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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.

Anonymous Referee #3

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Review of Berresheim et al. Missing SO2 oxidant in the coastal atmosphere? Summary Although I understand that the authors have attempted to rule out an incorrect background subtraction, the background signal of the CIMS seems to be a linear function of the OH signal. This is very suspicious and suggests to me that it is more likely an incorrect background subtraction than some SCI or other species. One of the authors is very experienced in measuring OH with CIMS and therefore should have noted this large background signal previously. Is there any evidence in older data sets in other regions? E.g Berresheim et al 2002 where a discrepancy was put down to DMS. OH and another species (esp. sCI) will have very different production and loss processes resulting in very different steady state concentrations and therefore diel cycles.

Again, there is no evidence presented in the manuscript that the instrument can detect SCI and so the authors should start from this point at least show that the instrument can detect SCI before speculating about a background signal that looks like a proportion of the OH signal. Even if the CIMS detects some SCI with some unknown sensitivity then the effect of each SCI on ambient chemistry with respect to its sinks is very varied (e.g. Vereecken et al.) and the SCI which may be detected may be different from those which can react with SO2 instead being destroyed by water vapor.

In the end, this paper is very speculative and needs further thought and much more work in the lab to demonstrate the points that are made. There are valid points made, such as the effect of possible production of SCI in the inlet system, but I really really would like to see some confirmation of detection before detailed speculation is made and certainly far more data.

Given the above point, there are other issues which further weaken the paper. Particular points.

Line 16 page 1161. The authors should not refer to CI as RO2. RO2 are peroxy radicals which are not CI also add some better reference on Criegee intermendiates than Calvert like (Criegee, 1975).

I am very skeptical that the background signal has its origins in an unknown species. From the data presented in the paper it is clear that the CIMS background correlates with the OH signal. I think it is more likely that the signal originates from OH itself and not some separate process. I know the authors have attempted to optimize the propane injection, but it is a very big stretch to invoke a separate species with different production and loss processes. For example, Novelli et al show a similar background with a LIF instrument and the background signal which owes its presence to some process producing OH within their instrument shows a very different diel signature to the OH signal. The authors should show as much data from the intensive as possible, even in supplementary information to show the relationship between the OH signal and the CIMS background. If the CIMS background originates from a separate species then one would expect at least some degree of variance from the OH signal in the day.

Before publishing this work the authors should ascertain that instrument will detect SCI in the lab before they invoke or deny speculative explanations.

It is also likely that at a marine location a wide variety of SCI will react in the main with water vapor, e.g CH2OO, and not contribute to SO2 formation and not get detected, (large losses = low steady state concentration) by the CIMS if indeed they are detected at all. As noted by Vereecken et al. (2014) the particular species of SCI is of import and therefore the sensitivity of the CIMS to SCI (again, if any) may not be relatable to the "extra" oxidation of SO2.

There is a paucity of data in the manuscript (there are two years of data???). I would like to see far more of the measured data and it would be good if all the campaign data could be archived and accessible. Also it would be good if very speculative hypotheses are backed up by all the data available to the authors. I assume there is a lot and a study of the background measured by the CIMS would be of use. Has this "extra" background been noted in historical CIMS data?

There needs to be far more detail on the theoretical calculations and a proper discussion of the limits and uncertainties of the numbers produced. This section seems like an add-on and needs a proper treatment. Detailed information on the calculations and all the important information should be included in the supplementary information. Is this the only alternative to sCI? Surely there is another reason for unexplained background counts. This point is also true for the condensational sink. What does the very large uncertainty do to the disagreement with the expected SO2 oxidation? What is the total uncertainty of the SO2/H2SO4 system? The uncertainty on the CS is very large. I would like to see a plot indicating the total uncertainty on the calculation.

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Interactive Discussion

Discussion Paper

A number of the references are incorrectly referred to. Luc Vereecken is known for his theory work why is his paper under field measurements? There are plenty of other references to work with Criegee intermediates earlier including Criegee himself. The Boy et al 2012 reference is referred to as theory when it is modeling work.

In figure 5 and 8 I would like to see a concentration scale in addition to the counts scale. The figure 8 diel profile show OH not following jO1D and so I would like to see how much OH is in the morning peak. The lack of relationship with jO1D also calls into question the parameterization used in figure 3. The authors cannot have their cake and eat it, either OH is related to OH or it isn't.

In figure 3 (and 5), what do the authors mean by parameterization?? Surely there was a measurement???? Anyway as noted early, the exemplary figure 5 shows no relationship between OH and jO1D (nicely with the background signal though) and so can the author really trust the method in such an environment?? I would say no. In general, please format the citations in the proper order following first the year than the name etc.

Why did the authors move from the hypothesis that DMS is responsible for the formation of H2SO4 with direct formation of SO3? Berresheim et al. 2002 is said that laboratory tests showed that the contribution of SCI on the background signal would be important during nighttime and 20% during the day. Where these tests repeated? Which kind of alkenes were tested? What changed between then and now? I am aware of the interest there is now in the Criegee intermediates chemistry, but the tests showed that this is unlikely not be a source for the discrepancy observed at Mace Head. In addition, as underlined by the authors, a large discrepancy was observed in Antarctica were it is unlikely to have a high concentration of VOCs. Mauldin et al 2012 showed that in Finland, in a forest during a very hot summer with a very high OH reactivity (Nölscher et al., 2012) and therefore VOCs concentration, the possible role of SCI in oxidizing SO2 is similar to the OH one. So I find it hard to believe that in Antarctica or at a "clean" coastal site there would be larger production of Criegee intermediates.

Berresheim, H., Elste, T., Tremmel, H. G., Allen, A. G., Hansson, H. C., Rosman, K., Dal Maso, M., Mäkelä, J. M., Kulmala, M., and O'Dowd, C. D.: Gas-aerosol relationships of H2SO4, MSA, and OH: Observations in the coastal marine boundary layer at Mace Head, Ireland, Journal of Geophysical Research: Atmospheres, 107, 8100, 2002.

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