

Interactive comment on “Strong anthropogenic control of secondary organic aerosol formation from isoprene in Beijing” by Daniel J. Bryant et al.

Anonymous Referee #1

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Summary and recommendation:

In this study, Bryant et al. examined the formation of isoprene-derived SOA (iSOA) during summer in Beijing (China) using a large suite of online and offline instruments. In particular, the authors focus on LC-MS data from filter extracts of PM_{2.5} and the detection, identification, and quantification of isoprene-derived organosulfates (OSs) and nitrooxy-organosulfates (NOSs). They determined an average concentration of iSOA OSs and NOSs of 82.5 ng m⁻³. Moreover, the authors claim that OS formation depends on a combination of photochemistry and particulate sulfate concentrations, and suggest that iSOA formation is strongly controlled by anthropogenic emissions in Beijing.

The authors acquired an impressive dataset with state-of-the-art instruments during

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their field study. Moreover, molecular-level identification and quantification of SOA constituents, such as OSs and NOSs, is challenging, yet highly desirable. However, I see several major weaknesses in the measurement approach, the data analysis and interpretation of the results, which need to be addressed before I can recommend the publication of the manuscript (as detailed below).

Major comments:

1) I have the impression that the main conclusion (which is also the title) of the manuscript is only weakly supported by the data shown in the manuscript. The authors claim that there is a “strong anthropogenic control of SOA formation from isoprene in Beijing”. However, only one figure (i.e., Figure 5) is actually showing a weak correlation of OSs to the product of ozone and sulfate concentrations, which can be considered to some extent as a metric for anthropogenic influences. Nonetheless, no correlations of total SOA mass to common anthropogenic pollutants is shown or discussed. It should also be noted that particulate sulfate could have been transported to the sampling site over longer distances, and thus, is not a direct anthropogenic emission factor.

2) In general, the discussion of the data remains quite superficial in several sections, which might also be one of the reasons for my comment above. For example, Fig. 1, which displays typical anthropogenic pollutants, is barely discussed in the results section (i.e. only four sentences, P8L315–318). This is similar for several other figures in the manuscript. Moreover, the authors should reconsider the order and layout of the figures, as the reader is often forced to jump between figures or to find essential data in the SI (e.g., Fig. S10).

3a) One of my most pressing concerns is the LC-MS method used for filter extract analysis and the selection of reversed-phase LC for the separation and detection of isoprene-derived OSs. As can clearly be seen from Table 1, the OSs are not retained on the column and probably elute together with inorganic salts such as sulfate. For example, 15 of the 31 identified species have a retention time of <0.8 min. For these com-

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pounds, it is actually impossible to exclude ionization artefacts, i.e., the corresponding compounds are formed from inorganic sulfate and organic compounds during electro-spray ionization. It would be necessary to give at least the dead time of the LC system, to make the reader aware of such potential artifacts.

3b) Moreover, the authors state that potential isoprene OSs were “identified” based on previous studies and then searched for in the LC-MS data (cf. P5L204f). However, even with high mass accuracy and resolving power, it is not possible to identify compounds without any reference standards. I can imagine that there were actually several isomers detectable for each of the “identified” OSs in Table 1 (actually, the authors even admit the presence of isomeric species in the following section 2.4). How did the authors decide which retention time to take for each of the OSs from the literature?

4) The authors claim that they account for matrix effects by calibrating the LC-MS through a standard addition approach. However, in my opinion, this approach is far from convincing, as only 6 of the 132 filters (i.e., 4.5%) of all filters were actually investigated. Moreover, it seems quite unreasonable to me to take the calibration curve of 2-MG-OS for all other detected OSs. As shown in Fig. S2, the slope of 2-MT-OS is about 4x larger than for 2-MG-OS. Eventually, such differences in sensitivity might lead to a large overestimation of OSs concentrations. This has to be discussed in more detail. Merely stating that the measurement uncertainty is 60% is not sufficient. How did the authors actually calculate this uncertainty?

Specific comments:

1) As one of the main aspects of the manuscript is the quantification of OSs and NOSs, I was wondering if the introduction may benefit from some more information on the general abundance of OSs also from other precursors such as monoterpenes and/or alkanes (e.g., Wang et al. JGR 2017, doi: 10.1002/2017JD026930; Brüggemann Environ. Chem. 2019, doi: 10.1071/EN19089; Riva et al. ACP 2016, doi:10.5194/acp-16-11001-2016)

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2) P5L174: As the samples were only extracted using H₂O, it is important to state that only the water-soluble fraction of the filter samples was analyzed.

