Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-1314-RC2, 2019

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Modeling and Numerical Simulation of the Recurrence of Ozone Depletion Events in the Arctic Spring" *by* Maximilian Herrmann et al.

Anonymous Referee #3

Received and published: 11 April 2019

[Summary]

Using a 1-D model of photochemistry and vertical diffusion in the lower troposphere, Herrmann et al. examine conditions leading to the self-oscillatory recurrences of ozone depletion events (ODEs) in the modelled polar boundary layer. This study finds that either the vertical diffusion of ozone from the free troposphere or the photochemical production of ozone via NOx chemistry can be a viable mechanism to recover the ozone mixing ratios after each episode of ODE in the boundary layer to drive a subsequent episode of bromine explosion and ozone depletion. Under some model conditions, the system can also approach the steady state after several recurrences of ODE.

Printer-friendly version

Discussion paper

I have a mixed feeling about the present study. On one hand, the authors have done very thorough model experiments on the emergence and disappearance of the ODE recurrences, expanding a brief report on similar ODE recurrences simulated with a much simpler box model by Evans et al. (2003). On the other hand, the timescales of simulated ODE recurrences are in most cases longer than 10-20 days, whereas the shortest recurrence period simulated is about 5 days with invariant meteorology (turbulent diffusion). The constant meteorology ensures the delineation of the self-regulatory oscillation of the system without external excitation. In the real environment, however, meteorological conditions will certainly vary more or less at this timescale or shorter. Dry (and wet) deposition of aerosols seems to be ignored in the model runs so that particulate bromide accumulating in the model aerosols during the ODEs will stay intact over the recurrence timescales and available for the subsequent bromine explosion event, which I am not sure is realistic enough.

Despite the novelty of this study, I rate its scientific significance somewhere between good and fair, because of the uncertain relevance of self-oscillatory ODE recurrences simulated here. I agree with Referee #2 in their opinion that the title of the paper is somewhat misleading and should be adapted to indicate that the authors have explored the likelihood of the chemically driven recurrence of ODEs in a more or less hypothetical fashion. However, who knows if someone will discover from the field data in the future the recurrent feature of ODEs similar to those simulated in this study? Yet it is fair to ask how the varying meteorological conditions can modify the self-oscillatory chemical behaviors.

In my opinion, the paper is publishable with relatively minor revisions. It is an interesting paper.

[Major comments]

1. P5, L30-, “To the authors’ knowledge, recurrences of ODEs are hardly discussed in the literature”: This sounds odd to me. Quite a few studies exist as the basis of our gen-

eral understanding that variability in the meteorological conditions is the major source of the recurring nature of ODEs. To name a few, in addition to Bottenheim and Chan (2006), Oltmans et al. (2012) reported the role of synoptic air mass transport. Jacobi et al. (2010) pointed out the role of changing local and mesoscale weather conditions including the turbulent diffusion. One may regard model studies by Toyota et al. (2011) and Cao et al. (2016) as the demonstration of meteorological (external) drivers for the occurrence and termination of ODEs. Moore et al. (2014) pointed out the potential role of narrow openings in the sea ice in creating vastly different vertical mass exchange rates between the boundary layer and the free troposphere during the horizontal air mass transport. The authors should rephrase the statement by reflecting on some of such existing studies and should stress that the main value of the present study is in the exploration of other mechanisms potentially causing the ODE recurrences. I also wonder if there is a possibility for resonances with time-varying (periodic) vertical diffusivity profiles, but I guess it will be worth an entirely new study.

2. P9, L17, "The pH value is fixed at 5": This assumption is probably good for the pH of moderately acidified sea-salt aerosols (Keene et al., 2002) and NH4-SO4-NO3 aerosols in the NH3-rich environment (Guo et al., 2017), but is perhaps too high for springtime haze aerosols (Li, 1994). Is there a rationale for your assumption and have you explored the role of aerosol acidity in your simulated results? You also mention, "HNO3 tends to dissolve quickly in aerosols" (P9, L9). If you assumed lower pH values, the behavior of HNO3 could be different.

3. It seems that the aerosol-phase species are not subject to dry deposition in the present model. Dry deposition velocities of fine aerosol particles are small but not necessarily negligible within the context of this study. If we take the dry deposition velocity of the order of 0.01-0.1 cm/s (e.g., Wu et al., 2018), the residence time of particle-bound species in the atmospheric boundary layer with the thickness of 200 m is estimated to be on the order of 2-20 days. This challenges the validity of neglecting the dry deposition of particle-bound species, in particular, bromide (Br-) (P17, L6-9;

P19, L2-5). It is probably useful to perform additional model experiments for exploring the impact of dry deposition of aerosols and/or to discuss its implications.

4. Evans et al. (2003) seem to have assumed the mixing ratio of CH3CHO at 18 pmol/mol (see the end of their paragraph 15), whereas the default initial mixing ratio assumed in the present model is 150 pmol/mol (Table 2). It is not mentioned explicitly whether this value is adjusted for comparison with model results by Evans et al. (2003) in Section 3.3, even though the rate of bromine explosion can be highly sensitive to the CH3CHO mixing ratio. If the simulated mixing ratios of CH3CHO are still on the order of 100 pmol/mol in this case study, it is worthwhile conducting new model runs with CH3CHO = 18 pmol/mol.

5. Processes that have been investigated in the past model studies but is missing in the present model study include in-snow multiphase photochemistry (e.g., Toyota et al., 2014) as a source of reactive bromine in the atmospheric boundary layer. They may accelerate the build-up of reactive bromine significantly and can thus modify the recurrent behavior of ODEs. This neglected aspect warrants some comments if not tested explicitly by extending the present model experiments.

[Minor comments]

1. The metric “alpha” (defined in Eq. (1)) is referred to when discussing the simulated growth and decay of gaseous reactive bromine. It would be interesting if you can indeed manage to calculate the values of alpha from the model runs and to show their time series along with the mixing ratios of ozone and bromine species. Is it possible at all?

2. P6, L17, “. . . Br instead reacts with HO2, aldehydes or alkenes to form HBr”: Models (including the one used in this study) often assume that Br + alkenes produce HBr exclusively, but this is a surrogate approach to simplify complex reactions leading to the production of halogenated VOCs (e.g., Sander et al., 1997; Toyota et al., 2004; Keil and Shepson, 2006). Please consider rephrasing the statement.

3. The model description in Section 2.1.1 appears to have significant overlaps with Cao et al. (2016). Please refer to (perhaps minor) changes from Cao et al. (2016) and consider shortening the description if possible.

4. From Table A2, I do not see the photolysis of HNO4 taken into account in this model. According to Stroud et al. (2003): “HNO4 thermal decomposition and IR photolysis are the important loss mechanisms for HNO4 in the arctic free troposphere. Our calculations result in IR photodissociation contributing 20% and 37% to the total HNO4 loss in February and May, respectively.” If you believe that this effect can notably change your model results in Section 3.4.2, please discuss.

5. P26, L5-6: Define what BrNOx represents. BrNO2 + BrONO2?

[Technical suggestions]

P1, L6: as low as -> as short as

P1, L13: formulated by Lotka (1909), which are formulated in analogy to -> formulated by Lotka (1909) in analogy to

P1, L16: in the order of -> of the order of

P4, L25: iodine I (I- and IO3-) -> iodine (I- and IO3-)

P4, L25: Specify the media (seawater, etc.?) being referred to concerning the relative abundance of iodine against bromine.

P4, L27: due to the reduction of Cl -> due to the reaction of Cl

P9, L1: It is mentioned that kf = 10 m2/s here, whereas Figure 1 indicates that kf = 1 m2/s. Please check the consistency between the two.

P9, L14: . . . heterogeneous reactions involving NOy ARE FORMULATED TO conserve gas-phase NOy.

P9, L19 and other places: Henry coefficients -> Henry’s law constants

P10, L4 and other places: uptake coefficient -> mass accommodation coefficient

P10, Eq. (12): Please double check if the factor “T/T0” is necessary

P17, L2-5: You may want to rewrite these two sentences. I do not quite understand the message.

P17, L15: nitrogen oxygen -> nitrogen oxides

P19, L2: starting at -> restarting from

P19, L3-4: the aerosols are not diffusion limited -> the multiphase reactions involving aerosols are not diffusion limited

P19, L4: All other EPISODES start FROM about 30 pmol mol-1 of BROMIDE. . .

P20, L1 and other places: aerosol transfer rates -> gas-aerosol mass transfer rates

P23, L5: regenerated -> replenished

P24, L13-15 (three times): upper troposphere -> free troposphere

P24, L22: transported much MORE SLOWLY

P24, L23: decreasing with larger kt,inv

P24, L23: I cannot see the connection between “drop to approximately 15 nmol mol-1” and “converging to 12 nmol/mol”. Can you rephrase to clarify?

P24, L24-25: reducing the ozone RECOVERY RATE in the boundary layer and also limiting the maximum LEVELS TO WHICH OZONE CAN BE RECOVERD

P24, L27-: Also, the time between the two recurrences tends to increase PROGRESSIVELY AFTER EACH RECURRENCE since a larger turbulent diffusion coefficient in the inversion layer causes A GREATER loss of bromine to the free troposphere, . . .

P24, L31: If -> In cases where

P26, L26: R59 -> R57?

P26, L28: R67 -> R65?

P26, L28: R86 -> R84?

P26, L29-30: I do not quite understand the message here. Do you mean: “The shift from PAN to HNO4 as the most abundant NOy species at the lower temperature decreases the net ozone destruction rate during an ODE, resulting in earlier terminations of the ODEs”?

P28, L6, “photolyzrefered”: Is this a word in German?

[References]

Le Cao, Ulrich Platt, Eva Gutheil, Role of the boundary layer in the occurrence and termination of the tropospheric ozone depletion events in polar spring, Atmospheric Environment, Volume 132, 2016, Pages 98-110, https://doi.org/10.1016/j.atmosenv.2016.02.034.

Hongyu Guo, Rodney J. Weber, and Athanasios Nenes (2017), High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific Reports, 7, 12109, doi:10.1038/s41598-017-11704-0.

Jacobi, H.-W., S. Morin, and J. W. Bottenheim (2010), Observation of widespread depletion of ozone in the springtime boundary layer of the central Arctic linked to mesoscale synoptic conditions, J. Geophys. Res., 115, D17302, doi:10.1029/2010JD013940.

Keene, W. C., Pszenny, A. A. P., Maben, J. R., and Sander, R., Variation of marine aerosol acidity with particle size, Geophys. Res. Lett., 29(7), doi:10.1029/2001GL013881, 2002.

Keil, A. D., and Shepson, P. B. (2006), Chlorine and bromine atom ratios in the springtime Arctic troposphere as determined from measurements of halogenated volatile organic compounds, J. Geophys. Res., 111, D17303, doi:10.1029/2006JD007119.

Li, S.-M. (1994), Equilibrium of particle nitrite with gas-phase HONO: tropospheric measurements in the high arctic during polar sunrise, J. Geophys. Res., 99, 25469-25478. Christopher W. Moore, Daniel Obrist, Alexandra Steffen, Ralf M. Staebler, Thomas A. Douglas, Andreas Richter, and Son V. Nghiem (2014), Convective forcing of mercury and ozone in the Arctic boundary layer induced by leads in sea ice, Nature, volume 506, pages 81-84.

Oltmans, S. J., B. J. Johnson, and J. M. Harris (2012), Springtime boundary layer ozone depletion at Barrow, Alaska: Meteorological influence, year-to-year variation, and long-term change, J. Geophys. Res., 117, D00R18, doi:10.1029/2011JD016889. Sander, R., Vogt, R., Harris, G. W. and Crutzen, P. J. (1997), Modelling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring. Tellus B, 49: 522-532. doi:10.1034/j.1600-0889.49.issue5.8.x

Craig Stroud, Sasha Madronich, Elliot Atlas, Brian Ridley, Frank Flocke, Andy Weinheimer, Bob Talbot, Alan Fried, Brian Wert, Richard Shetter, Barry Lefer, Mike Coffey, Brian Heikes, and Don Blake (2003), Photochemistry in the arctic free troposphere: NOx budget and the role of odd nitrogen reservoir recycling, Atmospheric Environment, 37, 3351-3364, https://doi.org/10.1016/S1352-2310(03)00353-4.

Toyota, K., Kanaya, Y., Takahashi, M., and Akimoto, H.: A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer, Atmos. Chem. Phys., 4, 1961-1987, https://doi.org/10.5194/acp-4-1961-2004, 2004.

Toyota, K., McConnell, J. C., Lupu, A., Neary, L., McLinden, C. A., Richter, A., Kwok, R., Semeniuk, K., Kaminski, J. W., Gong, S.-L., Jarosz, J., Chipperfield, M. P., and Sioris, C. E.: Analysis of reactive bromine production and ozone depletion in the Arctic boundary layer using 3-D simulations with GEM-AQ: inference from synoptic-scale patterns, Atmos. Chem. Phys., 11, 3949-3979, https://doi.org/10.5194/acp-11-3949-

Printer-friendly version

Discussion paper

2011, 2011.

Toyota, K., McConnell, J. C., Staebler, R. M., and Dastoor, A. P.: Air–snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS – Part 1: In-snow bromine activation and its impact on ozone, Atmos. Chem. Phys., 14, 4101-4133, https://doi.org/10.5194/acp-14-4101-2014, 2014.

Wu, M., Liu, X., Zhang, L., Wu, C., Lu, Z., Ma, P.-L., et al. (2018). Impacts of aerosol dry deposition on black carbon spatial distributions and radiative effects in the Community Atmosphere Model CAM5. Journal of Advances in Modeling Earth Systems, 10, 1150-1171. https://doi.org/10.1029/2017MS001219.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1314, 2019.