RC1: 'Review of Badia et al. 2016', Anonymous Referee #1, 19 January 2018

Review of ""Importance of reactive halogens in the tropical marine atmosphere: A regional modelling study using WRF-Chem" by Alba Badia et al.

The authors have completed an enormous amount of work, but unfortunately the paper
does not currently meet the requirements for publication in ACP.

This paper can be published after addressing the following major comments:
- The authors must provide a justification as to why they have not included chlorine cycling in the model. Even if there are no measurements of chlorine, the authors cannot focus on bromine and iodine cycling without some description of chlorine chemistry. The authors cannot simply ignore chlorine especially in the remote marine boundary layer. See for example Schmidt et al. (2016).

Response: Chlorine cycling is included in the model. This is mentioned in the Abstract "To do this the regional chemistry transport model WRF-Chem has been extended, for the first time, to include halogen chemistry (bromine, chlorine and iodine chemistry), Section 3.1 "This mechanism has been extended to include bromine, chlorine and iodine chemistry" and Section 3.2 "Chlorine chemistry is also included into the model, however, since our results are mainly focused on reactive bromine and iodine for which we have observed data, we have not included the chlorine chemistry in Fig 4." Moreover, Tables 1-5 describe all the reactions (including chlorine) that have been added to the model.

To make it clearer that chlorine is implemented in the model, we have added the following in the caption of Fig.4 "Chlorine chemistry has been added into the model, but since our results mainly focus on reactive bromine and iodine, chlorine chemistry is omitted from this figure (See Tables 1-5 for full list of additional reactions)."

In the 2 sections where we consider the impact of the halogen chemistry on VOCs (5.3) and on O_3 and O_X (5.4), we include a consideration of the Cl chemistry which was referred to several times in these two sections. We have added more on the Cl chemistry in Section 5.4 , a figure of the Cl_Y partitioning (Fig. 12) and the integrated odd oxygen loss rates for ClO_x cycles in Fig. 15. This new information has been included in the revised manuscript, as follows:
"When the VOCs react with Cl (WRF-DEBROM), almost all the inorganic Cl is in the form of HCl (see Fig. 12). When these reactions are not considered (WRF-NOHALVOCS), Cl_y increases and there is a shift in the partitioning to more reactive chlorine increases, in particular HOCl, but also ClO and the di-halogens."
"Moreover, the big change though is for the ClO_x which increases from < 1% to 26%. Cl is very important in the oxidation of the alkanes. When this chemistry is not included the concentrations of Cl_y increases and there is an impact on the partitioning increasing reactive species (see Fig. 12), hence, the ClO_x cycles play an important role in O_x loss. It should be noted that very little is known about the abundance and distribution of Cl_y so this is a large uncertainty."

We agree that not including the Cl chemistry would have been a significant weakness, but this simply was not the case. We hope this is now completely clear to readers and that the additions address the reviewer's concerns.
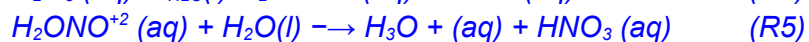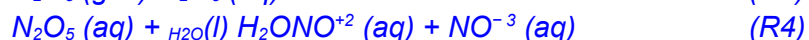
- A more complete description of heterogeneous chemistry already included in the model is needed. If the authors used the model as described, ClNO2 is formed on aerosols via reactions of N2O5. However, once formed ClNO2 is treated as an inert species. This should be updated prior to publication.

Response: This heterogeneous chemistry is included in this work. Moreover, $ClNO_2$ is not treated as an inert species but is broken down via photolysis and reaction with OH (see Table 2 and 4). Further information on this chemistry has now been added in the revised manuscript in which we cite another WRF-Chem paper (Archer-Nicholls et al., 2014) that provides more details of this chemistry as implemented in the model. This new information has been included in the revised manuscript, as follows:
"After uptake N_2O_5 is taken up onto the particle, it reacts reversibly with liquid water to form protonated nitric acid intermediate ($H2ONO^{+2}$). This then reacts with either liquid water, to form aqueous nitric acid (HNO_3), or with chloride ions to form $ClNO_2$. See Archer-Nicholls et al. (2014) for further description of this chemistry. In Archer-Nicholls et al. (2014) $ClNO_2$ was considered as an inert specie, however in our study $ClNO_2$ is not treated as an inert specie but is broken down via photolysis and reaction with OH (see Tables 2 and 4)."

Some text on this heterogeneous chemistry in Archer-Nicholls et al. (2014) is reproduced below for the purpose of this response, but we do not feel it necessary to repeat these details in the revised manuscript as it is published elsewhere:
"The reaction mechanism that is used for the hydrolysis of N_2O_5 is that of Thornton et al. (2003). They suggest that, after uptake onto the aerosol particle, aqueous phase N_2O_5 reacts reversibly with liquid water to form an (as yet unobserved) protonated nitric acid intermediate (H_2ONO^{+2}). This then reacts with either liquid water, to form aqueous nitric acid (HNO_3), or with halide ions to form nitryl halide (XNO_2; where X=Cl, Br, or I):

N_2O_5 (gas) N_2O_5 (aq)   (R3)
N_2O_5 (aq) + $_{H2O}$(l) H_2ONO^{+2} (aq) + NO^{-3} (aq)   (R4)
H_2ONO^{+2} (aq) + H_2O(l) $-\rightarrow$ H_3O + (aq) + HNO_3 (aq)   (R5)
H_2ONO^{+2} (aq) + X^- (aq) $-\rightarrow$ XNO_2 + H_2O(l).   (R6)

In applying the parameterisation of Bertram and Thornton (2009) we assume that the limiting step is the uptake of N_2O_5 to the condensed-phase, and that it reacts in a near instantaneous manner with H_2O and Cl^- to give NO^{-3} and $ClNO_2$ through Reactions (R4)–(R6). $ClNO_2$ is not added to the aerosol, but is instead assumed to out-gas in a near instantaneous manner, and has instead been added as an extra species to the gas-phase (currently as an inert tracer - no gas-phase reactions involving $ClNO_2$ have been added to the gas-phase chemistry scheme, although this could be added in the future, e.g. following Sarwar et al., 2012). In addition, for simplicity, we assume that the HNO3 molecules formed in Reaction (R5) undergoes ion dissociation to produce aqueous NO^{-3} ."

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., Hodnebrog, Ø., Denier van der Gon, H., and McFiggans, G.: Gaseous chemistry and aerosol mechanism

developments for version 3.5.1 of the online regional model, WRF-Chem, Geosci. Model Dev., 7, 2557-2579, https://doi.org/10.5194/gmd-7-2557-2014, 2014.

- As already pointed out by the other reviewer, Equation 2 is not an acceptable treatment for reactions on aerosols. This equation ignores the fact that reactions are limited by the rate at which gases can diffuse towards the aerosol surface (diffusion limitation).
There are clear descriptions of how to treat this correctly in the literature, for example in Schwartz (1986).
Response: See response to the other reviewer.

- While this paper was not submitted to Geoscientific Model Development (GMD), this is the first paper that describes a new model development. The paper should be held to the GMD standard for publication. For example, the subroutines that have been updated to perform the study should be included in an electronic supplement and/or the code used in the study should be provided as an electronic supplement.
Response: Copies of the code and data used in this study are readily available upon request from the corresponding authors. To our knowledge it is not a requirement to publish new model code for papers published in ACP, however, we are happy to be guided on this one by the editorial office.

The authors have attempted to study the influence of bromine and chlorine cycling in the tropical marine atmosphere. This can be an important study and hopefully the authors will make the effort to address these major comments so that the paper can be published in ACP.
Response: The authors wish to thank anonymous reviewer #1 for his/her valuable comments and suggestions. We have added further comments to clarify that chlorine chemistry has been included in the model and hope that this will avoid any future misunderstanding. We're very happy to make new code available to further scientific research and look forward to guidance from the editorial office regarding any requirement regarding supplementary information. Whilst we acknowledge the limitation in our representation of the heterogeneous chemistry, we see no reason for this being a barrier to publication as this approach is one that has been adopted in other recent studies that have been acceptable for publication. We have added new material from additional runs to illustrate the sensitivity of the results to the approach we have taken.

References:
Schwartz S.E. (1986) Mass-Transport Considerations Pertinent to Aqueous Phase Reactions of Gases in Liquid-Water Clouds. In: Jaeschke W. (eds) Chemistry of Multiphase Atmospheric Systems. NATO ASI Series (Series G: Ecological Sciences), vol 6. Springer, Berlin, Heidelberg.
Schmidt, J. A., et al. (2016), Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, J. Geophys. Res. Atmos., 121, 11,819–11,835, doi:10.1002/2015JD024229.

RC2: 'Review of Badia et al. 2016', Anonymous Referee #2, 12 December 2017

Review of ""Importance of reactive halogens in the tropical marine atmosphere: A regional modelling study using WRF-Chem" by Alba Badia et al.

The manuscript attempts to compare observations of reactive halogen species (containing Cl, Br, I) in the Pacific with model results. Comparison of model results with real observations are always important and n particular provide a test of the degree of our understanding of the modelled part of the reality. As such the authors have to be commended for their undertaking. The outcome of the inter comparison is the (not entirely new) finding that our knowledge of the relevant halogen chemistry and the source mechanisms of halogen species is very limited. Probably a meaningful modelling of abundance and distribution of reactive halogen species in the troposphere is not even possible at present. Nevertheless the modelling effort appears to be a useful exercise, however it is important to more clearly state what can be accomplished with models at present and what not.

In particular it would be very helpful if the following could be stated:
1) What are the real uncertainties in the model results taking into account our knowledge gaps. And what is the uncertainty of stated numbers (e.g. the tropospheric O3 loss due to halogen reactions and its vertical distribution as shown in Fig. 13). The real uncertainties are clearly much larger than the differences between the various scenarios (given in Table 7).
2) Where are the most important gaps in our knowledge, both in the area of input data (e.g. precursor fluxes) and regarding mechanistic data.
3) What could be done in the future to improve the situation
Response: We address each of the individual points below.

In detail there are many open questions and points to improve as shown in the (incomplete) numbered list below. For instance what is the Definitions of 'halogens' in the text (e.g. in the 1st line of the abstract certainly not just halogen molecules or halogen atoms are meant) and of 'reactive halogen' and 'Bry'.
Response: "Reactive halogens species, containing Cl, Br and I" from Saiz-Lopez and von Glasow (2012). Br_Y is defined as inorganic bromine. These definitions are now included in the updated manuscript as follows:
"This study investigates the impact of reactive halogen species (RHS, containing chlorine (Cl), bromine (Br) or iodine (I))".

Overall I feel that this manuscript has the potential to become an important contribution to our understanding of tropospheric halogen chemistry once the authors had a chance to make the above additions and to answer the many unclear points listed below. Unfortunately due to the simplistic implementation of aerosol reactions (Equation (2), see comment 22) below) the model runs must be repeated with a state of the art parameterisation of heterogeneous aerosol reactions. This is also likely to change many results of the manuscript. In view of the many required changes and the many unclear points a very major revision of the manuscript is required.

Response: The authors wish to thank anonymous reviewer #2 for his/her valuable comments and suggestions.

We agree with the reviewer that current understanding of the sources of halogen species and their chemistry is limited. Much of this is due to a lack of field observations with which to constrain model input and to evaluate models with. The new observations from TORERO provide a great opportunity to advance our understanding of the importance of reactive halogens in the tropical marine atmosphere and to highlight gaps in knowledge and this paper is part of that process. This contribution describes an important step in the understanding the tropospheric halogen chemistry because it is the first time that halogen chemistry (including bromine, chlorine and iodine) has been implemented into a regional online chemistry transport model. Of course there are limitations and the suggestions made by the reviewer in points 1 - 3 above are very valuable and we have made improvements to the manuscript to address them - see below.

Heterogeneous chemistry (uptake coefficients and surface aerosol area), photolysis rates (especially iodine photochemistry (Sommariva et al., 2012)), the chemical mechanism for the repartitioning of Br_y resulting from the reactions of Br with VOCs, interactions between halogens and the sulfur cycle (Chen et al., 2017, Chen et al., 2018), physical constants (such as Henry's Law value for HOI), deposition of halogenated species and inputs to calculate the oceanic fluxes (e.g. sea-water concentration, including iodide concentrations) are the most important gaps in our knowledge. We have discussed these more in the revised manuscript, in particular emphasizing how the results of our study contribute to this.

We are aware that our treatment of the aerosol chemistry is a simplification, but it is an approach in-line with many other studies published since the Schwartz and Freiberg paper in 1967. Due to computational resource limitations, large-scale models must be parameterized representations of reality. Furthermore, we are limited by the input data with which to constrain these parametrizations.

One important limitation is information with which to constrain a more detailed treatment of the heterogeneous chemistry. We have taken an approach similar to that used with other models such as TOMCAT (Yang et al., 2008), CAM-Chem (Ordoñez et al., 2012) and GU–WRF/Chem (Karamchandani et al., 2012). In this approach the heterogeneous chemistry is assumed to take place between a gas-phase species and an adsorbed species with an uptake coefficient (γ) used to calculate first-order rate constants for heterogeneous loss of the gas-phase species. There are large uncertainties in these uptake coefficients. Moreover, there are uncertainties in the ability of the model to simulate the aerosol size distribution (and thus aerosol surface area) and the mixing state and surface composition of the aerosols. In addition, there are a limited number of measurements with which to evaluate the model and these measurements have their own uncertainties. We agree that ignoring the diffusion limitation will artificially increase the heterogeneous reactions in the model, however we feel this is one of several uncertainties that will affect the rate of heterogeneous chemistry. Instead of focusing on one factor, we prefer to address the wider uncertainties in the heterogeneous chemistry through sensitivity studies in which γ is varied.

To illustrate the sensitivity of our results to this we have made a new run assuming that γ is reduced by a factor of 2 (WRF-GAMMADV2). Moreover, simulations WRF-NOALD, WRF-
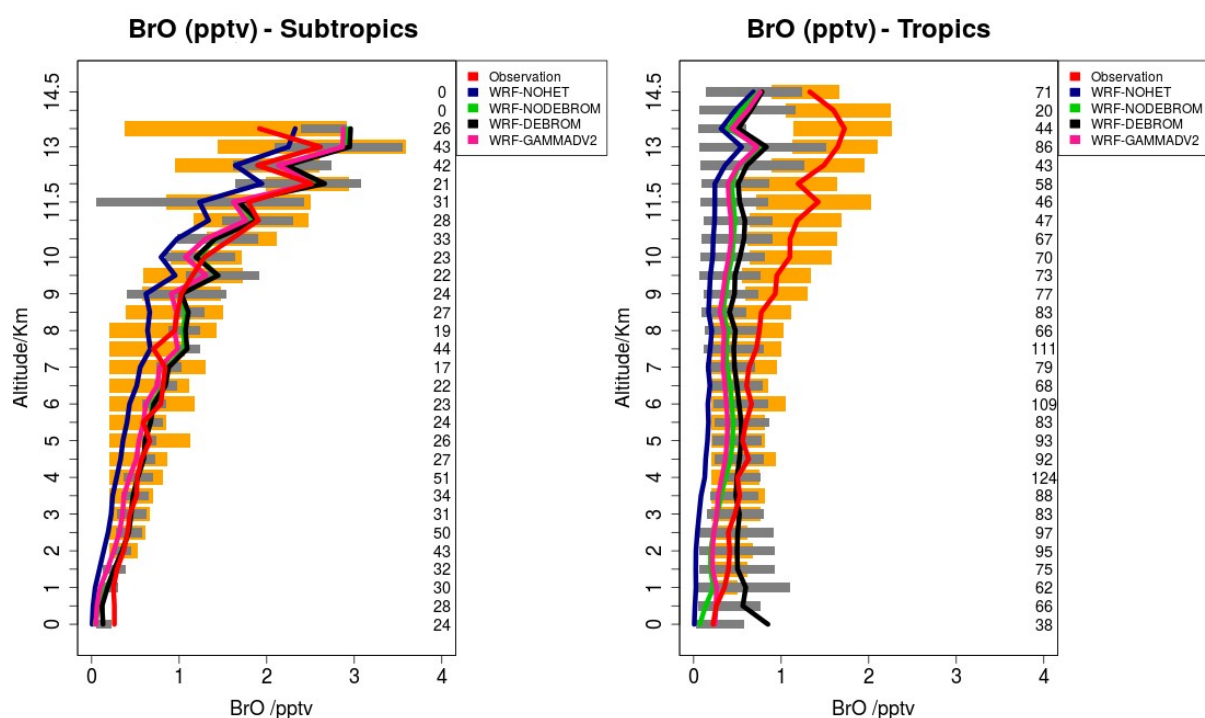
Figure 1. Mean vertical profile of BrO (pptv) over the subtropics (left) and tropics (right). An average over 16 flights of the TORERO campaign (red line) are compared to the 4 different WRF-Chem simulations: WRF-NOHET (blue line), WRF-NODEBROM (green line), WRF-DEBROM (black line) and WRF-GAMMADV2 (pink line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bins and the number of aircraft measurement points for each altitude are given on the right side of each plot.
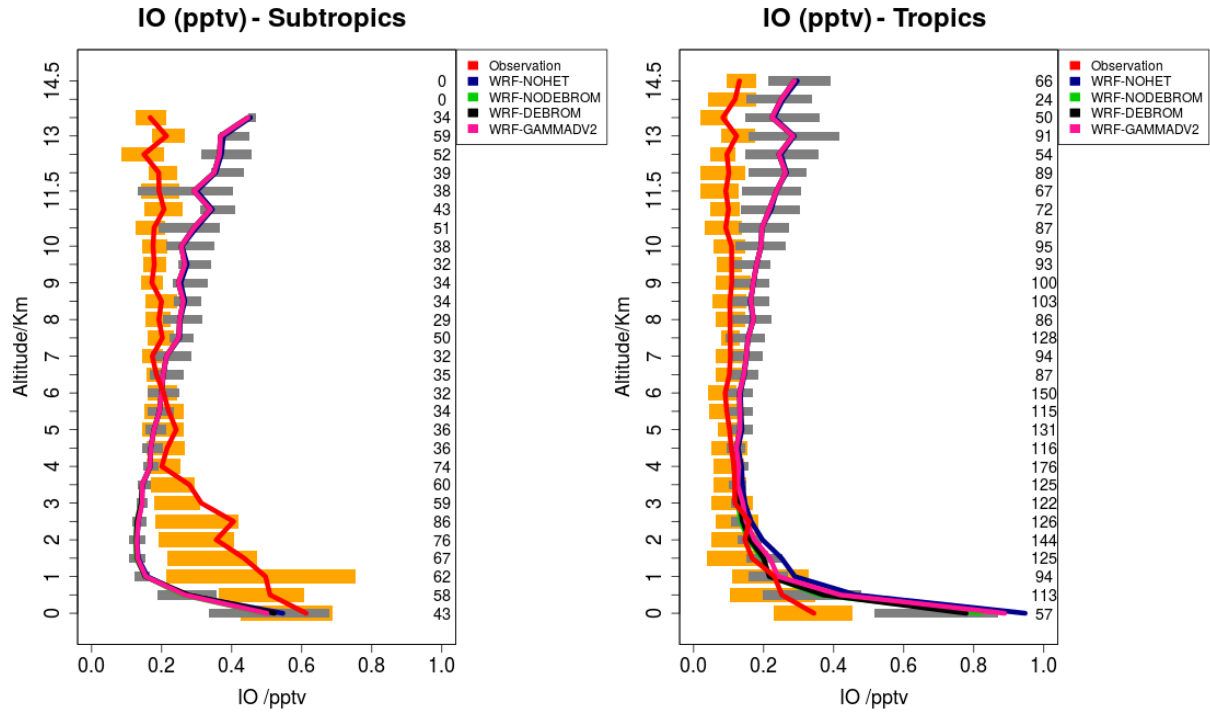
Figure 2. Mean vertical profile of IO (pptv) over the subtropics (left) and tropics (right). An average over 16 flights of the TORERO campaign (red line) are compared to the 3 different WRF-Chem simulations: WRF-NOHET (blue line), WRF-NODEBROM (green line), WRF-DEBROM (black line) and WRF-GAMMADV2 (pink line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bins and the number of aircraft measurement points for each altitude are given on the right side of each plot.

Figure 3: Regional average vertical partitioning of inorganic chlorine (Cl_y) for the two different simulations WRF-NOHALVOCS (left panel) and WRF-DEBROM (middle panel) during January and February 2012. Regional average vertical partitioning of reactive chlorine species (Cl^*) for WRF-DEBROM is also showed (right panel). Cl^* is defined as Cl_y gases other than HCl. Top panels are over the subtropical area and bottom panels over the tropical. Units are in pptv.

