

In Black the reviewer comments and in blue our responses

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.

The paper explains how we implemented the chemistry of halogenated compounds in a global tropospheric chemistry model LMDZ-INCA, an important component of the IPSL Earth System Model (ESM). LMDZ-ICA is often used for multiple long chemistry-climate simulations. We explain the methodology adopted, the capabilities and limitations of using such a model.

We should have stressed in the introduction that our aim was not to implement a very comprehensive description of tropospheric halogen chemistry with all the details or to simulate accurately the temporal and spatial evolution of all the halogenated compounds. The aim was to develop a simple and computationally cheap halogen chemistry scheme which is able to reproduce most of the effects of halogen species on climate-relevant species (e.g. ozone, methane), and then to assess for example whether iodine, bromine and chlorine chemistry can, beyond their already demonstrated impact on tropospheric ozone, also affect the sensitivity of ozone to its precursors, a potentially important considerations in chemistry-climate interactions. Having simplified models with an acceptable computation time makes it possible to carry out a large number of long global chemistry-climate simulations. The challenge is to find the right compromise between the level of realism and details (e.g. number of species and processes) acceptable for the chemistry-climate applications, and the computing efficiency. Our choices of chemistry representations and emissions are guided by results from global tropospheric chemistry models that include very detailed representations of halogen chemistry. Their results, notably the impact on the tropospheric ozone budget, are used as benchmarks in assessing the LMDZ-INCA simulations.

The heterogeneous component is the most complex part of halogen chemistry. It is also by far the most uncertain. In addition, we implemented the chemistry of I, Br and Cl in a version of INCA where aerosols (e.g. number/surface/mass concentration, composition) are not

prognostic variables but prescribed through climatologies. Nonetheless, although the (missing) explicit treatment of some heterogeneous processes (acid sensitivity of sea-salt dechlorination and heterogeneous reactions on aqueous aerosols and ice-crystals in clouds) can be important, especially to simulate the vertical distributions of halogenated compounds, it does not drive the overall impact of halogen chemistry on global tropospheric ozone in the model according to the comparisons with the more detailed reference chemistry-transport models (GEOS-CHEM and CAM-Chem). The comparisons show that, despite a simplified treatment of the heterogeneous halogen chemistry, our scheme is able to simulate satisfactorily the global levels of halogens and to account for the overall effect of halogen chemistry on tropospheric ozone. It represents a major model improvement still missing in almost all the global chemistry-climate modelling studies. As pointed out by the reviewer, it is “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.”

We recognize that the language was sometimes vague and some formulations were clumsy. We sincerely apologize and thank the reviewer for his/her recommendation. We did a thorough work on the manuscript in order to clarify the intent and better organize it to make the flow more logical. Below we give more details on how we respond more specifically to these general and further specific comments.

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 reviewer is correct. However, note that only the heterogeneous component of our halogen chemistry scheme is much simpler than in GEOS-Chem or CAM-Chem. It also is the most complex and uncertain part of this chemistry. The level of complexity of our heterogeneous representations was also limited by the fact that aerosols were prescribed instead of being calculated in our version of LMDZ-INCA. As a consequence, some heterogeneous processes could not be represented in a very detailed and interactive way, especially compared to GEOS-Chem or CAM-Chem in which the descriptions of halogenated tropospheric chemistry result from years of development. However, we show that our model is sufficient for some chemistry-climate applications, in particular investigating the impact of halogen chemistry on tropospheric ozone and its sensitivity to its main anthropogenic drivers. This is a novel result of our study.

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.

LMDz-INCA is a global model and, to keep computing costs reasonable in this development phase, it is used at a coarse resolution. At this stage, we assess the ability of the model to reproduce climatological datasets (i.e. averaged over time and location) which is the most appropriate scale for a first level of evaluation of a global chemistry-climate model. As explained previously, although we have not performed a comprehensive comparison with observations, the evaluation of our model performances relies largely on comparisons to

more complete and established models, CAM-Chem and GEOS-Chem, which have already been rigorously evaluated in a detailed manner against a wide variety of observations (as pointed out by the reviewer). The correct simulation of the global halogen species loading and of its contribution to the ozone budget, compared to CAM-Chem and GEOS-Chem, illustrates the relevance of our scheme, as implemented in LMDz-INCA.

