

Review of : Sensitivity of tropospheric ozone to halogen chemistry in the chemistry-climate model LMDZ-INCA vNMHC by Caram et al., 2022.

This is a resubmission of the original manuscript that was assessed by two previous independent referees. There was a general agreement between referees that the heterogeneous component of the model is lacking some key reactions, which are important for recycling and release/re-cycling of halogen species back into the gas-phase of the troposphere allowing photo-chemical destruction of e.g. Ozone (O_3) and methane (CH_4). Thus the accurate simulation of the mixing ratios of Cl, Br and I radicals is a prerequisite towards capturing the effects well with respect to climate impacts. Both of the previous referees suggested a major revision in order to achieve the quality necessary for publication in GMD. Looking at the modifications made to the manuscript I am not sure that issues have been fully addressed from the previous versions. There is the danger of formulating a scheme which doesn't simulate enough halogen radicals which, when applied in e.g. a chemical ensemble to predict CH_4 lifetimes, would increase uncertainty in the resulting projections due to the lack of key processes. The authors even admit that the simulated Chlorine component is not optimal, although both Bromine and Iodine have higher chemical destruction fluxes against the main tropospheric reactants therefore the under-estimate in total oxidative capacity is likely low. The evaluation of the scheme against observations is very weak and, this being a GMD development paper, needs addressing before publication to meet the requirements of the journal.

Major comments:

(i) Climate and oxidative capacity is moderated by photolysing light, which itself is attenuated by scattering processes involving clouds and aerosols. A large fraction of CH_4 is oxidised in the tropical region, which exhibits lower O_3 mixing ratios in the lower atmosphere than the more polluted Northern mid-latitudes meaning that the destruction via halogen radicals becomes most important. Sulphate production in clouds is enhanced by the oxidation in droplets via $HOCl(aq)$ and $HOBr(aq)$, but this process is missing from the update whereas there is a direct link to process important for determining future RF (with the S component in more remote regions being biogenic in origin via DMS oxidation). With low H_2O_2 in more remote locations, the halogen-sulphate production route could determine AOD over the oceans. Can the authors comment on why this omission was made considering the proposed application of LMDZ-INCA towards chemistry-climate studies.

(ii) The main acid catalysed routes are missing from the aqueous phase chemical scheme applied in the model, as acknowledged by the authors, but should be accounted for in some way. If the authors do not wish to implement a complex heterogeneous scheme they should apply a first-order generation rate to account for release of precursors e.g. $\rightarrow Cl_2(g)$ in s^{-1} (based on available cloud and/or aerosol SAD as a meteorological parameter for parametrizing the extent of activation). This could also be done for $BrCl(g)$ release. This could then act as a guide (and reference) for a scheme applicable in other chemistry-climate models rather than a more simplistic version of a CTM scheme. The influence of applying such an assumption should be

shown by comparing two simulations with respect to the tropospheric Cl burden, with and without such reactions active.

(iii) Section 3 : Both the total burdens in Sherwen et al. (2015) and Wang et al. (2021) should be put into the text and tables to show the underestimation in tropospheric Cl burden due to the omission of the heterogeneous chemistry discussed above. This avoids undermining the main conclusion in Wang et al., (2021) in that a complex description of heterogeneous chemistry is necessary for an accurate tropospheric Cl burden. A much more important inclusion would be values from a new run using the assumed release rates of halogen precursors.

(iv) Figure 2 shows the latitudinal and zonal mean impact on tropospheric O₃. There is no proof this moves the model towards a better description of the distribution of O₃ in the global troposphere. There are O₃ profile measurements readily available e.g. at the south pole which could be used to validate the substantial percentage reductions in O₃ burden for these latitudes. Currently the reader has no idea as to whether the inclusion of halogen chemistry is needed in this version of LMDZ (which would increase resources needed in any long-term run) or what the potential biases with and without are meaning confidence in the model capturing the correct global O₃ distribution is low. I find this not acceptable for a GMD paper, which doesn't need new scientific findings but rather some evaluation of the update to show the model performs well.

Minor comments

(i) When multiple references are used they should always be given in a chronological order throughout the text e.g. In 28.

(ii) Most of the reaction rates originate from the standard recommendations apart from some exceptions. For instance, Cl + C₂H₄ has a IUPAC recommendation but a single study value (which may not be the optimal choice) is applied. Why not use a full set of rate data from the recommendations? The IUPAC reaction for Cl + C₂H₄ is defined as a third-body reaction, whereas the rate applied here is second-order only. Although the impact of global modelling of O₃ will be small, a correct description of rate data should be applied.

(iii) There are no references for the assumed uptake parameters given in Table 5, even though many of these parameters have been measured and are available in the recommendations. This introduces a discontinuity in the basis upon which the gas-phase and aerosol-phase chemistry is sourced. The uptake values for various species currently applied are identical for both sea-salt and sulphate aerosol which doesn't seem to be correct. Sea-salt is typically 'wet' considering the Relative Humidity over oceans, with IUPAC providing e.g. an uptake value of 0.6 for HOBr higher than that used here, whereas for 60%wt H₂SO₄ it reduces to 0.06. Similar differences can be found for other halogen species. This will alter the global chemical budget terms provided.