Figure 4: A) Mean vertical profile of BrO (pptv) over the tropics in the left panel. A sub-set of 9 flights from the TORERO campaign (red line) are compared to the 4 different WRF-Chem simulations: WRF-NOBRALKE (blue line), WRF-NOBRALD (green line), WRF-NOBRVOCS (blue line) and WRF-DEBROM (black line). B) Regional average vertical partitioning of inorganic bromine (Bry) for the the WRF-NOBRVOCS run over the subtropical area (left panel) and over the tropical area (right panel) during January and February 2012. C) and D) the WRF-DEBROM (black line) simulation is compared with acetaldehyde and formaldehyde TORERO observations for the same flights (red line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bin and the number of points for each altitude is given on the right side of each plot. Units are in pptv.
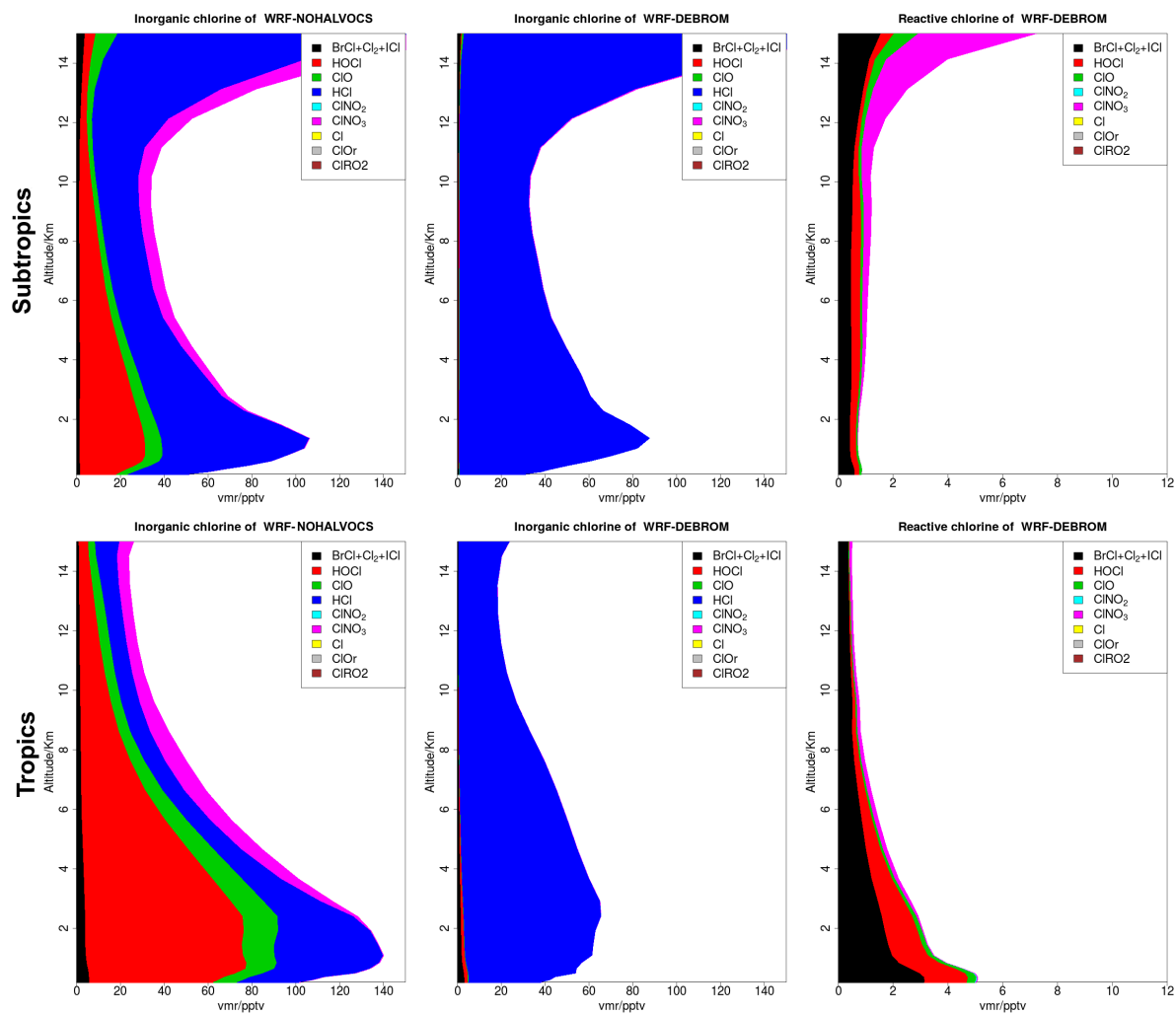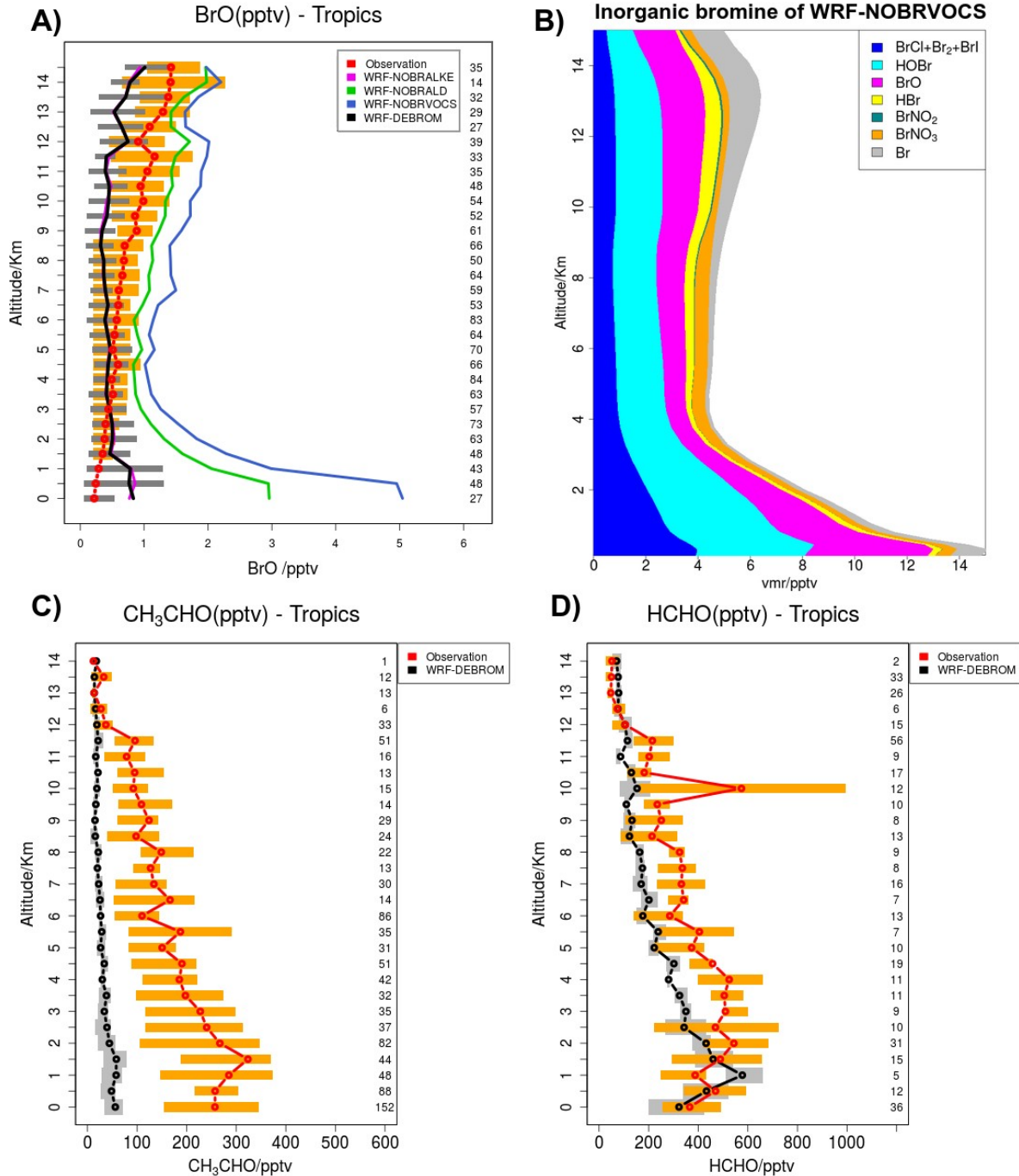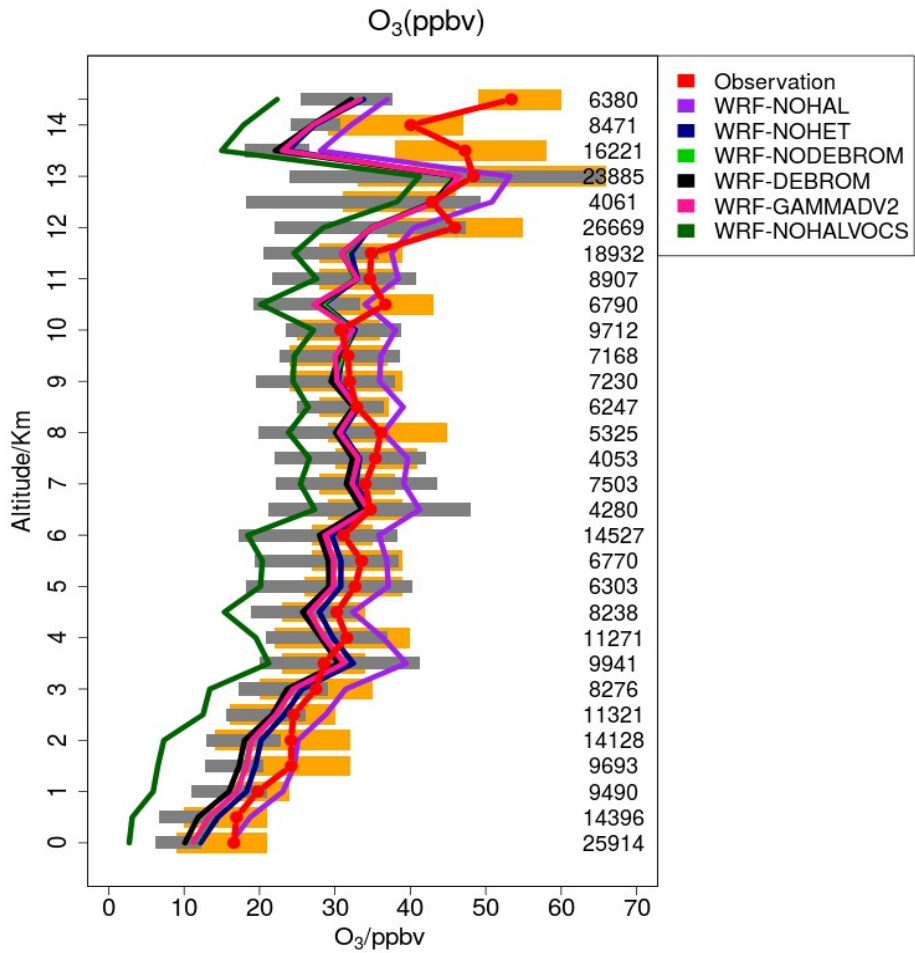
Figure 5. On the left, mean vertical profile of O_3 (ppbv) over the domain area using 13 flights from the TORERO campaign (red line) are compared to the 6 different WRF-Chem simulations: WRF-NOHAL (purple line), WRF-NOHET (blue line), WRF-NODEBROM (light green line), WRF-DEBROM (black line), WRF-GAMMADV2 (pink line) and WRF-NOHALVOCS(dark green line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bins and the number of aircraft measurement points for each altitude are given on the right side of each plot.
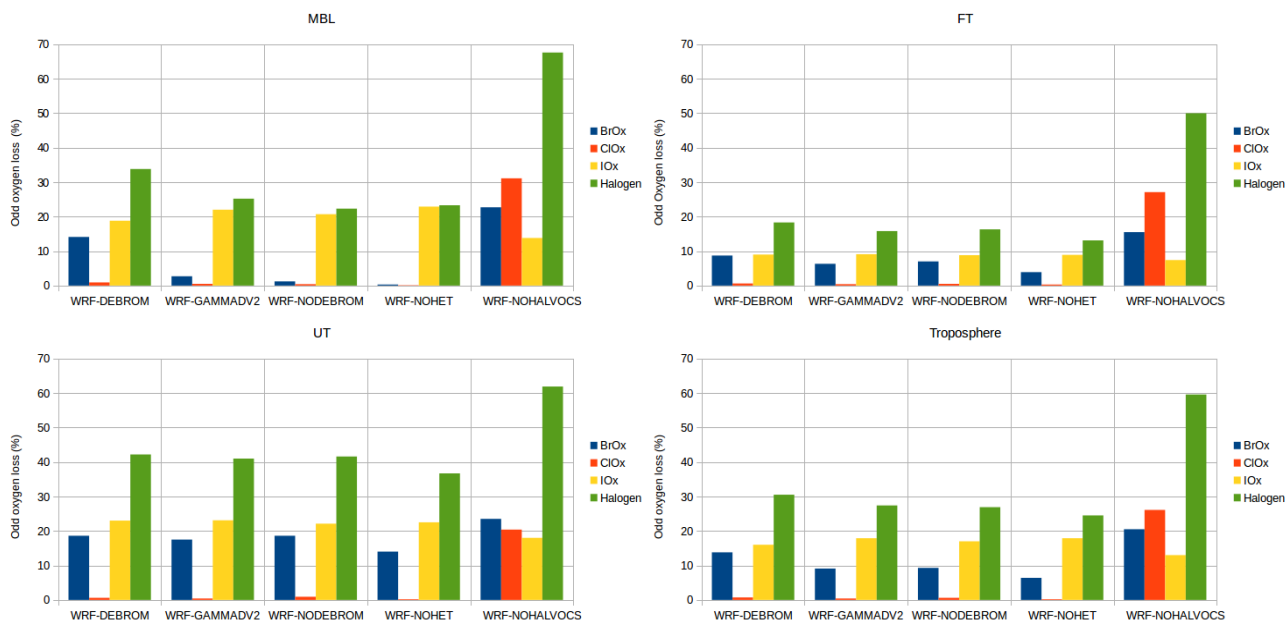
Figure 6. Integrated odd oxygen loss rates for each O3 depleting halogen family within the troposphere at different altitude levels: MBL (surface - 900 hPa), FT (900 hPa- 350 hPa), UT (350 hPa-tropopause) and troposphere (surface-tropopause) for the WRF-DEBROM, WRF-GAMMADV2, WRF-NODEBROM, WRF-NOHET and WRF-NOHALVOCS simulation.

New text has been added to the revised manuscript that discuss the results and the uncertainty of the stated numbers, such as the tropospheric O_3 loss due to halogen reactions and its vertical distribution. The main new points that have been added are:

"Areas, such as the tropics, where debromination dominates, the impact of halving gamma (WRF-GAMMADV2 run) is approximately half of the impact of including heterogeneous chemistry (i.e. the difference between the WRF-DEBROM run and the WRF-NOHET run) at least for the lower troposphere. Very little impact is seen in the UT, a slight decrease in BrO, when gamma is halved (WRF-GAMMADV2)."

"Changing GAMMA (difference between the WRF-DEBROM and WRF-GAMMADV2 runs) has very little impact on IO."

"The heterogeneous halogen chemistry has an impact on O_3 concentrations where a difference of up to 3 ppbv of O_3 is seen between the simulation with and without heterogeneous chemistry (WRF-DEBROM run WRF-NOHET run, respectively) mainly in the MBL. The modelled O_3 is highly sensitive to the inclusion of the reactions of the halogens with the VOCs (WRF-NOHALVOCS) where O_3 concentrations are much lower (between 12-7 ppbv) than in the WRF-DEBROM run."

"When comparing different simulations with the WRF-DEBROM run, the biggest difference is seen with WRF-NOHALVOCS simulation, where around 60% of O_x is removed by halogens. BrO is much higher when the VOC reactions are not included (see Fig. 11), which explains why the amount of O_x lost by BrO_x reactions is much larger (20.5%). Moreover, the big change though is for the ClO_x which increases from < 1% to 26%. Cl is very important in the oxidation of the alkanes. When this chemistry is not included the concentrations of Cly increases and there is an impact on the partitioning increasing reactive species (see Fig. 12), hence, the ClO_x cycles play an important role in O_x loss. It should be noted that very little is known about the abundance and distribution of Cly so this is a large uncertainty. Therefore, a large uncertainty in the impact of halogen cycling on the O_3 budget are the reactions of halogens with VOCs. In the model runs performed, excluding these reactions doubled the percentage contribution of halogens to O_x loss (i.e. increase it from 31% to 60%) in the troposphere. Heterogeneous chemistry (including debromination) has the effect of increasing the O_x loss by halogen cycling from 25 to 31% for the whole troposphere (i.e. comparision between WRF-NOHET and WRF-DEBROM runs). For the UT the equivalent values are 37% to 40%, for the FT 13% to 18% and for the MBL 23% to 34%. Hence, heterogeneous chemistry increases the percentage of the O_x loss that is attributable to the halogens by about 6% for the troposphere ranging from 3% to 11% depending on the region of the troposphere. Note that the gas phase halogen chemistry makes a bigger contribution of around 25% (WRF-NOHET run) to the O_x loss for the troposphere ranging from 13% to 37% depending on the region of the troposphere. Therefore, the overall impact of the halogen chemistry on O_x loss appears not to be very sensitive to the treatment of the heterogeneous chemistry."

Future steps should focus on providing more data from laboratory studies along with field observations to better constrain the modelled representation of halogen species. Only a few Br_y and I_y species are provided from field campaigns making it difficult to evaluate the model against observations and a very limited amount of data exist to compute the sea-water

concentration for the halocarbons, giving uncertainty in this input data when the halocarbon fluxes are computed. Furthermore, it is clear that we need to understand better the emissions and distributions of VOCs in the remote atmosphere, and the impact of their chemistry on halogen repartitioning.

Yang, X., J. A. Pyle, and R. A. Cox (2008), Sea salt aerosol production and bromine release: Role of snow on sea ice, Geophys. Res. Lett., 35, L16815, doi:10.1029/2008GL034536.

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G., and Saiz-Lopez, A.: 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, https://doi.org/10.5194/acp-12-1423-2012, 2012.

Karamchandani et al., 2012: Development of an extended chemical mechanism for global-through-urban applications, Atmospheric Pollution Research 3 (2012), doi:10.5094/APR.2011.047

Chen, Q., J. A. Schmidt, V. Shah, L. Jaeglé, T. Sherwen, and B. Alexander (2017), Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets, Geophys. Res. Lett., 44, 7069–7078, https://doi.org/10.1002/2017GL073812

Chen, Q., Sherwen, T., Evans, M., and Alexander, B.: DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry, Atmos. Chem. Phys., 18, 13617-13637, https://doi.org/10.5194/acp-18-13617-2018, 2018.

R. Sommariva, W.J. Bloss, R. von Glasow, Uncertainties in gas-phase atmospheric iodine chemistry, Atmospheric Environment, Volume 57, 2012, 219-232, 1352-2310,https://doi.org/10.1016/j.atmosenv.2012.04.032.

Detailed comments:
1) Page 2, line 4: Define the term 'reactive halogens'
Response: "Reactive halogens species, containing Cl, Br and I" from Saiz-Lopez and von Glasow (2012). This definition is now included in the revised manuscript (1st line of the abstract).

A. Saiz-Lopez and R. von Glasow. Reactive halogen chemistry in the troposphere. Chem. Soc. Rev., 41:6448–6472, 2012. doi:10.1039/C2CS35208G. URL http://dx.doi.org/10.1039/C2CS35208G.

2) Page 2, line 5: Only Cl-atoms 'reduce the lifetime of CH4'
Response: Amended. The manuscript has been changed.

3) Page 2, lines 6, 7: Define the term 'halogen species', also the statement '. . . play an important role in the oxidation capacity . . .' appears to be a repetition of the statements made above.

Response: Yes it is a repetition, so this sentence has been removed from the revised manuscript.

4) Page 2, line 10: what should be the effect on 'oxidation capacity' beyond the already mentioned CH4 and particles?
Response: We do not understand the reviewer's question. In the paragraph that the reviewer points to we already briefly explain how halogen chemistry affects the budgets of key oxidants in the atmosphere in order to provide relevance and justification for this study. The original paragraph with minor modifications in response to other comments is copied below and we cannot see what additional information the reviewer is asking for.

"Reactive halogens cause ozone (O_3) destruction, change the HO_X (HO_2 + OH) and NO_X (NO_2 + NO) partitioning, affect the oxidation of VOCs and mercury, and take part in new particle formation (Chameides and Davis, 1980; von Glasow et al., 2004; Saiz-Lopez and von Glasow, 2012). Moreover, reactive chlorine reduces the lifetime of methane (CH_4). Halogen species are known to play an important role in the oxidising capacity of the troposphere. The atmospheric oxidation capacity is to a large extent determined by the budgets of the hydroxyl radical (OH) and O_3; globally most tropospheric OH is found in the tropics (Bloss et al., 2005). Therefore a quantitative understanding of the composition and chemistry of the tropical marine atmosphere is essential to examine the atmospheric oxidative capacity and climate forcing."

5) Page 2, lines 12-15: What about fluorine? Are there not other cycles, e.g. XO self reactions and cross reactions like BrO + IO, . . .?
Response: We don't consider fluorine chemistry in the model.

"Fluorine atoms are so reactive that they form HF very rapidly and play no role in tropospheric chemistry." from Saiz-Lopez and von Glasow (2012).

A. Saiz-Lopez and R. von Glasow. Reactive halogen chemistry in the troposphere. Chem. Soc. Rev., 41:6448–6472, 2012. doi:10.1039/C2CS35208G. URL http://dx.doi.org/10.1039/C2CS35208G.

6) Page 2, lines 16-29: this paragraph should be edited for better structure. At present the authors talk about 'numerical models' in general then progress to global and regional models, then progress to specific models (e.g. WRF chem)
Response: This paragraph has been rewritten for better structure as follows:

"In the past, tropospheric halogen chemistry has been studied using a number of box models and 1D models (Sander and Crutzen, 1996; von Glasow et al., 2002a; Saiz-Lopez et al., 2006; Simpson et al., 2015; Lowe et al., 2009; Sommariva and von Glasow, 2012). Currently, there are several global models that have been used to study tropospheric halogens (Hossaini et al., 2010; Ordóñez et al., 2012; Saiz-Lopez et al., 2012a; Fernandez et al., 2014; Saiz-Lopez et al., 2015; Sherwen et al., 2016b; Schmidt et al., 2016). Numerical models predict that reactive halogen compounds account for 30% of O_3 destruction in the MBL (von Glasow et al., 2002b, 2004; Saiz-Lopez et al., 2015; Sherwen et al., 2016b) and 5-20% globally (Yang et al., 2005; Saiz-Lopez et al., 2015, 2012a; Sherwen et al., 2016b). Up to 34% of O_3 loss is calculated to be due to I and Br combined the tropical East Pacific

(Wang et al., 2015). However, there are only a few regional models that have studied tropospheric halogens. Chlorine chemistry was implemented into the WRF-Chem model (Lowe et al., 2015; Li et al., 2016) and into the CMAQ model (Sarwar et al., 2014) to study the formation of nitryl chloride ($ClNO_2$) from the uptake of dinitrogen pentoxide (N_2O_5) on aerosols containing chloride. Moreover, bromine and iodine chemistry was implemented in CMAQ in Gantt et al. (2017) and Sarwar et al. (2015), where the impact of iodide-mediated O3 deposition on surface ozone concentrations was studied, and in the recent work of Muñiz-Unamunzaga et al. (2018), that concluded that oceanic halogens and dimethyl sulfide (DMS) emissions need to be included into the regional models to accurately reproduce the air quality in coastal cities."

7) Page 2, line 30: Give definition of VSLH.
Response: Very Short Lived Halocarbons (VSLH) are defined as trace gases whose chemical lifetimes are generally under six months. This information is now included in the revised manuscript.

8) Page 3, line 1: What about the direct transport of XO?
Response: The lifetime of XO radicals is sufficiently short, ranging from minutes to one hour. Thus, direct transport of XO is not considered.

9) Page 3, line 11: Which OVOC species do the authors have in mind?
Response: Basically aldehydes. Aldehydes species that have been included in the model are formaldehydes and acetaldehydes. This is described in section 3.2.1.

10) Page 3, lines 15-19: Which heterogeneous reactions do the authors have in mind? Why is Cl not mentioned?
Response: Heterogeneous reactions involving reactive halogen species are included in the model. This is now clarified in the revised manuscript.
Cl is not mention here because we try to explain observations of BrO and IO and there are no reported direct observations of Cl.

How does debromination work? Is it different from heterogeneous Br-release through HOBr and BrNO3? Is there not also de-iodination and de-chlorination? Actually it would be good to have a list of sources of halogen atoms.
Response: Debromination is the process by which sea-salt aerosols are depleted in bromide (Br⁻) through the release of Br into the gas-phase. It occurs through the uptake of a gaseous species into the sea-salt and the subsequent reaction with Br⁻ (Yang et al, 2005). We represent this as release of Br through heterogeneous reactions that involve uptake of gases species including HOBr and $BrNO_3$. We described this in more detail on page 7. We changed the text on pages 3 and 7 to make it clearer what we mean by debromination:

Page 3: "Another source of reactive inorganic bromine in the troposphere is the release of bromide (Br⁻) from sea-salt aerosols into the gas-phase. This is known as debromination and occurs through the uptake of a gaseous species in the sea-salt and the subsequent reaction with Br⁻.
Page 7. "It is known that the chemistry involving the release of bromine from the sea-salt aerosol (debromination) is strongly pH dependent, being more efficient for acidified aerosol especially with a pH < 5.5 (Keene et al., 1998). Therefore, the pH value of the aerosol

particles is calculated in the model for each size bin (see Zaveri et al. (2008) for further description of the pH calculation). We then apply a pH dependence to the heterogeneous reactions that occur on the surface of the sea-salt. When the pH < 5.5 debromination reactions occur with the release of Br_2 and IBr resulting from the uptake of $BrNO_3$, $BrNO_2$, $HOBr$, INO_3, INO_2 and HOI (R11-R16). When the pH > 5.5 no debromination reactions occur, although uptake of INO_3, INO_2 and HOI on the sea-salt still occurs (R17-R19)".

Whilst the processes of deiodination and dechlorination do occur, they are not thought to be important sources of atmospheric I^- and Cl^- so we do not include them in the model.

List of sources of halogen atoms considered in this study: oceanic source of organic halogens ($CHBr_3$, CH_2Br_2, CH_3I, CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, CH_2I_2, CH_2IBr and CH_2ICl), debromination (Br_2, IBr) and inorganic I from the ocean (HOI and I_2). This list has been added in the revised manuscript in Sec. 3.

11) Page 3, lines 19-22: What does 'This source' refer to?
Response: This 'source' refers to the 'source' mention in the previous sentence i.e. 'debromination', the last word in the previous sentence. However, with the rewording made to address the previous point "This source has been included" has been replaced with "Debromination has been included as a source of gas-phase bromine".

What exactly is poorly understood?
Response: With the rewording of the previous sentence "this process" now clearly refers to debromination.

What do the authors mean with 'inconsistent levels' too high or too low?
Response: The authors mean inconsistent high levels of bromine species. This is now clarified in the revised manuscript.

12) Page 3, line 23: Do the authors really mean to state that all atmospheric models are largely untested or does this statement rather pertain to halogen chemistry in models?
Response: This statement pertains to halogen chemistry in models. We have rewritten the start of this sentence in the revised manuscript: "Halogen chemistry in atmospheric models...".

13) Page 3, line 33: 'heterogeneous recycling reactions' of what?
Response: The authors mean "Heterogeneous recycling reactions involving halogens". This is now clarified in the revised manuscript.

14) Page 4, lines 7-9: Here it would be good to have some information on the measurement techniques used.
Response: Air samples from the TORERO ship cruise were taken from a 10m bow mast and surface water samples were taken from the underway supply. Halocarbons in air and water phases were measured using two automated on- line GC-MS systems (Andrews et al., 2015) and calibrated using NOAA standard SX-3570. Ozone was measured by UV absorption (Coburn et al., 2014), OVOCs by the Trace Organic Gas Analyzer (TOGA) (Apel and UCAR/NCAR, 2016), and bromine oxide (BrO) and iodine oxide (IO) radicals were

measured by the University of Colorado Airborne Multi-Axis Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) instrument with typical detection limits of 0.5 pptv for BrO, and 0.05 pptv for IO (Volkamer et al., 2015; Dix et al., 2016).
This information is now included in the revised manuscript in Sec. 2.

S. Coburn, I. Ortega, R. Thalman, B. Blomquist, C. W. Fairall, and R. Volkamer. Measurements of diurnal variations and eddy covariance (EC) fluxes of glyoxal in the tropical marine boundary layer: description of the Fast LED-CE-DOAS instrument. Atmospheric Measurement Techniques, 7(10):3579–3595, 2014. doi:10.5194/amt-7-3579-2014. URL http://www.atmos-meas-tech.net/7/3579/2014/.

Apel, E., & UCAR/NCAR - Earth Observing Laboratory. (2011). Trace Organic Gas Analyzer (TOGA) for HIAPER. UCAR/NCAR - Earth Observing Laboratory. https://doi.org/10.5065/D6DF6P9Q Retrieved December 20, 2016

R. Volkamer, S. Baidar, T. L. Campos, S. Coburn, J. P. DiGangi, B. Dix, E. W. Eloranta, T. K. Koenig, B. Morley, I. Ortega, B. R. Pierce, M. Reeves, R. Sinreich, S. Wang, M. A. Zondlo, and P. A. Romashkin. Aircraft measurements of BrO, IO, glyoxal, NO 2 , H 2 O, O 2 –O 2 and aerosol extinction profiles in the tropics: comparison with aircraft-/ship-based in situ and lidar measurements. Atmospheric Measurement Techniques, 8(5):2121–2148, 2015. doi:10.5194/amt-8-2121-2015. URL http://www.atmos-meas-tech.net/8/2121/2015/.

S. J. Andrews, S. C. Hackenberg, and L. J. Carpenter. Technical Note: A fully automated purge and trap GC-MS system for quantification of volatile organic compound (VOC) fluxes between the ocean and atmosphere. Ocean Science, 11(2):313–321, 2015. doi:10.5194/os-11-313-2015. URL https://www.ocean-sci.net/11/313/2015/.

15) Page 4, first sentence of section 3.1: See comment 10, above.
Response*: See answer from comment 10 above.*

16) Page 4, line 29: How is Ka parameterised?
Response: *Ka is parameterized following Johnson (2010) which is mainly a function of wind speed and sea surface temperature (SST) taken from the model at each time-step. Following Johnson (2010), Ka = (1/ka+KH/kw)$^{-1}$, where ka is the rate of air-side transfer, kw is the rate of water-side transfer, and KH is the dimensionless gas over-liquid form of Henry's law constant. ka is based on Jeffrey et al. (2010) and kw is based on Nightingale et al 2000. We do not feel it necessary to explain this is the text of the manuscript beyond the first sentence where we cite Johnson (2010).*

Johnson, M. T.: A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas. Ocean Science, 6(4):913–932, 2010. doi:10.5194/os-6-913-2010. URL http://www.ocean-sci.net/6/913/2010/.

