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Comment

# ***Interactive comment on* “Emissions of organic carbon and methane from petroleum and dairy operations in California’s San Joaquin Valley” by D. R. Gentner et al.**

**D. R. Gentner et al.**

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We would like to thank the editor and the reviewers for their consideration of this manuscript and helpful comments. The manuscript has been revised to reflect many of the suggested changes. Responses to individual comments are shown following each comment.

Anonymous Referee #1

General Comments about “Emissions of organic carbon and methane from petroleum operations in California’s San Joaquin Valley”

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This paper provides a useful summary of the measurements of reactive gas phase organic compounds during the Calnex project. Their objectives stated in section 1 were to examine the magnitude, chemical composition, and spatial distribution of organic carbon emissions from petroleum and dairy operations in the San Joaquin Valley by using (1) Measurements at ground sites and aircraft (2) making a statistical source footprint using measurements (3) compare relative abundance of emissions from petroleum and dairy sources with other significant anthropogenic sources in the same region (4) compare petroleum and dairy source emissions to motor vehicle emissions for comparison to the CARB inventory. This paper adds additional characterization of emissions in an important region with air quality issues.

I recommend this paper for publication with minor updates as follows: Some of the key points discussed in section 3.4 (Implications for air quality and emissions inventories) should be included in the abstract (quantitative assessments of the emission inventories). In addition, further discussion of the exactly how the information provided in the paper can be used in an emissions inventory (perhaps a table to replace or augment the discussions on pp. 28251 (lines 5-30) and 28252 (lines 1-9) on p 28252. How would a person developing an emission inventory in the SJ Valley use the results?

Response: We have revised the last two sentences of the abstract to be more informative. The current discussion in the manuscript is intended as an assessment of the reactive organic gas (ROG) inventory including a relative comparison of motor vehicles, petroleum and dairy operations at the Bakersfield site. Per the recommendation, we have added a table to augment the discussion in Section 3.4. The objective of this paper was to better characterize the sources and assess their relative importance for emissions of methane, VOCs, and the potential impact of those VOCs on air quality. We have reviewed the manuscript to clarify our presentation of the assessment of the inventory.

A few Editorial Corrections are noted below:

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p. 28227, line 9 (missing period at end of sentence) p.28227, line 26 (missing period at end of sentence) Some of the fonts in figures 7, 8 and 9 are too small and are hard to read.

Response: We have resolved these typos and improved the clarity of the figures.

Anonymous Referee #2

The manuscript describes an analysis of a comprehensive set of methane and VOC measurements taken during CalNex in Central California to evaluate the influence of petroleum and dairy operations on regional air quality. The authors used a combination of chemical mass balance (CMB) modeling to assess contributions to emissions and a Lagrangian model to determine spatial emissions. The issue of dairy impacts is primarily a local one, but the work on petroleum sources is potentially important for other regions and the approach to determine statistical source footprints could clearly be applied in many other settings.

Specific Comments:

1. The value of the CMB model results clearly depends on the quality of the source profiles used for petroleum operations and dairy operations. I am not totally clear on the uncertainties in the source profiles used and their impacts on the reported source contributions.

Response: We reply to each subsection of comment #1 below. We agree with the reviewer that good a priori knowledge (and selection of dependent compounds used in the model) is critical to source apportionment through CMB modeling. So, we put considerable effort into developing our source profiles. We would like to clarify that only the petroleum source was used in the CMB model. The dairy operations source did not emit similar compounds to the other sources to model them in a CMB framework. To use the model, two or more compounds that vary dynamically with two or more sources are necessary (see source and compound choices in Gentner et al., 2012 (PNAS) and

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Gentner et al., 2009 (ES&T) for examples). The only similar compound was ethanol, and was thus insufficient to be included in the model. The dairy source was assessed via regression analyses using a mix of ground and flight data (discussed in methods Section 2.2.2).

a. Section 3.1. The authors note large standard deviations in the petroleum operations source profile and state that they used standard errors instead. However, the magnitude of the standard error is not stated and a justification for using these is not given beyond the inability to constrain the petroleum source without doing so. The authors also discuss the discrepancy between [methane]:[NMVOC] in the source profile and ambient measurements, and argue (not unreasonably) that this implies that petroleum operation emissions are primarily from storage and handling. It is noted that methane separation may impact the fraction of light alkanes emitted, but the authors argue that this effect is small based on the [ethane]:[butane] and [propane]:[butane] ratios in canister samples. However, couldn't this also potentially be observed with a lower fraction of light alkanes in the petroleum profile and a greater contribution from a different source of light alkanes at the site? What is the origin of the background propane and butane at the sampling site? Could the subtraction of these values affect the conclusions drawn from the [ethane]:[butane] and [propane]:[butane] ratios?

