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Atmospheric Chemistry and Physics Discussions
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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.

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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 concusions. 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 sCI radicals such as CH2OO may con-

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stitute 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 sCI 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. sCI 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 sCI 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 CH2OO 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 sCI 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 sCI potentially explaining all of nighttime and up to 20% daytime H2SO4 was based on ambient air experiments made at Hohenpeissenberg observatory, Germany, where nighttime H2SO4 levels were consistently above the detection limit, ranging sometime up to 106 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 sCI chemistry contributions to SO2 oxidation. In our current paper we conclude that at Mace Head H2SO4 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

sCI derived from ozonolysis of terpenes play no major role in the coastal environment of Mace Head.

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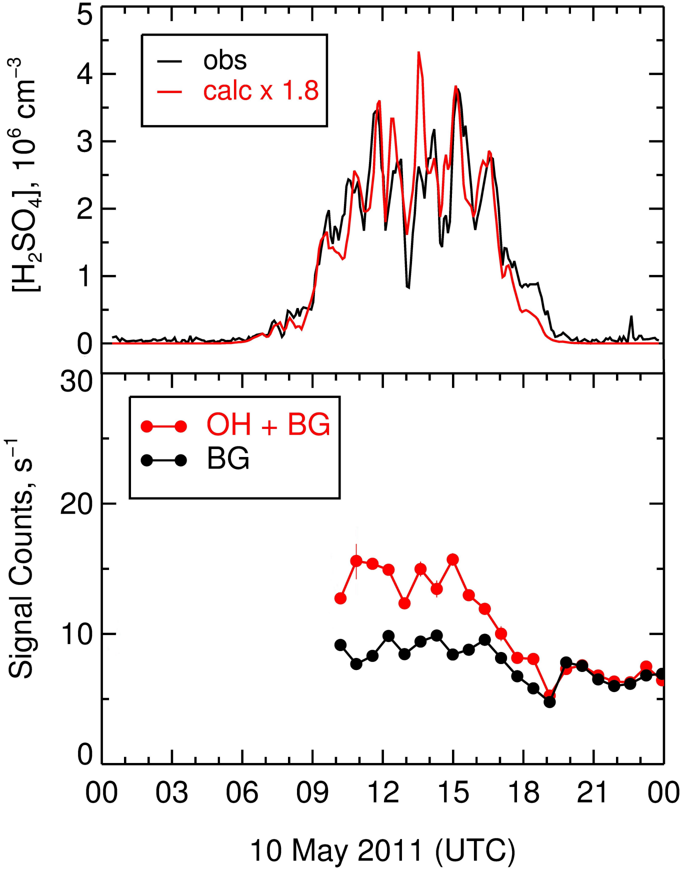

Fig. 1. Figure 5b

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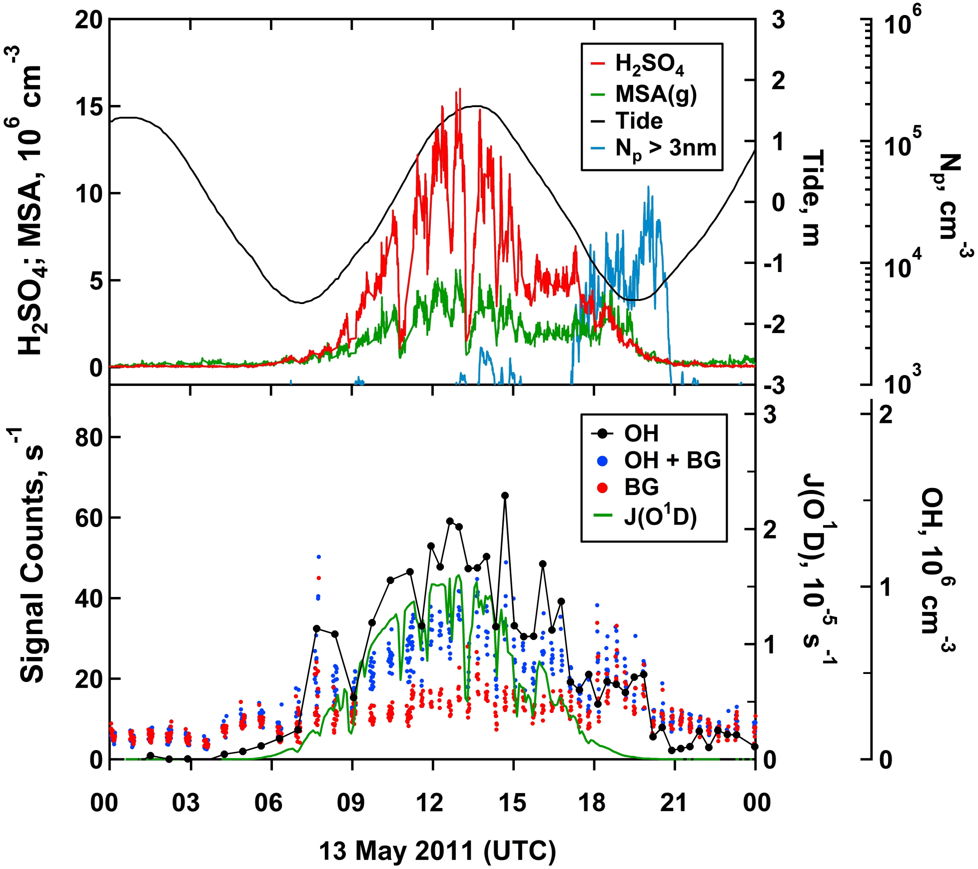