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.

Our aim is not to develop a scheme matching or more sophisticated than GEOS-Chem and CAM-Chem or carry out specific chemistry process studies with detailed comparisons against observations. The focus is on a simplified model with reasonable computational costs for chemistry-climate applications, in particular those involving the impacts of halogen species on global tropospheric ozone and oxidizing capacity. This also offers new scientific insights from the point of view of chemistry-climate interactions involving halogens.

This study introduces another model, an important component the IPSL ESM, which can be used for certain applications if not for all. Even with some limitations, the new scheme clearly helps to improve the ozone representation in our model, which is an important milestone in the model development. GMD is well suited for this type of work because it is 'dedicated to the publication and public discussion of the description, development, and evaluation of numerical models of the Earth system and its components'. We are convinced of the importance of this newly implemented chemistry scheme in LMDZ-INCA, to better assess the change in tropospheric ozone since the preindustrial era or in the future.

The necessity to have model ensemble is now well established and it requires the development of a diversity of models. Having already the halogenated chemistry in three global models cannot be a reason not to attempt to implement it in other models. There is not much scientific insight to gain if we all use the same models, perform the same studies and hence end up with the same results. Finally, even if it is just an illustration of the possible model applications, our results on the change in tropospheric ozone sensitivity to anthropogenic precursors produced by halogens are valuable and bring some new scientific insight on potential chemistry-climate interactions involving halogens (section 4.1).

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.

The main purpose of this part is to illustrate how the consideration of halogenated chemistry can perturb the model-calculated response of tropospheric ozone to changes since preindustrial times. First, regarding the ozone burden evolution, the main driver for atmospheric chemistry between preindustrial and present-day is definitely the emissions from anthropogenic sources. Second, emissions from natural sources have also changed but are not the primary driver, and the uncertainties around such changes are large. There is no

general consensus on the magnitude and sometimes even the sign on some of these changes.

One specific example is again acid displacement largely driven by HNO_3 , which, may be different between pre-industrial periods and present-day. These key assumptions need to be justified.

The aim was not to reproduce as faithfully as possible the distribution of the Cl-containing compounds. As the chlorine chemistry is less reactive than the bromine and iodine chemistries, it was not considered as a priority in this development focused on the impact of halogens on ozone. For chemistry-climate applications, chlorine is essentially significant as an additional sink for methane (which was estimated to 2 to 3% in recent literature not accounting for acid displacement and 1.0 % of the total methane chemical loss when considering the pH dependant chlorine chemistry (Wang et al. 2019)) but chlorine chemistry only plays a minor role in the halogen-driven ozone loss. The main reason for implementing some chlorine chemistry was to represent correctly the bromine recycling due to chlorine through the heterogeneous reactions involving HCl and BrCl.

The chemistry involving acid displacements leads essentially to a source of HCl from sea salt aerosols. This source is accounted for but its dependency to pH is not explicitly computed in an aqueous chemistry module. However, our total chlorine emissions (96Tg Cl.yr^{-1}), which corresponds to the flux in TOMCAT by Hossaini et al. (2015), is realistic and hence the global effect of chlorine on ozone and oxidation capacity is reasonably well reproduced in our model.

To consider acid displacement of HCl interactively in a realistic way, the LMDZ-INCA model should also account for aqueous-phase chemistry to consider reactions with Cl-. Aqueous-phase chemistry is beyond the scope of this first development phase, especially with the aim of minimising complexity and computational costs.

