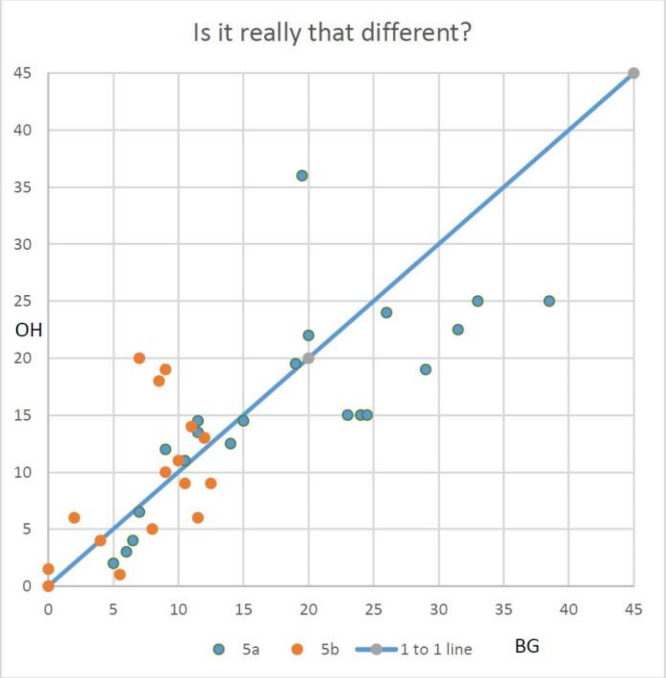
Reviewer Comment 1: Is the signal actually real?

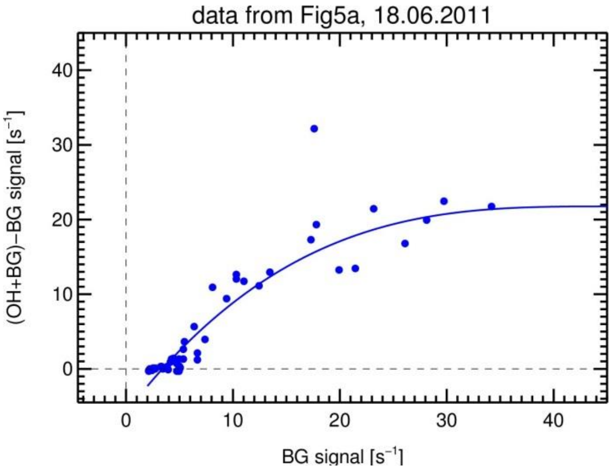
With reference to figures 5a and 5b. The authors differentiate between the two days shown in figures 5a and 5b. They make the point that the ratios of measured H2SO4 to calculated are very different and that this is related to different air masses. The authors also highlight the different behaviour in the OH + BG and BG signals. Unfortunately, the behaviour is not different. I have taken the liberty to read the data from the two plots and plot OH (calculated from [OH+BG]-BG) vs BG. There are two components to the BG signal, a systematic part of about 5 s-1 and a part which appears to be directly proportional the OH signal. I show both datasets overlaid to illustrate my point. Visually at least, the variability within the datasets is more the variability between the datasets.



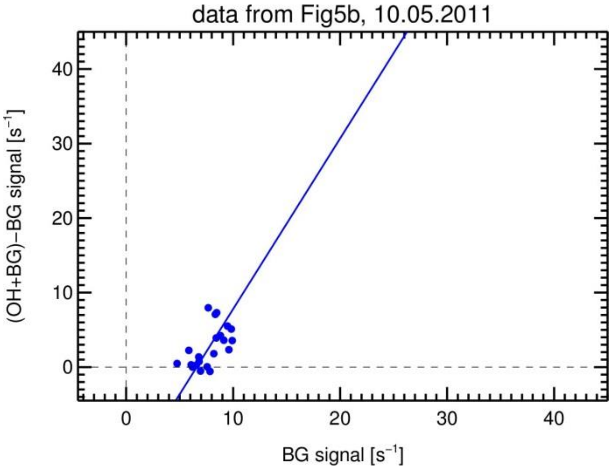
R 1: figure representing data from figures 5a and 5a of the revised manuscript prepared by the reviewer

If the conditions on both days are very different then why does the BG show the same relative behaviour to OH? This is another issue with the paper; I would suggest that this arises from some systematic signal on the m/Q measured superimposed on a signal due to OH from an incorrect background. The author's contention that they have been doing this for years is not really valid. There have been recently a number of instances of well-established techniques shown to suffer from interferences, e.g. HO2 and NO addition in FAGE see Fuchs et al.(2011) and the failure to subtract OH backgrounds correctly, see Mao et al. (2012)and Novelli et al. (2014) and the measurement of PAA with PAN CIMS (see Phillips et al. 2012). So, it is not a justification to say we have always done it like that. There is currently not much evidence other that general qualitative statements about associations, some of which bear no resemblance to the actual data, see above. There is a lack of quantitative rigour in the description of the data.

