Reply to second round of reviewers comments

We would like to thank the reviewers for their further comments on the manuscript. Reviewers comments are in red, author replies are in Black and added text is in blue.

Report#1

Major

a) The authors did a good job in comparing the results from HILIC and RPLC, however, I was wondering why only the peak areas of 2-MT-OS were correlated. What about the 2-MG-OS?

2-MG-OS was not targeted during the HILIC analysis. This analysis was undertaken in a different lab, so unfortunately further experiments cannot be undertaken.

b) I disagree with the conclusion that "there is no evidence of ion source induced artifacts" (L527). As the authors acknowledge, there is still some co-elution of sulfate and nitrate ions with detected OS species. Therefore, there is still a chance of adduct formation between inorganic ions and organic compounds. The "test for artefact formation" conducted by the authors is not convincing, as it is just proving that sulfate and 2-methylglyceric acid / 2-methyltetrol do not produce artifacts. This cannot be generalized for all organic compounds! (By the way, I totally agree with the authors' conclusion that all previous direct infusion studies suffer from in-source adduct formation. Therefore, I'm actually very happy to see that people are now more and more using chromatographic separation before ionization. Nonetheless, if the separation is not done appropriately, we will not get away from ion source artifacts.)

The reviewer states there is a chance that adduct formation happens. However they provide no evidence to show this is possible. In contrast, we directly show that for the two main species we targeted in this study, artefacts do not form under our conditions. It is true that this does not mean all that all organics act the same way but we do not say that in the paper. With the nature of such complex samples (rough analysis shows over 5000 species in one ambient sample) co-elution is inevitable, even with the best chromatographic method. Throughout the entire chromatogram, not just during the first few minutes there is the co-elution of species, which would be the same for every ambient study. So, unless there is complete separation of all species in ambient samples, matrix effects are a possibility. However, we have at least been able to rule out the adduct formation from two authentic standards which to our knowledge the best has done at this stage of our understanding. In response to this comment we have added text to highlight that adduct formation COULD be occurring, but we have ruled out that organosulfate formation is not occurring from the co-elution with sulfate for these two authentic standards, and have said that more evidence is needed to show if adduct formation is occurring or not for other organic species.

The following text has been added:

L220 : "This therefore rules out adduct formation for the two most important iSOA species, 2-MT-OS and 2-MG-OS, however due to the lack of authentic standards and the complexity of the samples, adduct formation throughout the entire chromatogram could still be occurring. At this stage, there is not enough evidence to say either way if adducts are forming or not."

c) The selected settings of the Q Exactive mass spectrometer are really far from appropriate for a quantitative analysis approach. With the settings applied here (i.e., full scan at R=70,000 combined with ddMS2 Top 10), the authors obtain ~1 full scan spectrum per second (i.e, full scan + 10 x ddMS2

= 256 ms + 10 x 64 ms = 896 ms). As a rule of thumb, for accurate quantification, about 12 data points are needed to get a good peak quality in the extracted ion chromatograms. Therefore, the chromatographic peak width needed here would have been roughly 11–12 seconds, which is a quite broad peak in typical UHPLC applications and only reached with quite concentrated samples. In particular, since all the OS peaks elute quite early, I would be surprised to see that the authors obtained more than ~5–6 data points for each of the peaks here. In principle, it is possible to increase data quality by measuring replicates. However, the authors decided to measure each sample only once. Therefore, I think the concentrations reported here are connected to very large uncertainties (which could have been avoided easily).

Here we strong object to the comments of the reviewer. All peaks have ample data points, with the peaks being around 10-14s wide. We agree that the peaks are wide compared to optimum UHPLC conditions, however this method was developed not just to target isoprene organosulfates, but a wide range of compounds. As such, our concentrations are not connected to large uncertainties due to the method. From the calibration curve you can see that the linear fit is very good for both the external and standard addition calibration methods. Also the repeatability is very good, with a low standard error. If we were under sampling our peaks, we would not be able to obtain this sort of calibration curve.

d) Regarding the uncertainties mentioned above, it is still unclear to me how the authors estimate an uncertainty of 60% for the measured OS concentrations.

We have taken the average ratio of standard addition to the 2-MG-OS external calibration values given in table S1 and S2 to get a mean correction factor of 1.83. The uncertainty (60 %) is calculated as 2$\sigma$ of the 6 values. This has been added to the text.

Following text has been added:

L456: “The uncertainty was calculated as 2$\sigma$ of the 6 values used to calculate the average correction factor of 1.83.”

