



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Emissions of organic carbon and methane from petroleum and dairy operations in California's San Joaquin Valley

D. R. Gentner¹, T. B. Ford², A. Guha³, K. Boulanger^{1,*}, J. Brioude^{4,5},
W. M. Angevine^{4,5}, J. A. de Gouw^{4,5}, C. Warneke^{4,5}, J. B. Gilman^{4,5},
T. B. Ryerson^{4,5}, J. Peischl^{4,5}, S. Meinardi⁶, D. R. Blake⁶, E. Atlas⁷,
W. A. Lonneman⁸, T. E. Kleindienst⁸, M. R. Beaver^{9,**}, J. M. St. Clair⁹,
P. O. Wennberg⁹, T. C. VandenBoer^{10,***}, M. Z. Markovic^{10,****}, J. G. Murphy¹⁰,
R. A. Harley¹, and A. H. Goldstein^{1,3}

¹Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA

²Department of Chemistry, University of California, Berkeley, CA, 94720, USA

³Department of Environmental Science, Policy and Management, University of California, Berkeley, CA, 94720, USA

⁴Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



⁵Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA

⁶Department of Chemistry, University of California, Irvine, CA, 92697, USA

⁷Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, 33149, USA

⁸National Exposure Research Laboratory, Environmental Protection Agency, Research Triangle Park, NC, USA

⁹California Institute of Technology, Pasadena, CA, USA

¹⁰Department of Chemistry, University of Toronto, Toronto, ON, CA

* now at: Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

** now at: National Exposure Research Laboratory, Environmental Protection Agency, Research Triangle Park, NC, USA

*** now at: Department of Chemistry, Memorial University of Newfoundland, NL, CA

**** now at: Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA; Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA

Received: 10 September 2013 – Accepted: 28 September 2013 – Published: 31 October 2013

Correspondence to: A. H. Goldstein (ahg@berkeley.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Petroleum and dairy operations are prominent sources of gas-phase organic compounds in California's San Joaquin Valley. Ground site measurements in Bakersfield and aircraft measurements of reactive gas-phase organic compounds were made in this region as part of the CalNex (California Research at the Nexus of Air Quality and Climate Change) project to determine the sources contributing to regional gas-phase organic carbon emissions. Using a combination of near-source and downwind data, we assess the composition and magnitude of emissions from these prominent sources that are relatively understudied compared to motor vehicles. We also developed a statistical modeling method with the FLEXPART-WRF transport and meteorological model using ground-based data to assess the spatial distribution of emissions in the San Joaquin Valley. We present evidence for large sources of paraffinic hydrocarbons from petroleum extraction/processing operations and oxygenated compounds from dairy (and other cattle) operations. In addition to the small straight-chain alkanes typically associated with petroleum operations, we observed a wide range of branched and cyclic alkanes that have limited previous in situ measurements or characterization in emissions from petroleum operations. Observed dairy emissions were dominated by ethanol, methanol, and acetic acid, and methane. Dairy operations were responsible for the vast majority of methane emissions in the San Joaquin Valley; observations of methane were well-correlated with non-vehicular ethanol, and multiple assessments of the spatial distribution of emissions in the San Joaquin Valley highlight the dominance of dairy operations for methane emissions. The good agreement of the observed petroleum operations source profile with the measured composition of non-methane hydrocarbons in unrefined natural gas associated with crude oil suggests a fugitive emissions pathway during petroleum extraction, storage, or processing with negligible coincident methane emissions. Aircraft observations of emission hotspots from operations at oil wells and dairies are consistent with the statistical source footprint determined via transport modeling and ground-based data. At Bakersfield, petroleum and

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



dairy operations each comprised 22–23 % of anthropogenic non-methane organic carbon and were each responsible for ~ 12 % of potential precursors to ozone, but their direct impacts as potential SOA precursors were estimated to be minor. A comparison with the California Air Resources Board emission inventory supports the current relative emission rates of reactive organic gases from these sources in the region.

1 Introduction

California's San Joaquin Valley contains a large density of dairy farms and is an important region for oil and natural gas production in the United States. Both sources are prominent in the California Air Resources Board (CARB) emission inventory of reactive organic gases (ROG) in the San Joaquin Valley (California Air Resources Board, 2010) Petroleum operations include extraction, storage, transport, and processing; all of these may have varying degrees of fugitive emissions of methane and other gas-phase organic carbon, such as Volatile Organic Compounds (VOCs) (Leuchner and Rappengluck, 2010; Buzcu and Fraser, 2006; Katzenstein et al., 2003; Petron et al., 2012; Gilman et al., 2013). Crude oil and unrefined natural gas are composed of a suite of organic compounds that span a range of vapor pressures, and are either produced by thermogenic or biogenic processes in the reservoirs (USGS, 2007). Thermogenic gas is geochemically produced via the cracking of larger compounds in oil and can either be termed associated or non-associated depending on the presence of oil (USGS, 2007). The vast majority of wells in the San Joaquin Valley are oil wells and most have associated gas, also known as wet thermogenic gas (USGS, 2007). Thermogenic wet gas is predominately found in oil wells and contains substantial amounts of non-methane hydrocarbons ranging from 3 to 40 % C₂ and greater content (Table 1) (USGS, 2007). Crude oil production in Kern County, located at the southern end of the San Joaquin Valley is 450 000 barrels day⁻¹, which represents 69 % of production within California and 8 % of national production (US EIA, 2010; California Energy Commission, 2010). There have been several studies on fugitive emissions from oil and gas op-

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



house Gas Analyzer) with 1 min time resolution. Acetic acid and other acids were measured using both Chemical Ionization Mass Spectrometry (CIMS) and Ambient Ion Monitor-Ion Chromatography (AIM-IC). These two methods were located at different heights on the sampling tower in Bakersfield and had different measurement frequencies. With both sets of data averaged to hourly resolution, the acetic acid data were well correlated to each other ($r = 0.84$) with a slope near unity. Details on their sampling and measurement methods have been published previously (Crouse et al., 2006; Markovic et al., 2012).

As part of the CalNex project, measurements were also made from the National Oceanic and Atmospheric Administration (NOAA) WD-P3 research aircraft. VOC canister samples were collected on the aircraft and analyzed offline (Barletta et al., 2013). High time resolution data on selected organic compounds and methane were collected on the aircraft using Proton Transfer Resonance Mass Spectrometry (PTR-MS) and a Picarro flight-ready greenhouse gas analyzer (model 1301-m), respectively (de Gouw and Warneke, 2007; Peischl et al., 2012). High resolution data was averaged to 1 min intervals and select flights in the central valley were used to evaluate the spatial distribution of methane concentrations and emissions from dairy operations (flight dates: 7 May, 11 May, 12 May, 14 June, 16 June, 18 June 2010).

2.2 Source apportionment methods

2.2.1 Petroleum operations

Using six weeks of in situ VOC data from the Bakersfield ground site, we assessed emissions from petroleum operations during spring and summer 2010. The magnitude of mass contributions from petroleum operations (along with other motor vehicle sources) was determined using a source receptor model with chemical mass balancing focused on hydrocarbon emissions from petroleum-related sources (Gentner et al., 2012) The model used ten compounds emitted from the sources of interest (petroleum operations, non-tailpipe gasoline emissions, gasoline exhaust, and diesel exhaust)

along with reliable information on the fractional composition of the ten compounds in each of the sources (i.e. source profiles). The ten compounds used were dependent species, but the model also calculated the predicted concentrations of all the independent compounds not included in the model, but still emitted by the petroleum-related sources.

The compounds used in the over-constrained (i.e. more tracer compounds than sources) source receptor model were propane, *n*-butane, *n*-pentane, iso-pentane, *m/p*-xylene, *o*-xylene, isooctane, *n*-nonane, *n*-undecane, and *n*-dodecane to model motor vehicle and petroleum operation sources. Due to high background concentrations, measurements of propane and *n*-butane were corrected by local background values of 500 and 100 pptv, respectively. The ten tracer compounds were carefully selected because together they captured the dynamics of all four petroleum-related sources. The atmospheric lifetimes of the most reactive species did not bias the model since the vast majority of contributions (i.e. emissions) were within short transport times to the site. The petroleum operations source had the longest transport times (up to 6 h) from source to field site, which did not present a problem because that source was represented and modeled by the least reactive species with negligible degradation during transport. Extensive details on these methods and model validation are described in detail in Gentner et al. (2012).

A priori source profile information for the model was constructed using US Geological Survey data on associated thermogenic natural gas composition from wells in the San Joaquin Valley (Table 1) (USGS, 2007) and regional gasoline/diesel fuel composition data (Gentner et al., 2012). Standard deviations for the petroleum operations source profile were ± 80 –300 %, due to the variability between wells and sampling methods in the data compiled by the USGS. This uncertainty was an order of magnitude greater than motor vehicle source profiles and would have otherwise been insufficient to constrain the petroleum source, so standard errors were used as uncertainties in place of standard deviations to model the petroleum operations source.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The source receptor model effectively modeled the compounds included in the initial petroleum operations source profile (Table 1), but there were an array of hydrocarbons (not among the compounds used in the model) that episodically exceed predicted concentrations based on emissions from motor vehicles. Many of the excess hydrocarbon concentrations were well correlated with each other and the petroleum operations source factor, likely indicating emissions from the petroleum operations source. Emissions of additional compounds from petroleum operations (not present in the initial limited petroleum gas profile) are derived from the residual mass that is well-correlated with the petroleum operations source. The residuals, or excess concentrations beyond contributions from motor vehicles, were filtered for values that exceeded the uncertainties of model calculations, which are determined in part by the 10–20 % variability in gasoline and diesel fuel. Similarly, we calculated the expected ethanol emissions from gasoline vehicles for hourly data. Taking the difference between these predicted concentrations and total observed ethanol results in non-vehicular ethanol concentrations that must be attributed to other ethanol sources, but were not correlated with the petroleum operations source

2.2.2 Dairy operations

A reliable source profile for dairy operations in the San Joaquin Valley was not available for all the compounds of interest in this study, so the source profile was established using a mix of aircraft and ground measurements. The emission ratios of organic compounds to methane were calculated using flight and ground data for compounds that had evident, quantifiable emissions from dairy operations to construct the source profile. The ratio of methanol to methane in dairy operation emissions was determined using 1 min aircraft data points sampled in the plumes from farms and facilities in the San Joaquin Valley. Acetic acid and ethanol ratios could not be determined using the flight data due to a lack of measurements and spatial incongruence of canister to methane data, respectively. Ratios of these two compounds to methane were determined using ground site data from Bakersfield. Dairies have been shown in previous studies to

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



be major sources of methane, methanol, ethanol, acetic acid, and other oxygenated species; and there is a large concentration of dairies in the San Joaquin Valley (Alanis et al., 2010; Chung et al., 2010; Howard et al., 2010a, b; Malkina et al., 2011; Sun et al., 2008; Shaw et al., 2007). So each compound is compared to methane via regression with close attention to enhancements from other sources that may skew the emission ratio from dairy operations.

