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Atmospheric Chemistry and Physics Discussions

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.

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Response to Reviewers We appreciate the two anonymous reviewers for their constructive criticisms and valuable comments, which were of great help in improving the quality of the manuscript. We have revised the manuscript accordingly and our detailed responses are shown below. All the revision is highlighted in the revised manuscript.

Reviewer #1

The authors presented hourly resolved measurements of volatile organic compounds

Printer-friendly version

Discussion paper

(VOCs) at a receptor site in the Pearl River Delta (PRD) region in China. A receptor model, positive matrix factorization (PMF), was used to apportion sources of VOCs, by taking into account of photochemical degradation of some VOCs. Results showed that four sources, including gasoline vehicular emission, diesel vehicular emission, biomass burning, and solvent usage, are major contributors to anthropogenic VOCs at the site. A photochemical box model with the master chemical mechanism was also used to evaluate the contributions of those VOCs to ozone formation, with vehicular emission found to be the most significant. Further analysis to test abatement scenarios was also performed for policy implication. Overall, this is a nice data set with thorough analysis. The manuscript is generally well written and is surely of interest to readers of ACP. I therefore recommend minor revision before publication, with below comments for the authors. Reply: Thanks for the reviewer's positive comments and helpful suggestions. We have addressed all of the comments/suggestions in the revised manuscript. Detailed responses to the individual specific comment/suggestion are as follows.

Major: 1. I do not understand that in Section 3.3, why did the authors sum up gasoline and diesel vehicular emissions in their discussion on the contributions of different VOC sources to ozone formation. It is of importance for policy making, as to which type of vehicular to control (e.g., with priority), if we have more detailed understanding on whether vehicles run on gasoline or diesel have more potential in VOC emission that is related to ozone formation. Can the authors justify and clarify? Reply: The reviewer's comment is highly appreciated. We thought that both diesel and gasoline vehicles belong to vehicle, so we combined them as a whole to discuss the vehicular emission. We agree with the reviewer that more detailed understanding on whether diesel or gasoline vehicles contribute more to O3 formation is important for policy making. Therefore, we discuss different factors separately in the revised manuscript. The text has been revised as follows: "Figure 8a-b showed the mean RIR values of different VOC sources and NO, together with the contributions of different VOC sources to photochemical O3 formation. The mean RIR values of various VOC sources were positive, while that of NO was negative, suggesting that O3 formation at the HS was in the

VOC-limited regime. Among the four main anthropogenic sources of VOCs, relatively higher mean RIR values of vehicular emissions and biomass burning than that of solvent usage were found, with the mean RIR value of gasoline vehicular emission higher than that of diesel vehicular emission. Furthermore, considering both the reactivity and abundance of VOCs in different sources, the results showed that the gasoline vehicular emission was the most important contributor to photochemical O3 production (Fig. 8b), with the mean percentage of 42%, followed by diesel vehicular emission (23%), biomass burning (20%) and solvent usage (15%), suggesting that controlling vehicular emissions (especially gasoline vehicular emission) and biomass burning could be a more effective way of reducing O3 pollution in the region." For detail, please refer to Lines 6-16, Page 20 in the revised manuscript.

Figure 8. The mean RIR values of different sources (a) and their contributions to photochemical O3 formation (b); The mean RIR values of different VOC groups (c) and their contributions to photochemical O3 formation (d); The mean RIR values of top 10 VOCs (e) and their contributions to photochemical O3 formation (f). The error bars represented one standard errors of the mean RIR values. Alkene* includes acetylene and alkenes except isoprene.

2. Using the same set of data, the same group of authors published in Journal of Environmental Science (JES) recently. Although the foci of the two papers are different, with the JES paper on isoprene and their oxidation products and this one on anthropogenic VOCs, I do like to see some connection between the two papers as they are based on the same data set (it was not even cited here). More importantly, what is the similarity and difference in methodology between these two papers? Would there be any bias if the whole chunk of biogenic VOCs were taken out from photochemical box model (e.g., the source/fate of OH radicals and ozone)? Reply: Thanks for the reviewer's comment. In the study published in JES (Ling et al., 2019), the source contributions of methacrolein (MACR) and methyl vinyl ketone (MVK) as well as their contributions to subsequently oxidation products were quantified. Both the study of

