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Atmospheric
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Discussions

Interactive comment on "The potential importance of frost flowers, recycling on snow, and open leads for Ozone Depletion Events" *by* M. Piot and R. von Glasow

Anonymous Referee #1

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Review of "The potential importance of frost flowers, recycling on snow, and open leads for Ozone Depletion Events", by M. Piot and R. von Glasow.

This paper basically follows the title, i.e. it investigates the impact of frost flowers (FF) as an Br- source, recycling of bromine on snow, and the impacts of open leads in the initiation and development of ozone depletion events in the Arctic marine boundary layer. They do this using a sophisticated 1D model with chemistry, microphysics and cloud formation used in a Lagrangian mode and by varying the horizontal extent of the FF patch, the width of the open leads, and the efficiency of recycling. Their model allows for the impact of strong heat and moisture input when traversing open leads and

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induces mixing. They also allow for the release of several other gases from the snow pack. Their approach is exhaustive, perhaps too exhaustive as it was quite an effort for this reviewer to try and assimilate the information contained in all the runs! 

Clearly this study Piot and von Glasow is based on a sophisticated modelling approach and contains quite a few original scenarios. We find several problems with the basics scenarios envisaged. If we understand correctly, all the calculations do not assume an initial presence of bromine along the trajectory. The surface release is thus constrained by what has been deposited at that instant and takes no cognizance of the fact that it would be possible for more bromine to be released that deposited since the surface really represents an accumulation of events, rather than a single pass. If the surface is an active source, which seems likely then the role of FFs must surely be less important in a instantaneous sense as is discussed in their paper - but perhaps more important as one of several continuing/ongoing source of bromine to the snow pack.

However, considering the primitive state of our understanding to the source of bromine and the mechanistic detail of ODEs in the polar boundary layer, this study seems very useful, but it should have an improved context set up in the introduction (which itself needs rewritten (see below)). Publication with some caveats added by the authors 9and perhaps a few less scenarios) would be useful in promoting further discussion of the issues raised in their work. It should be published with minor revision.

We would like the authors to take into consideration some of the following comments.

Major comments

1) For the further validation of the FF source function prescribed in the present work it would be useful if the authors emitted Na+ along with Cl- and Br- to the atmosphere and then compare the simulated Na+ and Cl- concentrations in the aerosols and irreversible deposition to the snowpack with any available observations. This appears feasible at least for the snowpack Na+ (or the Br/Na ratio) using the snowpack dataset by Simpson et al.(2005). For example, why not add something like Fig. 3 of Simpson et al. to Fig.

15 in the present work? From our comments above we are not convinced, from the present work in its current form, that the airborne transport of FF aerosols is a primary, perhaps ultimate source of bromine in the snowpack and in the polar boundary layer.

2) When discussing the simulated results for the impacts of FF aerosols and FFs themselves on the bromine deposition to the snowpack, the authors assume that snowfall is bromine-free (Sects. 3.6 and 3.8) But we consider that snowfall itself can be a source of bromine to the snowpack when looking at snowfall chemistry data at Alert (Toom-Sauntry and Barrie, 2002). We have done a preliminary calculation to see if this indeed can make a big difference and it appears that an amount ˜ 1.0E-10 mol/cm2/month of bromine can be delivered from the atmosphere to the snowpack via precipitation, which may be important for the snowpack a few hundreds km away from the FF field (cf. Fig. 15). It would be useful if the authors could put this issue into their context.

3) Strong surface temperature inversions are common and extensive features observed in the Arctic atmosphere and are believed to be linked strongly with ODEs (e.g. Bradley et al., 1992). It appears that the surface inversion persists most of the time and that the breakup of the surface inversion does occur but only once in a while when tracers are mixed efficiently down to ground level (Oltmans et al., 1989; Leaitch et al., 1994; Gong et al., 1997; Hopper et al., 1998; Morin et al., 2005). It is interesting to see that the present simulations by the authors never get the surface inversion for about 3 days (equivalent to a few hundred km downwind of the OL and/or FF fields) while the boundary layer air column is transported over the cold snow surface at 245 K. We wonder if the model runs ever get (or start from) the surface inversion when the air mass is transported long enough over the cold snow surface. Anyway it would be useful if the authors could show temporal changes in thermal stability in the lowest atmosphere, for example, by showing the potential temperature profiles and their relation to vertical diffusivity. Also it would be useful if the authors could state the relevance of the present model runs to those ODEs observed in the surface inversion.

