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Atmospheric
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Discussions

Interactive comment on "Synoptic-scale meteorological control on reactive bromine production and ozone depletion in the Arctic boundary layer: 3-D simulation with the GEM-AQ model" *by* K. Toyota et al.

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We would like to thank the referee #1 for his/her useful comments. We will answer each of the specific points raised by the referee below.

[Referee] - page 26212: "Cl-, which is typically 2 to 3 orders of magnitude more abundant than Br- in seawater and polar snowpack" This implies that the Cl-/Br- ratio in seawater is variable. However, the Cl-/Br- ratio is a very well defined number for sea water (e.g. Millero et al., Deep-Sea Res. I, 55, 50-72, 2008). Only for the snowpack this ratio shows some variation.

Of course, that was not the intent. We will rephrase to make it clear that the variability lies within the snowpack.

[Referee] - page 26216: "The sea-salt aerosols are assumed not to serve as a source of halogens" Why are halides in sea-salt aerosols not considered? Is it assumed that they are not important? Would it be possible to switch them on in the model and check if they have an effect on the results? As long as they are not included in the model, it is not possible to analyse their importance.

We did not consider gaseous halogen release from sea-salt aerosols generated on the open water surface because we wanted to simplify problems addressed in this study. According to references cited in the section 3.5 of our ACPD manuscript, observed gaseous and particulate bromine concentrations in the springtime Arctic boundary layer are generally too high to be explained by bromine release from sea-salt aerosols. In the revised manuscript, we will cite one of those studies at the sentence inquired by the referee.

As mentioned by the referee, however, it would need an additional model run before we can totally rule out the sea-salt aerosols emitted from the open water surface as a source of reactive bromine across the Arctic. But the numerical chemical solver used in this study does not deal with bromide (Br-) as an independent variable. Therefore autocatalytic halogen release from sea-salt aerosols cannot be simulated in an explicit manner as has been done by box models that include detailed multi-phase reactions in the gas and aqueous phases. Still, it would be able to simulate this process in a highly parameterized fashion. For instance, size-resolved sea-salt aerosol mass source fluxes simulated in GEM-AQ could be combined with a prescribed Br- deficit relative to seawater as a function of aerosol size, as was done in the p-TOMCAT model by Yang et al. (2005). This method, however, relies on observed Br- to sodium ratios in aerosols, which are "contaminated" in the polar region by aerosols derived from saline snow/ice surfaces including frost flowers as well as other bromine sources including direct volatilization from surface snowpack and blowing/drifting snow. Also uncertain is a source function of sea-salt aerosols from open leads in between sea ice with only short fetch available for wind-wave interactions.

Thus what the referee is suggesting here is, in fact, would be another study using GEM-AQ.

[Referee] - page 26216: "...our simple scheme of bromine chemistry but without chlorine chemistry." It is a pity that chlorine chemistry is not included because it is very important to understand the oxidation of NMHCs in polar regions. I understand that adding chlorine is probably beyond the scope of this study. However, maybe it could be done as the next step of the model development.

At the current stage of the model development, we felt that we should simplify the problem by not including the chemistry of reactive chlorine and its source problem. Also, we were/are not aware of the existence of intensive hydrocarbon measurements (or ClOx radical measurements) performed in the field from the Arctic during the simulated period (April 2001) which we could use for evaluating model runs even if the model had incorporated chlorine chemistry. We decided to simulate the spring 2001 case because we could avoid a long spin-up time by using global chemical weather fields from GEM-AQ available between the years 2001-2005 from our preceding work by Kaminski et al. (2008) whereas the quality of the GOME BrO data became degraded progressively after 2001. The chlorine chemistry in the polar boundary layer is indeed an interesting area to study further but was not our main goal at this time.

[Referee] - page 26216: "Zhao et al. (2008) developed another version of GEM-AQ" As far as I understand, both this work and Zhao et al. (2008) use GEM-AQ as their base model and implemented halogen chemistry. Also, there is some overlap in the list of authors of this work and Zhao et al. (2008). Was there a reason for splitting the model development? If yes, are you planning to merge the versions again?