Jeffery, C. D., Robinson, I. S., and Woolf, D. K.: Tuning a physically-based model of the air–sea gas transfer velocity, Ocean Model., 31, 28–35, doi:10.1016/j.ocemod.2009.09.001, 2010.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochem. Cycles, 14(1), 373–387, doi:10.1029/1999GB900091.

17) Page 5, lines 6-8: Give examples for OVOC's emitted from the ocean.
Response: OVOCs emitted from the ocean are acetaldehyde, ethanol and methanol. Those three are included into the model. This is now clarified in the revised manuscript:

"For the three OVOCs (acetaldehyde (CH_3CHO), ethanol (C_2H_6O) and methanol (CH_3OH)), the same online approach for the VSLH is used to calculate the marine fluxes where their sea-water concentrations are taken from Yang et al. (2014)."

18) Page 5, line 8: Which VOC's were included?
"the model as follows, the same... (2014); emissions for alkenes.. "
Response: Acetaldehyde, ethanol, methanol, propane, propene, ethane and ethene are included into the model. This is now clarified in the revised manuscript:

"Oceanic fluxes of several VOCs have been included into the WRF-Chem as part if this study. For the three OVOCs (acetaldehyde (CH_3CHO), ethanol (C_2H_6O) and methanol (CH_3OH)), the same online approach for the VSLH is used to calculate the marine fluxes where their sea-water concentrations are taken from Yang et al. (2014).
Emissions for alkenes and alkanes (C_2H_4, C_3H_6, C_2H_6, C_3H_8) are prescribed and based on the POET (Granier et al., 2005) global inventory."

19) Page 5, lines 16-17: Give some details on sea-salt emission parameterisation.
Response: The sea-salt aerosol emission parameterization from Archer-Nicholls et al. (2014) is used in this study. This parameterization is mainly a function of wind speed from the model and uses the emissions scheme from Gong et al. (1997) for particles with dry diameters of 0.45nm or more and for smaller particles uses Fuentes et al. (2010). This information is now included in the revised manuscript as follows:

"The sea-salt aerosol emissions parameterization used in this study is described in Archer-Nicholls et al. (2014). This parameterization is mainly a function of wind speed from the model and uses the emissions scheme from Gong et al. (1997) for particles with dry diameters of 0.45nm or more and for smaller particles uses Fuentes et al. (2010)."

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., Hodnebrog, Ø., Denier van der Gon, H., and McFiggans, G.: Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem, Geosci. Model Dev., 7, 2557-2579, https://doi.org/10.5194/gmd-7-2557-2014, 2014.

Gong, S. L., Bartie, L. A., and Blanchet, J.-P.: Modeling sea-salt aerosols in the atmosphere 1. Model development, J. Geophys. Res., 102, 3805–3818, 1997.

Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol – Part

1: Source fluxes, Atmos. Chem. Phys., 10, 9295–9317, doi:10.5194/acp-10-9295- 2010, 2010.

20) Page 5, lines 21-25: This description is not quite clear. When 'Most of the reactions come from ... MISTRA', which ones?

Response: Inorganic, organic and inter-halogens reactions from Tables 2, 3 and 4 come from MISTRA. Moreover, the chemical loss of VSLH through oxidation by the hydroxyl radical (OH) and by photolysis was included using data from Sander et al. (2011b).
This information is now clarified in the revised manuscript.

How is the high uncertainty of I2Ox reactions dealt with?

Response: We have not tested the sensitivity of the results to the uncertainty of these reactions. We have included the state-of-the-art knowledge of these reactions (Saiz-Lopez et al., 2014).

A. Saiz-Lopez, R. P. Fernandez, C. Ordóñez, D. E. Kinnison, J. C. Gómez Martín, J.-F. Lamarque, and S. Tilmes. Iodine chemistry in the troposphere and its effect on ozone. Atmospheric Chemistry and Physics, 14(23):13119–13143, 2014. doi:10.5194/acp-14-13119-2014. URL http://www.atmos-chem-phys.net/14/13119/2014/.

21) Page 5, lines 31-33: Explain 17 bins and give a few details on FTUV. It would also be good to give e.g. noontime values of the photolysis frequencies (e.g. in Table 4).
Response: The Fast Tropospheric Ultraviolet-Visible model (FTUV) photolysis scheme is based on the Tropospheric Ultraviolet-Visible model (TUV) model developed by Madronich (1987) and uses a modified wavelength grid between 121–850 nm, where the number of spectral bins is reduced from 140 to 17 (Tie et al., 2004).

FTUV is a well-known and often used photolysis scheme. It is included as a standard option within WRF-Chem. We believe it is sufficient to refer to the paper Tie et al (2003) which describes the scheme in detail.

Below are the photolysis frequencies for a specific latitude and altitude at solar noon and under clear skies in response to the reviewer. However, these will vary throughout the model domain as a function of solar zenith angle, altitude and cloud cover so we feel that it would be misleading to include them in Table 4 of the paper.

Table 1. Photolysis reactions of halogens included in WRF-Chem.

Photolysis reactions	Photolysis rates (s^{-1})
$Cl_2 \xrightarrow{h\nu} 2\ Cl$	2.5×10^{-3}
$OClO\ (+O_2) \xrightarrow{h\nu} O_3 + ClO$	8.2×10^{-2}
$HOCl \xrightarrow{h\nu} Cl + OH$	3.0×10^{-4}
$ClNO_2 \xrightarrow{h\nu} Cl + NO_2$	5.7×10^{-4}
$ClNO_3 \xrightarrow{h\nu} Cl + NO_3$	4.3×10^{-5}

Reaction	Value
$ClNO_3 \xrightarrow{h\nu} ClO + NO_2$	4.7×10^{-4}
$Br_2 \xrightarrow{h\nu} 2\,Br$	3.1×10^{-2}
$BrO \xrightarrow{h\nu} Br\ (+O_3)$	4.2×10^{-2}
$HOBr \xrightarrow{h\nu} Br + OH$	2.2×10^{-3}
$BrNO_2 \xrightarrow{h\nu} Br + NO_2$	2.6×10^{-2}
$BrNO_3 \xrightarrow{h\nu} Br + NO_3$	3.8×10^{-4}
$BrNO_3 \xrightarrow{h\nu} BrO + NO_2$	9.5×10^{-4}
$I_2 \xrightarrow{h\nu} 2\,I$	1.6×10^{-1}
$IO\ (+O_2) \xrightarrow{h\nu} I\ (+O_3)$	1.5×10^{-3}
$I_2O_4 \xrightarrow{h\nu} OIO + OIO$	7.3×10^{-3}
$OIO \xrightarrow{h\nu} I\ (+O2)$	2.0×10^{-1}
$I_2O_2 \xrightarrow{h\nu} I + OIO$	2.8×10^{-2}
$HOI \xrightarrow{h\nu} I + OH$	8.6×10^{-3}
$INO \xrightarrow{h\nu} I + NO$	3×10^{-2}
$INO_2 \xrightarrow{h\nu} I + NO_2$	3.3×10^{-3}
$INO_3 \xrightarrow{h\nu} I + NO_3$	1.0×10^{-2}
$I_2O_3 \xrightarrow{h\nu} OIO + IO$	3.0×10^{-2}
$IBr \xrightarrow{h\nu} I + Br$	7.3×10^{-2}
$ICl \xrightarrow{h\nu} I + Cl$	2.3×10^{-2}
$BrCl \xrightarrow{h\nu} Br + Cl$	1.0×10^{-2}
$CHBr_3\ (+O_2) \xrightarrow{h\nu} 3\,Br$	1.4×10^{-6}
$CH_3Br \xrightarrow{h\nu} Br + CH_3O_2$	3.2×10^{-22}
$CH_2Br_2 \xrightarrow{h\nu} 2Br$	1.6×10^{-9}
$CH_2BrCl \xrightarrow{h\nu} Br + Cl$	7.3×10^{-12}
$CHBrCl_2 \xrightarrow{h\nu} Br + 2\,Cl$	4.5×10^{-7}
$CHBr_2Cl \xrightarrow{h\nu} 2Br + Cl$	2.7×10^{-7}
$CH_2I_2 + (O_2) \xrightarrow{h\nu} 2\,I$	1.0×10^{-2}
$CH_3I \xrightarrow{h\nu} I + CH_3O_2$	8.7×10^{-6}
$CH_2ClI \xrightarrow{h\nu} I + Cl + 2\,HO_2 + CO$	1.8×10^{-4}
$CH_2IBr \xrightarrow{h\nu} Br + I$	5.3×10^{-4}

Tie, X., S. Madronich, S. Walters, R. Zhang, P. Racsh, and W. Collins (2003), Effect of clouds on photolysis and oxidants in the troposphere, J. Geophys. Res., 108, 4642, doi: , D20.

22) Page 6, Section 3.3, Equation (2) is simplistic in that it neglects diffusion limitations, which can be important at uptake coefficients higher than about 0.01, see e.g. Schwartz and Freiberg 1967. The authors should check likely changes in model results when more realistic parameterisations of heterogeneous reactions are used. Schwartz S.E. and Freiberg J.E. (1967), Mass-transport limitation to the rate of reac-

tion of gases in liquid droplets: Application to oxidation of SO2 in aqueous solutions, Atmospheric Environment 15, (7),1129-1144

Response: See response above.

23) Page 7, Lines 13-28: Are reactions R11 and R12 not occurring at pH > 5.5?

Response: Reactions R11-R16 occurs only when pH < 5.5 and reactions R17-R19 only when pH> 5.5.

This is clarified in the document "We then apply a pH dependence to the heterogeneous reactions that occur on the surface of the sea-salt. When the pH < 5.5 debromination reactions occur with the release of Br_2 and IBr resulting from the uptake of $BrNO_3$, $BrNO_2$, HOBr, INO_3, INO_2 and HOI (R11-R16). When the pH > 5.5 no debromination reactions occur, although uptake of INO_3, INO_2 and HOI on the sea-salt still occurs (R17-R19)"

 What about mass conservation in R13?
Response: In this simplification we do not model the chemistry within the sea-salt explicitly so reactions R11-R19 represent just the changes to the gas phase species. As such mass may not be conserved and in particular for reaction R11-R16 they are intended to add an extra source of Br. The same approach is used in the global models TOMCAT (Yang et al., 2008) and CAM-Chem (Ordoñez et al., 2012).

Yang, X., J. A. Pyle, and R. A. Cox (2008), Sea salt aerosol production and bromine release: Role of snow on sea ice, Geophys. Res. Lett., 35, L16815, doi:10.1029/2008GL034536.

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G., and Saiz-Lopez, A.: 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, https://doi.org/10.5194/acp-12-1423-2012, 2012.

Numbers or reactions are missing in Table 5
Response: No reactions are missing in Table 5.

24) Page 14, lines 15, 16: The model overestimates heterogeneous reactions on aerosol (see comment 22, above), thus the increase in the concentration of reactive species like BrO could be just a model effect.
Response: It is true that neglecting diffusion limitations will overestimate the impact of the heterogeneous reactions. As discussed above in response to the reviewer's earlier comment, there are many other uncertainties in the heterogeneous reactions. We have addressed this through sensitivity runs and revisions to the text described above.

25) Page 14, lines 19, 20: The underestimation of aldehydes could be due to neglect of Cl reactions in the model.
Response: The model chemical mechanism is of course a reduction of an explicit scheme, but it does include several reactions of Cl with VOCs that could lead to the formation of aldehydes including reactions of Cl with CH_4, C_2H_6, C_3H_8 and C_3H_6 (See Table 2 and Section 3.2.1). The problem may be a lack of VOCs in the model rather than specifically reactions of VOCs with Cl.

In fact heterogeneous oxidation of halogenides (by O3) is discussed in the text, but does not appear to be implemented in the model, since no reactions to that effect can be found in Table 5.

Response: We do not understand what the reviewer is referring to here. The heterogeneous oxidation of halogenides (by O_3) is not included. All the heterogeneous reactions discussed in the text are included in Table 5.

26) Page 14, line 22: What could be the reason for inorganic iodine emissions being lower than modelled in the tropics?

Response: The biggest uncertainty in the inorganic iodine emissions parameterization is the calculation of the iodide concentration in the sea water. This is now added in the revised manuscript. Other uncertainties in the flux calculation are in the Henry's law of HOI and suppression of flux from DOC (Shaw et al., 2013).

Shaw, M. and Carpenter, L. (2013). Modification of Ozone Deposition and I_2 Emissions at the Air-Aqueous Interface by Dissolved Organic Carbon of Marine Origin. Environmental science & technology. 47. 10.1021/es4011459.

27) Page 14, lines 23, 24: What is the reason for the minor importance of heterogeneous chemistry in the model?

Response: Unlike Br_Y, there is only a small change in the I_Y partitioning with the inclusion of the heterogeneous chemistry: The main change in I_Y with the inclusion of the heterogeneous chemistry occurs near the surface, due to the removal of the iodine oxides, and the production of more di-halogens in the MBL, especially when debromination is included.
Heterogenous iodine reactions (reactions R11-R19 from the manuscript) compete with the photolysis. Iodine species are more readily photolyzed (see Table 1), so less is taken up into the aerosol and the impact of heterogeneous chemistry is less.

28) Page 14, line 25: For which conditions was the 31% contribution to O3 loss calculated?

Response: In the first version of the manuscript, O_X loss calculations presented in the manuscript were from our base simulation, the WRF-DEBROM simulation, where its conditions were described in Sec. 4.1 and Table 7:
"Our base simulation, WRF-DEBROM, considered all main processes involving halogen chemistry (sea-salt debromination, heterogeneous chemistry and reactions between halogens and VOCs) and computes the oceanic halocarbons fluxes online."

However, in order to quantify the uncertainty of O_X loss calculations due to halogens, Fig. 12 have been updated and Fig. 14 has been included with calculations from other simulations. These results are discussed above in the general comment.

29) Page 14, line 26: How can the Ox loss be attributed to Br, I, Cl reactions when cross reactions play a major role (e.g. ClO + BrO)?

Response: Any cross reaction between XO species (where X is Br, Cl and I) will be counted as a loss of O_X and will be attributed to each family involved. i.e. BrO + IO means that the Br family is responsible for the loss of one O_X in the form of IO and at the same time the I family is responsible for the loss of one O_X in the form of BrO. This is clarified in the document "The tropospheric O_X loss due to the BrO_X, IO_X and ClO_X cycles" .

31) Page 14, lines 27-29: What is the meaning of 'negative bias', is it an overestimation of O3 loss?

Response: 'Negative bias' means that the simulation with halogens (WRF-DEBROM) is underestimating the observed O_3 values in the MBL where the oceanic emissions of the halogenated species are higher (see Fig. 12 of the manuscript). The manuscript has been changed to "The simulation with halogens (WRF-DEBROM) is underestimating the observed O_3 values in the MBL, where the oceanic emissions of the halogenated species are higher."

32) Page 14, lines 30-35: the reviewer can only agree with the statement in Line 30. What is the effect of these uncertainties for the conclusions drawn like 'Halogens constitute 31% of the overall ... O3 loss'? Should the conclusion not rather be 'Halogens reactions constitute a considerable fraction (10-60%) of the overall tropospheric O3 loss'?

Response: See comment 28.

33) Caption of Figure 5: It would be more clear if "obs" was changed to "observation". In the time series of CH3I there is a clear anti-correlation between observation and model results during Feb. 5 – 10, can this be explained?

Response: Amended. The word "obs" has been changed to "observation" in all Figures.

Results for low CH_3I during this period are already discussed in the manuscript in Sec. 5.1 "A possible explanation for the underestimation in halocarbon atmospheric concentrations might be due to the input data (e.g. wind speed, SST, sea-water concentration) that we used to compute these fluxes. In the case of the online fluxes, between 6-8 of February the model underestimates wind speed and this is directly accompanied by an underestimation for all three halocarbons atmospheric concentrations. "

F. Ziska, B. Quack, K. Abrahamsson, S. D. Archer, E. Atlas, T. Bell, J. H. Butler, L. J. Carpenter, C. E. Jones, N. R. P. Harris, H. Hepach, K. G. Heumann, C. Hughes, J. Kuss, K. Krüger, P. Liss, R. M. Moore, A. Orlikowska, S. Raimund, C. E. Reeves, W. Reifenhäuser, A. D. Robinson, C. Schall, T. Tanhua, S. Tegtmeier, S. Turner, L. Wang, D. Wallace, J. Williams, H. Yamamoto, S. Yvon-Lewis, and Y. Yokouchi. Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide. Atmospheric Chemistry and Physics, 13(17):8915–8934, 2013. doi:10.5194/acp-13-8915-2013. URL http://www.atmos-chem-phys.net/13/8915/2013/.

34) Table 6: The N2O5 heterogeneous chemistry is not listed in Table 5.

Response: N_2O_5 heterogeneous chemistry was already included in the model version we were using, which is why it was not included in Table 5 which lists the chemistry added as part of the current study. The N_2O_5 chemistry is described in Archer-Nicholls et al., 2014. We have clarified this in the Table 5 heading:

"Table 5. Halogen heterogeneous reactions added to WRF-Chem in this study."

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., Hodnebrog, Ø., Denier van der Gon, H., and McFiggans, G.: Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem, Geosci. Model Dev., 7, 2557-2579, https://doi.org/10.5194/gmd-7-2557-2014, 2014.

Importance of reactive halogens in the tropical marine atmosphere: A regional modelling study using WRF-Chem

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Abstract.

This study investigates the impact of ~~halogens~~ reactive halogen species (RHS, containing chlorine (Cl), bromine (Br) or iodine (I)) on atmospheric chemistry in the tropical troposphere and explores the sensitivity ~~of this~~ to uncertainties in the
5 fluxes of ~~halogens~~ RHS to the atmosphere and ~~the~~ their chemical processing. To do this the regional chemistry transport model WRF-Chem has been extended ~~,~~ to include Br, I as well as Cl chemistry for the first time, ~~to include halogen chemistry (bromine, chlorine and iodine chemistry),~~ including heterogeneous recycling reactions involving sea-salt aerosol and other particles, reactions of Br and Cl with volatile organic compounds (VOCs), along with oceanic emissions of halocarbons, VOCs and inorganic iodine. The study focuses on the tropical East Pacific using field observations from the TORERO campaign
10 (January-February 2012) to evaluate the model performance.

Including all the new processes, the model does a reasonable job reproducing the observed mixing ratios of BrO and IO, albeit with some discrepancies, some of which can be attributed to difficulties in the model's ability to reproduce the observed halocarbons. This is somewhat expected given the large uncertainties in the air-sea fluxes of the halocarbons in a region where there are few observations of their seawater concentrations.

15 We see a considerable impact on the inorganic bromine (Br_y) partitioning when heterogeneous chemistry is included, with a greater proportion of the Br_y in active forms such as BrO, HOBr and dihalogens. Including debromination of sea-salt increases BrO slightly throughout the free troposphere, but in the tropical marine boundary layer, where the sea-salt particles are plentiful
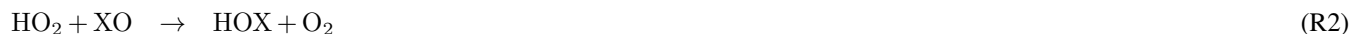
1

and relatively acidic, debromination leads to overestimation of the observed BrO. However, it should be noted that the modelled BrO was extremely sensitive to the inclusion of reactions between Br and the ~~VOCs~~oxygenated VOCs (OVOCs), which convert Br to HBr, a far less reactive form of Br_y. Excluding these reactions leads to modelled BrO mixing ratios greater than observed. The reactions between Br and aldehydes were found to be particularly important, despite the model underestimating the amount of aldehydes observed in the atmosphere. There are only small changes to the inorganic iodine (I_y) partitioning and IO when the heterogeneous reactions, primarily on sea-salt, are included.

Our model results show that ~~the~~ tropospheric O_x loss due to halogens ~~is 31~~ranges between 25-60%. ~~This loss is mostly due to I (16~~Uncertainties in the heterogeneous chemistry accounted for a small proportion of this range (25% ~~) and Br (14~~to 31%)~~and it is~~. This range in good agreement with other estimates from state-of-the-art atmospheric chemistry models. The upper bound is found when reactions between Br and Cl with VOCs are not included and, consequently, O_x lost by BrO_x, ClO_x and IO_x cycles is high (60%). With the inclusion of halogens in the troposphere O_3 is reduced by 7 ppbv on average. However, when reactions between Br and Cl with VOCs are not included O_3 is much lower than observed. Therefore, the tropospheric O_x budget is highly sensitive to the inclusion of halogen reactions with VOCs and to the uncertainties in current understanding of these reactions and the abundance of VOCs in the remote marine atmosphere.

1 Introduction

~~Reactive halogens~~ RHS cause ozone (O_3) destruction, change the $HO_{\sim x}$ (HO_2 + OH) and $NO_{\sim x}$ (NO_2 + NO) partitioning, affect the oxidation of VOCs and mercury, ~~reduce the lifetime of methane,~~ and take part in new particle formation (Chameides and Davis, 1980; von Glasow et al., 2004; Saiz-Lopez and von Glasow, 2012). Moreover, reactive chlorine reduces the lifetime of methane (CH_4). Halogen species are known to play an important role in the oxidising capacity of the troposphere. The atmospheric oxidation capacity is to a large extent determined by budgets of the hydroxyl radical (OH) , and O_3~~and their budgets and cycling~~; globally most tropospheric OH is found in the tropics (Bloss et al., 2005). Therefore a quantitative understanding of the composition and chemistry of the tropical marine atmosphere is essential to examine the atmospheric oxidative capacity and climate forcing.

In the troposphere, reactive halogen species catalyse ozone destruction cycles:

$$O_3 + X \quad \rightarrow \quad XO + O_2 \tag{R1}$$
$$HO_2 + XO \quad \rightarrow \quad HOX + O_2 \tag{R2}$$
$$HOX + hv \quad \rightarrow \quad OH + X \tag{R3}$$

where X= Cl, Br, I.

In the past, tropospheric halogen chemistry has been studied using a number of box models and 1D models (Sander and Crutzen, 1996; vo Currently, there are several global models that have been used to study tropospheric halogens (Hossaini et al., 2010; Ordóñez et al., 2012; Sa Numerical models predict that reactive halogen compounds account for 30% of O_3 destruction in the MBL (von Glasow et al.,

2002b, 2004; Saiz-Lopez et al., 2015; Sherwen et al., 2016b) and 5-20% globally (Yang et al., 2005; Saiz-Lopez et al., 2015, 2012a; Sherwen et al., 2016b). Up to 34% of O_3 loss is calculated to be due to I and Br combined in the tropical East Pacific (Wang et al., 2015). ~~In the past, tropospheric halogen chemistry has been studied using a number of box models and 1D models (Sander and Crutzen, 1996; von Glasow et al., 2002a; Saiz-Lopez et al., 2006; Simpson et al., 2015; Lowe et al., 2009; Sommariva and vo~~

5 ~~Currently, there are several global models that have been used to study tropospheric halogens (Hossaini et al., 2010; Ordóñez et al., 2012; S~~

However, there are only a few regional models that have studied tropospheric halogens. Chlorine chemistry was implemented into the WRF-Chem model (Lowe et al., 2015; Li et al., 2016) and into the CMAQ model (Sarwar et al., 2014) to study the formation of nitryl chloride ($ClNO_2$) from the uptake of dinitrogen pentoxide (N_2O_5) on aerosols containing chlo-

10 ride. Moreover, bromine and iodine chemistry was implemented in CMAQ in Gantt et al. (2017) and Sarwar et al. (2015), where the impact of iodide-mediated O_3 deposition on surface ozone concentrations was studied, and in the recent work of ~~?~~ Muñiz-Unamunzaga et al. (2018) , that concluded that oceanic halogens and dimethyl sulfide (DMS) emissions need to be included into the regional models to accurately reproduce the air quality in coastal cities.

Oceanic emissions provide a source of Very Short Lived Halocarbons (VSLH) to the atmosphere, defined as trace gases with

15 chemical lifetimes generally under six months, mainly in the form of bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and methyl iodide (CH_3I). Once in the atmosphere, VSLH (and their degradation products) can ascend into the lower stratosphere (LS) where they can contribute to the ~~inorganic bromine~~ (Br_y) and lead to ozone depletion. Several emissions inventories for the VSLH have been evaluated at a global scale ~~(Bell et al., 2002; Ziska et al., 2013; Ordóñez et al., 2012; Hossaini et al., 2013; Lennartz e~~ Recent measurements constrain the stratospheric injection of bromine from VSLH as $\sim$5pptv Br_y (Wales et al., 2018) , confirming

20 recent WMO estimates. About 40-50% of the bromine (2.1-2.6 pptv Br_y) is injected into stratosphere as product gases (Koenig et al., 2017; Wales et al., 2018) . Lennartz et al. (2015) presents a comparison of two simulations using the chemistry climate model EMAC. The first simulation computes the oceanic emissions online, mainly driven by the surface water concentrations and modelled meteorological variables, and the second uses prescribed emissions. These results reveal that calculating the air-sea fluxes online leads, in most cases, to more accurate atmospheric mixing ratios in the model in comparison with

25 the simulation using prescribed emissions. Emissions of inorganic iodine compounds (HOI and I_2) have been recognised as a significant source required to reproduce iodine oxide (IO) measurements over the open ocean (Mahajan et al., 2012; Carpenter et al., 2013) and have been included in some global models (Saiz-Lopez et al., 2014; Sherwen et al., 2016b).

There are indications that the chemistry of reactive halogens and oxygenated VOCs (OVOCs) in the tropics are inter-related. Model calculations suggest aldehydes are an important sink for bromine atoms and hence compete with the formation of BrO

30 (Br + O_3 $\rightarrow$ BrO). This illustrates a link between the cycles of halogens and OVOCs in the marine atmosphere (Sommariva and von Glasow, 2012; Toyota et al., 2004).

