Atmos. Chem. Phys. Discuss., 11, C2138–C2144, 2011
www.atmos-chem-phys-discuss.net/11/C2138/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “HOCl and Cl_2 observations in marine air” *by* M. J. Lawler et al.

Anonymous Referee #1

Received and published: 21 April 2011

General Comments:

This is a well written manuscript by a capable group of investigators that addresses an important issue, which is appropriate for publication in ACP. After suitable revision to address the specific comments listed below, I recommend that the manuscript be published and congratulate the authors on a nice piece of work.

Specific Comments:

Page 8116, line 14. It would be helpful to specify a range or median rather than an upper limit for CH4 destruction.

Page 8116, lines 21-22. While reactive Cl chemistry will catalytically destroy O3, available evidence suggests that this is a relatively minor sink for O3 in the troposphere under most conditions. I encourage the authors to either qualify or drop this statement.

Page 8116, lines 22-25. Relative reaction rates of Cl and OH with NMHCs vary greatly. In addition, it is potentially misleading to lump CH4 and NMHCs together in terms of their climate relevance. I suggest that the authors consider clarifying this section accordingly.

Page 8117, line 1. The authors may wish to add BrCl to the list since model calculations based on MECCA suggest that it is an important and sometimes dominant Cl-atom precursor over the open ocean.

Page 8117, lines 8-10. The cited studies evaluate the production of Cl-atom precursors initiated by N2O5 reaction with particulate Cl-. However, they did not explicitly address the importance of these activation pathways relative to others. In addition, the text should clarify that the pathways leading to ClNO2 and Cl2 involve reaction with particulate Cl- as opposed to generic "aerosols". N2O5 also reacts with aerosol via hydrolysis to produce HNO3.

Page 8118, lines 10-12. I understand what the authors mean but the terminology here is a little unclear. Relative to what would O3 "increase cycling." I think the authors mean to say that reaction with O3 sustains the cycle by converting Cl to ClO whereas most reactions of Cl with NMHCs produce relatively unreactive HCl, which slows radical recycling.

Page 8118, lines 19-20. To provide additional context, it would be helpful to include the detection limits for BrCl during these studies. Were detection limits sufficiently low to rule out BrCl as an important radical precursor?

Page 8119, line 8. Remove redundant "remote".

Page 8119, line 20. Suggest replacing "slightly higher" with a more quantitative descriptor.

Page 8119, line 22. Suggest adding additional details and/or a citation explaining the approach that was used to calculate the trajectories. In Fig. 1 and/or in the text, it would

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

also be helpful to provide additional information regarding the altitude of transport.

Page 8120, first two paragraphs. The manuscript indicates that ionic constituents of aerosols were measured and used to parameterize the model. A brief summary of what was measured, how it was measured, sampling frequency, and the relevant concentration ranges should be included here.

Page 8120, line 4. Suggest replacing "major contribution" with the range in actual contributions of particulate NO3- to NOy. Was particulate NO3- sampled quantitatively by the NOy instrument? If not, NOy measurements should be described as lower limits.

Page 8120, line 5. NOy includes species other than NO2, NO, HNO3, and NO3- so I don't understand the logic here. For example, model calculations and measurements suggest that BrNO3, ClNO3, and HNO3 may be present in marine air at roughly comparable mixing ratios [e.g., Keene et al., 2009].

Page 8120, line 18. It would be helpful to briefly describe how detection limits were estimated.

Page 8120, lines 21-22. It would be helpful to report the passing efficiency of the inlet.

Page 8121, lines 20-24. As described in the cited literature, the performance of Cl2 permeation tubes (both permeation rates and specificity) can vary over time and, thus, gravimetric loss may not be a reliable indicator of Cl2 permeation rates. The manufacturer of the tubes used for this study is aware of the problem and, upon request, will provide a procedure to restore specificity (but not necessarily permeation rate) after performance degrades. Consequently, the performance of one tube is not necessary indicative of the performance of another, particularly one that has been subject to different treatment (i.e., transported to and from a remote field site during which a power outage occurred). If performance of the tube used for calibration during this study was not verified via independent (i.e., iodometric) calibration or direct intercomparison with a traceable standard, it would be helpful to do so and to report the results in the revised version of the paper.

How much did sensitivity vary over the course of the study? How was "uncertainty in the instrument sensitivity" estimated and incorporated in the standard error calculation? The terminology is confusing. In this section, it appears that sensitivity refers to precision (i.e., random variability of replicate measurements). However, elsewhere the authors refer to directional changes in sensitivity between calibrations, which implies changes in instrumental response to a given signal strength. The text should be clarified in this regard.

Page 8122, lines 14 to 15. What does "roughly linear" mean? Suggest replacing with a quantitative descriptor such as the range in correlation coefficient for linear or quadratic calibration regressions.

Page 8122, line 18. What does "varied by less than 90%" mean? Relative to what did sensitivity vary? Do the authors mean that instrument response varied by something approaching a factor of two between daily calibrations? In light of this relatively large degree of variability, did the authors test the reliability of the assumption that response varied linearly between the daily calibrations? For example did pressure in the ionization region (to which response is highly sensitive) vary linearly over time? If not, what are the implications for data quality?

