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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 #2 for his/her detailed comments on the paper.

We recognize that we dealt with quite a few processes to simulate the chemistry of ozone and bromine in the Arctic boundary layer and to evaluate the simulated results. And, using a simplified scheme to describe what may be occurring at the air-snowpack interface, we could not answer some of the key questions related to the physical mechanism of reactive bromine release in a definitive manner. But we consider it useful and

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important for the research community to show that the occurrence of ODEs and “BrO clouds” can be simulated quite consistently across the Arctic by putting several pieces of information together in a 3D model like this, even though each of the implemented processes is “known” to some extent.

To our knowledge, this is the first 3D model study where the occurrence of “BrO clouds” is simulated at the spatial scales of synoptic weather patterns quite successfully as a result of bromine spontaneously released from the snow to the atmosphere based on parameterizations in the model. Such capability of the model also allowed us to show that reactive bromine can be actively released from the snow on the Arctic sea ice even at temperatures well above -20 degree Celsius. We thus consider that “synoptic-scale” is a good key word to describe this study. However, we agree with the referee regarding his/her comment that the title of the paper should reflect its real content. We will therefore change the title to “Analysis of reactive bromine production and ozone depletion in the Arctic boundary layer using 3D simulations with GEM-AQ: Inference from synoptic-scale patterns”.

We intended to stress our finding as regards surface temperature conditions during the occurrence of “BrO clouds”. But, after reading the comments from the referee, we reconsidered potential mechanisms behind bromine activation from the snow. We now consider that acidification via pollutant deposition could simply explain the active bromine release from the snow above -20 degree Celsius in the Arctic. We will revise our manuscript mainly by taking this into account.

Regarding the editorial concern, we will go over the revised manuscript with an extra caution especially by native English users among the authors of this paper.

We will answer each of the specific points raised by the referee below.

[Referee] 1. Much of the Introduction reads like a (5 page) review, without clearly laying out the questions the paper will address.

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We will shorten the introduction and put more emphasis on the questions addressed in this study.

[Referee] 2. Page 26213, line 14 - why is a pH below 6.5 "hardly attainable"? I believe they have frequently been measured to be below this. Deposition of sulfate/haze aerosol can do a good job of acidifying the surface snowpack.

The number of data is very limited over sea ice, but it does seem to occur in the Arctic. We will adjust our message by considering this possibility, in that acid-assisted bromine release mechanism may operate quite often in the springtime Arctic snowpack perhaps to explain the occurrence of "BrO clouds" at temperatures higher than -20 degree Celsius.

[Referee] 3. Page 26216: I think the paper should explain the impacts of ignoring chlorine chemistry. Chlorine chemistry is well known to be important, e.g. in terms of accelerating BrO conversion to Br atoms via the BrO + ClO reaction, by producing HCHO from Cl+ CH4, etc. Could you come to inappropriate conclusions by ignoring chlorine chemistry?

According to hydrocarbon concentration ratios measured in the field (e.g., Jobson et al., 1994), the Cl-atoms play no more than a secondary role in destroying ozone in the springtime Arctic boundary layer and that the importance of chlorine chemistry in the polar troposphere lies more in hydrocarbon chemistry itself. As indicated from photochemical box model and field measurement studies, hydrocarbon oxidation initiated via Cl-attack does appear to produce an appreciable amount of HCHO and CH3CHO in the springtime Arctic boundary layer, but the concentrations of these carbonyls would be controlled more by emissions from the snowpack associated presumably with photodegradation of dissolved organic compounds (e.g., Shepson et al., 1996; Tang and McConnell, 1996, Sander et al., 1997, Boudries et al., 2002).

On the other hand, measurements of ClO and OClO radicals sometimes indicated that the reaction BrO + ClO may play a role in the Arctic boundary layer (Tuckermann et

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al., 1997; Pöhler et al., 2010). But it appears that the instruments need to attain lower detection limits before we can assess the contribution of chlorine chemistry in the polar boundary layer confidently based on the measurements of ClO and OClO.

