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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of halogen chemistry on air quality in coastal and continental Europe: application of CMAQ model and implication for regulation" *by* Qinyi Li et al.

Anonymous Referee #1

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General comments

This work presents the evaluation of the halogen (Cl, Br, I) chemistry scheme from Sarwar et al [2015] within the CMAQ model on a regional scale (12km) for the month of July over Europe. The authors present an evaluation of halogen chemistry's impacts on air-quality metrics by comparing two runs, with chlorine ("CHL") or all halogens (HAL), against a model run without halogen chemistry ("BASE"). The focus is on how halogen chemistry impacts ozone in the European summer.

The authors argue the novel aspect of this study derives from the high resolution (12km) and focus on air quality impacts over Europe. However, this novelty is some-

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what challenged by the extensive referencing of a study in another model that considered also considered halogen chemistry within a nested model over Europe at ∼25km during the summer too [Sherwen et al 2017]. Furthermore, this work seems to omit reference to the follow-on work using the same nested model ∼25km for other seasons [Sommariva et al 2018] or using the model in a global for an entire year at 12km [Hu et al 2018]. It is not clear what the authors are suggesting is the main differences in between the nested global vs. nested hemispheric approaches, apart from the resolution.

Furthermore when considering the period of study: Halogen chemistry can be very seasonally dependent in Europe (e.g. ClNO2 - See Sommariva et al [2018]). So considering the existing literature on modelling halogens, further model runs should at least be presented for a winter month to give an equivalent novel value on understanding the air-quality impacts.

Some opportunities to make this work more novel seem to have been missed. For instance, coarse two bin comparisons ("coastal" vs. "inland") are made with regional ozone and NO2 observations instead of comparisons that show if the model captures chemical/physical processing (e.g. diel plots by the hour). Oxidants are analysed as "snapshots" of peak or average concentrations, rather than considered in terms of a given hour. Considering the diel cycle of oxidants by hour over Europe (e.g. contribution of Cl in the morning vs. OH at midday, then NO3) and how halogens effect this would really elevate this manuscript.

The description of the model setup needs to be clearer. From reading the manuscript, I think I correctly understand that the configuration uses a regional grid for Europe and then sets "boundary conditions" outside this grid from two additional hemispheric runs. Please add more information to the model configuration section and clarify this.

Writing is often verbose and would often benefit from re-wording to make the manuscript more concise. The introduction especially would benefit for re-writing for

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flow and clarity of the various different model studies cited. References (e.g. for observations) could be more up to date.

Specific comments

Page 1 - Lines 15-35 (Abstract) Please add headline numbers for changes seen in this manuscript to abstract.

What is the net effect of the domain on OH/HO2? The effect of halogens on OH /HO2 in box models and global models has been discussed at length by Stone et al. [2018].

Page 2 - Line 35 - 41 Earlier references should be used here to give fair credit to the original work on this, instead of recent reviews.

It would be cleaner and more instructive to the reader to include the following sentence, rather than just citing a recent review.

“The chemistry of halogens in the troposphere has been described in detail in recent reviews (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015), so we just briefly outline it here.”

Additionally, the effect of halogen nitrate hydrolysis on decreasing ozone production should be mentioned here as it has been shown to have a larger impact on ozone than increased loss [Schmidt et al 2016].

Page 2 - Line 46 “methane ch4” should read “methane (CH4)”

Page 2 - Line 52-55 “Evaluation of the complex role of halogen chemistry in air quality requires the employment of advanced, high-resolution chemical transport models”

Has this argument really been evidenced here? Could not the processed discussed be captured by existing coarse resolution approaches? Are the uncertainties on halogen modelling substantially small enough that horizontal resolution of models is the main limitation for the fidelity of simulation to observations and capturing chemical and physical processes?

Page 2 Line 56-61 Should not the faraday discussions paper you mentioned earlier be included here as you say in the manuscript it covered ClNO2 too? Other model studies have looked at this too and should be included here also. Adding "e.g. X et al., Y et al." to illustrate the reader that a couple of examples have been given would also be appropriate. There are other points in the manuscript where this would be appropriate too.

Page 3 - 61-71 It is hard for the reader to follow the way in which the previous work is being discussed. The authors have referred to another nested regional study in GEOS-Chem in the final intro paragraph [Sherwen et al 2017], but then did not include it in the discussion of existing regional modelling work here.

Page 3 - Line 71 It is arguable that 4km is a higher resolution. However, is a 4km horizontal resolution accepted to be sufficient to represent the processes going on in a city? I would suggest updating as follows:

From

"halogen sources on air quality at a city scale (4 km resolution) in Los Angeles, California, US."

