

Reply to RC2: 'Comment on acp-2022-556'

This paper aims to improve “bottom-up” estimates of OH concentrations by constraining chemical model simulations with observations of OH precursors. The paper is thorough, novel, well-written, and tackles a very important issue in atmospheric chemistry. I recommend it for publication in ACP, subject to some relatively minor corrections.

Response: We thank the reviewer for his/her helpful comments. All of them have been addressed in the revised manuscript. Please see our itemized responses below.

General comments

A simplified 0D model of atmospheric chemistry is used, gridcell-by-gridcell to determine the how the OH fields from a global 3D photochemical model would be adjusted by incorporating observations on OH precursors. One thing I felt was missing from the paper was a comparison of the OH fields predicted by the simplified model to that of the “parent” 3D model (i.e., how does $[OH]_{DSMACC_ref_model}$ compare to $[OH]_{model}$, using the terms from eq. 1?). It seems that this is important because large differences could lead to non-linear effects that could influence the results. Perhaps some simple comparisons could be presented in the Supplement.

Response: We agree and compare the $[OH]_{DSMACC_Ref_model}$ and $[OH]_{model}$ in the updated version of the text (L278-286): “The Ref_model experiments can well reproduce the spatial distribution of $[OH]_{trop-M}$ simulated by 3D models (Fig. S4), which indicate that the chemical box model DSMACC can generally capture the response of $[OH]$ to the changes in OH precursor concentrations and meteorological conditions. However, the Ref_model experiments overestimate the $[OH]_{trop-M}$ by 7% and 36% when compared with the global $[OH]_{trop-M}$ simulated by CESM1 CAM4-chem and GEOSCCM, respectively. Thus, the observation-based $[OH]$ ($[OH]_{obs}$) in each 3D model pixel for two different chemical mechanisms is estimated by correcting $[OH]$ as simulated by the corresponding 3D models ($[OH]_{model}$) by the ratio between $[OH]$ simulated by DSMACC experiments for the All_obs ($[OH]_{DSMACC_all_obs}$) and for the Ref_model ($[OH]_{DSMACC_Ref_model}$) case”

We include Figure S4 in the supplement:

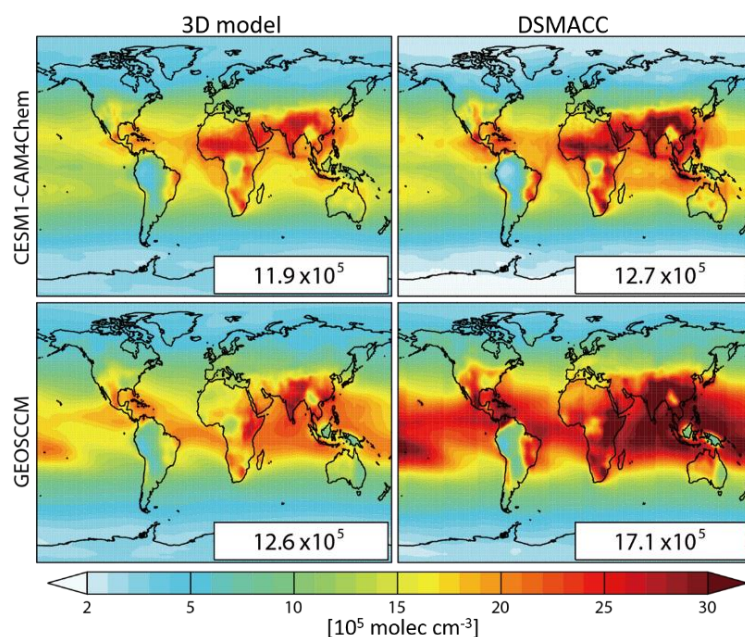


Figure S4. Spatial distributions of air mass-weighted tropospheric mean $[\text{OH}]$ ($[\text{OH}]_{\text{trop-M}}$) in 2010 from 3D model simulations (left) and chemical box model (DSMACC) simulations driven by the corresponding 3D model outputs (right). The global mean values are shown inset in molec cm^{-3} .

