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Interactive comment on “Numerical analysis of the chemical kinetic mechanisms of ozone depletion and halogen release in the polar troposphere” by L. Cao et al.

Anonymous Referee #2

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[Summary]

By using a photochemical box model, Cao et al. simulate and analyze timescales required for the buildup of reactive halogens released from saline snow/ice surfaces and resultant ozone depletion in the springtime polar boundary layer. This model employs a parameterization for the rate of air-snow transfer of reactive halogens based on the resistance model of dry deposition and thus constrains their simulation scenario in that saline ice/snow substrate as a source of reactive halogens to the atmosphere should reside primarily at/near the ground level. Also employed in the model is an assumption that the vertical transfer of HOBr and BrONO₂ from the overlying atmosphere essen-

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tially drives a net release of gaseous halogens from the saline ice/snow surfaces via the production of Br₂ and BrCl released back to the atmosphere. Reasoning by the authors for these simplifications sounds a little too blunt, even though physical and chemical mechanisms behind halogen activation in the polar boundary layer are not fully understood. However, their minimalist approach (if I may call so) works quite nicely to show the role of each reaction and physical parameter in the overall model behavior via sensitivity runs and the on-line calculation of local sensitivity matrices. Hence it would be fair if the authors admitted more clearly that the applicability of their model was potentially limited and/or that the minimalist approach was adopted intentionally in representing the real environment. This manuscript could be accepted for ACP after addressing the following issues.

[Major comments]

1. Introduction has been improved by dropping the redundant description of reaction cycles of potential significance, but it would read even better if the authors correct the following inaccuracy and incoherence in the context of cited studies: (1) all the papers cited at P24173, L9-10 only reported the measurements of XO radicals unlike what is indicated here by the authors, so the list of papers should be expanded in regard to halogen atoms, molecular halogens, etc.; (2) the work by Sander and Crutzen (1996) is not directly related to halogen activation in polar regions and should be dropped from citation at P24173, L21 and P24174, L2-3; (3) after all, the authors run the model at T = 258 K, which is above the eutectic of both NaCl-H₂O and NaBr-H₂O (e.g., Koop et al., 2000), making their argument in the paragraph of P24174, L1-13 rather irrelevant; (4) studies performed by the 1-D model MISTRA-SNOW (Thomas et al., 2011) are referred to as an example of coupled snow-gas phase chemistry “intensely studied” via modeling, right after a paragraph in which its methodology (the assumption of a liquid-like layer) is criticized; and (5) major difference between cited 3-D model studies lies in the types of halogen sources (wind-blown snow over sea ice – Yang et al., wind-blown frost flowers from refrozen leads – Zhao et al., snowpack over sea ice – Toyota et al.,

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or using satellite BrO measurements not by asking what the source is – Zeng et al.) rather than the treatment of turbulence in the model.

2. Given our poor understanding of physical chemistry of natural snow in regard to halogen activation, I do not feel that the authors are obliged to explain too much why they choose to represent halogen activation from the snow entirely by the ad-hoc choice of gamma values for HOBr and BrONO₂. Logics used by the authors to justify their approach in the fourth paragraph of Introduction just do not convince me enough, especially because there are also experimental studies that indicate the roles of gaseous ozone uptake and nitrate photolysis (as OH source) for the release of gaseous bromine presumably from the liquid-like layer on the salty ice surface (e.g., Abbatt et al., 2010; Oldridge and Abbatt, 2011). I already see the value of the paper in the analysis of how key metrics such as Lmix and beta affect the timescale of ozone depletion. So it would sound more compelling if the authors stated that they took a minimalist approach for the present purpose.

3. The parameterization described in Section 2.2.2 implies that the net source of halogens exist entirely at or very close to the bottom of the atmosphere. I will not criticize the authors for limiting their scope by this choice, but they should be cautious when they talk about the source of halogens in the model. It is not fully appropriate to indicate that this model accounts for sea-salt aerosols and/or wind-blown snow as a source of halogens (e.g., P24183, L2).

4. It would be useful if the authors could differentiate between “induction stage” and “depletion stage” in a more objective manner. Currently, the depletion stage is loosely defined as “the depletion rate is in the order of 1 ppb h⁻¹” (P24184, L1-2) and the authors seem to rely on the eye-ball examination of time-series plots for the assignment of the stages. I wonder if the authors could boldly define an exact threshold for the rate of ozone decrease in ppb per hour to differentiate between the “induction stage” and the “depletion stage”. That way, the authors’ discussion on the timescale of simulated ODEs would become more compelling, particularly for cases with shortened ozone

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depletion timescales by using high beta values. How long do the “induction” and “depletion” stages last respectively where the beta value approaches 100 and thereby the simulated ozone depletion is completed in about 2 days from the initiate state?

