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Atmospheric
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Discussions

Interactive comment on “Halogen cycling and aerosol pH in the Hawaiian marine boundary layer” *by* A. A. P. Pszenny et al.

Anonymous Referee #1

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"Halogen cycling & aerosol pH in the Hawaiian marine boundary layer", Pzenny, Moldanova, Keene, Sander, Maben, Martinez, Perner & Prinn.

Synopsis:

The paper presents an integrated investigation of boundary layer halogen chemistry incorporating a comprehensive suite of measurements with a detailed modelling study. The measurements were well targetted, providing most of the gas and aerosol speciation of halogen compounds to enable a meaningful comparison with the model, which is the most detailed available for the study of marine halogen chemistry. The methodology employed was to calculate the aerosol pH as a function of size based on the measured ionic composition, estimated liquid water content and degree of phase partitioning of HCl. This was compared with the modelled aerosol pH evolution, and the

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modelled gaseous and aqueous halogen compounds compared with the measured values. Good general agreement between the modelled and measured parameters was achieved. Gaseous chlorine species were present at around the predicted absolute concentrations and predictions of the diurnal variation of each chlorine species were consistent with the measurements for all but HCl. Bromine species were also present at around the predicted concentrations, but with a diurnal cycle opposite to that predicted. Cloud processing is tentatively postulated to explain the measured high daytime concentrations compared with the nighttime - see Roland von Glasow's interactive comment for a more full discussion. Modelled sensitivity of ozone destruction by halogen chemistry to the availability of seasalt aerosol showed a decrease in ozone of 16 percent with a seasalt increase within the observational uncertainty.

The paper is well written, well argued and makes a valuable contribution to the understanding of a subject area within the remit of ACP. It is therefore extremely worthy of publication. I have no major criticism of the script, but there are several points arising from the paper (not necessarily requiring explicit answers) that could help in future understanding of the subject area.

With direct reference to the measurement / sampling strategy:

The deployment of the instrumentation suite at the Bellows air force base on the Hawaiian coast ensured that background marine air was sampled, avoiding issues associated with coastal halogen hotspots where intertidal exposure of more gradually shelved macroalgal beds makes halogen chemistry difficult to interpret.

The authors are to be congratulated on the assembly of such a comprehensive measurement suite. Such deployments will inevitably lead to improved understanding of mbl halogen chemistry. There may have been one or two additions which could add value to the study.

i) It is stated that long path DOAS was used to measure BrO, NO2 and O3. Given that NO3 at night (through seasalt uptake of N2O5 and release of ClNO2 and BrNO2), and

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IO during the day (through reaction with HO2 and uptake of the HOI formed, followed by reaction with Cl- or Br- to form gaseous ICl and IBr) are two species readily observable by this technique (Allan et al., 2000a, Allan et al., 2000b, McFiggans et al, 2002), could they not be retrieved from the spectra and used to verify the predictions of halogen activation? In addition, it would be useful to verify the open ocean concentration of reactive nitrogen and iodine species.

ii) A possible addition to the arsenal could be the direct measurement of aerosol liquid water content. Such measurements would improve the calculation of aerosol pH and / or give a cross-check on the hygroscopicity models.

iii) Since di- and trihalocarbons may readily photolyse and continually supplement the halogen atom source from seasalt, an assessment of this relative contribution might be useful. With this in mind, measurements of these species would provide further constraint on the model's chemical mechanism. Alternatively, assuming the mechanism to be well understood, it should be possible to estimate an upper limit to their importance in the propagation of the cycling.

Concerning the model:

The coupling of gaseous and aqueous chemistry using multiple aerosol size bins is an entirely appropriate technique to address the multiphase cycling of halogens through seasalt aerosol; centering the bin diameters on those of the impactor stages allows direct comparison with the measurements. It would be helpful if the dynamics of the model were explained in the paper. I assume that a static sectional format is used. If this is the case, how sensitive to numerical diffusion is the condensational growth and evaporation scheme to bin spacing (14 bins in 2 distributions between 50 nm and 21 microns appears to be a very small number).

How sensitive is the model to the turnover rate of the aerosol? Since the modelled pH in the coarse fraction is higher than measured, is the size dependent aerosol deposition rate physically reasonable? How do the values from the Slinn model need to be

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adjusted to give the values calculated from measurements?

In the analyses:

On page 16 the median H+ activities are stated to be less in Hawaii than in Bermuda. Expressing the activity as pH is then confusing (lower activity being higher pH) and the sentence should be reworded.

It is interesting to note that fine, probably continental, aerosol are enriched in Br. Is there any evidence to suggest that the Br- is externally mixed with respect to the acidity in the fine fraction?

Throughout the analysis, there is little or no mention of iodine speciation in either gas or aqueous phase. Even if it were not possible to measure the iodine speciation, it would be useful to know whether the model predicts the iodine to be enriched in seasalt aerosol to the level measured in previous open ocean MBL studies. This would ensure that iodine-mediated halogen cycling was simulated at a reasonable magnitude.

A small point:

it is stated in the introduction that "photolysis of I-containing organic compounds ... may substantially increase production of new particles". In the light of recent observations of I2 at the coastal location where the new particle studies have been carried out, calculated I atom flux from I2 photolysis is of the order of 10000 times higher than from organic iodine. It is extremely unlikely that organic iodine is responsible for any new particle production.

In summary:

The paper presents a balanced and well considered study of MBL halogen cycling and contributes significantly to the state of the science.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4701, 2003.