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Comment

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.

H. Berresheim et al.

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1. The reviewer suggests applying a box model simulation to elucidate whether the observed diel profiles in the OH background signal were due to Criegee radicals produced from alkene ozonolysis. As there are – unfortunately – no concurrent data available from Mace Head on day-and-night variations of atmospheric alkene levels we think such an approach is rather futile and will not further curtail the underlying mechanisms. However, this will certainly have to be addressed in future work. We have

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pointed out, for example in the Conclusions section, that hydrocarbon emissions may be light dependent which could explain the low occurrence or absence of elevated OH background signals at nighttime. This is supported by previous measurements of diel cycles of alkene emissions at Mace Head which we now have included as references [Lewis et al., 1999]. We have also discussed the alternative possibility of Criegee intermediates being produced via photolysis which again might explain our observations that the background signal often closely follows the OH signal. 2. With respect to assuming a lower accommodation coefficient for H₂SO₄ we have clearly stated (in section 3.4, line 410) that this would reduce the discrepancy factor in the balance calculation by only 30% (assuming $\alpha = 0.5$ instead of 1.0). Any value even lower than 0.5 appears highly unlikely based on current literature (e.g., Kolb et al., 2010). 3. We have mentioned the possibility of H₂SO₄ formation from DMS+OH oxidation with SO₃ instead of SO₂ as intermediate product in the text (Abstract and section 3.2, line 262). We have now further emphasized this point by extending the discussion of Fig. 5a and in the Conclusions section. We have added a contrasting example in Fig. 5b showing near closure of the balance (ratio 1.8) for a day with no air mass advection from biologically active ocean regions and low insolation.

Replies to further comments (As the reviewer referred to page and line numbers in the ACPD article, we also adhere to this reference unless otherwise stated.)

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

Answer: Done.

Comment: 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.

Answer: We don't agree with this suggestion. Larin et al. only obtained an upper limit for IO + SO₂. We state on page 1170, line 24, that our TST result is consistent with

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this upper limit i.e. is less than it. It is surely better to use an actual estimate of the rate coefficient, rather than an upper limit.

Comment: pg 1163, line 15. "The ambient OH ... is completely converted to H₂SO₄ ..." 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?

Answer: With [H₂O] on the order of $\geq 10^{17}$ cm⁻³ in the marine boundary layer (see page 1171, line 13) the reaction of HOSO₂ with O₂ followed by SO₃ + H₂O occurs in the microsecond range which is well documented in the literature and needs no specific mention here.

Comment: Further down, re H₃SO₄⁻ 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?

Answer: On page 1163, line 27, we have stated that HSO₄⁻ is measured at m/z 97 (or m/z 99, depending on the sulfur isotope), i.e., the collisions with N₂ molecules in the CDC are tuned to remove the H₂O ligands. Also, in the first paragraph on page 1174 it was clearly discussed that the CIMS instrument measures the free monomeric H₂SO₄ and that intercomparison between our CIMS measurements at m/z 97 with the CI-API-TOF-MS measuring the H₂SO₄ clustered as HSO₄⁻-(HNO₃) at m/z 160 showed excellent agreement.

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

Answer: We have added the word "completely" in line 11.

Comment: 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

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a statistically significant difference between signal and background at night, and if so, at what magnitude.

Answer: Done.

Comment: 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).

Answer: We thank the reviewer for pointing out to us these two interesting references which we have now included in our discussion. However, we have also now mentioned that the isotopic del ratios observed in theses studies vary in the per mil range and thus had negligible effect on our measurements and the calculations in section 3.4.

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

Answer: Done. Driven by particle counts.

Comment: 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).

Answer: We have stated the RH range as suggested. We have also added that this factor can be as high as 2.0. As pointed out in the subsequent discussion, the uncertainty in this factor contributes to the uncertainty in CS which is estimated to be a factor of two. The reviewer may have misunderstood the last point. Bialek et al. did not

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determine aerosol surface areas, but only reported dry (<40%RH) and wet (90%RH) aerosol diameters. No assumption was made on the sphericity of aerosol particles to infer their surface area.

Comment: 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).

Answer: This is well noted and included now.

Comment: 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?

Answer: The lifetime of H₂SO₄ at Mace Head was around 7 minutes. This seems to be short enough to allow for steady-state-calculations to compare to 5 minute averages of H₂SO₄ observations. The excellent correlation between observed H₂SO₄ and JO1D (scaled JO1D as proxy for OH; see figures 5a and 5b) gave us the confirmation that this approach is adequate.

Comment: 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.

Answer: We have now added a detailed discussion of the air mass conditions on the day in question (18 June 2011) in comparison to two other days with similar high ratio

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(9.0; 11 June 2011) and very low ratio (1.8; 10 May 2011). We have added the 10 May 2011 measurements as Fig. 5b contrasting the example of 18 June 2011 as Fig. 5a. Corresponding air mass trajectories, tidal cycles, and solar irradiation conditions clearly contributed to the observed differences.

Comment: 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.

Answer: These uncertainties have been mentioned earlier. However, they cannot account for such high discrepancies.

Comment: 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.

Answer: See our reply to comment 1.

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

Answer: We think it is appropriate here to cite our earlier study with respect to the negligible role of nighttime NO₃ chemistry expected for Mace Head marine sector conditions.

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

Answer: Done.

Comment: 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.

Answer: See attached Table 1, which now includes an extra column with the Cartesian coordinates. We have added a sentence accordingly.

Comment: pg 1169, line 21 and Table 1. There are imaginary frequencies for the XO-

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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.

Answer: The reviewer has misunderstood the notation. These are transition states, not cluster geometries, which is why they each have one imaginary frequency. These transition states are indicated in the Table with the conventional # symbol. This is now pointed out in the caption for the Table.

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

Answer: This has been done in section 3.3 with reference to the studies by Saiz-Lopez and Plane.

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

Answer: We agree.

Comment: 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).

Answer: See our reply to comment 3. Those pathways have been pointed out already by Berresheim et al. in 1995. In the process of consecutive alterations of our manuscript focussing more on Criegee chemistry this important alternative pathway was somewhat unintentionally neglected but has now been re-emphasized. This is also the major reason why we have added a question mark in the paper's title.

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

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Answer: The data shown here are monthly averages for both compounds. The dots and bars are not meant to be assigned to a particular day or week of the month. They are separated for better viewing.

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

Answer: Interesting idea. However, as shown in Fig. 4, SO₂ levels varied only over a small range and the figure would probably lose clarity with all the data shown. Comment: Figure 4. Consider colour-coding CS by relative humidity. Answer: We will do this in a future study. There are other variables to consider as well, such as wind speed.

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

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