Response to the Reviewers

We thank the reviewers for their comments, and we have addressed them below:

Response to Reviewer #1

In the study by Anunciado et al., the authors explored the stability of two organosulfur compounds and two organosulfate compounds. In the experiment, the atomized solution was collected on PTFE filters, and the weight and Fourier transform infrared spectroscopy analysis at different time scales were carried out. Furthermore, the stability of four sulfur compounds and their changes over time were analyzed by ion chromatography and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). It is reported that MS has the highest stability and can be determined using FT-IR, while 2-MTS is unstable and easily decomposed into other organosulfates or inorganic sulfates. However, the current form still has the following major problems that need to be paid attention to and solved. As a result, the manuscript required minor revision before it could be considered for acceptance by the AMT.

Major comments:

- The authors themselves are supposed to highlight the use of Fourier transform infrared spectroscopy to quantify organic sulfur compounds and organosulfates. However, there seems to be no quantitative information in the manuscript, so the author needs to explain this clearly in the manuscript. In other words, how can compounds be quantified by FT-IR?

Response:

We acknowledge that there was no quantitative information provided by FTIR results. The authors would like to clarify that quantifying organic sulfur compounds and organosulfates is important and that the ultimate goal of this research is to do FTIR calibration using FTIR spectra. At this stage, however, understanding the stability of organosulfates and organosulfur compounds collected on PTFE filters was not known. Therefore, the primary focus of the paper was on characterizing their FTIR spectra over time. Only then when stable OS compounds are identified in the laboratory, we can pursue our research experiment quantifying OS directly from filters collected from different AQ stations. To support the qualitative information provided by FTIR spectra, we supplement our FTIR results with quantitative information, thus the gravimetric, IC and ICPOES results.

The following text has been added:

Last sentence of the abstract has been modified as follows

Future work includes the evaluation of these compounds in as ambient aerosol sample matrix to determine any differences in stability, identifing interferences that could limit quantification and developing calibrations to measure the compounds or functional groups in ambient samples.

Line 148 the following sentence has been added.

Organic sulfur compounds and organosulfate functional groups were not measured in these studies.

Line 162 was added at the beginning of the last paragraph of the intro:

The goal of this paper is to assess the stability of four organic sulfur and sulfate containing compounds on polytetrafluoroethylene (PTFE) filters and the suitability of Fourier-transform infrared (FT-IR) spectroscopy to measure these compounds in the IMPROVE network.

- The particles generated by the atomization method lack basic characterization of the size of the particles themselves, and to what extent can they represent the ambient particle samples?

Response: The atomizer produces submicron polydisperse particles. Organics, particularly SOA are expected to be submicron and vary in size within this range (Rayleigh scattering regime) does not impact FT-IR measurement as the attenuation, primarily due to absorption, scales with the total volume of particles (Bohren, C. F. and Huffman, D. R.: Absorption and Scattering of Light by Small Particles, John Wiley & Sons, Inc., 1983). The following text was added to address this point.

Aerosols were generated using an atomizer (Kamruzzaman et al., 2018; Ruthenburg et al., 2014) and dried with a diffusion dryer (Model 3074B Filtered Air Supply, TSI Inc., St. Paul, MN) **which produces a high concentration of poly disperse submicrometer sized particles allowing for short collection times and adequately representing the expected response from particles of similar size range in the atmosphere**.

- In the later time scale, why does the mass of the filter decrease and then increase? The author may need to analyze and give some reasons and explanations from different aspects. On this long time scale, how were the collected filter samples preserved, were they dried, and the moisture absorption of the filter might have contributed to the increased mass.

Response

Storage conditions were not controlled in the laboratory but are monitored over time. Filters were kept and stored at room temperature (21°C – 27 °C) and relative humidity of the lab are measured within 30±10% For this study, we want to mimic ambient air in the lab by not controlling environmental condition which could have led to water adsorption as discussed beginning on line 332 for MSA. Similar discussion are included for other compounds. The following two paragraphs discuss other causes of increase in mass including ammonium adsorption and chemical fragmentation. Text in line 222 was added to specify the storage conditions and the reasons for them.

Filters were stored at room temperature (21°C – 27 °C) and relative humidity (30%± 10%) to mimic the storage conditions for ambient IMPROVE Teflon filters.

- Why do the spectra curves coincide with the horizontal scale in all FT-IR spectra? It looks very ugly. Therefore, it is suggested that the author redraw the diagram so that the spectra is completely on the upper side of the axis. Also, the right panel coordinates in Figure 2 should start at 1500, not 500.

Response

Line 298: Figure 2 coordinates was modified. Figure 4 spectra were scaled and the figure replaced.

