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Comment

Interactive comment on “Source apportionment of methane and nitrous oxide in California’s San Joaquin Valley at CalNex 2010 via positive matrix factorization” by A. Guha et al.

A. Guha et al.

abhinavguha@gmail.com

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1) The paper needs editing to reduce excess words and improve clarity of the discussion.

Author’s changes: We have substantially edited the manuscript to reduce words and improve clarity of the discussion as requested. Changes suggested in the final PhD dissertation chapter associated with this manuscript have also been included to improve the document.

2) Given the strong latitudinal and vertical gradients in CH₄, comparison of measure-

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ments at Bakersfield and Mauna Loa Observatory are not appropriate. A suitable site at mid-latitudes would be more appropriate. (also related is reviewer's specific comment on p6085, I10-11)

Author response:

Along with comparison of our measurements to the observed backgrounds at Mauna Loa (~19.48 N latitude), we have also compared them to observations from the NOAA station at Trinidad Head (40.97 N latitude; only CH₄ data exists at THD) in Northern California simultaneously. The referee is correct that the CH₄ measurements at THD point to reasonably higher concentrations than at MLO, although the backgrounds at Bakersfield are even higher than that at THD. But there are two issues with using THD measurements for the comparison: firstly, the measured samples at THD are discrete flask samples collected very few days at a random time of day (not necessarily a daily low signal) while MLO measurements do contain information about daily minimum concentrations during the same measurement period as Bakersfield. Secondly, since we did not have N₂O data at THD, we prefer comparing the backgrounds at Bakersfield (35.36 N latitude) to MLO rather than THD just to be consistent using one station (MLO) for comparison of both CH₄ and N₂O backgrounds.

Author's changes: We have added the CH₄ background information from THD to Section 4.1 in the text for reference as well and also clarified why we use MLO data. I do not think the abstract can or should be altered to maintain brevity

3) Many experimental details, for example choice of standards, are glossed over. Was the water vapor correction checked experimentally? If so, how? If not, how can you trust it? (also related is reviewer's specific comment on p6085, I10-11)

Author's Response: Los Gatos Research Inc. is the manufacturer of the instruments that were used in this experiment and also our partners in this campaign. LGR supplied us with analyzers that were calibrated using the primary WMO standard from the Global Monitoring Division (GMD) at the NOAA Earth System Research Lab. The scuba tanks

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were secondary references and were calibrated before and after the experiments using the primary standards. The LGR co-author in this manuscript has responded that the calibration tests confirmed that there is no issue in short term stability of these species. The water vapor correction is a correction for the dilution effect of water. As water changes concentration, the effect is to dilute the target molecule. This is a mathematical formula applied to the wet values" $\{X\}_{dry} = \{X\}_{wet} / (1 - ([H_2O]/1e6))$ where $[H_2O]$ is the measured water concentration in ppm. We are not aware of published results confirming the LGR vapor correction and did not separately perform the test ourselves. I know it has been confirmed by researchers at NOAA and EMPA, but I do not think the results were published. Hence we assume the dry mole concentrations of the tracers based on the LGR internal correction to be sufficiently accurate. Author's changes: We have clarified these points in the main text in Section 3.1 (trace gas measurements and instrumentation).

4) Lack of benzene measurements seems odd, given the spectrum of VOCs reported.

Author's Response: There were instrumental and gas column related challenges that prevented us from being able to capture benzene in a quantitative manner. Author's changes: We have specifically added in Section 3.1 (trace gas measurements and instrumentation) as to why benzene was not included as a tracer in the analysis. Also a reference is added to a different manuscript that addresses this topic.

5) Uncertainties are not used consistently nor treated clearly. It seems odd to state the fraction of total emissions of a gas from a particular source as a range, then give an uncertainty.

Author's Response: I agree that the presentation of the averaged diurnal range with bootstrapping uncertainties is confusing and misleading as these two physical quantities are not related in the context of how they are derived.

Uncertainties in mass fractions derived from PMF analysis are calculated and reported in rather unconventional ways in past literature and often not mentioned at all. A de-

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tailed description of how the uncertainty in the relative apportionment of a particular gas, say CH₄, in each source type is documented in section S3 in the Supplement. The uncertainty of a tracer in each source factor is derived from the 1-sigma deviation of the averaged mass fraction of that tracer in that source from 100 bootstrapping runs. This is the quantity I report and call ‘uncertainty’ in the abstract and the main manuscript.