Fig. 2. Figure 8a

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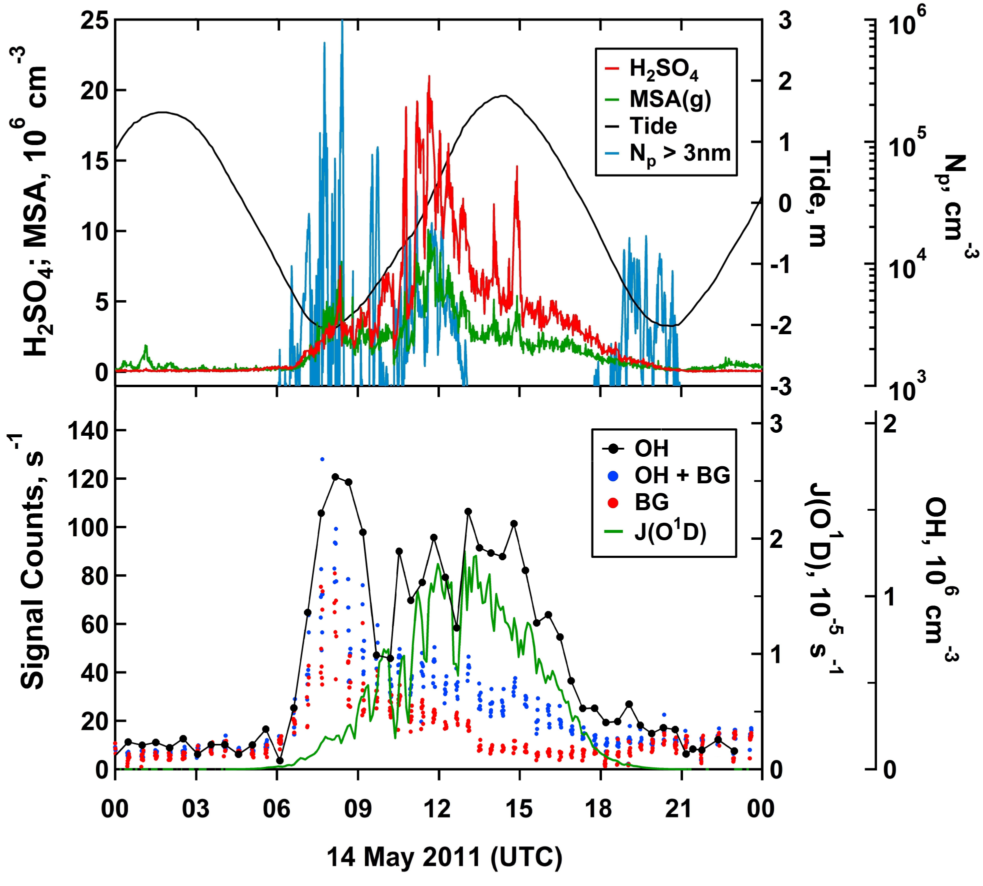

Fig. 3. Figure 8b