As indicated from field studies such as Impey et al. (1997) and Ramacher et al. (1999), radical reactions of bromine and chlorine occur somewhat at different times and/or locations if examined into detail. It is not necessarily trivial to simulate these changes and deserves a carefully designed, independent study. One may need to deal with poorly characterized controlling factors in the snow from which reactive bromine and chlorine species are released to the overlying atmosphere at different rates according to in-snow conditions that vary in time and space. The contention by Ramacher et al. was more about changes in the concentration ratio between Cl-atoms and Br-atoms via changes in chemistry in the air as ozone is depleted via bromine chemistry in air mass. This is probably a littler easier to simulate than the in-snow problem. Anyway, we were/are not aware 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.

In summary, we do recognize a potential role of reactive chlorine chemistry in the polar boundary layer but consider that we would not come to totally inappropriate conclusions (about ODEs) by ignoring the chlorine chemistry. We would rather think, at the current stage of the model development, that it made more sense to simplify the problem by not including the chlorine chemistry for this study.

In the revised manuscript, we will touch on some of these aspects in the conclusions section.

[Referee] 4. I do not understand Reaction G132 in Table 1. While the text says that HBr deposition only provides Br- to the snowpack, and that HOBr and BrONO2 deposition results in oxidation to produce Br2, Table 1 shows Reaction G132 pro-

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ducing Br2. That seems quite inappropriate, assuming it is not a typo. Explain.

Reactions listed in Table 1 describe gas-phase and aerosol chemistry only. As the footnote e of the table states, the rate of Br2 production via G132 is bound by the total uptake rate of HOBr and BrONO2 onto aerosols (G130-131). This is explained in the second paragraph of Section 2.2 as well. We meant to approximate heterogeneous aerosol reactions of HOBr/BrONO2 + HBr/HCl altogether by G130-132.

In the revised manuscript, we will indicate more clearly that heterogeneous reactions in Table 1 are meant to describe those reactions taking place on aerosols only. We will also adjust the title of Section 2.2 to “Gas-phase and heterogeneous aerosol chemistry”.

[Referee] 5. Page 26218, line 7. The only source of Br- on MY ice is HBr deposition? That seems unreasonable. After all, Br- is measurable on the surface of MY ice at all times. Can you justify this?

This is why we did sensitivity runs in which abundant Br- is assumed to exist on the MY ice as on the FY ice (Run 6-8) to make a contrast with Run 3-5. As such, we only simulated two possible extreme cases. Still, it is interesting to note that we simulated better BrO when we assumed Br- is more abundant in the FY ice than in the MY ice, in accord with what was argued by Simpson et al. (2007a).

That being said, we may have to admit that the present ACPD manuscript does not convey our intent efficiently enough to readers. We will correct this in the revised manuscript by rewriting the model description section.

[Referee] 6. Bottom paragraph, page 26218. It makes little sense to me that on MY ice, Cl- assumed to be "inexhaustible", but on the terrestrial snowpack, a x100 decrease means it is effectively gone? How would you reconcile that with measurements of Cl- the terrestrial snowpack (cf. Simpson et al., 2005), and with the measurements of BrCl above the terrestrial snowpack, by Foster et al.

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(2001)?

We came up with this snowpack bromine source scenario so as to release reactive bromine (as Br2) most efficiently on FY, less on MY and further less on land-surface snow in our simplified snowpack scheme for a large-scale 3D model. As mentioned by the referee, our rationale is based on perhaps an overly simplified assumption and thus contradicts some of the knowledge gained from the field data if examined in detail.

The land surface covered (either totally or partially) with snow often extends much farther from coastlines in the polar region than “BrO clouds” seen from satellite. It is true that there should be some halogen input and recycling mechanisms operating on the snowpack over land, as indicated from the field studies. But we do not consider that we have enough knowledge to describe this for a large-scale 3D model such as ours. If we attempted to do this, it could have called for a number of additional sensitivity runs to tune up parameters to match the observations. This indeed deserves to be studied further and 3D models perhaps with finer horizontal resolutions than ours can contribute. We simply could not do it in the frame of this study.