Ling et al. (2019) and this study applied PMF model for the source apportionment of VOCs based on the data collected at Heshan, but the aim of Ling et al. (2019) was to conduct the source apportionment of MACR and MVK, which included the primary emissions and secondary formation. Therefore, only species that are typical tracers of different emissions, including 18 NMHCs (i.e., isoprene, C6-C8 aromatics, C2-C4 alkenes), acetonitrile (ACN), methyl chloride (CH3Cl), methyl tert-butyl ether (MTBE) and peroxy acetyl nitrate (PAN) were selected as the input for the PMF model in Ling et al. (2019) (Song et al., 2006; Ho et al., 2009; Yuan et al., 2010, 2012b; Chen et al., 2014). On the other hand, different from that of Ling et al. (2019), this study aims to investigate and quantify the anthropogenic VOC sources which were all primary emissions. All anthropogenic VOCs except species with high uncertainties (i.e., cis-2-pentene, diphenyl methane, 1,3-diethylbenzene, etc. as more than a quarter of the samples for them were below the detection limits) were included in the PMF model. The total average concentration for the species in the PMF model accounted for ~99% of that for all anthropogenic VOCs. Furthermore, as the fact that source apportionments of VOCs using the PMF model was conducted based on the assumption of mass conservation, a photochemical-aged-based parameterization was applied to identify the influence of photochemical processing on source signature of VOCs before running the PMF model in this study (Yuan et al., 2012b; Ling and Guo, 2014). Moreover, in this study, only one biogenic species (isoprene) was quantified at the Heshan site. We agreed with the reviewer that if the whole chunk of biogenic VOCs were excluded as input in the photochemical box model, there will be bias for the model simulation. Actually, the simulation of PBM-MCM in this study included the observed levels of biogenic species, i.e., isoprene. To clarify the similarities and difference between this and previous study (Ling et al., 2019), the text has been revised as follows: “The detailed description of the model input is provided elsewhere (Guo et al., 2011a; Ling et al., 2014). The selection of species for the PMF model followed the following principles: 1) the chosen species had relatively high concentrations and/or were typical tracers for specific emissions, e.g., methyl tert-butyl ether (MTBE) as the

tracer of gasoline vehicular exhaust (Song et al., 2006; Ho et al., 2009) and acetonitrile (ACN) as the tracer of biomass burning (Holzinger et al., 1999; Yuan et al., 2010); 2) species with low abundance and/or high uncertainties were excluded, i.e., cis-2-pentene, diphenyl methane, 1,3-diethylbenzene, etc., because more than a quarter of the samples for those species were below detection limits, and 3) species related to biogenic emissions (i.e., isoprene) were excluded as this study focused on the source characteristics of anthropogenic emissions in the PRD region (Fuentes et al., 1996; Sanadze, 2004; Zheng et al., 2010a; Zhang et al., 2012). A total of 49 species (including 47 non-methane hydrocarbons (NMHCs), MTBE, and ACN) were selected for the input data, which accounted for ∼99 % of the total concentration of all measured anthropogenic VOCs. This was different from our previous study (Ling et al., 2019), where only species that are typical tracers of different emissions, including 18 NMHCs (i.e., isoprene, C6-C8 aromatics, C2-C4 alkenes), acetonitrile (ACN), methyl chloride (CH3Cl), methyl tert-butyl ether (MTBE) and peroxy acetyl nitrate (PAN) were input into the PMF model for the contributions of primary emissions and secondary formation to ambient methacrolein (MACR) and methyl vinyl ketone (MVK) based on the same data set collected at the HS. For the PMF modelling, detailed information of the data processes and evaluation of the model performance has provided in previous studies (Lau et al., 2010; Ling et al., 2019). ……" To clarify that biogenic species, i.e., isoprene, was input into the PBM-MCM model, the text has been revised as follows: "In this study, the hourly data of VOCs, including both anthropogenic and biogenic species, five trace gases (i.e., O3, NO, NO2, CO, and SO2) and two meteorological parameters (i.e., temperature and relative humidity) measured during the campaign were used as the model input." For details, please refer to Line 17, Page 6 – Line 12, Page 7 and Lines 17-19, Page 9 in the revised manuscript.

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3. Page 12, line 19-25. I do not understand the assertion here that correlation will be distorted if two VOCs from the same source have different photochemical reaction rates. The authors used the photochemical age concept in the paragraph right after it, which means that correction can still be retained if the two VOCs react in a proportional manner with OH radicals (and assuming no other fates). The rationale of these two paragraphs seems contradicting. Please clarify. Reply: Thanks for pointing it out. We agree with the reviewer that good correlation between two species from the same sources with different photochemical reaction rates would be retained if there were no other fates other than the oxidation by OH, NO3 and O3, as the fact that the reaction rates of these two VOCs are in a proportional manner. Therefore, the discussion on

the correlation between two species with different reaction rates has been deleted in the revised manuscript.

