012).
12. D. Wunch *et al.*, *Geophys. Res. Lett.* **36**, 10.1029/2009 GL039825 (2009).
13. J. S. Wang *et al.*, *Global Biogeochem. Cycles* **18**, 10.129/2003GB0021680 (2004).
14. A. Chambers, Optical Measurement Technology for Fugitive Emissions from Upstream Oil and Gas Facilities (Alberta Research Council, Edmonton, AB, 2004).
15. Clearstone Engineering, *Identification and Evaluation of Opportunities to Reduce Methane Losses at Four Gas Processing Plants* (Gas Technology Institute, Des Plaines, IL, 2002).
16. Innovative Environmental Solutions, *Field Measurement Program to Improve Uncertainties for Key Greenhouse Gas Emissions Factors for Distribution Sources* (Gas Technology Institute, Des Plaines, IL, 2009).
17. EPA, "Inventory of U.S. greenhouse gas emissions and sinks: 19902011" (EPA, 2013).
18. M. R. Harrison *et al.*, *Natural Gas Industry Methane Emissions Factor Improvement Study* (EPA, 2011).
19. K. E. Hummel *et al.*, *Methane Emissions from the Natural Gas Industry*, vol. 8, *Equipment Leaks* (EPA, 1996).
20. H. J. Williamson *et al.*, *Methane Emissions from the Natural Gas Industry*, vol. 4, *Statistical Methodology* (EPA, 1996).
21. National Gas Machinery Laboratory, Clearstone Engineering, Innovative Environmental Solutions, *Cost-Effective Directed Inspection and Maintenance Control Opportunities at Five Gas Processing Plants and Upstream Gathering Compressor Stations and Well Sites* (EPA, 2006).
22. Office of Inspector General, EPA, *EPA Needs to Improve Air Emissions Data for the Oil and Natural Gas Production Sector* (EPA, 2013).
23. EPA, *Fed. Regist.* 77(159), 49490 (16 August 2012); 40 Code of Federal Regulations, Parts 60 and 63.
24. EPA, *Greenhouse Gas Reporting Program*, subpart W, *Petroleum and Natural Gas Systems* (EPA, 2013).
25. M. A. Levi, *J. Geophys. Res.* **117**, (D21), 16 (2012).
26. D. T. Allen *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 17768 (2013).
27. C. L. Weber, C. Clavin, *Environ. Sci. Technol.* **46**, 5688 (2012).
28. R. A. Alvarez *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 6435 (2012).
29. Environmental Defense Fund, Natural gas: EDF is fighting for tough rules and enforcement (EDF, 2013); www.edf.org/climate/natural-gas.

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Supplementary Materials

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Comparative Life-Cycle Air Emissions of Coal, Domestic Natural Gas, LNG, and SNG for Electricity Generation

PAULINA JARAMILLO,*,† W. MICHAEL GRIFFIN,†,‡ AND H. SCOTT MATTHEWS†,§

Civil and Environmental Engineering Department, Tepper School of Business, and Department of Engineering and Public Policy, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213-3890

The U.S. Department of Energy (DOE) estimates that in the coming decades the United States' natural gas (NG) demand for electricity generation will increase. Estimates also suggest that NG supply will increasingly come from imported liquefied natural gas (LNG). Additional supplies of NG could come domestically from the production of synthetic natural gas (SNG) via coal gasification−methanation. The objective of this study is to compare greenhouse gas (GHG), SO_x, and NO_x life-cycle emissions of electricity generated with NG/LNG/SNG and coal. This life-cycle comparison of air emissions from different fuels can help us better understand the advantages and disadvantages of using coal versus globally sourced NG for electricity generation. Our estimates suggest that with the current fleet of power plants, a mix of domestic NG, LNG, and SNG would have lower GHG emissions than coal. If advanced technologies with carbon capture and sequestration (CCS) are used, however, coal and a mix of domestic NG, LNG, and SNG would have very similar life-cycle GHG emissions. For SO_x and NO_x we find there are significant emissions in the upstream stages of the NG/LNG life-cycles, which contribute to a larger range in SO_x and NO_x emissions for NG/LNG than for coal and SNG.

1. Introduction

Natural gas currently provides 24% of the energy used by United States homes (*1*). It is an important feedstock for the chemical and fertilizer industry. Low wellhead gas prices (less than $3/thousand cubic feet (Mcf) (*2*)) spurred a surge in construction of natural-gas-fired power plants: between 1992 and 2003, while coal-fired capacity increased only from 309 to 313 GW, natural-gas-fired capacity more than tripled, from 60 to 208 GW (*3*). Adding to this was the Energy Information Agency's (EIA) prediction of continued low natural gas prices (around $4/Mcf) through 2020 (*4*), lower capital costs, shorter construction times, and generally lower air emissions for natural-gas-fired plants that allowed power generators to meet the clean air standards (*5*). However, instead of remaining near projected levels, the average wellhead price of natural gas peaked at $11/Mcf in October 2005 (*6*). This price increase made natural gas uneconomical as a feedstock, so most natural-gas-fired plants are operating below capacity (*7*). Despite these trends, natural gas consumption is expected to increase by 20% of 2003 levels by 2030. Demand from electricity generators is projected to grow the fastest. At the same time, natural gas production in the United States and pipeline imports from Canada and Mexico are expected to remain fairly constant (*8*). The gap between North American supply and U.S. demand can only be met with alternative sources of natural gas, such as imported liquefied natural gas (LNG) or synthetic natural gas (SNG) produced from coal. Current projections by EIA estimate that LNG imports will increase to 16% of the total U.S. natural gas supply by 2030 (*8*). Alternatively, Rosenberg et al. call for congress to promote gasification technologies that use coal to produce SNG. This National Gasification Strategy calls for the United States to produce 1.5 trillion cubic feet (tcf) of synthetic natural gas per year within the next 10 years (*7*), equivalent to 5% of expected 2030 demand.

