



EGUsphere, referee comment RC1  
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## **Comment on egusphere-2022-854**

Anonymous Referee #1

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Referee comment on "OH measurements in the coastal atmosphere of South China: possible missing OH sinks in aged air masses" by Zhouxing Zou et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-854-RC1>, 2022

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The paper reports ground-based measurements of OH concentrations that were obtained in a coastal area in southern China in fall 2020. Additional measurements of trace gases (O<sub>3</sub>, NO, NO<sub>2</sub>, HONO, CO, VOCs, OVOCs) and meteorological parameters were used as input to a zero-dimensional box model to simulate the OH concentrations which are then compared to the observations. Modeled and measured OH concentrations agreed during the day when continental air arrived at the measurement site, but the model overestimates the observed OH concentrations in coastal air by a factor of 1.7. The disagreement is attributed to unmeasured atmospheric components which are supposed to be missing in the model as OH sinks. Atmospheric OH measurements are generally difficult and rare. New observations in previously understudied regions, as in this work, are therefore of potential interest. However, the paper in its current form has major shortcomings. In particular, since important quantities such as jO<sub>1</sub>D, HO<sub>2</sub>, and OH reactivity were not measured during the field campaign, few new insights can be gained from the reported OH observations that would expand our understanding of atmospheric OH chemistry. The manuscript would potentially qualify as a Measurement Report if (a) the documentation of the measurement instrument is improved, (b) the analysis of measured OH diurnal cycles is extended to include nocturnal values, and (c) the interpretation of the comparison between model and measurement is more balanced. The title of the paper would need to be adjusted accordingly.

General comments

### 1. Instrumental description

One problem is that the applied OH instrument is newly developed. The applied CIMS concept is well known in the literature, but the specific characterization, calibration and treatment of potential interferences of the present instrument is not well documented. The

authors refer to a preprint that was submitted to the journal AMT (Pu et al., Development of a chemical ionization mass spectrometry system for measurement of atmospheric OH radical, amt-2020-252), but was not accepted for final publication. Reference to that manuscript is problematic because it is not clear to the readers which of the statements made there are valid for the current work or led to a rejection. Without further explanation, the cited work is insufficient to support the quality of the measurements here. The present paper should stand on its own independently of the preprint in AMT.

The current manuscript provides sufficient references for the measurement principle of the instrument, but is lacking explanations how the specific calibration error, detection limits and overall accuracy of the new instrument were determined. Which factors contributed how much to the total accuracy of 44 %? How was the detection limit calculated and why was it larger in the field than in the laboratory? How large was the background compared to the OH signal? Were interference tests performed and what was the result? Were any corrections made for chemical interferences in the inlet as discussed by Berresheim et al. (2000)? These questions should be answered and supporting material could be presented in the Supplement. I also suggest to move Table 3 to the Supplement and give there some explanations of its contents.

## 2. Measured diurnal OH profiles

The measured diurnal OH profiles in Figure 7 show plausible variations during daytime as can be seen from the correlation with solar UV and the OH model simulation. However, the considerable nocturnal OH concentrations between  $0.5 \times 10^6 \text{ cm}^{-3}$  and  $1 \times 10^6 \text{ cm}^{-3}$  (Figure 5, 6) are an order of magnitude larger than the simulation shown in Figure 7. The unexpectedly high nighttime values are not commented or discussed. They could be due to a systematic instrumental offset or indicate real atmospheric OH at night. This needs to be discussed. For example, is there an instrumental baseline problem that cannot be eliminated by the chemical modulation in the CIMS inlet? Mauldin et al. (2012) reported a non-OH source of sulfuric acid in a Boreal forest (probably not applicable here) and Berresheim et al. (2014) found evidence for an unknown oxidant in coastal air that converts SO<sub>2</sub> to sulfuric acid in their CIMS inlet. Could these unknown oxidants play a role in the measurements reported here? What would happen if the unknown oxidant chemistry in the instrument inlet would be influenced by the OH scavenger? Have you tried a different scavenger other than C3F6? If there is a problem with the baseline, it could potentially affect the daytime OH measurements as well. If the nocturnal OH levels observed by CIMS indicated true OH levels, this would be of considerable atmospheric relevance. How do the values compare to previous observations of nighttime OH in PRD (Lu et al., *Atmos. Chem. Phys.*, 14, 4979–4999, 2014 ; Tan et al., 2019)?