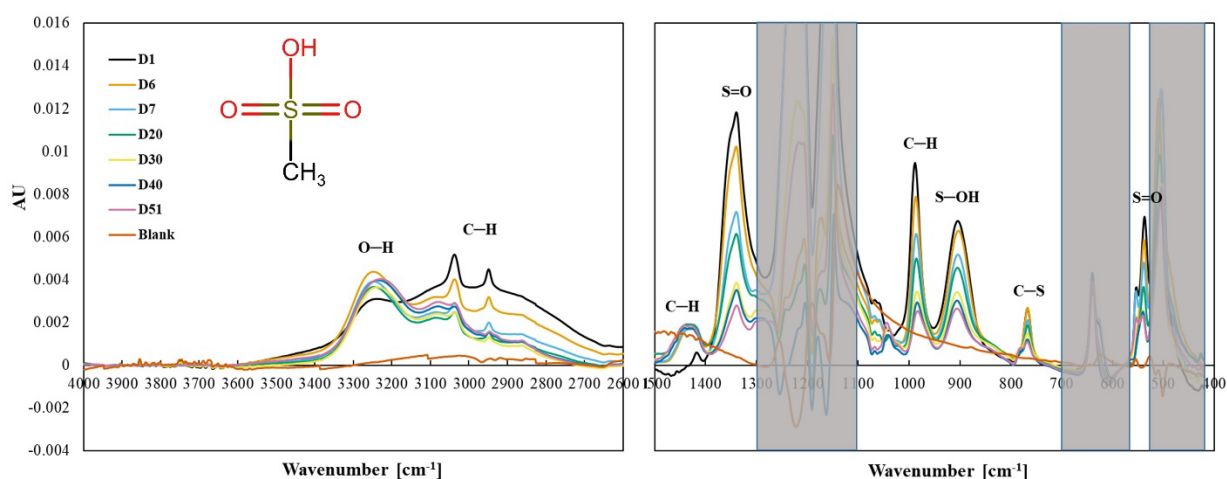



Figure 2

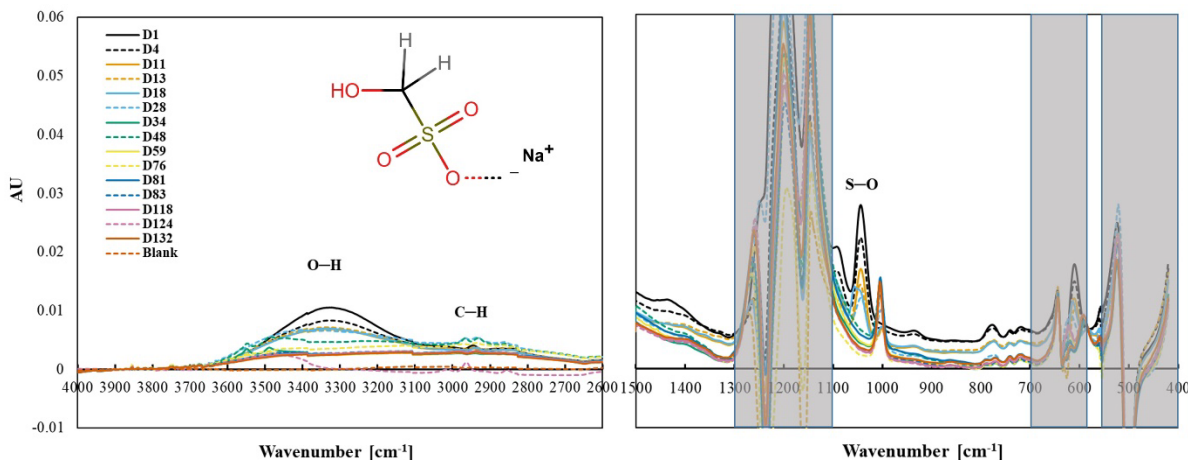



Figure 4

- What data did the author use to calculate the mass loss of 2-MTS, i.e., the amount of loss to generate different compounds? Is there any relevant literature? It is necessary for the author to explain this process clearly.

Response

Line 556: Theoretical mass loss calculations were performed based on the compounds molecular weight and the assumption that the moles of sulfate stayed constant. The end points we used (2-MGOS, GAS and ammonium sulfate) were based on Chen et al., 2020, Zhao et al., 2020; Wei et al., 2020, Harrill, 2020 as described in the paragraph just proceeding this discussion. Each conversion is assumed to go to completion as stated in each of the sentence stating the mass loss.

Following phrase was added to sentence starting in line 588.

To further evaluate the possible compounds on the filter at the end of the experiment, mass loss calculations were performed **using the molecular weight of 2-MTS and each product (MGOS, GAS and ammonium sulfate).**

The format of references is rough, and the names of quoted journals are either full name or abbreviated, which need to be carefully checked and unified.

