

Interactive
Comment

Interactive comment on “The chemistry influencing ODEs in the Polar Boundary Layer in spring: a model study” by M. Piot and R. von Glasow

Anonymous Referee #1

Received and published: 10 June 2008

[General comments]

I largely agree with Referee #4 on the weakness of this paper by Piot and von Glasow, but I still think that the paper can make a journal publication once significantly revised.

The work by Piot and von Glasow (acpd-2008-0008) is perhaps meant to complement their previous work which was based on 1-D model MISTRA published recently in ACP. The present work is based on the box model version of MISTRA and addresses a variety of chemical interactions between species (Br₂, Cl₂, BrCl, HCHO, H₂O₂, DMS, C₂H₄, C₂H₆, HONO, NO₂, and RONO₂) potentially emitted from and lost to the snow-pack as well as the ocean surface water, relevant to reactive halogen chemistry and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



ozone depletion in the springtime polar boundary layer. This is done by a series of sensitivity model runs with a single meteorological condition.

The topic fits well to the scope of the journal and current interest in this field. I can see some original and novel information in the manuscript, but the choice of model runs presented is rather arbitrary. Furthermore, in a majority of cases (Sect. 4.4 - H₂O₂; Sect. 4.6 - Cl₂; Sect. 4.7 - C₂H₄; Sect. 4.8 - C₂H₆), main discussion is dedicated to results from rather unlikely scenarios just for highlighting the role of specific chemistry emerging in those model runs. Some new concept such as "chlorine counter-cycle" is introduced from one of such discussions, but I feel that the authors have gone too far because the process is found to play a significant role only in very unlikely scenarios. Also, the manner of presentation is rather sketchy and often lacks quantitative analysis to support their statement. The model does not take into account the recycling of deposited bromine from the snowpack, which probably makes some of their discussion incomplete because dry deposition of HOBr and HBr sometimes plays a critical role in their model behaviors. But at least I consider it quite interesting and perhaps original that HO₂ radical is shown to be important in partitioning changes from Br/BrO radicals to HOBr with multifold implications for the air-snow fluxes of gaseous bromine, gas-aerosol partitioning of bromine, and the rate of ozone destruction via BrO self-reaction. In my opinion, the authors should have focused on these issues around HOBr and, for completeness, should have performed a sensitivity study in which the deposition of HOBr (and perhaps HBr and BrONO₂ as well) is recycled back to the atmosphere in the form of Br₂ such as in their own previous study using 1-D MISTRA or other box model studies such as Michalowski et al. (2000). Also, Table 4, which shows prescribed emissions of Br₂, BrCl and Cl₂ in order to induce ODEs at desired timescales, can be a useful reference for interested modelers in this field.

Overall, there are too many unlikely cases presented and discussed and therefore I suggest that the manuscript should be re-written mainly to discuss likely cases and to adjust its story line before it can be published in ACP.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



[Specific comments]

1) Choice of model runs presented

Throughout Section 4 the authors are not very consistent as to which ODE category (i.e. M1, M4, P4) to choose from their model runs to show and to discuss. In the last paragraph of Sect. 4.1 the authors state that they selected most relevant runs. But they switch their focus between M1, M4 and P4 in different subsections, distracting readers from linking/comparing the importance of each chemical species as a whole. It would be useful if the authors could summarize which chemical species (within likely scenarios of emissions or mixing ratios) could make substantial impacts on reactive halogen chemistry and ODEs for each of M1-Br₂, M1-BrCl, M4-Br₂, M4-BrCl, P4-Br₂, and P4-BrCl cases.

2) HCHO influence discussed in Sect. 4.3

All model runs in this section are based on quite likely scenarios and identify significant roles played by HCHO in bromine chemistry and ODEs. Not only HCHO itself in converting Br to HBr but also HO₂ produced via HCHO photocomposition in converting BrO to HOBr are shown to be important for promoting the dry deposition of gaseous bromine and also slowing down ozone destruction via BrO self-reaction. But I am very curious to know whether the conclusion about the impact of HO₂ can hold if HOBr deposited to the snow is recycled back to the atmosphere in the form of Br₂ or BrCl as assumed in some earlier models such as Tang and McConnell (1996) and Michalowski et al. (2000). Without sensitivity run(s) to investigate this possibility, the conclusion about indirect influence via HO₂ production appears rather too weak. The same holds for other species (such as H₂O₂) that produce HO₂ and subsequently HOBr discussed in other subsections.

3) H₂O₂ influence discussed in Sect. 4.4

The model run selected is from a scenario with H₂O₂ emission (therefore its mixing

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



ratio) higher than likely ranges during the polar springtime but perhaps within ranges for the late spring to the summer. Identified consequences to ODEs are qualitatively identical to what is found for HO₂ production from HCHO, so I believe that the length of present discussion is appropriate but even better if it could be shortened.

I also wonder if the authors intend to suggest that this process could be one of the factors to diminish bromine explosion in the polar boundary layer towards the summer.

4) DMS and DMSO discussed in Sect. 4.5

The model run selected is a scenario from Br₂-M4 under coastal conditions. This scenario prescribes the high Br₂ emission perhaps representing that from the snowpack on sea ice and at the same time the high DMS emission representing that from open water free from sea ice. I suspect that it is a rather unlikely scenario. Or, do the authors imply that the scenario shown could represent DMS emissions from ice algae?

There is no statement about the production of sulfate aerosols from DMS oxidation and its impact on bromine chemistry. Is it not important at all? Also, there is no statement about the relative role of sulfate aerosols versus sea-salt aerosols in the heterogeneous recycling of bromine in the entire manuscript. Even the description of how much sulfate aerosol is present in the model is totally missing. I believe that these points should be discussed in some detail, because a number of earlier modeling works have attributed the simulated recycling of bromine mostly to heterogeneous reactions on sulfate aerosols at least in the Arctic.