## 3. Comparison of modeled and observed OH concentrations

The authors report agreement of the modeled and measured OH in continentally influenced air and find that the model overestimates the observed OH in coastal air. What can be learned from this result? Unfortunately, measurements of HO<sub>2</sub> concentrations and OH reactivity were not performed in this campaign. Measurements of these quantities

have become standard in most field campaigns over the past decade and are absolutely essential if new insights into atmospheric OH chemistry are to be gained. For example, field studies have shown that the agreement between modeled and measured OH can be misleadingly good. Kanaya et al. (*Atmos. Chem. Phys.*, 12, 2567–2585, 2012) and Whalley et al. (2018) reported missing OH production in their MCM models that was coincidentally compensated for by the model's overprediction of HO<sub>2</sub>, resulting in good agreement between modeled and observed OH concentrations. These model deficiencies were only detected because HO<sub>2</sub> and OH reactivity measurements were available as additional constraints. These two parameters are of paramount importance for the understanding of OH since they dominate the chemical OH budget in most cases. For the same reasons, it is not clear if missing OH reactivity is the major reason for the overestimated modeled OH in coastal air. Without knowing how well the model reproduces HO<sub>2</sub>, it is difficult to quantify the amount of missing OH reactivity. The authors assume that unknown atmospheric trace gases react with OH and form products that do not undergo further reactions (page 13, line 23-24). The assumption that the products are inert is not very likely. Missing OH reactivity is most probably caused by unmeasured VOCs or OVOCs, which produce RO<sub>2</sub> and HO<sub>2</sub> when they react with OH. The additional peroxy radicals recycle some OH and thereby increase its total production rate (called P\_constrain in Eq 9). It means that the required amount of missing OH reactivity is probably higher than the authors' estimate that is based on a fixed OH production rate. Here, additional HO<sub>2</sub> measurements are missing to determine the total OH production independent of model assumptions.

#### 4. Quantification of VOCs

The total amount of VOCs is expressed in many places in the paper as the sum of the VOC mixing ratios (ppb). While the total mixing ratio is a useful quantity to indicate the amount of measured organic carbon, it tells us little about its relevance for the OH chemistry. Since the rate constants for different VOC species may differ by orders of magnitude, it is better to report the total organic OH reactivities of the measured VOCs and their subgroups (AVOC, BVOC, etc.) to characterize the chemical conditions.

#### 5. Ozone photolysis frequency

The photolysis of ozone forming O(1D) is one of the major processes that produce HO<sub>x</sub>. The corresponding *j*-value is calculated in the present work by using a clear-sky parametrization from Saunders et al. (2003). The values are then scaled with the ratio of modeled-to-measured *j*NO<sub>2</sub> (to correct for cloud effects?). The whole approach has a considerable error that is not discussed in the paper. *j*O(1D) depends on the total atmospheric ozone column and air temperature, which are both not considered in the parametrization. The parametrization is useful for pure modeling studies, but not a good choice for the description of real ozone photolysis frequencies in a field campaign. Ideally, *j*O(1D) is measured as is done by many groups. The next best approach would be to simulate the clear-sky values by a radiative transfer model (for example by the freely available Tropospheric Ultraviolet and Visible (TUV) Radiation Model from NCAR) taking total ozone and temperature into account. Also note that *j*O(1D) responds differently to cloudiness compared to *j*NO<sub>2</sub> (see for example, Walker et al., *Environ. Sci.: Atmos.*, DOI: 10.1039/d2ea00072e). The authors should attempt to estimate a more realistic *j*O(1D) by

means of the TUV or a similar radiative transfer model.

## 6. Literature review

In the introduction of the paper, the authors present Table 1 for an overview of previously published comparisons between modeled and measured atmospheric OH. The table takes up a large part of the paper, but is not very informative due to the lack of its discussion. In order to judge the listed comparison results, detailed explanations would be needed on how the past measurement techniques and chemical models have improved over the last 2-3 decades. To keep the paper focussed, I suggest to remove Table 1 and Figure 1. It is sufficient to refer to corresponding review articles (e.g., Heard and Pilling, *Chem. Rev.* 2003, 103, 5163-5198; Stone et al., 2012; Rohrer et al., 2014; Lu et al., *National Science Review* 6: 579-594, 2019).