4. P7/L37: I would strongly suggest the authors include more details on why a four-factor solution was chosen. Diagnostic analysis by comparing three-factor and five-factor solutions would be useful, even as supplementary materials. "a good fit to the data and the most meaningful results" is just too descriptive and not very convincing. Reply: Thanks for the reviewer's suggestion. To clarify the determination of PMF solution, the following text has been added as follows: "In this study, the source apportionments of a 4-factor solution from the PMF model was selected, which were able to sufficiently and completely explain the levels and variations of observed VOCs (Lau et al., 2010) (Sect. 3.2.2). Compared with those of the 4-factor solution, the solution with 3 factors coerced two profiles that would otherwise be attributed to solvent usage and biomass burning, while certain amounts of aromatics and heptane were added into the profile of gasoline vehicular emissions. On the other hand, when the factor number was 5, an additional factor split from the biomass burning with the presence of C6-C9 alkanes, together with about 10-25 % of aromatics (including toluene and xylenes) found in the 5-factor solution. To evaluate the performance of the 4-factor solution, various tests and verifications were conducted. Firstly, different numbers of start seed in the model run were tested and it was found that there were no multiple solutions during the simulation. Furthermore, the scaled residuals of all the selected species ranged between -3 and 3 for the 4-factor solution, while the ratios of Q(robust)/Q(true) in this solution was close to 1 (Paatero, 2000a). In the 4-factor solution, strong correlations were found between the concentrations extracted from the model and the observed concentrations of each species, with correlation coefficients ranging from 0.71-0.95, indicating that the 4-factor solution well reproduced the observed variations of VOCs (Lau et al., 2010). In the bootstrapped simulation for the 4-factor solution, all the factors were mapped to a basic factor in all runs, indicating that the solution was stable. Finally, in the F-peak model results of the simulation, the G-space plot with no oblique edges suggested that the solution was with little rotation (Paatero, 2000a; USEPA, 2008). Overall, the above

features proved that the 4-factor solution from PMF could reliably attribute the sources of VOCs in this study." For details, please refer to Line 17, Page 7 – Line 12, Page 8 in the revised manuscript.

References: Lau, A.K.H., Yuan, Z.B., Yu, J.Z., Louie, P.K.K.: Source apportionment of ambient volatile organic compounds in Hong Kong, Sci. Total. Environ. 408, 4138-4149, 2010. Paatero, P.: User's guide for positive matrix factorization programs PMF2 and PMF3, part 1: tutorial, Prepared by University of Heisinki, Finland, February, 2000a. USEPA (U.S. Environmental Protection Agency): EPA Positive Matrix Factorization (PMF) 3.0 Fundamental and User Guide. July, 2008.

Minor: 1. P2/L41: "complex, nonlinear" to "complex and nonlinear". Reply: It has been revised accordingly.

2. P2/L44: "VOCs and NOx limited" to "VOC- and NOx-limited"; "VOCs-limited" to "VOC-limited", and in other places as well. Reply: Thanks for pointing this out. It has been revised accordingly in the revised manuscript. Furthermore, all "VOCs-limited" in the manuscript has been revised as "VOC-limited".

3. P3/L60: "emission-inventory" to "emission inventory". Reply: It has been revised accordingly in Line 12, Page 3 in the revised manuscript.

4. P4/L84: did Ling et al., JES, 2019 take photochemical processing into account? Reply: Thanks for the reviewer's comment. Our previous study (Ling et al., 2019) did not take the influence of photochemical processing on the variations of VOCs into account before using the PMF model as the study was to investigate the sources of MACR and MVK, which included primary and secondary sources. Furthermore, the species used in Ling et al. (2019) have relatively long lifetime, and it was suggested that the influence of photochemical processing were not significant on these species (Zhang et al., 2012), which could be further confirmed by Fig. 4 in our manuscript. For details, please refer to Line 1, Page 15 – Line 3, Page 16 in the revised manuscript.

References Ling, Z. H., He, Z. R., Wang, Z., Shao, M., and Wang, X. M.: Sources of MACR and MVK and their contributions to methylglyoxal and formaldehyde at a receptor site in Pearl River Delta, J. Environ. Sci., 79, 1-10, 2019 Zhang, Y. L., Wang, X. M., Blake, D. R., Li, L. F., Zhang, Z., Wang, S. Y., Guo, H., Lee, F. S. C., Gao, B., Chan, L. Y., Wu, D., and Rowland, F. S.: Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China, J. Geophys. Res.-Atmos., 117, D15306, https://doi.org/10.1029/2011JD017356, 2012.

