

Geosci. Model Dev. Discuss., referee comment RC1
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Comment on gmd-2021-388

Anonymous Referee #1

Referee comment on "Sensitivity of tropospheric ozone to halogen chemistry in the chemistry-climate model LMDZ-INCA vNMHC" by Cyril Caram et al., Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2021-388-RC1>, 2022

In this manuscript, Caram and colleagues present the reactive halogen chemistry in the chemistry-climate model LMDZ-INCA, focusing on the sensitivity of tropospheric ozone. This work emphasizes a long-standing issue in the climate community that the impacts of halogen chemistry on key short-lived climate forcers (such as ozone and methane) have not been fully accounted for in most climate models.

The method section of this manuscript lacks key details of the model (LMDZ-INCA) that are relevant for the scientific goal of this work. For example, acid displacement is a major source of reactive chlorine in the atmosphere. To properly model acid displacement, several key processes need to be properly implemented in the model, such as the emissions, dry/wet depositions, and transport of sea salt, as well as its physical and chemical properties (especially acidity), not to mention the acidic gas(es) to displace HCl (e.g., nitric acid). It remains unclear how these processes are implemented in this model LMDZ-INCA. It does appear that the model uses highly simplified HCl emissions to account for this process, yet no details are given (i.e., spatial/temporal variability of such emissions). Similarly, debromination is a major source of reactive bromine in the troposphere. Yet, how this process is implemented in LMDZ-INCA is unclear. Fig 3 looks like the model only recycles HBr produced from other reactive bromine species (not a net bromine source); if this is indeed the case, essentially the only source of the reactive bromine is the organobromines. Key details like these should be clearly stated.

This work does take other more established models as benchmarks, especially GEOS-Chem and CAM-Chem. The halogen chemistry implemented in this model (LMDZ-INCA) appears to be much simpler than GEOS-Chem or CAM-Chem. The measurement-model (LMDZ-INCA) comparison is not adequately transparent and contains almost no specifics. A few major issues: the measurements and observations are not presented in consistent manners; the comparisons completely ignore the spatial and temporal variabilities revealed in the observational datasets. The level of detail presented in these comparisons does not adequately justify the performance of this model. Please see the next section for details. It is my opinion that this manuscript is not well written either, with numerous vague/confusing statements, which I will elaborate later. In light of these, it is unclear in

the current manuscript what new scientific insights this study offers, compared to other models such as GEOS-Chem and CAM-Chem, which are more comprehensive and have been rigorously evaluated against a wide variety of observations.

The way that the pre-industrial simulations are configured is based on key assumptions that are unverified/unjustified. For instance, this study essentially assumes several key processes of the Earth system (e.g., lightning, biomass burning, biogeochemistry in the ocean) remain the same between the pre-industrial period and the present-day. I am not fully convinced. One specific example is again acid displacement largely driven by HNO₃, which, may be different between pre-industrial periods and present-day. These key assumptions need to be justified.

Therefore, I do not recommend this manuscript for publication in Geosci. Model Dev. Please find my specific and technical comments below:

Line 26: Indeed the earliest study of the reactive halogen chemistry in the troposphere was perhaps a decade later than that for the stratospheric halogen chemistry, but since then there have been quite a few large-scale, comprehensive field experiments focusing on the tropospheric halogen chemistry. Therefore I do not think "...halogens in the tropospheric chemistry had been investigated but to a lesser extend..."

Line 40: reactive halogen species also greatly affect the chemical transformation of atmospheric mercury.

Line 51: halogen chemistry is also active in polluted atmosphere, e.g., Thornton et al 2010.

Line 58-59: please define HTAP, ACCMIP, and AerChemMIP. This is a great point. Please also elaborate how these model intercomparison projects have been used to evaluate the effects of international policies.

Line 87: consider deleting non-methane hydrocarbons (NMHC) since this category overlaps with volatile organic compounds.

Line 89: define ORCHIDEE.

Line 101: heterogeneous chemistry on sea salt: is this simply halogen recycling (i.e. not a net source) or debromination (net source)? Please clarify.

Line 105: "ice chemistry" is vague. What type of ice? What kind of chemistry on ice? What microphysics option/package is used? Please clarify. Also, I do not quite follow how discarding ice chemistry can *ensure* bromine cycling in the MBL.

Line 106-107: Does this mean that the model cannot reproduce bromine-mediated ozone loss if the so-called "ice chemistry" is included? This may be important information for the community.

Line 135: rephrase.

Line 181-196: in this section (chlorine), only a few ratios are roughly compared to a single model (GEOS-Chem) on the global scale (I guess the numbers are global means). Indeed the GEOS-Chem study cited here (Wang et al., 2019) is fairly comprehensive and probably state-of-the-art, but the level of detail presented in this manuscript does not adequately justify the performance of this model (LMDZ-INCA). Note that the GEOS-Chem study cited here (Wang et al., 2019) have been evaluated using a wide variety of observations (ground-based: particulate chloride, gaseous HCl, HNO₃, ClNO₂; airborne: HCl, ClNO₂, HOCl, Cl₂). I fail to understand why the rich reactive chlorine dataset used for model evaluation in Wang et al. (or even a subset of it) is not used to evaluate this model (LMDZ-INCA).