5. I agree with Referee #3 in that the analysis of ozone budget (P24184, L10-28) is performed somewhat in a different way than we usually learn at the school of atmospheric chemistry. We usually group species that are coupled via fastest reaction cycles and look at the net gain or loss of the grouped species. In the present case, I would rather look at $\text{NO} + \text{HO}_2$, CH_3O_2 , etc. as gross ozone formation reactions (but NO is absent in this run and therefore the gross ozone formation would be marginal) and $\text{BrO} + \text{BrO}$, $\text{BrO} + \text{HO}_2$, $\text{HO}_2 + \text{O}_3$, etc. as gross ozone loss reactions. If the authors want to stick to their current approach, I would like to see some more explanation by them as to why they choose to discuss the photochemical ozone budget in the way as currently done. Also, the inaccuracy of representation for the species “O” in the model (see the major comment #7) makes this paragraph quite confusing. I see the same kind of species grouping problem in Section 3.2 where the authors discuss the NO_x budget (P24187, L14-27).

6. I suppose that, owing to high mixing ratios (> 30 ppt) simulated for BrO, the self-reaction $\text{BrO} + \text{BrO}$ (R8 and R9) is a major cycle that leads to a net loss of Ox (= $\text{O}_3 + \text{O} + \text{BrO} + \dots$) at the “depletion stage”, rather than $\text{BrO} + \text{HO}_2$ (R13) (cf. Sander et al., 1997, Fig.2). Statement by the authors also indicates that this is the case (P24184, L21-24). With this argument in mind, implications from the local relative sensitivity matrix (Fig. 4) are very paradoxical in that changes in the rate constants for R8 and R9 do not appear to be a critical factor for the ozone loss in the system simulated here. I encourage the authors to discuss this issue in some details. I also wonder if the simulated HO₂ levels are in the right ball park, e.g., around 3 ppt as reported by Mao et al. (2010). On the basis of the calculated sensitivity matrix values, one may even drop R8 and R9 from a skeletal reaction scheme, which the authors plan to construct in future modeling studies (P24185, L1-15). If I understand correctly, such a paradox

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could be one of the major values of looking at the sensitivity matrices for chemical mechanism reduction in simulating ODEs.

7. There is some sloppiness in the chemical mechanism construction. As already raised by Referee #3, "O(1D)" is abbreviated as "O", which should make most atmospheric chemists puzzled. Also, there are a few missing reactions of potential significance in the polar boundary layer: $\text{HONO} + \text{hv}$ (sources for both NO_x and OH), $\text{HCHO} + \text{hv}$ (HO_x source) and $\text{O}(1\text{D}) + \text{N}_2$ (leading to the suppression of OH formation via $\text{H}_2\text{O} + \text{O}(1\text{D})$). The products of $\text{OH} + \text{OH} (+ \text{M})$ (R54) should be H_2O_2 rather than $\text{H}_2\text{O} + \text{O}_3$. The assumption that all the C_2H_5 formed via H-abstraction from C_2H_6 (R33 & R98) results in the formation of $\text{C}_2\text{H}_4 + \text{HO}_2$ via R34 (rather than $\text{C}_2\text{H}_5\text{O}_2$) seems unrealistic. The assumption that the photolytic reaction $\text{HNO}_3 + \text{hv} \rightarrow \text{OH} + \text{NO}_2$ is mediated by aerosols and its rate is limited by the uptake of HNO_3 from the gas phase (which is quite rapid) seems doubtful. As I see a major value of the paper in its minimalism and the extraction of key metrics, these problems may not be so detrimental as to discredit the entire story. But I do feel uneasy as to how much trust I could place on quantitative terms stated in the paper.

8. I wonder if the authors could examine the role of BrONO_2 hydrolysis from the viewpoint of simulated NO_x concentrations. I encourage the authors to plot NO_x versus O_3 correlations for different gamma values (cf. Evans et al., 2003, Fig. 5) and see if any insight can be gained into the likely range of gamma(BrONO_2)? The same thing could be done for PAN versus O_3 correlations (again have a look at Fig. 5 in Evans et al., 2003). Regarding the PAN variability during ODEs, it is also useful to refer to Bottenheim et al. (1986).