The percentage range for CH₄ and N₂O that I report for the major source types has nothing to do with the bootstrapping run. That range is derived from the relative apportionment of CH₄ and N₂O to the specific source from the 653 hourly samples collected during the experiment period in the PMF analysis. This range is reported to demonstrate the diurnal variation typically observed and also seen in Figure 7.

Author’s changes: I have used clarity and a further explanation when referring to the range and its related uncertainty throughout the text as a direct response to the comments from both reviewers. I have edited the abstract such that the bootstrapping uncertainty is not mentioned when reporting the diurnal range. In the main text, I provide a deeper explanation of the uncertainty estimates associated with tracer contributions and how are they derived.

6) Information in the introduction should be updated to the most recent IPCC report and original literature should be cited where possible.

Author’s changes: I have incorporated the suggestion and the requested change in the revised manuscript.

7) How is the footprint of the observations affected by differing night and day meteorology? Is it reasonable to lump measurements from both periods? Aren’t most of the enhancements coming from nighttime build-up of species in the shallow boundary layer when the site’s footprint would be much smaller? (also related Specific Comments p6088, I22)

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Author response:

It is true that the footprints differ between day and night and also based on wind speed and wind direction. But that is the advantage of this statistical technique that even in a nighttime buildup due to shallow boundary layer, difference in wind speeds and wind directions over the experiment period cause significant variations in the amplitude and timing of peak enhancements in various trace gas species. Similarly during day time, while the absolute enhancements are tinier as compared to nighttime for primary gases, the timing differences in day time lows, and high correlation with other species behaving similarly are important features that contribute to the overall statistical analysis. PMF is able to detect the differences in covariances of several groups of tracers varying together to create multiple sets of solutions with varying Q/Qexp ratio and allows the user to determine the most likely and plausible combination. If we split the daytime and nighttime data and attempt to run PMF on these separate periods (which we have done experimentally to verify), the PMF analysis is not conclusive because most importantly, a distinct diurnal profile of the enhancements being apportioned is missing which limits quality of the analysis and renders source factors that are not quite distinguishable and interpretable. You also cut down dramatically on the total number of samples (by half) by treating daytime and nighttime data separately so the degrees of freedom in the analysis suffer and impact the apportionment.

In the overall sense, since multiple biological and fugitive sources of GHGs are randomly distributed all across and also in close proximity to the experiment site at Bakersfield, we believe that the varying size of footprints does not cause certain GHG sources to go completely out of range except perhaps the larger oilfields to the east. But there are several operational oil pump jacks within and around the main urban core as well, and those are definitely within the footprints typically observed at the experiment site irrespective of day or night and wind direction.

Author's changes: None. I hope the reviewer/editor is satisfied with the explanation mentioned above

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8) Are comparisons appropriate of these results for the southern portion of the SJV with CARB inventories for the entire state?

Author response: The comparisons are made to point to some discrepancies in the bottom-up and top-down measurements and to provide a frame of reference to a reader who may not be aware of California's GHG inventory. We elucidate that emissions in the inventory are a product of combination of activity data and emission factors. Specific comparison of emission factors of the evaporative and fugitive source factor (Table 2) and the vehicle emission factor (Table 3) to those derived from southern SJV and Bakersfield-specific studies are used first to establish the origin of these PMF factors. These emission factors are then compared to the state-specific factors. Why? Because, in theory, the measured emission factors for specific source categories should not be significantly different from the state inventory emission factors although activity data (fuel sale, # of vehicles etc.) does vary greatly from region to region which we recognize. In our analysis, we point out to the mismatch of some of these emission factors when comparing local source factor to CARB sources. We are using this argument to suggest that CARB emission factors for certain sources need further validation through top-down data and by that extension question the accuracy of the inventory.

Author's changes: To make this point clear to other readers as well, I have added a sentence in the Implications section in paragraph 4 - "It should be noted that there is a significant difference in the regional vehicle activity data in the Bakersfield region as compared to the more urban Los Angeles and San Francisco regions of California and this can also be an important reason for difference in varying N₂O apportionment seen in regional vs state-specific N₂O inventory distributions. However, the discord of theoretical emission factors (EMFAC) from the measured vehicle emission factors in this study also points to the likelihood of erroneous estimates in any inventory when the theoretical but inaccurate emission factors are combined with activity data to calculate emissions."

All editing comments and specific comments by Referee # 1 have been attended to

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and addressed in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 6077, 2015.

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