Predicted concentrations in Bakersfield of methanol, ethanol, and acetic acid from dairy operations were estimated using the determined emission ratios to methane and measurements of methane at the Bakersfield ground site. A local background methane concentration of 1.87 ppbv was subtracted prior to multiplication by the emission ratio. These predicted concentrations were compared with observed concentrations to determine the fraction of each compound emitted from dairy operations.

OH reactivities and ozone formation potentials reported in this paper are from literature on OH reaction constants and maximum incremental reactivities (MIRs), respectively (Carter, 2007; Atkinson and Arey, 2003).

2.3 Methods to determine spatial distribution of emissions

Several methods are used in this work to assess the spatial distribution of organic carbon sources. In addition to the use of aircraft data collected from the NOAA WD-P3 mobile platform during the CalNex campaign, we developed a method that uses a Lagrangian transport and meteorological model (FLEXPART-WRF) to calculate the distribution of air parcels (i.e. back trajectory footprints) for each hourly sample prior to measurement at a ground site. We combine these footprints with ambient compound data from the CalNex site to assess the spatial distribution of emissions for a given compound in a region.

We generated 6 and 12 h back-trajectory footprints with 4 km resolution for each hourly sample using the FLEXPART Lagrangian transport model with WRF meteorological modeling (Fig. 1). Simulations were initiated from the top of the 18 m tower using WRF runs EM4N in Angevine et al. (2012); further details on FLEXPART and

WRF modeling can also be found in Brioude et al. (2012) and Metcalf et al. (2012). Here, we integrate this transport/meteorological model with statistical back-trajectory analysis to explore the distribution and relative magnitude of gas-phase organic carbon sources at ground level.

5 The back trajectory footprint produced by FLEXPART-WRF represents the area where the air parcel(s) of interest (i.e. a 30 min VOC sample) contacts the surface layer. The statistical source footprint (the final output) represents the calculated distribution of ground-level emissions. Utilizing concentration-weighted trajectory analysis
10 allows us to find the emission potential of every point in a region, which is represented by the average concentration of a compound in a cell (\overline{C}_{ij}) on a grided map with i and j representing the axes:

$$\overline{C}_{ij} = \frac{1}{\sum_0^t(\tau_{ijt})} \sum_0^t (c_t \cdot \tau_{ijt}) \quad (1)$$

where τ_{ijt} is the time the back-trajectory footprint spends at ground level (< 100 m) in the ij th cell for the VOC sample at time t and c_t is the measured concentration of
15 a compound at the ground site. Each cell has a corresponding n_{ij} value, representing the number of individual footprints included in each cell, which was determined as the number values contributing to a cell's average (\overline{C}_{ij}) (Seibert et al., 1994). To reduce bias from cells with few samples (i.e. low n_{ij} values), a weighting function multiplies the (\overline{C}_{ij})
20 result by a factor of 1, 0.7, 0.4, or 0.05 for cells with n_{ij} values above the Q_{90} , Q_{75} , Q_{50} or below the Q_{50} percentiles, respectively (Polissar et al., 2001). Contour maps were then plotted using these final values and shown with a 1 arc second elevation map obtained from the USGS National Map Seamless Server (<http://viewer.nationalmap.gov/viewer/>)
25 Our method builds upon previous techniques to estimate source location(s) using ground site data. It is insufficient to only consider the distribution of wind directions against compound concentrations when complex meteorology affects the transport of air masses. This is the case in California's central valley. Similarly, basic single HYSPLIT back-trajectory analysis can oversimplify the footprint of measurements into one

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



single path and not accurately represent the distribution of groundlevel residence times for an air parcel (Fig. 2).

3 Results and discussion

Figure 3 shows measurements of a selection of compounds plotted against carbon monoxide, a common technique to assess contributions from anthropogenic emissions (after filtering for biomass burning events). Several compounds have ratios to CO consistent with measurements from the Los Angeles air basin during the same time period (Borbon et al., 2013). However, there are several compounds with frequent enhancements above the slope from Los Angeles, indicating additional sources of these compounds that are not abundant in LA. Most of the compounds shown in Fig. 3 have been previously linked to petroleum and dairy operations, and their enhancements here are evidence for substantial emissions in the San Joaquin Valley.

3.1 Emissions from petroleum operations

Petroleum operations emit a substantial amount of hydrocarbons, with a smaller distribution of molecular weights than emissions from gasoline sources. The 25th percentiles for propane and *n*-butane are similar to other urban ground sites during the summer, but higher concentrations were observed for the 50th and 75th percentiles, by up to a factor of 2 compared to Pittsburgh, PA (2002) (Millet et al., 2005). The 75th percentiles in the San Joaquin Valley are also higher by 25–50 % compared to measurements from 2005 in Riverside, CA, a much more populated region (Gentner et al., 2009).

The non-methane composition of thermogenic wet gas reported by the USGS (Table 1) accurately represented the observed petroleum operations source. The composition of the unrefined natural gas has substantial variability among all the wells sampled, but the average composition is consistent with atmospheric observations using

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ance source receptor model. Most of the unexplained concentrations of these alkanes were well correlated ($r \geq 0.75$) with the petroleum operations source contribution from the model and are attributed to this source. The presence of the branched and cyclic alkanes in unrefined petroleum gas is not surprising as there are significant amounts of C_{5-7} straight chain alkanes in the reported composition (Table 1). Yet, there are limited previous in-situ measurements for many of the compounds reported here, especially many of the cyclic alkanes.

The additional compounds attributed here to the petroleum operations source profile increase the mass of emissions by 10 % as shown by the regression of the correlated “unexplained” compounds with the petroleum gas source ($r = 0.95$) (Fig. 5). The weight fraction of each correlated compound in the “unexplained” mass is shown in Table 2 with similar fractions in the overall source profile as the known C_{5-7} compounds in thermogenic wet gas (Table 1). Including these “new” compounds, the ozone forming potential of the source profile is calculated to be $0.67 \text{ gO}_3 \text{ g}^{-1}$ with the additional compounds increasing the reactivity from $0.58 \text{ gO}_3 \text{ g}^{-1}$ (this initial value is based on the non-methane source profile in Table 1). In all, the interquartile range of the unrefined petroleum gas source contribution was 8.3–90 ppbC, with a diurnal pattern that was strongly dependent on meteorological dilution (Fig. S3). This source represented a substantial fraction of anthropogenic emissions. For comparison, the mass concentration of compounds emitted by the observed petroleum operations source ranged from 30–40 % to 100–150 % of the sum of compounds from motor vehicles during the afternoon and nighttime, respectively (Fig. S4).

The remaining branched and cyclic compounds that were not highly correlated with the petroleum gas source represent a relatively small amount of mass and we could not confidently infer a specific source for these compounds. The excess C_{13-16} branched alkanes were well-correlated ($r \geq 0.80$) with each other, but not with any other compounds. The excess concentrations of C_{10-11} branched alkanes were correlated with each other, and one of the compounds, 2,6-dimethyloctane, was well-correlated ($r \geq 0.80$) with the three C_9 cycloalkanes that do not correlate well with the petroleum

operations source. These remaining compounds have ozone formation potentials similar to other observed compounds, ranging from 0.6 to 1.6 g O₃ g⁻¹, but their excess concentrations after modeling were minimal with average values from 0 to 0.15 ppb C each (Fig. 4).

Unrefined thermogenic wet gas is largely comprised of methane when extracted at the wells. Yet, at the Bakersfield ground site observations of methane and contributions from the petroleum operations source were not well correlated (Fig. S5). Additionally, the potential methane emissions expected based on the thermogenic wet gas source profile (Table 1) would equal or exceed all of the methane enhancements above background concentrations. Despite the absent methane emissions, the large source of hydrocarbons observed is well described by the VOC source profile of unrefined thermogenic wet gas associated with oil wells in the San Joaquin Valley. This is supported by the good agreement of the non-methane hydrocarbons in the unrefined gas profile with both the VOC canister measurements and source receptor modeling with in situ VOC measurements. Overall, this infers that the VOC source characterized in this analysis is not a major source of methane in this region.

In many cases, methane emissions are coincident with emissions of non-methane hydrocarbons at petroleum extraction or processing sites due to either co-emission from the same equipment/reservoir or co-located emission pathways at the same facility (Katzenstein et al., 2003; Petron et al., 2012; Gilman et al., 2013). The observations in our study are somewhat surprising and atypical of the aforementioned studies, but are not unique. Our observation of a major petroleum operations source with minimal coincident methane is consistent with some measurements of emissions from condensate storage tanks, which contain the separated non-methane liquids and have been shown in two Texas-based studies to be dominated by non-methane hydrocarbons (Armendariz, 2009; Hendler et al., 2006). The studies demonstrated that condensate tanks emit 4–6 times more VOCs than methane whereas all other emission pathways emit 3–15 times more methane than VOCs, and methane was on average only 15 ± 11 wt% of 20 vent gas samples from condensate tanks (Armendariz, 2009;

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Hendler et al., 2006). It should be noted that methane separation can also remove a fraction of very light alkanes (i.e. C₂₋₃) and affect their relative composition to other hydrocarbons in the condensate. This effect may be present in our measurements to a small, and potentially insignificant, extent. The propane to *n*-butane ratio in the in situ and canister data (2.0 and 2.2) were slightly lower than in unrefined gas data (2.9). Similarly, the ethane to *n*-butane ratio is slightly lower in the canister data (3.1) relative to the unrefined gas data (3.5).

Similar results can also be found in previous studies in the urban area of Houston, a prominent region for petroleum imports and refining. Studies there have reported considerable emissions attributed to oil/gas operations and petrochemical production of other chemicals (Leuchner and Rappengluck, 2010; Buzcu and Fraser, 2006). One evident source, termed oil/natural gas evaporation from refineries, was comprised of C₂₋₇ straight and branched alkanes, as well as cyclopentane, cyclohexane, and methylcyclopentane. In one study, this source accounted for 27 % of observed VOC mass at the urban site outside of the Houston shipping channel, and resulted in atmospheric concentrations ranging from 10–40 ppbC diurnally (Leuchner and Rappengluck, 2010).

