Atmos. Chem. Phys. Discuss., 3, S2508–S2515, 2003
www.atmos-chem-phys.org/acpd/3/S2508/

Atmospheric Chemistry and Physics Discussions

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

A. A. P. Pszenny et al.

Received and published: 3 February 2004

Prefacing note:

Our responses were delayed because four of the authors (Pszenny, Keene, Maben and Sander) were on a research cruise from mid-October to late November 2003 and were not able to consider the review comments during that period.

Re: Comments of R. von Glasow:

Dr. von Glasow mentions that "measurements [of Br- EF] ... peak around sunrise." We believe that this comment refers to measurements by B. Huebert and colleagues based on aerosol samples that were collected during the same experiment in parallel with those reported in this manuscript. Huebert and colleagues' measurements are described in Sander et al., Atmos. Chem. Phys., 3, 1301-1336, 2003. The data from our ˜12-hour samples do not allow resolution of variations on time scales of only a few hours.

Discussion with Dr. von Glasow following receipt of his comments led to discovery of a coding error that resulted in HBr not being included in Brt (the sum of volatile inorganic Br species). Figs. 4 and 11 (now 5 and 12, respectively; see below) have been corrected, the relevant discussion (paragraph bridging pp. 4721 and 4722 in the discussion version) has been replaced with the following, and the conclusions section and abstract have been revised accordingly:

"Maximum simulated mixing ratios of Brt varied between 1.5 and 7.0 pmol mol-1 (Fig. 5), which are within the range of measured concentrations (Fig. 8). The higher values were associated with the higher concentrations of sea-salt particles in simulation M3. Maximum simulated mixing ratios of individual Br species (HBr, HOBr, BrO, BrCl, and Br2) were each in the range of a few (1.5 to 3.0) pmol mol-1; HBr, HOBr and BrO peaked during daytime and BrCl and Br2 peaked at night. In all cases, Brt mixing ratios were highest in the early morning and lowest at dusk. In simulations M1 and M2 the Brt mixing ratio increased slowly overnight whereas, in simulation M3, the Brt mixing ratio increased quickly after dusk. These differences account for higher average daytime mixing ratios of Brt in simulations M1 and M2 compared to higher average nighttime mixing ratios in simulation M3. The diurnal variabilities of Brt in the model are thus quite in agreement with measurements, with higher daytime Brt mixing ratio on average but with some occasions when daytime mixing ratios were lower than those during the following night. Von Glasow et al. (2003) investigated the diurnal variability of Brt with the 1-dimensional model MISTRA and found that presence of clouds influenced diurnal variability of Brt. In simulations with clouds, Br2 and BrCl, which would otherwise accumulate in the gas phase, dissolved into the cloud droplets causing nighttime minima in mixing ratios of these two compounds. Diurnal variability in Br- and EFBr also differed between simulations M1 and M2 relative to M3. Under the conditions of less intensive halogen cycling, the bromine volatilisation took place only during daytime when there were significant concentrations of HOBr driving the Br activation reaction

R1. In simulation M2 no volatilisation took place at night and the EFBr increased due to the continuous air-sea exchange in the model replacing the bromine-depleted sea-salt particles with fresh ones. In simulations M1 and M3 with more intensive halogen cycling, larger gas phase mixing ratios of BrCl and Cl2 developed after dusk and bromine volatilisation occurred as BrCl and Cl2 dissolved into the sea-salt aerosol, volatilising Br2. In M3 with slower air-sea exchange this nighttime volatilisation led to the lower nighttime mixing ratios of Br- (and decreased EFBr) compared to daytime. In M1 with faster air-sea exchange the nighttime volatilisation was smaller than the relative increase of Br- due to air-sea exchange, and the diurnal pattern was similar to that of simulation M2. Differences between diurnal variabilities in M1 and M3 can be seen in Fig. 7. The model results can be compared to the measured Br- deficits (Fig. 8b) with slightly larger deficits during daytime than at night on average. Von Glasow and Crutzen (2003) recently compared diurnal cycles of Br- in 1-D MISTRA model simulations with intensive and less intensive bromine volatilisation. They obtained opposite diurnal cycles in agreement with our simulations, however with much larger amplitude in a low Br- volatilisation case. Rancher and Kritz (1980) reported diurnal variabilities of Brt and Br- over the equatorial Atlantic Ocean with consistently higher Brt and lower Br- during daytime."