Specific comments

Comment 1: On first reading, I was confused by the definition of the term: “ $[\text{OH}]_{\text{trop-M}}$ ”. When it is first introduced, both on line 44 and line 273, it is defined as a global value. E.g. “global tropospheric mean OH concentration” on line 44. However, it is later used to show regional distributions. I think that the authors are using $[\text{OH}]_{\text{trop-M}}$ to mean something like “column average airmass-weighted $[\text{OH}]$ ”, which is then sometimes averaged to produce a “global mean $[\text{OH}]_{\text{trop-M}}$ ”? I think the terminology needs to be tightened up a little here.

Response: We change “global tropospheric mean OH concentration” to “The global mean tropospheric column-averaged airmass-weighted $[\text{OH}]$ ($[\text{OH}]_{\text{trop-M}}$)” as suggested.

Comment 2: L83: “Such MCF-based top-down methods have...” rather than “method has”.

Response: We change “method has” to “methods have” as suggested.

Comment 3: L105 – 107: I don’t think these papers show that decreased $[\text{OH}]$ can explain the resumed CH_4 increase. Both have a high degree of uncertainty (such that no OH change is within the plausible range), and Rigby et al., 2017 has a coincident CH_4 emissions increase in their maximum-likelihood estimate. I would perhaps keep it more general and say that these papers indicate that MCF-based top-down methods indicate that $[\text{OH}]$ changes may have influenced recent CH_4 trends, although with a

high degree of uncertainty.

Response: We change “conclude that decreased [OH] and therefore CH₄ chemical loss after the mid-2000s can explain the resumed CH₄ increase since 2006” to “indicate that the [OH] changes may have influenced recent CH₄ trends, although with large uncertainties” as suggested.

Comment 4: L109: I don’t think the models show a monotonic increase in [OH], do they? i.e, does the use of “continuous increase” need to be softened to “decadal trend” or similar?

Response: We change “continuous increase” to “positive decadal trend” as suggested.

L111 – 125: It seems that the Nicely et al. (2017; 2018) papers would fit into the discussion here too?

Response: We add in the text:

(L120-122) “Nicely et al. (2017; 2020) found that the inter-model difference in tropospheric [OH] is mainly driven by the difference in model simulated ultraviolet light flux to the troposphere, the tropospheric O₃, CO, and NO_x mixing ratio.”

(L236-239) “Nicely et al. (2018) have estimated the response of [OH] to changes in OH precursors by conducting DSMACC model simulations for broad latitude and pressure bins. The results show that the H₂O_(g), NO_x, total column O₃, and tropical expansion can lead to a positive trend in tropospheric [OH], offsetting most of the negative trend led by the rising CH₄ concentrations from 1980 to 2015.”

We add reference:

“Nicely, J. M., Salawitch, R. J., Canty, T., Anderson, D. C., Arnold, S. R., Chipperfield, M. P., Emmons, L. K., Flemming, J., Huijnen, V., Kinnison, D. E., Lamarque, J.-F., Mao, J., Monks, S. A., Steenrod, S. D., Tilmes, S., and Turquety, S.: Quantifying the causes of differences in tropospheric OH within global models, *Journal of Geophysical Research: Atmospheres*, 122, 1983-2007, 10.1002/2016jd026239, 2017.”

“Nicely, J. M., Canty, T. P., Manyin, M., Oman, L. D., Salawitch, R. J., Steenrod, S. D., Strahan, S. E., and Strode, S. A.: Changes in Global Tropospheric OH Expected as a Result of Climate Change Over the Last Several Decades, *Journal of Geophysical Research: Atmospheres*, 123, 10,774-710,795, doi:10.1029/2018JD028388, 2018.”

