

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

Anonymous Referee #2

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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 in 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

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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

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'.

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.

Detailed comments:

1) Page 2, line 4: Define the term 'reactive halogens'

2) Page 2, line 5: Only Cl-atoms 'reduce the lifetime of CH₄'

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- 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.
- 4) Page 2, line 10: what should be the effect on 'oxidation capacity' beyond the already mentioned CH₄ and particles?
- 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, ...?
- 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)
- 7) Page 2, line 30: Give definition of VSLH.
- 8) Page 3, line 1: What about the direct transport of XO?
- 9) Page 3, line 11: Which OVOC species do the authors have in mind?
- 10) Page 3, lines 15-19: Which heterogeneous reactions do the authors have in mind? Why is Cl not mentioned? How does de-bromination 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.
- 11) Page 3, lines 19-22: What does 'This source' refer to? What exactly is poorly understood? What do the authors mean with 'inconsistent levels' too high or too low?
- 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?
- 13) Page 3, line 33: 'heterogeneous recycling reactions' of what?
- 14) Page 4, lines 7-9: Here it would be good to have some information on the measurement techniques used.

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- 15) Page 4, first sentence of section 3.1: See comment 10, above.
- 16) Page 4, line 29: How is K_a parameterised?
- 17) Page 5, lines 6-8: Give examples for OVOC's emitted from the ocean.
- 18) Page 5, line 8: Which VOC's were included?
- 19) Page 5, lines 16-17: Give some details on sea-salt emission parameterisation.
- 20) Page 5, lines 21-25: This description is not quite clear. When 'Most of the reactions come from ... MISTRA', which ones? How is the high uncertainty of I2Ox reactions dealt with?
- 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).
- 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 reaction of gases in liquid droplets: Application to oxidation of SO₂ in aqueous solutions, Atmospheric Environment 15, (7),1129-1144
- 23) Page 7, Lines 13-28: Are reactions R11 and R12 not occurring at pH > 5.5? What about mass conservation in R13? Numbers or 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.
- 25) Page 14, lines 19, 20: The underestimation of aldehydes could be due to neglect of Cl reactions in the model. In fact heterogeneous oxidation of halogenides (by O₃) is

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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.

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

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

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

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

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

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'?

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?

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

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