To

"halogen sources on air quality at a resolution of 4 km in the city of Los Angeles (California, US). "

Page 3 - Line 74 A URL in brackets is not an appropriate format here. If a URL must be used please include a reference to the EEA and a data accessed for the data. Referencing an EEA report would be preferable.

Page 3 - Line 72 to 82 It is hard for the reader to follow the semantic. The previous study is also a domain based study over Europe using boundary conditions from a model with a larger (global) domain with offline meteorology. Are the authors arguing that the main difference between the 12x12km CMAQ approach presented here and the existing

work, at the coarser resolution (25x25km), is just resolution? Both models use similar halogen chemistry are nested within larger domains, correct? Why is so much change in simulation skill expected to be seen between 12x12 km and 25x25km? Or would a higher resolution, say 4x4 km [MunÌČiz-Unamunzaga et al., 2018], be required to notable gains in capturing processes or differences? This leads to a more philosophical question: is it a model resolution or processes holding back science currently? Would not other uncertainties in halogen chemistry be greater than the difference caused by a change in resolution too? (e.g. emissions developed for coarser resolutions or new developments in the representation of halogen chemistry in models - Xuan et al [2019])

Page 3 - Line 84 Is “instrumented” the appropriate word here? “Including” would be a better choice or “which includes”.

Page 3 - Line 85 Why is “state-of-the-art” used here? It seems unnecessarily verbose, especially when referring to a paper that is at least four years old in a fast-moving part of the literature.

Page 4 - Line 90-96 The meteorology is offline? Or is CMAQ being run in coupled mode? Please explicitly state if the meteorology is offline.

Page 4 - Line 96 Why is the word “besides” used in this sentence. Please rephrase for clarity.

Page 4 - Line 111 How has coastal been defined here? More broadly, is 12km sufficient resolution to capture “coastal” effects?

Page 6 - Line 131 -132 Is this 12x12km domain nested within another domain not computed online? Or is the model run hemispherically at 12x12km here for all simulations? Please make this clearer.

Page 6 - line 143 The name “CHL” may make many readers from the Earth sciences community think of chlorophyll. I would suggest using “Cl” instead to make the paper more accessible to a broader readership.

Page 6 - Line 139 -145 Only 7 days spin up was used for a hemispheric simulation? Or is this for the European grid? Is this sufficient to ensure initial conditions are “washed” through the grid? Is there a reference showing this is sufficient? What spin up was used for “the hemispheric CMAQ simulations”/hemispheric grid? What initial conditions were used? This needs to be clearer. Global studies on halogens in CMAQ, GEOS-chem and CAM-Chem have highlighted the importance of changes in background concentrations. The relative contribution of boundary and local effects seems to be a core focus of the Sherwen et al [2017] manuscript, but not really given much attention or discussion here.

Page 6 - Line 152-160 The model is being run on a hemispheric grid of 12x12, but just analysed for the domain in Figure 1? The “Boundary conditions” are on the same grid, but global? and these are provided to the outside of the modelling domain? This needs to be explained more clearly.

Page 6 - Line 152 “Boundary conditions for the model were derived from the hemispheric CMAQ simulations.”

Which hemispheric CMAQ simulations? Where have these been described?

Page 7 - Line 161-163 Please include a table that shows which boundary conditions and chemistry used in each domain for each model experiment.

“the difference between CHL and BASE simulations represents the impact of the chlorine chemistry on air quality”

Don’t both of these simulations have the same boundary conditions (“Carbon Bond chemical mechanism and the chlorine chemistry”)? Surely then the most this difference can show is the contribution of chlorine chemistry locally. A preferable approach would be to use a “BASE” set of boundary conditions without halogen chemistry for the “BASE” simulation.

“the difference between HAL and BASE simulations represents the effect of halogen

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chemistry on air quality."

Again: according to the text, "BASE" includes the effects of chlorine globally as it includes chlorine in boundary conditions ("Carbon Bond chemical mechanism and the chlorine chemistry"). Therefore "BASE" - "HAL" is giving the effects of halogens minus the global effect of chlorine.

Although locally chlorine can provide an oxidant effect and lead to ozone formation, it also can act as a sink for ozone through the loss of chlorine nitrates on a global scale. This has been discussed in some of the global modelling papers cited here. What are the global effects of chlorine in this model? Can global effects be excluded here?

Page 7 - line 169 Please give a justification for the use for "within 24 km from the coast" definition. Coastal processes (notably halogens) can be confined to a very small area (e.g. macroalgae in tidal zones).