The natural gas system is one of the largest sources of greenhouse gas emissions in the United States, generating around 132 million tons of CO_2 equivalents annually (*1*). Significant emissions of criteria air pollutants also come from upstream combustion life-cycle stages of the gas. Emissions from the emerging LNG life-cycle stages or from the production of SNG have not been studied in detail. If larger percentages of the U.S. supply of natural gas will come from these alternative sources, then LNG or SNG supply chain emissions become an important part of understanding overall natural gas life-cycle emissions. Also, comparisons between coal and natural gas that concentrate only on the emissions at the utility plant may not be adequate. The objective of this study is to perform a life-cycle analysis (*9*, *10*) of natural gas, LNG, and SNG. Direct air emissions from the processes during the life-cycle will be considered, as well as air emissions from the combustion of fuels and electricity used to run the process. A comparison with coal life-cycle air emissions will be presented, in order to have a better understanding of the advantages and disadvantages of using coal versus natural gas for electricity generation.

2. Fuel Life-Cycles

The natural gas life-cycle starts with the production of natural gas and ends at the combustion plant. Natural gas is extracted from wells and sent to processing plants where water, carbon dioxide, sulfur, and other hydrocarbons are removed. The produced natural gas then enters the transmission system. The U.S. transmission system also includes some storage of natural gas in underground facilities such as reconditioned depleted gas reservoirs, aquifers, or salt caverns to meet seasonal and/or sudden short-term demand. From the transmission and storage system, some natural gas goes directly to large-scale consumers, like electric power generators, which is modeled here. The rest goes into local distribution systems that deliver it to residential and commercial consumers via low-pressure, small-diameter pipelines.

The use of liquefied natural gas (LNG) adds three additional life-cycle stages to the natural gas life-cycle described above. Natural gas is produced and processed to remove contaminants and transported by pipeline relatively short distances to be liquefied. In the liquefaction process, natural gas is cooled and pressurized (*11*). Liquefaction plants are generally located in coastal areas of LNG exporting countries and dedicated LNG ocean tankers transport LNG

* Corresponding author phone: 412-268-8769; fax: 412-268-7813; e-mail: pjaramil@andrew.cmu.edu.
† Civil and Environmental Engineering Department.
‡ Tepper School of Business.
§ Department of Engineering and Public Policy.

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to the United States. Upon arriving, the LNG tankers offload their cargo and the LNG is regasified. At this point the regasified LNG enters the U.S. natural gas transmission system.

The coal life-cycle is conceptually simpler than the natural gas life-cycle, consisting of three major steps: coal mining and processing, transportation, and use/combustion.

U.S. coal is produced from surface mines (67%), or underground mines (33%) (*1*). Mined coal is processed to remove impurities. Coal is then transported from the mines to the consumers via rail (84%), barge (11%), and trucks (5%) (*12*). More than 90% of the coal used in the United States is used by the electric power sector, which is modeled here (*8*).

The life-cycle of SNG is a combination of some stages from the coal life-cycle and some stages of the natural gas life-cycle. Coal is mined, processed, and transported, as in the coal life-cycle, to the SNG production plant. At this plant, syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2), is produced by gasification and converted, via methanation, to methane and water. The SNG is then sent to the natural gas transmission system, described above, and on to the electric power generator.

3. Methods for Calculating Life-Cycle Air Emissions

In our study we investigate the life-cycle air emissions from coal, natural gas, LNG, and SNG use. All fossil fuel options are used to produce electricity and combustion emissions are included as a component of the each life-cycle. For GHG, the emissions factors at power plants used are 120 lb CO_2 equiv/MMBtu of natural gas and 205 lb CO_2 equiv/MMBtu of coal. The SO_x and NO_x emissions at power plants are presented in the results section and in the Supporting Information

3.1. Life-Cycle Air Emissions from Natural Gas produced in North America. In 2003, the total consumption of natural gas in the United States was over 27 trillion cubic feet (tcf). Of this, 26.5 tcf were produced in North America (U.S., Canada, and Mexico) (*13*). According to the Environmental Protection Agency (EPA), 1.07% of the natural gas produced is lost in its production, processing, transmission, and storage (*14*). Total methane emissions were calculated using the percentage of natural gas lost. It was also assumed that natural gas has an average heat content of 1030 Btu/ft^3 (*13*), and that 96% of the natural gas lost is methane, which has a density of 0.0424 lb/ ft^3 (*14*).

In 1993 the U.S. EPA established the Natural Gas STAR program to reduce methane emissions from the natural gas industry. Data from this program for the reductions in methane lost in the natural gas system, as described in the Supporting Information, were combined with the data described above to develop a range of methane emissions factors for the North American natural gas life-cycle stages.

Carbon dioxide emissions are produced from the combustion of natural gas used during various life-cycle stages and from the production of electricity consumed during transport. EIA provides annual estimates of the amount of natural gas used for the production, processing, and transport of natural gas. In 2003, approximately 1900 billion cubic feet of natural gas were consumed during these stages of the natural gas life-cycle (*13*). Total carbon dioxide emissions were calculated using a carbon content in natural gas of 31.90 lb C/MMBtu and an oxidation fraction of 0.995 (*1*). According to the Transportation Energy Data Book, 3 billion kWh were used for natural gas pipeline transport in 2003 (*15*). The average GHG emission factor from the generation of this electricity is 1400 lb CO_2 equiv/MWh (*16*). These CO_2 emissions were added to methane emissions to obtain the upstream combustion GHG emission factors for North American natural gas.

SO_x and NO_x emissions from the natural gas upstream stages of the life-cycle come from the combustion of the fuels used to produce the energy that runs the system, as given in the Supporting Information. Total emissions from flared gas were calculated using the AP 42 Emission Factors for natural gas boilers (*17*). A range of emissions from the combustion of the natural gas used during the upstream stages of the life-cycle was developed using the AP 42 Emissions Factors for reciprocating engines and for natural gas turbines (*17*). Emissions from generating the electricity used during natural gas pipeline operations were estimated using the most current average emission factors given by EGRID: 6.04 lb SO_2/MWh and 2.96 lb NO_x/MWh (*16*). Note that EGRID reports emissions of SO_2 only. Other references used in this paper report total SO_x emission. For this paper, sulfur emission will be reported in terms of SO_x emissions.