Our reply: (line numbers in our reply refer to the new revised manuscript)
We can follow the concerns of the reviewer. We had the same. But since the reliability of our data analysis seems to be put into doubt by the reviewer we want to answer in some length here. First of all, we think the figure prepared by the reviewer by reading the data from our Figures 5a and 5b is misleading for two reasons. If we look to both data sets individually, we see a curved behavior "BG" vs "(OH+BG)-BG" for the data in figure 5a and a linear behavior for the data of figure 5b which has a more restricted dynamic range (see our figures R2a and R2b). At this point we want to mention that the data labeled "Fig5b" in the above figure R1 prepared by the reviewer seems to be related to our figure 5b, but shifted and scaled considerably.



R 2a: Data taken from Fig5a of the revised manuscript



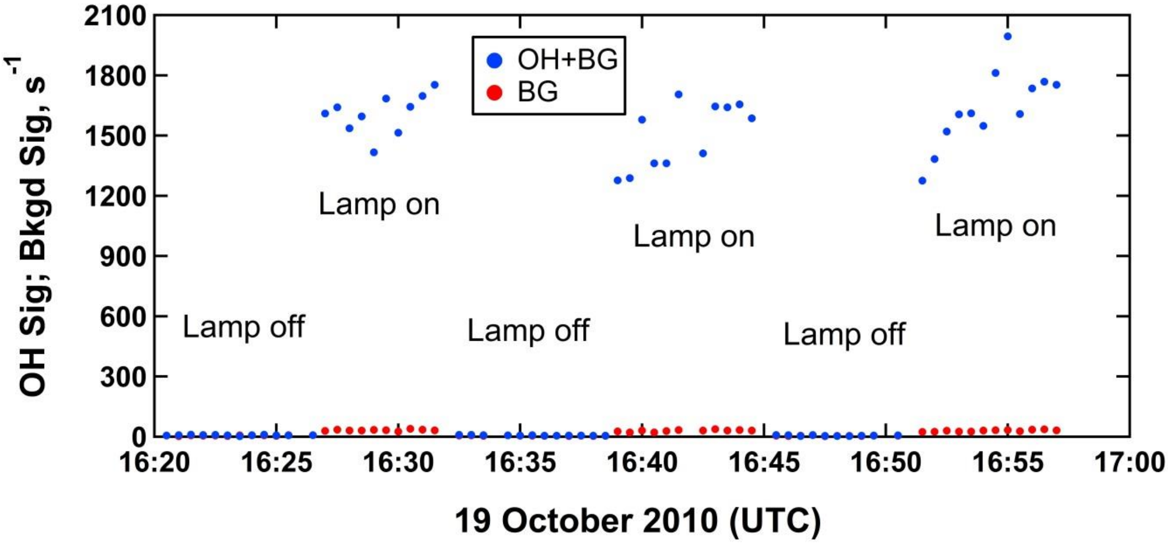
R 2b: Data taken from Fig5b of the revised manuscript

The fit in figure R2a is a third order polynomial, in figure 2b a linear relation. The result of the fit in figure 2a does not depend too much on the inclusion or exclusion of the outlier above (OH+BG)-BG=30 s^{-1}.

