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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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This is an interesting paper describing the first ambient measurements of HOCl in a marine environment. The authors reach the significant conclusion that additional chemistry may be needed to reproduce experimental results with models. While the experimental work is excellent, the modeling portion could, in my opinion, be strengthened considerably. I recommend acceptance of this manuscript for publication, provided that my concerns outlined below are addressed.

Comments on the measurements:

1. Since these are the first ambient measurements of HOCl, and the presence of sea spray is mentioned: Can the authors please discuss what interference (if any) could be expected from the presence of sea salt aerosol deposited on the inner walls of the inlet? For instance on pg 8122, line 20, it is stated that the inlet capillary clogged. Assuming that the clog consisted of mainly sea salt, how much of an interference could

that have caused? In other words, can the measured HOCl include part of HOCl(aq)? The answer is probably no, but it would strengthen the manuscript if this was discussed.

2. Fig. 2 shows two distinct periods (referred to as high Clx and low Clx days on line 19, pg 8123), separated by a "power outage". Prior to the power outage, high mixing ratios of HOCl and Cl2 are observed, whereas after the outage, the levels appear to be an order of magnitude lower. During a power outage, a lot of things can happen, including a full pressurization of the mass spectrometer. The coincidence of the power outage with such a large change in Cl2 and HOCl mixing ratios is suspicious. Can the authors strengthen the manuscript and make a more convincing case that the sensitivity of the mass spectrometer was not systematically affected by the power outage? Such a case could be made, for example, by including time series of calibrations.

3. On page 8123, it is stated that "The observed variability in Cl2 and HOCl is likely attributable to changes in air mass origin and chemistry." Can this be more substantiated, e.g., by using pollution tracers such as CO or NOy?

Comments on the modeling:

4. In Table 2, only one set of input parameters is given, even though in the data there are two distinct periods, identified as "high" and "low" Clx periods. Why is only the "high Clx" case modeled? It seems to me that the model outputs are in greater agreement with the "low Clx period". Consider widening the model-measurement comparison and also discuss how the model outputs compare to the low Clx case.

5. Section 5 "Model Simulations" (from page 8124 to the conclusion on page 8131, line 12 "The MECCA modeling results show that it is not possible to simulate the high observed levels of HOCl in aged polluted air at Cape Verde, without imposing unrealistic boundary conditions or introducing a new source of Clx.") could be condensed considerably. Personally, I am not convinced that turning reactions on or off in the model with the goal to match observed HOCl mixing ratios is the best approach as there are many unconstrained variables and a match could be due to a fluky cancellation of errors.

Overall, the entire section seems like a long way to go to conclude that there is missing chemistry.

6. Since the HOCl data are new, I would have personally preferred a narrower approach in the modeling, at least initially. For instance, why not constrain the model to observed levels of Cl2, BrCl, etc. and then answer relatively simple question such as: "Are the observed ratios of HOCl/Cl2 consistent with model predictions?" and go from there.

Minor comments

- the manuscript is internally inconsistent with respect to the use of the subscript (aq). For example, in R1, some ions have the subscript, others do not

- R11 and R12 are not balanced

- pg 8118, line 17 "In photochemical models of marine air, the photolysis of BrCl is a major source of oxidized chlorine in marine air (Pechtl and von Glasow, 2007; Vogt et al., 1996). Surprisingly, BrCl has not yet been detected in coastal or open ocean marine air (Finley and Saltzman, 2008; Lawler et al., 2009)." Is there any reason to trust the modeling work more than the observations? If not, consider rephrasing to say that model outputs and observations are not in agreement.

pg 8120, line 9. Insert "mixing ratios" between "ozone" and "ranged".

pg 8121, lines 23-24. "Instrument sensitivity was assumed to vary linearly between calibrations". Please state by how much the sensitivity typically changed between calibrations. Consider adding a time series of calibrations (e.g., as supplemental material)

pg 8122, line 18-19 "but it varied by less than 90% between calibrations under similar conditions." I am not sure I understand this correctly. Please rephrase. Is "less than 90%" close to a factor of 2?

pg 8124, line 24 and page 8125, line 10. "..... are listed in Tables 2 and 3." I am not sure the reader needs to be told this multiple times.

pg 8125, paragraph 5.1. "Best guess simulation"

This paragraph is very confusing. If it's a "best guess", why does this model give the worst results? Consider labeling this "first guess" or simply "Base case".

line 14 "... of only 23 ppt" Please add a statement how much HOCl you wanted the model to achieve (rather than expecting the reader to search for this in tables).

Line 14 - line 21 "Increasing O3 and gas phase acids ..." Sounds that model runs other than "base case" are described here. Consider summarizing these under a different heading and justifying each model perturbation. For instance, why increase ozone?

Line 21. "It seems likely that an additional source of Clx exists." Please add "other than reactions ..."

Page 8126, R13. Interesting hypothetical reaction. Is this reaction inspired by K W Oum et al., Science 279 (1998) 74-77?

page 8131 line 5 "We ran a total of 6 box model simulations". I lost count but it seems as if there are more (see comment on page 8125).

pg 8132 line 26. ".. and less acidic aerosols" Can you be more specific here? How much less acidic? In particular, how constrained is aerosol acidity? If aerosol acidity is a critical parameter, how is this used as a model input?

pg 8133. "This study suggests that human influence on Cl chemistry continues for several days over the oceans." I am confused by this statement. The back trajectories in Figure 1 appear to point to the middle of nowhere (or the Saharan dessert, which is sparsely populated) and it's earlier stated that there are no local sources of pollution. Please clarify.

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