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Atmospheric Chemistry and Physics Discussions

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

Alba Badia et al.

alba.badia.moragas@gmail.com

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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

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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 O3 and OX (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 ClY partitioning (Fig. 12) and the integrated odd oxygen loss rates for ClOx cycles in Fig. 15.

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

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species. This should be updated prior to publication.

Response: This heterogeneous chemistry is included in this work. Moreover, ClNO2 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. 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 N2O5 is that of Thornton et al. (2003). They suggest that, after uptake onto the aerosol particle, aqueous phase N2O5 reacts reversibly with liquid water to form an (as yet unobserved) protonated nitric acid intermediate (H2ONO+2). This then reacts with either liquid water, to form aqueous nitric acid (HNO3), or with halide ions to form nitryl halide (XNO2; where X=Cl, Br, or I):

N2O5 (gas) N2O5 (aq) (R3) N2O5 (aq) + H2O(l) H2ONO+2 (aq) + NO− 3 (aq) (R4) H2ONO+2 (aq) + H2O(l) −→ H3O + (aq) + HNO3 (aq) (R5) H2ONO+2 (aq) + X − (aq) −→ XNO2 + H2O(l). (R6)

In applying the parameterisation of Bertram and Thornton (2009) we assume that the limiting step is the uptake of N2O5 to the condensed-phase, and that it reacts in a near instantaneous manner with H2O and Cl− to give NO−3 and ClNO2 through Reactions (R4)–(R6). ClNO2 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 ClNO2 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.

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