Recent studies have highlighted the key role that heterogeneous chemistry plays in explaining observations of BrO and IO abundances in the tropical troposphere. Cycling of Br and I through HOBr, $BrNO_3$, HOI and INO_3 is very slow in the gas-phase, making it necessary to include heterogeneous reactions involving reactive halogen species to reproduce observed BrO

35 and IO abundances (von Glasow et al., 2004; Saiz-Lopez et al., 2015; Sherwen et al., 2016a). ~~Another source for~~

Another source of reactive inorganic bromine in the troposphere is the release of ~~bromine radicals by oxidation of bromide in~~ bromide (Br^-) from sea-salt ~~,~~ aerosols into the gas-phase. This is known as debromination ~~. This source~~ and occurs through the uptake of a gaseous species in sea-salt and the subsequent reaction with Br^-. Debromination has been included as a source of gas-phase bromine in several atmospheric models (Yang et al., 2005; Parrella et al., 2012; Ordóñez et al., 2012; Schmidt et al., 2016; Long et al., 2014). However, this process is poorly understood and its inclusion into the models can cause inconsistent high levels of bromine species (Schmidt et al., 2016).

~~Atmospheric~~ Halogen chemistry in atmospheric models remain largely untested due to lack of field observations of halogen species. However, during the last few years there have been four campaigns that provided vertically resolved measurements of halogen radicals: the Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO; Volkamer et al., 2015; Wang et al., 2015; Dix et al., 2016), the CONvective TRansport of Active Species in the Tropics ~~(CONTRAST; Pan et al., 2017; ?)~~ (CONTRAST; Pan et al., 2017; Koenig et al., 2017), the Coordinated Airborne Studies in the Tropics (CAST; Harris et al., 2017) and Airborne Tropical TRopopause EXperiment (ATTREX; Jensen et al., 2017).

The main objective of this study is to investigate the atmospheric chemistry in the tropical East Pacific with a focus on reactive halogens using the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem; Grell et al., 2005) and field data from the TORERO campaign (Volkamer et al., 2015; Wang et al., 2015). Our reaction mechanism in WRF-Chem is based on the MOZART-4 mechanism (Emmons et al., 2010; Knote et al., 2014) and has been extended to include halogen chemistry. Heterogeneous recycling reactions involving halogens have been included into the model, along with oceanic emissions of relevant VOCs and halocarbons. The observational data is described in Sec. 2. Model developments are described in Sec. 3. The model setup and the description of different sensitivity runs are in Sec. 4. The results of the model performance are discussed in Sec. 5. The last section summarizes the conclusions of this work.

2 Observational data

The TORERO campaign (Volkamer et al., 2015; Wang et al., 2015), from 15 January to 1 March 2012, was used to evaluate the model. Data on halocarbons are available from the TORERO ship cruise (Andrews et al., 2015) and flights of the NSF/NCAR GV aircraft, whilst observations of O_3, BrO, IO and ~~oxygenated VOCs (OVOCs)~~ OVOCs are available from the flights. The TORERO cruise aboard the NOAA RV Ka'imimoana (KA-12-01) took place from Honolulu, HI, to Puntarenas, Costa Rica, between 27 January and 1 March 2012. ~~BrO and IO were further measured aboard the NSF/NCAR GV aircraft~~ Air samples from the TORERO ship cruise were taken from a 10m bow mast and surface water samples were taken from the underway supply. Halocarbons in air and water phases were measured using two automated on- line GC-MS systems (Andrews et al., 2015) and calibrated using NOAA standard SX-3570. Ozone was measured by UV absorption (Coburn et al., 2014), OVOCs by the Trace Organic Gas Analyzer (TOGA) (Apel and UCAR/NCAR, 2016), and bromine oxide (BrO) and iodine oxide (IO) radicals were measured by the University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) instrument with typical detection limits of 0.5 pptv for BrO, and 0.05 pptv for IO (Volkamer et al., 2015; Dix et al., 2016). 13 flights provide O_3 data and 16 flights provide BrO and IO data. Fig. 1 displays the location of all the

observational data with an orange line for the cruise track, red lines for the flights in the tropics and green lines for the flights in the sub-tropics.

3 Model description

WRF-Chem (Grell et al., 2005) is a highly flexible community model for atmospheric research where aerosol-radiation-cloud
5 feedback processes are taken into account. Version 3.7.1 is used in this study.

The sources of halogen atoms considered in this study are: inorganic I from the ocean (HOI and I_2), oceanic source of organic halogens ($CHBr_3$, CH_2Br_2, CH_3I, CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, CH_2I_2, CH_2IBr and CH_2ICl) and debromination (Br_2, IBr). These sources are explained in detail below in the following sections.

3.1 Oceanic fluxes

10 The oceanic emission of inorganic iodine (HOI and I_2) follows the deposition of O_3 to the surface ocean and reaction with iodide (I^-) (Carpenter et al., 2013). We use Eqs. 19 and 20 in Carpenter et al. (2013) for the calculation of these emissions. Ocean surface I^- is parameterized using MacDonald et al. (2014) (see Fig. S1 in the supplementary information). Fig. 2 shows the average oceanic emission for inorganic iodine (I_2 in the left panel and HOI in the middle ~~panels~~panel) during January and February 2012. Higher emissions for inorganic iodine occurs in the tropics with HOI being the dominant species.

15 Two different approaches for the marine emissions of the halocarbons ($CHBr_3$, CH_2Br_2, CH_3I, CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, CH_2I_2, CH_2IBr and CH_2ICl) are examined in this model. The first approach uses prescribed monthly average oceanic fluxes from Ziska et al. (2013) and the second computes the oceanic fluxes online. Prescribed monthly average oceanic fluxes from Ziska et al. (2013) were calculated using 6-hourly means of wind speed and sea surface temperature from the ERA-Interim meteorological assimilation database (Dee et al., 2011) for the years 1989-2011 (1° x 1°). Computing the emissions online
20 accounts for an interaction between the modelled atmosphere and the ocean at each time step. Thus, this approach can respond to changes in meteorological parameters, like surface temperature and surface wind speed. ~~The~~ A two-layer model (Liss and Slater, 1974) is used to calculate the halocarbons air-sea fluxes:

$$F = -K_a \cdot (C_g - K_H \cdot C_l) \tag{1}$$

where K_a is the transfer velocity of the gas (s^{-1}), C_g (ppm) and C_l (nM) are the bulk gas and liquid-phase concentrations and
25 K_H is the Henry's law constant. K_a is parameterized following Johnson (2010) which is mainly a function of wind speed and sea surface temperature (SST) taken from the model at each time-step. C_g is also taken from the model. Halocarbon sea-water concentrations C_l are taken from Ziska et al. (2013). Fig. 3 shows the average air-sea fluxes for $CHBr_3$, CH_2Br_2 and CH_3I during January and February 2012 for the two approaches. Note that, the online calculation could increase, decrease or even reverse the fluxes in comparison with the prescribed emissions. This is the case for the online fluxes of $CHBr_3$ over the tropics
30 where the model calculates negative fluxes whereas the prescribed fluxes are positive.

Recent studies suggest that the ocean is an important source of OVOCs ~~(Coburn et al., 2014; Lawson et al., 2015; Mahajan et al., 2014; M~~ ~~the~~ such as acetaldehyde, ethanol and methanol (Coburn et al., 2014; Lawson et al., 2015; Mahajan et al., 2014; Myriokefalitakis et al., 20~~ models do not generally consider or are not able to capture (Millet et al., 2010; Sherwen et al., 2016a). ~~Thus, oceanic~~ Oceanic fluxes of several VOCs have been included into the ~~model. The same online approach is done for~~ WRF-Chem as part if this study. For the three OVOCs (acetaldehyde (CH_3CHO), ethanol (C_2H_6O) and methanol (CH_3OH))~~,~~ the same online approach for the VSLH is used to calculate the marine fluxes where their sea-water concentrations are taken from Yang et al. (2014).

Emissions for alkenes and alkanes (C_2H_4, C_3H_6, C_2H_6, C_3H_8) are prescribed and based on the POET (Granier et al., 2005) global inventory.

Deposition over the ocean for the halocarbons and OVOCs is included in the air-sea fluxes described above. For the rest of the species, dry deposition is calculated with the Wesely scheme (Wesely, 1989), which is used over land for several species. Washout of gases by precipitation is simulated using the scheme included in WRF-Chem (Grell and Dévényi, 2002; Zaveri et al., 2008) which was modified to include the Henry's law constants for the ~~halogens~~ RHS shown in Table 1.

The sea-salt aerosol emissions parameterization used in this study is described in Archer-Nicholls et al. (2014). This parameterization is mainly a function of wind speed from the model and uses the emissions scheme from Gong et al. (1997) for particles with dry diameters of 0.45nm or more and for smaller particles uses Fuentes et al. (2010) .

3.2 Gas-phase chemistry scheme

Our reaction mechanism is based on the MOZART-4 mechanism (Emmons et al., 2010; Knote et al., 2014). This mechanism has been extended to include bromine, chlorine and iodine chemistry and has been coupled with the MOSAIC 4-bin aerosol module (Zaveri et al., 2008). A total of 48 species and 159 halogen reactions have been included (see Tables 2, 3 and 4 for details). ~~Most of these~~ Inorganic, organic and inter-halogens reactions come from the 1D model MISTRA (Sommariva and von Glasow, 2012)~~which includes inorganic, organic and inter-halogens reactions~~. Production and loss reactions of the higher order of iodine oxides (I_2O_X, where X=2,3,4) reactions have been included into the model. Photochemistry of I_2O_X species is still an ~~aera~~ area of high uncertainty in atmospheric iodine chemistry (Sommariva et al., 2012; Saiz-Lopez et al., 2012b). Chemical loss of VSLH through oxidation by the hydroxyl radical (OH) and by photolysis is included using data from Sander et al. (2011b).

A schematic representation of the main bromine and iodine chemistry implemented in the model is shown in Fig 4. Chlorine chemistry is also included into the model, however, since our results are mainly focused on reactive bromine and iodine, we do not include chlorine chemistry in Fig 4.

Photolysis reactions included in the mechanism are listed in Table 4. To compute the photolysis rates the Fast Tropospheric Ultraviolet-Visible (FTUV) online scheme (Tie et al., 2003) is used. The quantum yields and cross section for the photolytic reactions of halogens are from JPL 10-6 (Sander et al., 2011b) and have been linearly interpolated onto the 17 wavelength bins used by FTUV. For I_2O_X we use the quantum yield and cross section data from Gómez Martín et al. (2005).
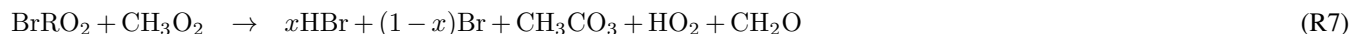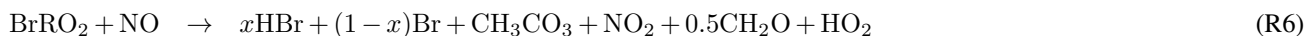
3.2.1 Halogens and VOCs reactions

Reactions between halogens and VOCs can be important for regulating reactive halogen chemistry in the MBL by promoting the conversion of Cl and Br atoms into HCl and HBr or more stable organic halogenated intermediates. The oxidation of methane (CH_4), formaldehyde (CH_2O), acetaldehyde (CH_3CHO), methanol (CH_3OH), methyl hydroperoxide (CH_3OOH),

5 methylperoxy (CH_3O_2), ethane (C_2H_6), ethene (C_2H_4) and propene (C_3H_6) by Cl is included in the chemical mechanism. In addition, the oxidation of CH_2O ~~and~~, CH_3CHO, C_2H_4 and C_3H_6 by bromine is also included in the chemical mechanism ~~. A~~ with a simplified version of the chemical scheme presented in Toyota et al. (2004) used for reactions of bromine with alkenes ~~is included~~:

$$Br + C_2H_4 + O_2 \rightarrow BrRO_2 \tag{R4}$$

10
$$Br + C_3H_6 + O_2 \rightarrow BrRO_2 \tag{R5}$$

where $BrRO_2$ is a brominated peroxy radical.

The ~~decay~~ loss of $BrRO_2$ is ~~defined as~~ represented by the following reactions:

$$BrRO_2 + NO \rightarrow xHBr + (1-x)Br + CH_3CO_3 + NO_2 + 0.5CH_2O + HO_2 \tag{R6}$$

$$BrRO_2 + CH_3O_2 \rightarrow xHBr + (1-x)Br + CH_3CO_3 + HO_2 + CH_2O \tag{R7}$$

15
$$BrRO_2 + HO_2 \rightarrow BrOR + H_2O \tag{R8}$$

The ~~decay~~ loss of BrOR is ~~defined as~~ represented by the following reactions:

$$BrOR + OH \rightarrow 0.5(xHBr + (1-x)Br) + 0.5BrRO2 + 0.5OH + 0.5CH_3CHO \tag{R9}$$

$$BrOR + h\nu \rightarrow xHBr + (1-x)BrOH + HO_2 + CH_3CO_3 + 0.5CH_2O \tag{R10}$$
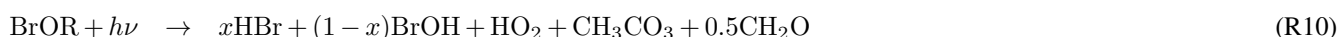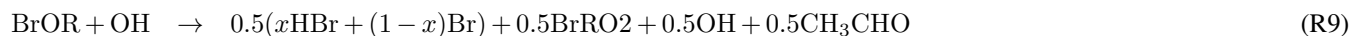
where BrOR is a brominated organic specie and x is a number between 0 and 1.

20 Reaction rates for these reactions and deposition velocities are taken from Toyota et al. (2004). Kinetic data for these reactions is poor, and the partitioning of the products (HBr/Br) is not clear. Based on the Toyota et al. (2004) description, it is assumed that $x = 0.2$ such that the partitioning for HBr/Br is 1/4 (Toyota, pers. comm., 2017).

3.3 Heterogeneous chemistry

Heterogeneous reactions on particle surfaces involving halogens are summarised in Table 5. The heterogeneous chemistry is
25 assumed to take place between a gas-phase species and an adsorbed species. Uptake coefficients are used to calculate first-order rate constants for heterogeneous loss of the gas-phase to the adsorbing surface (Jacob, 2000). Thus, the reaction rate constants, K (s^{-1}), are given by:

7

$$K = \frac{\gamma}{4} \cdot S \cdot A \tag{2}$$

where γ is the uptake coefficient, S is the root-mean-square molecular speed (m s^{-1}) and A is the total available aerosol surface area density (cm^2 cm^{-3}). Equation 2 does not take account of any diffusion limitation (i.e. the rate at which gases can diffuse towards the aerosol surface). We therefore test the sensitivity of our results to this - see section 4.1. Second-order reaction rate constants are calculated by dividing the first-order rate constant by the concentrations of the adsorbed species. Heterogeneous halogen activation is very efficient under cold or stratospheric conditions as compared to moderate temperatures. For this reason, we have made a distinction between moderate (> 243.15 K) and cold temperatures (< 243.15 K) in some reactions. Uptake coefficients for reactions in Table 5 are based on literature values where available (Jacob, 2000; Sander et al., 2006; Ordóñez et al., 2012).

Bulk aqueous phase chemistry in sea-salt aerosols is not treated in this study. Instead, we use a free molecular transfer regime approximation following McFiggans et al. (2000), where the reaction rate is the first-order rate constant computed as described above. There are 6 reactions implemented for sea-salt particles. The sea-salt surface area is calculated in the following way: 1) using the mass of Na and Cl and the associated H$_2$O for each bin and the individual dry densities (for Na, Cl and H$_2$O) the total volume of those particles for each bin is calculated and then, 2) assuming that sea-salt aerosols are spheres, the total surface area is calculated for each bin using this volume and the radius of aerosols in each bin.

It is known that the chemistry involving the release of bromine from the sea-salt aerosol (debromination) is strongly pH dependent, being more efficient for acidified aerosol especially with a pH < 5.5 (Keene et al., 1998). For this reason, we apply a pH dependence for debromination reactions in sea-salt considering two cases: when the pH > 5.5 and when the pH < 5.5. The pH Therefore, the pH value of the aerosol particles is calculated in the model for each size bin (see Zaveri et al. (2008) for further description of the pH calculation). Thus, the following debromination reactions in We then apply a pH dependence to the heterogeneous reactions that occur on the surface of the sea-salt are only considered if . When the pH < 5.5 debromination reactions occur with the release of Br$_2$ and IBr resulting from the uptake of BrNO$_3$, BrNO$_2$, HOBr, INO$_3$, INO$_2$ and HOI (R11-R16). When the pH > 5.5 no debromination reactions occur, although uptake of INO$_3$, INO$_2$ and HOI on the sea-salt still occurs (R17-R19) leading to a change in iodine speciation but no release of Br. See also Table 5.

If the pH < 5.5:

$$\text{BrNO}_3 \quad \rightarrow \quad 0.6\text{Br}_2 + \text{HNO}_3 \tag{R11}$$

$$\text{BrNO}_2 \quad \rightarrow \quad 0.6\text{Br}_2 + \text{HNO}_3 \tag{R12}$$

$$\text{HOBr} \quad \rightarrow \quad 0.6\text{Br}_2 \tag{R13}$$

$$\text{INO}_3 \quad \rightarrow \quad 0.5\text{IBr} + 0.5\text{ICl} + \text{HNO}_3 \tag{R14}$$

$$\text{INO}_2 \quad \rightarrow \quad 0.5\text{IBr} + 0.5\text{ICl} + \text{HNO}_3 \tag{R15}$$

$$\text{HOI} \quad \rightarrow \quad 0.5\text{IBr} + 0.5\text{ICl} \tag{R16}$$

~~When~~ If the pH > 5.5 ~~the following reactions are considered:~~

:

$$\text{INO}_3 \quad \rightarrow \quad 0.5\text{I}_2 + \text{HNO}_3 \tag{R17}$$

$$\text{INO}_2 \quad \rightarrow \quad 0.5\text{I}_2 + \text{HNO}_3 \tag{R18}$$

$$\text{HOI} \quad \rightarrow \quad 0.5\text{I}_2 \tag{R19}$$

~~These reactions change the iodine speciation and add a net source for bromine if the marine aerosol is acidic.~~

Due to the high uncertainty in the debromination process, the fraction of Br_2 formed ~~on~~ by reactions R11-R13 was chosen arbitrarily in order to add an extra bromine source in a simple way. A value of 0.6 was chosen. Fig. 2 shows the column-integrated fluxes for inorganic bromine (Br_2, right panel) during January and February 2012.

In addition, the heterogeneous uptake of N_2O_5 onto aerosol particles that contain Cl^- to form ClNO_2 is considered in the model ~~(see Lowe et al. (2015)~~. After uptake N_2O_5 is taken up onto the particle, it reacts reversibly with liquid water to form protonated nitric acid intermediate ($\text{H}_2\text{ONO}^{+2}$). This then reacts with either liquid water, to form aqueous nitric acid (HNO_3), or with chloride ions to form ClNO_2. See Archer-Nicholls et al. (2014) for further description of this chemistry. In Archer-Nicholls et al. (2014) ClNO_2 was considered as an inert specie, however in our study ClNO_2 is not treated as an inert specie but is broken down via photolysis and reaction with OH (see Tables 2 and 4).

4 Model setup

The model is set up with a horizontal grid spacing of 30 km x 30 km and 30 vertical layers up to 50 hPa. Simulations that study the oxidation of VOCs by Br over the tropical area (described in Sec. 4.1) are performed with more vertical layers than the standard case in order to capture the vertical mixing in this area. Thus, 52 vertical layers up to 50h Pa are used in this case. The meteorological initial and lateral boundary conditions were determined using the ERA-Interim (Dee et al., 2011) data and the meteorology was reinitialized every 3 days to reproduce the observed transport. Chemical initial and boundary conditions

(IC/BCs) are from the global atmospheric model GEOS-Chem described in Sherwen et al. (2016b). We conducted WRF-Chem simulations for January and February 2012 covering the TORERO domain (see Fig. 1). We performed a spin-up of 20 days. Table 6 describes the main configuration of the model.

4.1 Sensitivity studies

5 ~~Eight~~ Ten different simulations were performed in this study. Our base simulation, WRF-DEBROM, considered all main processes involving halogen chemistry (sea-salt debromination, heterogeneous chemistry and reactions between halogens and VOCs) and computes the oceanic halocarbons fluxes online. The WRF-ZIS simulation is the same as WRF-DEBROM but uses prescribed oceanic emissions for the halocarbons. To account for the diffusion limitation, a run was performed in which the values for the uptake coefficient (γ from Eq. 2) from Table 5 have been divided by two, WRF-GAMMADV2. To account

10 for the importance of the debromination in sea-salt particles, we ~~run~~ performed the simulation WRF-NODEBROM which is the same as the WRF-DEBROM simulation but without debromination. The WRF-NOHET simulation is the same as WRF-NODEBROM but without heterogeneous chemistry. A simulation with no halogen chemistry, WRF-NOHAL, is performed to study the effect of halogens on the tropospheric chemistry. All simulations except WRF-NOHAL use IC/BCs from the GEOS-Chem model that include halogens. WRF-NOHAL simulation uses IC/BCs from the GEOS-Chem model with no halogen

15 chemistry. Finally, to study the oxidation of VOCs by ~~Br three~~ halogens four simulations have been performed: 1) a simulation without the reactions of bromine reactions with alkenes (~~WRF-NOALKE~~WRF-NOBRALKE), 2) a simulation without the reactions of bromine with aldehydes (~~WRF-NOALD) and finally~~ WRF-NOBRALD), 3) a simulation without the reactions of bromine with VOCs, therefore neither alkenes nor aldehydes (~~WRF-NOVOCS~~WRF-NOBRVOCS) and 4) a simulation without reactions of bromine and chlorine with VOCs (WRF-NOHALVOCS). See Table 7 for a summary of all these simulations.

5 Model results

20

This section presents the model evaluation with observations of relevant trace gases. The model output is sampled at the nearest timestamp and grid box to the measurements. An ocean mask neglecting grid-boxes above land was applied to compute all model results.

5.1 Oceanic emissions: Halocarbons

25 Fig. 5 shows the time series of $CHBr_3$ (top-left panel), CH_2Br_2 (top-right panel) and CH_3I (bottom-left panel) mixing ratios (in ~~ppt~~pptv) for the WRF-ZIS (green line) and WRF-DEBROM (black line) runs. In addition, the modelled wind speed (black line) is also shown in Fig. 5 (bottom-right panel). Measurements for the halocarbons and wind speed are represented by the solid red lines. Fig. 6 presents the time series of $CHBr_3$, CH_2Br_2 and CH_3I water concentration (in pmol/L) from the measurements (dashed red lines) and from the Ziska et al. (2013) climatology (dashed blue lines) used to compute both the prescribed and

30 online fluxes.

10

In general, both simulations reproduce the concentrations of the halocarbons to the right order of magnitude, although there are specific periods with a negative bias. We see a tendency to underestimate CHBr$_3$ for both model simulations during most of the period. This result is similar to the study of Hossaini et al. (2016) who compared eleven global models using different emissions inventories. The majority of the models do not reproduce the observed concentrations in the tropical marine boundary layer. Over the tropics, high emissions observed are associated with tropical upwelling and active planktonic production (Class and Ballschmiter, 1988; Atlas et al., 1993). One reason for low CHBr$_3$ concentrations in our model simulations might be that the sea-water concentrations are too low in this area (see Fig. 6 for CHBr$_3$)~~and then the~~. The fluxes are also low (see Fig. S2 in the supplementary information). Note that Ziska et al. (2013) used only a very limited amount of data to ~~compute~~ derive the sea-water concentration for the halocarbons in ~~a~~ our domain, ~~giving uncertainty in this input data when the fluxes are calculated~~ ~~.~~which leads to uncertainty in the calculated fluxes. The modelled CHBr$_3$ is underestimated throughout the troposphere when is compared with aircraft observations (see Fig. S3 in the supplementary information). Atmospheric concentrations of CH$_2$Br$_2$ ~~is~~are in good agreement with the observations ~~despite a negative bias (~~although the model underestimates the observed values by ~~∼ -0.5ppt) between days~~ 0.5 pptv during the periods 6-10 and 22-25 ~~of February~~~~for both simulations~~February. Bromocarbon concentrations ~~in WRF-DEBROM~~ agree better with the measurements, ~~where the bias is decreased~~ when the oceanic fluxes are calculated online (WRF-DEBROM), in particular the underestimation is less for specific periods (e.g. 20th February for CHBr$_3$ and 10th and 22nd February for CH$_2$Br$_2$) in comparison with WRF-ZIS. Moreover, the ~~differences in~~ correlation coefficients between ~~simulations are~~the observations and the simulations are better for the WRF-DEBROM compared to WRF-ZIS: 0.48 and 0.3 for CH$_2$Br$_2$ and CHBr$_3$, respectively, in the case of WRF-ZIS and 0.65 and 0.43 for CH$_2$Br$_2$ and CHBr$_3$ in the case of WRF-DEBROM. Modelled CH$_3$I concentrations show a similar trend to the observations, although, like the bromocarbons, both simulations ~~present a negative bias~~ underestimate the observations during specific periods (days 6-10 and 18-28 of February). This underestimation is more prominent in the WRF-DEBROM simulation. One reason for that could be that the wind speed from WRF-Chem is lower than the wind speed used to calculate the prescribed emissions, producing lower online fluxes. ~~The correlation coefficients changes for~~ Nevertheless, the correlation coefficients between the observed and simulated CH$_3$I ~~,~~ ~~where~~ atmospheric concentrations are better for WRF-DEBROM than for WRF-ZIS: 0.19 is calculated for the WRF-ZIS and 0.40 for the WRF-DEBROM simulation.

