

## ***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 #3**

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This is a very detailed manuscript dealing with an interesting topic and containing a wealth of information. It provides results of modeling studies concerning the influence of surface properties in polar regions on the activation of reactive bromine compounds and the subsequent depletion of ozone in the atmospheric boundary layer. Such calculations are much needed because even more than 20 years after the discovery of the ozone depletion events (ODE) in the polar regions the exact mechanism and required conditions are not known. Most recently, the impact of salty frost flowers formed on new sea ice, the activation of reactive bromine compounds on snow or the existence of open leads have been discussed as important for the occurrence of ODEs. Therefore, modeling studies taking appropriately into account processes at all these different

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surfaces can provide valuable insight into their roles for the chemical processes. However, I have some mixed feelings about the manuscript, which I try to explain in my more specific comments and questions.

1. I'm not sure if the authors correctly model the processes occurring at the different surfaces considered in the calculations. These different surfaces are called frost flowers, open leads, and snow by the authors. I give some comments to these different types of surfaces.

1a. Frost flowers: In the model runs # 1 to # 18 frost flowers are considered as a source of sea salt aerosols. The aerosol source strength depends on wind speed and the sea salt concentrations in the aerosols are computed as three times the salt concentrations in standard seawater. The aerosols are considered being liquid. Only in model run # 19 frost flowers are considered as direct source of reactive bromine, but in this run no aerosols are generated (P. 4558, l. 13 'É but do not include the production of Ffaerosol'). Why are frost flowers regarded as either a direct source or a sea salt aerosol source? In my opinion, frost flowers are probably both and both at the same time. In model run # 19 with the direct production of Br<sub>2</sub> on the frost flowers the O<sub>3</sub> depletion is very efficient. Is that not an indication of the important role frost flowers can play for ODEs? The authors obviously don't see it this way, because they downplay the results of the model run # 19 in section 3.8. Why? It is correctly assumed that if the aerosols generated by frost flowers are liquid, they would exhibit sea salt concentrations as high as three times the standard seawater concentration. This is at the upper limit of salinities observed in frost flowers but it is justified for the model runs presented here. However, checking Figure 2H and 2I it seems like that at least in the lower 100 m of the model domain the temperatures after the frost flowers are lower and the relative humidities are equal or smaller (although very difficult to determine with the provided figures). Fig. 9E also shows a constant decrease in temperature in model runs # 1 and 11 after the frost flowers. Why should the frost flower aerosols, which are obviously solid at the beginning, under these conditions melt or become liquid?

This is very important because due to the formation mechanism of the frost flowers as discussed in the introduction the sea salt ions must be enriched in the QLL. In that case the solid particles generated by the frost flowers would be coated by a layer with significantly higher sea salt concentrations compared to the modeled aerosols. How does this affect the bromine activation in the model? By the way, such higher sea salt concentrations in the QLL would also apply to the frost flowers still on the ground. Is that taken into account for the model run # 19 with the direct Br<sub>2</sub> release from the frost flowers?

1b. Open leads: In the model open leads contribute water vapor and sea salt aerosols to the atmosphere and act as an irreversible sink for aerosols. The very strong effect of the increased humidity, the cloud formation and the break-up of the boundary layer structure as described on (P. 4541ff) is very interesting. The authors could stress these results much more.

1c. Snow: The way how the processes at this type of surface are modeled is either very obscure or I misunderstood the approach. I try to summarize how I read this. A downward flux of (reactive and less reactive) bromine compounds caused by deposition is calculated. As soon as these molecules touch the surface, 3 out of 4 bromine-containing molecules are (by whatever mechanism) immediately emitted back to the gas phase in the form of Br<sub>2</sub> and BrCl. (In some runs the ratio is varied between 0 and 2 out of 4.) Is that correct? Such a surface is then called 'snow'. The assumption is mainly based on the Br<sub>2</sub> and BrCl measurements above a snow surface by Foster et al. and Spicer et al. and the authors further refer to the Peterson and Honrath paper on reduced O<sub>3</sub> in the interstitial air of a snowpack. Actually, neither of these publications really demonstrates that there is such a bromine transformation mechanism on snow. I admit that there is some circumstantial evidence that such activation can take place on snow surfaces. However, the production rate would depend (among other parameters) on the concentrations of bromine compounds (or bromide if you take bromide as the initial source) in the snow, but it will certainly not depend on the downward flux! In

summary, this approach is not warranted and is not justified by any measurements I know of. The modeling approach certainly does not represent the processes occurring at the snow surface. I understand that in all model runs an efficient O<sub>3</sub> depletion was only possible if such a process at the ground is included (e.g. P. 4540, l. 8: 'the deposition/re-emission of halogens is a key process for the ozone depletion.'). In my opinion this result is very important, but my conclusion is very different. I think it suggests that a bromine activation process at the ground would be able (and sufficient) to activate necessary amounts of bromine for an ODE in the entire ABL. Aerosols are not needed in the model. (However, it could be that the aerosols generated by frost flowers are not correctly described in the model (see 1a) and that this could change for calculations with solid FF aerosols?). If that is true and if the snow would provide such a surface, why are ODEs not commonly observed over any given snow surface with a stable ABL? Or if you put it the other way round: which surface would have the appropriate properties to facilitate a mechanism as incorporated in the model runs? Frost flowers (or more general: new sea ice) comes to my mind