It is worth pointing out that this particular aqueous chemistry was added in GEOS-Chem only very recently (Wang et al., 2019) and thus our work is more comparable to the level of model descriptions reached in GEOS-Chem in Sherwen et al., 2016b and Sherwen et al., 2017. However, when we discuss the results from LMDz-INCA, we compare them to Wang et al. (2019) whose model version successfully simulates the observed mixing ratios of HCl. INCA is able to reproduce HCl concentrations of a hundred ppt over remote locations and the model-observation discrepancies are of the same magnitude as in GEOS-Chem. As the acid sensitivity is missing in INCA, the model is not able to faithfully capture the spatial variability of the mean HCl mixing ratios across locations, in particular the HCl enhancement at polluted coastal sites and northern midlatitudes. In GEOS Chem (Wang et al. 2019), HCl mixing ratios are highest over the oceans downwind of polluted continents due to the effective acid displacement from sea salt aerosol by HNO_3 and H_2SO_4 .

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 extent..."

The sentence was qualitative and not intended to minimize the efforts which have been done in particular in term of field experiments. We have removed "but to a lesser extent than for stratospheric chemistry".

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

yes, we agree that's why it is listed in the sentence

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

This paragraph aims to make the point of the importance of halogen chemistry in representing the overall chemistry of the pristine atmosphere.

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.

This point has been elaborated.

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

Thank you, it has been done.

Line 89: define ORCHIDEE.

Thank you, it has been done.

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

We have replaced "heterogeneous chemistry" by "Recycling through heterogeneous chemistry" to clarify. Note that the chemical scheme is now entirely provided in the manuscript itself (table 5).

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.

We apologize for the lack of clarity here. We mean reactions on ice crystals in clouds. We have rephrased the sentence here to clarify and removed the sentence about ensuring cycling in MBL which was confusing in this context.

We have also clarified in part 2.1.1. that the version of INCA used here does not compute aerosols interactively, climatologies are specified.

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.

As assessed by Badia et al. (2019) the loss of Ox due to the heterogeneous reactions of halogens (mainly bromine) is 6% of the total loss for the whole troposphere. In the marine boundary layer, these reactions account for about 11 % of ozone losses (see figure 15 in Badia et al., 2019 comparing the WRF-NOHET and WRF-DEBROM runs and text in their part 5.4). In-cloud chemistry (on clouds droplets, ice crystals) is the most important in the upper troposphere (Badia et al. 2019), but the loss of Ox due to the heterogeneous reactions involving halogenated compounds falls to less than 5%. Overall, most of the Ox losses by halogens take place in the lower layers of the troposphere where reactions on sea salts dominate and where the in-cloud chemistry has a minor effect.

Line 135: rephrase.

It has been rephrased.

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 GOES-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).

See above. The aim is not to reproduce Wang et al., 2019 study. GMD would not be the most suited journal for such a process study. LMDz-INCA is used here in a coarse resolution 3.75°x1.9° and is run over 1 year. Evaluations of global models against observations make sense only if these observations are gathered/averaged spatially and temporally to be representative of climatological compositions, on scales relevant to global chemistry-climate modelling. For the sake of simplicity, we compare the results from INCA to observational datasets already gathered in the literature by modellers who have the same purpose and we also compare the results to the most advanced versions of the models considering tropospheric halogenated chemistry. Again, chlorine chemistry is not central to the paper which is focused on ozone loss, mainly dominated by iodine and bromine.

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/...”

OK, it has been done.

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 GOES-Chem studies (Parella et al., 2012, Schmidt et al., 2016; Zhu et al., 2019).

The efficiency is assessed by quantifying the mass fluxes through the reactions. Fast production and loss of bromine radicals lead to large fluxes and thus an efficient recycling. A more detailed (but still schematic) representation of the bromine reaction fluxes in LMDz-INCA and in GEOS-chem (Schmidt et al. 2016) has been added to the supplementary material (Figure S1). Reaction fluxes are in a relatively good agreement despite differences in the representation of the chemistry.

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 GOES-Chem and CAM-Chem).