Specific periods of negative bias for both simulations demand further attention. A possible explanation for the underestimation in halocarbon atmospheric concentrations might be due to the input data (e.g. wind speed, SST, sea-water concentration) that we used to compute these fluxes. In the case of the online fluxes, between ~~days~~ 6-8 of February the model underestimates wind speed and this is directly accompanied by an underestimation for all three halocarbons atmospheric concentrations. Ziska et al. (2013) demonstrate that changes in the input parameters, especially wind speed and SST, affect the fluxes calculation. The same study suggests that CH$_3$I emissions are mainly influenced by variations of the wind speed. Moreover, the study of Lennartz et al. (2015), that uses the same sea-water concentration as our study, suggests that the negative bias in the modelled atmospheric concentrations could indicate regions where the sea-water concentration from the climatologies lacks hotspots, thus, missing an oceanic source regions. This is clearly seen for the sea-water concentrations of CHBr$_3$ (during most of the period), CH$_2$Br$_2$ (peaks around 15th February) and CH$_3$I (peaks around 20th February) used in this study that seem to be too

low in comparison with the observations (see Fig. 6). More data on the sea-water concentrations of these halocarbons in this region are required to better constrain the oceanic flux data sets available to models and so to improve the representation of these gases in the atmosphere.

5.2 Gas phase and heterogeneous chemistry: bromine and iodine partitioning

Fig. 7 compares model results sampled along 16 flight tracks with the observations for BrO (~~ppt~~pptv) separating tropical from subtropical flights for the ~~three~~ four simulations WRF-NOHET, WRF-NODEBROM, WRF-GAMMADV2 and WRF-DEBROM. Results indicate that there is an improvement of the modelled BrO throughout the troposphere in both the tropics and subtropics when the heterogeneous chemistry is included in both tropics and subtropics.

In the subtropics, higher values of BrO are found in ~~altitudes ranges~~ the altitude range 11-13 km due to the lower altitude of the tropopause. Some data points in this altitude range will be in the lower stratosphere. There is really good agreement with the observations particularly in the middle and upper troposphere where the model is able to capture the higher values of BrO. Within the model, aerosols over the subtropical area tend to be alkaline, thus, BrO does not increase in this area when sea-salt debromination is included. Over the tropics, where the aerosol is more acidic ~~, elevated BrO is seen with the inclusion of the debromination (WRF-DEBROM) in the MBL where the sea-salt~~ and where the sea salt aerosols are mostly located (see emissions of Br_2 in Fig. 2), elevated BrO is seen with the inclusion of the debromination (WRF-DEBROM) in the MBL. Debromination improves the simulation of BrO concentrations in the middle troposphere although it excessively increases BrO levels up to 1 ~~ppt~~ pptv in the MBL. ~~This overestimation is~~ Higher values are also seen in other modelling studies that include this process (Schmidt et al., 2016).

Areas, such as the tropics, where debromination dominates, the impact of halving gamma (WRF-GAMMADV2 run) is approximately half of the impact of including heterogeneous chemistry (i.e. the difference between the WRF-DEBROM run and the WRF-NOHET run) at least for the lower troposphere. Very little impact is seen in the UT, a slight decrease in BrO, when gamma is halved (WRF-GAMMADV2). Significant uncertainties still exist in the sea-salt debromination processes and the parameterisations used here might be too simple to represent them.

In addition, the conversion of BrO to HBr is dominated by the reaction between Br and ~~VOCs~~OVOCs, such that the BrO overestimation seen in the MBL could be reduced if the modelled aldehydes concentrations ~~increase~~ were increased (discussed in section 5.3). However, a reduction in the debromination would also reduce BrO concentrations. Thus, in order to capture the BrO concentrations in the MBL the right balance between these two chemical processes is needed.

BrO is underestimated in the model by 1 ~~ppt~~ pptv in the upper troposphere over the tropics. The breakdown of bromocarbons, such as $CHBr_3$, contributes to BrO concentrations in the UT, thus, a good representation of bromocarbons is needed. $CHBr_3$ is underestimated in the middle and upper troposphere especially over the tropics (see Fig. S3 in the supplementary information). The reason for that could be a combination of different factors: underestimation of the boundary conditions used in this study for $CHBr_3$, underestimation in the oceanic fluxes (see Fig. S2 in the supplementary information) and overestimation of the loss rates. Moreover, an underestimation in the heterogeneous chemistry or uncertainties in the reactions between the halogens and VOCs (discussed in section 5.3) can also contribute to the underestimation of BrO in the UT over the tropics.

Fig. 8 shows the vertical profile distribution for inorganic bromine (Br_y in ~~ppt~~pptv) for the three simulations WRF-NOHET (left panels), WRF-NODEBROM (middle panels) and WRF-DEBROM (right panels) over the subtropics (top panels) and tropics (bottom panels). Inorganic bromine concentrations increase with altitude with a maximum of 8 ~~ppt~~ pptv at 14 km in the subtropical area for all three simulations. This reflects the lifetime of the bromocarbon species that breakdown and release

5　Br in the UT and LS. Over the tropical area, inorganic bromine concentrations have a peak in the middle troposphere at 6 km and then decrease until 12 km then start to increase again. A big impact on the vertical Br_y partitioning is seen between the three simulations. With the inclusion of the heterogeneous chemistry, there is a decrease of HBr and an increase of more reactive species: di-halogens (BrCl, Br_2 and BrI) and BrO. HOBr increases and $BrNO_3$ decreases in the UT due to $BrNO_3$ hydrolysis. Over the tropics, Br_y increases in the MBL ($\sim$ ~~4ppt~~4 pptv) when debromination is included (WRF-DEBROM).

10　This enhancement is seen for all inorganic species with a maximum in the surface where the concentration of sea-salt aerosols is ~~higher~~highest. Over the subtropical area, little ~~differences are~~ difference is seen between WRF-NODEBROM and WRF-DEBROM.

Fig. 9 compares model results sampled along 16 flight tracks with the observations for IO separating tropical from subtropical flights for the ~~three~~ four simulations WRF-NOHET, WRF-NODEBROM, WRF-GAMMADV2 and WRF-DEBROM.

15　No clear impact is seen with the inclusion of the heterogeneous chemistry. At the surface, simulations with heterogeneous chemistry (WRF-DEBROM, WRF-GAMMADV2 and WRF-NODEBROM) have slightly lower IO concentrations than the simulation without heterogeneous chemistry (WRF-NOHET). The main reason for that reduction is the sink for the iodine oxides ($I_xO_y$$I_2O_X$, where X=2,3,4) included in the heterogeneous chemistry. Over the tropical region, the model overestimated surface IO. This overestimation might be explained by the ~~higher~~large modelled inorganic iodine oceanic fluxes in this area.

20　The biggest uncertainty in the inorganic iodine emissions parameterization is the calculation of the iodide concentration in the sea water. Over the subtropics, IO enhancements observed below 4 km are not captured by the model. Some studies suggest that there is abiotic CH_3I production when dust contacts seawater containing iodide ~~(Williams et al., 2007)~~ (Williams et al., 2007; Puentedura et Implementing this chemistry into the model is out of the scope of this paper and further investigation is needed to explain whether the production of CH_3I enhances the IO concentration or if there are other missing IO precursors. Gómez Martín et al.

25　(2013) presented an analysis of observations of several gas-phase iodine species ~~observations~~ made during a field campaign in the eastern Pacific marine boundary layer and suggested that the presence of elevated CH_3I does not have a big impact on the IO_x concentrations due to CH_3I in the MBL having a long lifetime ($\sim$2 days at the equator). An overestimation of modelled IO in the UT needs further investigation. This overestimation is similar to other modelling studies Sherwen et al. (2016a). Changing GAMMA (difference between the WRF-DEBROM and WRF-GAMMADV2 runs) has very little impact on IO.

30　Fig. 10 shows the vertical profile distribution for inorganic iodine (I_y) for the three simulations WRF-NOHET (left panels), WRF-NODEBROM (middle panels) and WRF-DEBROM (right panels) over the subtropics (top panels) and tropics (bottom panels). I_y is higher in the MBL where it is emitted, especially in the tropical region, with HOI being the dominant species. Concentrations start to decrease above the MBL due to the removal of soluble species by the wet deposition. Unlike Br_y, we do not see a big impact on the vertical ~~partitioning distribution~~ profile of I_y ~~partitioning~~ with the inclusion of the heterogeneous

35　chemistry. The only differences are the I_y decreases in the surface with the inclusion of the heterogeneous chemistry, due to the

removal of the iodine oxides, and the production of more di-halogens in the MBL, specially when debromination is included. Heterogenous iodine reactions (reactions R11-R19) compete with the photolysis. Iodine species are more readily photolyzed, so less is taken up into the aerosol and the impact of heterogeneous chemistry is less.

5.3 Impact on VOCs

Several VOCs oceanic fluxes have been included in the model (see section 3.2.1) as well as the oxidation of VOCs by halogens. In order to see the impact of halogen reactions with the VOCs, average loss rates of all organic compounds due to the Cl and Br families are calculated as % of the total tropospheric losses over the ocean for the WRF-DEBROM simulation. Bromine accounts for 9.2% of the oxidation of CH_3CHO, 1.4% of CH_2O, 0.8% of C_2H_4 and 4.1% of C_3H_6. Chlorine accounts for 0.6% of the oxidation of CH_3CHO, 0.3% of CH_2O, 7.7% of CH_3OH, 0.8% of CH_3OOH, 0.6% of CH_3O_2, 35.5% of C_2H_6 and 10.5% of C_3H_8.

A sub-set of 9 flights from the TORERO campaign over the tropics is compared with the WRF-DEBROM, ~~WRF-NOVOCS, WRF-NOALKE and WRF-NOALD~~ WRF-NOBRVOCS, WRF-NOBRALKE and WRF-NOBRALD simulations for BrO (~~ppt~~pptv) in Fig. 11. Comparisons between WRF-DEBROM and ~~WRF-NOVOCS~~ WRF-NOBRVOCS simulations show a clear difference (1-4 ~~ppt~~pptv) throughout the whole troposphere. VOCs play an important role in the MBL regulating the reactive halogens. Without the bromine reactions with the VOCs, ~~the model clearly overestimates BrO~~ BrO concentrations are higher than observed in the MBL. In the middle and upper troposphere, where VOCs emitted from the ocean and ~~large~~ forests are transported by convection, the model underestimates the ~~levels~~ amounts of BrO when these reactions ~~have been~~ are considered. The results obtained indicate that BrO is highly sensitive to the conversion of reactive bromine into more stable species by these reactions. The partitioning of the products of these reactions (HBr/Br), and thus the conversion of reactive bromine to more stable species, is highly uncertain (see section 3.2.1) and the results suggest that it might be too effective in these upper layers of the model.

In order to understand which families of VOCs have a higher impact on the BrO concentrations, the oxidation of alkenes and aldehydes by Br have been studied separately in ~~WRF-NOALKE and WRF-NOALD~~ WRF-NOBRALKE and WRF-NOBRALD simulations. Differences between WRF-DEBROM and ~~WRF-NOALD~~ WRF-NOBRALD are seen in the whole troposphere with higher differences up to 2 pptv in the MBL~~up to 2ppt~~, where the concentrations of both bromine and aldehydes are high. ~~Aldehydes concentrations~~ The concentrations of the aldehydes are underestimated by the model, especially for CH_3CHO, meaning that BrO modelled concentrations would be even lower if the modelled ~~aldehydes concentrations~~ concentrations of the aldehydes were reconciled with the observations. The model also seriously underestimates the observed glyoxal mixing ratios. The modelled values are typically ~1 pptv, whilst the observed values are around 30-40 pptv in the MBL decreasing to around 5-10 pptv in the upper troposphere (Volkamer et al., 2015; Sinreich et al., 2010) . This illustrates that there are large gaps in our understanding of OVOCs in the remote marine atmosphere. Small differences are observed between WRF-DEBROM and ~~WRF-NOALKE~~WRF-NOBRALKE. However, differences up to 2 ~~ppt between WRF-NOVOCS and WRF-NOALD~~ pptv between WRF-NOBRVOCS and WRF-NOBRALD are clearly seen especially in the MBL.

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These findings suggest that when aldehyde oxidation by Br is included, ~~Br$_Y$~~ reactive Br is reduced considerable, thus, limiting the amount of alkenes oxidation by Br (difference between WRF-DEBROM and ~~WRF-NOALKE~~WRF-NOBRALKE). However, when the oxidation of aldehydes is included, there is sufficient Br~~$_Y$~~$_y$ present for the oxidation of alkenes by Br to have an impact on the BrO (difference between ~~WRF-NOALD and WRF-NOVOCS~~WRF-NOBRALD and WRF-NOBRVOCS).

Fig. 11 also shows the vertical profile distribution for inorganic bromine (Br$_y$ in pptv) for the WRF-NOBRVOCS run over the tropics (top-right panel). When reactions of bromine with VOCs are not included the amount of Br$_y$ increases considerably (difference between WRF-DEBROM and WRF-NOBRVOCS from Figs. 8 and 11), reaching values of 14 pptv in the MBL over the tropics. Moreover, when this chemistry is included, the partitioning of Br$_y$ shifts to more stable bromine species such as HBr.

Fig. 12 shows the vertical profile distribution for inorganic chlorine (Cl$_y$ in pptv) for the two simulations WRF-NOHALVOCS (left panels), WRF-DEBROM (middle panels) over the subtropics (top panels) and tropics (bottom panels). Regional average vertical partitioning of reactive chlorine species (Cl*) is also shown (right panels) where Cl* is defined as Cl$_y$ gases other than HCl. When the VOCs react with Cl (WRF-DEBROM), almost all the inorganic Cl is in the form of HCl (see Fig. 12). When these reactions are not considered (WRF-NOHALVOCS), Cl$_y$ increases and there is a shift in the partitioning to more reactive chlorine increases, in particular HOCl, but also ClO and the di-halogens.

From this, we concluded that VOCs ~~have~~ play an important role in the reactive bromine ~~concentrations and VOCs marine emissions~~ and chlorine concentrations. Therefore marine emissions of VOCs as well as halogen reactions with VOCs need to be included ~~into the~~ in models. However, ~~uncertainty still exists~~ large uncertainties still exist in some of these reactions (see Sec. 3.2.1).

5.4 Impact on O$_3$ and O$_x$

Fig. 13 (left panel) presents a comparison of ~~2 model~~ modelled O$_3$ from 6 simulations (WRF-DEBROM, WRF-GAMMADV2, WRF-NODEBROM, WRF-NOHET, WRF-NOHALVOCS, and WRF-NOHAL) sampled along 13 flight tracks with the ~~observations for~~ observed O$_3$ (~~ppb). The model~~ppbv). O$_3$ is overestimated when halogens are not included (WRF-NOHAL) except in the upper troposphere. When halogens are included, the model (WRF-DEBROM) is in line with the observations, capturing the O$_3$ gradient and variability of data throughout the troposphere. The average difference between ~~the two~~ WRF-DEBROM and WRF-NOHAL simulations throughout the troposphere is ~~6.7 ppb~~7 ppbv. In the MBL, high concentrations of halogens due to ocean emissions destroy O$_3$ and contribute to a negative bias up to 8 ~~ppb~~ppbv for WRF-DEBROM run. In the middle troposphere, the model results (WRF-DEBROM) improve with the inclusion of halogens, where the average ~~bias~~ underestimation is reduced from ~~4. to -2.4 ppb~~4.0 to 2.4 ppbv. In the upper troposphere, where the differences between the ~~two simulations~~ the simulations (WRF-DEBROM and WRF-NOHAL) are mainly driven by the boundary conditions used for each simulation, both simulations underestimate the ozone concentrations. The heterogeneous halogen chemistry has an impact on O$_3$ concentrations where a difference of up to 3 ppbv of O$_3$ is seen between the simulation with and without heterogeneous chemistry (WRF-DEBROM run WRF-NOHET run, respectively) mainly in the MBL. The modelled O$_3$ is highly sensitive to

the inclusion of the reactions of the halogens with the VOCs (WRF-NOHALVOCS) where O_3 concentrations are much lower (between 12-7 ppbv) than in the WRF-DEBROM run.

Fig. 13 (middle and right panels) shows the regional effects of halogen chemistry on simulated O_3 concentrations at the surface. Surface mean bias (~~ppb~~ppbv) and relative mean bias (%) between the simulation with no halogen chemistry (WRF-NOHAL) and with halogen chemistry (WRF-DEBROM) for the simulation period are presented. We find that the regional

5 O_3 concentrations are reduced ~~between~~ by 2-18 ~~ppb~~ppbv, corresponding to 25-70 %, with the inclusion of the halogens. Over the tropics, there is a substantial decrease of O_3 (> ~~8ppb~~8ppbv, > 40%). As we see in Fig. 2 and 3, there are high iodine and bromocarbon emissions and especially ~~high~~ large amounts of bromine produced from debromination over this area. These destroy ozone and contribute to higher difference in O_3 concentrations in this area.

The odd oxygen O_x is defined as:

10 O_x = $O(^3P)$ + $O(^{21}D)$ + O_3 + NO_2 + $2\times NO_3$ + HNO_3 + HO_2NO_2 + $3\times N_2O_5$ + PAN + MPAN+ ONIT + ONITR+ $ISOPNO_3$ + PBZNIT + $MBONO_3O_2$+ XO + HOX+ XNO_2+ $2\times XNO_3$ + $2\times OIO$ + $2\times I_2O_2$ + $3\times I_2O_3$ + $4\times I_2O_4$ + $2\times OClO$,

where X=Cl, Br and I; PAN= peroxyacetyl nitrate, MPAN= methacryloyl peroxynitrate; ONIT= organic nitrate; ONITR= lumped isoprene nitrate; $ISOPNO_3$= peroxy radical from NO_3+ISOP; PBZNIT= peroxybenzoyl nitrate; $MBONO_3O_2$= peroxy radical from NO_3 + 2 methyl-3-buten-2-ol.

15 The O_x loss ~~is divided by~~ resulting from reactions with each of the ozone depleting families (O_x , HO_x, NO_y, VOCs, Br, Cl and I) is calculated. Note that to calculate the O_x loss due to the O_x depleting family we only consider reactions involving $O(^3P)$, $O(^{21}D)$ and O_3. The average tropospheric vertical profile of O_x loss grouped by ozone depleting families for the WRF-DEBROM simulation is given in Fig. 14. ~~Table ??~~ Fig. 15 summarises the relative contribution of each halogen family averaged at different altitude intervals for the WRF-DEBROM , WRF-GAMMADV2, WRF-NODEBROM, WRF-NOHET and

20 WRF-NOHALVOCS simulations.

The regional average O_x percentage loss due to the halogens in our model domain is 34%, 18% and 40% in the MBL (p>900hPa), FT (350<p<900hPa) and UT (350hPa<p<trop), respectively for the WRF-DEBROM simulation. The MBL O_x loss is in good agreement with Sherwen et al. (2016b) that reported 33% and Prados-Roman et al. (2015) reported 31%. The tropospheric O_x loss due to the ~~bromine, iodine and chlorine~~ BrO_x, IO_x and ClO_x cycles is 14%, 16%, 1% ~~, respectively~~throughout

25 the troposphere, respectively for the WRF-DEBROM simulation. The very fast catalytic reactions of iodine species make the iodine loss higher than for bromine and chlorine, especially in the MBL ~~(19~~for all simulations that include halogens-VOCs reactions (19-23%). With the inclusion of the sea-salt debromination, O_x loss due to the bromine is 14% in the MBL. In the upper troposphere, iodine contributes ~~21~~18-23% and bromine ~~19~~14-19% to the total O_x loss. ~~Thus, the overall~~ The impact of halogen chemistry on the tropospheric O_x loss is 31 % for the WRF-DEBROM simulation. This value is comparable with

30 other studies that reported 28% over the tropics (Saiz-Lopez et al., 2015) and 21.4% at the global scale (Sherwen et al., 2016b). Moreover, our results are in agreement with Wang et al. (2015), that used a box model and concluded that bromine and iodine are responsible for 34% of the column-integrated loss of tropospheric O_3. The tropospheric O_x loss due to the iodine is higher than the box model study of Dix et al. (2013), that concluded that the fraction of iodine-induced ozone loss generally is around 10%.

When comparing different simulations with the WRF-DEBROM run, the biggest difference is seen with WRF-NOHALVOCS simulation, where around 60% of O_x is removed by halogens. BrO is much higher when the VOC reactions are not included (see Fig. 11), which explains why the amount of O_x lost by BrO_x reactions is much larger (20.5%). Moreover, the big change though is for the ClO_x which increases from < 1% to 26%. Cl is very important in the oxidation of the alkanes. When this chemistry is not included the concentrations of Cl_y increases and there is an impact on the partitioning increasing reactive species (see Fig. 12), hence, the ClO_x cycles play an important role in O_x loss. It should be noted that very little is known about the abundance and distribution of Cl_y so this is a large uncertainty. Therefore, a large uncertainty in the impact of halogen cycling on the O_3 budget are the reactions of halogens with VOCs. In the model runs performed, excluding these reactions doubled the percentage contribution of halogens to O_x loss (i.e. increase it from 31% to 60%) in the troposphere. Heterogeneous chemistry (including debromination) has the effect of increasing the O_x loss by halogen cycling from 25 to 31% for the whole troposphere (i.e. comparision between WRF-NOHET and WRF-DEBROM runs). For the UT the equivalent values are 37% to 40%, for the FT 13% to 18% and for the MBL 23% to 34%. Hence, heterogeneous chemistry increases the percentage of the O_x loss that is attributable to the halogens by about 6% for the troposphere ranging from 3% to 11% depending on the region of the troposphere. Note that the gas phase halogen chemistry makes a bigger contribution of around 25% (WRF-NOHET run) to the O_x loss for the troposphere ranging from 13% to 37% depending on the region of the troposphere. Therefore, the overall impact of the halogen chemistry on O_x loss appears not to be very sensitive to the treatment of the heterogeneous chemistry.

6 Conclusions

We have presented a regional 3D tropospheric model that includes halogen chemistry (bromine, iodine and chlorine). A comprehensive description has been provided for the halogen gas-phase chemistry, the heterogeneous recycling reactions in sea-salt aerosol and other particles, reactions of ~~Br~~ reactive halogens with volatile organic compounds (VOCs) and the oceanic emissions of halocarbons, inorganic iodine and several VOCs. It is the first time that a comprehensive halogen chemistry mechanism has been ~~implemented~~ added into the online WRF-Chem model. Our results provide useful insight regarding the potential importance of reactive halogens in the tropical marine atmosphere and the many uncertainties that remain. Field data from the TORERO campaign (Jan-Feb 2012) has been used in the model evaluation.

Two different approaches to compute marine emissions, online and prescribed, for the ~~very short-lived halocarbons~~ VSLH are discussed here. There is an improvement using online fluxes, WRF-DEBROM, in comparison with prescribed fluxes, WRF-ZIS, especially for CH_2Br_2 and $CHBr_3$ atmospheric concentrations, where the ~~bias~~ overestimation seen for the model in comparison with ship measurements is decreased for specific periods. During the whole period, an underestimation is seen for both simulations for $CHBr_3$. This underestimation is similar to other modelling studies, which indicates the oceanic fluxes for $CHBr_3$ in this region are not well determined. Results indicate that the input data (especially wind-speed and water concentrations) used in this study to calculate marine fluxes underestimate halocarbon concentrations. Large underestimation of $CHBr_3$ and CH_3I concentrations throughout the troposphere is seen when compared to the aircraft observations.

Three sensitivity studies are compared in order to understand the impact of the heterogeneous chemistry for bromine and iodine species. Results show that the inclusion of heterogeneous chemistry on marine aerosol has a considerable impact on the Br_y partitioning, increasing reactive species like BrO. An increase of Br_y is seen in the tropical MBL when debromination processes are included, due to the presence of relatively acidic particles.

The oxidation of alkenes and aldehydes by bromine have been ~~studies~~ studied in three different sensitivity runs. These runs

5 suggest that reactions of bromine with ~~VOCs~~ OVOCs have a big impact on the BrO concentrations. The reactions between Br and aldehydes were found to be particularly important, despite the model underestimating the amount of aldehydes observed in the atmosphere.

The model shows an overall good agreement ~~for the~~ with the observed IO vertical profile. Higher modelled concentrations in the surface are seen over the tropics indicating that inorganic iodine emissions might be too high in this area. The model is

10 not able to capture the IO enhancements sometimes seen below 4 km over the subtropical area. Unlike, Br_y, the I_y partitioning is found to be relatively insensitive to inclusion of the heterogeneous chemistry.

~~Halogens constitute 31% of the overall tropospheric O_x loss. This value is comparable with other studies. The tropospheric O_x loss due to the bromine, iodine, and chlorine is 14%, 16%, 1%, respectively.~~ The model captures the O_3 vertical profile in the free troposphere. ~~However, a negative bias (< 8 ppb) is seen~~ The simulation with halogens (WRF-DEBROM) underestimates

15 the observed O_3 values in the MBL, where the oceanic emissions of the halogenated species are higher. Over the tropics, the regional surface O_3 concentrations are reduced between 2-18 ~~ppb~~ ppbv with the inclusion of the halogens. When heterogeneous chemistry is included O_3 concentrations is reduced by up to 3 ppbv in the MBL. The biggest difference (7-12 ppbv) in O_3 values is seen when reactions between Br and Cl and VOCs are not considered (WRF-NOHALVOCS run).

~~Large uncertainties in the halogen chemistry still exists: uptake coefficients~~ In our simulations, halogens constitute 25-60%

20 of the overall tropospheric O_x loss. This range of values is comparable with other studies. Uncertainties in the heterogeneous chemistry ~~, debromination process definition, photolytic rates (especially for the higher order of iodine oxides) , wet scavenging and dry deposition of halogenated species, the chemical mechanism for the repartitioning of Br~~ accounted for only a small proportion of this range (25% to 31% of the O_x loss). When reactions between Br and Cl with VOCs are not considered (WRF-NOHALVOCS), O_x loss by BrO_x, ClO_x and IO_x cycles is high (60%) which accounts for the upper limit of the overall

25 range. The model results are clearly very sensitive to the VOCs and this is a large uncertainty given that their emissions over these remote areas are poorly known.