9. As far as I skim through IUPAC and NASA/JPL recommendations, gamma values for BrONO_2 hydrolysis appear to be significantly higher than 0.01 whether on the liquid substrate at room temperature (~ 300 K) or on the ice/aerosol surfaces at lower stratospheric temperatures (~ 200 K) but unfortunately without any experimental evidence relevant to the present study (on salty ice surfaces at $T \sim 250$ K). I do, however, feel

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that the authors may suggest that the presence of NO_x in the polar boundary layer will likely accelerate reactive halogen release and ozone depletion, according to their present results. Please expand the discussion along this line if possible (P24190, L12-23).

10. Discussion in Section 3.3 (chlorine chemistry) seems flawless, but I am not sure if anything new is presented here. I would argue that the authors should move this section to the electronic supplement.

11. Though I see tremendous improvement from the initially submitted manuscript, there remain quite a few loose statements. Wording could be improved further in many places to make it sound more professional for journal publication in atmospheric chemistry. When revising the manuscript, please take an extra caution to editorial aspects again. I have picked up some examples in the editorial suggestions below.

[Minor comments]

Section 2.2.1: It is largely a repetition from Section 3.2 in Lehrer et al., (2004) and therefore should be shortened significantly. Instead, the authors should give some description of gamma values for BrONO₂ here.

Section 2.2.2: I find that the parameterization is borrowed largely from Huff and Abbatt (2000, 2002). It should be mentioned more explicitly. Although the impact would not be detrimental, I am not impressed by the inconsistent choice of the values of height (z) and wind speed (u) – by using the adopted formulation, the u value should be taken at the chosen height z, which does not seem to be taken care of seriously by the authors. Also, real-world z₀ would change with the wind speed (or friction velocity) as the authors adopted a formulation from König (1985) in their initially submitted manuscript.

P24172, L8: “sea-salt aerosols”: The parameterization adopted by the authors inherently excludes halogen release from particulate matters lofted well above the ground level.

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P24176, L22: Heterogeneous reactions on aerosols (R14, R128) do not change the total loading of halogens in the atmosphere. Hence the authors should modify the sentences around here.

P24182, L12-14: Please state values assumed for total column ozone and surface albedo and whether the presence of clouds and aerosols is assumed for photon absorption and multiple scattering in the atmosphere.

P24182, L15-19: How high is the H₂O mixing ratio (or relative humidity) assumed in the model?

P24182, L18: "CHBr₃" should be more appropriate than "CH₃Br" to be mentioned here (e.g., Tang and McConnell, 1996).

P24183, L1: "triggered from the saline surface and sea salt aerosols": I see two problems in this statement: (1) in this sentence, the authors are talking about bromine explosion rather than its trigger, hence they should rephrase from "triggered" to "released", and (2) the parameterization described in Section 2.2.2 implies that the bromine explosion is mediated by salty ice substrate residing very close to the surface level, hence the authors should drop the words "sea-salt aerosols", which are most likely mixed well into the surface boundary layer and above.

P24183, L19-20: It is not clear to me how Cao and Gutheil (2001) dealt with bromine release from the surface snow, but I am sure that a 1-D model by Lehrer et al. (2004) implicitly accounted for the effect of aerodynamic resistance imposed on the dry deposition of HOBr from the atmosphere and the release of Br₂ and BrCl back to the atmosphere. Hence the authors' statement should be corrected here.

P24185, L5 & P24211, Fig. 4 (caption): Are the sensitivity values shown here for daily mean or snapshot at a certain time of the day 6? Please clarify. There are other instances where the same vagueness occurs in the manuscript.

P24192, L20: I would not say that chemical mechanisms used in this study are so

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“detailed” as compared to models such as Thomas et al. (2011) and Toyota et al. (2013).

P24193, L25 to P24194, L2: This paragraph turns up out of the blue and is not substantiated by any part of the present study. I suggest dropping the entire paragraph, as it does nothing in the story line.

P24194, L3-7: Very confusing statement. If you neglect the heterogeneous reactions during the induction stage, what other mechanisms would account for the buildup of halogens in the atmosphere? Please be more specific here. Are you thinking of ad-hoc, 0-th order emissions or something similar? But a sensitivity study with NOx chemistry (Section 3.2) certainly indicates that BrONO₂ hydrolysis on the snow/ice surface shortens the induction stage, which seems to me negating the authors' conclusion. I also wonder if the computational benefit of neglecting just a few heterogeneous reactions in the chemical scheme is substantial at all.

