W. M. Keck Institute for Space Studies Postdoctoral Fellowship Final Report

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The earth's atmospheric composition is experiencing a perturbation unprecedented in the Holocene [Forster et al., 2007]. Various human activities, including large-scale deforestation, fossil fuel harvesting and combustion, and industrial scale crop fertilization have tremendously upset the planet's carbon and nitrogen cycles and led to large increases in the atmospheric abundance of greenhouse gases [Forster et al., 2007]. These changes are ongoing and dynamic. Anthropogenic greenhouse gas emissions are undergoing rapid alterations in response to technological, economic, and regulatory pressures. Quantification of anthropogenic greenhouse gas emissions is crucial to understanding the future of earth's climate.

My postdoctoral work focused on urban greenhouse gas emissions. Can we quantify urban greenhouse gas emissions with atmospheric observations? Can we do so from space? A description of result highlights follows below. Technical details can be found in the attached peer-reviewed manuscripts.

More than half the world's population now lives in urban areas, and over 70% of global energy-related CO_2 emissions are attributed to these areas. In efforts aimed at mitigation, some cities have enacted emissions reduction policies, but lack observation-based methods for verifying their efficacy. Atmospheric abundances of greenhouse gases (GHGs) in and around megacities are strongly impacted by local anthropogenic GHG emissions, and therefore have the potential to provide objective, independent assessment of GHG emissions trends due to urban emissions. Developing methods to observe, quantify, attribute, and track megacity GHG emissions would provide an invaluable tool for verifying true anthropogenic emission trends. Additionally, this improved quantification of anthropogenic contributions would greatly tighten top-down constraints on biospheric uptake, particularly crucial as we consider the future of the CO_2 land sink.

In work sponsored by KISS, we've shown megacity CO_2 can be observed and potentially tracked with space-based observations [Kort et al., 2012a]. We were able to demonstrate that even with satellites designed to study global carbon exchange, by focusing on megacities (Los Angeles and Mumbai), we could extract robust signatures of urban emissions, and make quantitative inferences about emission change with time.

Simulation studies were performed to assess NASA's Orbiting Carbon Observatory-2 ability to quantify anthropogenic emission in Los Angeles. Results suggest this new space-based sensor will provide a substantial improvement over current space-based observations. A nice summary of summer student findings on this project can be found at (http://develop.larc.nasa.gov/Summer2012Projects/LosAngelesHAQ.html).

As we've developed the space-based capability, we have also begun expanding ground-based observations in Los Angeles for tighter emissions constraints and validation of space-based methods. Using a high-resolution regional model, we've designed an optimal network layout for ground-based observations [Kort et al., 2012b]. We are now currently expanding the ground-based network using these simulation results as guidelines.

In working with Professor Wennberg [Wennberg et al., 2012], we considered methane emissions from the Los Angeles basin. Utilizing ground and airborne observations of methane and ethane, we were able to identify that LA appears to be emitting substantially more methane than attributed in inventory estimates. We furthermore discerned the atmospheric ethane:methane ratio had declined in lock-step with the supply to the basin, strongly suggestive that much of the observed excess methane was attributable to leakage of natural gas. This finding motivated the development of a continuous methane-ethane analyzer in a KISS technical development for follow-up studies.

We have now deployed this instrument throughout the basin in June of 2013, making mobile van observations in concert with the UC-Irvine mobile laboratory. Preliminary assessment of the data indicates it will be invaluable in attributing the source responsible for observed methane plumes. Ongoing analysis is planned and underway.

Ongoing work focused on investigating methane emissions in LA from space has shown great promise. Work with the GOSAT satellite has indicated we indeed can observe the methane dome of LA from space. Furthermore, we are able to use simultaneous methane and carbon dioxide observations to quantify the methane emissions from LA. Doing so with GOSAT observations, we find emissions numbers that agree well with those found with ground-based methods in Wennberg et al.   This demonstrates that even using non-ideal instruments and sampling techniques, space-based detection of methane is possible.

We have furthermore added the capability to measure boundary layer depth (critical for linking atmospheric concentrations to fluxes). These observational developments should help us better constrain GHG emissions from LA, and attribute the emissions to appropriate source category. Preliminary analysis of the boundary layer instruments in conjunction with ground-based and total column greenhouse gas observations has shown tantalizing results [Kort et al., AGU 2012].

In my time here at Caltech/JPL, substantial progress has been made in advancing urban greenhouse gas studies from space. We have demonstrated the first quantitative space-based observation of megacity emissions of carbon dioxide and methane. We have furthermore developed methods, and outlined recommendations, for developing supporting ground-based observations. This work will provide an important foundation as this research area continues to expand in coming years.

Forster P et al. (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon et al., Cambridge Univ. Press, Cambridge.

Kort EA et al. (2012a), Geophysical Research Letters, 39, L17806.

Kort EA et al. (2012b), *Surface observations for monitoring megacity greenhouse gas emissions: minimum requirements for the Los Angeles megacity*, J. Geophys. Res.

Wennberg PO et al. (2012), *On the Sources of Methane to the Los Angeles Atmosphere*, Environmental Science and Technology.

Acknowledgements
I would like to thank KISS for providing this wonderful opportunity to explore this exciting and interesting frontier of greenhouse gas research. Special thanks to the KISS family for providing such a supportive and fun environment—in particular Michelle Judd and Tom Prince. Much thanks to Chip Miller, Paul Wennberg, Christian Frankenberg, Debra Wunch, Riley Duren, Annmarie Eldering, Mike Gunson, Yuk Yung, Sally Newman, Dave Schimel, and many more for making JPL/Caltech such a exciting and fun place to study.

Talks & Posters (*invited)

Kort EA, Frankenberg C, Miller CE, Dubey M, Costigan K, Lindenmaier R, *Earth and Space-based observations of CO_2 and CH_4 to quantify and attribute anthropogenic emissions*, Gordon Research Conference, Mt. Snow, VT, 2013. (poster)
Kort EA, Angevine W, DeCola P, Duren R, Frankenberg C, Miller CE, Newman S, Oda T, Roehl C, Wennberg PO, Wunch D, *Detecting policy-relevant megacity greenhouse gas emission changes from space and earth-based observations*, NACP All-Investigators Meeting, Albuquerque, 2013
*Kort EA, Frankenberg C, Miller CE, Oda T, *Observing megacity greenhouse gas emissions from space*, AGU Fall meeting, San Francisco, 2012
*Kort EA, Angevine W, Decola P, Duren R, Miller CE, Newman S, Roehl C, Wennberg P, Wunch D, *Detecting policy-relevant greenhouse gas emission changes with atmospheric observations*, AGU Fall meeting, San Francisco, 2012
Kort EA, Frankenberg C, Miller CE, *Space-based Observations of Megacity Carbon Dioxide*, IWGGMS8, Caltech, 2012
Kort EA, *Urban CO_2 and CH_4 source attribution and network sensitivity*, Megacities Carbon Project workshop, Caltech, Pasadena, CA 2012
Kort EA, *Estimating emissions trends from Atmospheric Concentrations*, Megacities Carbon Project workshop, Caltech, Pasadena, CA 2012
Kort EA, Miller CE, Duren R, Eldering A, Sander S, Newman S, *Megacity Carbon: Observing system study for tracking Los Angeles greenhouse gas emission trends*, EGU Meeting, Vienna, Austria, 2012
Kort EA, Miller CE, Duren R, Eldering A, Sander S, Newman S, *Megacity Carbon: Initial network design for Los Angeles*, AGU Fall Meeting, San Francisco, CA, 2011
Kort EA, *High-resolution Inverse Modeling for LA*, Monitoring CO_2 in Megacities: Paris – Los Angeles workshop, Paris, France, 2011

Invited Seminars
Massachusetts Institute of Technology, Civil & Environmental Engineering (2013); University of Michigan, Atmospheric, Oceanic and Space Sciences (2013); Jet Propulsion Laboratory (2013); Pomona College, Physics (2012); UC Irvine, Earth System Science (2012); UCLA, Atmospheric and Oceanic Sciences (2012); Caltech, ESE & Society discussion group (2012); Caltech, Yuk Lunch seminar (2011)

Proposals: KISS technical development (selected, co-I)

Space-based observations of megacity carbon dioxide

Eric A. Kort,[1,2] Christian Frankenberg,[2] Charles E. Miller,[2] and Tom Oda[3,4]

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[1] Urban areas now house more than half the world's population, and are estimated to contribute over 70% of global energy-related CO_2 emissions. Many cities have emission reduction policies in place, but lack objective, observation-based methods for verifying their outcomes. Here we demonstrate the potential of satellite-borne instruments to provide accurate global monitoring of megacity CO_2 emissions using GOSAT observations of column averaged CO_2 dry air mole fraction (X_{CO2}) collected over Los Angeles and Mumbai. By differencing observations over the megacity with those in nearby background, we observe robust, statistically significant X_{CO2} enhancements of 3.2 $\pm$ 1.5 ppm for Los Angeles and 2.4 $\pm$ 1.2 ppm for Mumbai, and find these enhancements can be exploited to track anthropogenic emission trends over time. We estimate that X_{CO2} changes as small as 0.7 ppm in Los Angeles, corresponding to a 22% change in emissions, could be detected with GOSAT at the 95% confidence level.
Citation: Kort, E. A., C. Frankenberg, C. E. Miller, and T. Oda (2012), Space-based observations of megacity carbon dioxide, *Geophys. Res. Lett.*, *39*, L17806, doi:10.1029/2012GL052738.

