

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

Anonymous Referee #2

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Comments on “Halogen cycling and aerosol pH in the Hawaiian marine boundary layer” by Pszenny et al.

The manuscript by Pszenny et al presents a combined observational and modeling investigation of the multiphase halogen chemistry and aerosol pH in the marine boundary layer (MBL). Comprehensive measurements of the chemical composition of aerosols and various gas-phase species show acidic particles with a median pH of 5.1 in the super μm size range and lower pH for smaller particles. The modeled pH values agreed well, considering the limitations of the box-model that was used in the analysis. The observed chlorine depletion in particles seem to correlate well with the measured HCl* during the day. The nocturnal correlation was less obvious. No clear diurnal variability was found for HCl mixing ratios, although the model clearly showed elevated HCl levels in the early morning, illustrating that other parameters than solar radiation influence

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HCl levels. In general, the modeled chlorine levels agreed well with the observations. Simulated daytime bromine levels were similar to the observations. However, the reason behind the higher nocturnal values is not clear. Finally the paper illustrates the importance of halogens on marine boundary layer ozone, finding a considerable decrease of ozone mixing ratios in the presence of sea salt particles.

This is a very interesting and well written paper and I strongly support its publication. The text clearly illustrates the current state of knowledge of halogen and sea salt aerosol chemistry and its importance for ozone levels in the MBL. The manuscript also points out some unsolved problems, such as the cloud processing of halogens, which need to be further addressed (see interactive comment by R. von Glasow). The authors employed a comprehensive set of aerosol and gas-phase instruments to provide a detailed data set on the multiphase processes, and offer an excellent description of their different measurement techniques and the methods used to derive aerosol properties, such as pH and total acidity. I would also like to commend the authors for their comprehensive and detailed discussion of the measurement uncertainties. The model is well suited for the purpose of this study and agrees generally well with the observations.

While I have found no major problems with the manuscript, I found a number of smaller issues that the authors may want to address before the final publication:

- The manuscript is somewhat unclear on how the data shown in figure 9 were derived. Was the difference between the two atmospheric spectra used in the analysis always 3 hours, or was there a variable time difference? If so, was the data in figure 9 scaled to show the equivalent temporal change in 3 hours? It would also be helpful to show errors of the data, and to make a statistical analysis to determine whether the negative values in the morning are statistically significant.

- Can the statement on page 4724 that "Observed O₃ variations between 15 - 35 nmol mol⁻¹ during the campaign may thus explain some of the variability in the measured halogen species" be further supported by a correlation analysis between ozone and

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halogen species?

- The DOAS system also measured NO_2 and most likely HCHO. How do these observations relate to the initialization of the model? Also, is there any information on iodine oxides and chlorine oxides that can also be measured by DOAS?

- The manuscript currently does not consider the possible impact that the presence of iodine radicals would have on the presented results, in particular with respect to the recycling of halogens and the destruction of ozone. The DOAS instrument can, in principle, measure IO and OIO and thus at least give an upper estimate of the concentrations of these species. With the help of the chemical model a brief assessment of the impact of iodine on the results would round up the manuscript nicely.

Technical comments:

Page 4725: R11 it should be HOX, without the subscript of the "X".

R12 $\text{XNO}_3 + \text{Y}^- \rightarrow \text{XY} + \text{NO}_3^-$ would be a better way to write this equation, since the most important reaction path produces BrCl (see further below in manuscript).

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

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