

***Interactive comment on* “Halogens and their role in polar boundary-layer ozone depletion” by W. R. Simpson et al.**

Anonymous Referee #1

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Review of “Halogens and their role in polar boundary layer ozone depletion”, by W. R. Simpson et al.

This paper is one part of a comprehensive review of surface (on and in) and atmospheric chemistry and physical processes associated (largely) with polar regions of the atmosphere. This review focuses on the atmospheric chemistry associated with ozone depletion events (ODEs) while also touching base with other elements of the overarching review, such as the atmospheric boundary layer, snow chemistry and mercury depletion events (MDEs). Thus, for this reviewer, the process is more akin to reviewing a book and estimating if all the areas that he or she feels are important are touched on. A list of sections, which is unusual I admit, will give the reader some idea of the range of topics covered.

1. History of discovery of ODEs 1.1 Introduction 1.2 Historic Overview of the discovery of ODEs 1.3 Key reactions and cycles 1.4 Observational, modelling and laboratory methods 2. Halogens and their roles in ODEs 2.1 Bromine 2.1.1 Groundbased measurements of bromine compounds 2.1.2 BrO Satellite observations: Spatial and temporal scale 2.1.3 The link to other places 2.2 Chlorine 2.3 Iodine 2.4 Interhalogen interactions 3. Key environmental processes and their effects on ODEs 3.1 The role of sea ice 3.1.1 Brine formation and aerosol production 3.1.2 Precipitation processes and modification of pH 3.1.3 Sources of reactive halogens 3.1.4 Frost Flowers as a direct halogen source 3.1.5 Frost flower-derived aerosol as a halogen source 3.1.6 Saline surfaces as a halogen source 3.1.7 Satellite remote sensing of frost flowers 3.2 The role of meteorology and boundary layer physics 3.2.1 Polar boundary layer description 3.2.2 Meteorological influences on ozone destruction events 3.2.1 Termination of ozone depletion events 3.3 The role of surface fluxes and snow photochemistry 3.3.1 HOx and NOx fluxes 3.3.2 Haloorganic fluxes 4 Impacts of ODEs on polar chemistry 4.1 Effects on halogen - mercury intereactions 4.2 Effects on hydrocarbons and aldehydes 4.3 Effects on radiation and of radiation 4.4 Effects on bromine export to the free troposphere 4.5 Effects on the sulfur cycle 4.6 Effects on aerosol production 4.7 Effects on ice core chemistry 5. Future scenarios of ozone depletion and open questions 5.1 Anthropogenic influences and atmospheric change 5.2 Global relevance of ODEs 5.3 Open questions 5.4 Future needs and plans 6. Summary Supplement 38 pages of measurements and locations with references compiled by Rolf Sander.

In addition, the comprehensiveness of the review also presents problems for a reviewer since very few people have expertise in all these areas.

The review deals very well with the presentation of the current state of the art of polar halogen chemistry. One of the major problems underscored (but perhaps not sufficiently) is the lack of definitive knowledge of the how chlorine and bromine from sea salt get transferred to the atmosphere and also the idea of the “bromine explosion”. The latter idea is concerned with the rapidity of release of bromine from the surface.

There are a few schemes but none are really very satisfyingly complete. The release of iodine is also important but here organic sources may be important as opposed to bromine and chlorine where it appears that inorganic sources dominate.

Once in the atmosphere bromine oxides have lifetimes of only a few hours yet they have a clear satellite signature which strongly suggests a longer lifetime. Thus the conclusion is that recycling of BrOx in the atmosphere must be occurring. Part of the review thus deals with the recycling chemistry.

The review also documents the major campaigns that have taken place in polar regions. It is clear that much effort has gone into these campaigns: design of new instruments that can survive at polar temperatures both in summer and winter, the actual physical effort required sometimes to make measurements in often very cold temperatures, wondering if the ice that one is camping on is stable etc. Perhaps this aspect is the stuff of an interesting book! 61514;

Overall, this is a very impressive review and given that many authors have been involved care has been taken to ensure continuity and cross referencing and differences in writing style are not too obvious and certainly not abrasive. I certainly can recommend this as a starting point for someone entering the field.

Lastly, the important problems are outlined and summarized at the end of the review.

One of the levels of detail (p4297 L27) "However at low ozone (O_3), Br can become more abundant than BrO." I would just point out that this statement is based on calculations not observations and this should be pointed out. Also it would be useful if there were some discussion about what might happen to Br-atoms at putative (based on calculations) at very high densities when there is no O_3 for recycling and HCHO is gone.

Typos and such like: except that I found the word "like" a wee bit over used. How about "such as" for a break! 61514;

P4289 L28: Example is volatile organic compounds

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P4291 L4: The main source for of reactive bromine species L14: Ozone depletion events occur...

P4297 Last line. "The cross reaction between BrO and ClO may be is important in stratospheric ...". Calculations based on measurements indicated that this reaction can account for about 30-40% of polar ozone loss in the stratosphere (WMO reports) so "is" is more appropriate that "may be".

P4298 L5: The channel leading to OXO is uncommon except for the case of iodine .." : In fact the reaction $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$ is about 25% or so of the total BrO/ClO reaction and occurs in the stratosphere. And although it photolyses rapidly OCIO has been observed from ground and space and is a useful indicator of Cly processing by PSCs.

P4298 L16/17: The bromine explosion reactions: It is probably more accurate to point out that the sequence of reactions is a theoretical sequence - I am not convinced that the observations can categorically pin down that sequence at present.

P4303 L15: Global maps of the total tropospheric and stratospheric column. . ." would be clearer to the reader.

L23-25: "Compared to stratospheric measurements, this technique is less accurate etc". Accuracy is a function of amount etc. Perhaps it is clearer to say that the method is less sensitive due to quenching of the resonance signal (so that is also done at lower pressures to try and reduce this effect.)

P4305 L14: "One example for of the involved complications.."

P4308 L8: "occurred" - spelling L28: Metop and GOME-2 are in space as we write and producing BrO amounts etc..

P4309 L25: Free tropospheric BrO: Could mention that reactive/short-lived halocarbons are also potential sources of free tropospheric BrO (WMO) in addition to the polar MBL.

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P4311 L12: “The could showed that . . .” tense

P4313 L3: “However, the nature of the chlorine atom precursor s in not necessarily well understood. . .” P 4313 L23. “frost flowers will be are considered as possible sources..”

P4322 L3. “Alkaline for to supporting bromine explosion..”

P4326 L24. Figure 7 is in the wrong order.

P4328 L20. “ this apparent seasonal asymmetry has been a point for discussion ever since.”

P4328 Section 3.2.3 this section is a bit weak. And it is important because I suspect it contains some of the clues as to why ODEs occur.

P4344 L14. Antarctic - spelling

P4384 Figure 2. Useful to give the location of the measurements P4388 Figure 6. Same as above, ie location required. P4389 Figure 7. Location (and also out of order) P4398 Figure 16. Location (e.g. near Alert etc or “see text”) P4402 Figure 20. Location.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4285, 2007.

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