We did not state clearly that the aim was to develop a simple and computationally cheap halogen chemistry scheme which is able to reproduce most of the effects of halogen species on climate-relevant species, i.e. ozone, methane via oxidizing capacity, and then explore how halogen chemistry can affect the sensitivity of ozone (and the related oxidizing capacity) to its precursors, a potentially important considerations in chemistry-climate interactions. The challenge is to find the right compromise between the level of realism and details (e.g. species and processes) acceptable for the chemistry-climate applications, and the computing efficiency for the long chemistry-climate simulations. Therefore, we only represent the reactions and species which are dominant for the impact of halogens on global ozone destruction. Some reactions can be of importance in specific environments but only marginally impact global ozone destruction and thus were not prioritized in such development. None of the global models which have been used in recent multi-model projections of atmospheric chemistry for climate takes into account the halogenated chemistry despite the fact they assess ozone budget. The fact that 3 models have developed, over more than ten years, a very comprehensive representation of halogenated chemistry does not mean that other models should not start such implementation even if gradually and thus, in the first stage, less comprehensively. A figure (Figure 3) has been added to show the Ox destruction in the troposphere in INCA. It can be compared with similar figures for GEOS-chem (Sherwen 2016a for scheme with Br and I chemistry and Sherwen 2016b for Br, I and Cl chemistry). It illustrates that the model is able to reasonably simulate the effect of halogenated chemistry on ozone.

We modified the introduction and flow of the paper to better reflect its intent.

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.

The sentence has been rewritten “The branching ratios are found to be consistent with Schmidt et al., (2016) even though reaction fluxes can differ up to a factor of 2”

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

In the sentence “concentrations” has been changed in “burden” and a more detailed figure is now shown.

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.

The sentence has been removed.

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).

These figures aim to present the budget. Only a few chemical pathways and the main compounds or reservoirs are represented. The chemical scheme for halogenated compounds is now included in the main text as tables 1-5 (instead of supplementary material). Some compounds/fluxes have been added (e.g. BrNO₂, HBr production) The legends now make clear that it represents the main terms in the budget rather than the complete tropospheric cycle.

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?

Physical losses are wet and dry deposition. It has been clarified in the Figures.

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.

Corrected.

7) The percentage values in the square brackets are not defined.

The percentages correspond to the branching ratio for the sinks of HOBr and BrO, it has been clarified in the legend.

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”??

Added to the iodine figure in the manuscript.

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

“LMDZ-INCA underestimates the continental ClNO₂ content for many sites” has been replaced by “ClNO₂ over continental areas does not exceed a few tens of ppt in INCA whereas observations at several continental locations gathered by Wang et al. 2019 (their Table 5) show concentrations of a few hundreds to thousands ppt over such locations for hourly maximums. “

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.

This is the way it is considered in GEOS-chem as well. These are not elementary reactions but a representation of dechlorination and debromination of sea salts, and the resulting bromine and chlorine in that specific reaction comes from the chloride and bromide in the sea-salt particle.

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.

-> We do not make comparisons to individual compounds because the papers we compare the results to report the values in a similar way. We had to adapt to other papers' results. We use for Cl* the same definition as Wang et al., 2019.

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)?

Measurements correspond to average of several 24 hours mean measured over 1 or 2 months. These results have been aggregated by Wang et al. 2019, we use them in a similar way.

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.

Not applicable, the Table has been removed.

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.

Not applicable, the Table has been removed.

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?

The model has a $3.75^\circ \times 1.75^\circ$ resolution, it does not make sense to compare to individual observations. Observations can be used if they have a climatological representativity.

4) again it makes no sense to compare the modeled diurnal averages to the measured daily max.

Not applicable, the Table has been removed.

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

It has been clarified in the text

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

The formulation was clumsy, it has been modified to avoid confusion.

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

Sorry, the sentence has been clarified.

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

For sake of clarity, this paragraph has been removed.

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

For sake of clarity, this paragraph has been removed.

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

For sake of clarity, this paragraph has been removed.