4) The authors have proposed an intriguing possibility for the impacts of boundary-layer

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clouds on the vertical mixing of ozone from aloft and on the suppression of bromine radical chemistry. It might be a good idea for the authors to stress the difference between the usual forms of vertical mixing mechanisms such as turbulent diffusion by wind shear (Gong et al., 1997; Strong et al., 2002) and topography-induced disturbance (Morin et al., 2005). The influence of clouds on bromine chemistry in the mid-latitude marine boundary layer was addressed by an earlier study by von Glasow et al. (2002) in which gas-phase bromine species are also taken up by clouds (and aerosols) but only during the nighttime. There is a nice explanation for this behaviour in the paragraph 43 of the von Glasow et al. paper, which is never mentioned in the present paper by Piot and von Glasow. Is it indeed by the different reason that lead to the simulated suppression of bromine radical chemistry in the cloudy Arctic boundary layer? It would be useful to know whether this is the case or not, in terms of difference in the cloud influence between the mid-latitude and polar boundary layers.

5) Lidar measurements detected cloud plumes of buoyant convection from Arctic open leads reaching 3-4 km altitude and it was estimated that open leads as wide as 10 km could produce such intensive plumes during the wintertime (Schnell et al., 1989; Serreze et al., 1992). McElroy et al. (1999) suggested this possibility for free tropospheric BrO measured in the Arctic spring. On the other hand, the present simulations do not see that level of intensive plumes even for the 1-hour long overpass of open leads (equivalent to 18 km, Runs 4 and 5). We wonder why. Is it because the boundary conditions are totally different? Or, is the MISTRA model intrinsically not capable of handling free convection?

6) The authors investigated the impacts of NO, NO2, HONO, H2O2, HCHO, and C2H4 emissions from the snowpack individually and concluded that only the HONO emission could exert a notable influence on bromine chemistry (Sect. 3.7). It seems to us that this conclusion is somewhat constrained by their choice of the emission fluxes in the first place. The HONO emission of 5.0E+8 molec/cm2/sec is larger than any numbers prescribed for other species emitted. I wonder how representative the present choice

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of the emissions is. There seem to be alternative choices for the NOx and HCHO emissions. If the authors took the HCHO emission estimate of 2.0E+9 molec/cm2/sec from Grannas et al. (2002) and the NOx emission estimate of 40 nmol/m2/hour (ca. 6.7E+8 molec/cm2/sec) from Beine et al. (2002), the present conclusions by the authors might have changed. The authors should at least try these cases as well before concluding that only the HONO emission is important. Also, the insignificance of C2H4 could have arisen from the MISTRA's chemical mechanism in which Br + C2H4 produces HBr that is recycled to Br2/BrCl quite rapidly on aerosols. If it is assumed to produce organically-bound bromine compounds that are rather hard to get recycled (Sander et al., 1997; Toyota et al., 2004), the present conclusion might change. A significant amount (several tens of pmol/mol) of bromoacetaldehyde, which is one of the degradation products from the reaction Br + C2H4, has been detected in-situ near Barrow recently (Keil and Shepson, 2006). Finally, it would be useful if the authors also showed/reported the simulated concentrations/profiles for HCHO, C2H4, etc. and compared with previous observations if available. Among NO, NO2, HONO, H2O2, HCHO, and C2H4, only the NOx profiles are shown in Fig. 2B, although having complained above about the number of scenarios perhaps this should only be considered if the amount of other information/figures decrease.

7) We consider that the authors can significantly improve the readability of the manuscript by more careful and extensive proofreading. I was rather distracted especially in Results and discussions (Sect. 3) when I read basically the same kind of message repeated twice or more in one paragraph after another.