Response:

The authors reviewed the references and updated all this incomplete information.

Minor comments and suggestions:

- Page 7: "arctic region"→"Arctic region"

Response:

Line 122: arctic changed to "Arctic"

- Page 11: "cadmium telluride (MCT) detector" →"mercury cadmium telluride (MCT) detector"

Response:

Line 215: mercury was added to "cadmium telluride (MCT) detector"

- Page 14: A mistake (24 C˚C).

Response:

Line 279: the extra "C" deleted

- Figure 7: The position of the first S-O-C is incorrectly marked

Response:

Line 467: Figure 7 was modified

- Figure 9: The labeling range of CH_3 functional groups is too broad

Response:

Line 506: label was reduced

- Page 28: "at3426 cm^{-1}", the author should add a space

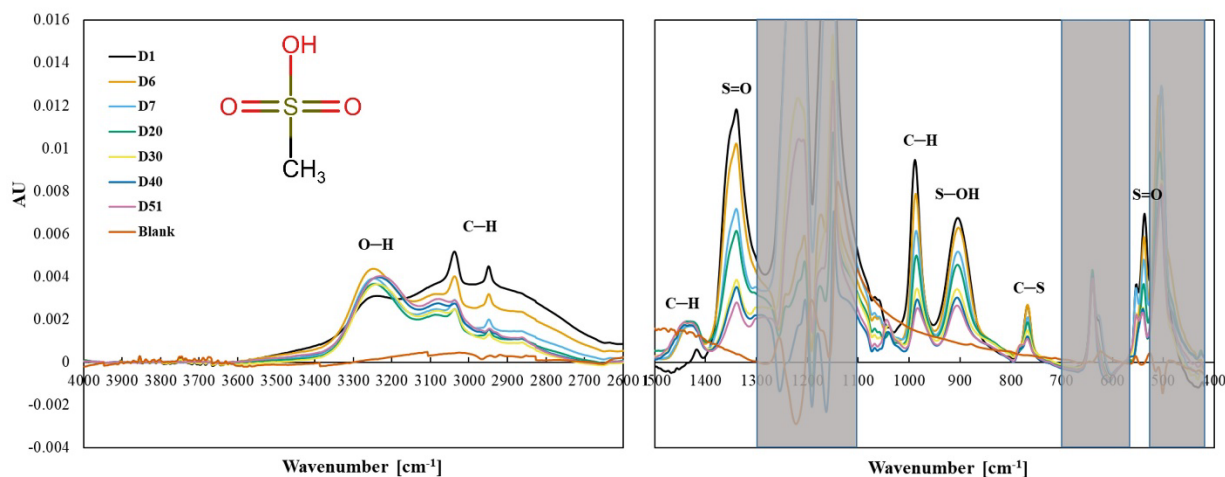
Response:

Line 523: space was added

Response to Reviewer #2

- The paper would be improved by the addition of a figure that shows the structures of the materials investigated (and their degradation products) with the acronyms used, rather than just describing the molecules in the text.

Response:

Thank you for this excellent suggestion to improve readability of the paper. We added the molecular structures of the four organic sulfur compounds to the spectra figures. Here is an example of the first figure.

- The details of the infrared measurements must be clarified. Are the filters measured in transmission or by attenuated total internal reflection (ATR) or by some other method?

Response:

Line 231: Add the language "transmission mode" to the below statement.

Transmission mode measurements were made using 512 scans for each filter at 4 cm^{-1} resolution and ratioed to the most recent (less than 1 h) background spectrum to obtain absorbance spectra using OPUS software (Bruker Optics, Billerica, MA)(Debus et al., 2019).

- Are the spectra presented difference spectra (i.e. [PTFE + sample] - [PTFE])?

Response

To clarify how we manipulated the spectra to remove interferences from PTFE, he following paragraph was modified (bold text) to explain the spectra manipulations that were performed.

To better visualize functional groups in the organosulfur compounds **and minimize the impact of the PTFE scattering and absorption on the spectra, several steps were taken**. Spectra were baseline corrected from 1500 cm^{-1} to 500 cm^{-1}, using blank correction and smoothing spline

fitting (Kuzmiakova et al., 2016)   The spectral region from 4000 cm^{-1} to 1500 cm^{-1} were baselined using an automated version of the Kuzmiakova et al., 2016 smoothing spline process in AirSpec (Reggente et al., 2019). Regions with large PTFE absorption (1300-1100 cm^{-1}, 700-600 cm^{-1} and 500-420 cm^{-1}) were grayed out in spectra plots and are not considered for peak identification.