

Interactive comment on “Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications” by Z. He et al.

Anonymous Referee #3

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General comments

The manuscript enhances current understanding of ozone formation in the Pearl River Delta, China. The authors analyze one month of measurements made at a receptor site using positive matrix factorization (PMF) and a parameterization of photochemical age to identify and quantify contributions of four emission source types to VOC mass concentration. A box model is used to calculate relative incremental reactivities (RIR) and source contributions to ozone formation. The model is also used to develop ozone response surfaces as a function of VOC and NO_x emission reductions.

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The manuscript states that one important motivation for their study is the need to determine how photochemical processing affects the accuracy of PMF applications to VOC source apportionment in the study region (p 4, l 80 - 85). It would be informative to know how much difference the calculation of photochemical processing made to the PMF results (sections 3.2.1 and 3.2.2). A simple comparison of PMF results with and without the adjustment for photochemical losses would clarify how important it is to do the photochemical loss calculation and adjustment of species concentrations. Such a comparison might make the manuscript more general and of greater interest to a wider audience.

The authors correctly note that their “results could provide valuable information, facilitating local and regional policy-makers...” Their findings are indeed valuable for the specific region studied. The manuscript could have wider significance if the authors provided more comment about how their methods or their results would be of interest to researchers or policymakers in other geographical areas.

The absence of biogenic VOC (e.g., isoprene) contributions to ozone formation is of concern (please see specific comments). Since the results were determined for a one-month autumn sampling period, additional discussion of the applicability of the findings to other seasons is merited.

Readers will need some additional information to evaluate the accuracy of the box model simulations (please see specific comments).

Specific comments

Please note that the “hundreds” digits of the line numbers are not visible in the PDF, so I refer to both page number and line number throughout this review.

p. 7, l 32 – 34. The exclusion of biogenic VOC measurements as inputs to PMF is a limitation. Because the measurement period was October 22 to November 20, 2014, it is possible that biogenic emissions were much lower than would be typical of spring

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or summer and the exclusion of biogenic VOC concentrations from the PMF inputs may not affect the conclusions for this study period. However, there should be some acknowledgment that the results pertain to a fall study and may not represent other seasons.

p 8, l 52 – 54. Please clarify if biogenic VOCs were included among the inputs to the box model. The RIR values will not be correct if biogenic VOCs were excluded from the inputs to the box model.

p 8, l 52 – 54. Please clarify that the model was applied to each individual day in the study for the RIR calculations (rather than that hourly data were averaged across days and then input as averages to the model as was later done to generate the ozone isopleths). The citations to Lyu et al. (2016) and Wang et al. (2017) imply that the model was applied to each individual day (as done in those studies) for the RIR calculations but it would be helpful to be explicit in this paragraph.

p 8, l 64. It might be helpful to say “net O₃ production plus NO consumed” rather than “net O₃ production and NO consumed” (the equations are correct).

P 9, l 95 – 96. If O₃ formation at the site is VOC-limited as previously discussed, it isn't likely that photochemical processing of the arriving air masses is truly complete. Even if NO_x mixing ratios are too low to sustain further O₃ production in the arriving air, injection of fresh NO_x emissions into aged air masses would permit further photochemical processing. The next section (3.2.1) indicates that photochemical aging was relatively incomplete (high correlations between more reactive and less reactive species; similarities between initial and observed VOC species concentrations except for highly reactive species such as some alkenes and aromatics).

P 11, Table 1. It would be helpful to include summary statistics for NO and NO₂.

P 17, section 3.3. For readers to understand the accuracy of the box model, it would be helpful to provide model performance statistics for the base case at the beginning

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of this section.

P 18, Figure 8 and related text. The RIR calculation for each species depends on the concentrations of all other species. If biogenic VOCs (e.g., isoprene) were not included as inputs to the box model, the reported RIR values will not represent the “real-world” condition. If biogenic VOCs were included as inputs to the box model, Figure 8 should show their RIRs and relative contributions. Please note in the caption what the error bars represent (e.g., one or two standard errors of the means or a different measure of variation?)

P 18, l 37 - 38. The phrase “based on the average diurnal variation” suggests that hourly data were averaged across days to provide a single base-case input for the box model's generation of ozone isopleths, which would be consistent with the approach described by Lyu et al. (2016). Please expand this description slightly. Do the 58 VOCs include isoprene and alpha- or beta-pinene?

P 19, l 61. Even in the NO_x-limited regime, VOC reductions never increase ozone formation. Consistent with past studies, the isopleths are nearly vertical on the left side of Figure 9b and indicate a very small ozone decrease in response to VOC reductions at fixed NO_x.

Pages 21 – 22. Many readers will not be able to follow this discussion as written.

p. 23, l 34 – 35. Does this conclusion apply to other seasons?

Minor comments

Abstract. The abstract uses a term (“abatement ratio”) that is defined in the text (page 21), requiring a full page of explanation there. Another full page (p 22) is needed to define and discuss the abatement ratios of the individual source types. To aide readers of the abstract who will not have already read pages 21 - 22, I suggest revising the following sentence:

“Sensitivity analysis indicated that in order to prevent the increment of O₃ concentra-

tion, the abatement ratios of the individual VOC source vs. NO_x should be higher than 3.8, 4.6, 4.6, and 3.3, respectively, for diesel vehicular emission, solvent usage, biomass burning, and gasoline vehicular emission, respectively.”

A sentence such as the following appears to me to better convey the intended meaning: “Sensitivity analysis indicated that combined VOC and NO_x emission controls would effectively reduce incremental O₃ formation when the ratios of VOC-to-NO_x emission reductions were higher than 3.8 for diesel vehicular emission, 4.6 for solvent usage, 4.6 for biomass burning, and 3.3 for gasoline vehicular emission.”

P 3, l 71-73. Please clarify if the percentages refer to percent of VOC mass or percent of VOC reactivity.

P 5, l 99-100. The map shows that the site is southwest of Guangzhou and Foshan, not northeast (alternatively, the cities are northeast of the site).

P 13, eq. 6 and l 53 – 54. For consistency, please use either kVOC or kNMHC in both eq. 6 and the text.

p. 20. Figure 9 is confusing for two reasons. First, it would be easier to understand the figure if the two panels were swapped (right replacing left). Second, the axes are also reversed from the more common presentation format. Reversing the vertical and horizontal axes and then placing the current left panel above the current right panel would be consistent with customary presentations (NO_x reductions on the vertical, VOC reductions on the horizontal axis).

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