2. I fully disagree with the comparison of the model results with the measurements by Simpson et al. (2005) regarding the bromine concentrations in the snow as a function of the distance from the open water. The comparison between the model results and the measurements rather highlight the wrongly assumed process at the 'snow' surface in the model as discussed in 1c. Only if it is assumed that the modeled deposition lasts for several day (8 to 24) you get snow concentrations comparable to the measurements. This clearly demonstrates that the reservoir of bromine species in the snow is much larger than just the small amount deposited during the model run. Clearly a much less effective release process but using this higher initial bromide concentration can have the same effect in the calculations. The authors correctly state in their conclusions: 'In reality, of course, bromine deposited at night (I would add here 'and in the days and nights before') could be recycled on the next day after sunrise.' (P.462, l. 25-26). I recommend deleting this paragraph (P. 4556, l. 6ff) and also Figure 15.

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3. Taking into account the above misrepresentations of the processes occurring at frost flower and snow surfaces conclusions like 'È that bromide activation is unlikely to occur on frost flowers crystals.' (P. 4560, l. 16) or ' È the best agreement with observations if the recycling of halogens on snow is considered' (P. 4560, l. 10-11) are not justified. These should be deleted. This also affects the title, which should be changed accordingly. The calculations rather show that surface processes and properties are very important for the development of ODEs and that mixing in the ABL would be efficient enough to delete the O3 in the entire ABL.

4. I find the figures showing the concentrations and the meteorological data very difficult to read even in the electronic version of the paper. The printed versions are essentially unreadable. This concerns Figures 2 - 4, 6 - 11, and 13.

Further minor comments:

P. 4523, l. 25: 'This might significantly impact the global tropospheric ozone budget': Any evidence for this statement?

P. 4528, l. 7: 'Ludwig-Soret effect': As far as I know the Soret effect has hitherto been applied to mixtures of two neutral organic liquids. I haven't seen any evidence that it can also be applied to a system of ions dissolved in the QLL of ice. Maybe it can, but the presented model runs do not provide any insight into the mechanism of the migration of the salt ions into the frost flowers. At the end the higher salinities of frost flower measured in the field are used as starting points for the frost flower aerosols. Therefore, this sentence should be deleted. If you keep the Zhang et al. paper: it is not correctly cited (issue and page numbers).

P. 4530, l. 6: 'Photolysis rates are calculated onlineÈ': I couldn't find any further information on the photolysis rates. Maybe I missed it? Are they calculated for a certain date and latitude? What about the diurnal cycle? Later on there is the information that in some model runs certain emissions are during the night and so on. What are the maximum photolysis rates? More information on that (maybe in the supplement) would

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be good.

P. 4534, I. 13: 'J(H<sub>2</sub>O<sub>2</sub>) and J(HCHO) are used to obtain spring values for hydrogen peroxide and formaldehyde fluxes.': Previous measurements of the exchange of H<sub>2</sub>O<sub>2</sub> and HCHO between the atmosphere and snow have demonstrated that the fluxes of both compounds are stronger related to temperature-dependent equilibria than to radiation intensities. Moreover, higher photolysis rates would rather destroy both compounds in the snow than increase the production and thus the flux to the atmosphere. In the model runs presented here, the snow temperatures are sufficiently low so that I would rather expect a flux from the atmosphere to the snow instead of emissions. Since the fluxes do not show any effect according to section 3.7 I recommend repeating the model runs without any fluxes of H<sub>2</sub>O<sub>2</sub> and HCHO.

P. 4537, I. 22: 'temperature inversion at around 300 m': The height of the BL is an important parameter. Unfortunately, it is not clear to me how you determined it: by the temperature inversion or using the profiles of the relative humidity (like also sometimes mentioned in the manuscript). It would be good to clarify this. I also recommend showing the BL height (for example as a black line) in all plots of the temperature and the relative humidity in Figures 2 - 4, 6 - 11, and 13.

P. 4553, I.2: Delete 'Due to important climatic implications': As far as I know 'Arctic Haze' has been investigated for several reasons. Better to include an appropriate reference here.

Plots of O<sub>3</sub> concentrations in Figures 3, 4, 6 - 11, and 13: I suggest adding the 25 nmol mol<sup>-1</sup> isopleths to all O<sub>3</sub> plots where appropriate.

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

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