Our model results suggest that including halogen chemistry has a large affect on O_3 (7 ppbv) and contributes typically about 25-30% of O_x loss. Including heterogeneous halogen chemistry has a big impact on the Br_y ~~resulting from the reactions of Br with VOCs, inputs to calculate the oceanic fluxes (e. g. sea-water concentration) , etc. Some of these processes counteract each~~

30 ~~other, e.g. inclusion of debromination increases BrO, whilst reactions between Br and VOCs decrease BrO, making it difficult to assess through evaluation against observations of a limited number of chemical species if any one process improves the modelled representation of the chemistry, or not.~~ partitioning, but not on the I_y partitioning. However, it does not have a large impact on the O_3 concentrations or the percentage of O_x loss via halogen chemistry. Therefore, although the uncertainties in the heterogeneous chemistry are large the O_x appears to be relatively insensitive to these uncertainties. However, the modelled O_3

35 and O_x loss are very sensitive to the reactions between the halogens and the VOCs. Excluding these reactions leads to greater amounts of the reactive halogen species (Figs. 11 and 12) less O_3 (Fig. 13) and greater O_x loss from halogens (60%) (Fig. 15), in particularly from ClO_x. Very little is known about the abundance and distribution of Cl_y so this is a large uncertainty. There are also large uncertainties in the degree to which Br is recycled or converted to the more stable product HBr in the reactions following Br reactions with the alkenes. Moreover, there is considerably uncertainty in the emissions and distributions of the
5 VOCs in the remote marine atmosphere.

More data is required at the process level from laboratory studies along with field observations of, for example, more Br_y ~~and~~ , I_y and Cl_y species, to better constrain the modelled representation of these processes and to verify if halogens really do have such a large impact on O_x in the tropical troposphere. This is important given that the oxidising capacity of this region of the atmosphere has a large impact on the lifetime of many pollutants including methane, a key greenhouse gas.

Figure 1. Flight and cruise tracks from the TORERO campaign (January-February 2012). Cruise track is represented by an light orange line. Flights are grouped by the following regions: tropical (red lines) and subtropical (green lines). Two different domains where defined: domain to evaluate the cruises (dark orange square) and domain to evaluate aircrafts (green square).
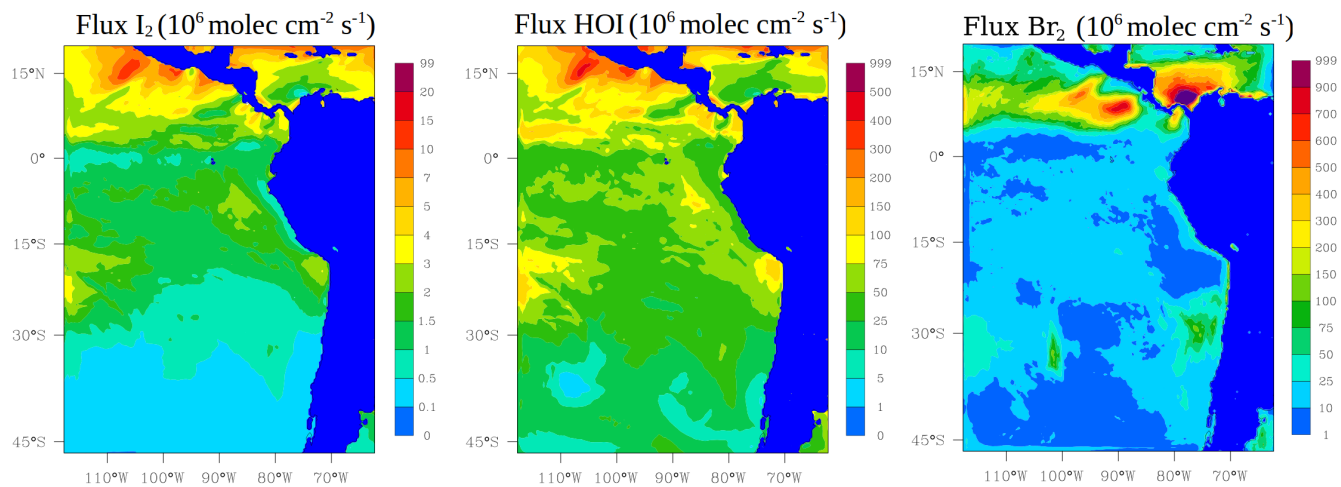
Figure 2. Mean oceanic surface fluxes for inorganic iodine: I_2 (left panel) and HOI (middle panel). The column-integrated fluxes for inorganic bromine (Br_2, right panel) from the debromination process during January and February 2012 are also shown. Values are given in 10^6 molec cm^{-2} s^{-1}.
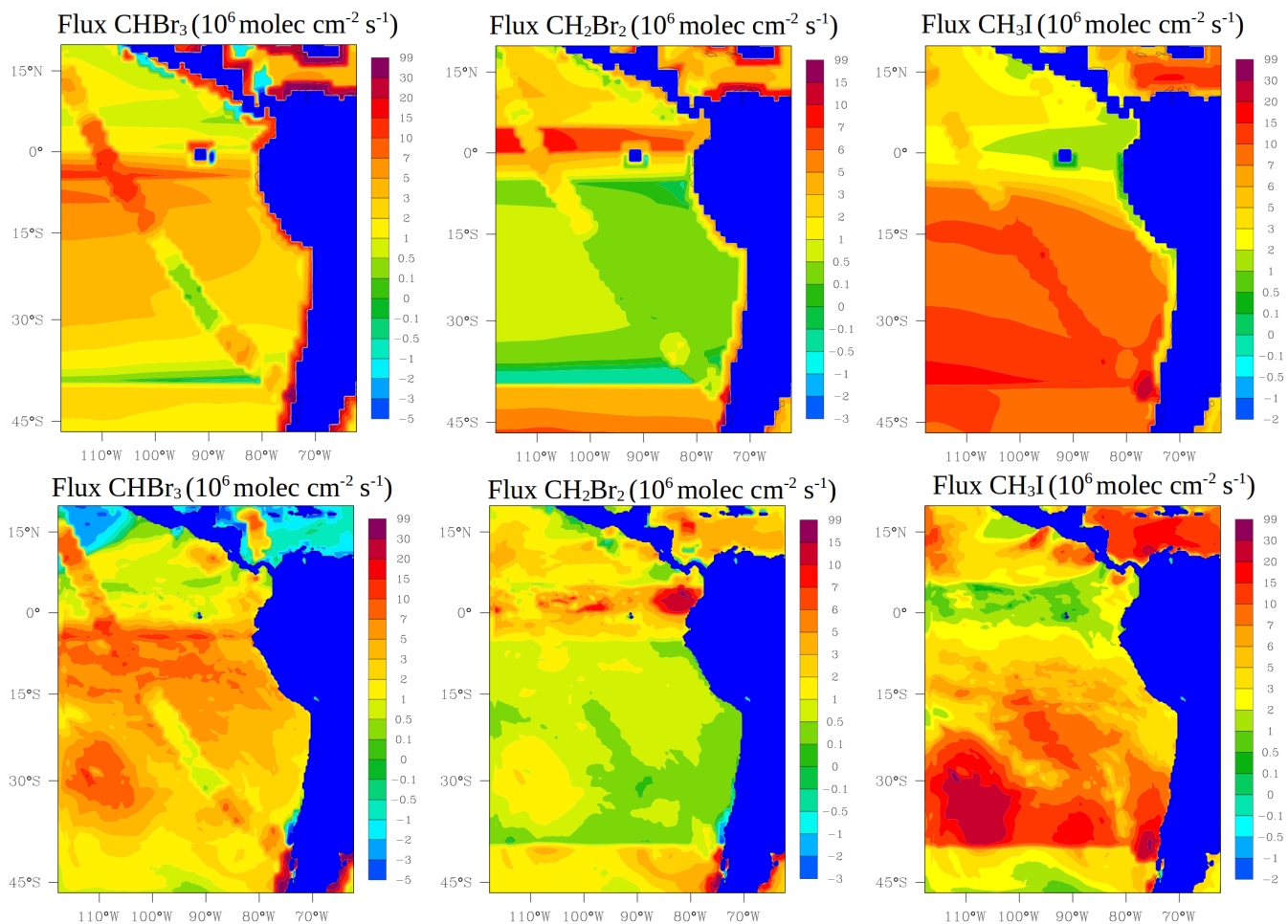
Figure 3. Mean oceanic fluxes for halocarbons ($CHBr_3$, CH_2Br_2 and CH_3I) during January and February 2012. Prescribed fluxes are shown on the top and online fluxes on the bottom. Values are given in 10^6 molec cm^{-2} s^{-1}.
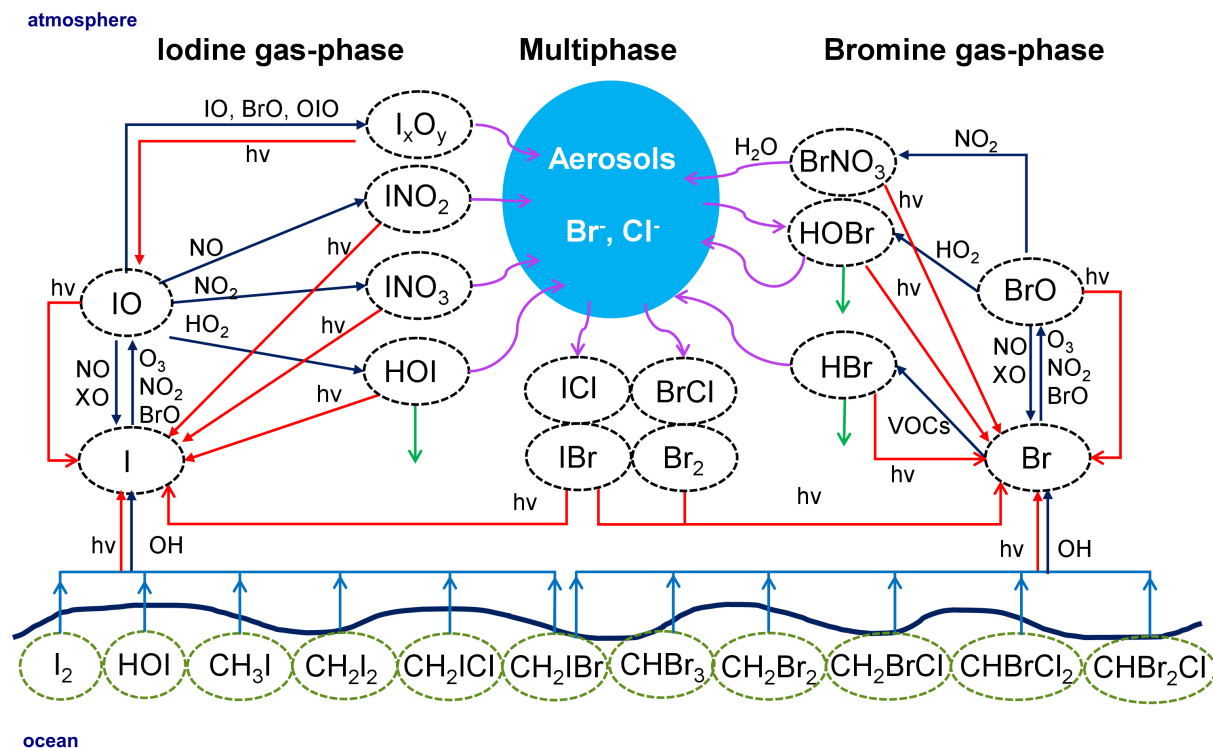
Figure 4. Schematic representation of the implemented iodine and bromine chemistry in WRF-Chem. Chlorine chemistry have been included into the model, since our results are mainly focused on reactive bromine and iodine, we decide not to include chlorine chemistry in this figure. Red lines represent photolytic reactions, dark blue lines gas-phase pathways, light blue lines fluxes, green lines deposition and purple curved lines heterogeneous pathways.
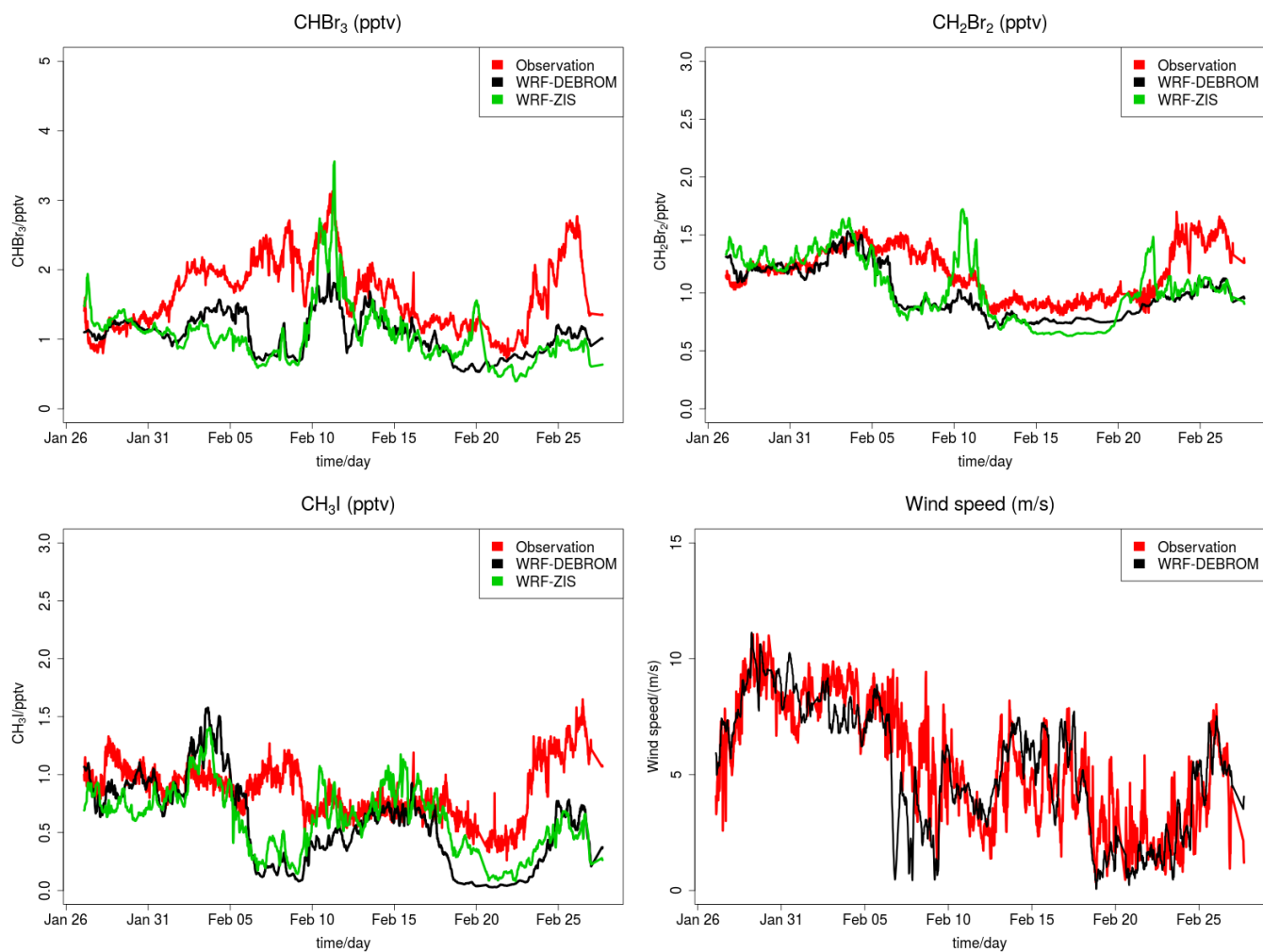
Figure 5. Time series of CHBr$_3$ (top left), CH$_2$Br$_2$ (top right) and CH$_3$I (bottom left) mixing rations (in ~~ppt~~pptv) for the WRF-ZIS (green line) and WRF-DEBROM (black line) runs ~~.~~ during the period of the TORERO campaign in 2012. On the bottom-right, the wind speed (m s^{-1}) of the model is shown with a black line. ~~Observations~~ Measurements during the TORERO campaign are depicted with red lines.
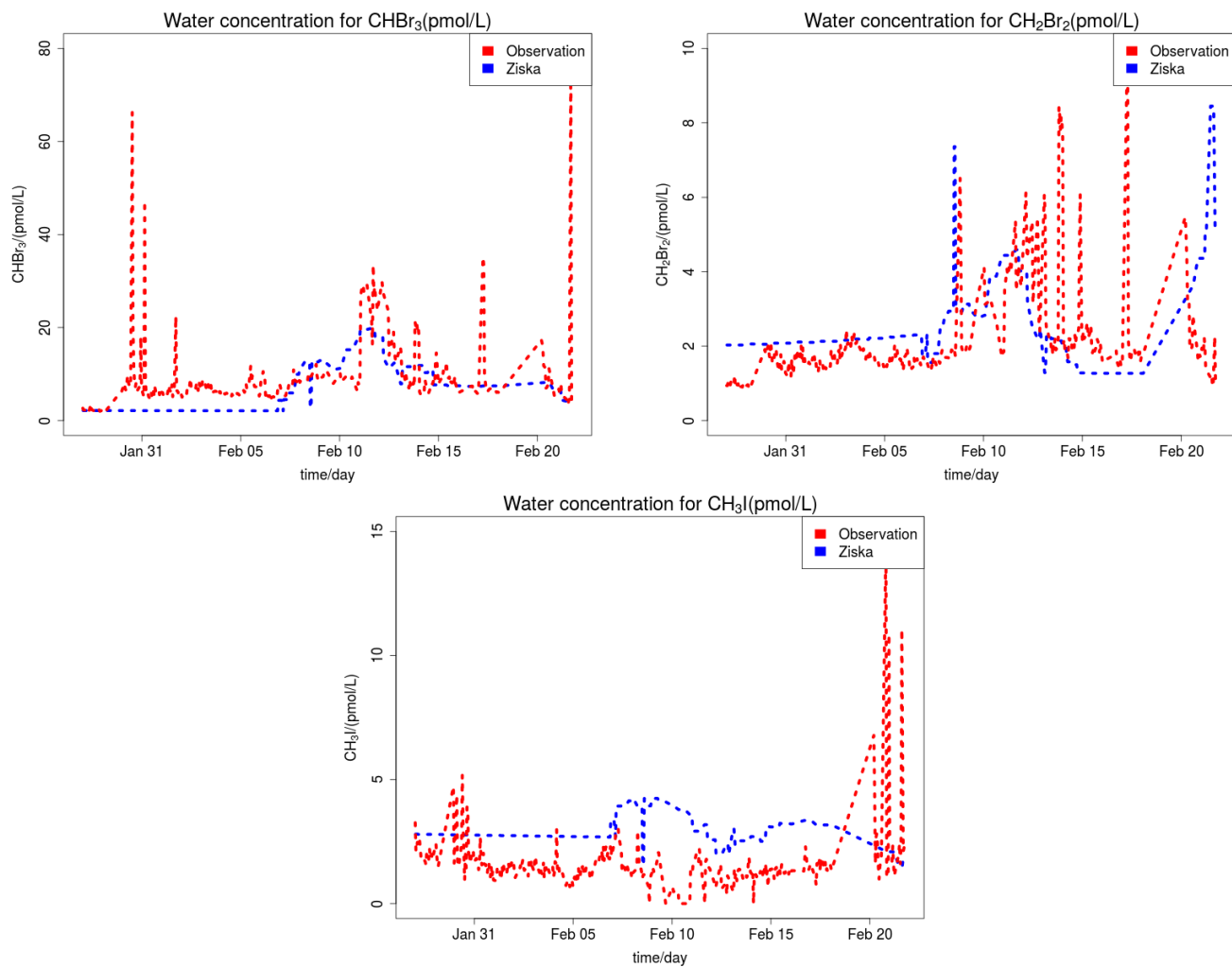
Figure 6. Time series of measured CHBr$_3$ (top left), CH$_2$Br$_2$ (top right) and CH$_3$I (bottom) water concentration (in pmol/L) ~~derived from during~~ the ~~measurements~~ TORERO campaign (red dashed line) and from the Ziska et al. (2013) climatology (blue dashed line).
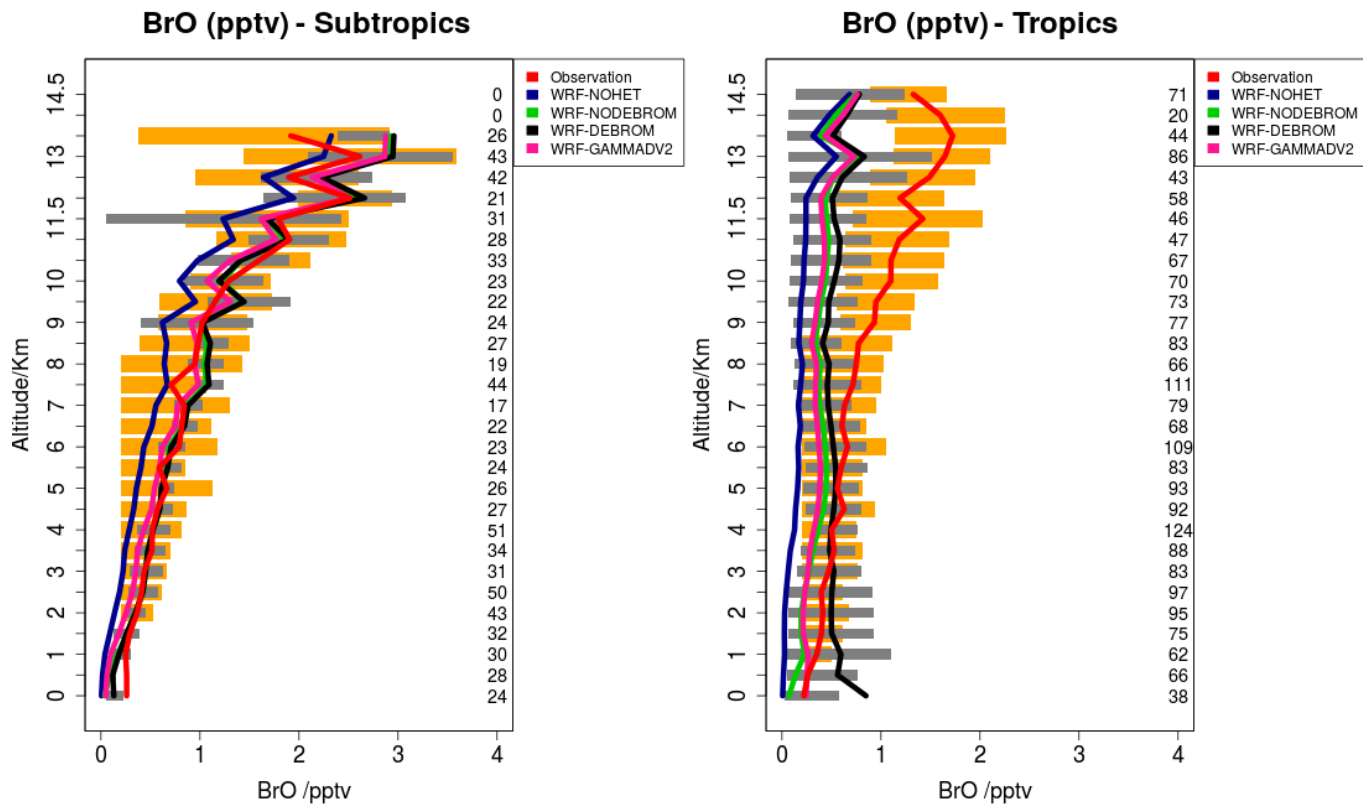
Figure 7. Mean vertical profile of BrO (~~ppt~~pptv) over the subtropics (left) and tropics (right). An average over 16 flights ~~from~~ of the TORERO campaign (red line) are compared to the ~~3~~ 4 different WRF-Chem simulations: WRF-NOHET (blue line), WRF-NODEBROM (green line)~~and~~, WRF-DEBROM (black line) and WRF-GAMMADV2 (pink line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bins and the number of aircraft measurement points for each altitude ~~is~~ are given on the right side of each plot.
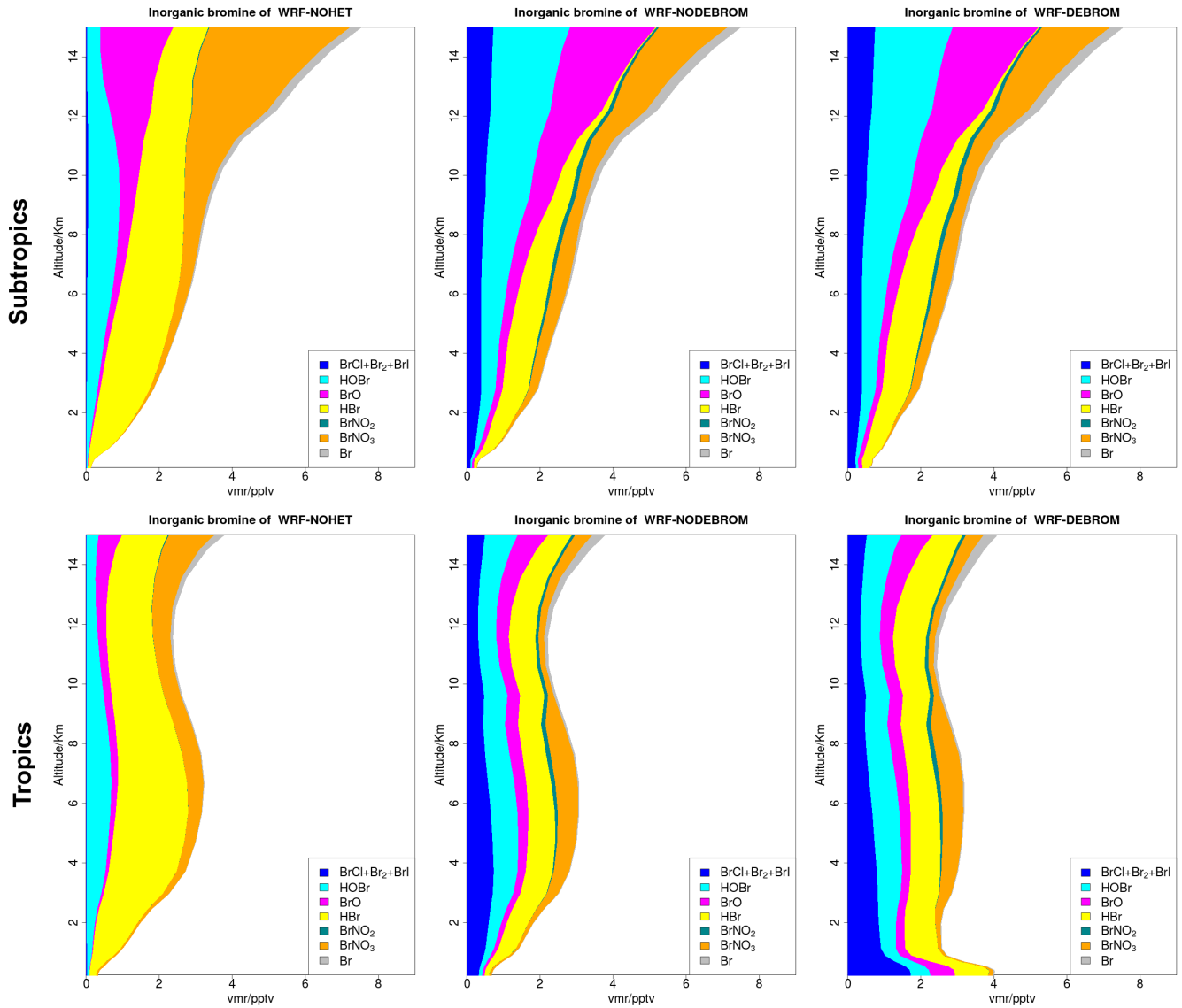
Figure 8. Regional average vertical partitioning of inorganic bromine (Br$_y$) for the three different simulations WRF-NOHET (left panel), WRF-NODEBROM (middle panel) and WRF-DEBROM (right panel) during January and February 2012. Top panels are over the ~~tropical~~ subtropical area and bottom panels over the ~~subtropical~~tropical. Units are in ~~ppt~~pptv.
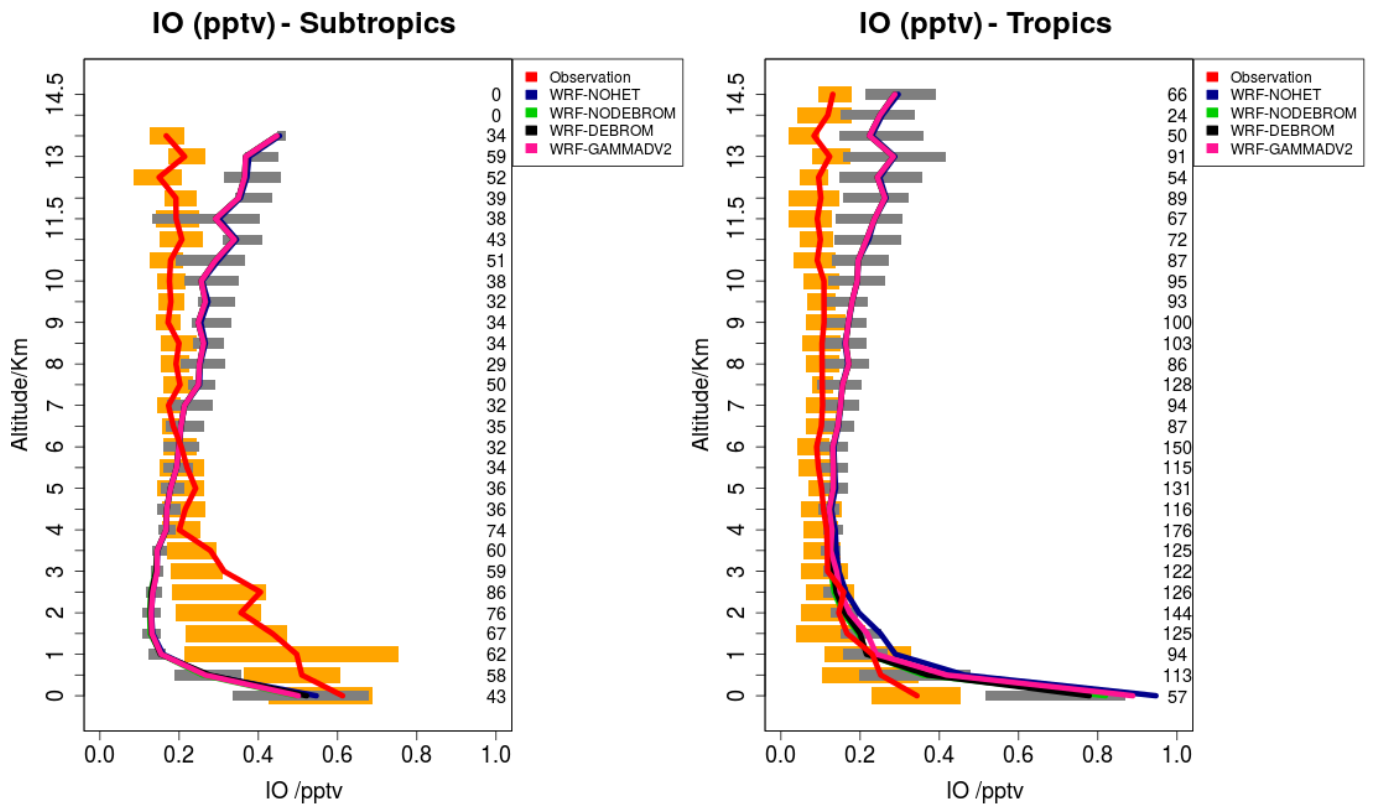
Figure 9. Mean vertical profile of IO (~~ppt~~pptv) over the subtropics (left) and tropics (right). An average over 16 flights ~~from~~ of the TORERO campaign (red line) are compared to the ~~3~~ 4 different WRF-Chem simulations: WRF-NOHET (blue line), WRF-NODEBROM (green line)~~and~~, WRF-DEBROM (black line) and WRF-GAMMADV2 (pink line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km ~~bin~~ bins and the number of aircraft measurement points for each altitude ~~is~~ are given on the right side of each plot.
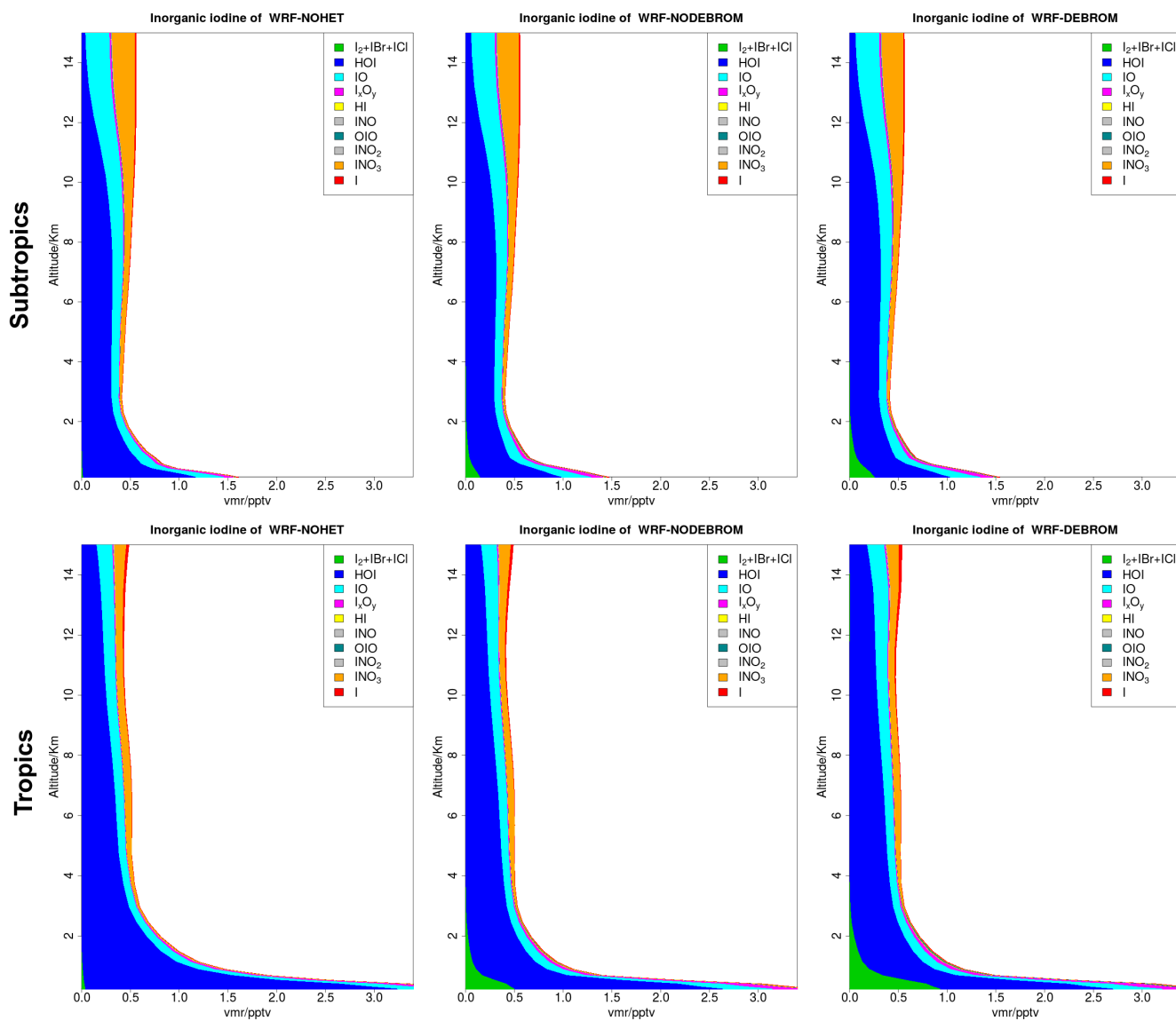
28

