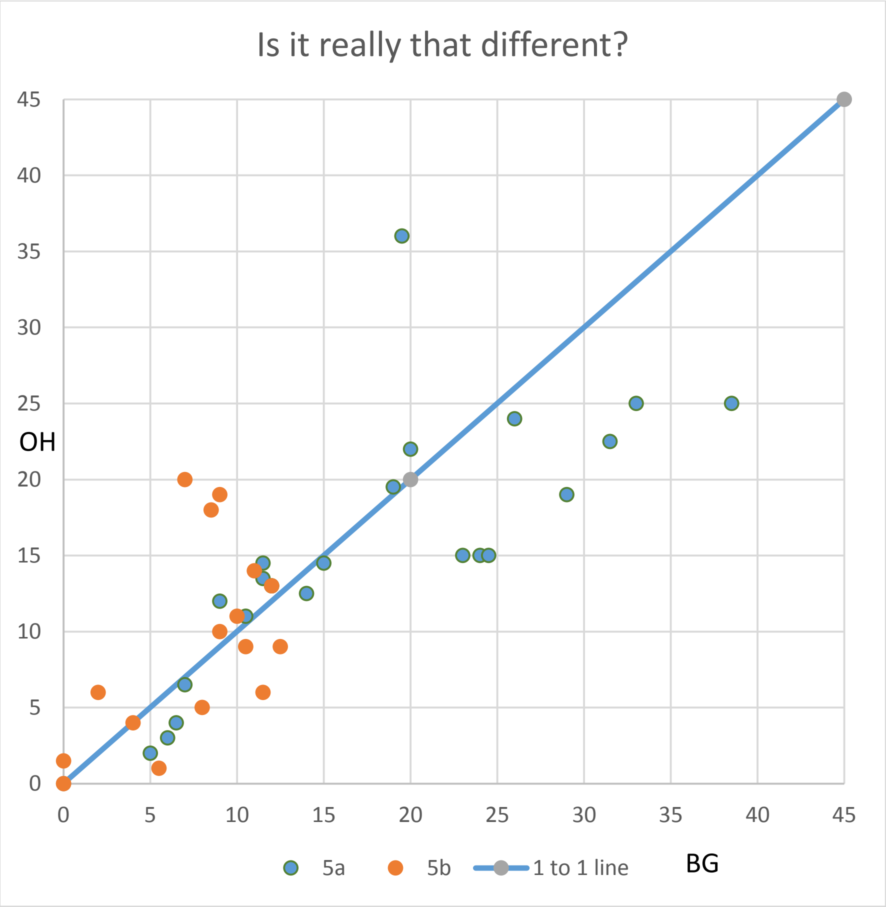
Second review of Berreshiem et al.

I am still very worried about this paper. The authors have ignored a number of my queries and there are still a number of issues which need to be dealt with.

I will be clear and list them as individual points so that the authors can be clear as to their response to each one.

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 H_2SO_4 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.



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. HO_2 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.

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 sceptical about the results and the more data the better along with some good correlation plots in addition to the time series.

3: If the authors have a clear idea of what is forming H_2SO_4 then why write this paper??

The authors state in the conclusion that the extra H_2SO_4 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 CH_2I_2 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.

Some particular points

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.

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 SO_2 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 SO_2?

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 CH_2I_2 there would be the formation of only the CH_2OO Criegee intermediate.

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?

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

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?

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?

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.

Page 19 line 418: I would remove the bracket (monoterpenes + SO_2) because it might mislead the reader into thinking that the rate used is between monoterpenes and SO_2 and not between Criegee intermediate coming from ozonolysis of monoterpenes, and SO_2.

Page 19 lines 428-445: This is true for reaction with SO_2, not totally true for reaction with water. Stone et al. (2014) actually find the reaction with CH_2OO 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 H_2O and SO_2 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 CH_2OO of 75 s^{-1} is given for CH_2OO. Why not use this value and do the calculation for CH_2OO as well? Also, the authors make a point in underlining the use of 2 different rate coefficient for the reaction between *syn* and *anti*-CH_3CHOO 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*-CH_3CHOO (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 SO_2 and on the background observed by the CIMS.

