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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric oxidation capacity in Chinese megacities during photochemical polluted season: radical budget and secondary pollutants formation" *by* Zhaofeng Tan et al.

Anonymous Referee #2

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This manuscript describes constrained photochemical modeling of four large urban areas in China. The paper is difficult to read due to organization, presentation and grammar. I found it difficult to understand what exactly was modeled or measured and how. The conclusion that all four cities are VOC limited is probably correct and probably worth noting for these cities. However, some of the conclusions such as the importance of some radical sources is more difficult to justify as they are not based on observations. I have included major and minor comments below. However, please note the manuscript needs significant editing for style and grammar beyond my suggestions.

I think this paper is only publishable after major revisions. 1) The title and abstract indicate that the "atmospheric oxidation capacity" is the focus of the paper. That is fine but this term should be defined instead of vaguely described as in the first line of the abstract. Once defined the values for the different cities should be reported – preferably in the abstract and in the results. I would define the AOC as the reactions of OH, ozone, NO3, etc. that lead to oxidation of an atmospheric component. I would expect units of something like the amount of oxidized molecules per time. The authors only include OH in their reporting of AOC and only vaguely report the values. This needs to be tightened up. I am sure that OH dominates but ozone and NO3 may be important at night and this should needs to be at least mentioned. 2) When I read the abstract, I thought this was going to be more of an observational study than a modeling project. I expected to see observations of OH, HO2, etc. So I recommend stating clearly that this is a photochemical modeling study constrained by observations of NOx, ozone, etc. For example, I initially thought that OH reactivity was measured in this study instead of being calculated from VOC observations. So please make it clear what is measured and how. The lack of any detail in the instrumentation section is unacceptable in my opinion. I suggest that a table be made of every parameter that is measured, including the method, and a reference. I realize standard commercial instruments perform some of the measurements such as ozone and CO. However, many of the measurements are not run of the mill. In particular, there needs to be a reference to the VOC measurement method and a list of measured compounds and detection limits listed in the supporting information. In addition, I do not know what NO2 chemical conversion to NO means as stated on line 25 of page 3. This needs to be described and the probability of interference from PAN needs to be discussed. I would expect at least 5 ppbv of PAN in areas such as Beijing during the day. This could lead so a significant interference in NO2. Please also report in more detail on the VOC observations. I think at least averages of the top 10 or 5 VOC in terms of OH loss should be listed for each city. I like the graphs in the supplement but the scales on many of the graphs don't make sense. Often the parameter graphed only

goes up to 10 or 20% of full scale making it impossible to see what is going on. I don't think keeping consistent axes between different cities is worth not being able to read the graph. 3) The reporting of OH reactivity could be made much more simple as well. Perhaps having a section in the results showing the VOC observations separately would be less confusing. You could then have a following section on the calculated OH reactivity. I really recommend limiting the discussion in these sections and focusing on the results. For example, the paragraph on line 1 page 5 stating that OH reactivity can be measured in 3 ways made me think for some time that this was a measured quantity in this work. 4) I highly recommend being more explicit on what is derived from the model or parameterized. For example, I don't think formaldehyde or acetaldehyde are measured but are model predicted. If so this needs to be described and predicted levels compared to observations if available. This will certainly impact the radical budget as well as the production rate of PAN relative to HNO3. So I suggest a table of model parameters that are predicted, constrained, and parameterized. I also suggest that the model results be presented in an organized manner in the results section. There is a lot of discussion throughout section 3 that should probably be in section 4. 5) The very simple parameterization of HONO as being 2% of NO2 is somewhat troubling. I am surprised that it would be that simple especially as a function of the time of day. I think this assumption needs to be better justified and probably looked at to determine the sensitivity, i.e. some case studies with different assumptions are probably needed. This is also another reason to describe the NO2 measurement in more detail. 6) I am not sure the ISOROPPIA modeling adds much to the paper especially as there are no measurements of ammonia or nitric acid. I certainly realize that if there is a large excess of ammonia that this will drive nitric acid into the aerosol. However, I am not sure the nitric formation rate vs. loss rate to aerosol versus dry and wet deposition can be suitably treated in this work to allow for quantitative predictions of ammonium nitrate aerosol. So I recommend removing from the paper and perhaps replacing with a simple discussion. This discussion could also mention that cutting down NOx may lead to enhanced ozone production but it will cut down on particulate nitrate as well.

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