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Atmospheric
Chemistry
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Discussions

Interactive comment on "Consistent simulation of bromine chemistry from the marine boundary layer to the stratosphere, Part I: model description, sea salt aerosols and pH" *by* A. Kerkweg et al.

Anonymous Referee #3

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General Comments:

The subject matter addressed in this manuscript is appropriate for publication in ACP and, in general, the investigation is sound. The specific comments below offer a number of suggestions for clarifying the presentation. My major concern relates to general lack of discussion regarding potential implications of some elements of the modeling approach for the reliability of simulated results. Most important among these are the treatment of sea salt $>$1-μm dry diameter as a single (rather than multiple) bin, the treatment of chemical processes in freshly emitted aerosols, and ignoring transformations involving the accumulation mode aerosol in Br cycling. While I appreciate the

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Discussion Paper

need to adopt a relatively simple scheme (compared to that for a box model) in the context of global modeling, this does have potentially important consequences for the representativeness of results. A concise, explicit discussion of these issues would be a valuable addition to the manuscript.

After suitable revision to address comments herein, I recommend that the manuscript be published and congratulate the authors on a nice piece of work.

Specific Comments:

Page 7220, line 21. It would be helpful to mention here the number (or range) of vertical layers that typically fall within the modeled boundary layer.

Page 7224, Section 2.4, pages 227-228, section 2.5, and tables 1 and 2. These sections briefly summarize how aerosol characteristics and processing were modeled. Much of this information (e.g., aerosol nucleation, dust fluxes, etc.) is somewhat peripheral to the primary focus of the investigation. In contrast, the physical and chemical processing of coarse mode sea salt is central to the analysis but, with the exception of the chemical scheme, is not discussed in much detail. I appreciate that modeling at the global scale imposes limits on the complexity of the scheme that can be considered. However, it would be helpful to provide readers with some perspective on these limitations and the associated implications for results. For example, the size-resolved processing of sea-salt aerosols between 1- and ˜30 μm diameter is highly nonlinear in time and space. What are the potential implications in terms of atmospheric lifetimes, vertical mixing, and chemical evolution of treating all coarse-fraction sea salt as a single bin? Although not addressed in the manuscript, presumably aerosols emitted from the ocean surface are instantaneously mixed with aged aerosols. This approach precludes consideration of chemical processes involving fresh alkaline sea salt over large regions of the global ocean. What are the associated implications particularly in more remote regions where rates of acidification are relatively slow? While some of these issues may be addressed in the cited literature, given their relevance to the subject investigation, they should, in my view, be mentioned and briefly evaluated in this manuscript.

Page 7226, Sections 2.4.2 and 2.4.3 and Figure 1. The dry deposition of particles to the ocean surface is typically considered as the combined influence of gravitational settling, diffusion, and impaction involving two layers - the mixed turbulent layer and the laminar sublayer [e.g., Slinn and Slinn, 1980; Lewis and Schwartz, 2004; both cited in the manuscript]. Consequently, it seems potentially and unnecessarily confusing to characterize "sedimentation" and "dry deposition" as mutually exclusive processes. Virtually all studies of which I am aware (including many cited in the manuscript) consider the former to be a subset of the latter. I suggest that the terminology be revised accordingly.

Page 7228, lines 7-19. It would be helpful if the authors added a brief assessment of the implications for modeled results of ignoring transformations involving accumulation mode aerosol. Model calculations suggest that reactions involving aerosols in this mode accelerate Br cycling. In contrast, the as yet unexplained accumulation of Br in smaller size fractions under some conditions, particularly in more polluted regions, may act to quench Br-radical chemistry.

Page 7229, line 4. Suggest citing Table 2 here to provide quantitative context for "short atmospheric lifetime."

Page 7230, lines 5-10. In the context of lifetimes and column burdens, it would be useful to compare the simulated vertical profiles of sea salt with measured profiles reported in the literature [e.g., Maring et al., 2003, JGR; and references therein]. Are the large measured gradients reflected in the modeled results?

Page 7230, line 22. Should be "... significantly LONGER (not shorter) in models ..."

Page 7230, last couple lines. It would be helpful to specify the data sets that correspond to a 10-μm cut diameter. Presumably, this cut is based on ambient not dry diameter. It would also be helpful to provide a range in the potential magnitude of error associated with excluding particles $>$10-μm diameter. Although important in terms of the salt flux, particles in this size range account for relatively minor fractions ambient salt mass in marine air under most conditions.

Page 7231, lines 12-17. When I checked, the "AEROCE" data were not available through either the AeroCom or IGAC web sites. The authors may wish to add a citation for the source of these data.

Page 7231, lines 18-26. To my knowledge, none of these programs "measured" or reported "sea-salt aerosol concentrations." How was sea-salt mass estimated from the reported data? Concentrations of particulate-phase species measured by IMPROVE in continental air over North America and by EMAP at higher elevation stations in Europe are largely irrelevant to the topic addressed in this paper and the tracers typically used to estimate sea salt mass (e.g., Na+ or Mg2+) are not conservative in continental air. In addition, the authors indicate that the simulations cannot be reliably interpreted in the context of these data. I suggest that these comparisons be dropped. In their place, the authors may wish to add comparisons with longer-term data records at other marine sites [e.g., see Gong et al., 1997, JGR]. Also the acronyms IMPROVE, EMAP, and AEROCE should be defined in the text when first used (or in the legend on page 7245).