[2] Carbon dioxide (CO_2) holds a central role in the earth's climate system, acting as a potent greenhouse gas [*Forster et al.*, 2007]. It is the single most important human-influenced (anthropogenic) greenhouse gas, with atmospheric abundances increasing over the last 50 years from less than 320 ppm to present day values approaching 400 ppm, with a significant associated radiative forcing perturbation [*Forster et al.*, 2007]. Future agreements to abate and reduce emissions will require independent Measurement, Reporting, and Verifying (MRV) [*Duren and Miller*, 2011]. Atmospheric observations can provide independent MRV, as anthropogenic emissions are reflected in atmospheric CO_2 concentrations. However, other processes, including atmospheric transport, also influence atmospheric carbon dioxide levels, obfuscating source attribution, presenting a major challenge in using atmospheric observations for MRV. In particular, the exchange of carbon dioxide due to photosynthesis (uptake) and respiration (release) produces a large diurnal and seasonal impact on observed mixing ratios. Though land-based biospheric fluxes only represent a net sink of ~1/4 of annual anthropogenic emissions [*Pan et al.*, 2011], this represents the interplay between seasonally varying large uptake and release that greatly impact observed atmospheric CO_2. For MRV, we must disentangle the anthropogenic and biospheric signals.

[3] One approach is to exploit the spatial disaggregation of the fluxes [*Pacala et al.*, 2010]. Anthropogenic emissions are largely concentrated in urban areas. Net fluxes per unit area in urban regions greatly exceed that of forests (i.e., +20 kg CO_2 m^{-2} yr^{-1} for Los Angeles compared to -0.9 kg CO_2 m^{-2} yr^{-1} at Harvard Forest [*Pacala et al.*, 2010]). Megacities in particular are large anthropogenic emitters, with the ten largest greenhouse gas emitting cities having emissions comparable to those of Japan [*Hoornweg et al.*, 2010]. These emissions result in very large localized urban CO_2 domes that are easy to detect [*Pataki et al.*, 2007; *Rigby et al.*, 2008]. The large signal can often be attributed to fossil fuel emissions, which can overwhelm the influence of the urban biosphere [*Newman et al.*, 2012]. Fossil fuel signals in the total column have been estimated to range from ~0.5 to ~2.0 ppm for some representative large cities [*Pacala et al.*, 2010], though ground-based total column observations over Los Angeles indicate this signal ranges from 2–8 ppm [*Wunch et al.*, 2011]. Though megacities have been a research target for air quality, most recently by *Beirle et al.* [2011], the opportunity for monitoring anthropogenic greenhouse gas emissions is only beginning to be explored [*Pataki et al.*, 2007; *Rigby et al.*, 2008; *Mays et al.*, 2009; *Strong et al.*, 2011; *Newman et al.*, 2012]. The potential for space-based observation of point source emissions has been discussed for future satellite missions [*Bovensmann et al.*, 2010], and multi-year averaging of SCIAMACHY data has suggested enhancements of CO_2 over industrial Germany are observable [*Schneising et al.*, 2008]. A recent study highlights the potential of tracking urban emissions, and suggests column observations (such as those made from space) of urban CO_2 are likely the optimal method for tracking emissions trends [*McKain et al.*, 2012].

[4] Here we present and analyze column averaged CO_2 dry air mole fraction (X_{CO2}) derived from observations collected by the Greenhouse gases Observing Satellite (GOSAT) [*Morino et al.*, 2011] from June 2009 through 2011. GOSAT spectra, collected near midday, are fit using the ACOS v2.9 level 2 algorithm [*Wunch et al.*, 2011; *O'Dell et al.*, 2012; *Crisp et al.*, 2012]. In normal operations, GOSAT records three to five footprints, each ~10 km in diameter, across its 700 km swath with a revisit time of three days. Occasionally, GOSAT performs dedicated measurements over specific sites of interest, including some megacities as part of the GOSAT Research Announcement "Estimation of the anthropogenic CO_2 and CH_4 emissions from the spatial concentration distribution around large point sources" (http://www.gosat.nies.go.jp/eng/proposal/proposal.htm). Due to limitations of the GOSAT sampling coverage, we focus our study on Los Angeles and

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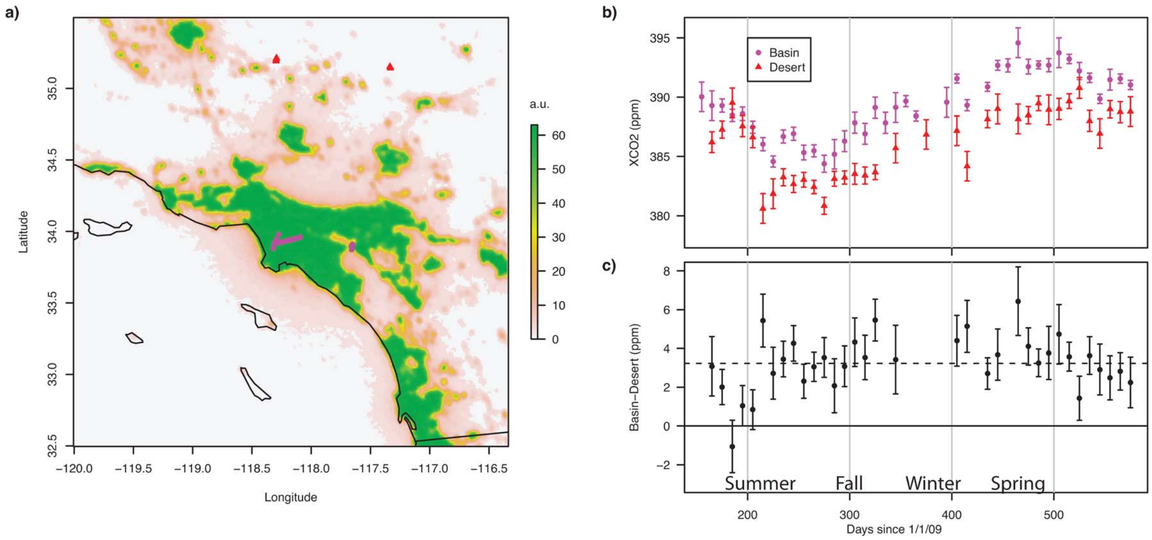

Figure 1. Observed X_{CO2} urban dome of Los Angeles from June 2009 to August 2010. (a) Nightlights map of the Los Angeles megacity and surroundings. Selected GOSAT observations within the basin (pink circles near 34°N, 118°W) and in the desert (red triangles near 35°N, 117–118°W). (b) Time-series for basin and desert observations averaged in 10-day bins. (c) The difference between 10-day block averages of basin and desert observations. The dashed black line shows the average difference (3.2 ± 1.5 ppm). All error bars plotted are one-sigma. Note Bakersfield is located near 35.4°N, 119.0°W.

Mumbai, where sufficient observations for our strategy exist. We find that statistically significant enhancements of X_{CO2} are observable throughout the year, and that these enhancements can be exploited to track anthropogenic emission trends in time.

[5] Key to our approach is the ability to differentiate X_{CO2} observations over the megacity with nearby 'clean' observations representative of background air. This relative difference isolates the CO_2 enhancement caused by megacity emissions. Relative differences are robust results that minimize sensitivity to global or zonal observational biases, and eliminate many sources of error in the satellite retrieval, as light path, viewing angle, and surface pressure are essentially identical for the megacity and clean scenes. Aerosols, surface albedo, and O_2 A-band radiance are potentially different between megacity and 'clean' observations [*Wunch et al.*, 2011].

[6] Though GOSAT has been recording operational science observations since June 2009, the need for observations both within the megacity and in a nearby background location limits the data we can use. For Los Angeles this requirement is met from June 2009 to August 2010. In August 2010 the GOSAT viewing strategy changed, resulting in a loss of the standard background desert observations. For the chosen time window, we select X_{CO2} observations within the basin, and in rural area north of the basin (termed desert). Figure 1a shows these 'basin' and 'desert' points over a nightlights map, delineating the extent of the LA megacity (nightlights image and data processing by NOAA's National Geophysical Data Center. DMSP data collected by US Air Force Weather Agency). Typical midday circulation exhibits on-shore winds with low wind-speeds [*Lu and Turco*, 1995]. This leads to large X_{CO2} enhancements where the basin observations are located, in downtown LA, and east towards Riverside. The desert observations typically sample a similar 'background' column without the anthropogenic influence (though outflow from Bakersfield and LA can influence these observations). Large-scale transport or fluxes would be expected to impact the desert and city observations similarly ('background' variability), whereas the desert observation point has little local fluxes to perturb the column. Since very few days have both basin and desert observations, we take 10-day block averages of basin and desert points. The column over this time frame clearly tracks a seasonal cycle, with basin observations systematically higher than the corresponding desert point (Figures 1b and 1c). This persistent enhancement is found to be 3.2 ± 1.5 (1σ) ppm. This enhancement is consistent with ground-based X_{CO2} observations made in Los Angeles in 2008, which observed column enhancements from 2–8 ppm attributed to anthropogenic emissions [*Wunch et al.*, 2009]. This agreement strongly supports the GOSAT observations, and validates that the differencing technique indeed produces the enhancement attributable to LA emissions. Furthermore, the value of 3.2 ± 1.5 ppm agrees well with the column enhancement predicted by a simple box model with an emissions inventory (~3.8 ppm [*Wunch et al.*, 2009]), again supporting the observations and differencing technique.