Figure 10. Regional average vertical partitioning of inorganic iodine (I_y) ~~)~~ for the three different simulations WRF-NOHET (left panel), WRF-NODEBROM (middle panel) and WRF-DEBROM (right panel) during January and February 2012. Top panels are over the ~~tropical~~ subtropical area and bottom panels over the ~~subtropical~~ tropical. Units are in ~~ppt~~ pptv.
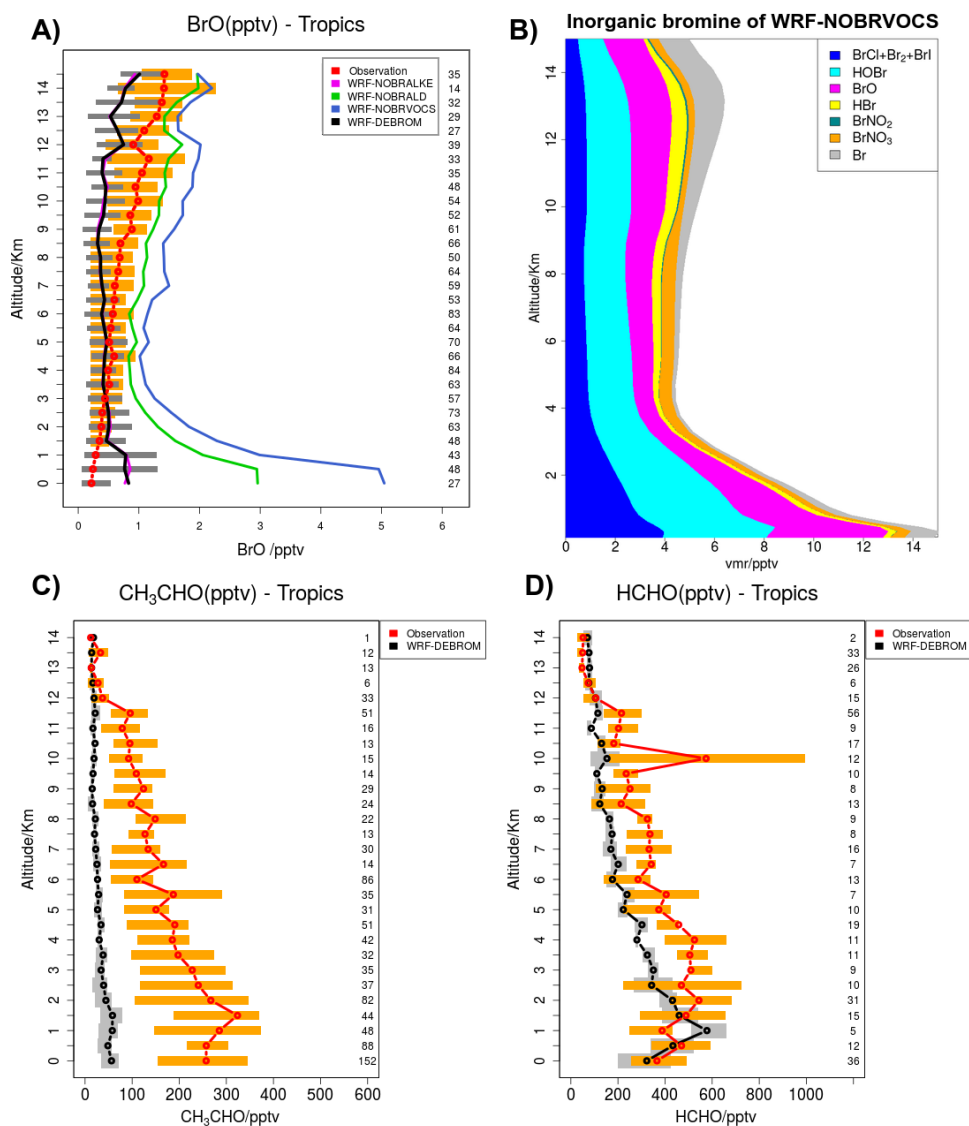
Figure 11. A) Mean vertical profile of BrO (~~ppt~~pptv) over the tropics in the left panel. A sub-set of 9 flights from the TORERO campaign (red line) are compared to the 4 different WRF-Chem simulations: ~~WRF-NOALKE~~ WRF-NOBRALKE (blue line), ~~WRF-NOALD~~ WRF-NOBRALD (green line), ~~WRF-NOVOCS~~ WRF-NOBRVOCS (blue line) and WRF-DEBROM (black line). ~~In~~ B) Regional average vertical partitioning of inorganic bromine (Br$_y$) for the ~~middle~~ the WRF-NOBRVOCS run over the tropical area during January and ~~right panel,~~ February 2012. C) and D) the WRF-DEBROM (black line) simulation is compared with acetaldehyde and formaldehyde TORERO observations for the same 9 flights (red line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bin and the number of points for each altitude is given on the right side of each plot. Units are in ~~ppt~~pptv.
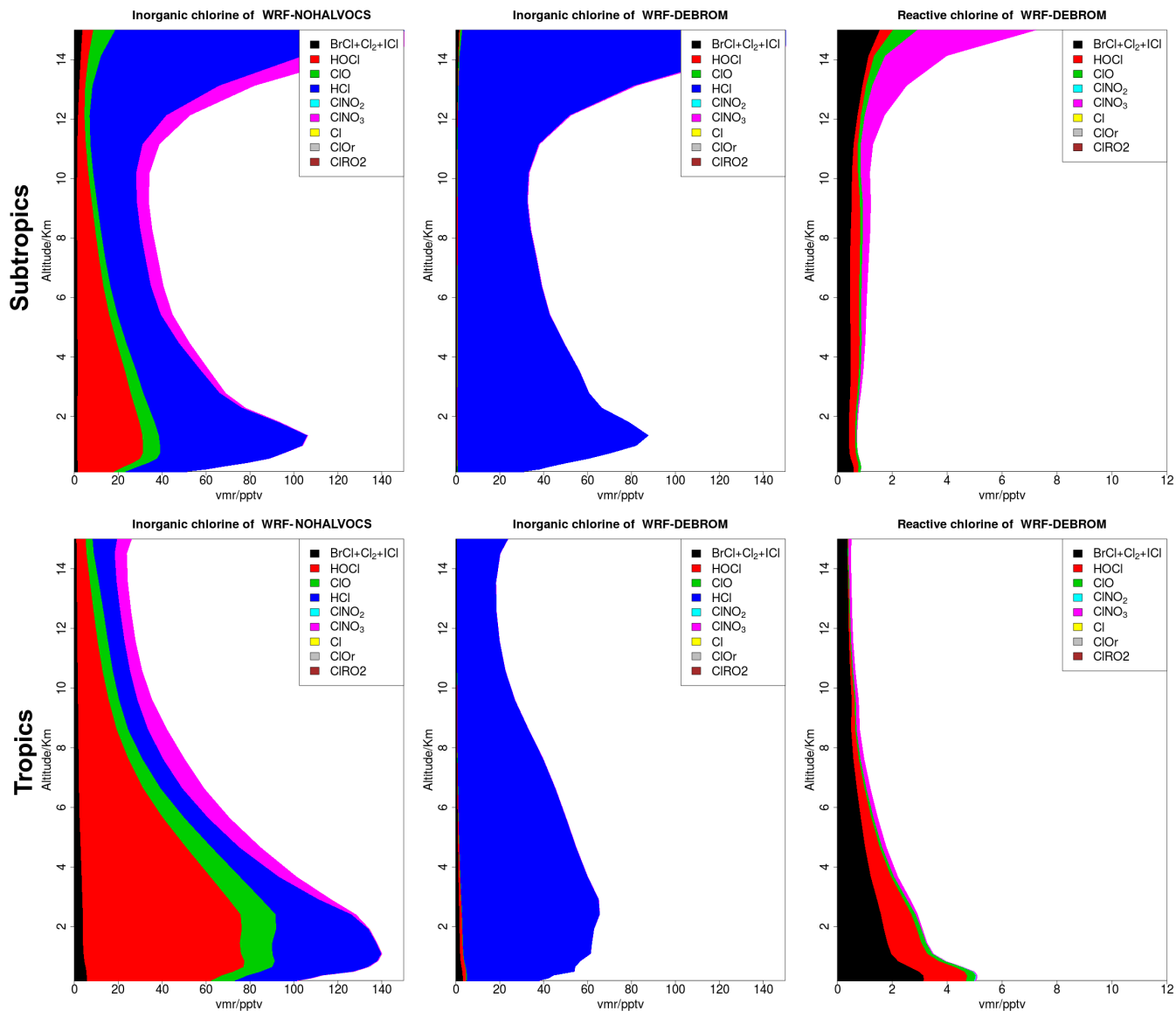
30

Figure 12. Regional average vertical partitioning of inorganic chlorine (Cl_y) for the two different simulations WRF-NOHALVOCS (left panel) and WRF-DEBROM (middle panel) during January and February 2012. Regional average vertical partitioning of reactive chlorine species (Cl^*) is also showed (right panel). Cl^* is defined as Cl_y gases other than HCl. Top panels are over the subtropical area and bottom panels over the tropical. Units are in pptv.
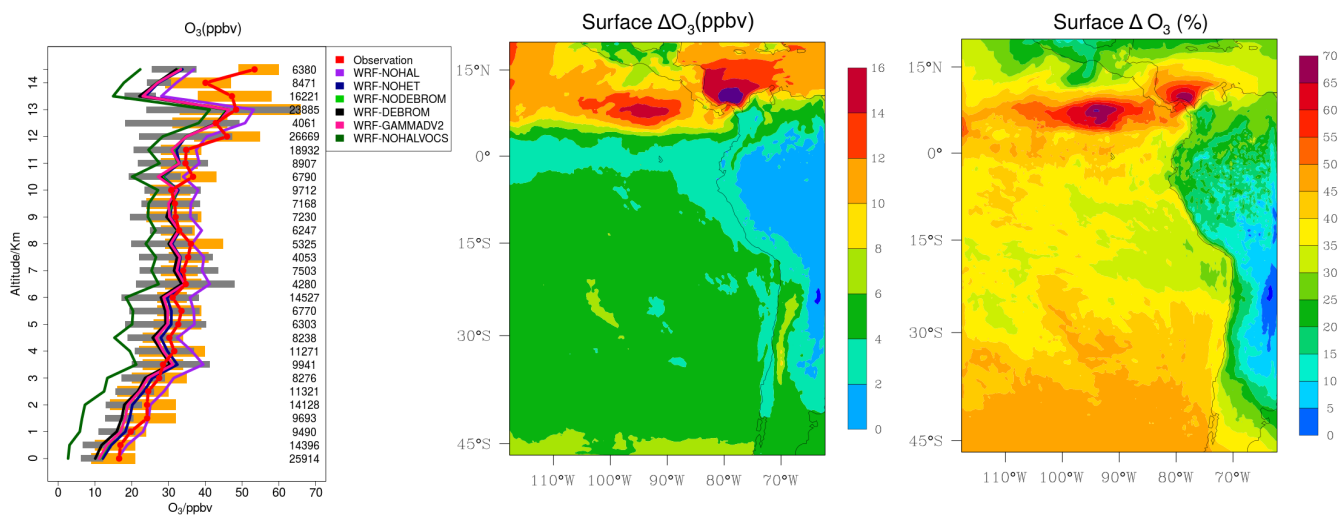
Figure 13. On the left, mean vertical profile of O$_3$ (~~ppb~~ppbv) over the domain area using 13 flights from the TORERO campaign (red line) are compared to the ~~2~~ 6 different WRF-Chem simulations: WRF-NOHAL (purple line), WRF-NOHET (blue line)~~and~~, WRF-NODEBROM (light green line), WRF-DEBROM (black line), WRF-GAMMADV2 (pink line) and WRF-NOHALVOCS (dark green line). Orange and grey horizontal bars indicate the 25th-75th quartile interval for the observations of the TORERO campaign and WRF-DEBROM simulation, respectively. Values are considered in 0.5 km bins and the ~~number~~ numbers of aircraft measurement points for each altitude ~~is~~ are given on the right side of each plot. On the middle and right, mean O$_3$ difference between the simulation with no halogen chemistry (WRF-NOHAL) and with halogen chemistry (WRF-DEBROM) for January and February 2012. Surface mean bias (~~ppb~~ppbv) is shown in the left panel and surface relative mean bias (%) in the right panel. Relative mean bias (%) is calculated as (WRF-NOHAL - WRF-DEBROM)/WRF-NOHAL $\times$ 100.
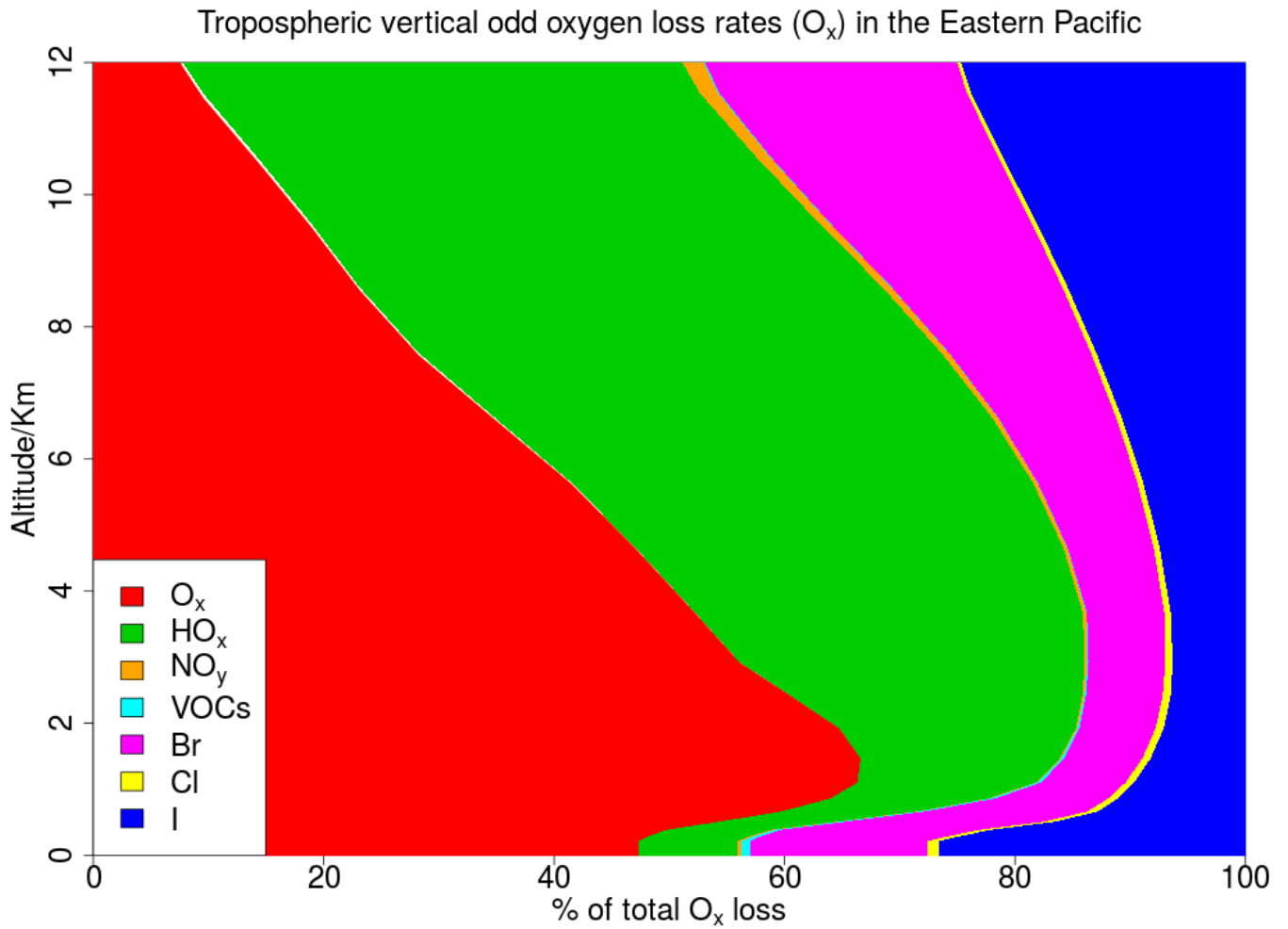
Figure 14. Regional average percentage contribution of each ozone depleting family to the total tropospheric vertical odd oxygen loss (O_x) for the WRF-DEBROM simulation.