Page 7231, last paragraph. Only a subset of these stations were operated by the AEROCE program. Most of the others were operated under the auspices of SEAREX and a few involved related programs [check with Joe Prospero at U. Miami; some of these details are also specified in Acknowledgement Section in Gong et al. 1997, JGR]. The text should be corrected. To provide additional context, it would be helpful to include the duration of the record at each station.

Figure 3, legend. It would be helpful to specify the depth of the lowest layer in the model either here or in the text. If relatively deep, differences between observations

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near the surface and simulated values in the bottom layer of the model may reflect the influence of sharp vertical gradients.

Figures 4 and 5. Do the concentrations based on measurements correspond to monthly arithmetic means, geometric means, median values, or something else? It would be helpful to specify that the simulated values correspond to the lowest level in the model. Do differences between simulated and observed concentrations fall within the ranges of variability in each? To provide relevant context in this regard, it would be helpful to add bars depicting variability (e.g., standard deviations around the means or ranges around medians) for average concentrations based on both measurements and model calculations.

Page 7232, line 13 to end of section. This section would be easier to follow and could be consolidated substantially if comparisons between measured and simulated number concentrations were compiled into a table rather that interspersed through the text.

Page 7232, line 16. Presumably, the authors refer here to "... CLOUD droplets."

Page 7232, line 18. Under many conditions, NO3- is a major chemical constituent of aged sea-salt aerosols.

Page 7233, general. The text should indicate whether these sizes refer to radius or diameter. Both are used earlier in the manuscript. The text should also indicate whether the sizes correspond to ambient or dry aerosol.

Page 7233, lines 17-22. Since number concentrations of marine aerosols increase substantially with decreasing size between 1.0- and 0.3- (or 0.6-) μm diameter, much of the inferred difference between the measurements reported by O'Dowd et al. and the coarse mode simulated in the model ($>$1.0 μm-diameter) reflects differences in the corresponding lower size limits for the number counts. Also, to my knowledge, the top of the tower at Mace Head is above the surf zone and measurements are sector controlled. Consequently, it is unlikely that local influences account for these differences.

Page 7234, lines 26-26. I don't understand this point. If the chemical and meteorological measurements, hygroscopicity models, and thermodynamic data are unbiased and the system is in equilibrium, any acid or base that partitions significantly between phases as a function of pH will yield unbiased estimates of the same pH. I believe that the authors are referring to the fact that the accumulated uncertainties in this approach are relatively large and/or that one or more of the underlying assumptions may not be valid. Consequently, paired estimates based on different acids (or bases) may diverge. However, any systematic divergence does not result from inherent aspects of the acids (or bases) themselves.

Page 7235, first few lines. Depending on the saturation state, phase disequilibia can result in positive or negative bias in pH estimated using this approach. For example, for fresh aerosol injected into marine air containing HNO3 and HCl, Cl- will be supersaturated with respect to HCl vapor whereas NO3- will undersaturated with respect to HNO3 vapor. Consequently, pH inferred from the measured phase partitioning and the corresponding thermodynamic properties of HCl would be biased high whereas that inferred from HNO3 would be biased low. For fresh marine aerosol, which contains virtually no NO3-, the relative disequilibria in HNO3/NO3- is typically greater than that in HCl/Cl- and, consequently, the corresponding magnitude of bias in pH based on HNO3 would be relatively greater than that based on HCl.

Page 7235, par. 2. Presumably, this model does not generate organic acids or consider their influence on aerosol pH. Formic and acetic acids, in particular, are major natural sources of acidity in remote marine regions [e.g., see Keene and Galloway, 1988, Tellus]. Oxalic and methanesulfonic acids are also important under some conditions. Based on their thermodynamic properties, formic and acidic acids will partition preferentially with the higher-pH, coarse marine aerosols and contribute to alkalinity titration. As such, modeled pHs that do not account for the influence of these and other organic acids should be considered upper limits.

Also, the authors should briefly explain how the average pH for each grid cell and time period was calculated. Do these data correspond to 1) H+ concentration averaged over time and altitude within the MBL and expressed as pH, 2) H+ per square meter averaged over time and altitude and dissolved in the corresponding average aerosol liquid water per square meter and expressed as pH, 3) pH averaged over time and altitude, or 4) something else? Because pH corresponds to a log scale, direct averaging would seem inappropriate. Also, given the large vertical gradients in sea-salt concentrations and RH through the MBL, were the non-linear influences of water content on the phase partitioning of soluble acids and pH considered in the averaging?

Table 4. As discussed in the text, H+ was "measured" in only two of these studies. For the others, H+ concentrations were estimated based on either paired gas- and particulate-phase measurements of species that partition between phases as a function of solution pH or thermodynamic model calculations.

Page 7236, last paragraph, and Figure 13. Again, most of the pHs referred to as "measured" were not measured but inferred. The figure legend should be corrected. Also, the legend should clarify that the indicated pHave corresponds to the simulated values. Finally, do the simulated values correspond to the lowest level in the model? These would be the most relevant for comparison with estimates based on near-surface measurements.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7217, 2008.