We would like to remind that our snowpack scheme allows some re-emission of reactive bromine even on the snow over land, so we would argue that our approach is still consistent with some aspects of the findings reported by Simpson et al. (2005) and Foster et al. (2001).

We would also like to remind that both of these field studies were conducted at places not very far from coastlines from the perspective of our model resolution. Roughly speaking, elapsed time for a specific boundary-layer air mass from the input of reactive bromine (via emissions from the surface snowpack) to near-complete ozone depletion would be 1-2 days at least, during which period the air mass is transported by 250-500 km horizontally even at the wind speed of 3 m/s and much farther if the wind is stronger and thus active bromine release from snowpack and/or blowing snow is anticipated. Spatial scales involved in ODEs may be sufficiently large quite often that the model can

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simulate boundary-layer ozone variations reasonably well even if it does not reproduce field measurements of Foster et al. (2001) and Simpson et al. (2005) at locations where those data were obtained. We will mention this in the revised manuscript.

[Referee] 7. Page 26219: The discussion of O3 reaction with Br- to produce Br2 should also cite Wren et al., JGR, 2010.

We will add this reference in the revised manuscript.

[Referee] 8. The top paragraph on page 26221 raises the question of how you control NOx, if you are not releasing it and HCHO from the surface. If you have no source of NOx, there would quickly be none with which to form BrONO2. Is it held constant? What are the initial conditions for the model, in terms of chemical concentrations?

In our model, NOx (or NOy) is supplied to the Arctic boundary layer by long-range transport from lower latitudes and/or from higher altitudes. So, the answer is no - NOx was not held constant in the model. 3D models of tropospheric chemistry generally do not account for snowpack emissions at all, but of course such models do not intend to simulate halogen chemistry in the polar boundary layer either.

Actually, we did a sensitivity run with NO2 emissions from the snowpack as well during the preliminary stage of this study. But it was not mentioned in the manuscript. It is absolutely true that, by switching on bromine chemistry in the model, BrO quickly scavenges NO2 in the Arctic boundary layer. But the snowpack flux of NO2 at 4E+8 molecule cmˆ-2 sˆ-1 apparently impacted less on our surface ozone simulation than the HCHO flux at 4E+9 molecule cmˆ-2 sˆ-1 did (both flux values were taken from the Michalowski et al. box model study in 2000). We will refer to this in the revised manuscript.

[Referee] 9. Bottom of page 26223: to take an increase in R from 0.56 to 0.68 to imply that "the model realistically represents reactive bromine release from the

surface snowpack" is just too big a leap. One could easily hypothesize that met. is not perfectly represented in the base model and that adding halogen chemistry fortuitously improves the agreement. This comment should be removed.

We will rephrase this to a modest statement. But we consider that the improvement was not totally fortuitous, because we are not talking about a single episode but statistical metrics calculated from time series over a month. We will also refer to MB and RMSE values for Alert and Barrow much improved with bromine release in the model, in order to reinforce our reasoning.

[Referee] 10. Top page 26224: of the places you are studying, Barrow may well have the most tractable meteorology. Why don't you make use of the extensive ozonesonde data from Barrow? The data are readily accessible.

Actually, Barrow is not one of NOAA's regular balloon-borne ozonesonde sites. NOAA/ESRL did launch a few for a short period in the late 1980's and also during recent campaigns in Feb-March, 2008 and 2009 (Bryan Johnson, personal communication, 3 January 2011). There would be some other campaign-based ozone soundings performed to date, but as far as we know there are no ozonesonde data obtained at Barrow during April 2001. At WOUDC (www.woudc.org), we can only find an archive of several ozonesonde profiles obtained in 1974.

[Referee] 11. Starting with Figure 4, the Figures are not discussed in order. They should be referred to in order, or renumbered.

We will correct this mostly by renumbering the figures, except Fig. 14c for which we will change the order we refer to it in the text.

[Referee] 12. Page 26226, starting line 7: these points might be more clearly presented as a color-coded map of the Arctic showing the distribution of BL ozone.