“Nicely, J. M., Duncan, B. N., Hanisco, T. F., Wolfe, G. M., Salawitch, R. J., Deushi, M., Haslerud, A. S., Jöckel, P., Josse, B., Kinnison, D. E., Klekociuk, A., Manyin, M. E., Marécal, V., Morgenstern, O., Murray, L. T., Myhre, G., Oman, L. D., Pitari, G., Pozzer, A., Quaglia, I., Revell, L. E., Rozanov, E., Stenke, A., Stone, K., Strahan,

S., Tilmes, S., Tost, H., Westervelt, D. M., and Zeng, G.: A machine learning examination of hydroxyl radical differences among model simulations for CCMI-1, Atmos. Chem. Phys., 20, 1341-1361, 10.5194/acp-20-1341-2020, 2020.”

Comment 5: L221: “... DSMCC is/was run forward” (insert is or was)

Response: We add “is” as suggested

Comment 6: L223: “DAMSCC” should be changed to “DSMACC”

L235: “observation-based”, rather than “observational-based”

Response: We changed these typos as suggested.

Comment 7: L239: I suggest “... [OH] simulated by DSMACC experiments for the All_obs ($[OH]_{DSMACC_all_obs}$) and for the Ref_model ($[OH]_{DSMACC_Ref_model}$) case” (add “case”, or “simulation”, or similar).

Response: We add “case” as suggested.

L282 (and 315, 316 and 325): To improve readability, and given that it is only mentioned a couple of times, I suggest just referring to Spivakovsky et al. each time, rather than defining another term (S2000).

Response: We change “the S2000 OH field” to “the OH field estimated by Spivakovsky et al. (2000) as suggested”.

Comment 8: L300: should this be $[OH]_{Trop-M}$, rather than [OH]?

Response: Yes, we change “[OH]” to “[OH]_{trop-M}”.

L307: “which is larger than that over ...” (remove “the”)

Response: we remove “the” in the text.

Comment 9: L375: “over the 15 – 60N region” (insert “region” or similar)

Response: we add “region” as suggested.

Comment 10: L384: “... by 0.07, but still cannot explain...” (insert “but”)

Response: We add “but” as suggested.

Comment 11: L395: “NO2 results in a positive bias” (insert “a”)

Response: We add “a” as suggested.

Comment 12: L404: Remove “The” from the start of the second sentence, or add “model” after “CESM1 CAM4-chem”

Response: We change “CESM1 CAM4-chem” to “CESM1 CAM4-chem simulation” as suggested.

Comment 13: L481: “... loss of CH4 in the previous GCP...” (add “the”)

L522: “... respectively, dominating the bias” (dominating, rather than

“dominant”)

Response: Changed as suggested.

Comment 14: Section 4 (Conclusions): This section could be made more concise and readable. I suggest thinking about the paragraph structure so that ideas are grouped together more concisely and start each paragraph with a sentence describing the main point of the paragraph (at present lots of paragraphs start with phrases like “In addition”, or “Also”, which don’t help to orientate the reader).

Response: we summarize the uncertainties led by model chemical mechanisms and the one led by the availability of the observation data and model outputs (L632-692):

“Although the observation-based 3D OH fields presented in this study can capture the global tropospheric OH burden and chemical loss of CH₄, unresolved uncertainties and limitations remain:

(1) The method presented in this study cannot improve the chemical mechanisms in the models and does not fully explain the overestimation of the N/S ratios of [OH].

The differences in global [OH]_{trop-M} between the two observation-based OH fields estimated from CESM1 CAM4-chem and GEOSCCM simulations is 0.6×10^5 molec cm⁻³. Besides precursor concentrations, the inter-model difference in tropospheric [OH] is partly attributable to their differences in chemical mechanisms (Nicely et al., 2018; 2020). As discussed in Murray et al. (2021), the oxidative efficiency of NMVOCs and lifetime of NO_x simulated by different models can largely determine inter-model differences in tropospheric [OH] and their responses to changes in precursors. Reducing the uncertainties due to the modeled chemical mechanisms relies on additional observations to improve the simulation of NMVOCs oxidative efficiency and NO_x lifetime, which is beyond the scope of our study.