The results of this section along with the following sections form and augment the conclusion that the vast majority of methane enhancements observed in the San Joaquin Valley are due to emissions from dairy operations. In particular, Sect. 3.3 shows the statistical source footprint of emissions from petroleum operations in stark contrast to both the statistical source footprint of methane emissions and the spatial distribution of methane concentrations measured via aircraft in California's central valley with large spikes over areas with high concentrations of dairies. It is very possible that there are emissions of methane in the San Joaquin Valley from other petroleum operations that are downstream from our observed source, perhaps related to natural gas marketing. The results of this study infer that these emissions are minor or negligible compared to dairy operations, and are predominantly not co-located with our characterized petroleum operations source.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

urban and continental mixing ratios globally, as reported by Kirstine et al. (2012). However, a comparison of methanol concentrations is within the typical range of observed values globally (Heikes et al., 2002).

The methanol to methane emission ratio in dairy operation plumes measured on the aircraft was $7.4 \pm 0.6 \text{ mmol mol}^{-1}$ (aka ppbvppmv⁻¹); this slope of the regression ($r = 0.89$) is nearer to the lower limit within a range of 7–16 mmol mol^{-1} in the plumes (Fig. 6). This ratio was constructed from multiple transects and shows a range of ratios indicating some near-source variability in emissions from the different pathways of emissions. This ratio could be improved by collecting a wider, and perhaps more representative, range of data from more locations in future source characterization studies.

Ground site ethanol and acetic acid data were compared to methane to determine their emission ratios with close attention to enhancements from other sources. For ethanol and somewhat for acetic acid, there is a clear slope that emerges (Figs. 7 and 8) against methane with occasional enhancements in ethanol or acetic acid that are coincident with high concentrations of VOCs that represent tracers of other sources. In contrast, there were no enhancements in methane concentrations past these baseline slopes in the data. This is indicative of a singular major source of methane that is clearly related to ethanol and acetic acid. This result, along with the results of Sect. 3.3 showing the agreement of dairy locations with the spatial distribution of concentrations (measured via aircraft) and the statistical source footprint of both methane and ethanol, supports the conclusion that dairies are the predominant source of methane in the San Joaquin Valley and emissions from petroleum are negligible in comparison. To calculate emission ratios, data points with enhancements due to other sources (determined and shown by correlation with other tracer compounds) were filtered from the emission ratio assessment. This allows ethanol and acetic acid to become source-specific tracers of dairy operations. With dairy (and other cattle) operations responsible for the vast majority of methane emissions observed at the Bakersfield site, the emission ratios of ethanol and acetic acid to methane are effectively calculated by taking the lower limit of

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



slopes vs. methane when enhancements from other sources of ethanol or acetic acid are at their minimum.

At the Bakersfield ground site, concentrations of non-vehicular ethanol (calculated via the source receptor model) were well correlated with methane except for outliers with enhancements in ethanol that were coincident with large enhancements in tracers of other potential ethanol sources (Fig. 7). Other potential sources of alcohols and oxygenated gas-phase organic carbon are wastewater treatment, vegetation, soil processes, motor vehicles, and landfill/composting facilities. At low concentrations of these tracers, non-vehicular ethanol is very well correlated with methane with a slope of 18 mmol mol^{-1} . Chloroform, trichloroethylene, and carbon disulfide correlate with different points that deviate from the emission ratio, suggesting multiple other minor sources of ethanol.

The results of the acetic acid vs. methane assessment (Fig. 8) at the Bakersfield ground site produced similar results to that of non-vehicular ethanol vs. methane. The enhancements of acetic acid above the emission ratio slope coincided with tracers of other primary and secondary sources. We calculated an emission ratio for acetic acid to methane of $1.3 \text{ mmol mol}^{-1}$. This value represents a lower limit of acetic acid emissions associated with dairy operations. There is remaining uncertainty in this emission ratio and, based on the data shown in Fig. 8, the ratio of acetic acid to methane could be up to 50 % greater. The diurnal profile of acetic acid also suggests emissions from local/regional sources since concentrations are at their maxima during the night as emissions accumulate in the nocturnal boundary layer when there is minimal horizontal or vertical dilution. The results of our study show that there are high concentrations of acetic acid that are sometimes associated with methane, formic acid, acetone, or isoprene. This indicates that there are multiple major biogenic and anthropogenic sources of acetic acid in the San Joaquin Valley.

Rice cultivation could also be an important source of light alcohols and methane (Peischl et al., 2012), but there is little rice cultivation in the San Joaquin Valley. The bulk of Californian rice cultivation is located in the Sacramento Valley – the northern portion

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Midwestern US, with the remainder being anthropogenic. Heikes et al. (2002) reports a similar value with primary biogenic emissions responsible for 81 % of non-oceanic emissions. Dairies are an important source of methanol in the San Joaquin Valley along with emissions from agriculture and natural vegetation. The methods used in these studies to allocate emissions will determine whether dairy (and other cattle) operations are categorized as biogenic or anthropogenic sources. In this work we consider emissions from dairy operations to be anthropogenic, similar to the CARB inventory.

3.3 Spatial distribution of sources

Using FLEXPART-WRF meteorological data and methods for the region, distributions of back-trajectories were calculated for 6 and 12 h prior to arrival and measurement at the Bakersfield site. Overall averages, as well as day and nighttime averages are shown for the entire campaign in Fig. 1. The influence of local emissions near the site is important at all times. Daytime measurements are largely impacted by transport from the north-northwest due to consistent up-valley flows during the day. In contrast, at night the wind speeds and direction are more variable and irregular with flows that arrive from all directions, but originate from up-valley flows from the north-northwest. Extensive reviews of meteorology and flow patterns in the San Joaquin Valley found elsewhere are consistent with the results presented in this work (Bao et al., 2007; Beaver and Palazoglu, 2009). The footprint analysis used in this study provides a good representation of the distribution of surface-level areas that influence parcels' contact with the surface layer and associated sources.

Statistical meteorological modeling using ground site data resulted in a spatial distribution of petroleum gas emissions similar to that of oil wells in the southern San Joaquin Valley (Fig. 10). Additionally, canister samples taken via aircraft in the region show higher propane (a major component of the source profile) concentrations for some points in the southern part of the valley (Fig. 10c). Given the co-location of oil wells in the region and the spatial distribution of elevated concentrations of petroleum

gas compounds, it is possible that the observed emissions occur at or near the wells during extraction, storage, and initial processing.

The statistical distribution of emissions of non-vehicular ethanol and methane were similar for both 6 and 12 h back-trajectories. The map of emissions is consistent with the distribution of dairies in the San Joaquin Valley (Figs. 11 and 12) and aircraft measurements of ethanol and methane (Figs. 13 and 14). While there are dairy operations within the 12 h footprint and the emitted methane and light alcohols have long atmospheric lifetimes, the dairies within the 6 h footprint are much more influential in elevated concentrations, especially at night. The spatial distributions of petroleum and dairy operation emissions clearly show that they are coming from different parts of the valley. The maps in this section provide strong supporting evidence that the vast majority of methane is comin from dairy (and other cattle) operations.

The statistical emissions mapping method developed in this paper is an useful integration of concentration-weighting trajectory methods with the FLEXPART-WRF modeling platform. This emissions mapping tool is effective at locating point and area sources. The analyses of the spatial distribution of emissions from petroleum and dairy operations shown in this work are two applications of this technique. For these purposes, either concentration data or modeling outputs (e.g. source receptor models) can be used, both of which are used in this work. Further development of this approach will continue to improve its utility and quantitative outputs, but caution must be given to the transport timescales and tracer lifetime. Overall, this work demonstrates the efficacy and usefulness of this tool, and future work should apply it on regional and continental scales, as appropriate, to locate primary sources of pollution.

3.4 Implications for air quality and emissions inventories

Both petroleum and dairy (and other cattle) operations are important sources of reactive organic carbon in the San Joaquin Valley. On a mass basis observed concentrations of VOCs from petroleum extraction/processing were on the same order as emissions from motor vehicles. Yet, they represent a relatively minor contribution to potential

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



important, but emissions from petroleum and dairy operations will make up a greater fraction of non-methane organic carbon in the atmosphere and will be responsible for a greater fraction of ozone formation. These results confirm the importance of emissions from dairy operations in the San Joaquin Valley, but further work is necessary to confirm the conclusions of Howard et al. (2010a) who stated that dairy operations are major contributors to ozone production relative to other sources across the whole Central Valley. Our results on the relative contributions from each source indicate a mix of influential sources. Given our location in an urban area in the Southern San Joaquin Valley, where oil wells are concentrated, emissions from motor vehicles and petroleum operations are likely higher than other parts of the valley. Future work to address the valley-wide importance of dairy operations vs. biogenic and other anthropogenic sources would require repeating the source apportionment analyses in this paper at numerous locations throughout the San Joaquin and Sacramento Valleys.

The San Joaquin Valley has an abundance of agriculture and is surrounded by a lot of natural vegetation that is a large source of emissions. Future work should focus on biogenic emissions of reactive organic gases from both agriculture and natural vegetation. Emissions from natural vegetation in the surrounding hills and mountains are potentially a major source of non-methane organic carbon following transport to other parts of the valley.

Comparing different assessments for emissions from multiple sources presents challenges relating to the definition of sources and spatial boundaries. Here, we provide a comparison of our relative emissions magnitudes at the Bakersfield site to the CARB emission inventory for the San Joaquin Valley. To promote consistency with our observed sources, we compare our petroleum operations source to emissions from oil/gas production and refining, and exclude petroleum marketing (and combustion from petroleum operations) since our observed source is clearly related to unrefined petroleum. While there are likely some differences in emissions, it is difficult to separate dairy cattle from other cattle, so we have assumed that we are observing all cattle in this study and include them with dairy operations. Although in the CARB inventory,

dairy cattle represent almost 80 % of cattle-related emissions in the San Joaquin Valley. Similarly, we compare these sources to on-road mobile sources as that is the best representation of the observed motor vehicle sources in this study. However, some fraction of off-road sources may be included in the ambient measurements used for source apportionment.

