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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 #2

This manuscript presents an analysis of hourly VOC data from the Pearl River Delta re-

gion including PMF and VOC sources important for ozone formation. There is also an analysis of VOC and NOx limitation and what effect controlling each of these may have on ozone. In general the manuscript is well written with only a few sections needing clarification. 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.

Specific Comments: P8 Line 62-63: Is this a result from this study or from elsewhere? It is confusing to have these papers cited without more explanation. Reply: Sorry for the mistake and confusion it caused. We have revised this part to clarify it, and the improved text is as follows: "As ethane, acetylene, ethene, and propane had been suggested to be the tracers of incomplete combustion from vehicle exhaust, biomass or coal (Liu et al., 2008a; Lau et al., 2010; Guo et al., 2011b; Yuan et al., 2012a), the characteristic of abundant species at the HS indicated that incomplete combustion was likely the dominant source of VOCs during the measurement period." For details, please refer to Line 24, Page 10 – Line 4, Page 11 in the revised manuscript.

Table 1: Add a line dividing the individual species from the categories. This will make the table easier to read. Reply: Thanks for the reviewer's great suggestions. It has been revised accordingly in the revised manuscript (Table 1, Page 12).

P9 Line 73-78: The use of these correlations seems to be overstated both in terms of widespread use (1 paper cited) and what these correlations mean for photochemistry impacts. Weak correlations may exist due to strength of impact from different sources in addition to changing photochemistry. Adding some statements about the degree of correlation or lack of correlation between other species would strengthen this section. A more convincing argument would be to look at photochemically formed species from these precursor compounds – I'm not sure if these compounds are available. This simple analysis and the extended analysis using the parameterization suggests little photochemistry is taking place. Is this due to the time available for photochemistry to take place or atmospheric conditions. What is the estimated air mass age?

(using chemical tracers, proximity to sources and average wind speed, or from the parameterization). Reply: Thanks for the reviewer's comment. We agree with the reviewer that weak correlation between two species may exist due to different impact on them from different sources. Furthermore, the reviewer#1 pointed out 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. We agreed with both reviewers, and the discussion on the correlation between two species with different reaction rates has been deleted in the revised manuscript. In this study, we applied the photochemical-aged-based parameterization method to estimate the initial concentrations of VOCs after emissions. The OH exposure ([OH] Δt) is calculated and used to represent photochemical age, as [OH] and Δt always appear together in the parameterization equation (Shao et al., 2009; Yuan et al., 2012b). [OH]Δt=1/((k_E-k_X))$\times$[ln [E]/[X] |_(t=0)-ln [E]/[X]] (5) The OH exposure ([OH]Δt) was calculated as 6.47$\times$109 moleculeÂůcm-3Âůs. With the hourly concentrations of OH during the measurement period simulated by PBM-MCM, the air mass age Δt was calculated as about 3 hours. As the lifetimes of most of species in this study ranged from 2.8 hours to 6 months (Simpson et al., 2010), the air mass age calculated by the parameterization method suggested that there was not enough time for these species to be degraded completely by OH radical. Indeed, from the parameterization method, the difference between initial and observed concentrations were small for most of the VOC species, i.e., the species with the OH reaction rate constant < 5.64$\times$10-11 cm3Âůmolecule-1Âůs-1, and the ratio of initial/observed concentrations ranging from 1.00-1.23. For those species with relatively higher photochemical reactivity (with the OH reaction rate constant ranging from 5.64$\times$10-11-6.40$\times$10-11 cm3Âůmolecule-1Âůs-1), the initial concentrations were 1.44-1.51 times the observed levels (Fig. 4). It should be noted that these relatively higher reactive species only accounted for a small fraction of the concentrations and the ozone formation potential (OFP) of all the observed VOCs due to their relatively lower abundance (data not

shown). Furthermore, to roughly identify the potential source areas of VOCs, 24-h air masses backward trajectories in 3-h intervals were calculated, and 7 main types of backward trajectories were obtained through cluster analysis (Fig. S2), which were mostly passing through the center cities of PRD before arriving at the Heshan site. As the air mass age was calculated as about 3 hours by the photochemical-aged-based parameterization method, the position of 3-h backward trajectories of each type was extracted to determine the source areas. It was found that $\sim$70% air masses were from the center cities of PRD (i.e., Foshan and Guangzhou), while $\sim$30% were from the southeast of Jiangmen city and from the center of Zhongshan city, indicating that the air masses at the Heshan site were from or through the urban areas with significant anthropogenic emissions. The above discussion was provided in the revised manuscript (Lines 8-14, Page 14) and the supplementary.