[Minor comments]

A) It appears that sulfate aerosols are present for the recycling of bromine even in non "Arctic-Haze" runs from what I read in Sect. 3.7 (page 4557, lines 10-11). But I miss the aerosol number density and size distribution parameters assumed in those non-haze runs (cf. Table 2).

B) What are the date and latitude conditions for J-value calculations? Also, what time are the sunset and the sunrise in the simulations?

C) Reaction (20), i.e. BrO + HCHO = HOBr + CHO. The rate constant on which the present work is based was derived rather theoretically than experimentally (i.e. via kinetic experiment) by Hansen et al. (1999). The rate constant was derived from a more recent kinetic experiment (although by fitting to complex mechanism) by Orlando et al. (2000) and was found to be significantly smaller than Hansen's. Based on this newer rate constant Grannas et al. (2002) estimated that its contribution to the HOBr production may be as low as 1% or less in the Arctic springtime. We would like the authors to put a few words about this issue in Sect. 3.2 when discussing the impact of Reaction (20).

D) The CHBr3 deposition is simulated to comprise a non-negligible fraction of the bromine deposition to the snowpack, which is actually a little surprising, but we cannot find its dry deposition velocity in the manuscript and the supplement. How large is it exactly and is there any observational support for it?

E) The authors did sensitivity runs to see what happens if nighttime recycling of bromine from the snowpack does not take place but did not definitively conclude that the active nighttime recycling is rather unlikely. But we would rather think that the nighttime recycling of bromine from the snowpack is indeed not very active because it would release too much gaseous bromine to the wintertime Arctic when the frost flower formation is even more prevalent than in the spring.

[Technical suggestion]

Please make sure that the Figures are printed big enough to see in the final ACP version of the paper. Please also take into account the fact that North American readers print to letter-size (8.5 x 11 inches) papers which results in some minor shrinkage to the plots. The lines for TCBr, TCg, TCa, TCd, and IDBr should be annotated in each plot.

Page4527, line 15: than PFF -> than to PFF

P4527, L16: sea-ice zone -> marginal sea-ice zone (?)

P4527, L19: chemical heterogeneous reactions -> heterogeneous chemical reactions

P4531, L26: It should be stated that temperature at the surface of the FF field is "fixed" at 255 K (or 260 K) more explicitly. It was not clear to us until we read through the Results and discussion section.

P4539, L 25: along -> over

P4541, L 22: with 17 pmol mol-1 -> 17 pmol mol-1 which is

P 4542, L 19: his -> her (perhaps)

P4546, L 19 (also page 4552, L 19): quasi -> almost

P4547, L 4: beneath -> below

P4547, L 24: humidity -> relative humidity

P4549, L 14: at the surface -> at the particle surface (or ground surface?)

P4550, L 26: showed -> shown

P4552, L 1: Now, -> Then,

P4557, L 21: Seems to be an inappropriate use of colon. Please rephrase. Also, the entire paragraph (Ls 16-21) appears rather too rough. What do "the chemistry explained above" and "as explained in this section" point to?

P4566, Ls 13-14: I suppose that the authors are trying to cite an article from the Boundary-layer Met. journal but not properly in its current form.

P4524, L14 and following. The introduction could be tidied up a wee bit. For example the wording of the first few paragraphs could be cleaned up a bit. Also as it is an introduction it would be useful to set the scene by mentioning the “source problem” and the “recycling problem” and also the problem as to how an ODE effectively appears to shut down in the summer and not appear in the fall.

P4525, L12: “a significant amount of halogens ..” The authors haven’t discussed the loss processes of BrOx at this point - again this is part of the introduction that really does need tidied up.

P4525, L19, eq (14): this equation appears a bit out of the blue.

P4527, L13: “This might indicate an implication of FFs” sounds odd. Suggest “This would suggest that FF could be implicated in the generation of BrO”.

P4527, L16: There is no (clear) discussion of the FF aerosol production mechanism in this study. We feel that some words should be allocated to letting the reader know what is going on without have to backtrack to the Rankin et al paper, particularly as this really is the major novelty of the paper.