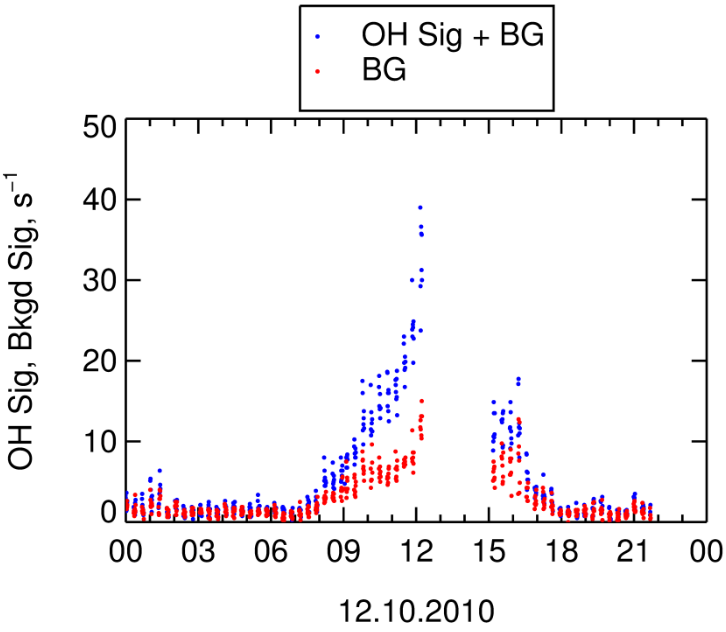
It is our interpretation that the background signal often seems to have a diurnal behavior similar to OH but with a slightly different shape with respect to the width of this shape centered at noon time. This seems to indicate the involvement of photolysis reactions with slightly different wavelength dependencies. Such similarly driven diurnal behaviors are difficult to distinguish from an experimental artefact like the reviewer presumes. There is no proof for or against both lines of arguments without additional information. Such information can be extracted from the calibration procedure of the CIMS instrument. In principle, a H2SO4-CIMS instrument uses an absolute measurement technique related to dimensions of the instrument and to physical constants, in this case the residence time inside the ionization tube and the rate constant for the H_2SO_4+NO_3^- reaction. This is caused by the fact that the raw signals of the $H_2SO_4^-$ ions are related to the available NO_3^- ions which are both measured at the same time. For this reason the CIMS instrument is not calibrated frequently. But as an example we demonstrate here a calibration (figure R3) and adjacent ambient observations (figure R4) showing the BG signals as described in our paper in close temporal proximity to the calibration procedure. During such a procedure, a calibrated Hg lamp illuminates part of the CIMS inlet tube and generates relatively large amounts of OH from the photolysis of ozone and the following reaction with water vapor. Figure R3 shows such an example with intervals when the Hg lamp was switched on and off in a regular pattern. In case of an artefact of the sort the reviewer presumes like insufficient quenching of OH by the added propane gas, BG and (OH+BG) signal should be related and the BG considerable enhanced. This is clearly not the case. At least 98% of the OH is quenched by the propane added during the BG mode of the instrument. Also, system operation was set to detect any significant changes in flow rates and automatically generate a flag for the corresponding data.

The reviewer did mention difficulties of OH-FAGE instruments connected to the determination of the background signal by shifting the wavelength of the detection laser on and off the OH line. Difficulties of this sort are avoided for FAGE systems by using chemical quenching of ambient OH as described in the paper of Mao et al., 2012. Such a method for the determination of the background signal is used in OH-CIMS instruments from the very beginning.

We think such a lengthy explanation was required in our answer to this important and noteworthy reviewer comment. Accordingly, we have further clarified in the manuscript our precautions taken to exclude potential instrument artefacts including checkups during the calibration runs (see Experimental section, lines 160ff.).



R 3: calibration at 19.10.2010 showing BG and (OH+BG) raw signals related to the switching of the Hg lamp used to generate OH inside the inlet tube of the CIMS instrument



R 4: 30s raw signals of the CIMS instrument for ambient observations during 12.10.2010

Reviewer Comment 2: Is it measured OH data? And where is it all?
This may seem like a confusing question, but I am confused by the legend on figure 5a which says that the OH concentrations used in the calculation were derived from OH-jO1D relationship. Is the data in this paper parameterized or measured? Surely the whole point of the paper is use the measured data otherwise the whole paper falls over. If it parameterized then show the difference between the measured data and the calculated data for the entire period. Is a parameterisation which only uses JO1D appropriate for this dataset; as the authors show, the OH does not always relate to jO1D? If the time series of OH is not as frequent, would it not have been more appropriate to interpolate? Is the calculated data the same, different? The authors show in figure 8a that parameterizing to JO1D is inappropriate.

In addition the authors should show all the OH data for the entire period for the campaign described. I am becoming increasingly skeptical about the results and the more data the better along with some good correlation plots in addition to the time series.