Figure S2. The seven clusters of 24-h air masses backward trajectories with Heshan as the ending point (the trajectories were simulated for 3-h intervals at the ending point of 200 m above sea level) (Ling et al., 2013).

References: Ling, Z.H., Guo, H., Zheng, J.Y., et al.: Establishing a conceptual model for photochemical ozone pollution in subtropical Hong Kong. Atmos. Environ. 76, 208-220, 2013. Shao, M., Lu, S.H., Liu, Y., Xie, X., Chang, C.C., Huang, S., and Chen, Z.M.: Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, J. Geophys. Res., 114, D00G06, https://doi.org/10.1029/2008JD010863, 2009. Simpson, I.J., Blake, N.J., Barletta, B., et al.: Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C2-C10 volatile organic compounds (VOCs), CO2, CH4, CO, NO, NO2, NOy, O3 and SO2, Atmos. Chem. Phys., 10.11931-11954, 2010. Yuan, B., Chen, W.T., Shao, M., Wang, M., Lu, S.H., Wang, B., Liu, Y., Chang, C.C., Wang, B.G.: Measurements of ambient hydrocarbons and carbonyls in the Pearl River Delta (PRD), China, Atmos. Res., 116, 93-104, https://doi.org/10.1016/j.atmosres.2012.03.006, 2012a.

Figure 2: Consider showing as the difference between the measured and estimated initial concentration instead. It will be easier to see the delta for all species than infer it from the difference between bars. Reply: Thanks for the reviewer's great suggestions. Figure 4 was 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).

Figure 5: Why are both diesel and gasoline vehicles together if they were different factors? Reply: The reviewer's comment is highly appreciated. The similar comment was also made by reviewer #1. 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 pho-

tochemical 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 acetylenes and alkenes except isoprene.

Sect 3.3 How does this compare for the different classes of VOCs? This would be good to include to inform which measurements would be most important to make long-term or in the future. Or if new industry moved into the area and the mix of VOCs was different. Reply: The reviewer's suggestion is highly appreciated. The relevant discussion on different VOC species and groups has been added in the revised manuscript as follows: "Furthermore, Fig. 8c-f also showed the mean RIR values and the contributions to photochemical O3 formation for the top 10 VOC species and groups at the HS. Aromatics had the highest RIR value, with the average contribution of $\sim$82% to the sum RIR of all VOCs, followed by alkenes ($\sim$11%) and alkanes ($\sim$7%). Among the individual VOC species, toluene and m/p-xylene made most significant contribution (with a relative contribution of $\sim$40% and $\sim$34%, respectively) to O3 formation at the site when both the reactivity and abundance of VOC species were considered. The PMF results suggested that aromatics (including toluene, xylenes, and ethylbenzene) were mainly from gasoline vehicular emission and solvent usage, while alkenes were mainly related to diesel vehicular emission. The results suggested that gasoline vehicular emission was the dominant contributor to O3 formation at the HS, and greater efforts should be devoted to toluene, xylenes, ethylbenzene, ethene, and 1-pentene for effectively controlling photochemical pollution." For detail, please refer to Line 17, Page 20 – Line 7, Page 21 in the revised manuscript.

Sect 3.4.2 – something about the tenses used (past and present) is confusing or not consistent. I suggest going through the section and checking verb use for consistency and clarity. Reply: Thanks for the reviewer's patience and revision. For better expression, we have rewritten section 3.4.2 and double-checked the whole manuscript.

