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Discussions

Interactive comment on “Missing SO₂ oxidant in the coastal atmosphere? – Evidence from high resolution measurements of OH and atmospheric sulfur compounds” *by* H. Berresheim et al.

Anonymous Referee #1

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Using measurements of OH, sulfuric acid, SO2, and particle size distributions at Mace Head, the authors show that observed daytime H2SO4 concentrations are larger (by factors of 4.8 on average) than can be rationalized using OH+SO2 as the only H2SO4 source and heterogeneous uptake as the only H2SO4 sink. The discrepancy scales with OH. The authors speculate about the existence of one or more missing SO2 oxidants by a process of elimination, ruling out NO3 and several halogen and halogen oxide oxidants (for which rate constants were calculated using ab initio molecular structures and transition state theory). The authors suggest Criegee biradicals as the

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missing daytime oxidant of SO2. The results are interesting and, if confirmed, have significant implications for atmospheric sulfur budgets and sulfate aerosol formation. However, I recommend revisions to this paper as I find parts of the discussion not (yet) convincing. For instance, I would have expected Criegee chemistry (from O3 + alkenes) to produce a different diel profile than was observed; perhaps this could be cleared up with a box model calculation? Another weakness is that the analysis relies on assumed (high) aerosol uptake of H2SO4; what if this uptake was slower? Finally, SO3, which is produced during the oxidation of DMS and OH, was mentioned but was neglected in the analysis without stating a reason why.

Specific comments

pg 1160, line 8 Please specify if the aerosol diameters are aerodynamic.

pg 1160, line 25. Since the rate constants for some of these reactions are known (e.g., Larin et al, Kinet Catal 41, 437-443, 2000), consider stating that the ab initio methods were used to estimate reaction rates for cases for which the reaction rates are not available experimentally.

pg 1163, line 15. "The ambient OH ... is completed converted to H234SO4 ..." OH + SO2 gives HSO3 as the initial product. Please state the reaction that converts HSO3 to H2SO4. Is there sufficient water vapour to convert HSO3 to H2SO4 (pg 1168, lines 13/14) considering the short residence time?

Further down, re H34SO4- product ion. Sulfate is hygroscopic and has a high binding constant for H2O. Are the sulfate+water clusters observed in this CIMS? Or is the CDC operated to dissociate these clusters?

pg 1164, line 4. "Propane ... [is added] to scavenge any OH ... recycled from peroxy radicals." Wouldn't the propane scavenge all of the OH?

pg 1164, line 7. "nighttime OH measurements showed no major increase in the background signal compared to the OH signal" The phrase "no major increase" is vague and suggests that there was a minor increase. Please state whether there was a statistically significant difference between signal and background at night, and if so, at what magnitude.

pg 1164, line 18. The ratio of 34S to 32S in SO2 can vary somewhat (e.g., Seguin et al, Atmospheric Environment 44, 1139-1144, 2010; Lin et al, Atmospheric Environment 62, 615-621, 2012). Please comment on the (systematic) error this may have introduced in the measurements presented here (which may have been negligible).

pg 1166, line 4. Please state whether the variability in Figure 4 (bottom) is driven by changes in RH, particle counts, or both.

pg 1166, line 12-13. Please state that the hygroscopic growth factor 1.7 correspond to a certain RH range (90% vs 40% RH). Bialek et al identified several clusters and growth factor modes ranging from 1.2 to 2.1. The single growth factor of 1.7 presented here seems like an oversimplification. Since there is overlap of the Bialek et al. and this study for the year 2010, it may be a worthwhile exercise to compare the CS calculated using a GF of 1.7 with the more refined aerosol surface area reported by Bialek et al. (for 2010).

pg 1166, line 17. The assumption that biogenic sources dominate the sulfur budget is consistent with isotope data (e.g., Seguin et al, Atmospheric Environment 44, 1139-1144, 2010; Lin et al, Atmospheric Environment 62, 615-621, 2012).

pg 1167, equation (1). Following up on my comments on pg 1163, line 15: The reaction of OH with SO2 does not give H2SO4 directly. Please discuss the appropriateness of equation (1), which relies on an assumed steady state in H2SO4. For example, can it be assumed that the chemistry is faster than the typical transport times of these molecules?

pg 1167, line 26. "Comparison with measured H2SO4...". It would have been nice if the reader were shown more data here rather than only a single day (Figure 5), which is a bit of a tease. There appears to a lot of day-to-day variability in the ratio of observed over calculated H2SO4. Consider presenting a few representative days (e.g., poor agreement, really poor agreement) and discussing differences (e.g., meteorological conditions, gas-phase concentrations, particle area and relative humidity) between those days.

pg 1168, line 8. There are other possible explanations: For example, the surface area and/or uptake coefficients used in the calculation were too large.

pg 1168, line 19. Criegee biradicals form mainly from reaction of O3 with alkenes ... which I would not expect to have a diel cycle consistent with the missing oxidant shown in Figure 5. Consider performing a box model simulation.

pg 1168, line 25. Since the discrepancy occurs mid-day, there is probably no need to discuss nighttime oxidation pathways as a possible reason.

pg 1169, line 4. Please cite the original paper, not a web site.

pg 1169, lines 18-19, Figure 7. Please also include a table of the geometries (i.e., x,y,z coordinates of all atoms). That’s more useful than a pretty picture.

pg 1169, line 21 and Table 1. There are imaginary frequencies for the XO-SO2 clusters, which suggest that the saddle points (the transition geometry) were not actually found. In light of this, please defend the choice of transition state geometry.

pg 1169, line 20 (entire paragraph). Please compare the theoretical results with experiment, where available.

pg 1170, line 15. The diel profile of the discrepancy also rules out many of the halogens.

pg 1170, prior to section 3.4. I am not clear why the authors choose to neglect SO3 as a major intermediate producing H2SO4. It is well known that DMS yields "biogenic sulfate" via both SO2 and SO3 intermediate. SO3 is produced from CH3SO3, which in turn is produced by many reactions, including OH+MSA and many others (see for example Figure 3 in Barnes et al., Chem Rev. 106, 940, 2006).

Figure 2. MSA and H2SO4 are offset relative to each other by about one week, which is confusing. Please make appropriate changes.

Figure 3. Consider colour-coding the data by SO2 concentration.

Figure 4. Consider colour-coding CS by relative humidity.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1159, 2014.