Our reply:
We agree that our applications of the OH-JO^{1}D relationship to calculate H_2SO_4 concentrations were perhaps not adequately stated. We have now clearly justified and explained it in the text (line 262ff., following eq. 1; and Figure 5 caption). We also included in figures 5a and 5b the H2SO4 calculated using the observed OH concentrations together with the results using the OH-JO1D relationship. The reason for doing this in the first place was the high precision of the H2SO4 observations and their obvious strong correlation with photolysis frequency. OH was measured for the first 5min within each 30min period, H2SO4 was measured all the time. The precision (Berresheim et al., GRL, 2013) for 5min OH concentrations around 1x10^6 cm^{-3} was 13%, for H_2SO_4 around 13x10^6 cm^{-3} (both the maximum values in figures 5a and 5b) was 2.5%. The precision of observed H2SO4 was 5 times better, its frequency 6 times higher than those of OH. The precision estimate for OH covers a confidence interval of +- 30%, almost a factor of 2. For these reasons we used the highly precise JO^{1}D observations to calculate H_2SO_4. It is obvious that a large part of the variability of observed H_2SO_4 is explained by this approach. One can clearly see now in the new figures 5 that the observed OH concentrations are too sparse to show that adequately. The observed high variability of photolysis frequency does not allow for a linear interpolation of the OH observations as the reviewer proposes. In fact, we used JO^{1}D as a proxy to do that interpolation. The argument that the relation OH-JO^{1}D is adequate to describe OH is based on the previous publication about the OH dataset from Mace Head (Berresheim et al., GRL, 2013). Especially the average difference between observed and calculated H_2SO_4 will not be affected by this approach. The cases where OH and JO^{1}D are significantly not correlating are very sparse. We had to look very careful into the data set to find these occasions. One of these exceptions is shown in figure 8. And the circumstance that this is an exception is clearly stated in the text (lines 514ff).

Reviewer Comment 3: If the authors have a clear idea of what is forming H2SO4 then why write this paper??
The authors state in the conclusion that the extra H2SO4 is likely formed from DMS emission. Would not make more sense to write the paper about that and show why it cannot

be caused by Criegee intermediates, or not completely caused. There can be still a contribution From Criegee intermediates but without alkenes measurement or CH2I2 it is difficult to assess how much. As underlined in the conclusion monoterpenes are likely not to be present, and have a different diel pattern, so they cannot be the cause. It is quite obvious, and a semi-quantitative calculation (see below) is unnecessary.

Our Reply:
We present here for the first time the observation of the seasonal variation of both H_2SO_4 and MSA in the NH marine atmosphere and a rigorous evaluation of the H_2SO_4 mass balance in comparison with measured data for the lifetime and an important production pathway of H_2SO_4, namely the reaction $OH+SO_2$. For an explanation of the observed large deficit in this H_2SO_4 mass balance we first looked into the raw data of the CIMS instrument which is designed to directly observe any production of H_2SO_4 from SO_2. Since one of several possible production pathways of H_2SO_4 from DMS+OH oxidation has previously been proposed to occur via SO_3 (instead of SO_2) as intermediate (see below) we assume that the H_2SO_4 produced this way would already be present in ambient air and not be formed in the CIMS instrument.

We found that approximately half of the total CIMS signal, which in fact is the $H_2{}^{34}SO_4$ produced inside the CIMS inlet, was due to a non-OH reactant with $^{34}SO_2$. Since there are speculations in the literature that this CIMS background signal is caused by Criegee radicals and that these substances have a significant impact on the ambient H_2SO_4 production we considered this idea by looking into the details of the chemistry taking place inside the CIMS inlet. The result was that in contrast to the H_2SO_4 signal produced by OH which can be attributed one-to-one to an OH concentration, the relation between CIMS background signal and the oxidative power of its precursor with respect to SO_2 strongly depends on the kinetic parameters of this precursor and its production pathway. We show that for certain large Criegee radicals discussed in the literature (formed via ozonolysis of monoterpenes) their oxidative power with respect to SO_2 deduced from the CIMS background signal would be negligible. On the other side of the spectrum, special Criegee radicals like the very small ones such as CH_2OO or CH_3CHOO, which would have the potential to impact on the ambient H_2SO_4 concentration at Mace Head due to their fast reaction with SO_2, would also be negligible for the H_2SO_4 budget if the CIMS background signal would be entirely caused by them if they are produced via ozonolysis. But if they are produced photolytically, the situation would be quite the contrary. These two opposing possibilities are now clearly stated throughout the text. In addition, the available kinetic information about these small Criegee radicals, notably on their reaction with H_2O, is quite ambiguous.

That being stated, our analysis uncovers that a simple attribution of the CIMS background signal to the oxidative power of ambient air masses with respect to SO_2 is not possible. It is only possible to do this inversely, i.e., assuming first a particular source of the background signal it is then possible to induce the oxidation power with respect to SO_2 for this special case given that the relevant kinetic parameters of production and destruction for the compounds under consideration are sufficiently established. We may not have appropriately stated this point in the abstract and in the conclusions. Therefore, we have now changed both paragraphs.