In addition to emissions from the energy used during the life-cycle of natural gas, SO_x emissions are produced in the processing stage of the life-cycle, when hydrogen sulfide (H_2S) is removed from the sour natural gas to meet pipeline requirements. A range of SO_x emissions from this processing of natural gas was developed using the AP 42 emissions factors for natural gas processing and for sulfur recovery (*17*). To use the AP 42 emission factors for sulfur recovery, we found that in 2003 1945 thousand tons of sulfur were recovered from 14.7 trillion cubic feet of natural gas resulting in a calculated average natural gas H_2S mole percentage of 0.0226. This was then used with the AP 42 emission factors for natural gas processing.

3.2. Air Emissions from the LNG Life-Cycle. In 2003, 500 billion cubic feet of natural gas were imported in the form of LNG (*13*). In 2003, 75% of the LNG imported to the United States came from Trinidad and Tobago, but this percentage is expected to decrease as more imports come from Russia, the Middle East, and Southeast Asia (*13*). According to EIA, the LNG tanker world fleet capacity should have reached 890 million cubic feet of liquid (equivalent to 527 billion cubic feet of natural gas) by the end of 2006 (*18*). There are currently 5 LNG terminals in operation in the United States, with a combined base load capacity of 5.3 billion cubic feet per day (about 2 trillion cubic feet per year). In addition to these terminals, there are 45 proposed facilities in North America, 18 of which have already been approved by the Federal Energy Regulatory Commission (FERC) (*19*).

Due to unavailability of data for emissions from natural gas production in other countries, it is assumed that natural gas imported to the United States in the form of LNG produces the same emissions from the production and processing life-cycle stages as North American natural gas. Those stages are incorporated for LNG. Most of the natural gas converted to LNG is produced from modern fields developed and operated by multinational oil and gas companies, so they are assumed to be operated in a similar way to those in the United States.

It is expected that transportation of natural gas from the production field to the liquefaction plant would have emissions similar to those of pipeline transport of domestic natural gas. But the emission factor for the U.S. system (which is included in the LNG life-cycle) is based on total pipeline distances of over 200 000 miles (*20*). Because LNG facilities are closely paired with gas fields, it is expected that the average distance from production field to a LNG facility would be much smaller than 200 000 miles. Also, because there were no reliable data for the myriad of fields and facilities and suspected impact on the overall life cycle would be minimal, this transport from the fields to the liquefaction terminals was ignored. This would slightly underestimate the emissions from the LNG life cycle.

Additional emission factors were developed for the liquefaction, transport, and regasification life-cycle stages of LNG. Tamura et al. have reported emission factors for the

liquefaction stage in the range of 11−31 lb CO_2 equiv/MMBtu (*21*). The sources of these emissions are outlined in the Supporting Information.

LNG is shipped to the United States via LNG tankers. LNG tankers are the last ship type to use steam turbine technology in their engines. This technology allows for easy use of boil-off gas (BOG) in a gas boiler. Boil-off rates in LNG tankers range between 0.15% and 0.25% per day when loaded (*22*, *23*). When there is not enough BOG available, a fuel oil boiler is used to produce the steam. In addition to this benefit, steam turbines require less maintenance than diesel engines, which is beneficial to these tankers that have to be readily available to leave a terminal in case of emergency (*22*).

Most LNG tankers currently in operation have a capacity to carry between 4.2 and 5.3 million cubic feet of LNG (2.6 and 3.2 billion cubic feet of gas). There are smaller tankers available, but they are not widely used for transoceanic transport. There is also discussion about building larger tankers (8.8 million cubic feet), however none of the current U.S. terminals can handle tankers of this size (*18*).

The rated power of the LNG tankers ranges between 20 and 30 MW, and they operate under this capacity around 75% of the time during a trip (*24*, *25*). The energy required to power this engine is 11.6 MMBtu/MWh (*26*). As previously mentioned, some of this energy is provided by BOG and the rest is provided by fuel oil. A loaded tanker with a rated power of 20 MW, and 0.12% daily boil-off rate would consume 3.88 million cubic feet of gas per day and 4.4 tons of fuel oil per day. The same tanker would consume 115 tons of fuel oil per day on they way back to the exporting country operating under ballast conditions. A loaded tanker with a rated power of 30 MW, and a 0.25% daily boil-off rate would get all its energy from the BOG, with some excess gas being combusted to reduce risks of explosion (*22*). Under ballast conditions, the same tanker would consume 172 tons of fuel oil per day.

For LNG imported in 2003 the average travel distance to the Everett, MA LNG terminal was 2700 nautical miles (*13*, *27*). In the future LNG could travel as far as far as 11 700 nautical miles (the distance between Australia and the Lake Charles, LA LNG terminal (*27*)). This range of distances is representative of distances from LNG countries to U.S. terminals that could be located on either the East or West coasts. To estimate the number of days LNG would travel (at a tanker speed of 20 knots (*22*)), these distances were used. This trip length can then be multiplied by the fuel consumption of the tanker to estimate total trip fuel consumption and emissions, and these can then be divided by the average tanker capacity to obtain a range of emission factors for LNG tanker transport between 2 and 17 lb CO_2 equiv/MMBtu.

Regasification emissions were reported by Tamura et al. to be 0.85 lb CO_2 equiv/MMBtu (*21*). Ruether et al. report an emission factor of 3.75 lb of CO_2 equiv/MMBtu for this stage of the LNG life-cycle by assuming that 3% of the gas is used to run the regasification equipment (*28*). The emission reported by Tamura et al. differs because they assumed only 0.15% of the gas is used to run the regasification terminal, while electricity, which may be generated with cleaner energy sources, provides the additional energy requirements. These values were used as lower and upper bounds of the range of emissions from regasification of LNG.

As done for the carbon emissions, natural gas produced in other countries and imported to the United States in the form of LNG is assumed to have the same SO_x and NO_x emissions in the production, processing, and transmission stages of the life-cycle as for natural gas produced in North America. Emission ranges for the liquefaction and regasification of natural gas were calculated using the AP 42 emission factors for reciprocating engines and natural gas turbines (*17*). It is assumed that 8.8% of natural gas is used in the liquefaction plant (*21*) and 3% is used in the regasification plants (*28*). Emissions of SO_x, and NO_x from transporting the LNG via tanker were calculated using the AP 42 emission factor for natural gas boilers and diesel boilers, as well as the tanker fuel consumption previously described.