5. P6/L19: remove "," after "contributions". Reply: Removed.

6. P7/L32: "the detection limit" to "their detection limits". Reply: Corrected. 7. P7/L35: why MTBE and ACN so special and not considered as "VOCs"? Reply: Sorry for the mistake. Indeed, MTBE and ACN were VOCs. It has been revised as follows: "A total of 49 species (including 47 non-methane hydrocarbons (NMHCs), MTBE, and ACN) were selected for the input data. . ." In addition, the following text has been added in the revised manuscript: ". . .the chosen species had relatively high concentrations and/or were typical tracers for specific emissions, e.g., methyl tert-butyl ether (MTBE) as the tracer of gasoline vehicular exhaust (Song et al., 2006; Ho et al., 2009) and acetonitrile (ACN) as the tracer of biomass burning (Holzinger et al., 1999; Yuan et al., 2010); . . ." For details, please refer to Lines 3-4, Page 7 and Lines 18-21, Page 6 in the revised manuscript.

8. P8/L58: add "divided by" after "production"? Reply: Thanks for pointing this out. "divided by" has been added accordingly in the revised manuscript (Line 1, Page 9).

9. P9/L89&L91: "that" to "those". Reply: Corrected.

10. P9/L94-96: how can variations of VOCs suggest photochemical processing? It could be just variations on sources. Please clarify. Reply: The reviewer's comment is highly appreciated. We agreed with the reviewer that variations of VOCs were related to the variations on sources other than photochemical processing. Therefore, the text has been deleted accordingly in the revised manuscript. For details, please refer to

Line 24, Page 10 in the revised manuscript.

11. P9/L96: delete “to be”. Reply: Deleted. 12. P12/L34-35: these rate constants appeared later in the next page and look redundant. Please remove. Reply: Thanks for pointing this out. Those redundant rate constants in Line 2, Page 14 have been deleted in the revised manuscript.

13. P13/Eq 6: k_VOC instead of k_NMHC? It would be good to have a table showing the rate constants for each VOCs and appropriate citation. Reply: Thanks for pointing this out. It has been revised accordingly in the revised manuscript (Line 13, Page 14). In addition, a table showing the OH reaction rate constants for each VOC has been added as Table S1 in the supplement.

14. P14/L60&L62: “reaction rate” should be “reaction rate constant”? Reply: Corrected.

15. P14/L71: add “the” before “rest species”. Reply: Added

16. P15/L89: remove “,” after “VOCs”. Reply: Removed.

17. P15/L93: “acetonitrile” to “ACN" (you defined it early). Reply: Thanks for pointing this out. It has been revised accordingly in the revised manuscript (Line 1, Page 17).

18. P15/L00: “peak” or “valley”? Reply: Sorry for the mistake. It has been corrected to “valley” in the revised manuscript (Line 10, Page 18).

19. P17/L22: “relative” to “relatively”. Reply: Corrected. 20. P18/L29: add “a” before “more”. Reply: It has been revised accordingly.

21. P23/L31: remove “cluster”. Reply: Removed.

22. P24/L44-P25/L65: I would suggest to shorten this paragraph to a few sentences to make the point: although there are some control measures on VOC emission from vehicles, there is limited control on biomass burning etc. Reply: Thanks for the great suggestion. To condense this paragraph and to make brief description on the policy

implication, the text has been revised as follows: “Indeed, many additional policies on VOCs have been and continue to be implemented and formulated in the PRD region. A series of policies regarding the control of vehicular emission have been conducted in the PRD region, the purposes of which can be mainly divided into two categories: 1) improve the environmental standards of the main air pollutants and standards of emissions; and 2) improve the quality of the fuel used in vehicles. Policies on controlling biomass burning, however, are relatively limited. Nevertheless, some policies have been effective, and levels of NOx (another important O3 precursor), have decreased in the PRD region in recent years. On the other hand, for VOCs, most relevant policies only control the total mass and/or the total emissions of VOCs, and the level of O3 continues to increase in this region. ……” For details, please refer to Lines 13-21, Page 27 in the revised manuscript.

23. Figure 4: can the authors use another panel to show ratios too? Reply: Thanks for pointing this out. Figure 4 has been revised to show the ratios of initial to observed concentrations of VOCs in the revised manuscript. (Fig. 4, Page 15).

Figure 4. Ratios of initial to observed concentrations of volatile organic compounds (VOCs).

24. Figures in general: it would be more reader friendly if the authors can use a bigger font size for most of the figures. Reply: The reviewer’s suggestion is highly appreciated. The font size for most of the figures have been bigger in the revised manuscript. âĂČ

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-1293/acp-2018-1293-AC2-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1293, 2019.