

Review of the manuscript “Sensitivity of tropospheric ozone to halogen chemistry in the chemistry-climate model LMDZ-INCA vNMHC” Caram et al., GMDD, 2023.

The paper describes the implementation of a halogen chemistry scheme into the LMDZ-INCA model, which is based on previous developments of short-lived chlorine, bromine and iodine chemistry in CAM-Chem and GEOS-Chem. This is of major importance, as tropospheric halogen chemistry has been shown to influence the ozone budget as well as the methane burden, and many works have highlighted the importance of including this chemistry in future chemistry-climate projections. Even though the halogen chemical scheme LMDZ-INCA does not contain the full scheme presented in other models, the authors have selected the main reaction and processes as a compromise between detailed chemistry and computational costs during this initial implementation, which can be updated in future steps as the model is used for climate studies. Despite the paper focuses on the technical implementation, they provide a very interesting evaluation of how sensitive is the global tropospheric ozone budget to perturbations in the emissions of air-pollutants, comparing results for different configurations including and neglecting the contribution of chlorine, bromine and iodine; as well as a comparison of results for pre-industrial and present-day scenarios.

The paper is well organized and provides details on the new processes that are currently implemented in LMDZ-INCA, although there are several technical details and/or inconsistencies that are not clear on some of the tables, figures and descriptions presented in Sections 2 and 3. Thus, and even though I do not find any relevant scientific issues that must be solved before publication, given the large number of technical details that must be corrected and/or clarified in the manuscript, I would like to see them implemented in a revised version of the manuscript before publication. I hope the detailed list provided below helps the authors to finalize the description of the model.

Main Comments:

P4, L122: Following other reviewer’s request during previous revisions, the authors explicitly state that *“Recycling through heterogeneous chemistry on sea salt and sulfate aerosols is included while the heterogeneous bromine reactions in water droplets and on ice crystals in clouds are not”*. Even though this is fine for the initial and simplified halogen implementation in LMDZ-INCA, something should be mentioned (either here or below in the text where

sources are described) that the model does not include any type of inorganic bromine source from sea-salt aerosols, while in CAM-Chem and GEOS-Chem this is the dominant bromine source to the troposphere. I also suggest this issue to be mentioned in the discussion and/or conclusions when the range of impacts of halogens on tropospheric compositions is quantified. In relation to this, P15, L321-323: It is expected that tropospheric bromine burden in LMDZ-INCA is in the low range of other models and observations due to the missing source of SSA-recycling. Later on L330, you indicate that *“Our choice to include, in this first step, reactions on sea salt and sulfate aerosols only is ...”* but the bromine heterogeneous reactions you mention here do not represent a net bromine source from SSA. Please make this clarification explicit to avoid conclusion.

P10, L184-187: The authors explicitly state that: *“The inorganic iodine distribution of emissions (HOI and I₂) are prescribed from Prados-Roman et al., (2015a) ...”*. Based on this, I understand that an emissions file is read off-line from the model instead of being computed on-line as in CAM-Chem. If this is the case, this should be explicitly indicated. In addition, some discussion about how these “prescribed” emissions are considered for pre-industrial conditions should be provided, because for example, changes of surface ozone between pre-industrial and present-day in CAM-Chem and LMDZ-INCA differ. How these changes translate into changes in iodine emissions in LMDZ-INCA? In line L198 you state that emissions are 40% lower. Is this based on INCA O₃ changes or taken from Prados-Roman et al.?

Minor Comments:

P2, L46: In addition to Iglesias-Suarez et al., 2020, another study from the group focused on halogen influence on ozone budget and the oxidative capacity of the atmosphere is Badia et al, 2021. This paper should be cited when the budget results presented in Table 7 are discussed.

P2, L58-74: When the discussion about the compromise between detailed atmospheric chemistry mechanisms vs. computational costs is presented, the authors could refer to Fernandez et al., 2020, where Surrogate, Explicit and Full halogen schemes for bromine are compared.

P3. L105: Are biogenic emissions for pre-industrial times identical to present? Please clarify.

P3, L110: Authors should add a reference for HTAP.

P9, L154: The resolution is longitude x latitude, or vice versa? Also, 39 levels up to which height?

P9, L157: All simulations used the same meteorology from ECMWF, including the pre-industrial ones? This is common procedure in many other modeling works, please make sure to make it explicit.

P9, L161: Could you provide at least in the text the CH₄, NO_x and NMVOCs emission values for present-day and pre-industrial conditions? Absolute values are necessary to compare with other models and to estimate how much represents -20% change.