The N/S ratio of [OH]_{trop-M} after observation-based adjustment is still higher than the one obtained from MCF-inversions (less than 1.0). This difference indicates that the overestimation of the N/S ratio by atmospheric models cannot be fully explained by the underestimation of CO and overestimation of O₃ over the Northern Hemisphere as mentioned in previous studies (Naik et al. 2013). The overestimation of the N/S ratio may also attributable to chemical mechanisms included in the atmospheric chemistry models. Both CESM1-CAM4chem and GEOSCCM do not include the OH recycling by isoprene and simulate low OH values in regions with high NMVOC emissions, such as rain forests in the Southern Hemisphere (Zhao et al., 2019). Including the chemical mechanism such as OH recycling by isoprene (Lelieveld et al. 2008) would help further reduce the N/S ratio for model-simulated OH fields.

(2) The constraints brought on tropospheric [OH] are limited by observations quality and time resolution of available model outputs.

Data constraining the OH precursors come mainly from satellite observations and reanalysis data, of which the uncertainties are not considered in this study. For example, the MERRA-2 reanalysis data significantly overestimate $\text{H}_2\text{O}_{(\text{g})}$ in the upper troposphere (Jiang et al., 2015); The QA4ECV tropospheric NO_2 vertical column density is lower compared with surface observations under the extremely high-pollution case compared with surface observations (Compernelle et al., 2020). The performance of this method depends on the accuracy of observations used to constrain individual factors. Data products regularly improve and, since the sensitivity of [OH] to each precursor is estimated by the chemical box model, we can easily improve the [OH] using the updated observational datasets.

OMI measures concentrations of chemical species around local time 13:30, but most of the CCMI models only provide monthly means for 3D distribution of chemical concentrations. The monthly mean NO_2 and O_3 concentrations simulated by 3D models are therefore constrained only by such afternoon observations. For O_3 , of which the tropospheric mean lifetime is 23.4 ± 2.2 days (Young et al., 2013),

we assume that not considering diurnal variations has only a small influence. This is not the case for NO_2 with a much shorter lifetime (~ 1 day, Jaffe et al., 2003). By comparing the tropospheric NO_2 VCDs observed by SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric Chartography; overpass time around local time 10:00) with OMI, previous studies show that the tropospheric NO_2 VCDs have significant diurnal variations (Boersma et al., 2008; 2009). Diurnal variations of NO_2 VCDs are controlled by complex factors including local emissions, photochemistry, deposition, advection, etc., and vary among different seasons over different regions (Boersma et al., 2008; 2009). Considering the diurnal cycle of NO_2 photolysis, tropospheric NO_2 VCDs over remote regions should be lower during daytime than nighttime (Cheng et al., 2019). Constraining the model simulated monthly mean NO_2 VCDs with satellite data at the overpass time leads to an overestimation of the high bias of modeled tropospheric NO_2 VCDs. Thus, the 0.3×10^5 molec cm^{-3} estimated in this study gives an upper limit of the high bias in global $[\text{OH}]_{\text{trop-M}}$ due to boundary layer NO_2 .

Since we only have the tropospheric NO_2 VCDs, another key factor that could influence the tropospheric OH burden but is unconstrained in this study is NO_2 in the free troposphere. Although the NO_2 mixing ratio is usually less than 1 ppbv in the free troposphere, the sensitivity of [OH] to NO_2 can be very high in low NO_2 regions. However, a potential model bias due to lightning NO_x emissions, which had proven to contribute significantly to the upper-tropospheric [OH] burden (Murray et al., 2013; Turner et al., 2018), is not adjusted in our study. Satellite retrievals for upper tropospheric NO_2 (e.g. Belmonte Rivas et al., 2015; Marais et al., 2021) could help quantify [OH] biases due to free tropospheric NO_2 and the

contribution of lightning NO_x emissions. ”

Comment 15: L526: add “major” before “global CH_4 sink”, to make it clear that you’re referring to one of the methane sinks (i.e., you’re not also investigating Cl, etc.)

