

Dear editor,

please find enclosed a point-by-point response to the comments of reviewers #1 and #3. In the open discussion we have also answered the comments made by D. Stone and made by you.

Best regards

Franz Rohrer

Reply to comments made by Reviewer #1

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 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 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 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 ^{34}S to ^{32}S in SO_2 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 these 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 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 (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-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.

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.

Reply to comments made by Reviewer #3

1. We disagree with the reviewer that our paper is "highly speculative". The reviewer has misinterpreted our data, specifically those shown in Fig. 5 and Fig. 8. However, his/her comments have been helpful in further clarifying our results and conclusions. First, we have modified some of our statements, including the title, which may have given reason for misunderstandings. We have now made it very clear at several text locations, that SO₂ oxidation by highly reactive sCl radicals such as CH₂OO may constitute one possible pathway for H₂SO₄ formation not accounted for in eq. (1) and thus, explain the discrepancy between solely OH based calculations and measurements of the atmospheric H₂SO₄ concentration. On the other hand, we have shown that sCl species derived from terpene ozonolysis such as proposed by Mauldin et al. cannot explain our observations.

We have added Figure 5b as a contrasting example showing very little diel variation in the OH background signal in contrast to the OH concentration. This could be clearly related to the tidal cycle and relatively low insolation in comparison to the case shown in Figure 5a. Furthermore, we have also added Figure 8a, complementary to Figure 8b, demonstrating clearly the strong relation between aerosol nucleation events (due to organic iodine and H₂SO₄ chemistry) and peaks observed in both OH and the OH background signal. The known involvement of organic iodine emissions from seaweed during low tide (O'Dowd et al.) strongly suggests that a relevant precursor oxidant species, such as CH₂OO, may have been responsible for both effects and that it has photolytic source(s) such as the photolysis of CH₂I₂ first proposed by Welz et al. Even more so, our observations in these cases also showed increased H₂SO₄ and MSA(g) levels, overcompensating for increased new particle surface area concentrations.

The reviewer had misinterpreted the 30 s resolved signal count rates for OH and OH background in the lower half of Figure 8 as "tracing each other but not showing a relation with J(O¹D)." We have now eliminated the OH concentration data in the upper half of each Figure 8a and 8b and instead introduced the 5 min resolved OH concentration data in the respective lower halves of each Figure. These clearly show the good correlation of [OH] with J(O¹D), as the OH concentration is derived from the difference (!) between the signals of OH+BG and BG.

2. The uncertainties in the condensational sink (CS) have been discussed in detail and found to still fall short in explaining the observed deficit.

3. We have now, in the revised version, even more clearly discussed, that direct formation of H₂SO₄ via SO₃ instead of SO₂ as intermediate in the DMS oxidation could still be a valid and equally ranking alternative explanation for the H₂SO₄ not accounted for by eq. (1). Our current paper is not intended to present a complete survey of all data with respect to air mass analysis and possible contributions from

DMS hot spot emissions. This will be the focus of a future paper, we have clearly stated this.

4. Following the suggestion made by the reviewer we have now added two case observations of OH vs. OH Background signals NOT correlating during daytime (Fig. 5b, Figs. 8a & 8b) which corroborates that our measurements are not subject to a hidden artefact formation of OH in the CIMS instrument. With respect to the latter point, we have emphasized our propane experiments, previous field intercomparisons involving CIMS and LIF instruments, as well as work by other teams (Mauldin et al., Eisele et al.) with similar or identical CIMS prototype instruments as we use at Mace Head.

5. With respect to laboratory experiments we would like to refer the reviewer to the fact that we work with the same type of CIMS instrument and operating conditions as used by Mauldin, and that for example Mauldin as well as Berndt et al. have carried out extensive lab experiments proving that the observed background signal is not due to artefact OH formation in the system. Also, our current paper is not meant to be a complete survey of the two years of measurements made at Mace Head with regard to the importance of DMS-SO₃-H₂SO₄ chemistry vs. sCl chemistry. We have added in our Conclusions that this will be the subject of a future paper. We are also working with RL Mauldin to prepare an extensive review of previous CIMS OH background measurements in various natural environments to study the possible importance of sCl contributions to H₂SO₄ more systematically.

6. We have added a number of recent references (e.g., Taatjes et al., 2014) which have been published on the relevant subjects since our paper was open for discussion in ACPD. With respect to the reviewer's criticism of our former Figure 5 (now Figure 8) we want to point out here that the reviewer made a false deduction by comparing the OH and Background signals with the diel cycle of J(O¹D). What actually needs to be shown is the Difference OH(sig) – Bkgd(sig) in relation to J(O¹D), or the actual OH concentration. We have now included the diel OH concentration profile in the lower part of the Figure which now clearly shows the good correlation between OH and J(O¹D). We are nevertheless grateful for the reviewer's comments as they helped to significantly clarify the discussion in the text: This example of 14 May, 2011, and the preceding day, 13 May, 2011, now also shown as a case study in a complementary Figure, clearly documents the near absence of a diel cycle in the Background signal during high tide (and relatively low photolysis) whereas during low tide, with nucleation occurring, definite spikes are observed in both X and OH signals. This again strongly suggests a connection to iodine chemistry, possibly the generation of CH₂O through photolysis of CH₂I₂. The original Figure also erroneously contained flagged "low" OH signal data points which have now been eliminated.

7. The SCATE Antarctic campaign led by Berresheim et al. has clearly documented both high DMS emissions in summer from coastal Antarctic waters as well as the

major presence of wildlife (penguins, seals etc.) on land in these regions. Both algae as well as land fauna are major sources of VOC's and thus potentially of photolytic formation of atmospheric sCl and/or halogen radicals.

8. All other (minor) comments have been addressed as suggested by the reviewer. The former argument made by Berresheim et al. (2002) about sCl potentially explaining all of nighttime and up to 20% daytime H_2SO_4 was based on ambient air experiments made at Hohenpeissenberg observatory, Germany, where nighttime H_2SO_4 levels were consistently above the detection limit, ranging sometime up to 10^6 cm^{-3} . Isoprene and monoterpene concentrations are high during summer in this rural environment. It was a speculative argument in regard to assuming the same for the marine/coastal atmosphere at the time, as relatively few measurements were made during the PARFORCE campaign. However, it served to evoke the question of sCl chemistry contributions to SO_2 oxidation. In our current paper we conclude that at Mace Head H_2SO_4 levels also appear to be above the detection limit, however, not as high and consistent as at MOHp. We state that this might be due to the different strengths and types of reactive VOC emissions in both environments. And again, we clearly show that sCl derived from ozonolysis of terpenes play no major role in the coastal environment of Mace Head.