With respect to the alternate possibility of a direct pathway from DMS+OH to H_2SO_4 without SO_2 as intermediate the reviewer is misquoting us. We do *not* make the statement "that the extra H_2SO_4 is likely formed from DMS emission". Clearly, we conclude that "CH_2OO formed via photolysis of CH_2I_2 appears to be a likely candidate to explain the observed increase in the OH background signal during daytime aerosol nucleation events at low tide". With respect to the DMS->SO_3-> H_2SO_4 pathway we concluded in the original submission "that marine DMS emissions from biologically active waters in polar latitudes may dominate H_2SO_4 formation in marine air at Mace Head during summer and that SO_2 may not be the major precursor in this process". We have rewritten this sentence at the end of the conclusions to make clear that the look into DMS chemistry as a possibility for the deficit in the H_2SO_4 budget will be our next step.

Again, the motivation for writing this paper originated from the fact that for the first time all major components were measured for evaluating the H_2SO_4 balance in marine background air (i.e., SO_2 , OH, H_2SO_4, and CS). Following our presentation of seasonal atmospheric OH levels at Mace Head in a preceding paper [Berresheim et al., 2013] we are now presenting the seasonal variations of H_2SO_4 and MSA in marine air. However, the central and most important point for us was to probe the closure of the H_2SO_4 budget as mentioned above. This was triggered by the study of Mauldin et al. [2012] and Welz et al. [2012] suggesting a missing SO_2 oxidant in the atmosphere which might be a Criegee radical. Such a suggestion was already previously made by Berresheim et al. [2002] for the marine atmosphere at Mace Head and presented as early as 1998 at the EGU symposium in Dordrecht, NL. Numerous discussions with F. Eisele, R.L. Mauldin (a contributing investigator in our OH measurements, see Acknowledgment) and other colleagues strenghtened our view that the CIMS OH Background signal may contain valuable information about the presence and possibly identity of such a "missing X-oxidant". The discussion of the CIMS background signal and its possible origins dates back at least as far as the early paper by Eisele et al. [1991]. Knowing from our own extensive previous research about the possibility of alternate sources of H_2SO_4 in marine air based on the proposal by Lin and Chameides [1993], i.e., the potential DMS + OH (+X?) ->SO3->H_2SO_4 route without SO_2 as an intermediate we also wanted to look into case studies involving air masses advected from highly productive marine waters. We have clearly stated that we found evidence that both mechanisms may be significant in coastal marine air and that this needs more systematic research in the future (and this of course needs to include VOC alkene measurements which is obvious to us as well). We had no pre-conceived view of how to interpret our data as the reviewer falsely seems to suggest and we don't think that our paper appears to make such a rather amateurish impression on the general reader in view of the numerous positive (and constructive) comments we have already received during the discussion phase.

Eisele, F.L., and D.J. Tanner, Ion-assisted tropospheric OH measurements, *J. Geophys. Res., 96*, 9295-9308 (1991). Lin, X., and W.L. Chameides, CCN formation from DMS oxidation without SO_2 acting as an intermediate, *Geophys. Res. Lett., 20,* 579-582 (1993).

Reviewer Comments **Page 3 line 27:** Photolysis of CH_2I_2 will lead to the formation of a single Criegee intermediate, CH_2OO. In addition, a recent study by Berndt et al. (2014) shows how the reaction between CH_2OO and water dimer is fast enough to allow this gas to be lost solely on reaction with water and water dimers. Thought it is unlikely it will have such a big role in the oxidation of SO_2 and consequent detection by the CIMS instrument.

Reviewer Comments **Page 19 lines 428-445:** This is true for reaction with SO2, not totally true for reaction with water. Stone et al. (2014) actually find the reaction with CH2OO and water to be very slow. Anyway, as until this point no consideration on the different conformers created was highlighted, how is the calculation done? Which yields of syn vs. anti are used? In addition, on line 435 it says that the unimolecular decomposition rate of 250 s-1, is not considered as it would make only a small contribution on the estimate. Does this mean that the rate of SCI towards H2O and SO2 is a lot faster therefore there is no unimolecular decomposition is happening? Or what is the meaning? It would be interesting if the authors could provide the starting concentration of SCI used for the calculation so the reader could understand the meaning of such a sentence. In Taatjes et al. (2012) a limit for the unimolecular decomposition of CH2OO of 75 s-1 is given for CH2OO. Why not use this value and do the calculation for CH2OO as well? Also, the authors make a point in underlining the use of 2 different rate coefficient for the reaction between *syn* and *anti*-CH3CHOO with water vapor. This is good as they do have a different behaviour. What is it not clear is why consider these two conformers. The authors start the calculation considering monoterpenes and in particular pinene and limonene. As these two molecules are both cyclic, the typology of Criegee formed and their reactivity differs quite a lot from *syn* and *anti*-CH3CHOO (Nguyen et al., 2009). So I do not see the point on using two different rate coefficients for reaction with water vapour as the calculation is anyway so approximate that such a distinction makes actually no difference what so ever.