[7] Ideally we would difference basin and desert observations from the same day. Fortunately, changes in the X_{CO2} background occur on synoptic time scales, and the X_{CO2} enhancement in the basin is a robust daily feature of the Los Angeles urban dome [*Wunch et al.*, 2009; *Newman et al.*, 2012]. Daily transport variation will impact the magnitude of the enhanced CO_2 dome. This variation may in fact be responsible for some of the spread in the observed basin-desert difference. Interestingly, 20-day or 30-day block averages yield enhancements that are statistically equivalent to the 10-day block averages (Figure S1 in the auxiliary material).[1] This finding indicates the LA basin enhancement is a robust feature of the region attributable to anthropogenic emissions,

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GL052738.

and not affected by seasonally varying changes in biospheric fluxes or transport patterns. We rule out aerosol, albedo, and radiance effects (see auxiliary material). Continuous in-situ observations of $CO_{2(excess)}/CO_{(excess)}$ validated by periodic comparison with $^{14}CO_2$ from whole air flask samples, indicate that up to 100% of the midday enhancement can be attributed to emissions from fossil fuel combustion [*Newman et al.*, 2012]. The lack of any seasonality in the basin-desert difference (Figure 1b) further suggests that no significant biospheric or oceanic CO_2 fluxes are impacting our retrieved difference, as either biospheric or coastal upwelling contributions would exhibit strong seasonality. This is expected for both the city and desert observation locations, as both exhibit relatively low photosynthetic activity, demonstrated by the very low chlorophyll fluorescence signal observed in the LA region [*Frankenberg et al.*, 2011].

[8] Local meteorological conditions explain the cases when the basin-desert difference drops to zero or becomes negative. During Santa Ana conditions, the circulation changes dramatically, with strong winds travelling from the desert into the LA basin. These events carry urban emissions out to sea, expelling the urban CO_2 dome and reducing the basin-desert difference to near zero. At times the desert observation is directly downwind of Bakersfield, and therefore influenced by anthropogenic emissions and not representative of background X_{CO2}. Back trajectory calculations (using HYSPLIT [*Draxler and Rolph*, 2012]) indicate that these two conditions explain observations near day 200 in Figure 1.

[9] The data in Figure 1 demonstrate conclusively that space-based observations can detect enhanced X_{CO2} over the LA basin. With such observations we ask: What is the smallest change in emissions that could be detected? We focus on the question of change rather than absolute fluxes for a number of reasons. Even with very dense surface observational networks, retrieval of accurate absolute fluxes is hampered by the presence of unaccounted for bias errors. This often is a product of transport error in the inverse method [*Lauvaux et al.*, 2012]. When looking for changes in fluxes rather than absolute values, many bias errors do not influence our assessment. Furthermore, by looking at the change in emissions, we are insensitive to potential biases present in the differencing technique (such as the background 'desert' site being offset from a truly representative background site). We are insensitive to daily CO_2 variations attributable to transport, as we consider the full year statistical aggregate. We assume on average the transport (most importantly the basin ventilation time), does not change annually.

[10] The basin-desert difference distribution is quite Gaussian (Figure S3), enabling the use of simple statistical tools. Assuming we have the same observation set (i.e., identical statistics) for a different $\sim$1 year time frame, a simple t-test suggests we could detect a minimum change of 0.7 ppm (22% of the observed enhancement) in the basin-desert difference with 95% confidence using GOSAT observations. The basin-desert difference measures the additional CO_2 molecules within the basin due to local emissions. Assuming no trend in basin ventilation time, this difference value is therefore linearly dependent on the flux. Consequently, the t-test implies GOSAT-like space-based observations could detect emissions changes of 22% or greater. California has a goal to reduce greenhouse gas emissions back to 1990 levels by 2020 (30% below current trends [*Croes*, 2012]). By 2030 Los Angeles plans to cut greenhouse gas emissions 35% vs. 1990 levels [*Villaraigosa et al.*, 2007]. To achieve these goals, emissions reductions will need to exceed 22% from 2009/2010 levels. If these reductions were spatially heterogeneous through the LA basin, these reductions would appear to be observable and verifiable with appropriate sustained observations from space. Ground-based observations of CO_2 and meteorological variables would be necessary to support and validate such space-based verification.

[11] The question arises whether similar X_{CO2} enhancements can be observed over other megacities. Mumbai also exhibits a CO_2 urban dome observable from space. When appropriate GOSAT observations are available (e.g., during the dry season of 2011), we can apply the same technique used to analyze Los Angeles X_{CO2}. We identify city and rural observations, and find a robust X_{CO2} enhancement of 2.4 $\pm$ 1.2 (1σ) ppm in Mumbai (Figure S4). In fact, on specific observing days in March of 2011, GOSAT observations captured the city-rural X_{CO2} gradient (Figure 2). Further interpretation of the Mumbai observations is hampered by the limited data and the total lack of observations in the wet season. There is a potential biospheric influence on the background sites. The current observational capability over Mumbai would be challenged to detect robust emissions changes, but these observations do demonstrate that satellite observations of this precision can identify enhanced X_{CO2} due to megacity emissions as well as map their spatial extent and variability.

[12] The meteorology in both Los Angeles and Mumbai enables us to apply our simple technique. Both are coastal cities with consistent wind patterns that commonly form urban CO_2 domes. Nearby background locations with smaller anthropogenic and biogenic influence exist. Many megacities are near other major urban sources or strong biogenic influences. This leads to significant daily perturbations to the megacity CO_2 concentrations that are not attributable to local anthropogenic emissions. To monitor CO_2 concentrations under these conditions requires numerous observations in space and time both around and within the megacity. Additionally, atmospheric transport must be explicitly considered.

[13] Although our simple approach works for Los Angeles and Mumbai, the current GOSAT observing strategy limits its use for systematic monitoring and assessing global megacity emission trends. There are few observations directly over the small areas occupied by megacities, or in a nearby background location. Filtering of cloudy or other contaminated retrievals reduces the number of usable observations further. It is rare to have a day with observations both within the city and over a nearby rural/background location. In spite of the sparseness of megacity observations, care should be taken when using special observations in global inversion studies, as these are non-random samples in space, and are biased towards point-emitters poorly represented in global models.

[14] We suggest a program of "Special Observations" focused on megacities, with particular emphasis on rapidly growing population centers (e.g., Delhi, Dhaka, Karachi, Lagos, Shanghai). The program should include dense observations within each urban center combined with nearly simultaneous observations of appropriate nearby rural/background sites (see Figure 1a).

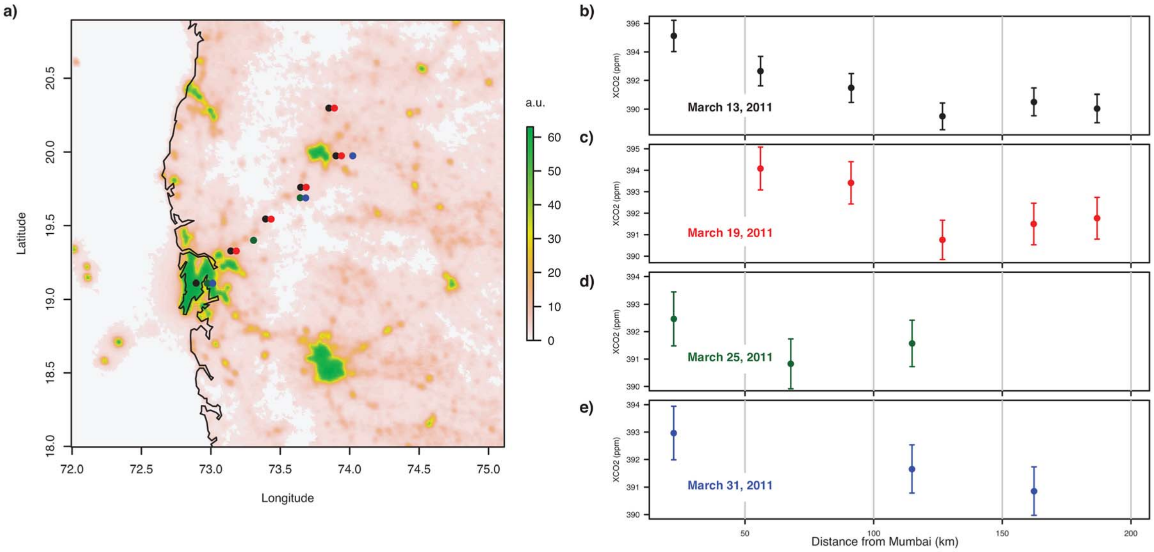

Figure 2. Spatial mapping of Mumbai X_{CO2} urban dome in March 2011. (a) Nightlights map of the Mumbai megacity and surroundings. Selected GOSAT observations, corresponding to days in Figures 2b–2e. Overlaying footprint locations are offset for visibility. (b–e) X_{CO2} urban dome gradient observed over Mumbai. Error bars are one-sigma retrieval error.

