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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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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

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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.

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?

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

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oversimplification. Are transport times to the sampling site long enough to average out temporal variations in these ratios?

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?

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

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?

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