I do not think that by doing a calculation in this way it is actually possible to estimate any impact of Criegee on the oxidation of SO2 and on the background observed by the CIMS.

Reviewer Comments **Page 21 lines 466-470:** Their studies show that the rate coefficient between CH2OO and SO2 is fast. That doesn't quite mean that the reaction is relevant in the atmosphere as there are several other coreactants that will compete with SO2. The study of Berndt et al. (2014) indicates that reaction with water monomers and dimers is likely to be the main loss process for CH2OO in the atmosphere. It would be worth mentioning it.

Our reply:
These three comments of the reviewer seem to be related, so we answer them in a common context. The background signal of the CIMS instrument might be caused by a combination of processes all working at the same time. One possibility are Criegee radicals which might produce H_2SO_4 by oxidizing SO_2. The background signal itself is not specific to make any differentiation possible. So all we do is we try to answer the following question: “If the background signal is in total caused by a specific precursor which oxidative power would this precursor have with respect to ambient SO_2”? So all we do is we assume that one specific precursor X_i is responsible for the BG signal and calculate how an observed average ratio OH/BG of 1:1 would be transformed into the ratio $(k_{OH+SO2}*[OH]*[SO_2])/(k_{Xi+SO2}*[X_i]*[SO_2])$ for ambient air if we take ongoing production of X_i inside the CIMS inlet into account. To do this we selected three types of Criegee radicals which are discussed in the literature as X_i and show that the range of possibilities for the ratio of oxidative power of OH to X_i with respect to SO_2 at Mace Head is going is not significant with respect to the large deficit observed. Without external knowledge about the concentrations of different X_i the BG signal of CIMS is not specific enough to give a more detailed answer. That is the reason why we did not discuss more examples of Criegee’s. For CH_3CHOO we used the kinetic information for both

conformers to make the reader aware that even for one Criegee type there might be different results in this calculation depending on the kinetic parameters of subtypes of these species. Further on, since we attribute the CIMS BG signal in total to a specific Criegee intermediate (see the new Table 2) to make an upper limit estimate, we do not need to know the yields for different conformers.

Replies to minor comments:

"Though it is unlikely it will have such a big role in the oxidation of SO_2 and consequent detection by the CIMS instrument." Even if the Criegee under consideration would react very fast with H_2O in ambient air and therefore would not react with ambient SO_2 it might still produce a significant BG signal in the CIMS instrument because the SO_2 concentration in the CIMS instrument is so large. This has to be considered correctly. We think our equation is doing that. Quantitative examples are shown in the new Table 2.

"I do not think that by doing a calculation in this way it is actually possible to estimate any impact of Criegee on the oxidation of SO2 and on the background observed by the CIMS." Such an estimate is already in the literature (Mauldin et al., NATURE 2012), but we think, the CIMS inlet chemistry was not considered enough since neither the ongoing production of Criegee's in the inlet nor the ratio of the reaction coefficients with SO_2 by Criegee and OH has been taken into account. So our calculation of the impact of the inlet chemistry is worth to be published in this context.

"It would be interesting if the authors could provide the starting concentration of SCI used for the calculation…" That kind of information was already in the text: "Therefore, if X is indeed a sCI compound (of the kind considered here), the measurement signal resulting from sCI would have to be weighted by 1:3.6 with respect to the OH signal to obtain the corresponding ambient air [sCI] concentration", but maybe it was not clear enough. We introduced equation 4 and 5 to make that point more clear.

"The study of Berndt et al. (2014) indicates that reaction with water monomers and dimers is likely to be the main loss process for CH2OO in the atmosphere. It would be worth mentioning it." done.