The CARB emissions inventory for the San Joaquin Valley reports an average of 28 tons ROG per day from petroleum operations (production and refining), which is equal to 39 % of on-road mobile source emissions (72 tons per day) in the air basin (California Air Resources Board, 2010). This value is somewhat higher than the daytime ratio observed at the Bakersfield site (27 %) when vehicular emissions are greatest, but is similar to nighttime ratios and average ratios (42 %). Nighttime ratios are significantly higher since Bakersfield is in much closer proximity to potential petroleum operations sources compared to other parts of the air basin. A comparison on a smaller scale for the portion of Kern County in the San Joaquin Valley illustrates this as much of the San Joaquin Valley's petroleum operation emissions are in this county. For this area, petroleum production/refining emissions in the CARB inventory are 180 % that of on-road mobile sources (California Air Resources Board, 2010). This observation is consistent with the statistical footprints shown in this work as daytime footprints encompass a larger area that stretches into other counties while nighttime footprints are more heavily influenced by local emissions.

According to the CARB emission inventory, dairy and other cattle operations in the San Joaquin Valley emit 57 tons ROG per day, which is 80 % of non-vegetation farming-related emissions (California Air Resources Board, 2010). These emissions from dairy and cattle operations are equivalent to 80 % of on-road motor vehicle emissions in the inventory, which is higher than the average non-methane organic carbon (NMOC) mass comparison at the Bakersfield measurement site (40 %). The CARB inventory for the San Joaquin Valley states that emissions from dairy operations are twice those from petroleum operations (dairy and other cattle operations ROG emissions = $2.0 \times$ oil/gas production and refining ROG emissions). The average measured contributions from

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

petroleum and dairy sources were nearly equivalent at the Bakersfield site (Fig. 15). This is largely dependent the distribution of dairy operations relative to petroleum operations, which is greatest in the southern part of the San Joaquin Valley (e.g. Bakersfield) where the oil wells and related operations are concentrated. Thus, the ratio of petroleum to dairy operation contributions goes up by several factors with decreased dilution and a greater influence of local sources (Table 4). This is likely also the reason for the greater contribution from motor vehicles relative to dairy operations at the Bakersfield site vs. the inventory. The greater prevalence of motor vehicles near the site increases its impact relative to the whole valley.

A comparison of the dairy operations source profile (Table 3) with the CARB emission inventory reveals that the ratio of methane to NMOC is consistent between our results and the inventory, 93 % vs. 92 % methane. Additionally, the existing CARB inventory for the San Joaquin Valley reflects the difference in the magnitude of methane emissions between the two sources with total methane emissions from dairy (and other cattle) operations being an order of magnitude greater than petroleum production operations, with minor methane emissions from production/refining and 81 % of fugative emissions from oil/gas marketing (California Air Resources Board, 2010). Overall, these intercomparisons, while rough, provide validation of the CARB emission inventory for relative emission rates of dairy and petroleum operations in the San Joaquin Valley.

The San Joaquin Valley, and the central valley as a whole, contains a complex mixture of both anthropogenic and biogenic sources of reactive gas-phase organic carbon on both regional and urban scales. Our focus in this paper has been quantifying regional emissions from petroleum and dairy operations, comparing their emission rates to other anthropogenic sources, and evaluating their importance for air quality in the urban area of Bakersfield and the San Joaquin Valley. The dairy and petroleum sources are clearly relevant to air quality on both local and regional scales for ozone formation, but are likely not very important as sources of precursors to secondary organic aerosol. This study provides important new information expanding knowledge on the

suite of compounds emitted from these sources and providing new useful information on their sources profiles.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/13/28225/2013/acpd-13-28225-2013-supplement.pdf>.

Acknowledgements. For their support, we would like to acknowledge the California Air Resources Board (Contract 08-316), the National Oceanic and Atmospheric Administration (GRANT #NA10OAR4310104), and the U.C. Berkeley undergraduate chemistry summer research fellowship. We would also like to thank Joe Fisher and Jim Nyarady (CARB), Jason Surratt and Caitlin Rubitschun (U. North Carolina, Chapel Hill), and John Offenberg (US EPA) for their contributions and feedback. The US Environmental Protection Agency through its Office of Research and Development collaborated in the research described here. The manuscript has been subjected to external peer review and has not been cleared for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- Alanis, P., Ashkan, S., Krauter, C., Campbell, S., and Hasson, A. S.: Emissions of volatile fatty acids from feed at dairy facilities, *Atmos. Environ.*, 44, 5084–5092, 2010.
- Angevine, W. M., Eddington, E., Durkee, K., Fairall, C., Bianco, L., and Brioude, J.: Meteorological model evaluation for CalNex 2010, *Mon. Weather Rev.*, 140, 3885–3906, 2012.
- Armendariz, A.: Emissions from natural gas production in the Barnett Shale Area and opportunities for cost-effective improvements, available at: http://www.edf.org/sites/default/files/9235_Barnett_Shale_Report.pdf (last access: October 2012), 2009.
- Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605–4638, 2003.

ACPD

13, 28225–28278, 2013

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Bao, J. W., Michelson, S. A., Persson, P. O. G., Djalalova, I. V., and Wilczak, J. M.: Observed and simulated low-level winds in a high ozone episode during the central California ozone study, *J. Appl. Meteor. Climatol.*, 47, 2372–2394, 2007.

Barletta, B., Carreras-Sospedra, M., Cohan, A., Nissenson, P., Dabdub, D., Meinard, S., Atlas, E., Lueb, R., Holloway, J. S., Ryerson, T. B., Pederson, J., VanCuren, R. A., and Blake, D. R.: Emission estimates of HCFCs and HFCs in California from the 2010 CalNex study, *J. Geophys. Res. Atmos.*, 118, 2019–2030, 2013.

Beaver, S. and Palazoglu, A.: Influence of synoptic and mesoscale meteorology on ozone pollution potential for San Joaquin Valley of California, *Atmos. Environ.*, 43, 1779–1788, 2009.

Brioude, J., Angevine, W. M., McKeen, S. A., and Hsie, E.-Y.: Numerical uncertainty at mesoscale in a Lagrangian model in complex terrain, *Geosci. Model Dev.*, 5, 1127–1136, doi:10.5194/gmd-5-1127-2012, 2012.

Borbon, A., Gilman, J. B., Kuster, W. C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky, C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J. S., Stutz, J., McKeen, S., Petetin, H., Beekmann, M., Warneke, C., Parrish, D. D., and de Gouw, J. A.: Emissions of anthropogenic VOCs in northern mid-latitude megacities: observations vs. emission inventories in Los Angeles and Paris. *J. Geophys. Res.*, 118, 2041–2057, 2013.

Buzcu, B. and Fraser, M. P.: Source identification and apportionment of volatile organic compounds in Houston, TX, *Atmos. Environ.*, 40, 2385–2400, 2006.

California Air Resources Board: The California Almanac of Air Quality & Emissions – 2009 Edition, available at: <http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php> (last access: May 2012), 2010.

California Air Resources Board: Flash Emissions of Greenhouse Gas and other Compounds from Crude Oil and Natural Gas Separation and Storage Tank Systems, available at: http://www.arb.ca.gov/cc/oil-gas/flash_test_procedure_apr24.pdf (last access: September 2013), May 2013 Draft.

Carter, W. P. L.: SAPRC Atmospheric Chemical Mechanisms and VOC Reactivity Scales, available at: <http://www.engr.ucr.edu/~carter/SAPRC/> (last access: August 2012), 2007.

Chan, A. W. H., Isaacman, G., Wilson, K. R., Worton, D. R., Ruehl, C. R., Nah, T., Gentner, D. R., Dallmann, T. R., Kirchstetter, T. W., Harley, R. A., Gilman, J. B., Kuster, W. C., deGouw, J. A., Offenberg, J. H., Kleindienst, T. E., Lin, Y. H., Rubitschun, C. L., Surratt, J. D., Hayes, P. L., Jimenez, J. L., and Goldstein, A. H.: Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: insights into emission sources, atmo-

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



spheric processing and secondary organic aerosol formation, *J. Geophys. Res.*, 118, 1–14, 2013.

Chung, M. Y., Beene, M., Ashkan, S., Krauter, C., and Hasson, A. S.: Evaluation of non-enteric sources of non-methane volatile organic compound (NMVOC) emissions from dairies, *Atmos. Environ.*, 44, 786–794, 2010.

Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry, *Anal. Chem.*, 78, 6726–6732, 2006.

de Gouw, J. A. and Warneke, C.: Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spec. Rev.*, 26, 223–257, 2007.

Gentner, D. R., Harley, R. A., Miller, A. M., and Goldstein, A. H.: Diurnal and seasonal variability of gasoline-related volatile organic compound emissions in Riverside, California, *Environ. Sci. Technol.*, 43, 4247–4252, 2009.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, *P. Natl. Acad. Sci. USA*, 109, 18318–18323, 2012.

Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L., Dallmann, T. R. Wood, E. C. Herndon, S. C, Goldstein, A. H., and Harley, R. A.: Chemical speciation of gas-phase organic carbon emissions from motor vehicles and implications for ozone production potential, *Environ. Sci. Technol.*, 47, 11837–11848, doi:10.1021/es401470e, 2013.

Gilman, J. B., Lerner, B. M., Kuster, W. C., and de Gouw, J. A.: Source signature of volatile organic compounds from oil and natural gas operations in Northeastern Colorado, *Environ. Sci. Technol.*, 47, 1297–1305, 2012.

Hendler, A., Nunn, J., Lundeen, J., and McKaskle, R.: VOC Emissions from Oil and Condensate Storage Tanks, report prepared for the Houston Advanced Research Center, available at: <http://files.harc.edu/Projects/AirQuality/Projects/H051C/H051CFinalReport.pdf> (last access: October 2012), 2006.

Heikes, B. G., Chang, W. N., Pilson, M. E. Q., Swift, E., Singh, H. B., Guenther, A., Jacob, D. J., Field, B. D., Fall, R., Riemer, D., and Brand, L.: Atmospheric methanol budget and ocean implication, *Global Biogeochem. Cy.*, 16, 1133, doi:10.1029/2002GB001895, 2002.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Howard, C. J., Kumar, A., Mitloehner, F., Stackhouse, K., Green, P. G., Flocchini, R. G., and Kleeman, M. J.: Direct measurements of the ozone formation potential from livestock and poultry waste emissions, *Environ. Sci. Technol.*, 44, 2292–2298, 2010a.

Howard, C., Kumar, A., Malkina, I., Mitloehner, F., Green, P. G., Flocchini, R. G., and Kleeman, M. J.: Reactive organic gas emissions from livestock feed contribute significantly to ozone production in Central California, *Environ. Sci. Technol.*, 44, 2309–2314, 2010b.