### Specific comments

- Abstract and Introduction. OH reactivity and missing OH reactivity need to be defined.
- Page 2 – line 4. The hydroxyl radical (OH) dominates ...
- Page 2 – line 9. The sentence can be deleted since heterogeneous losses of OH on particles are generally excluded from atmospheric models. If you want to keep the sentence, you may explain that OH is too short-lived to experience significant loss by collisions with particles.
- Page 2 – line 22. The paper by Hard et al. 1979 is not a good choice to inform interested readers about LIF techniques that have been used internationally in the last three decades. Hard et al. were pioneers of the FAGE concept, but the laser spectroscopy described in their 1979 paper used 282 nm excitation that was significantly affected by self-generation of OH and abandoned later (see overview by Crosley, *J. Atmos. Sci.* 1995, Vol 52 No 19, 3299). More recent descriptions can be found, for example, in Heard and Pilling, *Chem. Rev.* 2003, 103, 5163-5198 and Schlosser et al., *Atmos. Chem. Phys.*, 9, 7923-7948, 2009.
- Page 3 – line 5-6. OH underprediction is not restricted to biogenic environments, but was also observed in urban atmospheres when NO was below 1 ppb. See, for example, Whalley et al., 2018 and Tan et al., 2017, 2019.
- Page 3 – line 12. The results in the Zhang et al. (2006) paper are outdated because the OH data used had a significant calibration error that was later corrected. The revised TRACE-P data show good agreement with model results (Ren et al., *Journal Geophysical Research*, Vol. 113, D05310, doi:10.1029/2007JD009166, 2008).
- Page 3 – line 8-23. Specify the locations or type of environments for which OH was overestimated by models.
- Page 3 – line 16-19. It should be mentioned that numerous studies in all types of environments (marine, rural, forest, urban) have demonstrated missing OH reactivity by direct measurements of OH reactivity that was compared to the reactivity calculated from measured VOCs. Overviews can be found, for example, in Lou et al. *Atmos. Chem. Phys.*, 10, 11243-11260, 2010, and Yang et al., *Atmospheric Environment* 134 (2016) 147-161.
- Page 3 – line 19-23. Which measurement techniques are discussed here?
- Page 7, line 12. The value for the absorption cross section of H<sub>2</sub>O for the Hg 184.9 nm

line given by Cantrell et al. is  $7.14 \times 10^{-20}$  cm (not  $7.22 \times 10^{-20}$  cm<sup>2</sup>).