Reviewer Comments **Page 3 lines 29-32:** As underlined by the authors, there are no VOC measurements for the period described in the manuscript. It is not clear on what basis the statement that larger SCI play no significant role for SO2 oxidation in the marine environment is made. If larger SCI are not present because of lack of precursors then they cannot have a role; they just are not there. So what is the meaning of the sentence? Also, from Lewis et al. (1999) it is clear that small alkenes such propene, iso-butene, *do* follow a diel cycle with a peak at noon (cf. OH and the background). So what if the Criegee intermediate formed from these alkenes have a role in the oxidation of SO2?

Our reply:

The reviewer refers to conclusionary statements in our Abstract. We have added a clarification here and the corresponding discussion has now been further clarified in lines 460ff., denoting the sCI compounds resulting from ozonolysis of monoterpenes as "relatively large" in contrast to "smaller" and more reactive CI such as CH_2OO. We are not aware of previous measurements of monoterpenes in marine air. Therefore, we cannot - as the reviewer suggests - simply state that “they are not present” in this environment (e.g., significant isoprene levels have previously been recorded by various groups, see our references on p. 18 to both Broadgate et al. and Lewis et al.).

We go here the other way around. In any case, Criegee intermediates capable of oxidizing SO_2 would induce a BG signal of the CIMS instrument. As it happens, the CIMS instrument does show a significant BG signal. So we target the question, if all of that CIMS BG signal would be caused by a specific Criegee intermediate, what would be its ambient concentration and impact? This is a kind of upper limit estimate. Based on the kinetic data available from the literature (Mauldin et al., 2012) our calculations for ozonolytically produced Criegee intermediates show that “larger” (monoterpene derived) types of sCI are not likely to be significant for SO_2 oxidation in the coastal atmosphere even if all of the CIMS BG signal would be caused by such a type of Criegee intermediate. The same line of argument is used for the other Criegee intermediates discussed in our paper. With regard to the presence of such sCI formed from alkene-ozonolysis reactions some discussion is in lines 592ff. In our Conclusions we state: “Whether this oxidant might be a Criegee radical with its production mainly determined by strong light-induced emissions of marine hydrocarbon species and/or atmospheric photolysis of iodine species remains an open question.” Clearly, it is obvious from this statement what type of future measurements have to be included in further research on this subject.

Reviewer Comments **Page 3 line 33:** The authors might want to state at least which small SCI they are referring to because to my knowledge from the photolysis of CH2I2 there would be the formation of only the CH2OO Criegee intermediate.

Our reply: Done

Reviewer Comments **Figure 2:** What is the meaning of the bars in the plot? Is one limit of the bar always touching zero? Does this mean that H2SO4 and MSA concentrations could be zero all the time?

Our reply:

Bars denote standard deviations. We have added a corresponding explanation in the figure caption. The bars just show the variability of the individual samples in the averaging process. The fact that the lower wing of the bars touch zero all the time might be an effect of the distribution of the samples. A log-norm distribution would give such a result.

Reviewer Comments **Figure 3:** Why not perform a York fit (York et al., 2004) that takes into account the accuracy on both measurements (that seems to be rather high)? There is a load of OH data here, could there be a time series too?

Our reply:

We are aware of the problem for a linear regression with errors in both variables. Since we did use OH calculated from JO^1D in figure 3 this problem does not have to be taken into account because the JO^1D data are extremely precise. We did use this parameterization because MSA was not measured in the 5min period used for the measurement of OH but only in the 25min for the H_2SO_4 measurement. The measurement sequence has been 5min

OH and H_2SO_4, 25min MSA and H_2SO_4. We have already shown now for the calculation of the mass balance of H_2SO_4 that the average results taking the OH proxy from JO^1D and taking direct OH observations are almost identical.
The OH time series have been shown and analyzed in our preceding paper (Berresheim et al., 2013) so we would like not to show them again here.

Reviewer Comments **Page 13 lines 278-279:** I would like to see the atmospheric OH concentration plot. Again, if the data for OH+Bg and Bg were available, why not show measured OH with BG?

Reviewer Comments **Figure 6:** This plot shows OH measurements (right?) for the entire period of the campaign, May till August. So if there is availability of the data, why not show all of them?

Our reply:
Both points of the reviewer are dealing with the data shown in figure 6. The time period for the data used to calculate this average diurnal pattern is 2010-2011 which was stated within the text line 280 at the first occurrence of figure 6. We regret that we have missed to give this information in the figure caption. This is done now. The OH time series have been shown in our preceding paper (Berresheim et al., 2013) so we would like not to show them again here. Figure 6 shows already OH (green line) and BG (red line) as the reviewer wants to see. The reason for figure 6 is to show that OHsig and BGsig have on average the same magnitude, This average ratio of 1:1 is used in the calculation of the effect of Criegee's in the application of equations 3-5.