Hu, L., Millet, D. B., Mohr, M. J., Wells, K. C., Griffis, T. J., and Helmig, D.: Sources and seasonality of atmospheric methanol based on tall tower measurements in the US Upper Midwest, *Atmos. Chem. Phys.*, 11, 11145–11156, doi:10.5194/acp-11-11145-2011, 2011.

Katzenstein, A. S., Doezema, L. A., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Extensive regional atmospheric hydrocarbon pollution in the southwestern United States, *P. Natl. Acad. Sci. USA*, 100, 11, 975–11, 979, 2003.

Kirstine, W. V. and Galbally, I. E.: The global atmospheric budget of ethanol revisited, *Atmos. Chem. Phys.*, 12, 545–555, doi:10.5194/acp-12-545-2012, 2012.

Klouda, G. A., Lewis, C. W., Stiles, D. C., Marolf, J. L., Ellenson, W. D., and Lonneman, W. A.: Biogenic contributions to atmospheric volatile organic compounds in Azusa, CA, *J. Geophys. Res.*, 107, ACH 7-1–ACH 7-13, doi:10.1029/2001JD000758, 2002.

Leuchner, M. and Rappengluck, B.: VOC source–receptor relationships in Houston during Texas, *Atmos. Environ.*, 44, 4056–4067, 2010.

Lillis, P. G., Warden, A., Claypool, G. E., and Magoon, L. B.: Petroleum systems of the San Joaquin Basin Province – geochemical characteristics of gas types, Ch. 10, in: *Petroleum Systems and Geologic Assessment of Oil and Gas in the San Joaquin Basin Province, California*, edited by: Scheirer, A. H., US Geological Survey, available at: <http://pubs.usgs.gov/pp/pp1713/> (last access: April 2013), 2007.

Malkina, I., Kumar, A., Green, P. G., and Mitloehner, F.: Identification and quantification of volatile organic compounds emitted from dairy silages and other feedstuffs, *J. Environ. Qual.*, 40, 28–36, 2011.

Markovic, M. Z., VandenBoer, T. C., and Murphy, J. G.: Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases. *J. Environ. Monitor.*, 14, 1872–1884, 2012.

Metcalf, A. R., Craven, J. S., Ensberg, J. J., Brioude, J., Angevine, W. M. M., Sorooshian, A., Duong, H. T., Jonsson, H. H., Flagan, R. C., and Seinfeld, J. H.: Black carbon

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

aerosol over the Los Angeles Basin during CalNex, *J. Geophys. Res.*, 117, D00V13, doi:10.1029/2011JD017255, 2012.

Millet, D. B., Donahue, N. M., Pandis, S. N., Polidori, A., Stanier, C. O., Turpin, B. J., and Goldstein, A. H.: Atmospheric volatile organic compound measurements during the Pittsburgh Air Quality Study: Results, interpretations, and quantification of primary and secondary contributions, *J. Geophys. Res.*, 110, D07S07, doi:10.1029/2004JD004601, 2005.

Peischl, J., Ryerson, T. B., Holloway, J. S., Trainer, M., Andrews, A. E., Atlas, E. L., Blake, D. R., Daube, B. C., Dlugokencky, E. J., Fischer, M. L., Goldstein, A. H., Guha, A., Karl, T., Kofler, J., Kosciuch, E., Misztal, P. K., Perring, A. E., Pollack, I. B., Santoni, G. W., Schwarz, J. P., Spackman, J. R., Wofsy, S. C., and Parrish, D. D.: Airborne observations of methane emissions from rice cultivation in the Sacramento Valley of California, *J. Geophys. Res.*, 117, D00V25, doi:10.1029/2012JD017994, 2012.

Petron, G., Frost, G., Miller, B. R., Hirsch, A. I., Montzka, S. A., Karion, A., Trainer, M., Sweeney, C., Andrews, A. E., Miller, L., Kofler, J., Bar-Ilan, A., Dlugokencky, E. J., Patrick, L., Moore Jr., C. T., Ryerson, T. B., Siso, C., Kolodzey, W., Lang, P. M., Conway, T., Novelli, P., Masarie, K., Hall, B., Guenther, D., Kitzis, D., Miller, J., Welsh, D., Wolfe, D., Neff, W., and Tans, P.: Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study, *J. Geophys. Res.*, 117, D04304, doi:10.1029/2011JD016360, 2012.

Polissar, A. V., Hopke, P. K., and Harris, J. M.: Source regions for atmospheric aerosol measured at Barrow, Alaska. *Environ. Sci. Technol.*, 35, 4214–4226, 2001.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D. T., Schwikowski, M., Kasper, A., and Puxbaum, H.: Trajectory analysis of aerosol measurements at high alpine sites, in: *Transport and Transformation of Pollutants in the Troposphere*, edited by: Borrell, P., Borrell, P. M., Cvitas, T., Kelly, K., Midgley, P., and Seiler, W., Academic Publishing, Den Haag, 689–693, 1994.

Shaw, S. L., Mitloehner, F. M., Jackson, W., DePeters, E. J., Fadel, J. G., Robinson, P. H., Holzinger, R., and Goldstein, A. H.: Volatile organic compound emissions from dairy cows and their waste as measured by proton–transfer–reaction mass spectrometry, *Environ. Sci. Technol.*, 31, 1310–1316, 2007.

Sheridan, M.: California Crude Oil Production and Imports, California Energy Commission, available at: <http://www.energy.ca.gov/2006publications/CEC-600-2006-006/CEC-600-2006-006.PDF> (last access: August 2012), 2006.

Sun, H., Trabue, S. L., Scoggin, K., Jackson, W. A., Pan, Y., Zhao, Y., Malkina, I. L., Koziel, J. A., and Mitloehner, F. M.: Alcohol, volatile fatty acid, phenol, and methane emissions from dairy cows and fresh manure, *J. Environ. Qual.*, 37, 615–622, 2008.

5 US Energy Information Administration: US Crude Oil Production by State, available at: http://www.eia.gov/dnav/pet/PET_CRD_CRPDN_ADC_MBBLPD_A.htm (last access: August 2012), 2010.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Unrefined natural gas profile for thermogenic wet wells in the San Joaquin Valley from USGS samples ($N = 49$ wells).

| | wtC% | Std. Dev. | k_{OH} | MIR |
|-------------------|-------|-----------|----------|-------|
| Methane | 82.3 | 9.2 | 0.0064 | 0.014 |
| Ethane | 5.33 | 3.46 | 0.248 | 0.28 |
| Propane | 4.42 | 3.50 | 1.09 | 0.49 |
| Isobutane | 0.920 | 0.837 | 2.12 | 1.23 |
| <i>n</i> -butane | 1.55 | 2.17 | 2.36 | 1.15 |
| Isopentane | 0.223 | 0.401 | 3.6 | 1.45 |
| <i>n</i> -pentane | 0.273 | 0.405 | 3.80 | 1.31 |
| neo-pentane | 0.061 | 0.182 | 0.825 | 0.67 |
| <i>n</i> -hexane | 0.105 | 0.108 | 5.20 | 1.24 |
| <i>n</i> -heptane | 0.049 | 0.041 | 6.76 | 1.07 |

Notes: k_{OH} is in $\text{cm}^3 \text{s}^{-1} \text{molecules}^{-1} \times 10^{12}$ from Atkinson and Arey, (2003).

MIR is in $\text{gO}_3 \text{g}^{-1}$ from Carter, 2007.

The observed source profile for petroleum gas emissions at the Bakersfield site is well represented by the composition of non-methane organic carbon shown here.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. Continued.

| Compound Name | # in Fig. 4 | Interquartile Range [pptv] | WtC% of Unexplained Mass | MIR [$\text{g O}_3 \text{g}^{-1}$] |
|---|-------------|----------------------------|--------------------------|--------------------------------------|
| C13 branched alkanes (2 unknown isomers) | 34 | 2.3–5.8 | | 0.6 |
| C14 branched alkanes (6 unknown isomers) | 35 | 4.4–11.3 | | 0.55 |
| C16 branched alkane (unknown) | 36 | 1.3–3.1 | | 0.47 |
| cyclopentane | 37 | 36.7–164.5 | 4.04 | 2.39 |
| methylcyclopentane | 38 | 57.4–315.3 | 8.86 | 2.19 |
| cis-1,3-dimethylcyclopentane | 39 | 14.8–100.1 | 5.23 | 1.94 |
| trans-1,3-dimethylcyclopentane | 40 | 16.4–177.7 | 7.86 | 1.94 |
| ethylcyclopentane | 41 | 7.9–44.4 | 1.93 | 2.01 |
| ctc-1,2,4-trimethylcyclopentane | 42 | 5.4–52.2 | 4.19 | 1.53 |
| ctt-1,2,4-trimethylcyclopentane | 43 | 1.7–15.5 | 1.32 | 1.53 |
| Unknown methylethylcyclopentane | 44 | 0.7–4.3 | | 1.6 |
| iso-propylcyclopentane | 45 | 1.1–5.9 | 0.35 | 1.69 |
| <i>n</i> -propylcyclopentane | 46 | 2.1–10.0 | 0.58 | 1.69 |
| cyclohexane | 47 | 27.5–154.0 | 6.22 | 1.25 |
| methylcyclohexane | 48 | 20.4–147.0 | 7.30 | 1.70 |
| cis-1,3- and 1,1-dimethylcyclohexane | 49 | 4.6–38.4 | 3.02 | 1.4 |
| trans-1,2-dimethylcyclohexane | 50 | 4.6–42.4 | 3.37 | 1.41 |
| trans-1,3-dimethylcyclohexane | 51 | 2.9–17.8 | 0.95 | 1.52 |
| cis-1,2-dimethylcyclohexane | 52 | 1.9–9.8 | 0.52 | 1.41 |
| ethylcyclohexane | 53 | 4.8–31.9 | 2.36 | 1.47 |
| ccc-1,3,5-trimethylcyclohexane | 54 | 1.0–6.6 | | 1.15 |
| 1,1,3-trimethylcyclohexane | 55 | 2.0–20.4 | 2.32 | 1.19 |
| 1,1,4-trimethylcyclohexane | 56 | 1.1–8.8 | | 1.2 |
| ctt-1,2,4- and cct-1,3,5-trimethylcyclohexane | 57 | 0.7–3.9 | | 1.2 |
| ctc-1,2,4-trimethylcyclohexane | 58 | 1.2–9.6 | | 1.2 |
| 1,1,2-trimethylcyclohexane and isobutylcyclopentane | 59 | 0.7–2.0 | | 1.3 |
| methylethylcyclohexane isomer #1 | 60 | 0.8–4.5 | 0.32 | 1.4 |
| methylethylcyclohexane isomer #2 | 61 | 0.7–3.7 | 0.28 | 1.4 |
| iso-propylcyclohexane | 62 | 0.9–5.2 | | 1.3 |
| <i>n</i> -propylcyclohexane | 63 | 2.9–15.5 | | 1.29 |
| unidentified C10 cyclohexane | 64 | 2.5–7.8 | | 1.07 |
| unidentified C10 cyclohexanes | 65 | 0.7–2.7 | | 1.07 |
| unidentified C9 cycloalkane | 66 | 1.2–11.0 | 1.26 | 1.36 |