P9, L171: I can imagine that CH₂BrCl, CHBr₂Cl and CHBrCl₂ were not included due to the compromise between computational cost and number of species/reactions. But as those species are included in the original Ordoñez et al., 2012 inventory, at least something should be said about them.

P11, L221-223: I would expect that the ozone percentage changes in the SH are larger because, at least partially, the absolute abundance are smaller.

P12, L248: I suggest pointing at the individual reactions numbers in each table.

P12, L255: Please indicate how the ozone lifetime is computed (e.g., burden / losses?).

P13, L263: Here you mention (but do not define) X*, which is not used until L360, where it is only defined for Chlorine. Please clarify its definition and usage.

P13, L272: Why do you exclude IBr, ICl and aerosols for the burden computation?

P14, L298-299: The implementation of HOI and IONO₂ recycling on ice-crystals in Saiz-Lopez et al. 2015 allowed to reproduce IO upper tropospheric abundance by “increasing” ly lifetime against washout. I would expect including those reactions here will even increase the LMDZ-INCA IO overestimation. Can you comment on this?

P15, L321: There is a misunderstanding of the captioned values: Both (2.0 +/- 1.5 pptv) and 3.2 +/- 1.6 pptv) BrO values are observations at different heights performed by Dorf et al. (2008) in the tropical tropopause, which Fernandez et al. (2014) indicates are in agreement

with CAM-Chem modeling results. But those are observations, not modeling results. Please correct.

P19, L416: The emissions of photo-oxidant precursors has been perturbed by 20% compared to present-day values, isn't it? Please make it clear. Why did you chose to reduce instead of increase by 20% the air-pollutants emissions?

Figures and Tables

Table 1: I found a few inconsistencies between the table and the text, as well as to how LMDZ-INCA has mapped the halogen chemistry scheme from CAM-Chem. In particular:

T1a: Methyl Bromide (CH₃Br) emissions are not considered in CAM-Chem, this model uses a LBC approach as for Long-lived halogens. Also, I'm surprised that Bromoform (CHBr₃) is omitted in the table. Is there a typo or an omission here?

T1b: HCl in LMDZ-INCA is emitted both from the surface as well as from sea-salt, isn't it? Then both circle and square symbols should be included.

T1c: I'm surprised that dry-deposition is considered for VSL compounds like CH₂IBr and CH₂ICl. Why is that and following which model? Why this is not considered for other VSL compounds like CH₂Br₂. Is this a typo?

Table 2: The title of the table contains too much information that would much better fit as a table footnote. In particular, reference to J29, J30, and quantum-yields 2 and 30 are mentioned, but no number assignation for any of the photolysis reactions is given. Please make it consistent. Also, I noticed there is no photolysis of HCl and HBr, while this process is considered for HI. Could this be affecting the partitioning of chlorine species where, for example, HCl is the most abundant of all chlorine reservoirs?

Table 3: Please move the detailed information from the table title to an appropriate and well referenced footnote (e.j., define A0 and Ea). Replace reation by reaction.

Table 4: Please update table title and footnotes as for previous tables.

Table 5: Please define I2Ox. Also note that footnote c is applied only to the first reaction on the table, although I believe it corresponds to all reactions with 2 reactants.

Table 6: Please move details from the title to footnotes as for previous tables. Most importantly, note that emission values are provided in Gg yr⁻¹, and not Tg an.⁻¹. In particular, the HOI-I2 emissions published in Prados-Roman et al. (2015) is 1.9 Tg I yr⁻¹, where in your table it is aprox. 2.5 Tg yr⁻¹. How can you explained those differences if emissions, as stated above, are prescribed to Prados-Roman et al.? Have the original Prados-Roman emissions been scaled to surface O3 deposition in LMDZ-INCA? Finally, bromine emission from sea-salt increases from PI to PD, while for the case of HCl it remains constant. Why is that? Is this due because acidification is not considered?

Table 7: Based on the numbers compiled in the table, the halogen impact over ozone seems to be larger than for other models (e.g., Badia et al., 2021). Indeed, I believe the ozone burden for LMDZ-INCA are lower than for CAM-Chem and GEOS-Chem. I'm more familiar with positive STE values, why do you present them as negative?. Anyhow, your results show that in absolute terms STE is smaller when halogens are considered ... Which makes me ask: Does LMDZ-INCA include a prescribed representation of the stratosphere? Or is the stratosphere chemically-coupled to the troposphere? P12, L239-240: I would expect that the different coupling to the stratosphere between models also affects results here.