Reviewer Comments **Page 17 lines 391-398:** Why use data for α-pinene and limonene that are more common in forest than on the coast and show a correlation with temperature and not with solar radiation and not do the calculation with propene or isoprene previously measured at the site? There is far more information on smaller alkenes, and therefore Criegee formed after their ozonolysis, than for larger ones. Additionally, the simplification applied here is quite extreme: the Criegee coming from both monoterpenes do not have exactly the same unimolecular decomposition rate and do not react at the same speed with water. I agree that it is not simple to do an estimation of the impact of Criegee intermediate, but if the simplification is excessive than the results obtained are meaningless.

Our reply:
As stated at several occasions in this reply we analyse the CIMS signals the other way around. We are not asking how much BG signal a particular concentration of a specific Criegee intermediate would give. In this case we would need observations of precursor concentrations or correlations with temperature etc.

We ask how large the contribution of a specific Criegee intermediate to the H_2SO_4 budget would be if all of the observed CIMS BG signal would be caused by this specific Criegee. We restrict this question to the monoterpene type of Criegee's (which do not have the potential to impact the ambient H_2SO_4 budget if we take the BG signal of the CIMS instrument as a measure for their abundance) and to the small Criegee's which would have this potential due to their faster-than-OH reaction constant with SO_2. And we do not exclude that these small Criegee intermediates are formed in the ozonolysis of small alkenes.

We do not think that we apply an extreme simplification. On the contrary. We calculate the Criegee chemistry in the CIMS inlet system and the transfer to ambient Criegee concentration and SO_2 oxidation potential correctly. But our result depends on the kinetic parameters for these reactions which might be wrong.

Reviewer Comments **Page 19 line 418:** I would remove the bracket (monoterpenes + SO2) because it might mislead the reader into thinking that the rate used is between monoterpenes and SO2 and not between Criegee intermediate coming from ozonolysis of monoterpenes, and SO2.

Our reply:
This has been changed.

Figure 8a and b: It would be nice to see a figure showing only the measured (or calculated, because it is not clear to me) OH and the JO1D together without the additional backgrounds signals. As a lot of the OH used for the calculation of the H2SO4 is derived from the OH-JO1D relationship, it would be good to see if this assumption can be made, especially during low tidal period when there is actually no correlation between measured OH and JO1D.

Our reply:
This has all been addressed in our Reply to point 2 made by the Reviewer (see above). These figures 8 show only observations. We scaled JO^1D so that the correlation with (observed) OH is clearly visible. We would like to keep the raw signals BG and BG+OH in this plot since this allows for more insight especially during the situations of interest. As we have stated now in the revised text the usage of OH_obs or OH_calc makes almost no difference for the average of the mismatch in the H_2SO_4 budget or its range of variability.

Reviewer Comments **Page 22 line 497:** The CH_2OO intermediate is unlikely to decompose forming OH as it has a high energy and it misses a methyl group *syn* to the oxygen (Vereecken and Francisco, 2012). In Berndt et al. (2012) there is no reference to the CH_2OO as it is not formed from the alkenes studied. Kroll et al. (2001) shows how it is unlikely that stabilised CH_2OO are involved in the formation of OH as the yields of OH (that is in general quite low) does not change by changing the pressure.

Our reply:
We have not stated that “specifically” CH_2OO could decompose to OH. The exact excerpt reads *“We interpret our observations as strong formation of X-oxidant(s) (e.g., CH2OO from photolysis of CH2I2; Welz et al. [2012]) and OH (perhaps via thermal decomposition of sCI; Berndt et al. [2012], Kroll et al. [2001]) followed by …”*. We only generally state that OH may be formed “perhaps via thermal decomposition of sCI “. In this we followed Berndt et al. (2014) who neither specify nor exclude this possibility for CH_2OO according to their introductory remark: “The gas-phase reaction of ozone with olefins produces an energy-rich primary ozonide, which decomposes very rapidly, forming a carbonylic substance and a

biradical, the so-called Criegee intermediate (CI). This still energy-rich CI can undergo unimolecular reactions or can be collisionally stabilized by the pressure gas. The unimolecular pathways lead to the formation of an excited vinyl hydroperoxide (VHP) that rapidly decomposes producing OH…" We have now also cited the Berndt et al. (2014) paper. To be more clear we also changed "and OH" into "or of OH" at line 537.