[15] Future satellites will offer new opportunities to monitor megacity CO_2 emissions. Improved spatiotemporal coverage with small footprints, such as offered by 'mapping' or geostationary observations are particularly attractive for megacity emissions studies.

[16] **Acknowledgments.** This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA. EAK thanks the W. M. Keck Institute for Space Studies for support. GOSAT Level 1B products (spectral data) were provided by the GOSAT Project (JAXA, NIES, and Ministry of the Environment Japan) through its collaboration with NASA's Atmospheric CO_2 Observations from Spaces (ACOS) team. The X_{CO2} data used in this work were processed by the ACOS team using software build 2.9. The authors thank the GOSAT and OCO/ACOS teams for continued collaboration and detailed technical discussions. The authors wish to thank Paul Wennberg, Yuk Yung, Michael Gunson, and Annmarie Eldering for insightful and constructive suggestions and comments.

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Surface observations for monitoring urban fossil fuel CO_2 emissions: Minimum site location requirements for the Los Angeles megacity

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[1] The contemporary global carbon cycle is dominated by perturbations from anthropogenic CO_2 emissions. One approach to identify, quantify, and monitor anthropogenic emissions is to focus on intensely emitting urban areas. In this study, we compare the ability of different CO_2 observing systems to constrain anthropogenic flux estimates in the Los Angeles megacity. We consider different observing system configurations based on existing observations and realistic near-term extensions of the current ad hoc network. We use a high-resolution regional model (Stochastic Time-Inverted Lagrangian Transport-Weather Research and Forecasting) to simulate different observations and observational network designs within and downwind of the Los Angeles (LA) basin. A Bayesian inverse method is employed to quantify the relative ability of each network to improve constraints on flux estimates. Ground-based column CO_2 observations provide useful complementary information to surface observations due to lower sensitivity to localized dynamics, but column CO_2 observations from a single site do not appear to provide sensitivity to emissions from the entire LA megacity. Surface observations from remote, downwind sites contain weak, sporadic urban signals and are complicated by other source/sink impacts, limiting their usefulness for quantifying urban fluxes in LA. We find a network of eight optimally located in-city surface observation sites provides the minimum sampling required for accurate monitoring of CO_2 emissions in LA, and present a recommended baseline network design. We estimate that this network can distinguish fluxes on 8 week time scales and 10 km spatial scales to within ~12 g C m^{-2} d^{-1} (~10% of average peak fossil CO_2 flux in the LA domain).

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1. Introduction

[2] Carbon dioxide (CO_2) is the single most important anthropogenic greenhouse gas [*Forster et al.*, 2007]. Atmospheric levels of CO_2 have increased from a preindustrial level of 280 ppm to nearly 400 ppm today, and anthropogenic emissions continue to rise [*Hofmann et al.*, 2009]. This 40% increase in CO_2 significantly perturbs the Earth's radiative balance, and provides potential incentive for a reduction in emissions. Atmospheric observations have the potential to provide independent validation for any future agreement on carbon emissions. However, to extract information on anthropogenic emissions from atmospheric observations, the role of transport and biospheric fluxes must be untangled. Current global assimilation frameworks are incapable of disentangling these components to the level required for monitoring of anthropogenic CO_2 at 300 km spatial scales [*Hungershoefer et al.*, 2010]. By developing a framework specifically focused on small area, large magnitude anthropogenic sources, we can potentially overcome transport and biospheric obfuscation. Improved observational constraints on anthropogenic emissions will also improve biospheric flux estimates.

[3] Megacities present an excellent target from both an atmospheric and policy perspective. Megacities concentrate large emissions in a small area, often producing an urban dome with significant anthropogenic enhancement of CO_2 [*Pacala et al.*, 2010]. Urban areas are estimated to be responsible for over 70% of global energy-related carbon emissions [*Rosenzweig et al.*, 2010]. Urban populations are expected to grow, with projections of global urban population almost doubling by 2050. Some megacities already have

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climate plans in place, including aggressive greenhouse gas emissions reductions objectives (i.e., Los Angeles, *Villaraigosa et al.* [2007]).

[4] Many measurements of CO_2 in urban environments have been made, with a particular focus on the diurnal variation of CO_2 and its relation to boundary layer height and emissions [*Pataki et al.*, 2007; *Rigby et al.*, 2008; *Strong et al.*, 2011]. Recent examples have started to attempt to specifically attribute emissions [*Turnbull et al.*, 2011; *Newman et al.*, 2012] and perform trend detection over time [*McKain et al.*, 2012]. These studies suggest that attribution and trend detection with atmospheric observations are possible. However, although optimal global monitoring network design has been studied [*Gloor et al.*, 2000; *Suntharalingam et al.*, 2003; *Hungershoefer et al.*, 2010], optimal strategies for monitoring urban emissions have yet to be determined.

[5] *McKain et al.* [2012] posited that total column CO_2 observations may be preferable for urban monitoring. This notion, in concert with the excellent spatiotemporal coverage of satellite-based observations, suggests space-based observations would be an ideal manner in which to sample urban emissions. *Kort et al.* [2012] succeeded in detecting enhanced CO_2 over the Los Angeles and Mumbai megacities using observations from the Greenhouse gases Observing SATellite (GOSAT), but noted that current space-based urban CO_2 observing capabilities are quite limited, and still require as yet nonexistent ground-based validation. With long temporal averaging, SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) has exhibited sensitivity to persistent CO_2 emissions from industrial Germany [*Schneising et al.*, 2008], and future satellites with designs optimized for urban studies may significantly improve space-based studies [*Bovensmann et al.*, 2010].

[6] In this study, we use a high-resolution regional model to study the ability of different CO_2 observing systems to constrain anthropogenic flux estimates in the Los Angeles megacity. We consider different observing system configurations based on existing observations and realistic near-term extensions of the current ad hoc network. We evaluate the difference between in-city surface observations and more remote, downwind observing sites. We compare the information gained from surface and ground-based total column observations. We then assess the current observing network's sensitivity to emissions, and compare with proposed network enhancements.

[7] The remainder of the paper is structured as follows. Section 2 presents the inversion scheme and transport model employed. Section 3 outlines the different observing systems considered in our study. Section 4 discusses model results, comparing and contrasting different individual observations, urban observational networks, and identifies the minimum sampling required for accurate monitoring of CO_2 emissions in Los Angeles (LA), and recommends a baseline network design.

2. Methods

[8] Monitoring of urban greenhouse gas emissions is a burgeoning area of research, and there are many open questions about the best approach to take. There will be different optimal observing strategies depending on whether questions focus on bulk anthropogenic flux changes with time, or the evolving contribution from specific source sectors. In this analysis, we are interested in (1) determining the sensitivity of different observations to LA anthropogenic emissions, and (2) quantifying the relative ability of different observations (and networks) to constrain anthropogenic CO_2 emissions estimates for the Los Angeles megacity using average fluxes for ~8 week time windows.

2.1. Inversion Method

[9] To probe observations sensitivity to emissions at a fine spatial scale, we employed the Stochastic Time-Inverted Lagrangian Transport (STILT) model [*Lin et al.*, 2003], driven by wind fields generated with the Weather Research and Forecasting (WRF) model (as in *Nehrkorn et al.* [2010]). STILT and STILT-WRF have been described and used extensively in regional inversions of various trace gases [*Gerbig et al.*, 2003; *Kort et al.*, 2008; *Miller et al.*, 2012] as well as in urban studies [*McKain et al.*, 2012]. Key to the work here is the ability of this model to produce a footprint for any hypothetical observation. The footprint represents the sensitivity of the observation to surface emissions (units ppm m^2 s μmol^{-1}), and can be used to construct the Jacobian matrix (**H**). Once **H** has been calculated for an observation or set of observations, a Bayesian framework can be used to solve for optimized fluxes by minimizing the cost function

$$J(f) = \frac{1}{2}\left[(z - \mathbf{H}f)^T \mathbf{R}^{-1}(z - \mathbf{H}f) + \left(f - f_{\text{prior}}\right)^T \mathbf{C}_{\text{prior}}^{-1}\left(f - f_{\text{prior}}\right)\right] \quad (1)$$

[10] Here z is an $n \times 1$ vector of observations, **H** is an $n \times m$ Jacobian, f is an $m \times 1$ vector of fluxes in the domain, f_{prior} is an $m \times 1$ vector of a priori fluxes, **R** is an $n \times n$ model-data mismatch covariance matrix, and $\mathbf{C}_{\text{prior}}$ is an $m \times m$ a priori error covariance matrix representative of uncertainty in the prior flux field. An analytical solution to the minimization of (1) exists, yielding the optimized flux field (f_{post}), as well as the posterior error covariance matrix ($\mathbf{C}_{\text{post}}$), representative of the error in the optimized flux field

$$\mathbf{C}_{\text{post}} = \left[\mathbf{H}^T \mathbf{R}^{-1} \mathbf{H} + \mathbf{C}_{\text{prior}}^{-1}\right]^{-1} \quad (2)$$

[11] The posterior error covariance matrix $\mathbf{C}_{\text{post}}$ calculated using this analytical approach provides a powerful tool for evaluating different hypothetical observing systems. By simply calculating **H** for a hypothetical observing system, and defining model-data mismatch and prior flux uncertainty (**R** and $\mathbf{C}_{\text{prior}}$, respectively), we can calculate the percentage error reduction due to this set of hypothetical observations. Because the framework is analytic and the calculations rapid, many different observing systems can be quantitatively assessed and compared for their ability to constrain urban CO_2 emissions. This same analytical technique has been exploited to study global observing systems [*Hungershoefer et al.*, 2010].