In the revised manuscript, we will add a new figure similar to this suggestion: color-coded circum-polar maps of total hours when simulated surface ozone is lower than 5 ppbv in April 2001 for Runs 3-8. The plots indicate that, if one deploys perhaps 5-10 buoys that measure surface ozone continuously across the Arctic Ocean, difference between FY ice and MY ice as a source of reactive bromine may be gauged much better than we did in this study.

[Referee] 13. The middle paragraph on page 26227 should cite Sjostedt et al. 2007, and their discussion of possible bromine chemistry at Summit. The paper should also state clearly why comparison of model output to measurements at Summit, which is very different from the other sites, is important.

We intended to look at surface ozone data from Summit initially to check if our ozone simulation in the Arctic free troposphere was not biased significantly, assuming (initially) minimal impacts from halogen chemistry. We will refer to this more clearly in the revised manuscript.

Also, we will refer to Sjostedt et al. (2007) in that bromine transport from the marine boundary layer (not necessarily over sea ice) along with local blowing snow could act as a driver for active bromine chemistry at Summit. It is actually interesting to see that surface ozone decrease observed during the blowing snow event (Fig. 12 of Sjostedt et al.) was somewhat modest compared with what we see during the later half period of April 2001.

[Referee] 14. Figure 8 can be removed, as not much is done with it.

We consider that we should keep it. Without Figure 8, we cannot adequately discuss that high BrO columns in the troposphere often occur where surface air temperatures are elevated well above -20 degree Celsius with accompanying surface ozone increase. This is among the most important messages we wanted to convey to readers.

But, after carefully looking at the corresponding paragraph in the manuscript, we noticed that Fig. 8b had not been referenced properly from the text. We also feel that

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paragraphs referring to Fig. 8a (surface met) and Fig. 8b (surface ozone) need some rework in order to convey our message more clearly about boundary layer meteorology and ozone variations. We will correct these in the revised manuscript.

[Referee] 15. Page 26230, line 17: you should explain this observation of improved simulation at higher T, as it is somewhat counterintuitive.

In the revised manuscript, we will direct readers by noting that this “counterintuitive” result is discussed in Section 3.5. As we mentioned, however, we will rewrite the discussion of potential mechanisms behind this behavior by taking into account a possibility of snowpack acidification by acid deposition from the atmosphere.

[Referee] 16. Page 26233, line 18, should cite Salawitch et al., 2010. However, the discussion of VSL bromocarbons should also discuss how these compounds get into the stratosphere. If they are actually VSL, their presence should be sporadic and spatially heterogeneous, related to deep convection and transport.

VSL bromocarbons are believed to enter the stratosphere in the tropics and that by the time air is mixed to high latitudes then inhomogeneities will be mixed out. As we mention in Section 3.3, the mean age-of-air in the Arctic lower stratosphere is estimated to be older than 6 months.

The two main VSL Br species are CHBr3 and CH2Br2. CHBr3 has a lifetime of around 30 days but CH2Br2 has a lifetime around 6 months. These species (especially CH2Br2) are also transported by large-scale vertical motion and so the upper troposphere is probably not as spatially heterogeneous as it would be for really short-lived species anyway.

For all these reasons we would argue that the contribution from VSL species to bromine should be smeared out at high latitudes. Hossaini et al. (2010), ACP, has run a 3D model with an explicit treatment of tropospheric VSL bromocarbons and degradation products and looked at transport into the stratosphere. From those runs the lower

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stratosphere looks well mixed.

One caveat to all this might be that the Salawitch et al. (2010) paper inferred some very large contributions of VSL species (but with a large error bar). Globally the contribution is expected to be about 5 pptv but if there is indeed more present in the high latitude lower stratosphere then that points to a more spatially inhomogeneous distribution, which might indicate the injection to the stratosphere not confined to the tropics. However, there are large uncertainties in this and the spatial variation that Salawitch et al. (2010) sees may be due to other factors.

For instance, another important feature reported by Salawitch et al. (2010) was an existence of fairly abundant BrO measured in-situ above the near-surface boundary layer, which actually had been inferred by McElroy et al. (1999) using a nadir-viewing optical instrument on board an aircraft. Moist convection over open leads and/or polynyas implied as a mechanism involved in carrying bromine upwards was not accounted for even implicitly in our present model or any other 3D chemical models published to date.

