

Interactive comment on “Observations and explicit modeling of isoprene chemical processing in polluted air masses in rural areas of the Yangtze River Delta region: radical cycling and formation of ozone and formaldehyde” by Kun Zhang et al.

Anonymous Referee #1

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The manuscript "Observations and explicit modeling of isoprene chemical processing in polluted air masses in rural areas of the Yangtze River Delta region: radical cycling and formation of ozone and formaldehyde" by Zhang et al. is a modelling study of isoprene chemistry in a rural region near Shanghai, China. The main focus of the study is the role of isoprene and oxygenated VOCs in the HOx radical cycle, a subject that has been studied elsewhere but not in this particular region. As such, the results in the paper provide an interesting, if not especially surprising, insight in the atmospheric chemical processes of this part of the world. The paper certainly fits in the remit of ACP,

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but I have some serious concerns about the methodology that need to be addressed by the authors before the manuscript can be considered for publication.

MAJOR COMMENTS

I find two main issues with the analysis presented in sections 3.2 and 3.3. One is the lack of heterogeneous chemistry in the model. This is likely to impact both the levels and the budget of OH (because of the heterogeneous sources of HONO), of HO₂ (because of HO₂ uptake on aerosol), and of NO₃ (because of the equilibrium with N₂O₅). I don't think that a complete analysis of radical chemistry can just ignore these processes. If the authors think that heterogeneous chemistry is negligible under the conditions of this study (and it may well be so), they should provide some evidence or reason why that is the case.

The other important issue is the HONO/NO₂ ratio which is set here to 2%, based on the Tan et al., 2019 paper. However that study examined Chinese megacities and I would expect HONO and NO₂ levels to be different in rural areas. I appreciate that without HONO measurements it is not possible to be very accurate on this point, but since the paper shows that HONO is a major source of OH, this issue should be discussed somewhere in the manuscript. I suggest at least a sensitivity study to assess how the estimate of HONO impacts the model results and hence the conclusions of the paper. If, on the other hand, the conditions in this study and in the Tan et al., 2019, paper are similar, that would bring into question the classification of the measurement site as "rural", which would necessarily reframe the subject and the conclusions of the paper.

With regards to the analysis of ozone and formaldehyde I am confused about the model setup. On line 141 it is said that O₃, NO_x and VOCs (does it include HCHO?) are constrained in the model. However, on lines 147-151 and in Figure S1, "simulated ozone" is discussed. It is also not clear if HCHO is constrained or not. A species can be either constrained or calculated (simulated) in a model, but not both. The larger point, however, is that if O₃ and/or HCHO are constrained, then the results in sections

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3.4, 3.5, 3.6.2 and 3.6.3 need to be revised. It does not make much sense to look at the rate of production of a constrained variable because its value is set by the model and not calculated based on the values of the other variables. So the authors should first clarify whether O₃ and HCHO are constrained or calculated in the model and then amend the discussion in sections 3.4, 3.5, 3.6.2 and 3.6.3 accordingly.

MINOR COMMENTS

In Table 1, and in the related text, I believe "42i" and "43i" need to be exchanged. Also, I suggest the detection limits and/or uncertainties are added to the Table 1.

line 103: correct to "Vaisala"

line 115: I imagine you mean 15m above the 5th floor?

line 142: correct to "RH"

lines 143: correct to "nitrous acid".

line 149: please define these indices (IOA, MB, NMB).

lines 199-201: I assume you are talking about simulated NO₃ here. Please always make clear in the text, figures and captions, when you are talking about measurements and when about model results.

lines 205-207: I am not aware of RO+NO₃ reactions forming RO₂. Can you please clarify and/or correct?

line 212: correct to "ozonolysis".

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