2.2. Transport Model Details

[12] The simulations in this study were all performed using the WRF meteorological fields developed by *Angevine*

et al. [2012] for California during the CALNEX campaign (May–June 2010). Many configurations were tested and optimized for this time frame. We focused on the configuration referred to by Angevine et al. as GM4, which was found to have optimum representation of Los Angeles basin dynamics (note that usage of the EM4N runs, with different initialization fields and land surface model, produces nearly equivalent results). The GM4 simulation has a horizontal grid spacing of 4 km within the Los Angeles basin, with initial and boundary conditions from the U.S. National Centers for Environmental Prediction Global Forecast System analyses. The extensive evaluation performed with these wind fields [*Angevine et al.*, 2012] indicates considerable systematic and random uncertainties. For much of the analysis presented here, our findings should be relatively insensitive to these errors—particularly as we consider relative performance of different observations. These errors will have a larger impact when we consider absolute flux reductions.

[13] A Jacobian (of 0.1° × 0.1° spatial resolution, domain delineated in Figure 1) was generated for each potential observing site for a midday observation (2 P.M. local time) each day for ~2 months (7 May to 30 June 2010). Simulations were focused on midday observations for two major reasons: (1) the model best captures the atmospheric dynamics at this time of day due to the well-developed boundary layer, and (2) radiocarbon measurements indicate midday observations within the LA basin are ~100% fossil fuel derived [*Newman et al.*, 2012], meaning biospheric contributions can safely be neglected in this study. One hundred air parcels were released back in time 24 h for each potential observing site, with 10 m above ground level as the default release height for surface sites. For simulating column CO_2 observations at Caltech, 100 air parcels were released from 10 different heights above ground level of 10, 310, 610, 910, 1210, 1510, 1810, 2110, 2410, 2710 m. The column footprint was then generated as the weighted average (by pressure) of these receptors multiplied by the mass fraction of the atmosphere we have modeled (~30%). All site locations simulated are presented in Table 1.

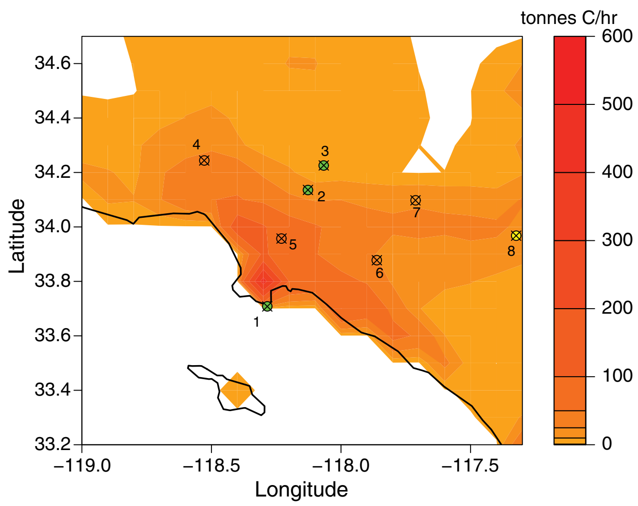

Figure 1. Vulcan emissions (average for May 2002). Targets indicate locations of observing sites, green sites currently exist, the yellow site is forthcoming, and hollow sites are proposed expansion locations.

Table 1. Surface Site Locations Used in Simulations

Identifier	Latitude	Longitude
1. Palos Verdes	33.708	–118.285
2. Caltech	34.200	–118.180
3. Mt. Wilson	34.226	–118.067
4. Northridge	34.244	–118.528
5. Downtown	33.957	–118.230
6. Anaheim	33.878	–117.862
7. Claremont	34.098	–117.713
8. Riverside	33.968	–117.324
9. Palm Springs	33.874	–116.506

[14] Comparison of modeled and observed winds at Los Angeles international airport indicates the land-sea breeze circulation is captured by the model [cf. *Angevine et al.*, 2012, Figure 4]. This suggests evening emissions that are pushed offshore and recirculated into the basin the next day are simulated. This feature of the LA basin dynamics indicates that midday observations exhibit some sensitivity to evening rush-hour emissions. It should be noted that this recirculation, and the model representation of it, is rather inefficient and uncertain. Future analyses using observations made throughout the full daily cycle would likely improve fossil-fuel emissions constraints, provided diurnal boundary layer features are captured by the model and validated by observations.

2.3. Error Covariance Matrices

[15] To reduce the influence of prior assumptions on our evaluated uncertainty reduction, we consider the simplest possible error covariance matrices. The model-data mismatch matrix (**R**) is defined as diagonal, with uncertainties (1σ) set at 5 ppm for surface observations, and 0.5 ppm for column observations. Note these values are representative of model-data mismatch, not observational uncertainty, and are approximations based largely on confidence in model representation. Thus, these values entrain uncertainty attributed to different processes including boundary condition and boundary layer height errors. The prior flux uncertainty ($\mathbf{C}_{prior}$) is based on the Vulcan CO_2 emissions inventory [*Gurney et al.*, 2009]. The average emissions for May is calculated, and uncertainty is defined as 66% of the emissions, with a floor of 3 μmol m^{-2} s^{-1}, where grid boxes with uncertainty less than this value are assigned this number. Usage of Vulcan enables us to account for the spatial heterogeneity of emissions throughout the basin, and defining an uncertainty floor enables the inversion to capture emissions from regions where Vulcan predicts negligible emissions.

[16] Note that bias errors are not included in this simple Bayesian formulism. This has a minimal impact on our relative comparison of different observations, but may impact absolute flux estimates, in particular through potential error in boundary layer height. We anticipate that the use of boundary layer observations to quantify and account for bias errors will be essential for accurate urban CO_2 flux estimates from inversions of actual observations.

3. Observing Systems

3.1. Single-Site Observations

[17] In this section we compare the information from different individual observing sites as well as from different measurement techniques. We first assess the benefits of

surface in situ observations from a site within the LA basin compared with a remote downwind site by analyzing observation at Caltech (where the actual measurement record extends back for more than a decade, *Newman et al.* [2012]) and Palm Springs, one of the LA basin's outflow regions. We also weigh the value of Caltech observations versus the near-remote site located on Mt. Wilson. We then explore whether urban CO_2 emissions can be monitored accurately with a single in-city site. Finally, we test the conclusion of *McKain et al.* [2012] that integrated column measurements are preferable for urban trend detection for Los Angeles by comparing whether surface in situ CO_2 measurements or ground-based measurements of column averaged CO_2 dry air mole fraction (XCO_2) from a single in-city location more accurately capture emissions in the LA urban CO_2 dome. Pasadena is selected for these simulations, as actual observations of each type are now being made (in situ: *Newman et al.* [2008, 2012]; column: observations began Spring 2012, similar to those in *Wunch et al.* [2009]).

3.2. Multisite Observations

[18] We consider three different observing system scenarios based on present and realistic near-term network expansions.

S1: Current observational capability in basin (Palos Verdes, Caltech, Mt. Wilson, Sites 1–3 in Table 1)

S2: S1 augmented by a downwind site in the Riverside area (Site 4, planned deployment)

S3: S2 augmented by 4 new sites (Sites 5–9, proposed deployment)

[19] The locations of existing and proposed sites are illustrated in Figure 1. Also plotted is the average anthropogenic CO_2 emissions predicted for May 2002 by the Vulcan inventory [*Gurney et al.*, 2009]. Notice the strategy proposed entails placing numerous sites in and around the high emissions concentrated in the LA basin. When actually deploying urban monitoring stations, site-specific selection details not accounted for here are critical. For this analysis we assume all sites sample air masses representative of the location on the ~1 km scale and are not dominated by "local" sampling effects. Thus, similar data would be observed for any location within ~1 km range of the sites in Table 1. From this perspective, ideal monitoring is performed from elevated height on towers, removed from very localized emission dynamics (i.e., individual roads or power plants) or submodel-scale meteorological dynamics (i.e., canyoning). Measurement accuracy, achieved though careful calibrations, is essential to prevent site-to-site biases (constant or evolving) from being falsely interpreted as atmospheric signatures from fluxes.