L586: “Such a difference is partly attributable to...” (remove “be”)

L593: Remove “In addition”

L627: Remove “Also”

Response: Changed as suggested.

Comment 16: Figure 5: Consider making this a 2-panel plot (well, really a 6-panel plot) merged with Figure 2.

Response: We merged Fig.5 with Fig.2 as suggested:

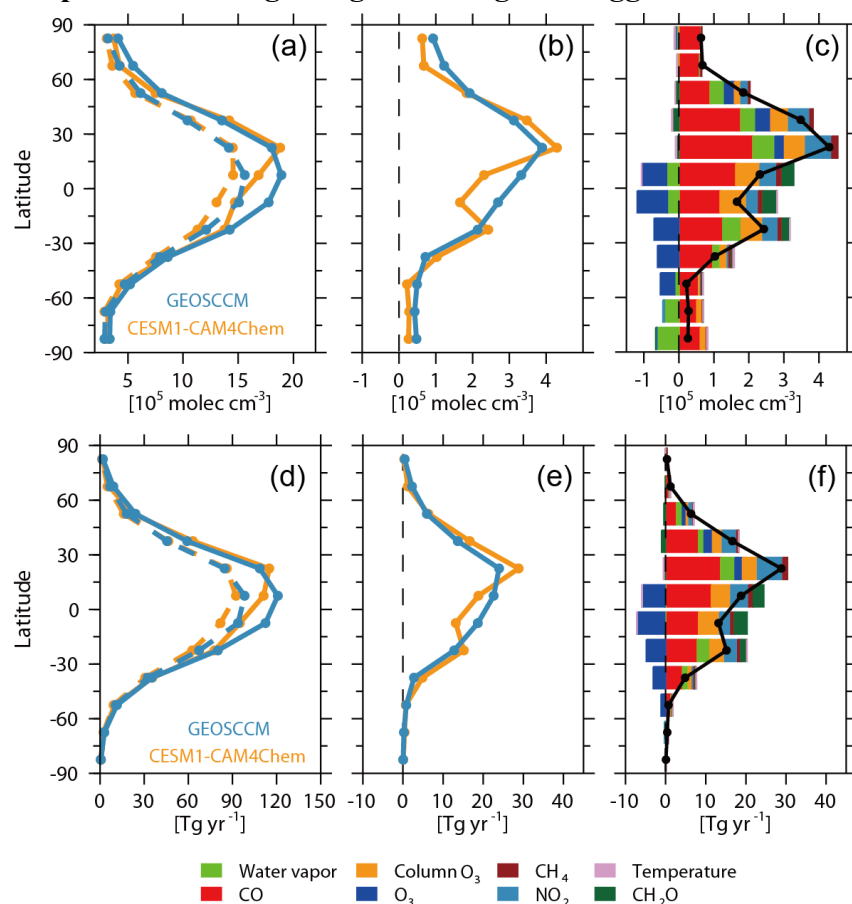


Figure 2. (a) Zonal averaged $[\text{OH}]_{\text{trop-M}}$ of modeled (solid lines) and observation-based OH field (dashes lines) estimated from CESM1 CAM4-chem (yellow) and GEOSCCM (blue) simulations. (b) Difference of zonal averaged $[\text{OH}]_{\text{trop-M}}$ between modeled and observation-based OH fields. (c) Difference between CESM1 CAM4-chem simulated and observational-based zonal averaged $[\text{OH}]_{\text{trop-M}}$ (black line) and the contribution from each OH precursor (colored bars) for zonal averaged difference. (d-f) Same as (a-c) but for the tropospheric CH_4 sink by reaction with OH.