

Interactive comment on “Halogens and the chemistry of the free troposphere” by D. J. Lary

Anonymous Referee #1

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David Lary presents a very interesting study on the potential importance of halogen chemistry in the free troposphere. He uses a chemical data assimilation analysis with input from several platforms to obtain fields of some halogen species in the atmosphere. Combined with model calculations he concludes that the contribution of atomic chlorine to methane oxidation in the free troposphere might be more than 10% and regionally up to 50%. Furthermore hydrolysis of BrONO_2 could contribute 35% to the HNO_3 production rate in the free troposphere. He also points to shifts in the $\text{OH}:\text{HO}_2$ and $\text{NO}:\text{NO}_2$ ratios which are influenced by reactive halogen chemistry and can be used as indirect evidence for the presence of halogens.

Major comments:

The paper is very brief and to-the-point which I like a lot, however, this comes with a description of the analysis/modeling procedure that is too short to understand. It is merely stated that a "chemical data assimilation analysis" (p. 5368) or a "careful constraint of

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a photochemical modeling system using chemical data assimilation" (conclusions) is being used. It is still unclear to me how much photochemical modeling is involved in his study or what the chemical reaction set is. Apparently the only observed species are sulfate aerosol (but which property: number, size, effective radius,.. ?), O_3 , HNO_3 , HCl , H_2O , CH_4 - therefore it is even more important to explain the approach used in this study because the main conclusions of this paper are about HO_x , NO_x , $BrONO_2$, $HOBr$, BrO , Cl - all species that are not observed and only loosely constrained by the observations. Especially the calculation of the relative contribution to reaction cycles of non-observed species requires a lot of additional information to be put into the model, an important one being heterogeneous chemistry. This is not at all explained in the manuscript. Some of the more important questions regarding this point are: what are the sources and sinks for Cl and Br in his model, how are they determined, what is the uncertainty of them? How strong are the constraints of the satellite data assimilation for the presented results?

On p. 5369, l. 2 it is stated that the analysis "start[ed] in October 1991" but only 2 months are presented (October 1991 and February 1993). Is there any information about seasonal cycles or year-to-year variability or are these 2 months the only ones completely analyzed? Do the presented results refer to these 2 months only or to a longer time span?

These are critical questions that should be addressed.

Minor comments:

p. 5368, l. 24/25: One such study appeared around the time of submission of Lary's manuscript in ACPD: von Glasow et al., 4, 4877 - 4913, 2004

p. 5369, l. 18: please explain what "equivalent PV latitude" is. The description in this whole paragraph was a bit too short for me.

p. 5369, l. 19: "coordinates. With.." maybe change into: "coordinates, with .."?

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p. 5370, reaction 4: this reaction is extremely slow and not referred to again - are there any results regarding the (likely negligible) contribution of R4?

p. 5372: HNO_3 formation via BrONO_2 hydrolysis: does this refer to gas phase or particulate phase HNO_3 ? The hydrolysis of BrONO_2 on particles is likely to produce NO_3 - which hardly increases the gas phase mixing ratios of HNO_3 .

Conclusions: the text is almost the same as in the abstract!

Figures:

They are VERY hard to read. On a color printout I couldn't read the legends, please enlarge!

Why is the caption of some figures (esp. fig 4) repeated in the text?

References:

There are some problems with capitalization in some of the references which might be due to problems with the EGU bibtex style. There is a new style available that should solve these problems.

Please use consistent names for the journals (esp J. Geophys. Res.)

Crutzen et al: add the u-umlauts to Muller and Bruhl

Lary et al, 2003 appears twice in the literature list

Reber et al: Mcneal → McNeal

Sander et al: add the o-umlaut to Honninger

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5367, 2004.

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