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 4. Quartiles [ppbC] for ambient concentrations from major anthropogenic sources measured at the Bakersfield site (does not include methane emissions) shown with Maximum Incremental Reactivity (MIR) and Secondary Organic Aerosol (SOA) Yields for each source.

| | Q_{25} | Q_{50} | Q_{75} | MIR [$\text{g O}_3 \text{g}^{-1}$] | SOA Yield [g SOA g^{-1}] |
|-----------------------|----------|----------|----------|--------------------------------------|-------------------------------------|
| Gasoline Exhaust | 12.1 | 20.4 | 34.0 | 4.5 | 0.023 ± 0.007 |
| Diesel Exhaust | 14.9 | 27.8 | 53.9 | 2.5 | 0.15 ± 0.05 |
| Non-tailpipe Gasoline | 4.19 | 8.41 | 20.4 | 2.0 | 0.0024 ± 0.0001 |
| Petroleum Gas Source | 8.25 | 20.2 | 89.8 | 0.67 | ~ 0 |
| Dairy Operations | 5.66 | 11.2 | 26.1 | 1.3 | ~ 0 |

Note: Gasoline and diesel exhaust include both emissions of unburned fuel and products of incomplete combustion. MIR and SOA yield values for motor vehicle sources shown for comparison from Gentner et al. (2013) and Gentner et al. (2012).

Dairy operations includes other cattle farming in the San Joaquin Valley, and the MIR value is for NMOC fraction of source profile.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

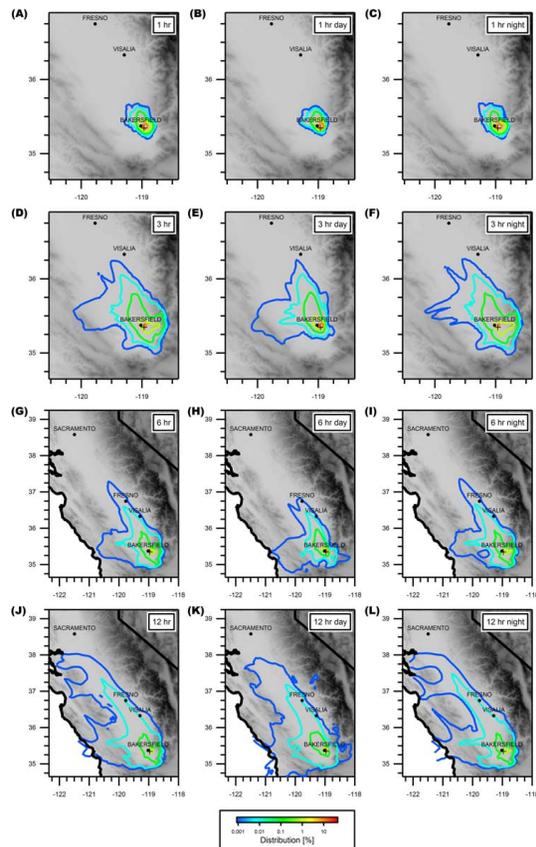


Fig. 1. 1, 3, 6 and 12 h statistical footprints for the Bakersfield ground site (marked by +) averaged across the entire CalNex campaign (y- and x-axis represent latitude and longitude). Day (**B, E, H, K**) and nighttime (**C, F, I, L**) average are filtered for 08:00–20:00 PST and 21:00–06:00 PST, respectively, and are shown with overall averages (**A, D, G, J**).

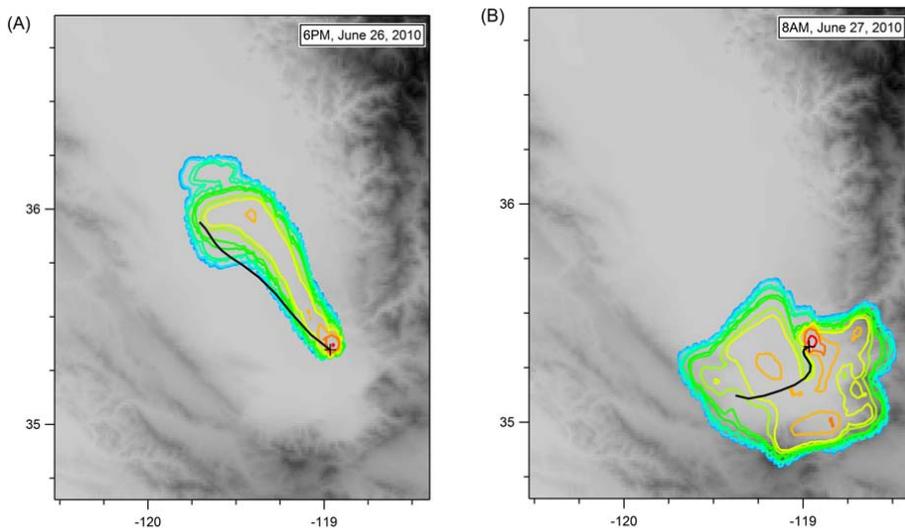


Fig. 2. Examples of individual probability distribution back-trajectory footprints produced using FLEXPART-WRF (contours with log color scale – red: max, blue: min) for the Southern San Joaquin Valley with air parcels arriving at the CalNex-Bakersfield ground site. Two examples show previous 6 h with air parcels coming **(A)** along a concentrated northwest flowpath and **(B)** a more dispersed footprint from the southern tip of the valley. Dates and arrival times are superimposed on the panels. Also shown are comparisons of single-path HYSPLIT back-trajectories (black lines) and FLEXPART-WRF footprints. Flexpart methods show some disagreement with HYSPLIT and over-simplification.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

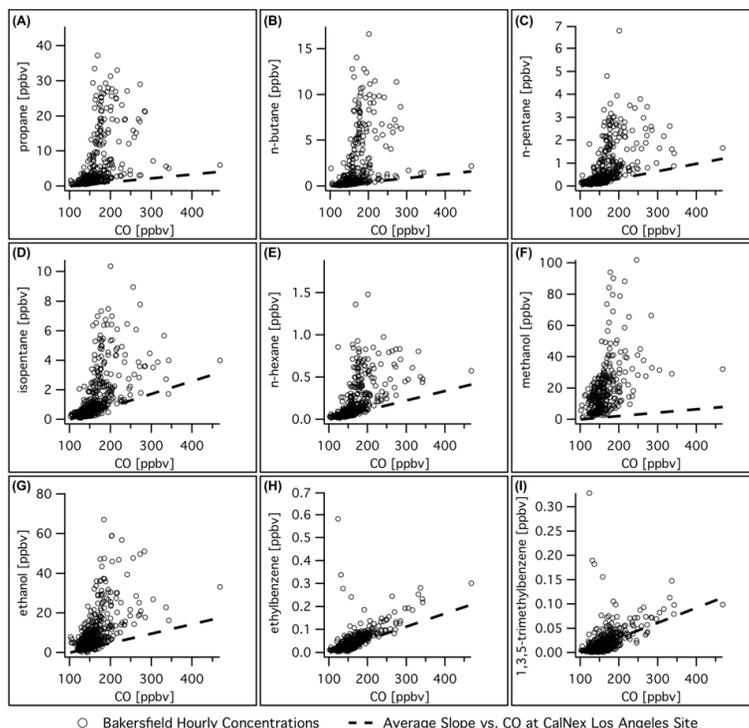


Fig. 3. Concentrations of several compounds from Bakersfield, CA shown against carbon monoxide with the average slope of compounds vs. CO during the same time period at the CalNex-LA site in Pasadena, CA (Bourbon et al., 2012). Concentration enhancements above VOC/CO line are due to emissions from **(A–E)** petroleum operations and **(F–G)** dairy operations, neither of which emit CO. **(H–I)** are shown as examples of compounds who agree well between Bakersfield and Los Angeles.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

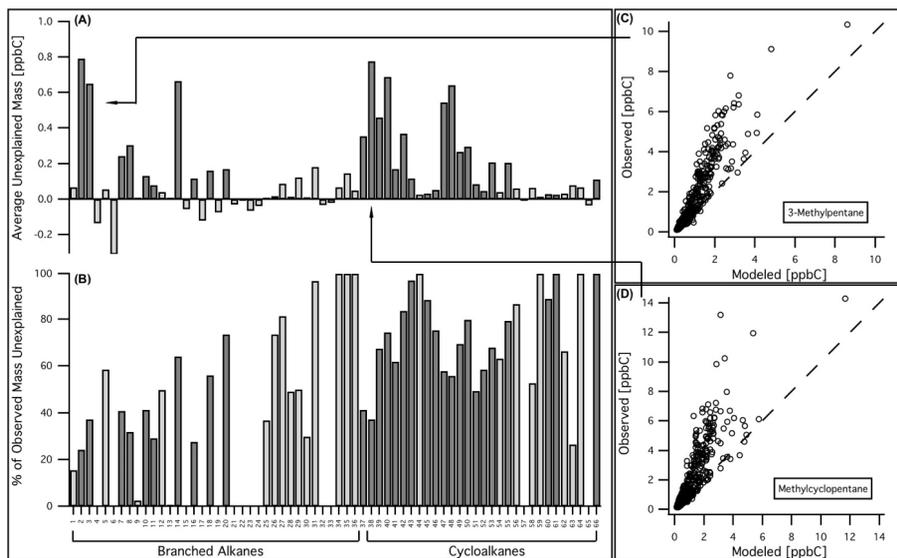


Fig. 4. Many branched and cyclic alkanes exceeded predicted concentrations based on source profiles for motor vehicles. **(A, B)** The average unexplained concentration of each compound and the percentage of unexplained mass out of total observations. Compounds that are well correlated ($r \geq 0.75$) with the petroleum gas source are shown with shaded bars. A few compounds have negative residuals. **(C, D)** Examples of exceedances of observed over-predicted values are shown with a 1 : 1 line.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