4. Results

4.1. Caltech

[20] Observations have been made discontinuously at Caltech since the early 1970s [*Newman et al.*, 2008]. Analysis of carbon isotopes from whole air flask samples has been performed to assess the observed CO_2 attributable to local emissions, and it was found that ~10 ppm more CO_2 was attributable to local emissions in the 1970s than the early 2000s, in seeming contrast to the known emissions increase in that time frame [*Newman et al.*, 2008]. This finding can possibly be explained by analysis of the footprint of the Caltech site, seen in Figure 2a. Observations at Caltech exhibit sensitivity to emissions in the historic downtown LA region. This downtown area was already well developed in the 1970s, and the increase in LA basins emissions in the past 40 years is more connected to urban sprawl, and an increase in emissions east in the basin. The center of LA has actually experienced a decrease in emissions, presumably largely attributable to improved transport efficiency (fuel economy) in this time frame. This highlights the value of an in-city site to track emissions trends, but emphasizes the limitations of such a site, which will only be sensitive to a portion of the regions emissions trends.

4.2. Caltech vs. Palm Springs

[21] Footprint analyses for individual observing sites explicitly show the sensitivity of observations at that site to CO_2 fluxes throughout the Los Angeles megacity. Figure 2 illustrates the average midday footprint for the previous 24 h—a good metric for a site's ability to constrain flux estimates in an inversion. Included are the footprints for surface observing sites at Caltech and Palm Springs (Figure 2a), Mt. Wilson (Figure 2b), and a total column CO_2 observation at Caltech (Figure 2c). Predominant midday wind patterns exhibit onshore flow into the basin. The Caltech surface observation footprint clearly illustrates this pattern, because the footprint is strongest southwest of the site. Wind patterns outside the basin exhibit more variability, and this is clearly exhibited in the Palm Springs footprint, showing sensitivity to emissions both to the west and southeast. Although Palm Springs has sensitivity to the LA basin on some days, many days there is little to no influence from the basin. The average footprint from Palm Springs is relatively weak in the basin compared to the site at Caltech, indicating it will not provide the same level of constraint on CO_2 emissions as the Caltech site can provide. Although a remote downwind site such as Palm Springs has days where it sees an integrated LA signal, this signal is diluted and mixed with other upwind fluxes, and is only sampled intermittently. For urban emissions monitoring, observations within the urban environment with daily sensitivity to emissions, larger signals, and fewer confounding fluxes appear superior.

4.3. Caltech vs. Mt Wilson

[22] Midday surface observations made on Mt. Wilson are thought to provide an integrated picture of the greater Los Angeles basin [*Hsu et al.*, 2010]. Mt. Wilson is located in the San Gabriel Mountains along the northern edge of the Los Angeles basin at an elevation of ~1700 m above sea level. Surface observations from Mt. Wilson sample the free troposphere in the evening, night, and morning. Midmorning upslope flow from the basin can start to reach the site. By midday, the well-established boundary layer of the LA basin can rise above the Mt. Wilson site. Therefore, the midday footprint from Mt. Wilson shows sensitivity within the LA basin (Figure 2b). Although the footprint is a bit more distributed throughout the basin than the Caltech footprint, the Mt. Wilson footprint still only exhibits sensitivity to a portion of the basin, and therefore does not contain information on the integrated basin's activities. The sensitivity to the

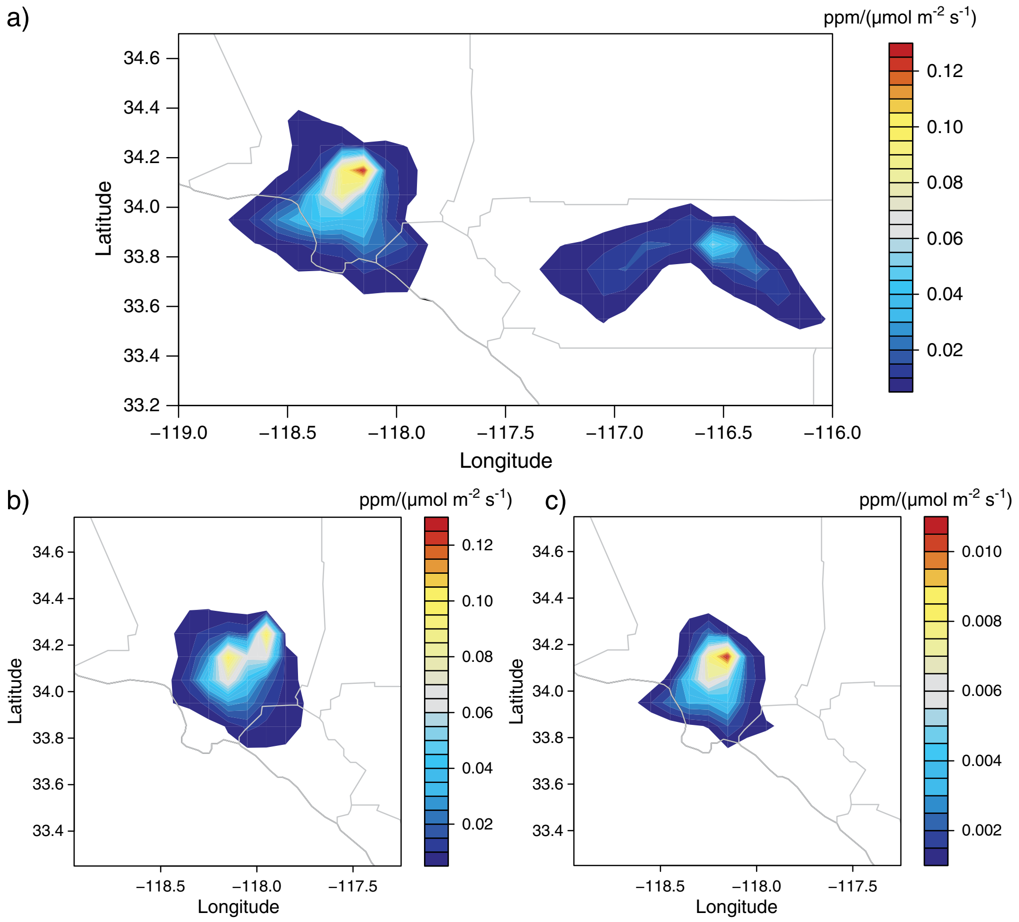

Figure 2. Average midday footprint for (a) Caltech surface site and Palm Springs surface site, (b) Mt. Wilson surface site, (c) and Caltech total column observation. Note all are shown on linear scale, where values less than 0.005 (0.001 for Figure 2c) are left white.

basin is also weaker than the in-city Caltech site, as illustrated in Figure 3, which displays the uncertainty reduction. An observation at Caltech has the ability to reduce flux uncertainty to more than 50%, while the site on Mt. Wilson can only achieve a reduction of up to 15%. Mt. Wilson is potentially a useful site for urban monitoring, particularly to define boundary conditions, as the free troposphere values sampled in evening, night, and morning, provide nice constraints on boundary CO_2 values entering the basin, but is does not provide tight constraints on emissions nor an integrated picture of the entire basin.

4.4. Caltech: Surface vs. Total Column

[23] It has recently been suggested that total column observations may be ideal for urban CO_2 emissions trend detection [*McKain et al.*, 2012]. This suggestion arises from

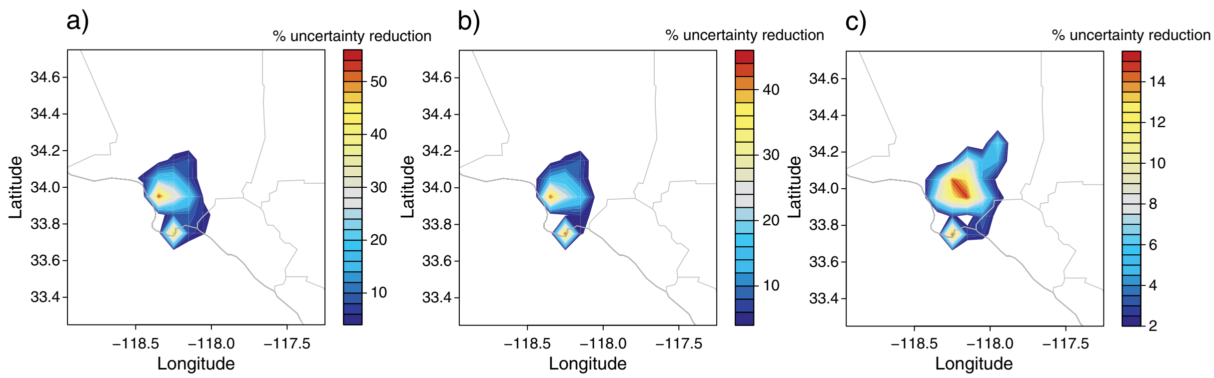

Figure 3. Uncertainty reduction in fluxes using (a) midday observations at the surface site at Caltech, (b) with a total column observation at Caltech, (c) and for observations on Mt. Wilson. Note that each panel uses a different uncertainty scale.

the notion that total column observations have lower sensitivity to small-scale emissions and meteorological dynamics, while simultaneously having sensitivity to the entire urban region. Though this may be true in a small city such as Salt Lake City, this does not hold in Los Angeles. The observation still has lower sensitivity to small-scale dynamics, but no longer is sensitive to the entire urban area. In fact, the near-field footprint of the total column observation is extremely similar to that of a surface observation in the same location (Figure 2). Interestingly, the uncertainty reduction attributable to total column versus surface observations are also very similar. This result is a product of the total column seeing smaller signals (and having a smaller **H**) but also being easier to model (having a smaller model-data mismatch error, largely attributed to reduced sensitivity to planetary boundary layer dynamics, **R**). Hence, although the total column observation will provide valuable information, and facilitate any linkage to space based observations, it does not solve the problem of having a network sensitive to the entire urban region.