Zhao et al. (2008) addressed an issue of reactive halogen release from airborne sea salt particles emitted from open/refrozen leads potentially covered with frost flowers. Considering relatively short timescales involved in mass transfer between gas and aerosol phases, perhaps on the order of minutes, it made sense for that study to use a chemical solver that could handle autocatalytic halogen release via multiphase reactions in an explicit manner by introducing aerosol bromide and chloride concentrations as independent variables. It was then decided to use the MESSy/MECCA photochemistry module (Sander et al., 2006) incorporated to GEM-AQ. One downside of this choice was an extra computational burden to the model by dealing explicitly with differential equations of multiphase reactions. For the present study to simulate the snowpack source of reactive bromine, it was felt not necessarily required to rely on such a sophisticated but computationally demanding numerical solver. We did not have an opportunity to merge these two versions of GEM-AQ in the frame of this study, but may consider it as a choice when we pursue the simulation of polar and/or tropospheric halogen chemistry further if resources permit.

[Referee] - page 26217: "Br2 is emitted to the atmosphere at a rate prescribed from the dry deposition fluxes of HOBr, BrONO2, HBr and O3" The aqueous-phase reaction HOBr + HBr produces Br2 only at low pH. Is this taken into account? I am not aware of a mechanism that acidifies brine created from seawater.

In our present model we did not handle the effect of changing pH values in the snow. As pointed out by the referee, it remains unknown whether the uptake of HOBr to unacidified brine can release Br2 (and/or BrCl) to the gas phase well above -20 degree Celsius. We meant to stress this point in the section 3.4. The role of the acidity, however, was not phrased adequately there. We will add a statement to remind readers on the requirement of low pH conditions for liquid halide solutions to release Br2 and/or BrCl via HOBr uptake at least at room temperature, i.e. above the freezing point of water. In particular, the surface snowpack in the Arctic may be acidified rather frequently by a deposition of haze pollution material transported from distant sources, as pointed by another referee. In that case, a surface reaction of HOBr which requires acidity to release Br2 such as at the room temperature may well operate. We will adjust our message from the paper by considering this possibility, which indeed seems likely.

[Referee] - page 26222: "Run 1 is to simulate a benchmark case without bromine chemistry" The term "Benchmark" is normally only used for analyzing the model performance, see e.g.: http://en.wikipedia.org/wiki/Benchmark_%28computing%29 Thus, it is probably better to call Run 1 the "base case" or "reference case" instead.

We will change the word and use the “reference case”.

[Referee] - page 26228: "It appears that surface ozone mixing ratios [...] were depleted much too frequently [...], indicating either the irrelevance of frost flowers as a source of reactive bromine or inaccuracy in the PFF algorithm employed by Kaleschke et al. (2004)." It should be noted that PFF only represent conditions that _potentially_ create frost flowers. Maybe the discrepancy can be reconciled when considering that PFF are just an upper limit for the occurrence of real frost flowers.

Until pointed out by the referee, we (at least the first author) were not clearly aware that the PFFs should be regarded as an upper limit for the occurrence of real frost flowers in the field. It now seems that this could provide another plausible explanation for why Zhao et al. (2008) simulated more frequent ODEs at coastal stations than we do in the present work. We will change our statement in the paper accordingly.

[Referee] - page 26235: "There are more than a few reasons to believe that heterogeneous bromine activation is favored at lower temperatures:" Here, several reasons are listed again which have already been mentioned on page 26213. Is there a reason why shifting the equilibrium constants of R10 towards Br2 formation is not mentioned here again?

Opps, a slip of the hand/keyboard. We will repeat this item in page 26235.

[Referee] - page 26235: "decreasing alkalinity via carbonate precipitation from freezing seawater as envisaged theoretically by Sander et al. (2006)" Although Sander et al. (2006) was only a theoretical study, it could be mentioned that CaCO3 precipitation was indeed found in the Arctic by Dieckmann et al. (The Cryosphere, 4, 227-230, 2010).

We see that the Dieckmann et al. paper reported the existence of ikaite, which was argued by Morin et al. (2008) to be a likely form of carbonate precipitated from sea ice, rather than calcite, which Sander et al. (2006) assumed to precipitate from freezing brine. This field evidence suggests that brine laid on the surface snowpack does not titrate alkalinity as efficiently as calculated by Sander et al. (2006), and yet it appears to support the feasibility of a titration mechanism mediated by “evapoconcentration” in brine-derived aerosols as proposed in their follow-up study (Sander and Morin, 2010). We will rephrase the corresponding statement in page 26235 to “decreasing alkalinity via carbonate precipitation from freezing brine (Dieckmann et al., 2010; Sander and Morin, 2010).”

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