Table 8: Given that the implementation of halogen chemistry is based on CAM-Chem, I recommend to include methane lifetimes values from Li et al., (2022) in the table.

Figure 4: The caption indicates that numbers in boxes represent the mass balance of the species, but does not explain what the numbers above each colored arrow are.

Figure 5. *"Percentages in brackets represent the branching ratios"*. I do not understand what the values in brackets are, not how they are computed.

Figure 7: I like a lot the schematic representation of how halogens modify the ozone budget for pre-industrial and present day conditions. I suggest including in parenthesis the percentage change of each of the reported burden changes printed on the side of each arrow.

Supplement Header: Affiliations are missing. They should be made consistent with the main text.

Figure S2: Please indicate a reference for the HCl observations, and if possible, a range of values. Do not use capital letters for “Mixing Ratio” and “pptv” in the title.

Table S2: Reference for VSL chlorocarbon emissions in Table S2 are incorrect, at least for CAM-Chem. None of the papers cited in footnote considered anthropogenic VSL chlorocarbons. Note that the Ordoñez inventory only consider natural oceanic emissions.

Language editing comments and Typos:

P1, L14: I suggest replace with “... and evaluate halogen effects on the tropospheric ozone burden”.

P1, L24: I was surprised the first sentence of the introduction started with “If ...”. I suggest rephrasing unless strictly necessary.

P1, L34: “oxide radicals”

P3, L83: “... and their effect on ozone by using ...”

P4, L122: Replace “modellers” by “other models”.

P9, L195-196: Revise grammar when defining CH₃Br LBCs for pre-industrial periods.

P10, L207: “simulating the climatology of halogen species”.

P11, L213: “which include Cl, Br and I”

P11, L236: Ox = Odd Oxygen.

P14, L293-295. Please revise the sentence grammar and if there is something missing.

P19, L421: “the chemical lifetime of CH₄ reflects the lifetime of CH₄ to removal by OH”. Please revise.

P20, L452: “CO and NMVOC”

Fig. S1: missing →mixing

References

Many references and citations include a,b letters that are not correct (e.g., Fernandez et al., 2014b; Ordoñez et al., 2012a,b). See for example (P3,L13). This should be corrected all over the manuscript.

P2, L44; P2, L55; P3, L113 and elsewhere: Note that sometimes citations in the text are in chronological order, and some others in alphabetical order. Please follow the journal guidelines.

P9, L181: Check parenthesis in citation to Schmidt et al., 2016.

P22, L531: Fernandez et al., 2014b is incorrect, it corresponds to Saiz-Lopez et al., 2014.

P24, L611: Ordoñez et al., 2012 is duplicated.

Badia, A. et al. The Role of Natural Halogens in Global Tropospheric Ozone Chemistry and Budget Under Different 21st Century Climate Scenarios. *J. Geophys. Res. Atmos.* 126, e2021JD034859 (2021).

Dorf, M., et. Al.: Bromine in the tropical troposphere and stratosphere as derived from balloon-borne BrO observations, *Atmos. Chem. Phys.*, 8, 7265–7271, doi:10.5194/acp-8-7265-2008, 2008.

Fernandez, R. et al., Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection. *Atmos. Chem. Phys.* 14, 13391–13410 (2014).

Fernandez, R. et al. Intercomparison Between Surrogate, Explicit, and Full Treatments of VSL Bromine Chemistry Within the CAM-Chem Chemistry-Climate Model. *Geophys. Res. Lett.* 48, e2020GL091125 (2021).

Iglesias-Suarez, F. et al. Natural halogens buffer tropospheric ozone in a changing climate. *Nat. Clim. Chang.* 10, (2020).

Li, Q. et al. Reactive halogens increase the global methane lifetime and radiative forcing in the 21st century. *Nat. Commun.* 13, 2768 (2022).

Ordóñez, C. et al. Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources. *Atmos. Chem. Phys.* 12, 1423–1447 (2012).

Prados-Roman, C. et al. A negative feedback between anthropogenic ozone pollution and enhanced ocean emissions of iodine. *Atmos. Chem. Phys.* 15, (2015).

Saiz-Lopez, A. et al. Iodine chemistry in the troposphere and its effect on ozone. *Atmos. Chem. Phys.* 14, 13119–13143 (2014).

Saiz-Lopez, A. et al. Injection of iodine to the stratosphere. *Geophys. Res. Lett.* 42, (2015).