Re: Comments of Anonymous Referee #1:

i) Even though it is possible to measure NO3 with our instrument, we did not because NO3 absorbs in a different spectral region and its measurement would therefore have required a significant amount of measurement time we preferred to dedicate to get a good time resolution of BrO. We have added a statement to the end of Section 2.2 indicating that IO was measured, but always remained below the detection limit, which was 1.5 pptv on average. No temporal variations were evident even when the measurements were time-differenced (as in Fig. 9 for BrO). For this reason we elected not to discuss the IO measurements further.

ii) We agree that direct measurements of aerosol LWC would be very helpful in future field studies.

iii) Some iodocarbons were measured during the experiment by E. Atlas (presented at the CACGP/IGAC conference in Crete in September 2002). However, with only upper limits for IO mixing ratios and no aerosol iodine data at all we do not believe that discussion of I chemistry is warranted here. We have added the following sentence to the end of the introduction:

"Although evidence is now mounting that the cycling of reactive iodine compounds may also significantly influence the chemical evolution of MBL air (e.g., McFiggans et al., 2000, and reference therein), measurements of aerosol I species were beyond the scope of this effort. Due to this lack of multiphase observational constraints on I cycling the discussion is limited to Cl and Br chemistry."

Analyses points:

Re: Fine particle Br enrichment: We are not aware of definitive evidence of external mixing of Br and "acidity" in fine particles. Sander et al. (Atmos. Chem. Phys., 3, 1301-1336, 2003) discuss fine particle Br enrichment in their recent review.

Re: I speciation: As noted above, we do not feel that a discussion of I chemistry is warranted in this paper.

Re: Photolysis of organic I compounds: The key word in our original sentence was "initiates". To our knowledge, molecular iodine is not emitted from the ocean to the atmosphere. It is produced in situ as part of a cycle that begins with photolysis of organoiodine compunds (see, e.g., McFiggans, G., B. Allan, H. Coe, J.M.C. Plane, L.J. Carpenter, and C. O'Dowd, A modeling study of iodine chemistry in the marine boundary layer, J. Geophys. Res., 105, 14,371-14,385, 2000). We have not revised the sentence.

Concerning the model:

The dynamics in the model are truly static. Bin sizes and humidity are kept constant in the simulations so there is no condensational growth involved; there is also no coagulation. Consequently, there is no "transport" of particles across size bins. In this sense, there in no numerical diffusion. As described in the paper, the air-sea exchange of aerosol mass is treated in the model by replacing reacted particles in each size bin with fresh sea-salt particles in proportion to their (size-dependent) atmospheric lifetimes against dry deposition. This approach introduces disequilibria into the particle solution in each bin. This is certainly different from the real world where the particles have different ages and therefore different degrees of disequilibrium within each size bin, but this is impossible to describe with our model. The sensitivity of aqueous phase equilibria to the turn-over rate of the particles can be seen by comparing concentrations in the individual size bins. Fig. 2b and Fig. 6 in the discussion version of the paper show concentrations in individual bins of the sea salt particles in simulation M1 and M3 (Fig. 6b). Because of their short atmospheric lifetimes, only the largest particles maintain large undersaturation with respect to HCl. Those in all smaller size bins approach saturation.

This also partly answers the reviewer's next comment about the exchange rate needed to maintain equilibrium. However, since direct measurements of aerosol pH were not made, we do not know the actual equilibrium state of the mixed particles within each sampled size fraction. The pH values presented in Table 3 were calculated assuming equilibrium with gas-phase HCl. The differences between pHs inferred from the measured phase partitioning and thermodynamic properties of HCl relative to those simulated with the model reflect a difference in calculation approach rather then a difference between actual and modelled pH.

Re: Comments of Anonymous Referee #2:

Re: Derivation of data shown in Figure 9: As stated in the figure caption, the detection limit, or 2-sigma error, was about 2 pmol mol-1, too large to show in the figure. Therefore there is a lot of scatter (the minimum hourly average is about equal to its standard deviation) and the values derived from measurements could be due to instrumental artifacts. Even though the BrO measurements were all below the 2-sigma detection limit, the time-differenced values do show a noticeable diurnal variation, which we feel is worth showing. We have added a sentence to the figure caption to clarify how the time differences were calculated.