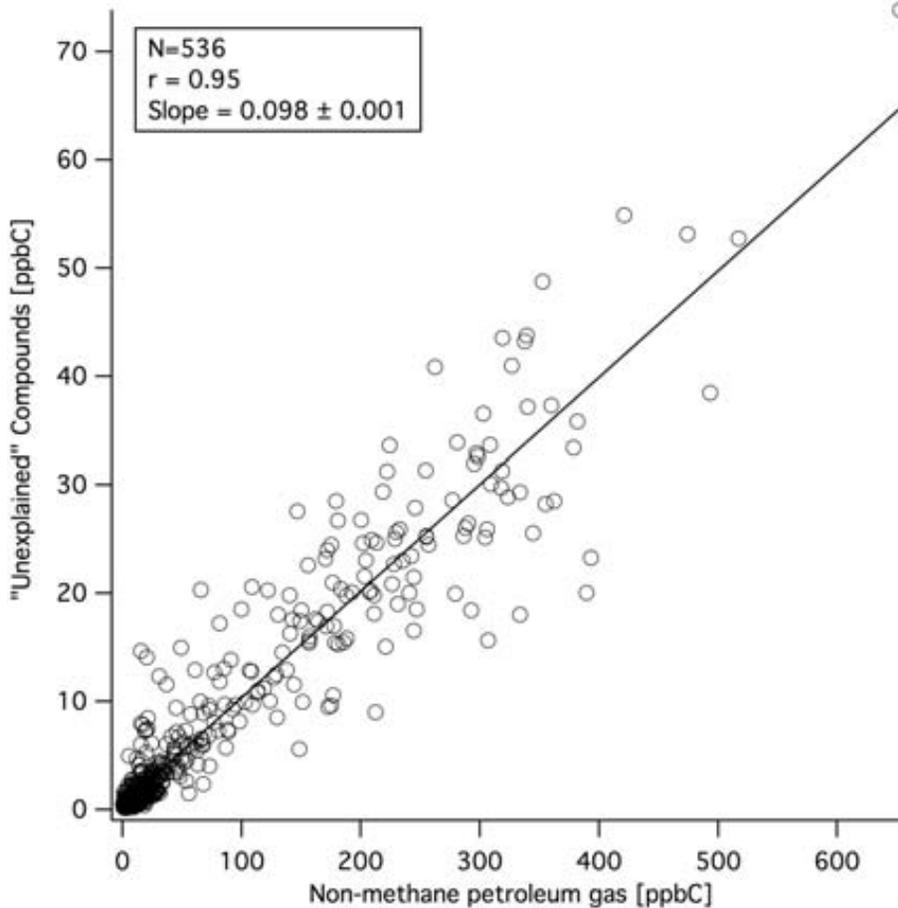


Fig. 5. The sum of unexplained compounds was very well correlated with gas-phase emissions from the modeled petroleum operations source with a slope of 0.098. This increases emissions by 10% from the original profile.

28268

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



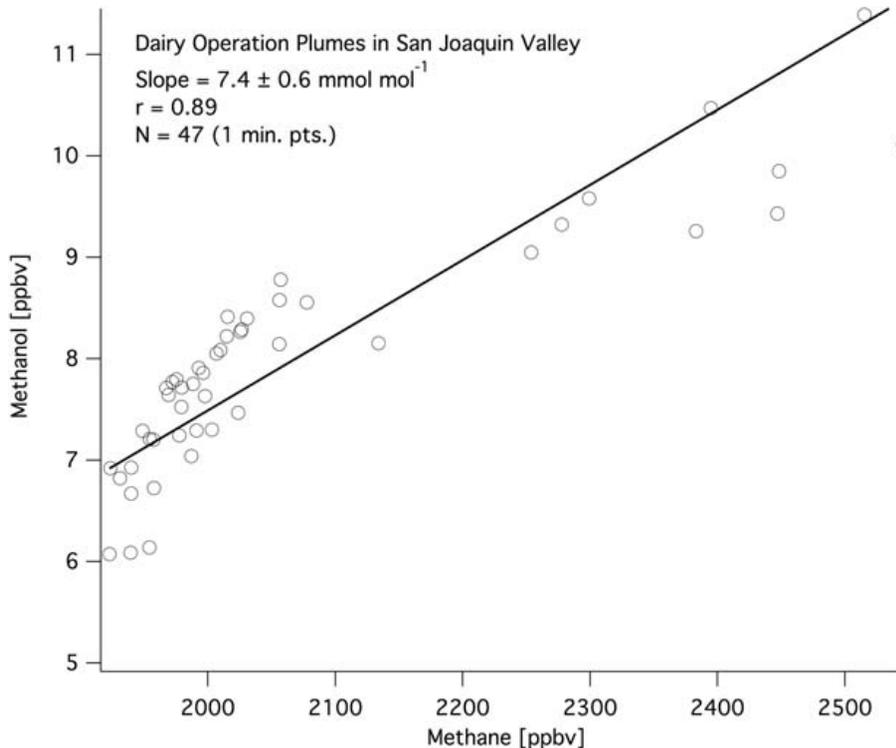


Fig. 6. Methanol and methane concentrations are well-correlated in dairy operation plumes sampled via aircraft (flight dates: 7 May, 14 June 2010). Ratios of methanol to methane average $7.4 \pm 0.6 \text{ mmol mol}^{-1}$ and range up to 16 mol mol^{-1} due to the heterogeneity in emission pathways at dairy operations. Note: the data shown here represent a subset of dairies in the valley measured during CalNex.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

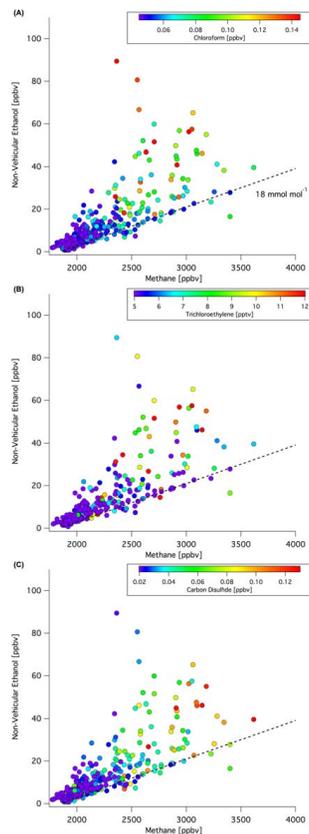


Fig. 7. Observations of non-vehicular ethanol vs. methane are correlated and shown with the inferred emission ratio from dairy operations. Enhancements of ethanol from another source than the dominant source of methane and ethanol are shown by enhancements in **(A)** chloroform, **(B)** trichloroethylene, and **(C)** carbon disulfide. No major enhancements of methane are observed beyond the inferred slope with non-vehicular ethanol.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

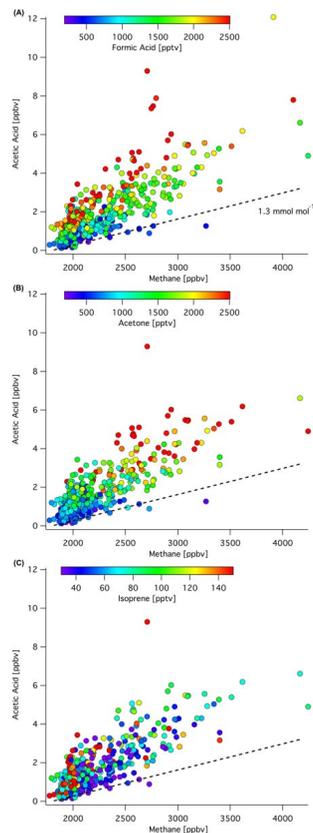


Fig. 8. Acetic acid vs. methane shown with the inferred acetic acid:methane emission ratio from dairy operations. Acetic acid exceedances above the emission ratio are due to other sources of acetic acid coincident with sources of **(A)** formic acid, **(B)** acetone, and **(C)** isoprene.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

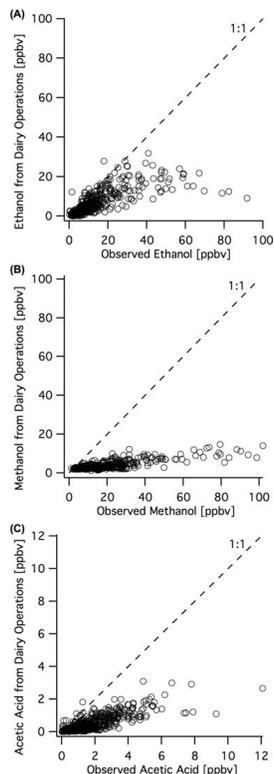


Fig. 9. Estimated concentrations of non-methane organic compounds emitted by dairy operations shown against ambient observations at the Bakersfield ground site. Emissions are apportioned to dairy operations using emission ratios the methane determined using aircraft and ground site measurements. On average, 45 % of observed **(A)** ethanol is from dairies. Whereas, smaller fractions of **(B)** methanol (27 %) and **(C)** acetic acid (28 %) are from dairy operations. These fractions vary with time of day and source strength. Diurnal patterns of percent contributions from dairy operations are shown in Fig. S8.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

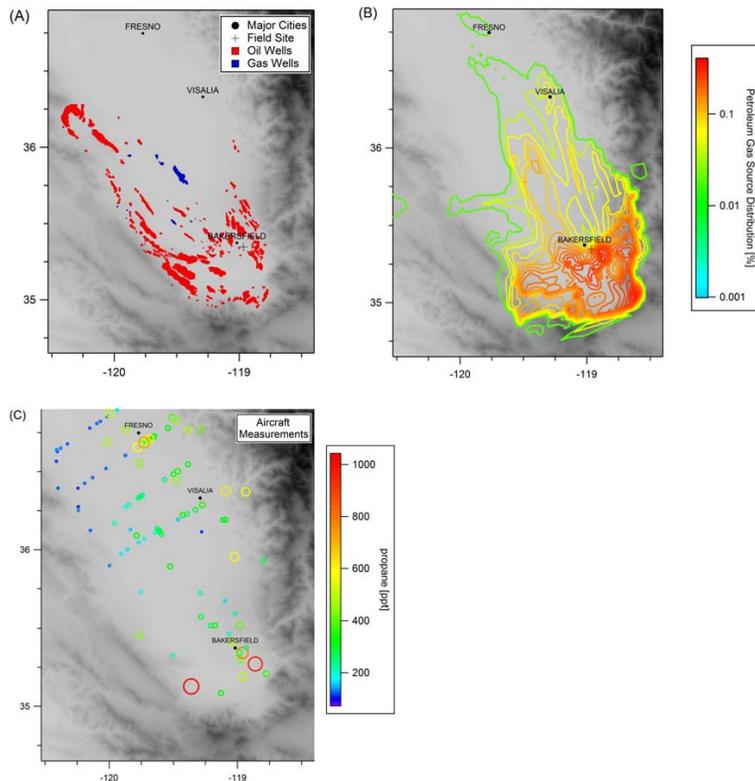


Fig. 10. Maps of southern part of the San Joaquin Valley with **(A)** the location of oil and gas wells, **(B)** the spatial distribution of petroleum gas emissions determined using statistical footprint analysis, and **(C)** aircraft canister measurements of propane, sized and colored by concentration. Together the maps show a similar distribution of wells and emissions in the region. Note: meteorological conditions and local dilution varies between canister measurements.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