4.5. Networks

[24] The current CO_2 observing network for Los Angeles is anchored by the long-term observation record at Caltech (Figure 1, Site 2). Observations at Mt. Wilson (Figure 1, Site 3) and Palos Verdes (Figure 1, Site 1) contribute boundary condition constraints and some additional sensitivity to portion of the LA megacity poorly sampled by the Caltech site. We designate this three-site network S1. As seen in Figure 4a, S1 shows good sensitivity to the urban core of the LA megacity. An inversion using observations from this network would significantly reduce CO_2 flux uncertainties over much of the megacity (>50% from prior uncertainty, Figure 5a). However, S1 lacks sensitivity to much of the megacity, especially the San Fernando and San Gabriel Valleys where much of the recent emission growth has occurred.

[25] The California Air Resources Board plans to place a new CO_2 observing site in the Riverside area (Figure 1, Site 8). Adding the Riverside site to S1 creates the four-site network we designate S2. The Riverside site will add sensitivity in the eastern section of the basin (Figure 4b). However, S2 only reduces flux uncertainty within the basin modestly compared to S1 (Figure 5b), and still lacks sensitivity to the entire basin.

[26] Following numerous trial analyses, we find that the eight-site network S3 represents a minimum design that provides sensitivity to emission throughout the basin (Figure 4c). Figure 1 shows the full S3 network, S2 augmented by in-city sites at Northridge (Figure 1, Site 4), Downtown (Figure 1, Site 5), Anaheim (Figure 1, Site 6), and Claremont (Figure 1, Site 7). Predicted uncertainty reductions now reach throughout much of the basin (Figure 5c). There are still regions of the LA megacity with weaker flux sensitivity (notably in Riverside and Northridge), but note these regions coincide with lower emissions as well. In fact, the suggested

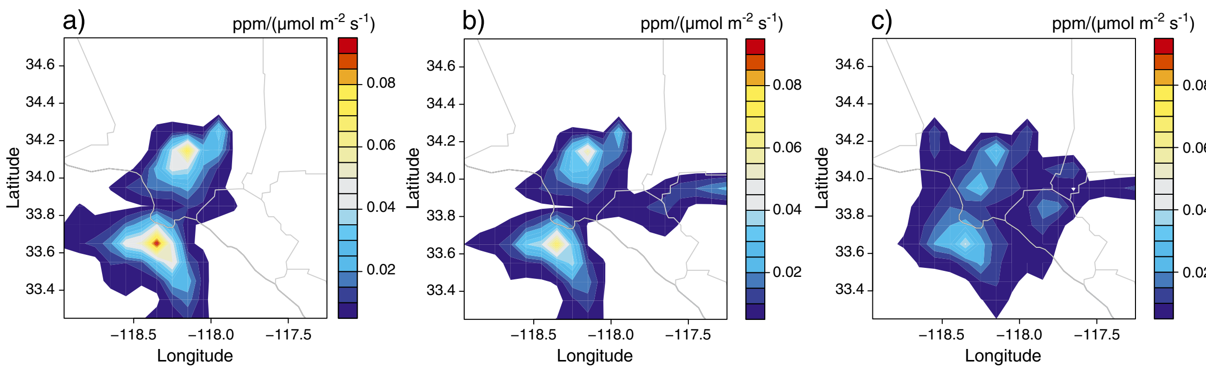

Figure 4. Average midday footprint for scenarios (a) S1, (b) S2, and (c) S3.

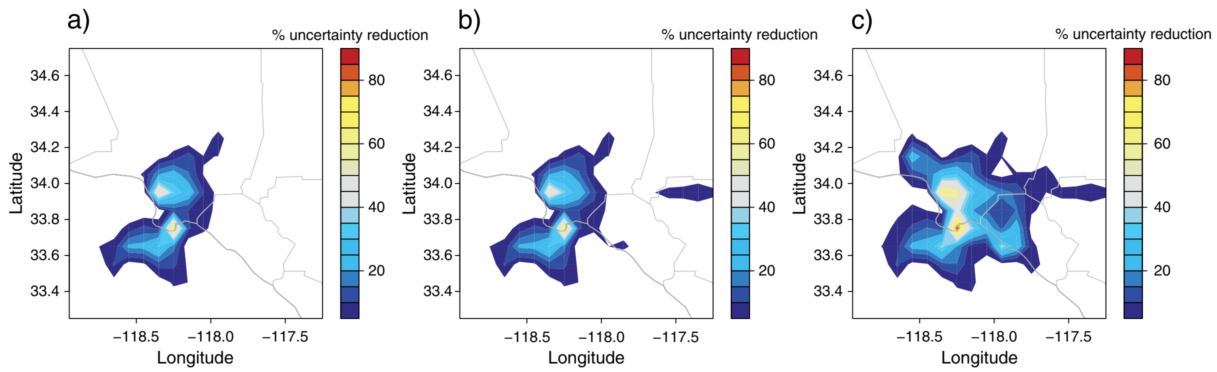

Figure 5. Uncertainty reduction in fluxes using midday observations for scenario (a) S1, (b) S2, and (c) S3.

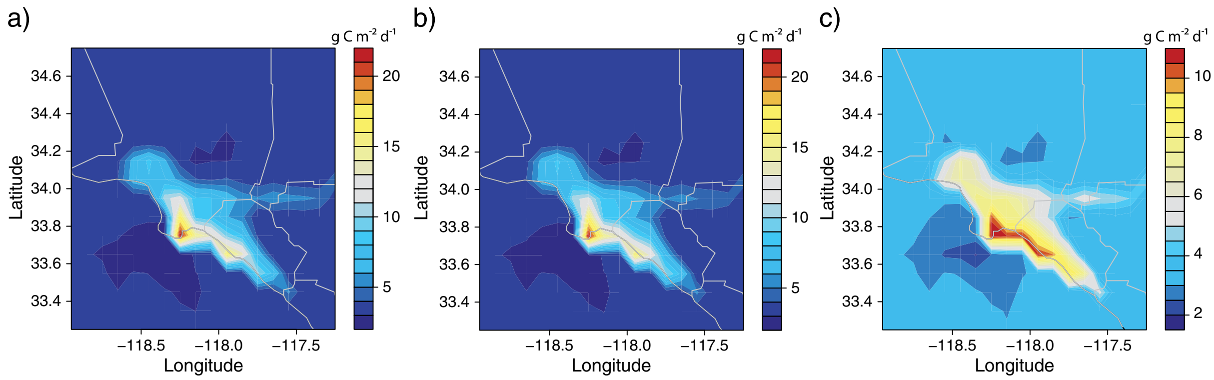

Figure 6. Posterior uncertainties for scenario (a) S1, (b) S2, and (c) S3. Note the reduced uncertainty scale for panel C.

network exhibits high sensitivity to almost the entirety of the high intensity emissions area (>10 tons C/h), suggesting this properly sited network would be able to provide observational constraints on the LA basin's emissions behavior.

4.6. Target Flux Requirements

[27] The inversion method applied is this work provides a robust answer for comparing the relative uncertainty reductions of different observing network strategies. We can also use this approach to evaluate absolute flux error reductions; however, absolute flux uncertainty estimates are highly dependent on the construction of the inversion. Even small changes to the prior error covariance matrices can significantly impact the results, whereas changes to the error covariance matrices have comparatively little impact on comparisons of relative uncertainty reductions.

[28] We consider two quantitative requirements: (1) Ability to distinguish fluxes on ~8 week time frames and ~10 km spatial scales to within 12 g C m^{-2} d^{-1}, equivalent to 10% of average peak fossil CO_2 flux in the LA domain for May 2002. Being able to reduce flux uncertainty in peak emitting areas to 10%, and be able to spatially attribute fluxes at 10 km scales begins to reach potential policy relevance. (2) Ability to distinguish 10% of average ~ monthly flux for the entire LA domain. For both policy and regional carbon balance questions, constraining the net flux of the domain is of primary importance.

[29] Figure 6 shows the spatial distribution of posterior uncertainties; demonstrating that only scenario S3 meets our requirement for high spatial resolution uncertainty. This indicates that such a network should be able to significantly reduce uncertainty of large emission regions, and be able to spatially identify the location of large emissions. None of the proposed networks with the inversion framework as constructed meet the requirement of reducing net flux uncertainty to 10%. This result is largely driven by the large uncertainty defined in the prior error covariance matrix—leading to prior net uncertainty of the high emission region (>65% of net flux) of ~100%. Scenario S3 does substantially reduce this net uncertainty of the higher emitting region to less than 50%. This inversion finding does not mean that the evaluated observing systems could not constrain fluxes at the 10% level—because inversion methods are not necessarily even required for constraining fluxes to the ~15% level [*McKain et al.*, 2012].