Re: Correlation of measured O3 with measured halogen species: Good suggestion! Spearman's rank correlation coefficients (rho) for measured Br species with O3 (averaged over aerosol and filter pack sampling intervals) were as follows:

Brt vs. O3: nighttime: 0.555; daytime 0.213

EFBr vs. O3: nighttime: -0.427; daytime -0.556

The DOAS was not operational during the first intensive so n = 10 for each of these calculations. The signs of the four rho values are all in agreement with MOCCA simulation results, however null hypotheses of no correlation between variables could not be rejected at the alpha = 0.05 level in any of the four cases (rho-critical = 0.636). It should also be noted that the DOAS was generally operated for only brief periods at night due to local permitting restrictions, making comparison with the Br parameters somewhat unfair. And the model does not consider externally caused changes in O3 such as enhancements due to transport of polluted continental air, as was evident during the last intensive. Thus, non-significant correlations are not surprising. We have not revised the text in light of this.

Re: DOAS measurements of HCHO and other species: HCHO was always below the detection limit of about 400 pmol mol-1, whereas NO2 was above detection limit of 60 pmol mol-1 only during brief periods of offshore flow. The largest such spike was recorded on 11 September between 0600 and 0800 local time when mixing ratios reached 2 nmol mol-1. IO and OClO were measured, but always remained below the detection limit, which was 1.5 pmol mol-1 on average, and no temporal variations were evident even when time-differenced (as in Fig. 9 (now Fig. 10) for BrO).

Re: Discussion of I chemistry: As noted with respect to a similar comment by the other anonymous reviewer, we do not believe that such a discussion is warranted here.

Additional revision not directly in response to a review comment:

Shortly after submission of this manuscript the publication of a paper by A. Laskin et al. (Laskin, A., Gaspar, D.J., Wang, W., Sherri W. Hunt, S.W. Cowin, J.P., Colson, S.D., and Finlayson-Pitts, B.J., Reactions at interfaces as a source of sulfate formation in sea salt particles, Science, 301, 340-344, 2003) inspired us to examine our cascade impactor data closely for evidence of day/night pH and nss-SO42- variations. The new text below has been inserted between lines 5 and 6 on page 4717 of the discussion version and a new figure (#2) has been added. Subsequent figures have been renumbered and figure call-outs updated accordingly.

"Laskin et al. (2003) recently hypothesized based on laboratory experiments that the reaction OH + Cl –> OH- + Cl at the surfaces of deliquesced sea-salt aerosols slows aerosol acidification and, thus, speeds S(IV) oxidation by O3 during daytime in clean marine air. Data generated during this experiment were examined for evidence in support of this hypothesis. Median pH values inferred from HCl phase partitioning for each of the six largest size fractions did not differ statistically day vs. night (Mann-Whitney U tests, alpha = 0.05), although the median in each fraction was 0.1 to 0.2 pH unit lower during the day than at night (Fig. 2a). Nss-SO42- distributions also differed insignificantly day vs. night (Fig. 2b). Both of these observations are in agreement with MOCCA simulation results (Fig. 3b). HCl* mixing ratios, with 2-hour time resolution, provide a diagnostic of aerosol acidity during midday. HCl is infinitely soluble in alkaline solution and its uptake is diffusion limited. Significant production of alkalinity during midday would favor HCl partitioning into the aerosol and, thus, smaller HCl mixing ratios in the gas phase. Systematic midday decreases in HCl* were not evident (Fig. 4). Indeed, during the two cleanest sampling periods (intensives 2 and 5, Table 2), HCl* mixing ratios peaked during midday (Fig. 4). These results suggest that the Laskin et al. (2003) mechanism of alkalinity production via surface reaction of OH with

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

Cl- in sea-salt aerosols did not affect S cycling appreciably under these clean marine conditions."

Caption for new Figure 2:

"Box-whisker plots of (a) aerosol pH during daytime (narrow blue boxes) and nighttime (wide black boxes) inferred from HCl phase partitioning, and (b) measured nss-SO42- as a function of particle size. Box tops and bottoms indicate quartile values, whiskers indicate decile values, and thick horizontal bars indicate median values. Eleven daytime and eleven nighttime values were available for constructing each box."

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