P4528, L28: Before launching into details, first let the reader know what you are going to do.

P4529, L7: “we HAVE used the one dimensional model” sounds better. Or “We use”

P4530, L1: explicitly (spelling)

P4532, L17: OL “provide a source region for sea salt aerosols” Is this true? I would have thought that the associated fetch associated with a small Polyna or OL would not generate large enough waves for aerosol generation.

General: Could the FF aerosols be replaced with blown snow with deposited bromide and still have the same impact?

We don’t think that leapfrogging is the best description of the process of bromine movement: It seems more like hopping as the air parcel passes that way only once and a fraction of the bromine deposited at that instant is released.

This also leads to another more serious point. If we understand correctly, all the calculations do not assume an initial presence of bromine along the trajectory, to that it would be possible for more bromine to be released that deposited since the surface really represents an accumulated of events, rather than a single pass.

What is the initial temperature profile?

P4538, L6: ID(Br) as defined, although accumulated deposition, this is not a local quantity as the air parcel continues to move. Rather it is the integral of deposition along the path. This should be made clearer.

P4542, L17. I estimate the ozone loss due to surface deposition is about 10 ppbv in 4 days . Or assuming a 100 m MBL would imply a VD of about 0.02 cm/s. If the MBL remains at about 100 m this seems rather rapid as it would remove the ozone is a few weeks whereas 40 ppbv can persist in transit through the Arctic for a few weeks with no perceptible depletion. Hmmmm

In general: OL. The size of the leads used sound rather large - what sort of statistics are available? Also what are the aspect ratios of the leads? Surely the wind doesn't always blow across the leads?

What about ubiquitous ice crystals? They can act as surfaces for heterogeneous reactions and if there is an inversion they are almost always present.

P4554, Role of acids? SO2 sources in Russia in the high Arctic appear to have been decreasing. This is likely to have affected the general acidity of aerosols over the last 20 years. Has it impacted ODEs?

[References]

Beine, H.J. et al., J. Geophys. Res., 107(D21), 4584, doi:10.1029/2002JD002082, 2002.

Bradley, R.S. et al., J. Geophys. Res., 97, 15,699-15,712, 1992.

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Gong, S.-L. et al., Atmos. Environ., 31, 969-981, 1997.

Grannas, A.M. et al., Atmos. Environ, 36, 2733-2742. 2002.

Hansen, J.C. et al., J. Phys. Chem. A, 103, 8543-8546, 1999.

Hopper, J.F. et al., J. Geophys. Res., 103, 1481-1492, 1998.

Keil, A.D., and P.B. Shepson, J. Geophys. Res., 111, D17303, doi:10.1029/2006JD007119, 2006.

Leaitch, W.R. et al., J. Geophys. Res., 99, 25,499-25,517, 1994.

McElroy, C.T. et al., Nature, 397, 338-341, 1999.

Morin, S. et al., Geophys. Res. Lett., 32, L08809, doi:10.1029/2004GL022098, 2005.

Oltmans, S. et al., Atmos. Environ., 23, 2431-2441, 1989.

Orlando, J.J. et al., Geophys. Res. Lett., 27, 2633-2636, 2000.

Sander, R. et al., Tellus, 49B, 522-532, 1997.

Schnell, R.C. et al., Nature, 339, 530-532, 1989.

Serreze, M.C. et al., J. Geophys. Res., 97, 9411-9422, 1992.

Simpson, W.L. et al., Geophys. Res. Lett., 32, L04811, doi:10.1029/2004GL021748, 2005.

Strong, C. et al., Atmos. Environ., 36, 2641-2652, 2002.

Toom-Sauntry, D. and Barrie, L.A., Atmos. Environ., 36, 2683-2693, 2002.

Toyota, K. et al., Atmos. Chem. Phys., 4, 1961-1987, 2004.

von Glasow, R. et al., J. Geophys. Res., 107, 4323, doi:10.1029/2001JD000942, 2002.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4521, 2007.