CH₃CHO: What is the range of its simulated mixing ratios during the model runs? This species seems to play some significant roles in the present model runs in converting Br atoms to HBr (Fig. 4) and as a precursor of PAN (Section 3.2). These are consistent with what we know could be happening in the Arctic boundary layer, but I would like to see if the simulated CH₃CHO mixing ratios change significantly from the initial value of 100 ppt (Table 2). I can see that emissions from the snow are not assumed unlike HCHO (Table 1). From the list of reactions in the supplement, I suppose that CH₃CHO is produced photochemically via the degradation of C₃H₈ (1.2 ppb initially – Table 2) to C₂H₅O₂ and its subsequent reactions. Both of C₃H₈ and C₂H₅O₂ appear to be surrogates of actual compounds, so the authors are playing a little risky game here.

While the present paper is under review, a new paper that follows up the present study appears to have been submitted and accepted in a different journal (Cao, L. and Gutheil, E., Numerical simulation of tropospheric ozone depletion in the polar spring, *Air Qual. Atmos. Health*, doi:10.1007/s11869-013-0208-9, Received: 31 July 2013,

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Accepted: 30 September 2013). It would be appropriate if the authors could give a few words to explain how it is related to the present study.

[Editorial suggestions]

P24172, L2: "In recent years": This sounds odd, unless your experience in atmospheric chemistry is well beyond 50 years. :-) It has been 25 years since the community recognized the role of bromine chemistry for ozone depletion in the springtime polar boundary layer.

P24172, L4-5: "auto-catalytic chemical cycle including key self reactions": If you are talking about HOBr releasing Br₂ and/or BrCl from the snow for the former and BrO + BrO destroying ozone for the latter, I think you should phrase so more explicitly here, particularly because the BrO + BrO reaction is not really a part of the auto-catalytic cycle of halogen release.

P27172, L5-6: "several chemical reaction schemes are investigated" → perhaps better by "three sets of reaction schemes are tested by sequentially introducing bromine, nitrogen oxides and chlorine species to the scheme"

P24172, L7: "A category of ...": Awkward sentence, but I cannot come up with a suggestion. Please rephrase.

P24172, L14: "ozone depletion process" → perhaps better by "substantial ozone decrease"

P24172, L15: "Ozone depletion duration" → perhaps better by "Time required for the major ozone depletion ($[O_3] < X$ ppb) to be achieved" where X = 1 or whatever the authors feel appropriate.

P24172, L16: Drop "a value of".

P24172, L19: "in the order of" → "on the order of"

P24172, L20: "atomic chlorine radicals" → "chlorine atoms"

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P24173, L3: “tropospheric layer” → “atmospheric boundary layer”

P24173, L3: “reduce” → “decrease”

P24173, L3: “normal” → “background”

P24173, L14: “bromine concentration in the boundary-layer air”

P24173, L17: “fully” → “thoroughly”

P24173, L19-20: “since the 90’s of the last century” → “to date”

P24173, L26: “techniques” → “scenarios” (?)

P24174, L1: “... apply the deposition ...” → “... apply the empirically adjusted deposition ...”

P24174, L24: “confirming” → sounds too strong, perhaps better by “addressing”

P24176, L15: “atmospheric pressure” → “1 atm”

P24176, L21: “halogen stock” → “halogen loading in the atmosphere”

P24182, L11: “radicals” → “atoms”

P24182, L15-16: Reads better by “The initial mixing ratios of gas-phase species are...”

Unit explanation in the parentheses should move to a caption in Table 2 and then add “ppb = parts per billion”.

P24182, L27: Drop “active”.

P24183, L3-7: Here the words “concentration” and “mole fraction” are used interchangeably, but actually they should not be. If you refer to tracer abundance in the unit of ppb and ppt, you should say “mole fraction” or “mixing ratio”. I would normally choose the word “mixing ratio” and stick to it in the whole sentence.

P24183, L12-15: I would rephrase: “When the boundary layer height (L_{mix}) is raised to 500 m and 1000 m (Figs. 1b-c), the depletion stage commences only after 15 days

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and even more than 30 days, respectively, and its duration itself is extended to about 3-5 days." Here I assume that the authors have defined what "induction stage" and "depletion stage" are before this sentence in the revised manuscript.

P24183, L15-17: I would rephrase: "The speciation profiles of bromine species and their changes with the progress of ozone depletion are similar to those simulated at $L_{mix} = 200$ m (Fig. 1a), but the peak concentrations are considerably lower. The maximum values of BrO are in the range of 30–40 ppt, as compared to 60 ppt at $L_{mix} = 200$ m."

P24184, L4: "keeps stable" → "remains almost constant"

P24185, L24: "state" → "stage"

I will stop here, but I think there are a lot more phrases that should or can be improved.

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