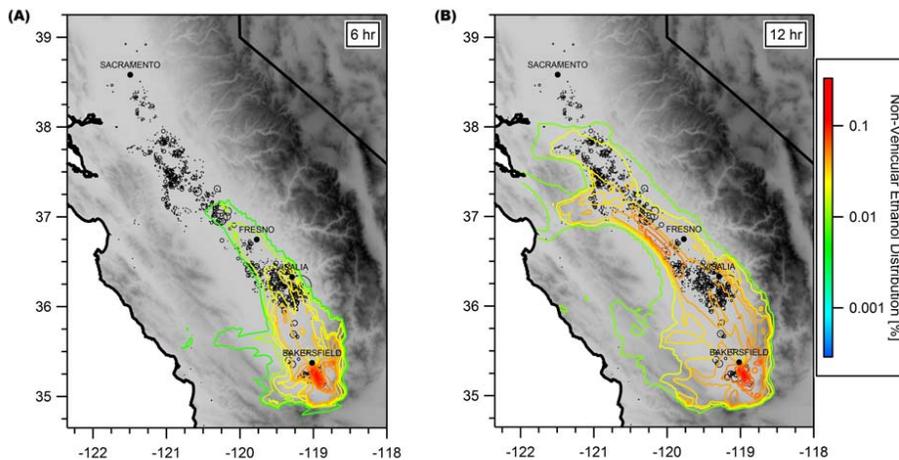


Fig. 11. Statistical distribution of emissions of non-vehicular ethanol in the San Joaquin Valley shown as colored contours for 6 and 12 h footprints. Modeling results shown with the location of dairies as markers (o) scaled by the size of each dairy.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

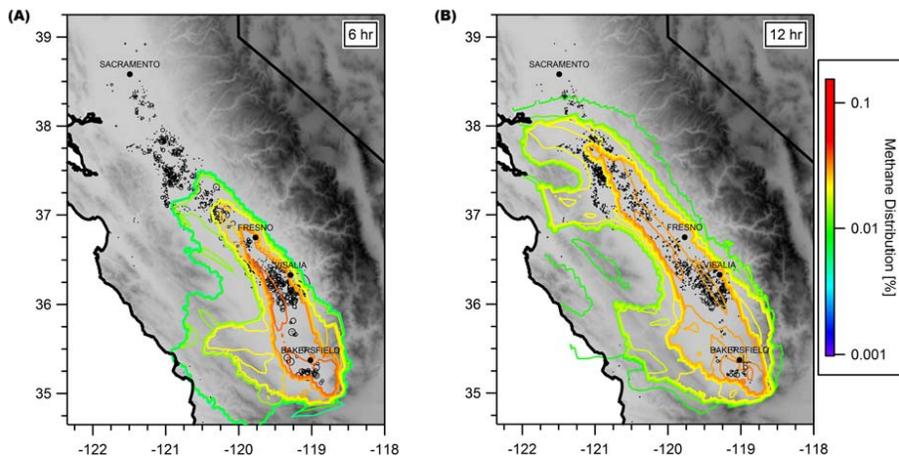


Fig. 12. Statistical distribution of emissions of methane in the San Joaquin Valley shown as colored contours for 6 and 12 h footprints. Modeling results shown with the location of dairies as markers (o) scaled by the size of each dairy.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

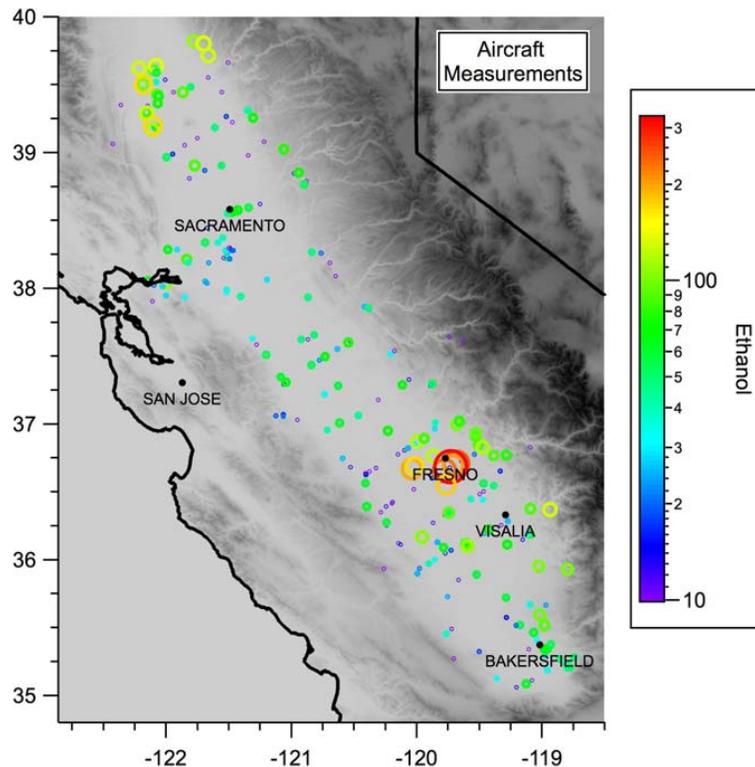


Fig. 13. Aircraft canister measurements of ethanol in California's Central Valley shown as individual circles, sized and colored by ethanol concentration. Data were taken at varying altitudes above and below the boundary layer with general filter for below 1000 m. Vertical gradients are responsible for some variability, but aircraft data support conclusions of other analyses showing large ethanol sources in the central valley: dairy operations in the San Joaquin Valley and rice cultivation in the Sacramento Valley. Note: meteorological conditions and local dilution varies between canister measurements. Also, alcohol measurements made using the canisters were prone to significant losses, so their use is only relative.

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

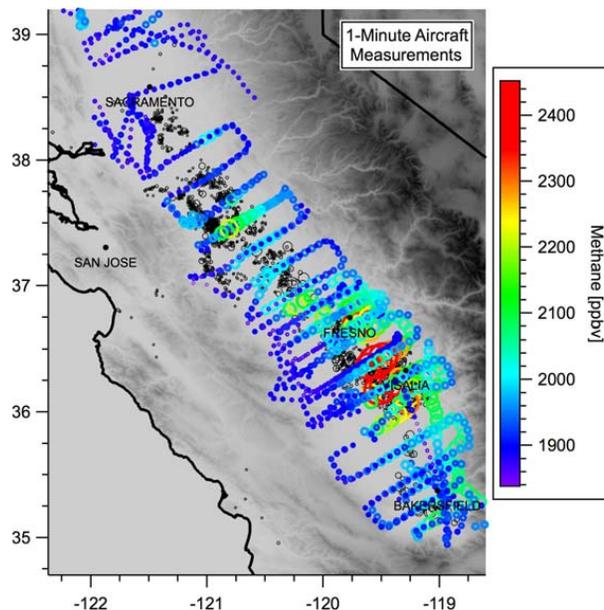


Fig. 14. Map of observed methane concentrations over 7 flights in California's Central Valley shown as individual circles, sized and colored by methane concentration. Data were taken at varying altitudes above and below the boundary layer with general filter for below 1000 m. Vertical gradients and multiple flights are responsible for some variability, but methane enhancements in aircraft data show good correlation with the location of dairy operations (open black circles sized by bovine population). A map including the all of the Sacramento Valley can be found in the Supplement (Fig. S11).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Emissions of organic carbon and methane from petroleum

D. R. Gentner et al.

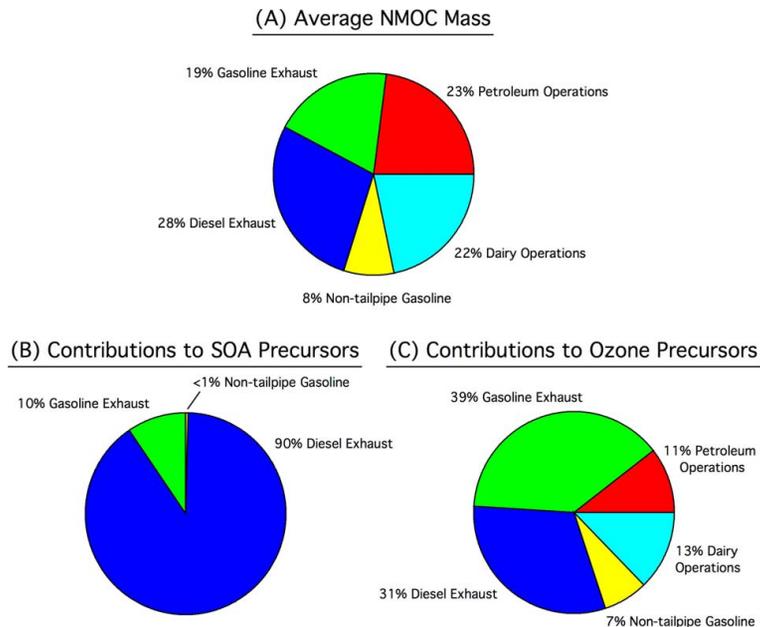


Fig. 15. Breakdown of the contributions of prominent anthropogenic sources in Bakersfield for **(A)** total non-methane organic carbon (NMOC) mass, **(B)** precursors to secondary organic aerosol (SOA), and **(C)** precursors to ozone. The exhaust values here include unburned fuel emissions and products of incomplete combustion, and dairy operations include other cattle farming. Biogenic emissions from natural vegetation are excluded, and are likely to have important contributions to emissions and air quality in the San Joaquin Valley, but less so in the urban core of Bakersfield, CA. Note: The NMOC mass comparison mass in **(A)** is in terms of mass (similar to inventories), so ratios of sources will be slightly different from Table 4 where they are in mol Carbon.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion