**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Modelling multi-phase halogen chemistry in the remote marine boundary layer: investigation of the influence of aerosol size resolution on predicted gas- and condensed-phase chemistry" *by* D. Lowe et al.

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We thank Roland for his helpful comments, and address specific issues that he raises below.

- *Which 3rd order Rosenbrock solver are you using - ROS3 or RODAS3?*

  We use the RODAS3 solver. We have adjusted the following text on page 5292, line 8: "Rosenbrock solver *(RODAS3, Sandu et al., 1997)* packaged with KPP."

- *I couldn't find information about temperature and relative humidity - are you keeping these parameters constant? What are the values that you used?*

  Apologies, we forgot to include these details. We have added the following sentence to page 5293, line 19: "Temperature, pressure, and relative humidity are held constant through out all model runs at values of 285.15 K, 1014 hPa, and 89.4% respectively."

- *Even though this is the easiest way to describe wet deposition in a box model it is physically not correct because precipitation is not a process that streches over days but over short periods of time where a drastic reduction in aerosol and soluble gas concentrations occurs. What is your 8-day lifetime based on - global wet-deposition lifetime estimates?*

  The 8-day deposition lifetime was chosen to match that used by Toyota et al. (2001). For this study, like Toyota, we have represented all aerosol removal resulting from deposition as a 1st order continuous process analogous to a dry deposition removal process. It is merely used as an indicative loss process to represent all physical aerosol removal and hence, in our representation, the aerosol turnover rate.

- *You do calculate phase exchange for* NH_3 *- don't you?*

  Yes. Gas-phase NH_3 is kept constant in order that we can get a realistic ammonia loading without having to include sources and sinks. Condensed-phase NH_3 is not kept constant, and NH_3 exchange between the gas- and condensed-phases is dealt with in a fully dynamic manner.

- *Do you calculate the entrainment of* O_3 *as a function of time, dependent on the calculated* O_3 *concentrations or do you simply prescibe a flux? How do you calculate the entrainment velocity?*

The entrainment of O_3 from the free troposphere into the marine boundary layer is simulated using two opposing reactions, one for transport of O_3 into the marine boundary layer, the other for transport of O_3 from the marine boundary layer. The entrainment velocity is proscribed at $1.3\,\mathrm{cm\,s^{-1}}$, the O_3 emission flux given in Table 2 is calculated using the free troposphere O_3 concentration and entrainment velocity. The, badly-named, O_3 deposition velocity given in Table 3 is, in fact, the sum of both the entrainment velocity to the free troposphere, and the deposition velocity to the sea surface. We have corrected Table 3 to indicate that it lists both entrainment and deposition velocities.

- *Why do you think that the atmosphere is in steady state? There is cloud formation and dissipation, discrete precipitation events, airmass changes and mixing, all acting to drive the atmosphere away from steady state. Unless your long spin-up time is due to very non-steady state initial conditions or initialisation of key parameters with 0., I would conclude from your estimate of the time it takes to establish steady state in the model that the atmosphere is usually not in steady state — at least with regard to the parameters that you are studying. The fact that you do very long model runs is probably also the reason why your absolute gas phase reactive halogen levels are rather high.*

The direct representation of atmospheric conditions was not the point of the paper. We agree that the atmosphere will not be in steady-state and hence the spin-up conditions are unphysical, as we note in the paper (p. 5295). They are also, as you say, why the absolute gas phase halogen levels are a little high. Our interest with this study is not, however, to directly study realistic atmospheric processes, but rather to investigate the influence of specific microphysical assumptions that we as a community make on the behaviour of mixed-phase chemistry models. This can be facilitated by stepping away from reality for a while, reducing the number of degrees of freedom in the system in order to empathise the influence of the assumptions we're interested in studying. Once we understand

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the influence of these assumptions in an ideal testcase we can then carry that knowledge through to more realistic testcases.

- *A slightly semantic comment: would it not be better to refer to "reservoirs" instead of "sources", after steady state has been established? The aerosol will still be a net source (due to replenishment of deposited aerosol) but the gas phase is a mere reservoir unless you have significant concentrations of organic bromine.*

  We agree, and have amended our text to differentiate between these two roles.

- *Could you please add the lifetime of the largest particles? I am somewhat surprised that you have very small S(VI) production in these particles as oxidation by O_3 should be really fast (see e.g. Chameides and Stelson, 1992 or von Glasow, 2006, Fig. 3).*

  Our largest particles have wet radii of approximately 34 μm, and lifetimes of 1.7 hours (in comparison our particles with wet radii around 5 μm, comparable to the particles in von Glasow (2006) have lifetimes of 1.3 days). S(VI) production does occur, however the rapid turnover of these particles limits the build up of S(VI) to $\sim$0.001 mol kg_{H2O}^{-1}. We have changed the text in lines 21–22 of page 5298 to include these details.

- *You should mention which accommodation coefficients have been measured and which haven't as currently the reader might assume that the uncertainty is the same for all accommodation coefficients, which is not the case (e.g. Wachsmuth et al., 2002, for HOBr).*

  We have added notes to Table 7 to indicate for which halogen species the accommodation coefficients used in the Pechtl et al. (2006) scheme are based on measurements and which are estimated.

- *p. 5299, l. 2 vs. caption table 7: Please use a consistent term to describe case Base/Pechtl.*

It might be better to use "HOX" instead of "HO$_X$" as the latter might be confused with "HO$_x$ = OH + HO$_2$".

p. 5300, l. 2: "reduce" → "reduced"

These three errors have now all been corrected in the text.

- *From Figure 3 I would conclude that the scenario "1 bin, S/V" reproduces the results of the full model rather well. Please comment.*

For this study (remote, non-cloudy marine MBL) the "1 bin, S/V" model does reproduce the results of the full model well. This is both because the model captures the important microphysical characteristics of the aerosol phase, has been initialised with turnover rates calculated with the full model, and because the it is the bulk of the seasalt distribution of which dominates the halogen processing and source term. However it's not clear that this would be applicable for other scenarios. For all scenarios we would need to use the full model to calculate the turnover rates. Other microphysical properties could also become more important, i.e. particle number for cloudy scenarios. Also we have found that the response of HNO$_3$ was not fully captured by the "1-bin, S/V" model: it would be interesting to see if increasing the pollution load of the atmosphere exacerbates this difference, or if the influence of the condensed-phase on the gas-phase is drowned out.

- *Table 1,2: Could you add references what these mixing ratios and fluxes are based on?*

References have now been added to Tables 1, 2, and 3.

- *Table 4: Could you please specify whether you are refering to log10 or ln?*

Apologies, these should be natural logs, and have been changed to reflect this.

- *Table 5: The formatting of the blank lines is a bit odd, please improve.*

This has been tidied up.

- *Overall the figures are rather small, some at the limit of what can be read. Please make sure that the figures in the final version of the paper are not smaller and if possible larger than in the ACPD version.*

  We will ensure that Figures 3, 4, 5, 6, and 8 are either full page or re-formatted (or split) to fit the page better.

- *It might be useful to add a figure similar to figure 5 but for the case "N/V" as larger scale models might aim to reproduce cloud microphysics and chemistry and for cloud processes the number of aerosol particles/CCN is crucial.*

  We agree that information pertaining to the N/V initialisation could be useful. We have plotted the ozone mixing ratios, and NO_x and HO_x ratios, for the 1- to 16-bin N/V initialised models. Also rhe text of Section 3.2 has been extended to reflect these changes.

- *Figure 2 and 9: Please add "loss" between "ozone per" in the caption.*

  Ozone destruction is plotted as a percentage of the ozone concentration, not the total ozone loss per hour. However the captions are misleading, and have been changed to read "in the percentage *loss* of total ozone per hour".

- *Figure 4 and 10: Please add the unit for the molality.*

- *Figure 7: What is the unit for the aqueous phase concentrations?*

  The units of molality are moles per litre of solvent (water): $mol\ kg^{-1}_{H_2O}$. This has been added to the captions.

- *Figure 7: Why do you have a rather strong diurnal variation in the pH of the largest particles? What are the reasons for the morning peak of NO_3^- in the small sea salt particles? What is the source and what is the sink?*

The strong diurnal variation in the pH of the large particles is caused by their very short lifetimes (1.7 hours), which leads to the rapid replacement of aerosol acidified during the day. Diurnal variations in pH in smaller ($<21\mu m$ diameter) seasalt particles have already been measured (as well as variations in pH across the particle size range, Pszenny et al., 2004) – so it should be possible to test our model predictions with their impactor measurements. We have added text to Section 3.2 to explain this.

The morning peak of NO_3^- is due to the rapid uptake of $XONO_2$ by the smallest seasalt particles: when the accommodation coefficients for these compounds are reduced the peak in NO_3^- becomes less pronounced (Figure 10), while the gas-phase concentrations of these compounds increases (Figure 8). The elevated levels of NO_3^- in the smallest seasalt particles leads them to out-gas HNO_3, creating a morning peak in gas-phase HNO_3 too, a feature not see in the Low accommodation coefficient testcase (Figure 8). As NO_2 levels decrease the production of $XONO_2$ slows, until it can't match the uptake rate of these compounds onto the smallest seasalt particles, allowing the out-gassing of HNO_3 to reduce the levels of NO_3^- until equilibrium with gas-phase HNO_3 is reached again.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5289, 2009.

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