Overall, we do not consider that we should stress too much on the possibility for inhomogeneous Bry distribution in the Arctic stratosphere, based on evidence available to date. In the revised manuscript, we will briefly touch on Hossaini et al. (2010), Salawitch et al. (2010) and McElroy et al. (1999) in the context mentioned above.

[Referee] 17. Page 26235, line 10: should an increase in R from 0.64 to 0.68 be regarded as significant?

We did not intend to stress too much on this increase in the R value, but rather wanted to state that the offset for the linear regression could be removed without decreasing the R value. So, we will rephrase from "...not only removes the offset for the linear regression but also improves the correlation coefficient from 0.64 to 0.68" to "...removes the offset for the linear regression and also slightly improves the correlation coefficient".

[Referee] 18. Page 26236, line 13 should cite Fickert et al., 1999. Line 21 should

cite Cho et al., 2002.

We will refer to these references there in the revised manuscript.

[Referee] 19. Page 26236, line 27: this last statement is inappropriate; this conclusion cannot be drawn from the information presented in this paper.

We will adjust our message from the paper, including the statement noted here by the referee, by taking into account the possibility of snowpack acidification via deposition of haze material to drive bromine release from the snow.

[Referee] 20. Page 26237, title line: the answer to this question was published by Foster et al., in 2001.

We will refer to Foster et al. (2001) there in the revised manuscript. The Foster et al. paper reported in-situ measurements of Br2 in and above the Alert snowpack to demonstrate that reactive bromine production could occur in the snowpack. But what we tried to address in this section was more of the quantitative aspects whether or not bromine release directly from the surface snowpack is indeed substantial enough to account for the occurrence of “BrO clouds” that can be seen from satellite. Br2 mixing ratios in the range of a few ppt reported by Foster et al. are far less than total inorganic bromine mixing ratios (50-100 ppt for more) that can reach Alert (as indicated from the Impey et al. study, for example).

[Referee] 21. Page 26238, line 7: This conclusion was made in the 1997 paper by Impey et al., and should be cited.

We will add this reference in the revised manuscript.

[Referee] 22. Given the last paragraph in section 3, one again wonders what the focus of the paper should be, and what the new information is.

We will rephrase several statements in the section 3.5, including the paragraph noted by the referee. We will stress that active bromine release can take place almost everywhere particularly on first-year sea ice in the springtime Arctic as well as on the multi-year sea ice perhaps with less efficiency, driven mainly by boundary-layer wind speed and ozone increase no matter what the exact physical mechanism occurring near the air-snowpack interface is.

We recognize that we could not answer the questions listed in the section 3.5 in a definitive manner. But we consider it useful and important to show that the occurrence of ODEs and “BrO clouds” can be simulated consistently across the Arctic by putting several pieces of information together in a 3D model like this, even though each of the implemented processes is “known” to some extent.

[Referee] 23. Page 26240, line 2: this statement is way too strong. You simply cannot prove that with a model study such as this.

We still believe that our present study serves as a circumstantial evidence that Arctic snowpack can release a lot of bromine well above -20 degree Celsius. In the revised manuscript, however, we will refer to a possibility of haze-acidified brine in the surface snowpack driving the production of reactive bromine above -20 degree Celsius, which was overlooked in the ACPD manuscript.

[Referee] 24. Table 4: the R values do say one thing clearly - that halogen chemistry has little impact on the correlations, and that other factors (mixing?) are more important. This is not reflected in the content of the paper.

That actually led us to feel that it indeed made sense to use both ground-based ozone and satellite BrO data, which complemented each other, for evaluating our model scenarios.

We believe that such a result for the R values was obtained because a potential source of bromine is almost everywhere on the Arctic sea ice in the spring as assumed in our model. Without bromine chemistry, dry deposition of ozone on the snow/ice surface does a similar job in decreasing (to a much lesser extent) Arctic boundary-layer ozone mixing ratios in the model. One should also look at improved MB and RMSE values when reactive bromine is released ubiquitously from sea ice in the model.

[References (not cited in our ACPD manuscript)]

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