5) Cl₂ influence and "chlorine counter-cycle" discussed in Sect. 4.6

In this subsection it is shown in the first place that ODEs cannot be explained only by chlorine chemistry. But this is what we already knew from previous studies in which ambient Cl atom concentrations were inferred. So perhaps we do not need to argue that HCl production becomes unrealistically large in a scenario with Cl₂-based ODEs for refuting the reality of the scenario. The authors go on to point out that HCl is

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

produced from a variety of reactions in addition to $\text{Cl} + \text{CH}_4$, but there is not a sufficient amount of quantitative analysis/statement given here. The authors name this process as "chlorine counter-cycle" with a fancy schematic presented in Fig. 9, but I do not believe in a lot of benefit from this whole discussion/presentation detailed as it is now.

In the latter part of this subsection, the concept of "chlorine counter-cycle" is extended to indirect impacts on bromine chemistry as a result of the production of HO_2 and HCHO from methane. However, its impact is only as large as 10% to change the stoichiometry of Br surface emission flux (emitted as either Br_2 or BrCl) needed to cause the same timescale/magnitude of ODEs.

6) C_2H_4 influence discussed in Sect. 4.7

The role of C_2H_4 in suppressing reactive bromine chemistry in the polar boundary layer was addressed by Sander et al. (1997). What is new in the present work is indirect influence through changes in HO_x abundance at relatively C_2H_4 low mixing ratios. The authors state in Sect. 3.4 that further reactions of $\text{H}_2\text{C}(\text{OH})\text{CH}_2\text{OO}$ radical (produced via $\text{OH} + \text{C}_2\text{H}_4$) are not detailed, but it appears that the further reactions of $\text{H}_2\text{C}(\text{OH})\text{CH}_2\text{OO}$ (or EO_2) are almost completely detailed as listed in Table 2 of supplementary material. If that is the case, then a significant amount of HO_2 is produced via subsequent reactions, meaning their interpretation of C_2H_4 influence on bromine chemistry may need to be adjusted.

Also, as recently evidenced by Keil and Shepson (2006) and admitted by the authors themselves, the reaction $\text{Br} + \text{C}_2\text{H}_4$ in reality ends up with organically bound bromine compounds that are potentially quite stable against photochemical degradation (see also Toyota et al., 2004) rather than produces HBr as assumed in the present work. This actually corresponds to the case in which Sander et al. (1996) argued that C_2H_4 can exert a significant impact. Without addressing the case of producing organically bound bromine at least in a simplistic/parameterized manner, discussion in this subsection sounds rather incomplete.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

7) C₂H₆ influence discussed in Sect. 4.8

It is shown that there is no significant impact on reactive halogen chemistry within likely ranges of C₂H₆ mixing ratios in the polar boundary layer. But the authors presented model results with unrealistically high C₂H₆ mixing ratios (ca. 15 nmol/mol) to show what exactly are species involved in the impacts on reactive halogen chemistry. Since nothing is very different from processes identified in other subsections, I suggest that this whole subsection should be deleted or reduced to just a few words of statement if the authors are keen to address the issue of C₂H₆ at all.

8) HONO, NO₂ and RONO₂ influences discussed in Sect. 4.9

Scenarios discussed are all something very likely to take place in the springtime polar boundary layer.

The role of HONO emission has been already found to be important in their previous ACP paper based on 1-D version of MISTRA and briefly presented in there. Therefore, the finding itself is not new, and the authors should make sure that the present work adds a substantial new information - which is perhaps achieved by the discussion of HCl release from SSAs. It is also discussed that the role of HO_x derived from HONO makes a significant difference in bromine chemistry. But their discussion is rather sketchy and sounds like NO production from HONO photolysis may also be important. If so, I wonder what would happen to bromine chemistry and ODEs if NO₂ were released from the surface at 5.0E+8 molec. cm⁻² sec⁻¹ (I think it is likely), which is the same flux as used for HONO.

Evans et al. (2003) stated that the heterogeneous conversion of BrONO₂ is important for HNO₃ production, whereas the present manuscript states that HNO₃ is produced via OH + NO₂ and BrONO₂ is important mainly for sequestering otherwise reactive bromine radicals - there seems to exist some major difference between the two model studies in terms of heterogeneous reaction rate of BrONO₂. I wonder why.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

9) Sea-salt aerosols (SSAs)

How much Br⁻ is accumulated in the model box after 2 days of spin-up? As presently shown in the unit of mmol/L, one cannot evaluate/guess how important the SSAs are as a source of reactive bromine in model runs presented. Especially for coastal conditions with continuous supply of SSAs over the entire period of model runs (as I suppose), how important are the SSAs as a source of bromine compared with the surface snowpack emissions of Br₂ assumed?

Any rationale for giving the flux of SSAs as presently assigned? Can it be supported by any measurements of aerosol Na⁺ or Cl⁻ in the polar boundary layer? See, for example, Rolf Sander's supplementary table in the Simpson et al. (2007) review article.

10) 'Bromine explosion'

The authors refer to autocatalytic bromine release from SSAs as 'bromine explosion' in the present work. But the word 'bromine explosion' has also been used to autocatalytic bromine release from snowpack especially because the same kind of chemistry involving HOBr (Reaction 14) is believed to play a role. Adding some footnote in Introduction may be appropriate.

[Minor technical comments]

1) Use of the words "strong" and "strongly" (English)

I suspect that they should be rephrased in many places.

2) Table 2 of supplementary material

It would be more useful if "Special rate functions" for gas-phase rate constants were described explicitly.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7391, 2008.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)