3) P5L175: Did the authors account for potential artifacts from sonication of the filter samples, for example, as shown by Mutzel et al. (Atmos. Environ. 2013, doi:10.1016/j.atmosenv.2012.11.012)

4) P5L191: What is “full scan MS²”? Do the authors mean full scan combined with data-dependent fragmentation (i.e., full scan-ddMS²)? If so, how many different ion species were fragmented after each full scan? And how were they selected? Moreover, the authors should state at which resolution the mass spectra were obtained, as this will also determine the chromatographic time resolution of the MS method. Besides, it also remains unclear if and how many replicate injections were performed for each sample.

5) P6L216: Here, it is necessary to explain what standards were used for the calibration curves. Without this knowledge, it is very confusing for the reader to follow this discussion.

6) Section 2.5: The filter extraction method for the HILIC-MS analysis is very different from the LC-MS method. In this case, pure methanol was used for extraction. Did the authors investigate how this affects the presence of certain OSs and NOSs?

7) P8L300: It is stated that a SIFT-MS was used to measure isoprene, however, there are no data shown from these measurements. The authors merely claim that there is a good correlation to the DC-GC measurements (P8L321)

8) Fig. 1: I would recommend avoiding interpolation over periods of missing data. Again, as mentioned above, there is almost no discussion of the data.

9) P8L328: Give values for k_{ox} in the main text and not only in the caption of the figure.

10) Fig. 3a: I would recommend giving the loss rate in ppb h⁻¹, as this would help

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the reader to compare the numbers to the actual measurements. Moreover, you could try to estimate a lower limit for isoprene emissions here and compare it to previous studies.

11) P9L349 / Fig. S2-S4: The calibration curves are not of high quality. Especially, for the lower concentrations the data seem to deviate quite strongly from the determined fits (Fig. S2). It would be nice to see errorbars for the variability / standard deviation of the data. Why is the standard addition only shown for one filter sample each? You could normalize the data and show how the slopes of the calibration curves compare to the external calibration for the two compounds.

12) P9L354 / Table S1 and S2: How did the authors select these filter samples? There is no further information given on how these filters were selected and whether they are representative for the campaign period. Moreover, Tables S1 and S2 are very difficult to comprehend.

13) P10L372: Where do these scaling factors come from?

14) P10L374: How did the authors calculate an uncertainty of 60% for their concentrations? If there is such a high uncertainty, it should clearly be stated also in Table 1.

15) Fig. 4: It is misleading to represent the concentrations of the quantified compounds by single data points and to interpolate in between. Better display concentration steps with corresponding lengths to the sampling time.

16) P10L394: The reader has to believe the authors that the three-hourly data are consistent with the hourly samples. No evidence is shown for this assertion.

17) P10L398–P11L413: It would be helpful for the reader to see all the data discussed in this section in one figure. Furthermore, it would be much more convincing to see correlation plots instead of time series (also in other parts of the manuscript).

18) Fig S7 / P11L416: It is obvious that especially OSs with similar retention times

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(i.e., 0.71–0.73 min) strongly correlate with each other. This is a strong indication that ionization artifacts produce these species (e.g., fragments, adducts, complexes, etc.), as they are all ionized at the same time in the ESI source. The authors should discuss and clearly state this in the manuscript.

19) P11L421: Any references which support this hypothesis?

20) Fig. S8: The figure has a bad quality and typos in the title. Moreover, the caption is not sufficient to understand the content of the figure.

21) P11L445: Do the authors mean regional background sites? (also at P12L450)

22) Fig. S10 / P12L463: Why is the Figure in the SI? It is an essential part of your data. Any hypothesis why the concentrations are higher at night?

23) Fig. 6: It would be beneficial to see a comparison to total PM or OM mass concentrations in the figure.

24) P13L526: There are no corresponding data shown to this discussion.

25) P14L546: So far, there was no clear discussion of NO_x levels and how they affect iSOA formation in Beijing.

Technical comments:

1) P5L184: What is “UPLC-MS2”? I think this term is very misleading here. If I understood the methods section correctly, the authors use full scan data for the quantification of the target analytes.

2) P9L341: The wording “high throughput screening” is quite exaggerated. The method described here is more like a standard data processing method of LC-MS data.

3) P9L355: I do not understand what the sentence “50 μ L of filter sample extract and ...” should tell the reader here.

4) P9L367: Use the notation “Table S1 and S2” to avoid confusion

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5) P10L389: I do not understand what this sentence should tell us here. Is this an important comparison to AMS data?

6) P14L540: Instead of “heterogeneous products”, better use “products from heterogeneous reactions”.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-929>, 2019.

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