Page 8124, lines 22-24, and Table 2. To facilitate comparison with published measurements, it would be helpful to add temperature, relative humidity, and the air concentrations of a sea-salt tracer and of non-sea-salt SO42- to Table 2. Presumably particulate ions were allowed to vary. The rationale for initializing species that were not measured should also be explained.

How did the authors account for the turnover of species that were allowed to vary? For example, volatile inorganic Br in marine air is typically greater than the corresponding deficit relative to sea salt because it has a longer atmospheric lifetime against deposition than does the parent aerosol. Realizing this aspect of "steady state" in the simulations would require that aerosols turnover in the model. Did they and if so at what rate? If not, the text should so indicate and briefly discuss the implications of ignoring the deposition and emission of reactive species.

Page 8125, lines 20-21 and onward. An additional source is only one of several possible explanations for the discrepancy between simulated and measured HOCl. These results suggest that HOCl vapor is produced more rapidly and/or lost more slowly in ambient air relative to the model. This could be explained by the same sources and sinks but with different rate constants in air relative to the model. Indeed, slower uptake of HOCl by aerosols is considered as a possible explanation later in the manuscript. Alternatively, as the authors suggest, an additional source or sources not considered in the model could be involved.

Pages 8127-8128, Section 5.3. Based on similar pathways in chlorinated water supplies, it seems reasonable to speculate that some HOCl reacts with organics associated with marine aerosol to form organochlorine products. However, the almost completely unconstrained nature of the model parameterization renders simulated results little more than a wild guess. In the absence of additional evidence, I suggest that authors consider dropping this section although the speculation may warrant a sentence or two that could be consolidated in the preceding section.

Page 8129, line 20. Relative to HNO3, SO2 and other acids including HCl, HCOOH, and CH3COOH are typically present at much higher mixing ratios in this region [e.g., Lee et al., 2010, ACP]. Consequently, most alkalinity associated with fresh marine aerosols will be titrated by acids other than HNO3. SO2 uptake and oxidation via O3 slows greatly after all alkalinity has been titrated but HNO3 continues to accumulate towards thermodynamic equilibrium, which would displace the less soluble acids (HCl and carboxylics) that would have been scavenged by freshly produced, alkaline aerosol. In addition, Chameides and Stelson [1992] investigated the potential role of S(IV) in acidifying sea salt. HNO3 was not evaluated explicitly. Erickson et al. [1999] (cited elsewhere in the manuscript) modeled the roles of HNO3, SO2, and HCl in the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

initial chemical evolution of fresh marine aerosol.

Page 8130, lines 16-19. This interpretation is potentially misleading. As mentioned at the end of this section, the production and processing of halogen nitrates significantly accelerates oxidation of NOx to HNO3. In the absence of halogen chemistry, NOx mixing ratios would be substantially higher, which would in turn sustain higher OH and O3 mixing ratios. However, in the simulations, NOx was held constant and consequently the overall impact of halogens on oxidation processes is not realized in the simulations. This important point should be mentioned. The indirect effects of halogen chemistry on oxidation processes via accelerated NOx destruction are of comparable magnitude to the direct influences via halogen-atom reactions.

Pages 8133, lines 1-5. I'm a bit confused by this interpretation. Model calculations cited in the manuscript suggest that, under the moderately polluted conditions considered by the authors, fresh marine aerosol would be rapidly acidified in a matter of seconds to a few minutes, which implies that conversion of Cl2 to HOCl would be relatively unimportant. Acidic aerosol should be a net source not sink for Cl2. In contrast, some evidence cited in the manuscript indicates that uptake of HOCl by marine aerosol may be overestimated in the model. This latter explanation for the discrepancy between modeled versus measure ratios of Cl2 to HOCl seems equally (if not more) plausible than that based on significant conversion of Cl2 to HOCl in fresh aerosol.

If an organic film slows HOCl uptake by aerosols, presumably, it would also slow HOBr uptake, which could help explain a long-standing puzzle. MECCA consistently overestimates rates of Br cycling through the aerosol relative to expectations based on observations (i.e., Br- deficits relative to sea salt in simulations based on the MECCA scheme are consistently greater than those measured [e.g., Sander et al., 2003, ACP; Keene et al., 2009, ACP; among others]). Slower uptake of HOBr would slow rates of Br activation via BrCl and Br2 production, which presumably would result in higher, more representative steady-state concentrations of particulate Br- in the aerosol.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

A related issue that the authors may wish to address involves the potential implications for simulated Cl chemistry associated with the unreasonably rapid Br cycling in the model. For example, lower particulate Br- concentrations in modeled versus ambient aerosols implies more efficient production of BrCl relative to Br2 in the model (R11 and R12, respectively, on page 8118) compared to ambient air [Fickert et al., 1999, JGR]. Relative to a model that reliably simulates Br cycling, the greater simulated production of atomic Cl by the photolysis of the 'extra' BrCl would yield additional HOCl (via R8 and R9 on page 8118) but no Cl2. In other words, relative to the MECCA scheme as currently configured, slower, more realistic Br chemistry in a model should yield relatively lower simulated ratios of HOCl to Cl2, which would exacerbate the discrepancy between the measured and modeled results.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8115, 2011.