5. Conclusions

[30] In this study, a high-resolution regional model was used to study the minimal observational requirements to track anthropogenic CO_2 emissions trends for the Los Angeles megacity. We find that no single fixed-site CO_2 observation (surface in situ or total column) or within or downwind of the LA basin are sufficient for capturing the behavior of the entire megacity emissions trends. A minimum network of sites distributed optimally across the basin is needed to ensure sensitivity to emissions behavior throughout the LA basin. Although the present study was optimized for Los Angeles CO_2 emissions patterns and meteorology, the framework presented here can readily be applied to designing observing networks for other megacities. Additionally, because observational sensitivity to CO_2 emissions falls off exponentially with distance from the observing site, our conclusion that robust monitoring of megacity CO_2 emissions requires multiple in-city sites with location carefully selected based on local meteorology is completely general. Our proposed network here identifies the minimum sites required to detect emissions behaviors throughout the basin. We find the network proposed for Los Angeles, S3, can distinguish fluxes on 8 week time scales and 10 km spatial scales to within ~12 g C m^{-2} d^{-1}. If higher-resolution inversions are planned, and the intention is to also identify varying source locations, an even higher density network of sites with overlapping footprints would be required. We have also only focused on CO_2 observations. Use of other tracers, such as CO_2 isotopes or carbon monoxide, would facilitate in looking at specific questions relating to attribution.

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On the Sources of Methane to the Los Angeles Atmosphere

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

■ INTRODUCTION

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

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

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

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

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

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

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

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

DATA SOURCES

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

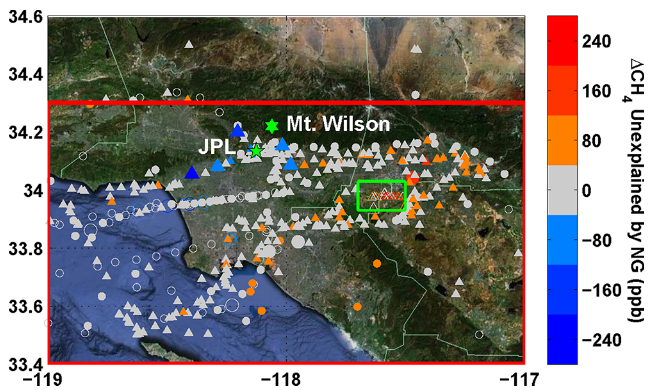

Figure 1. The locations of the ARCTAS (circles) and CalNex (triangles) measurements in the greater Los Angeles Basin overlaid on a Google Earth satellite image. The open symbols are measurements excluded from this analysis, either because they are samples that explicitly targeted dairy farms (green box),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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

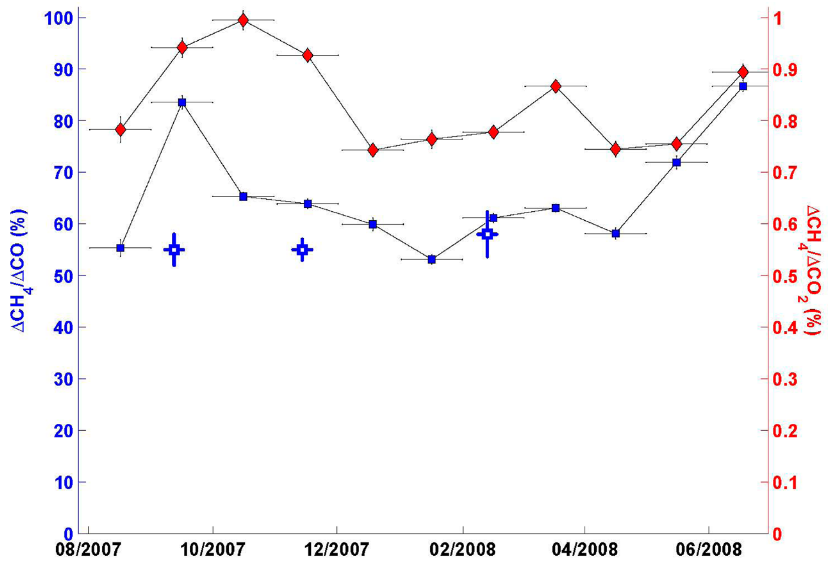

Figure 2. The monthly ratio of $\Delta CH_4/\Delta CO$ (blue squares, left axis) and $\Delta CH_4/\Delta CO_2$ (red diamonds, right axis) measured by a remote sensing technique at the campus of NASA's Jet Propulsion Laboratory (closed symbols) and at the top of Mt. Wilson (open symbols) by in situ sampling.

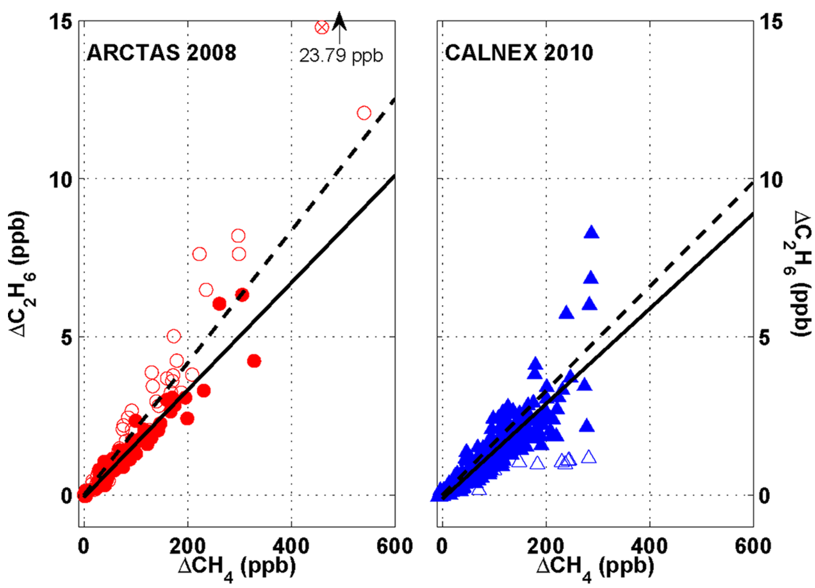

Figure 3. ΔC_2H_6 and ΔCH_4 during the ARCTAS 2008 and CalNex 2010 aircraft campaigns. The solid lines are the best fit lines to the data, and the dashed lines are the ratios of C_2H_6 to CH_4 in the natural gas delivered to the greater Los Angeles basin at the times of the measurements. The open symbols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

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

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

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

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

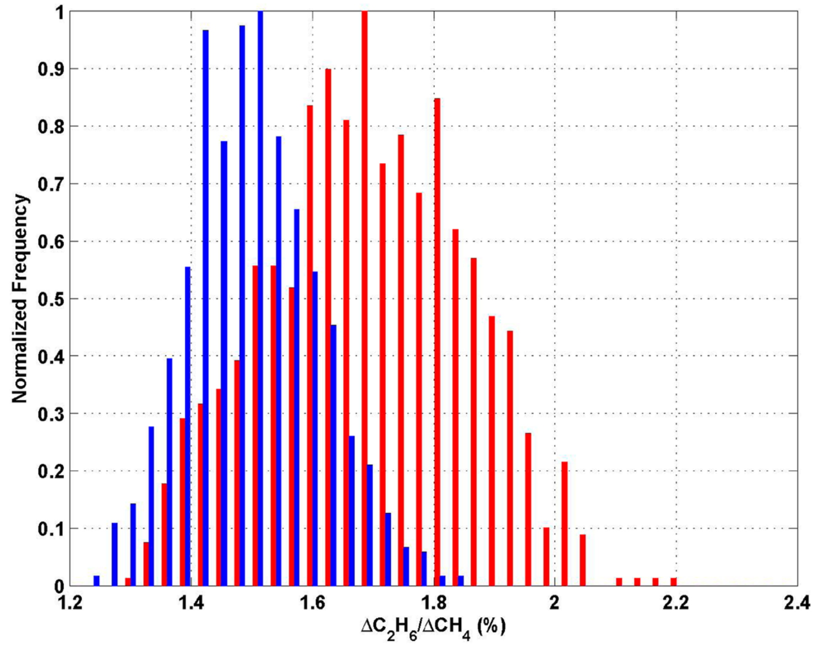

Figure 4. Histograms of the distributions of the slopes of the possible linear fits to the data in Figure 3 from the bootstrap analysis. The data in red (to the right) are computed from the ARCTAS measurements, and the data in blue (to the left) are from CalNex.

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

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

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

DISCUSSION

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

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

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

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

For C_2H_6, we assume that only the petroleum and natural gas sectors have associated emissions. For petroleum, we assume that the ratio of C_2H_6 to CH_4 is 10%,[14,34] while for the natural gas sector we use the measured C_2H_6:CH_4 ratio in 2008 from the Southern California Gas Company (Table 1).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED IN PROOF

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

■ NOTE ADDED AFTER ASAP PUBLICATION

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