Response: For the petroleum operations source profile, the standard errors are the standard deviations divided by  $(49)^{0.5} = 7$  (note added in text). We re-ran our model as a sensitivity analysis with all the sources in the CMB with source profile uncertainties defined with standard errors. Standard error, while a less inclusive definition of uncertainty than standard deviation, is an acceptable measure of uncertainty for use in a chemical mass balance model. The U.S. EPA uses it in their CMB 8.2 model (see ref. in paper). The results of our model re-run were essentially equivalent, which is not surprising since the modeled source profiles fit the data well. We have changed the paper to reflect this fact. The background subtractions were only used for propane and butane going into the CMB model. The aforementioned hydrocarbon ratios (from

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both canisters and in-situ data) were all calculated via linear regression, which is not affected by background concentrations. We investigated other potential sources of light alkanes and couldn't find any evidence; including liquefied petroleum gas, but the propane: butane ratios were not consistent with ambient data from the site. For these reasons, and the very good fit of observations to the source profile of unrefined natural gas for the region (Table 1) we are confident that we have correctly ascribed and estimated the source contributions.

b. Section 3.2. Ground site data are used to estimate [ethanol]:[methane] and [acetic acid]:[methane] ratios from dairy emissions. Clearly the sampling site used, a location several hours downwind of the major concentrations of dairy operations in the region, is not optimal for determining this ratio. As the authors state on P. 28244, the methane and VOC sources are co-located but are not the same. VOC emissions are primarily from animal feed. The authors state that methane is primarily from enteric fermentation and not from animal waste (lines 9-10), but the literature indicates that emissions from manure stored in lagoons may exceed those from enteric fermentation. Since the VOC and methane sources are different and given that environmental factors are likely to have a substantial (and different) impact on VOC and methane emissions, using a single [VOC]:[methane] ratio to apportion dairy emission contributions is likely an oversimplification. Are transport times to the sampling site long enough to average out temporal variations in these ratios?

Response: We agree that the downwind sampling site is not optimal for determining the ratio of an individual operation, but it is very helpful to look at the net effect of all the operations in the region. Since the Bakersfield site is a few hours downwind of the largest distribution of dairies (South of Fresno), this provides a good opportunity to evaluate the overall source profile. This is largely because there is sufficient transport time for samples to be mixed in the atmosphere and further averaged by the 30-minute sample collection prior to analysis. We do agree that calculating one source profile is potentially an oversimplification if you are looking at another region or only a few dairies,

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but there is no work currently that provides an overall source profile since most of the literature focuses on a single source pathway at a dairy operation. Thus we contend that our contribution is a valid and useful one, provided it is applied with attention to differences in future studies. We have revised our comments to clarify our intentions and justification in the manuscript.

2. Section 3.3. Given that the lifetimes of the tracers used are relatively long, is there a reason why the longest trajectories used were 12 hours? Is it possible that sources further upwind contribute significantly to the tracer concentrations at the sampling location?

Response: Yes, it is possible, but it becomes increasingly unlikely that there are strong influences outside the 12-hour footprint for the compounds that we are examining due to the location of potential sources and effects of dilution during transport. Extending the footprint would include a larger distribution of samples from the coast (beyond what is already shown in Figure 1J-L). This may be appropriate if we were studying compounds that we expected transport of emissions from the coast that also had minor emissions in the rest of the footprint (e.g. DMS). If used in this study, there is more likely a potential to reduce the local resolution of sources. The scope of this work is focused on prominent sources (with some a priori knowledge on their source profiles) in the San Joaquin Valley (which has a number of large sources for the compounds studied). So, we are confident that the modeling methods are suited to the area of interest and the boundaries set by the footprint time. Nevertheless, we have revised the manuscript to improve our discussion of the method used and the limitations inherent to its application.

3. Section 3.4. The authors calculate contributions of dairy operations to ozone formation using the observed dairy-attributed methanol, ethanol and acetic acid. However, it is possible that more reactive species in dairy emissions that are depleted before reaching the sampling site, such as alkenes, may contribute to significantly to ozone formation and that the estimated contribution in this work is systematically low. Some

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of these (potentially) unmeasured species could also contribute to SOA.

Response: We agree with the reviewer that there is potentially a bias from the exclusion of compounds that are more reactive or were otherwise not measured in ambient samples in Bakersfield. We did not observe any alkene or aldehyde emissions in the section of these compounds we were able to measure. Despite this potential underestimate, it is uncertain based on this work and the literature whether additional emissions will be large enough to boost the ozone formation potential significantly. We have revised Sections 3.2 and 3.4 to emphasize this discussion more clearly. We have also added a reference to Hafner et al. (2013) to compare other compounds that may contribute to ozone formation.

4. The manuscript compares the source contributions reported here to those in the CARB inventory. The authors discuss potential impacts of the site location compared to the CARB inventory, which deals with the entire region. However, I did not see a discussion of seasonal effects. The CARB inventory is an annual average, whereas this work was conducted during a 6-week period. Can the authors comment on potential contributions from these sources at other times of the year?

Response: We compare our results to the CARB inventory for the San Joaquin Valley and, at a finer scale, the portion of Kern County in the San Joaquin Valley, where Bakersfield is located. There are potential among the 5 sources shown in Table 4 and Figure 15 for seasonal effects. The composition of gasoline will change from the winter to summer due to the reduction of fuel volatility (removing the most volatile components in the summer). With regards to the sources focused in this manuscript, emissions from dairy operations and petroleum production and refining have no seasonal change in the CARB almanac between summer and winter. The emissions we observe from both sources could be hypothesized to volatilize more in warmer weather, but we have insufficient data to assess the seasonal changes and other effects than temperature may potentially play a role. We have added a short paragraph to the manuscript mentioning these potential seasonal effects.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 28225, 2013.

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