3.3. Air Emissions from the Coal Life-Cycle. Greenhouse gas emissions from the mining life-cycle stage were developed from methane releases and from combustion of fuels used at the mines. EPA estimates that methane emissions from coal mines in 1997 were 75 million tons of CO_2 equivalents, of which 63 million tons came from underground mines and 12 million tons came from surface mines (*1*). CO_2 is also emitted from mines through the combustion of the fuels that provide the energy for operation. The U.S. Census Bureau provides fuel consumption data for mines in 1997 (*29*). These data are available in the Supporting Information. Fuel consumption data were converted to GHG emissions using the carbon content and heat content of each fuel and an oxidation fraction given in EPA's Inventory of U.S. Greenhouse Gas Emissions Sources and Sinks (*1*) (see Supporting Information). Emissions from the generation of the electricity consumed were calculated using an average 1997 emission factor of 1400 lb CO_2 equiv/MWh (*16*). These total emissions were then converted to an emission factor using the amount of coal produced in 1997 and the average heat content of this coal.

Emissions from the transportation of coal were calculated using the EIO-LCA tool developed at Carnegie Mellon University (*30*). To use this tool, economic values for coal transportation were needed. In 1997, the latest year for which the EIO-LCA tool has data, 84% of coal was transported via rail, 11% via barge, and 5% via truck. The cost for rail transport, barge, and truck transport was 13.9, 9.5, and 142.7 mills/ton-mile respectively (*12*). For a million ton-miles of coal transported, EIO-LCA estimates that 43.6 tons of CO_2 equivalents are emitted from rail transportation, 5.89 tons of CO_2 equivalents from water transportation, and 69 tons of CO_2 equivalents from truck transportation (*30*). These emissions were then converted to an emission factor by using the average travel distance of coal in each mode (796, 337, and 38 miles by rail, barge, and truck, respectively), the weighted average U.S. coal heat content of 10 520 Btu/lb (*31*) and the coal production data for 1997 (see Supporting Information).

The energy consumption data used to develop carbon emissions from the mining life-cycle stage were used to develop SO_x and NO_x emission factors for coal. AP 42 emissions factors for off-road vehicles, natural gas turbines, reciprocating engines, light duty gasoline trucks, large stationary diesel engines, and gasoline engines were used to develop this range of emission factors (*17*, *32*). In addition, the average emission factors from electricity generation in 1997 (3.92 lb NO_x/MWh and 7.86 lb SO_2/MWh (*16*)) were used to include the emissions from the electricity used in mines.

SO_x and NO_x emissions for coal transportation were again calculated using EIO-LCA (*30*). EIO-LCA estimates that a million ton-miles of coal transported via rail results in emissions of 0.02 tons of SO_x and 0.4 tons of NO_x. A million ton-miles of coal transported via water would emit 0.07 tons of SO_x, and 0.36 tons of NO_x. Finally, a million ton-miles of coal transported via truck would emit 0.06 tons of SO_x, and 1.42 tons of NO_x (*30*). These data were added to emissions from mines to find the total SO_x and NO_x emission factors for the upstream stages of the coal life-cycle.

3.4. Air Emissions from the SNG Life-Cycle. Performance characteristics for two SNG plants are given in the Supporting Information. These plants have a higher heating value efficiency between 57% and 60% (*33*, *34*). Using these efficiencies, emissions from coal mining, processing, and

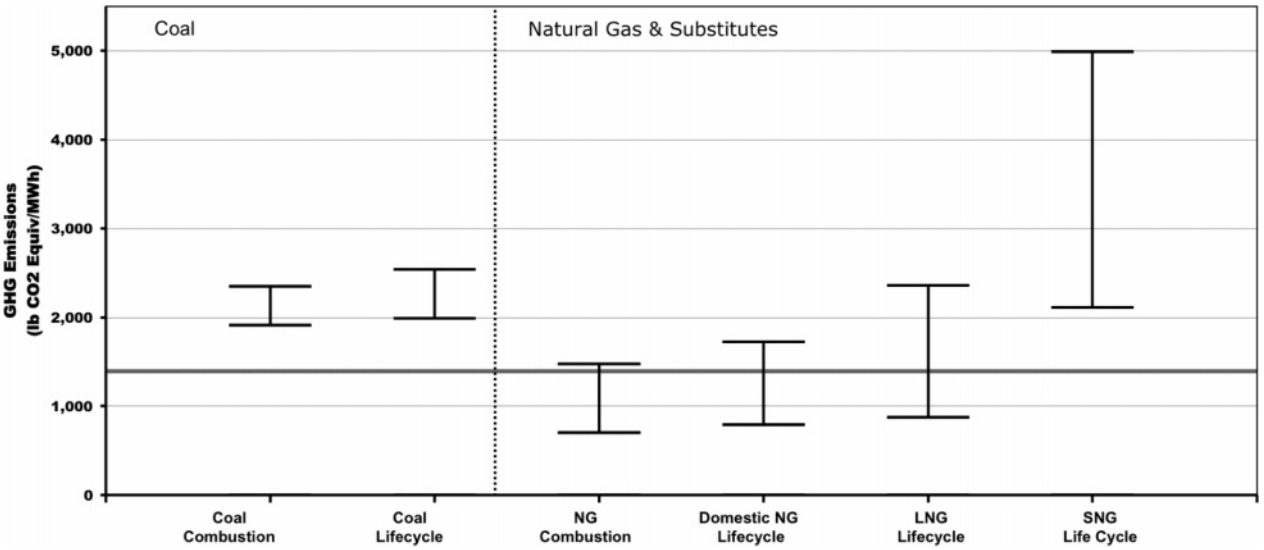

FIGURE 1. Fuel Combustion and Life-Cycle GHG Emissions for Current Power Plants.

transportation previously obtained were converted to pounds of CO_2 equiv/MMBtu of SNG. The data were also used to calculate the emissions at the gasification−methanation plant using a coal carbon content of 0.029 tons/MMBtu and a calculated SNG storage fraction of 37% (*1*). Finally, the emissions from transmission, storage, distribution, and combustion of SNG are the same as those for all other natural gas.

To develop the SO_x and NO_x emissions from the life-cycle of SNG, the emissions from coal mining and transport developed in the previous section in pounds per MMBtu of coal were converted to pounds per MMBtu of SNG using the efficiencies previously discussed. In addition, the emissions from natural gas transmission and storage were assumed to represent emissions from these life-cycle stages of SNG. The emissions from the gasification−methanation plant were taken from emission data for an Integrated Coal Gasification Combine Cycle (IGCC) plant, which operates with a similar process. Bergerson (*35*) reports SO_x emissions factors from IGCC between 0.023 and 0.15 lb/MMBtu coal (0.026−0.17 lb/MMBtu of coal if there is carbon capture), and a NO_x emission factor of 0.0226 lb/MMBtu coal (0.0228 lb/MMBtu of coal if there is carbon capture). These were converted to lb/MMBtu of SNG using the same coal-to-SNG efficiencies previously described.

4. Results

4.1. Comparing Fuel Life-Cycle Emissions for Fuels Used at Currently Operating Power Plants. Emission factors for the fuel life-cycles were calculated as pounds of pollutants per MMBtu of fuel produced, as presented in the Supporting Information. Since coal and natural gas power plants have different efficiencies, 1 MMBtu of coal does not generate the same amount of electricity as 1 MMBtu of natural gas/LNG/SNG. For this reason, emission factors given in Table 10S and Table 11S in the Supporting Information were converted to pounds of pollutant per MWh of electricity generated. This conversion is done using the efficiency of natural gas and coal power plants. According to the U.S. Department of Energy (DOE), currently operating coal power plants have efficiencies ranging from 30% to 37%, while currently operating natural gas power plants have efficiencies ranging from 28% to 58% (*36*). The life-cycle GHG emissions factors of natural gas, LNG, coal, and SNG described in the Supporting Information were converted to a lower and upper bound emission factor from coal and natural gas power plants using these efficiency ranges. Figure 1 shows the final bounds for the emission factors for each fuel cycle. The life-cycle for each fuel use includes fuel combustion at a power plant. The combustion-only emissions for each fuel are shown for comparison. The solid horizontal line shown represents the current average GHG emission factor for U.S. electricity generation: 1400 lb CO_2 equiv/MWh (*16*). Note that in this graph no carbon capture and storage (CCS) is performed at any stage of the life-cycle. CCS is a process by which carbon emissions are separated from other combustion products and injected into underground geologic formations such as saline formations or depleted oil/gas fields. A scenario in which CCS is performed at power plants as well as in gasification−methanation plants will be discussed in the following section.

It can be seen that combustion emissions from coal-fired power plants are higher than those from natural gas: the midpoint between the lower and upper bound emission factors for coal combustion is approximately 2100 lb CO_2 equiv/MWh, while the midpoint for natural gas combustions is approximately 1100 lb CO_2 equiv/MWh. This reflects the known environmental advantages from combustion of natural gas over coal. Figure 1 also shows that the life-cycle GHG emissions of electricity generated with coal are dominated by combustion, and adding the upstream life-cycle stages does not change the emission factor significantly, with the midpoint between the lower and upper bound life-cycle emission factors being 2270 lb CO_2 equiv/MWh. For natural-gas-fired power plants the emissions from the upstream stages of the natural gas life-cycle are more significant, especially if the natural gas used is synthetically produced from coal (SNG). The midpoint life-cycle emission factor for domestic natural gas is 1250 lb CO_2 equiv/MWh; for LNG and SNG it is 1600 lb CO_2 equiv/MWh and 3550 lb CO_2 equiv/MWh, respectively. SNG has much higher emission factors than the other fuels because of efficiency losses throughout the system. It is also interesting to note that the range of life-cycle GHG emissions of electricity generated with LNG is significantly closer to the range of emissions from coal than the life-cycle emissions of natural gas produced in North America. The upper bound life-cycle emission factor for LNG is 2400 lb CO_2 equiv/MWh, while the upper bound life-cycle emission factor for coal is 2550 lb CO_2 equiv/MWh.

To compare emissions of SO_x and NO_x from all life-cycles, the upstream emission factors and the power plant efficiencies from the Supporting Information are used. Emissions of these pollutants from coal and natural gas power plants in operation in 2003 were obtained from EGRID (*37*). Table 1

TABLE 1. SO_x and NO_x Combustion and Life-Cycle Emission Factors for Current Power Plants

fuel		SO_x (lb/MWh)		NO_x (lb/MWh)	
		min	max	min	max
current electricity mix		6.04		2.96	
coal	combustion	1.54	25.5	2.56	9.08
	life-cycle	1.60	25.8	2.83	9.69
natural gas	combustion	0.00	1.13	0.12	5.20
	life-cycle	0.04	1.49	0.17	9.40
LNG	life-cycle	0.094	2.93	0.25	15.4
SNG	life-cycle	0.30	3.88	0.65	8.08

shows life-cycle emissions for each fuel obtained by adding the combustion emissions from EGRID to the transformed upstream emissions. The current average SO_x and NO_x emission factors for electricity generated in the United States are also shown (*16*).

It can be seen that coal has significantly larger SO_x emissions than natural gas, LNG, or SNG. This is expected since the sulfur content of coal is much higher than the sulfur content of other fuels. SNG, which is produced from coal, does not have high sulfur emissions because the sulfur from coal must be removed before the methanation process.

For NO_x, it can be seen that the upstream stages of domestic natural gas, LNG, and even SNG make a significant contribution to the total life-cycle emissions. These upstream NO_x emissions come from the combustion of fuels used to run the natural gas system: for domestic natural gas, production is the largest contributor to these emissions; for LNG most NO_x upstream emissions come from the liquefaction plant; finally, for SNG most upstream NO_x emissions come from the gasification−methanation plant.

4.2. Comparing Fuel Life-Cycle Emissions for Fuels Used with Advanced Technologies. According to the DOE, by 2025 65 GW of inefficient facilities will be retired, while 347 GW of new capacity will be installed (*8*). Advanced pulverized coal (PC), integrated coal gasification combined cycle (IGCC), and natural gas combined cycle (NGCC) power plants could be installed. PC, IGCC, and NGCC plants are generally more efficient (average efficiencies of 39%, 38%, and 50%, respectively (*38*)) than the current fleet of power plants. In addition, CCS could be performed with these newer technologies. Experts believe that sequestration of 90% of the carbon will be technologically and economically feasible in the next 20 years (*5*, *38*). Having CCS at PC, IGCC, and NGCC plants decreases the efficiency of the plants to average of 30%, 33%, and 43%, respectively (*38*).

Figure 2 was developed using the revised efficiencies for advanced technologies and the GHG emission factors (in lb/MMBtu) described in the Supporting Information. This figure represents total life-cycle emissions for electricity generated with each fuel. Notice that emissions are shown with and without CCS. In the case of SNG with CCS, capture is performed at both the gasification−methanation plant and at the power plant. The solid horizontal line shown represents the current average GHG emission factor for electricity generation in the United States (1400 lb CO_2 equiv/MWh) (*16*). The upper and lower bound emissions in this figure are closer together than the upper and lower bounds in Figure 1, because only one power plant efficiency value is used, while for Figure 1 the upper and lower bound efficiency from all currently operating power plants was used (this is especially obvious for the domestic natural gas (NGCC) cases). It can be seen that, in general, life-cycle GHG emissions of electricity generated with the fuels without CCS would decrease slightly compared to emissions from current power plants that use the same fuel (due to efficiency gains). The most efficient natural gas plant currently in operation, however, could have slightly lower emissions than the lower bound for NGCC, LNGG, and SNGCC, due to efficiency differences. Three of the cases, however (PC, IGCC, and SNGCC), would still have higher emissions than the current average emissions from power plants. If CCS were used, however, there would be a significant reduction in emissions for all cases. In addition the midpoints between upper and lower bound emissions from all fuels are closer together, as can be seen in Figure 3. This figure also shows how the upstream from combustion emissions of fuels become significant contributors to the life-cycle emission factors when CCS is used.

Table 2 was developed using the upstream SO_x and NO_x emission factors obtained in this study and the combustion emissions reported by Bergerson (*35*) for PC and IGCC plants and by Rubin et al. for NGCC plants (*38*). These reported combustion emissions can be seen in the Table 12S in the Supporting Information.

As can be seen from Table 2, if advanced technologies are used there could be a significant reduction of NO_x and SO_x emissions, even if CCS is not available. It is interesting also to note that a PC plant with CCS could have lower life-cycle emissions than an IGCC plant with CCS. In the PC case all sulfur is removed through flue gas desulfurization. The removed sulfur compounds are then solidified and disposed of or sold as gypsum. In an IGCC plant with CCS, sulfur is removed from the syngas before combustion. In these plants, however, instead of solidifying the sulfur compounds removed and disposing them, the elemental sulfur is recovered in a process that generates some additional SO_x emissions (*35*). For NO_x, only LNG has higher life-cycle emissions than the average generated at current power plants.

5. Discussion

Natural gas is an important energy source for the residential, commercial, and industrial sectors. In the 1990s, the surge in demand by electricity generators and relatively constant natural gas production in North America caused prices to increase, so that in 2005 these sectors paid 58 billion dollars more than they would have paid if 2000 prices remained constant. Cumulative additional costs of higher natural gas prices for residential, commercial, and industrial consumers between 2000 and 2005 were calculated to be around 120 billion dollars. LNG has been identified as a source of natural gas that might help reduce prices, but even with an increasing supply of LNG, EIA still projects average delivered natural gas prices above $6.5/Mcf in the next 25 years. This is higher than the $4.5 /Mcf average projected price in earlier reports before the natural-gas-fired plant construction boom (*4*).

In addition to LNG, SNG has been proposed as an alternative source to add to the natural gas mix. The decision to follow the path of increased LNG imports or SNG production should be examined in light of more than just economic considerations. In this paper, we analyzed the effects of the additional air emissions from the LNG/SNG life-cycle on the overall emissions from electricity generation in the United States. We found that with current electricity generation technologies, natural gas life-cycle GHG emissions are generally lower than coal life-cycle emissions, even when increased LNG imports are included. However LNG imports decrease the difference between GHG emissions from coal and natural gas. SNG has higher life-cycle GHG emission than coal, domestic natural gas, or LNG. It is also important to note that upstream GHG emissions of NG/LNG/SNG have a higher impact in the total life-cycle emissions than upstream coal emissions. This is a significant point when considering a carbon-constrained future in which combustion emissions are reduced.

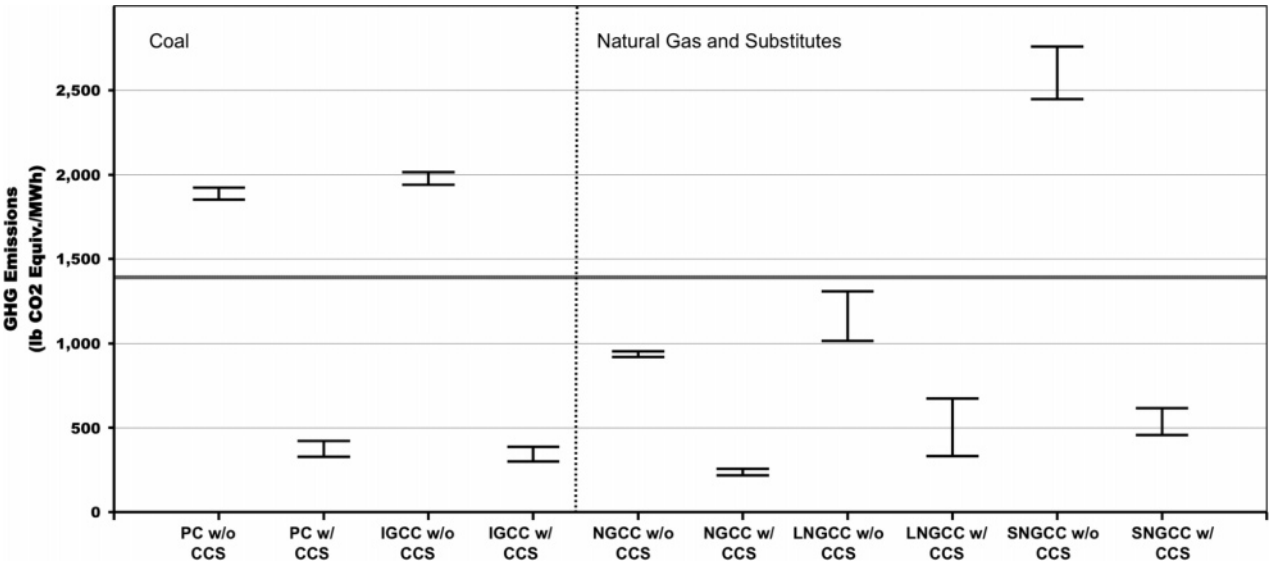

FIGURE 2. Fuel GHG Life-Cycle Emissions Using Advanced Technologies.

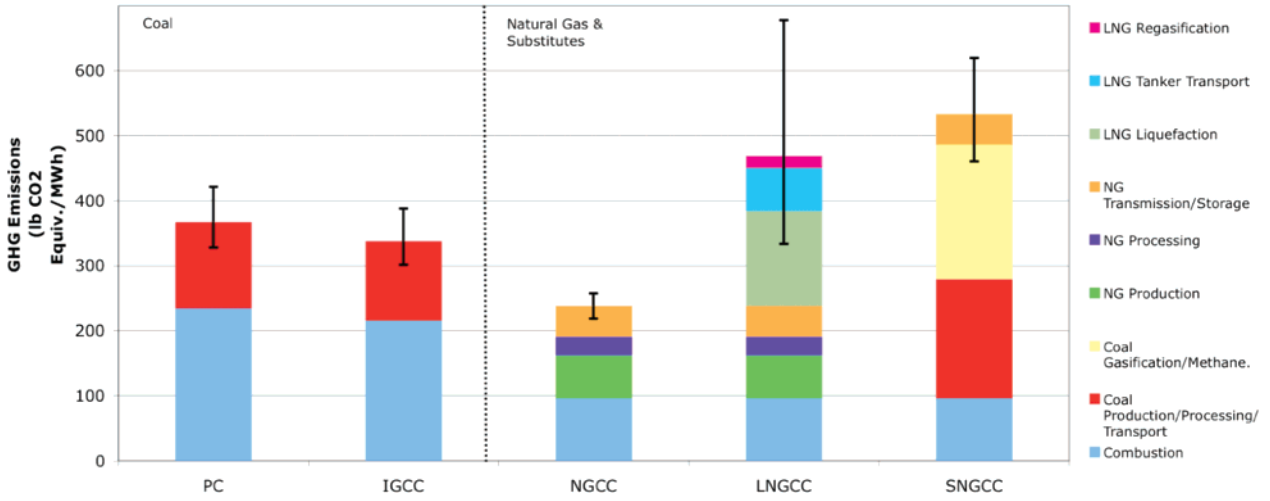

FIGURE 3. Midpoint Life-Cycle GHG Emissions Using Advanced Technologies with CCS.

TABLE 2. SO_x and NO_x Life-Cycle Emission Factors for Advanced Technologies

fuel		SO_x (lb/MWh)		NO_x (lb/MWh)	
		min	max	min	max
current electricity mix		6.04		2.96	
coal	PC w/o CCS	0.24	1.54	1.42	2.46
	PC w/ CCS	0.08	0.34	1.90	3.61
	IGCC w/o CCS	0.27	1.57	0.47	0.70
	IGCC w/ CCS	0.32	1.83	0.54	0.78
natural gas	NGCC w/o CCS	0.04	0.20	0.30	2.57
	NGCC w/ CCS	0.05	0.24	0.36	3.01
LNG	NGCC w/o CCS	0.25	1.04	0.39	5.89
	NGCC w/ CCS	0.30	1.23	0.46	6.91
SNG	NGCC w/o CCS	0.35	2.15	0.88	1.85
	NGCC w/ CCS	0.45	2.80	1.03	2.18

For emissions of SO_x, we found that with current electricity generation technologies, coal has significantly higher life-cycle emissions than any other fuel due to very high emissions at current power plants. For NO_x, however, this pattern is different. We find that with current electricity generation technologies, LNG could have the highest life-cycle NO_x emissions (since emissions from liquefaction and regasification are significant), and that even natural gas produced in North America could have life-cycle NO_x emissions very similar to those of coal. It is important to note that while GHG emissions contribute to a global problem, SO_x and NO_x are local pollutants and U.S. policy makers may not give much weight to emissions of these pollutants in other countries.

In the future, as newer generation technologies and CCS are installed, the overall life-cycle GHG emissions from electricity generated with coal, domestic natural gas, LNG, or SNG could be similar. Most important is that all fuels with advanced combustion technologies and CCS have lower life-cycle GHG emission factors than the current average emission factor from electricity generation. For SO_x we found that coal and SNG would have the largest life-cycle emissions, but all fuels have lower life-cycle SO_x emissions than the current average emissions from electricity generation. For NO_x, LNG would have the highest life-cycle emissions and would be the only fuel that could have higher emissions than the current average emission factor from electricity generation, even with advanced power plant design.

We suggest that advanced technologies are important and should be taken into account when examining the possibility of doing major investments in LNG or SNG infrastructure. Power generators hope that the price of natural gas will decrease as alternative sources of natural gas are added to the U.S. mix, so they can recover the investment made in

natural gas plants that are currently producing well under capacity. We suggest that these investments should be viewed as sunk costs. Thus, it is important to re-evaluate whether investing billions of dollars in LNG/SNG infrastructure will lock us into an undesirable energy path that could make future energy decisions costlier than ever expected and increase the environmental burden from our energy infrastructure.

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Supporting Information Available

Graphical representation of the fuel life-cycles, emissions calculation information, summary of emissions from fuel life-cycles, power plant efficiency information, emissions from advanced technologies, and references, This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) U.S. EPA. *Inventory of US Greenhouse Gas Emissions and Sinks: 1990−2002*; Office of Global Warming: Washington, DC, 2004.
(2) U.S. DOE. *Historical Natural Gas Annual: 1930 Through 2000*; Energy Information Administration: Washington, DC, 2001.
(3) U.S. DOE. *Electric Power Annual*; Energy Information Administration: Washington, DC, 2003.
(4) U.S. DOE. *Annual Energy Outlook*; Energy Information Administration: Washington, DC, 1999.
(5) Granger, M.; Apt, J.; Lave, L. *The U.S. Electric Power Sector and Climate Change Mitigation*; Pew Center on Global Climate Change: Arlington, VA, 2005.
(6) U.S. DOE. *U.S. Natural Gas Wellhead Price: 1973 to 2006*; Energy Information Administration: Washington, DC, 2006.
(7) Rosenberg, W. G.; Walker, M. R.; Alpern, D. C. *National Gasification Strategy: Gasification of Coal & Biomass as a Domestic Gas Supply Option*; Harvard University, John F. Kennedy School of Government: Cambridge, MA, 2005.
(8) U.S. DOE. *Annual Energy Outlook*; Energy Information Administration: Washington, DC, 2006.
(9) ISO. *ISO 14040 - Environmental Management - Life Cycle Assessment: Principles and Framework*; International Organization for Standardization: Geneva, Switzerland, 1997.
(10) Hendrickson, C.; Lave, L.; Matthews, H. S. *Environmental Life Cycle Assessment of Goods and Services: An Input-Output Approach*; Resources for the Future: Washington, DC, 2006.
(11) U.S. DOE. *U.S. LNG Market and Uses: June 2004 Update*; Energy Information Administration: Washington, DC, 2004.
(12) U.S. DOE. *Coal Transportation: Rates and Trends in the United States, 1979 - 2001*; Energy Information Administration: Washington, DC, 2004.
(13) U.S. DOE. *Natural Gas Annual 2003*; Energy Information Administration: Washington, DC, 2004.
(14) U.S. EPA. *Methane Emission From the Natural Gas Industry*; Environmental Protection Agency: Washington, DC, 1996.
(15) Davis, S. C.; Diegel, S. W. *Transportation Energy Data Book*, 25th ed.; Oak Ridge National Laboratory: Oak Ridge, TN, 2006.
(16) U.S. EPA. *EGRID Data Highlights*; http://www.epa.gov/cleanrgy/egrid/samples.htm#highlights (accessed September 14, 2006)
(17) U.S. EPA. *AP 42 Emission Factors Volume I: Stationary Point and Area Sources*; Technology Transfer Network: Clearinghouse for Inventories and Emission Factors: Washington, DC, 1995.
(18) U.S. DOE. *The Global Liquefied Natural Gas Market: Status & Outlook*; Energy Information Administration: Washington, DC, 2005.
(19) FERC. *Existing and Proposed North American LNG Terminals as of May 2006*; Office of Energy Projects: Washington, DC, 2006.
(20) Tobin, J. *Expansion and Change on the U.S. Natural Gas Pipeline Network - 2002*; Energy Information Administration: Washington, DC, 2002.
(21) Tamura, I.; Tanaka, T.; Kagajo, T.; Kuwabara, S.; Yoshioka, T.; Nagata, T.; Kurahashi, K.; Ishitani, H. M. S. Life Cycle CO_2 Analysis of LNG and City Gas. *Appl. Energy* **2001**, *68*, 301−319.
(22) Sharke, P. In *Mechanical Engineering Magazine*, July 2004.
(23) U.S. DOE. *Worldwide Natural Gas Supply and Demand and the Outlook for Global LNG Trade*; Energy Information Administration: Washington, DC, 1997.
(24) Corbett, J. J. In *LNG Tankers and Air Emissions: Context, Inventory Methods, Implications*; 2006.
(25) Corbett, J. J.; Koehler, H. W. Updated Emissions from Ocean Shipping. *J. Geophys. Res.* **2003**, *108*.
(26) Endresen, O.; Sorgard, E.; Sundet, J. K.; Dalsoren, S. B.; Isaksen, I. S. A.; Berglen, T. F.; Gravir, G. Emission from International Sea Transportation and Environmental Impact. *J. Geophys. Res., [Atmos.]* **2003**, *108*.
(27) WorldNewsNetwork., World Port Distance Calculator; www.distances.com (accessed May 31, 2006)
(28) Ruether J.; Ramezan, M. G. Eric Life Cycle Analysis of Greenhouse Gas Emissions for Hydrogen Fuel Production in the US from LNG and Coal; *Second International Conference on Clean Coal Technologies for our Future*; 2005.
(29) U.S. Department of Commerce. *1997 U.S. Economic Census*; U.S. Census Bureau: Washington, DC, 2001.
(30) CMU. Economic Input-Output Life Cycle Assessment Model; www.eiolca.net (accessed May 9, 2006).
(31) U.S. DOE. *Coal Industry Annual 1997*; Energy Information Administration: Washington, DC, 1997.
(32) U.S. EPA. *AP 42 Emission Factors Volume II: Mobile Sources*; Technology Transfer Network: Clearinghouse for Inventories and Emission Factors: Washington, DC, 1995.
(33) Beychok, M. R. *Process & Environmental Technology for Producing SNG & Liquid Fuels*; U.S. Environmental Protection Agency: Washington, DC, 1975.
(34) Gray, D.; Salerno, S.; Tomlinson, G. *Potential Application of Coal-Derived Fuel Gases for the Glass Industry: A Scoping Analysis*; National Energy Technology Laboratory, DOE: Pittsburgh, PA, 2004.
(35) Bergerson, J. A. *Future Electricity Generation: An Economic and Environmental Life Cycle Perspective on Options and Policy Implication*; Carnegie Mellon University, Pittsburgh, PA, 2005.
(36) U.S. DOE. *Combined (Utility, Non-Utility, and Combined Heat & Power Plant) Database in Excel Format*; Energy Information Administration: Washington, DC, 2003.
(37) U.S. EPA. *EGRID Emission Data, 2002*; Clean Energy Office: Washington, DC, 2002.
(38) Rubin, E. S.; Rao, A. B.; Chen, C. In *Proceedings of 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7)*, Vancouver, Canada 2004.

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