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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An analysis of the impacts of VOCs and NO_x on the ozone formation in Guangzhou" *by* Y. Zou et al.

Anonymous Referee #1

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This manuscript reported one-year online measurement data of NOx, VOC and O3 collected at a suburban site of southern China. The authors studied seasonal variations of O3 and its precursors. They also investigated the ozone formation potential of VOCs. However, this manuscript does not have novelty at all. The methods used for data analysis are out of date and discussions show lack of basic atmospheric chemistry knowledge. Also, the English language needs to be significantly polished. The manuscript is not worthy to be published in ACP.

General comments 1. VOC/NOx ratio should only give a rough idea as to whether it is a NOx-sensitive or VOC-sensitive environment, which is crucial for ozone formation. However, VOCs are a complex mixture of compounds with large difference in reactivity with respect to ozone formation. The true impact of VOCs to ozone formation is more

relevant to the reactivity of individual VOC species rather than to the total amount of VOCs. 2. Only one site located in suburban Guangzhou is not appropriate for the formulation and implementation of ozone control strategies in Guangzhou. 3. There is no QA/QC of online VOC measurements. Any inter-comparison? Are all the instruments calibrated and how?

Specific comments 1) Very poor quality of Fig 1. Also, much more detailed map and surroundings should be plotted. 2) Page 5 lines 10-12: why? 3) How did you identify VOC species with GC-FID? What standards were used? 4) Lines 23-24, page 5: I don't know how the analyzer contacted enriched concentration at 13°C, given that C1-C4 HCs have negative boiling points. In other words, it is impossible to concentrate these low boiling-points HCs at 13°C. More info about the operation principle of GC-FID is needed. Zou et al. (2013) is in Chinese. 5) Lines 19-21, page 6: this is not fully correct. What about the emission strength of air pollutants? 6) Lines 16-24, page 6: no statistical analysis was conducted for all the comparisons. Are they really statistically different? 7) Lines 25-26, page 6: I did not see this pattern from Fig 3. 8) Line 26 page 6 – lines 1-2 page 7: how? What is the law of atmospheric photochemical reactions? 9) Lines 10-19, page 7: the discussion contains a conceptual mistake. The most important factor to affect the net production of ozone is not NO titration but the level of OH radicals which initiate the photochemical reactions. Simply, during nighttime, there was zero O3 generation because there was no OH radical. NO titration could still consume O3. 10) The title of Fig 5 is not accurate. It should be diurnal variations of NO2/NO and O3. 11) Lines 1-10, page 8: low morning O3 is caused not only by NO titration but also low OH radicals. How could "NO2/NO ratio subsequently reaches its maximum by further photochemical reaction (eq.2)"? The diurnal patterns of NO2/NO are related to both primary emissions such as vehicles which can emit NO2 as well, and secondary formation via photochemical reactions. The discussion here shows the lack of basic atmospheric chemistry knowledge. 12) Section 3.3 Impact of VOCs on ozone formation potential: To assess the reactivity and the contribution to photochemical O3 formation of individual VOC, a propylene-equivalent concentration method proposed by Chamei-

des et al. (1992) and a maximum incremental reactivity (MIR) method proposed by Carter (1994) are used in this study. The MIR method is based on a scenario in which O3 formation is derived under optimum conditions, such as high actinic flux and a scenario with NMHC/NOx ratios, which yield a maximum O3 formation, whereas the propylene-equivalent concentration method simplifies the estimation by solely taking into account the OH reaction rate coefficients and concentrations of a NMHC. However, there is no unique relationship between the competitive reaction rates of a set of organic compounds with hydroxyl radicals and their ability to produce O3 in atmosphere because the latter depends on the subsequent reaction mechanisms of the products of the OH radical attack. Both methods are used to assess the OFPs simply by summing up the products of measured NMHC amounts and their corresponding MIR and kOH factors, neither of which considers actual meteorology and transport influence. The OFPs and reactivities assessed by these two methods are not meant to represent actual O3 concentrations in that area, because it will also be affected by meteorology and transport factors. As such, more comprehensive methodologies are necessary to study the impact of VOCs on the ozone formation, i.e. numerical models available nowadays to simulate O3 pollution in the atmosphere from the level of box models like observation-based model (OBM), and photochemical trajectory model (PTM-MCM) to three-dimensional chemistry and transport models such as the Weather Research and Forecasting-Chemistry mode (WRF-Chem), and the U.S. Environmental Protection Agency's Community Multi-scale Air Quality (CMAQ), because one of the most important components in these AQS models is the chemical mechanisms that describe the formation of O3 from VOCs and NOx. 13) It is dangerous to use VOC/NOx ratio to judge VOC-limited or NOx-limited regimes, as stated in "General Comments".

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