Figure 15. Integrated odd oxygen loss rates for each O_3 depleting halogen family within the troposphere at different altitude levels: MBL (surface - 900 hPa), FT (900 hPa- 350 hPa), UT (350 hPa- Tropopause) and troposphere (surface-Tropopause) for the WRF-DEBROM, WRF-GAMMADV2, WRF-NODEBROM, WRF-NOHET and WRF-NOHALVOCS simulation.

Table 1. Henry's Law constant for relevant halogen species implemented in WRF-Chem. INO_2 Henry's law constant is assumed equal to that of $BrNO_2$. Iodine oxi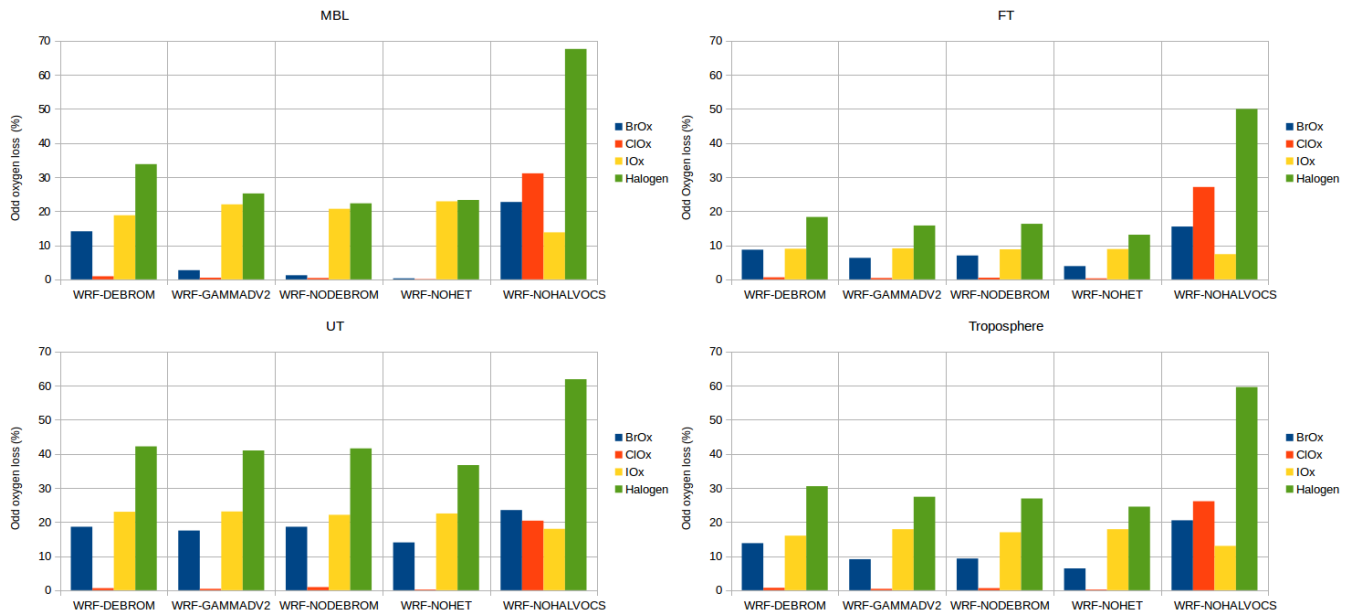des (I_2O_X) Henry's law constants are assumed to be infinity by analogy with INO_3. Virtually infinity solubility is represented by using a very large number (2.69×10^{15}).

Species	Henry's Law Constant (H) at 298K (M atm^{-1})	$\frac{d(lnH)}{d(1/T)}$ (K)	Reference
$ClNO_3$	∞	-	Sander (2015)
$BrNO_3$	∞	-	Sander (2015)
INO_3	∞	-	Sander et al. (2006)
$HOCl$	6.5×10^2	5900	Sander (2015)
$HOBr$	1.9×10^3	-	Sander (2015)
HOI	4.5×10^2	-	Sander et al. (2011a)
HCl[a]	7.1×10^{15}	5900	Sander (2015)
HBr[a]	7.5×10^{13}	10200	Frenzel et al. (1998); Schweitzer et al. (2000)
HI[a]	7.43×10^{13}	3190	Sander (2015); Sander et al. (2006)
$BrCl$	0.9	5600	Sander (2015)
IBr	2.4×10^1	-	Sander (2015)
ICl	1.1×10^2	-	Sander (2015)
$BrNO_2$	$3. \times 10^{-1}$	-	Sander (2015)
$ClNO_2$	4×10^{-2}	-	Sander (2015)
INO_2	$3. \times 10^{-1}$	-	see caption text
I_2	2.63	4600	Sander (2015)
Br_2	0.8	4000	Sander (2015)
I_2O_2	∞	-	see caption text
I_2O_3	∞	-	see caption text
I_2O_4	∞	-	see caption text

[a] Effective Henry's law of HX is calculated for acid conditions (pH = 4.5): $K_H^*(T) = K_H(T) \times (1 + \frac{K_a}{[H^+]})$, where X= Cl, I or Br and $K_a = 1 \times 10^9$M is the acid dissociation constant (Bell, 1973).

Table 2. Bimolecular and thermal decomposition halogen reactions included in WRF-Chem. These reactions are given in the Arrhenius form with the rate equal to $A \times e^{\frac{-Ea}{RT}}$.

Reactions	A (cm^3 molecules^{-1} s^{-1})	$\frac{Ea}{R}$ (K)	Reference
Cl + O$_3$ → ClO + O$_2$	2.8×10^{-11}	250	Atkinson et al. (2007)
Cl + HO$_2$ → HCl + O$_2$	7.8×10^{-11}	620	Atkinson et al. (2007)
Cl + HO$_2$ → ClO + OH	7.8×10^{-11}	620	Atkinson et al. (2007)
Cl + H$_2$O$_2$ → HCl + HO$_2$	1.1×10^{-11}	980	Atkinson et al. (2007)
Cl + H$_2$ + O$_2$ → HCl + HO$_2$	3.9×10^{-11}	2310	Atkinson et al. (2007)
ClO + OH → Cl + HO$_2$	6.8×10^{-12}	-300	Atkinson et al. (2007)
ClO + OH → HCl	4.38×10^{-13}	-300	Atkinson et al. (2007)
ClO + HO$_2$ → HOCl	2.2×10^{-12}	-340	Atkinson et al. (2007)
ClO + O$_3$ → Cl + 2O$_2$	1.5×10^{-17}	-	Atkinson et al. (2007)
ClO + NO → Cl + NO$_2$	6.2×10^{-12}	-295	Atkinson et al. (2007)
HCl + OH → Cl + H$_2$O	1.7×10^{-12}	230	Atkinson et al. (2007)
HOCl + OH → ClO + H$_2$O	3.0×10^{-12}	500	Burkholder et al. (2015)
Cl + ClNO$_3$ → Cl$_2$ + NO$_3$	6.2×10^{-12}	-145	Atkinson et al. (2007)
ClNO$_3$ + OH → 0.5ClO + 0.5HNO$_3$ + 0.5HOCl + 0.5NO$_3$	1.2×10^{-12}	330	Atkinson et al. (2007)
ClNO$_2$ + OH → HOCl + NO$_2$	2.4×10^{-12}	1250	Sander et al. (2011b)
ClO + ClO → Cl$_2$ + O$_2$	1.0×10^{-12}	1590	Sander et al. (2011b)
ClO + ClO → OClO + Cl	3.5×10^{-13}	1370	Sander et al. (2011b)
ClO + ClO → 2Cl	3.0×10^{-11}	2450	Sander et al. (2011b)
Cl + CH$_4$ → HCl + CH$_3$O$_2$	6.6×10^{-12}	1240	Atkinson et al. (2006)
Cl + CH$_2$O → HCl + HO$_2$ + CO	8.1×10^{-11}	34	Atkinson et al. (2006)
Cl + CH$_3$CHO → HCl + CH$_3$CO$_3$	8.0×10^{-11}	-	Atkinson et al. (2006)
Cl + CH$_3$OH → HCl + HO$_2$ + CH$_2$O	5.5×10^{-11}	-	Atkinson et al. (2006)
Cl + CH$_3$OOH → HCl + CH$_3$O$_2$ + OH	5.7×10^{-11}	-	Atkinson et al. (2006)
Cl + CH$_3$O$_2$ → 0.5CH$_2$O + 0.5CO + 0.5H$_2$O + 0.5HO$_2$ + 0.5HCl+ 0.5ClO	1.6×10^{-10}	-	Burkholder et al. (2015)
ClO + CH$_3$O$_2$ → Cl + CH$_2$O + HO$_2$	3.3×10^{-12}	115	Atkinson et al. (2008)
Cl + C$_2$H$_6$ (+ O$_2$) → HCl + C$_2$H$_5$O$_2$	7.2×10^{-11}	70	Sander et al. (2011b)
Cl + C$_3$H$_8$ (+ O$_2$) → HCl + C$_3$H$_7$O$_2$	7.85×10^{-11}	80	Sander et al. (2011b)
Cl + C$_3$H$_6$ (+ O$_2$) → HCl + PO2	3.6×10^{-12}		Sander et al. (2011b)
CH$_3$Cl + Cl → HO$_2$ + CO + 2HCl	3.20×10^{-11}	1250	Sander et al. (2011b)
CH$_3$Cl + OH → Cl + H$_2$O + HO$_2$	2.40×10^{-12}	12509	Sander et al. (2011b)

Reactions	A (cm^3 molecules^{-1} s^{-1})	$\frac{Ea}{R}$ (K)	Reference
Br + O$_3$ → BrO + O$_2$	1.7×10^{-11}	800	Atkinson et al. (2007)
Br + HO$_2$ → HBr + O$_2$	7.7×10^{-12}	450	Atkinson et al. (2007)
BrO + OH → Br + HO$_2$	1.8×10^{-11}	-250	Atkinson et al. (2007)
BrO + HO$_2$ → HOBr + O$_2$	4.5×10^{-12}	-500	Atkinson et al. (2007)
BrO + NO → Br + NO$_2$	8.7×10^{-12}	-260	Atkinson et al. (2007)
BrO + BrO → 2Br + O$_2$	2.4×10^{-12}	-40	Sander et al. (2011b)
BrO + BrO → Br$_2$ + O$_2$	2.8×10^{-14}	-840	Sander et al. (2011b)
HBr + OH → Br + H$_2$O	6.7×10^{-12}	-155	Atkinson et al. (2007)
BrNO$_3$ + Br → Br$_2$ + NO$_3$	4.9×10^{-11}	-	Orlando and Tyndall (1996)
Br + NO$_3$ → BrO + NO$_2$	1.6×10^{-11}	-	Sander et al. (2011b)
Br$_2$ + OH → HOBr + Br	2.1×10^{-11}	-240	Sander et al. (2011b)
Br + CH$_2$O → HBr + CO + HO$_2$	1.7×10^{-11}	800	Sander et al. (2011b))
Br + CH$_3$CHO → HBr + CH$_3$CO$_3$	1.8×10^{-11}	460	Atkinson et al. (2006)
Br + C$_2$H$_4$ (+ O$_2$) → BrRO$_2$	1.3×10^{-13}	-	Atkinson et al. (2006)
Br + C$_3$H$_6$ (+ O$_2$) → BrRO$_2$	3.6×10^{-12}	-	Atkinson et al. (2006)
BrRO$_2$ + NO → 0.2 HBr + 0.8 Br + CH$_3$CO$_3$ + NO$_2$ + 0.5 CH$_2$O + HO$_2$	4.06×10^{-12}	-360	Toyota et al. (2004)
BrRO$_2$ + CH$_3$O$_2$ → 0.2 HBr + 0.8 Br + CH$_3$CO$_3$ + HO$_2$ + CH$_2$O	1.48×10^{-12}	-	Toyota et al. (2004)
BrRO$_2$ + HO$_2$ → BrOR + H$_2$O	7.5×10^{-12}	-	Toyota et al. (2004)
CH$_3$Br + OH → Br + H$_2$O+ HO$_2$	2.35×10^{-12}	1300	Sander et al. (2006)
CH$_2$Br$_2$ + OH → 2Br	2.0×10^{-12}	840	Sander et al. (2006)
CH$_2$BrCl + OH → Br + Cl	2.4×10^{-12}	920	Sander et al. (2006)
CHBrCl$_2$ + OH → Br + 2Cl	9.0×10^{-13}	600	Sander et al. (2006)
CHBr$_2$Cl + OH → 2Br + Cl	9.0×10^{-13}	600	Sander et al. (2006)
CHBr$_3$ + OH → 3Br	1.35×10^{-12}	600	Sander et al. (2006)
I + O$_3$ → IO (+ O$_2$)	2.1×10^{-11}	830	Atkinson et al. (2007)
I + HO$_2$ → HI (+ O$_2$)	1.5×10^{-11}	1090	Atkinson et al. (2007)
I + NO$_3$ → IO + NO$_2$	1.0×10^{-10}	-	Atkinson et al. (2007)
I$_2$ + OH → HOI + I	1.8×10^{-10}	-	Burkholder et al., (2015)
IO + HO$_2$ → HOI (+ O$_2$)	1.4×10^{-11}	-540	Atkinson et al. (2007)
IO + NO → I + NO$_2$	7.15×10^{-12}	-300	Atkinson et al. (2007)
IO + IO → I + OIO	2.16×10^{-11}	-180	Atkinson et al. (2007)
IO + IO → I$_2$O$_2$	3.24×10^{-11}	-180	Atkinson et al. (2007)
OIO + NO → NO$_2$ + IO	1.1×10^{-12}	-542	Atkinson et al. (2007)

Table 2: Continued from previous page

Reactions	A (cm^3 molecules^{-1} s^{-1})	$\frac{Ea}{R}$ (K)	Reference
OIO + OIO → I$_2$O$_4$	1.5×10^{-10}	-	Gómez Martín et al. (2007)
IO + OIO → I$_2$O$_3$	1.5×10^{-10}	-	Gómez Martín et al. (2007)
I$_2$O$_2$ → IO + IO	1×10^{-12}	9770	Ordóñez et al. (2012)
I$_2$O$_2$ → OIO + I	2.5×10^{-14}	9770	Ordóñez et al. (2012)
I$_2$O$_4$ → 2OIO	3.8×10^{-2}	-	Kaltsoyannis and Plane 2008
HI + OH → I + H$_2$O	1.6×10^{-11}	-440	Atkinson et al. (2007)
HOI + OH → IO + H$_2$O	5.0×10^{-12}	-	Riffault et al., 2005
INO$_2$ (+M) → I + NO$_2$	9.94×10^{17}	11859	McFiggans et al. (2000)
INO$_3$ → IO + NO$_2$	1.1×10^{15}	12060	Atkinson et al. (2007)
INO + INO → I$_2$ + 2NO	8.4×10^{-11}	2620	Atkinson et al. (2007)
INO$_2$ + INO$_2$ → I$_2$ + 2NO$_2$	4.7×10^{-12}	1670	Atkinson et al. (2007)
I$_2$ + NO$_3$ → I + INO$_3$	1.5×10^{-12}		Atkinson et al. (2007)
INO$_3$ + I → I$_2$ + NO$_3$	9.1×10^{-11}	146	Kaltsoyannis and Plane 2008
IO + CH$_3$O$_2$ + O$_2$ → CH$_2$O + HO$_2$ + I + 0.5O$_2$	2.0×10^{-12}	-	Dillon et al., 2006
I + BrO → IO + Br	1.2×10^{-11}	-	Sander et al. (2011b)
IO + Br → I + BrO	2.7×10^{-11}	-	Bedjanina et al. 1997
BrO + ClO → Br + OClO	1.6×10^{-12}	-430	Atkinson et al. (2007)
BrO + ClO → Br + Cl + O$_2$	2.9×10^{-12}	-220	Atkinson et al. (2007)
BrO + ClO → BrCl + O$_2$	5.8×10^{-13}	-170	Atkinson et al. (2007)
IO + ClO → 0.33ICl + 0.67I + 0.33Cl + 0.33OClO + 0.67O$_2$	9.4×10^{-13}	-280	Atkinson et al. (2007)
IO + BrO → Br + I + 0.5O$_2$	3.0×10^{-12}	-510	Atkinson et al. (2007)
IO + BrO → Br + OIO	1.2×10^{-11}	-510	Atkinson et al. (2007)
CH$_3$I + OH → I + H$_2$O + HO$_2$	2.9×10^{-12}	1100	Sander et al. (2011b)

Table 3. Termolecular reactions for halogens species included in WRF-Chem. The lower pressure limit rate (K_0) is given by $A_0 \times (\frac{T}{300})^a$. The high pressure limit (K_∞) is given by $B_0 \times (\frac{300}{T})^b$. F_c describes the fall of curve of the reaction described by Atkinson et al. (2007). Then the reaction rate (k) is defined as $K_0[M]/(1+\frac{K_0[M]}{K_\infty}) \times F_c^n$ and n as $(1+ (\log_{10} \frac{K_0[M]}{K_\infty})^2)^{-1}$.

Termolecular reactions	A_0 (cm^6 molecules^{-2} s^{-1})	a	B_0 (cm^3 molecules^{-1} s^{-1})	b	F_c	Reference
Cl + NO$_2$ $\overset{M}{\rightarrow}$ ClNO$_2$	1.8×10^{-31}	-2	1.0×10^{-10}	-1	0.6	Sander et al. (2011b)
ClO + NO$_2$ $\overset{M}{\rightarrow}$ ClNO$_3$	1.8×10^{-31}	-3.4	1.5×10^{-11}	-1.9	0.4	Sander et al. (2011b)
Br + NO$_2$ $\overset{M}{\rightarrow}$ BrNO$_2$	4.2×10^{-31}	-2.4	2.7×10^{-11}	0.0	0.55	Sander et al. (2011b)
BrO + NO$_2$ $\overset{M}{\rightarrow}$ BrNO$_3$	5.2×10^{-31}	-3.2	6.9×10^{-12}	-2.9	0.6	Sander et al. (2011b)
I + NO $\overset{M}{\rightarrow}$ INO	1.8×10^{-32}	-1	1.7×10^{-11}	0.0	0.6	Atkinson et al. (2007)
I + NO$_2$ $\overset{M}{\rightarrow}$ INO$_2$	3.0×10^{-31}	-1	6.6×10^{-11}	0.0	0.63	Atkinson et al. (2007)
IO + NO$_2$ $\overset{M}{\rightarrow}$ INO$_3$	7.7×10^{-31}	-5	1.6×10^{-11}	0.0	0.4	Atkinson et al. (2007)

Table 4. Photolytic reactions of halogens included in WRF-Chem.

Photolysis reactions
$Cl_2 \xrightarrow{h\nu} 2\ Cl$
$OClO\ (+O_2) \xrightarrow{h\nu} O_3 + ClO$
$HOCl \xrightarrow{h\nu} Cl + OH$
$ClNO_2 \xrightarrow{h\nu} Cl + NO_2$
$ClNO_3 \xrightarrow{h\nu} Cl + NO_3$
$ClNO_3 \xrightarrow{h\nu} ClO + NO_2$
$Br_2 \xrightarrow{h\nu} 2\ Br$
$BrO \xrightarrow{h\nu} Br\ (+O_3)$
$HOBr \xrightarrow{h\nu} Br + OH$
$BrNO_2 \xrightarrow{h\nu} Br + NO_2$
$BrNO_3 \xrightarrow{h\nu} Br + NO_3$
$BrNO_3 \xrightarrow{h\nu} BrO + NO_2$
$I_2 \xrightarrow{h\nu} 2\ I$
$IO\ (+O_2) \xrightarrow{h\nu} I\ (+ O_3)$
$I_2O_4 \xrightarrow{h\nu} OIO + OIO$
$OIO \xrightarrow{h\nu} I\ (+ O2)$
$I_2O_2 \xrightarrow{h\nu} I + OIO$
$HOI \xrightarrow{h\nu} I + OH$
$INO \xrightarrow{h\nu} I + NO$
$INO_2 \xrightarrow{h\nu} I + NO_2$
$INO_3 \xrightarrow{h\nu} I + NO_3$
$I_2O_3 \xrightarrow{h\nu} OIO + IO$
$IBr \xrightarrow{h\nu} I + Br$
$ICl \xrightarrow{h\nu} I + Cl$
$BrCl \xrightarrow{h\nu} Br + Cl$
$CHBr_3\ (+O_2) \xrightarrow{h\nu} 3\ Br$
$CH_3Br \xrightarrow{h\nu} Br + CH_3O_2$
$CH_2Br_2 \xrightarrow{h\nu} 2Br$
$CH_2BrCl \xrightarrow{h\nu} Br + Cl$
$CHBrCl_2 \xrightarrow{h\nu} Br + 2\ Cl$
$CHBr_2Cl \xrightarrow{h\nu} 2Br + Cl$
$CH_2I_2 + (O_2) \xrightarrow{h\nu} 2\ I$
$CH_3I \xrightarrow{h\nu} I + CH_3O_2$
$CH_2ClI \xrightarrow{h\nu} I + Cl + 2\ HO_2 + CO$
$CH_2IBr \xrightarrow{h\nu} Br + I$

Table 5. Halogen heterogeneous reactions added to WRF-Chem in this study.

Heterogeneous reactions	Note	Uptake coefficient
$INO_3 \rightarrow 0.5\ IBr + 0.5\ ICl + HNO_3$	Sea salt only if pH < 5.5	0.01
$INO_3 \rightarrow 0.5\ I_2 + HNO_3$	Sea salt only if pH > 5.5	0.01
$INO_2 \rightarrow 0.5\ IBr + 0.5\ ICl + HNO_3$	Sea salt only if pH < 5.5	0.02
$INO_2 \rightarrow 0.5\ I_2 + HNO_3$	Sea salt only if pH > 5.5	0.02
$HOI \rightarrow 0.5\ IBr + 0.5\ ICl$	Sea salt only if pH < 5.5	0.06
$HOI \rightarrow 0.5\ I_2$	Sea salt only if pH > 5.5	0.06
$BrNO_3 \rightarrow 0.6\ Br_2 + HNO_3$	Sea salt only if pH < 5.5	0.08
$BrNO_2 \rightarrow 0.6\ Br_2 + HNO_3$	Sea salt only if pH < 5.5	0.04
$HOBr \rightarrow 0.6\ Br_2$	Sea salt only if pH < 5.5	0.1
$I_2O_2 \rightarrow I(aerosol)$		0.02
$I_2O_3 \rightarrow I(aerosol)$		0.02
$I_2O_4 \rightarrow I(aerosol)$		0.02
$ClNO_3 \rightarrow HOCl + HNO_3$	Hydrolysis	0.001[a]/0.01[b]
$BrNO_3 \rightarrow HOBr + HNO_3$	Hydrolysis	0.03[a]/0.8[b]
$ClNO_3 + HCl \rightarrow Cl_2 + HNO_3$		0.1
$ClNO_3 + HBr \rightarrow BrCl + HNO_3$		0.1
$HOBr + HBr \rightarrow Br_2 + H_2O$		0.1
$HOBr + HCl \rightarrow BrCl + H_2O$		0.1

[a] Uptake coefficient for moderate temperature

[b] Uptake coefficient for cold temperatures

Table 6. Model details and experiment configuration

Chemistry	
Chemical mechanism	MOZART-4 (Emmons et al., 2010; Knote et al., 2014)
Halogen chemical mechanism	MISTRA (Sommariva and von Glasow, 2012)
Photolysis scheme	FTUV (Tie et al., 2003)
Dry deposition	Wesely (1989)
Wet deposition	Grell and Dévényi (2002)
Biogenic emissions	MEGAN (Guenther et al., 2006)
Halocarbons and OVOCs air-sea fluxes	Online calculation (Liss and Slater, 1974; Johnson, 2010)
Alkenes and alkanes oceanic emissions	POET (Granier et al., 2005)
Sea-salt emissions	$seas\_opt = 4$, Archer-Nicholls et al. (2014)
N_2O_5 heterogeneous chemistry	$n2o5\_hetchem = 2$, Lowe et al. (2015)
Resolution and Initial conditions	
Horizontal resolution	30 km x 30 km
Vertical layers	30 or 52
Top of the atmosphere	50 hPa
Chemical initial condition	GEOS-Chem (Sherwen et al., 2016b)
Meteorological initial condition	Era-Interim (Dee et al., 2011)
Chemistry spin-up	20 days

Table 7. Summary of all the simulations to investigate the main processes involving reactions between halogen chemistry.

Simulation name	Oceanic fluxes	Debromination	Heterogeneous	Br-Alkenes	Br-Aldehydes	Cl-VOCs	Halogens
WRF-DEBROM	Online	√	√	√	√	√	√
WRF-GAMMADV2	Online	√ (γ divided by 2)	√ (γ divided by 2)	√	√	√	√
WRF-ZIS	Prescribed	√	√	√	√	√	√
WRF-NODEBROM	Online		√	√	√	√	√
WRF-NOHET	Online			√	√	√	√
WRF-NOBRALKE	Online	√	√		√	√	√
WRF-NOBRALD	Online	√	√	√		√	√
WRF-NOBRVOCS	Online	√	√			√	√
WRF-NOHALVOCS	Online	√	√				√
WRF-NOHAL	-						

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