- Page 8 – line 4-6. The measurement site was located at a coast, where halogen chemistry could play a role for OH. Since it is not mentioned, I assume that halogen chemistry was not included in the model? How much could your model results be affected by BrO or IO if you assume mixing ratios as reported in literature (e.g., Fan et al., *Atmos. Chem. Phys.*, 22, 7331–7351, 2022).
- Page 8 – line 7. Which HOx recycling mechanisms do you mean?
- Page 9 – line 4. Molecular weight must be molecular mass.
- Page 9 – line 8-10. I do not understand how the authors constrained their model with NO and NO<sub>2</sub>. Did you use measured values or concentrations that were calculated from a PSS assumption? As NO and NO<sub>2</sub> have a strong influence on OH, the handling of the NO<sub>x</sub> data should be explained in detail. Figure S1 needs to be explained and its relevance should be discussed.
- Page 9 – line 11-12. How sensitive are the modeled OH concentrations to the assumed VOC concentrations?
- Page 9 – line 17-19. In Table 4, the OH production and destruction is calculated from concentrations of species that were not measured (e.g., H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>). How were the concentrations of these species determined? Did the model consider deposition of products that are build up in the model over three days? Was the three day spin-up simulated with constant photolysis frequencies and constant deposition?
- Page 10 – line 1-2. In the literature, it is more custom to look at the correlation between jO<sub>1</sub>D and OH (e.g., Ehhalt and Rohrer, *J. Geophys. Res.* 105, No. 03, 3565-3571, 2000; Rohrer and Berresheim, 2006; Ma et al., 2019; Tan et al., 2017). How comparable is your correlation for jO<sub>1</sub>D?
- Page 10 – line 29. What is a continental air mass cluster?
- Page 11 – line 11-26. It would be of interest to see also plots of the model results for HO<sub>2</sub> the OH reactivity, which both have a large influence on OH. How does the simulated OH reactivity compare to the reactivity that can be calculated from measurements (CO, NO<sub>x</sub>, VOCs, OVOCs)? How does the modeled HO<sub>2</sub> concentration compare to observations in PRD (e.g., Tan et al., 2019)?
- Page 12 – line 3-4. The meaning of 'p < 0.05' needs to be explained.
- Page 12 – line 24. Table 4 does not fit here. Do you mean Table S1?
- Page 18 – line 28. Check the author list.
- Figure 1: I suggest to remove this figure and Table 1 as explained above.
- Figure 4. Use different colors to make it easier to distinguish the NO and NO<sub>2</sub> data. It is difficult to see any temporal structure in the shown NO<sub>2</sub> photolysis frequencies. I suggest to draw jNO<sub>2</sub> as a solid line. CO, HCHO, jO<sub>1</sub>D and the total reactivity of VOCs and OVOCs should be shown since they have an important influence on OH. What is the reason for the gaps in the OH time series? The OH concentrations are determined from the difference of two noisy signals (Eq. E1). Near the limit of detection, the difference can become occasionally negative. Were any negative OH data calculated that are not shown in the figure?
- Figure 5. As mentioned before, it would be good to see jO<sub>1</sub>D and the total OH reactivities of VOCs and OVOCs. How large were the NO nighttime values?
- Figure 7 + 8. Explain the shown error bars of measured OH. Do they denote precision (signal noise) or errors of calibration? Here and in other figures: which time zone is used for the x-axis? It would be more informative to see the OH reactivity of AVOC, BVOC, OVOC plotted rather than the total sum of mixing ratios.
- Table 2. Some of the measured trace gases that are used as model input (Table S1) are missing and should also be listed (e.g., CO, SO<sub>2</sub>, NH<sub>3</sub>). For which signal-to-noise ratio is the detection limit defined? The table should also specify the accuracies of the measurements.
- Table 3. The table needs explanations. The listed quantities (e.g., sample flow [SO<sub>2</sub>], elimination rate, switching time, reaction time etc.) should be explained and defined. What is the purpose of sample flow [NO]? What is the purpose of C<sub>3</sub>F<sub>6</sub> in the sheath flow? What are the main gas components in the SO<sub>2</sub> and NO mixtures? Specify the

purity of the main components in the gas mixtures and of the other used gases (N<sub>2</sub>, zero air, HNO<sub>3</sub>). Who is the supplier of the gases? Define 'sccm'. Is the OH accuracy (44 %) given for 1 or 2 sigma? Why is the value larger than in the text (38 %)?

- Table 4. O1D should read O1D+H<sub>2</sub>O. Which reaction is meant by CH<sub>3</sub>CCH<sub>3</sub>O<sub>2</sub>B and CH<sub>3</sub>CCH<sub>3</sub>O<sub>2</sub>C? A large fraction of 36-40 % of the OH loss is attributed to 'Other' species. Which species are lumped in 'Other'?
- Figure S3 + S4. Remove the labels 'good matched' and 'overestimated'. Which species are included in 'Other'? The OH reactivity shown in Figure S4 is better called simulated reactivity or modeled reactivity. Then it is clear that the reactivity includes the contributions of measured and modeled species as well.
- Table S1 is difficult to understand. What are the units of the concentration measurements? All symbols and abbreviations (e.g., OH\_DL, PM\_SUR) need to be defined. Unusual names for organic compounds, e.g. IC<sub>4</sub>H<sub>10</sub>, EBENZ, TEXs\_PTR, C<sub>5</sub>H<sub>8</sub>deri, should be replaced by their chemical names. Indicate for each organic species which technique (GC or PTRMS) was used for its measurement. Indicate which of the listed parameters/species were actually used as model input.