Minor / Technical comments:
1) There are several mentions of “corplot” and “PollutionRose plot” in the manuscript, which might be disturbing to readers less familiar with R. I would recommend replacing these R-specific names with more general terms (e.g., corplot = correlation plot).

The terminology has been changed for the corplot, and a more detailed description added for the pollution rose plot.

Following text has been added:

L414: “in a correlation plot (R, Openair, CorPlot)”

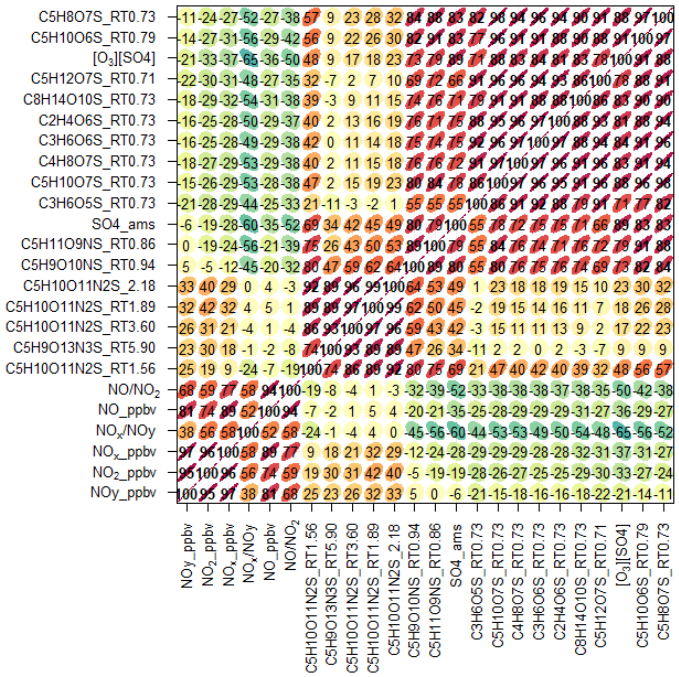
L415: “The correlation plot”

Figure 5 caption: “Correlation plot (R, Openair, CorPlot)”

Figure 2 caption: “Figure 2. PollutionRose plot (Openair) of particulate sulfate measured by AMS, for the sampling period. Highlighting under what wind conditions the highest concentrations of sulfate occur.”

2) Figure 5: Some of the label names capitalized and some not.

These have been capitalized.

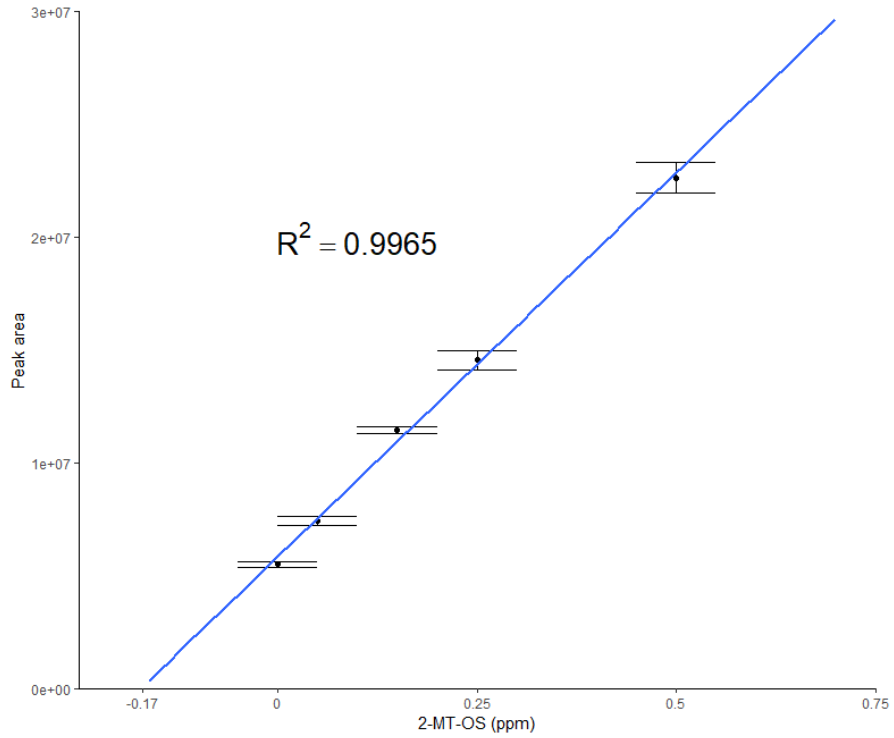



3) L901: Ultra-performance liquid chromatography (UPLC) is actually specific for components from Waters Corporation. The more general term is ultra-high performance liquid chromatography (UHPLC).