Page 21 lines 466-470: Their studies show that the rate coefficient between CH_2OO and SO_2 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 SO_2. The study of Berndt et al. (2014) indicates that reaction with water monomers and dimers is likely to be the main loss process for CH_2OO in the atmosphere. It would be worth mentioning it.

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 J_{O1D} together without the additional backgrounds signals. As a lot of the OH used for the calculation of the H_2SO_4 is derived from the OH-J_{O1D} 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 J_{O1D}.

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.

Summary

The authors have not demonstrated that their mystery signal does not arise from a prosaic source needing no explanation. The purpose of the paper is also a slight mystery as the author already seem to know what causes the addition H_2SO_4, DMS, and so it is not clear why the paper has been written in the first place. It is also not clear when the authors use calculated OH and when they use measured OH. This should be made clear and if calculated OH is being used then a comparison should be presented with all the measured OH data. But, if calculated OH has been used, the authors cannot have their cake and eat it, they cannot say there are strange sources of OH and then use a parameterization which only include jO1D to study the differences.

References

Berndt, T., Jokinen, T., Mauldin, R. L., Petaja, T., Herrmann, H., Junninen, H., Paasonen, P., Worsnop, D. R., and Sipila, M.: Gas-Phase Ozonolysis of Selected Olefins: The Yield of Stabilized Criegee Intermediate and the Reactivity toward SO_2, J. Phys. Chem. Lett., 3, 2892-2896, 2012.

Berndt, T., Voigtländer, J., Stratmann, F., Junninen, H., Mauldin Iii, R. L., Sipilä, M., Kulmala, M., and Herrmann, H.: Competing atmospheric reactions of CH_2OO with SO_2 and water vapour, Phys Chem Chem Phys, doi: 10.1039/c4cp02345e, 2014. 2014.

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and Wahner, A.: Detection of HO_2 by laser-induced fluorescence: calibration and interferences from RO_2 radicals, Atmos. Meas. Tech., 4, 1209-1225, 2011.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L., and Donahue, N. M.: Mechanism of HOx Formation in the Gas-Phase Ozone-Alkene Reaction. 2. Prompt versus Thermal Dissociation of Carbonyl Oxides to Form OH, The Journal of Physical Chemistry A, 105, 4446-4457, 2001.

Lewis, A. C., McQuaid, J. B., Carslaw, N., and Pilling, M. J.: Diurnal cycles of short-lived tropospheric alkenes at a north Atlantic coastal site, Atmos Environ, 33, 2417-2422, 1999.

Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, Atmos. Chem. Phys., 12, 8009-8020, 2012.

Nguyen, T. L., Peeters, J., and Vereecken, L.: Theoretical study of the gas-phase ozonolysis of beta-pinene (C(10)H(16)), Phys Chem Chem Phys, 11, 5643-5656, 2009.

Novelli, A., Hens, K., Tatum Ernest, C., Kubistin, D., Regelin, E., Elste, T., Plass-Dülmer, C., Martinez, M., Lelieveld, J., and Harder, H.: Characterisation of an inlet pre-injector laser induced fluorescence instrument for the measurement of ambient hydroxyl radicals, Atmospheric Measurement Techniques Discussions, 7, 819-858, 2014.

Phillips, G. J., Pouvesle, N., Thieser, J., Schuster, G., Axinte, R., Fischer, H., Williams, J., Lelieveld J. and Crowley J. N.: Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionization mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes, *Atmos. Chem. Phys*., 13, 1129-1139, 2013.

Stone, D., Blitz, M., Daubney, L., Howes, N. U., and Seakins, P.: Kinetics of CH_2OO reactions with SO_2, NO_2, NO, H_2O and CH_3CHO as a function of pressure, Phys Chem Chem Phys, 16, 1139-1149, 2014.

Taatjes, C. A., Welz, O., Eskola, A. J., Savee, J. D., Osborn, D. L., Lee, E. P. F., Dyke, J. M., Mok, D. W. K., Shallcross, D. E., and Percival, C. J.: Direct measurement of Criegee intermediate (CH2OO) reactions with acetone, acetaldehyde, and hexafluoroacetone, Phys Chem Chem Phys, 14, 10391-10400, 2012.

Vereecken, L. and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, Chemical Society Reviews, 41, 6259-6293, 2012.

York, D., Evensen, N. M., Martínez, M. L., and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, American Journal of Physics, 72, 367-375, 2004.