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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observationally constrained modelling of atmospheric oxidation capacity and photochemical reactivity in Shanghai, China" *by* Jian Zhu et al.

Anonymous Referee #1

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The authors present measurements of a number of important atmospheric species, including O3, NOx, HONO, SO2, HCHO and VOCs, made in an urban environment in Shanghai during a five month period between May and September 2018. These measurements are used to constrain box model simulations, using the Master Chemical Mechanism (MCM), to study the atmospheric oxidising capacity (AOC, the sum of the rates of VOC oxidation reactions by OH, O3, and NO3), OH reactivity (the inverse of the OH lifetime), and the OH chain length (the ratio of OH recycling to OH termination). The authors focus on three short periods during the five month observation period, and determine that the main species contributing to ozone formation during these periods were formaldehyde, toluene, ethylene, and m/p-xylene, which have lower concentra-

tions than other species but have greater contributions in terms of reactivity.

While the analysis and results reported in the paper will be of general interest to the atmospheric science community, the manuscript is somewhat limited in its scope. It is not entirely clear why the three short periods out of the full measurement period have been chosen for detailed study, or whether any of these three periods are representative of typical conditions. Some further discussion regarding the choice of these three periods is necessary, particularly since the authors comment several times on measurements made over five months but focus only on six days.

Details of the model simulations could also be expanded. How are model intermediates treated? Does the model include deposition terms to avoid build-up of high concentrations of model intermediates? If so, what were the deposition lifetimes and how do they impact the modelled AOC, OH reactivity and OH chain length? It would also be useful to include some discussion of the concentrations of modelled OH, HO2 and RO2 species.

Minor comments are given below.

Page 1, line 19: 'Five months of observation' to 'Five months of observations'.

Page 1, line 21: State clearly what the 92.2 % refers to, presumably of the observation period?

Page 1, line 28: '... of the OH lifetime'.

Page 1, line 29: 'condition' to 'conditions'.

Page 1, line 31: 'the HONO photolysis' to 'HONO photolysis' and 'the O3 photolysis' to 'O3 photolysis'.

Page 1, line 32: The statement regarding the reaction with NO2 completely dominating seems over-exaggerated, there are surely some other contributions. 'radicals termination' to 'radical termination', and 'reactions of radical-radical' to 'radical-radical

reactions'.

Page 2, line 56: Hydroperoxy is preferred over hydroperoxyl.

Page 3, line 76: There are more recent measurements in London than those referenced.

Page 3, line 85: 'a emissions' to 'an emissions'.

Page 3, line 98: 'suburban' to 'suburban areas'.

Page 4, line 111: 'vehicle' to 'vehicles'.

Page 4, line 113: Please expand on what you mean by a clean environment. Clean air? Free of rubbish waste?

Page 4, line 117: Please clarify what is analyzed further? How is the initial analysis performed? Why is further analysis necessary and what does it achieve?

Page 4, line 122: 'Photolysis frequency of...' to 'The photolysis frequency of...'.

Page 5, line 135: How were deposition rates implemented in the model, if at all? What was the impact of these?

Page 5, line 137: 'last' to 'latest'.

Page 5, line 144: How reliable is the use of measured JNO2 to scale calculated JO1D? They are known to be affected differently by cloud cover.

Page 5, line 155: There are better references to provide for the definition of OH reactivity (similarly for OH chain length). The equation given could be generalised more widely instead of showing several species explicitly and 'other'.

Page 6, line 170: 'pollutants' to 'pollutant'.

Page 6, line 173: 'concentrations' to 'mean concentrations'. It would be helpful to include the standard deviation and median (and elsewhere where mean concentrations

are referred to).

Page 7, Figure 1 caption: 'of Shanghai' to 'in Shanghai'.

Page 7: Are any of the cases chosen for detailed study representative of typical behaviour?

Page 7, line 189/Figure 1: The differences in wind speed are difficult to see in the figure. 'the unfavourable diffusion condition is' to 'unfavourable diffusion conditions are'.

Page 7, line 192: 'lead' to 'leads'. 'the JNO2' to 'when the JNO2'.

Page 8, line 204: 'an average total VOCs' to 'average total VOC'.

Page 9, line 213: 'highest concentrations in alkanes' to 'highest concentration alkanes' and 'the main species in alkenes' to 'the main alkene species'.

Page 9, line 215: Define the meaning of 'maximum incremental reactivity'.

Page 10, line 220: 'due to acetylene is' to 'since acetylene is' or 'due to acetylene being'. Would it be more sensible to group as saturated aliphatic hydrocarbons and unsaturated aliphatic hydrocarbons?

Page 10, section 3.2: What was the AOC in Berlin?

Page 11, Figure 2: It would be interesting to be able to see the nighttime data as well, perhaps a log scale for the y-axis or a separate plot?

Page 11, line 251: 'lower than that of Case 2 and Case 3' should be 'lower than that of Case 1 and Case 2'? Do the calculated losses of OH include reactions of OH with model generated oxidation intermediates or are the values reported given for observed concentrations only? If model generated oxidation intermediates are included, what are the impacts of deposition rates on the calculated reactivity? On page 12 it is stated that measured species are used to calculate OH reactivity, but intermediates from the model simulations could be included. If they haven't been, why not?

Page 12, line 258: There are also measurements of OH reactivity in urban regions in London.

Page 12, Figure 3: The y scale chosen is not ideal, the plots would be clearer if a smaller scale were used.

Page 13, line 277: 'Case 1 about' to 'Case 1 was about'. The statement 'may be caused' could be strengthened – the data are there to show this either way without conjecture.

Page 13, line 284: Do the authors mean to say that OVOCs are the main contribution or the second highest contribution? The use of 'predominant' indicates they are the main contributions, but the following discussion states alkenes represent the largest contribution.

Line 13, line 290: Please quantify the statements 'similar' and 'negligible'.

Line 13, line 291: Are there any alcohol concentrations in similar locations? Do the authors expect significant contributions from these species?

Page 14, line 305: 'evaluating the HOx' to 'evaluating HOx'.

Page 14, line 310: 'within' to 'less than'?

Page 15, line 322: Why were contributions from peroxides excluded?

Page 15, line 324: 'sinks of HOx was' to 'sinks of HOx were'.

Page 15, line 331: 'generation rate of HOx was' to 'generation rates of HOx were'.

Page 15, line 332: 'loss rate was' to 'loss rates were'. Please include 'and' before the final value.

Page 15, line 336: What were the concentrations of HONO and O3? Did the HONO concentration change significantly between cases?

Page 16: It would be helpful to include some discussion of the concentrations of OH,

HO2 and RO2, and any details of the main RO2 species in the model, with comparison to measured values in similar locations. Some discussion of the nighttime chemistry would also be of interest.

Page 17, line 373: 'VOCs concentrations' to 'VOC concentrations'.

Page 18, line 386: 'VOC groups' to 'VOC group'.

Page 18, line 390: 'OVOCs shows its significant contribution' to 'OVOCs show significant contributions'.

Page 18, line 401: Is this 14.6 % of the total NMVOC concentration?

Page 20, line 430: 'increase of radicals level' to 'increase of radical levels'.

Page 20, line 433: If each radical could generate more O3, why is the O3 level lower? Data availability: It would be preferable to host the data at a secure and available site/database rather than needing to contact the corresponding author.

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