This has now been changed throughout. On lines 45, 173, 175, 205, 206, 248, 426, 482, 530, 532, 659

4) Figure S3: I suppose the x-axis label should read 2-MG-OS.

This has now been changed.




Report#2

Major:

Since AMS data is available in this campaign (L984), could the authors look into the tracer of IEPOX-SOA (i.e., m/z 82 or C_5H_6O^+) to see what is the relationship between the measured tracers and that ion tracer in AMS? Presumably NOx conditions may also affect the channels of IEPOX or OS formation if the chemistry is similar in other regions with SOA from isoprene.

The measured tracers (2-MT-OS and 2-MG-OS) showed limited correlation towards the C5H6O+ tracers with R2 values of 0.3837 and 0.4079 respectively. This is likely due to the low levels of IEPOX-SOA at this location and that a fraction of the C5H6O+ peak comes from other sources, such as methyl-furan. We do not feel this adds to the overall story of the paper and have not included it.

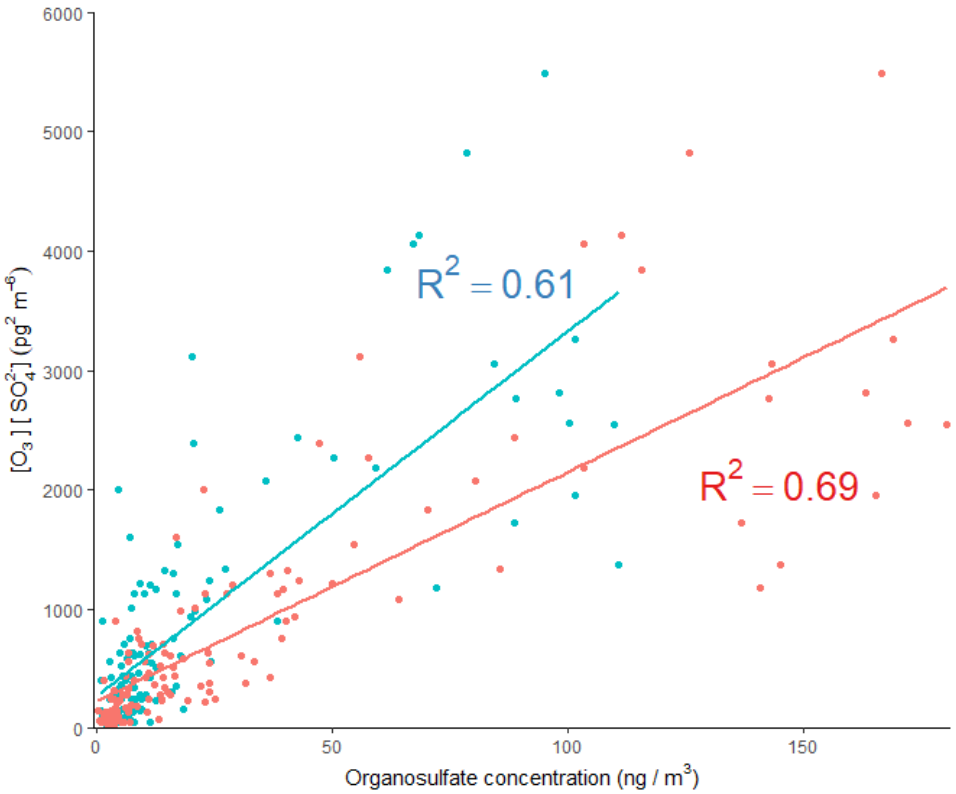
Minor:

1. The authors used “ultra-pressure liquid chromatography” in the Abstract, but “ultra-performance liquid chromatography” in L901. Please be consistent.

The terminology has now been changed to ultra-high performance liquid chromatography (UHPLC) throughout. On lines 45, 173, 175, 205, 206, 248, 426, 482, 530, 532, 659

2. Figure 7. Please use [O3] × [SO_4^2-] in the title of y axis. And better to use SO_4^2- for sulfate as there is no such thing as SO_4.

This has now been changed.


6000
5000
4000
3000
2000
1000
0
0
50
100
150
$[O_3]\,[SO_4^{2-}]\,(pg^2\,m^{-6})$
Organosulfate concentration (ng / $m^3$)
$R^2 = 0.61$
$R^2 = 0.69$