Line 186: "atomic chlorine evolves..." this is confusing and inaccurate from the chemistry perspective. Consider rephrasing to something like "atomic chlorine has two main sinks/reaction pathways/..."

Line 202: What is considered as "efficient"? How is this efficiency quantified in this model and in the cited GEOS-Chem studies? Note that the bromine schemes are very different in these GEOS-Chem studies (Parella et al., 2012, Schmidt et al., 2016; Zhu et al., 2019).

Line 210: This entire paragraph is problematic: 1) "Since our goal is to simulate the impact on global and ground-level ozone, rather than simulating a state-of-the-art partition within inorganic bromine..." I fail to follow the logic here. What is a point of simulating the impact on global and ground-level ozone if the model does not represent the state-of-the-art understanding of bromine chemistry? Especially, the "impacts on global and ground-level ozone" have been examined using more comprehensive models (like GEOS-Chem and CAM-Chem). 2) "... we make sure that the bromine cycle is chemically active..." This sounds like a very low bar. One can have an active bromine chemical mechanism as long as a few key reactions are included. 3) "...even though reaction fluxes are a factor of 1 to 2 smaller..." please clarify what fluxes the authors are referring to here.

Line 222: "the concentrations of HI, INO₂, and O₂ are lower..." where can the readers find the concentrations of these compounds??

Line 230: if the authors do not bother to clarify how geographical representation of organic/inorganic iodine sources affect iodine burden, might as well delete this sentence because it serves no purpose as currently written.

Figure 2-4: these schematic diagrams are so simplified that they are very difficult to follow and may be confusing for readers who are not experts in this area. I'll list a few here: 1) Many important pathways are not shown (e.g., the production of HBr, BrNO₂ chemistry). 2) In Fig 3, BrO photolysis and the reactions with other compounds (NO, BrO, ClO) are not separated and some reactions may lead to a net loss of ozone (or odd oxygen) but some don't. 3) In Fig 3, Br (a very short-lived radical), Br₂ and BrCl (both stable compounds) are placed in one box, and it's unclear where some of the arrows are pointing at. 4) it is not immediately clear how the bottom center box (HOI, INO_x, N₂O₅) affects chlorine (Fig 2) and bromine budget (Fig 3). 5) It remains absolutely unclear what "physical loss" is and how it works, e.g., is this wet or dry deposition?? What compound(s) exactly? 6) the number formatting is very confusing. For instance, the Cl burden in Fig 2 is written as "3,0.10⁻⁴". I am aware that comma is also commonly used to separate the integral part of the number from the decimal part (which is perfectly fine), but then the full stop is used in the scientific notation (not even the dot multiplication symbol). All together it looks like two numbers (3 and 0.10⁻⁴). Please follow the commonly accepted number formatting in scientific publications as well as journal guidelines. 7) The percentage values in the square brackets are not defined. 8) In Fig 4, not one single reaction rate is given (while Figs 2 and 3 do list a few rates) and what exactly are "gas phase reactions"??

Line 247-248: this sentence offers virtually no specifics. Where are these sites located? Where are the ClNO₂ comparisons presented?

Table S5: the last four reactions appear to rely on underlying assumptions. Essentially the yields and branching ratios used in these four reactions need to be justified. Also, some of these reactions do not obey mass conservation, e.g., HOI → 0.85 ICl + 0.15 IBr + HNO₃. This reaction makes chlorine, bromine, and nitrogen out of nothing, which might not be complete nonsense under very specific conditions but are certainly dangerous and should be avoided in modern chemical transport models.

Table S9: The way the comparisons are conducted in this table does not make much sense and definitely is not "satisfactory" (Line 251). 1) Is Cl* the sum of total reactive chlorine or some individual compound (Cl₂, HOCl, ClNO₂, ClNO₃)? Either way, such comparison offers practically no scientific insights. I fail to understand why the comparisons are not conducted for each individual compound. 2) if the measurements are shown as 24-hour means, please also show standard deviation or something like that to represent the variability of these observations. 3) I do not understand why monthly means (modeled) are compared to 24-hour means (measured)?

Line 253: Table 2 is also problematic. 1) the measurements are shown in very different styles: some given in a range, some with a plus/minus (unclear what these are), and some are given a single value. The table caption does not help. 2) the use of "<" is also confusing. It says in the caption that this symbol indicates that mixing ratios are below detection limit, yet in the table the symbol appears to be used differently. For instance, in the first line of the table reads like the measured BrO was below 2.0 ppt. 3) many of the observations contain rich information on the spatial variability (vertical, geographic) which is wasted completely here. Why don't the authors show a few vertical profile plots for the airborne measurements and a few time-series or alike for the ship-based measurements? 4) again it makes no sense to compare the modeled diurnal averages to the measured daily max.

Line 279: averaged across the entire atmosphere or troposphere or what?

Line 282: why ozone column carries the unit of ppbv?

Line 303-304: the total ozone chemical annual loss decreased by 2.4% in the simulation with halogen chemistry, I assume?

Line 347: please provide evidence (perhaps a few citations) to support this statement.

Line 349: what is this "NO_x concentration threshold"?

Line 350: "... NO_x from 24-27 pptv to 39-41 pptv" it is completely unclear what these values are.