Page 7 - Line 169-171 The level of the evaluation presented needs to be increased to be in line with the high-resolution output the authors argue is notable here.

Please plot ozone and NO2 as a diel (24-hour) comparison compared with the model, preferably showing a few regions in Europe. Regions like the coastal Mediterranean should not just be lumped together with the coastal Scandinavian, as they have very different seasonal characteristics. Simply using a table to do a very coarse two bin comparison does not provide much insight and it is not really in line with the current level analysis presented in the literature (e.g. Schnell et al. 2015), instead, it smooths out the extra information gained.

Page 7 - Line 179-181 Please provide references for the proposed explanations for model bias or expand this discussion.

Page 7 - Line 184-186 Only a single table of comparisons has been provided to back up this statement. More evidence is needed. Please provide diel plots of core species (e.g. CO, NO2, O3).

Page 7 - Line 182 How does this comparison look on a diel basis? Is there an offset or difference in the diel cycle at certain times of the day? Does the model capture the diel cycle before or after or is there a structural issue in the model (e.g. caused by emissions or boundary layer mixing?)?

Page 11 - Line 223-255 The coastal influence or inland nature of observations should be made clearer. At the resolution presented here (12x12km) it would not be fair to expect the model to reproduce many of these observations (e.g those influenced by local emissions from the tidal zone).

Page 11 - Table 1 This table of observations does not seem in line with current literature (e.g. observations for ClNO2 are available across seasons in Northern Europe [Sommeriva et al 2018]). Please expand these comparisons.

Page 11 - Line 249 The largest IO dataset has been published since Saiz-Lopez and von Glasow [2012] by Prados-Roman [2015]. Did this not this start and end in the Mediterranean? How does the model compare against this? What other more recent datasets are there?

Page 12 - Line 261-264 Please see earlier comments about the inclusion of chlorine in boundary conditions for both “BASE” and “CHL” simulations.

Page 13 - Line 267 Please give OH units in the more commonly used units of molecules cm-3 or at least show this in brackets throughout the text. Please do the same for Cl (atoms cm-3).

Page 13 - Line 290 What about the resolution difference could cause this? What other differences could explain this? Are there any differences in the chemistry between the Sarwar et al (2015) and Sherwen et al (2017) Mechanism?

Page 15 - Line 305 “Our study, along with the previous work, highlights the vital role of halogen chemistry in the nighttime chemistry.”

Which previous work? How is this chemistry constrained by lab work/observations?

Is it based on theoretical calculations? If So, then the uncertainty on this should be highlighted here.

page 15 Line 307 - 309 Cly is in the boundary conditions for both “BASE” and “CHL”, correct? How much Cly is transported into the domain?

Page 15 - 312-318 How do these values compare against known constraints on tropospheric chlorine (e.g. Gromov et al [2018])? Are there any explanations for the differences? (e.g. It is worth noting too that Hossani et al [2016] used unrealistic anthropogenic chloride emissions - see Xuan et al [2019] for details on this)

page 15 Line 320 “The current study and the previous works simulated a broad range of the surface Cl concentrations although they were all within the scope of the reported observed (observation- based calculation) values of 103 to 105 atom cm-3 ($\sim$ 4.0 $\times$ 10-5 to 4.0 $\times$ 10-3 pptv) according to the review of Saiz-Lopez and von Glasow (2012).”

Why is a review that is > seven years old being used as the basis for comparison? There have been a large amount of Cly measurements since then (e.g. Gromov et al [2018], Haskins et al [2018] etc ...) and more work to constrain tropospheric Cl [Gromov et al 2018].

page 22 Fig 8 AOT40 is calculated over a growing season. Why is this shown for a single month in Fig. 8 and discussed in the text? It would be more appropriate to give output in units of exceedances for a given month as this usage of “AOT40” could mislead readers. What over relevant ozone thresholds are there? What about the particulate matter if the oxidants have changed (e.g. PM10, PM2.5)?

page 23 Lines 430-432 “These models do not include the comprehensive halogen chemistry, potentially leading to [an] unrealistic simulation of O3 concentration responsiveness to the predicted NOx and/or VOCs emission changes in Europe.”

As only a coarse comparison is provided for ozone (table 1) and no diel cycles are shown it is hard to see if halogens are aiding the capture of processes seen within the

observations. This weakens the argument that halogen processes are needed to gain a “realistic” simulation in air quality models. Please back up this claim with figures.

page 24 Lines 460-465 The final paragraph of the conclusion comes across as vague. Please provide a few examples of uncertainties that are more specific than just “chemical mechanism”.

References

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