Line 19 Line 40: Which of your reduction scenarios reflect these changes? I ask that for the majority of this section. The listing of all these policies without more direct connection to your findings is superfluous. Only the last paragraph in the section touches on this but still doesn't connect how much these policies are expected to change VOC and NOx levels. The importance and relevance of this section needs to be considered. If it is important figure out a way to make it easier to follow and more connected to the rest of the paper. Reply: The reviewer's suggestion is highly appreciated. In this study, we summarize briefly the policy for controlling VOC emissions conducted/being conducted in the PRD region based on the source apportionments of anthropogenic VOCs and their contributions to O3 formation at a receptor site of the PRD region. Though the results, i.e., the source apportionments of VOCs, their contributions to O3 formation and the appropriate reduction ratios, indeed provided scientific support and indication for devising controlling strategies on photochemical pollution in this region, this study could not evaluate the benefits and dis-benefits of the control measures, i.e., how much the policies influence on the abundance of VOCs and NOx, only by one-month measurement data collected in a specific season. Therefore, to shorten the summary of the policy as suggested by reviewer #1 and to connect the results of this study to the implication for policy development, the policy implication section has been combined with the conclusion section and revised as follows: "The PRD region has long been facing severe photochemical air pollution, and VOCs has been the limiting factor of O3 formation in this region. To better understand the contribution of different anthropogenic VOCs to O3 formation in this region, we performed in-depth analyses on data obtained from intensive measurements of VOCs and related species at a downwind rural site (Heshan site, HS) of the PRD region during October – November, 2014. Four anthropogenic sources were identified by the PMF model with the consideration of the influence of photochemical processing. The O3 formation at the HS was generally VOC-limited, with the vehicular emission (especially gasoline vehicular emission) as the most important anthropogenic VOC source contributing to O3 formation, followed by biomass burning. It indicated that priority should be given to controlling vehicular

emission and biomass burning. Furthermore, with the current industries operating in the PRD region, particular attention should be given to toluene, xylenes, ethylbenzene, ethene and 1-pentene in efforts to control photochemical pollution. 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. To prevent net O3 increment, the VOCs and NOx should be controlled in an appropriate ratio since VOCs and NOx are frequently controlled simultaneously. Furthermore, long-term monitoring is still needed to evaluate the benefits and dis-benefits of the control measures on vehicular emissions and/or photochemical pollution in the PRD region. Overall, the results of this study will be valuable for facilitating local and regional policy-makers to propose appropriate strategies and effective control measures of VOCs and photochemical pollution in other regions of China, especially where O3 formation is VOC-limited. However, it is noteworthy that the above results were obtained based only on measurements taken over one month, and in a specific season (i.e., autumn), which may only represent the characteristics of photochemical pollution in autumn at a receptor site in the PRD region." For details, please refer to Line 2, Page 27 – Line 6, Page 28 in the revised manuscript.

P9 Line 77: little instead of insignificant. Insignificant implies statistics were used. Reply: Thanks for pointing this out. The relevant text has been deleted in the revised manuscript.

P11 Line 11: adjusted instead of compensated Reply: Thanks for pointing this out. It has been revised accordingly in the revised manuscript (Line 16, Page 15).

P12 Line 26: C6-C7 alkanes? Reply: Sorry for the mistake. It has been revised accordingly in the revised manuscript (Line 17, Page 16). P13 Line 39: why “again”? I don’t think you’ve presented PBM-MCM data yet. Reply: Thanks for pointing this out. It has been deleted in the last manuscript.

P19: Line 32-33: This suggests. . .in the region. Reply: Thanks for the reviewer’s suggestion. The relevant passage had been deleted in the last manuscript.

P19 Line 42: closely instead of strictly Reply: Thanks for the reviewer’s suggestion. The relevant passage had been deleted in the last manuscript.

P19 Line 42: What are new energy automobiles? Reply: [P24 54] Sorry for the mistake and confusion it caused. The relevant passage had been deleted in the revised manuscript to shorten the policy implication section as suggested by the reviewer#1. The accurate expression should be “new energy vehicles”. The term new energy vehicles (NEVs) is used to designate plug-in electric vehicles eligible for public subsidies in China, and includes only battery electric vehicles (BEVs), plug-in hybrid electric vehicles (PHEVs), and fuel cell electric vehicles (FCEV). (https://en.wikipedia.org) âĂČ

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-1293/acp-2018-1293-AC3-supplement.pdf

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