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Reply on Anonymous Referee #2

Alexandra J. Boris et al.

Author comment on "Quantifying organic matter and functional groups in particulate matter filter samples from the southeastern United States – Part 2: Spatiotemporal trends" by Alexandra J. Boris et al., Atmos. Meas. Tech. Discuss.,
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Interactive comment from Anonymous Referee #2

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Please see responses in italics

This manuscript describes FTIR analysis coupled with multivariate calibration of specific functional groups (aliphatic C-H, carboxylic COOH, oxalate O=C-O-, non-acid and carbonyl C=O and alcohol O-H) in filter-based fine PM samples collected at the surface over 8 years at 4 sites in the southeastern United States as part of the former SEARCH air quality network. The authors find that there is a decline in organic mass that is driven primarily by carboxylic acid and oxalate functional groups. They attribute this to reductions in anthropogenic emissions of SO₂ and/or VOCs. There is a lot of analysis and the supplemental information is extensive.

We appreciate your positive assessment of our work.

Control experiments and quality assurance are discussed in the supplemental information (SI). It is difficult to understand the impact of not storing samples frozen over several years, and the SI indicates there is chemical change. Looking at Figure 4, my first instinct was the annual trend is related to sample degradation - I actually think a more thorough discussion in the main text would help the authors' case.

This critique provides an important perspective for us on this matter. We have moved material from the SI to the main text to more visibly discuss the possibility of sample degradation as a cause of OM decline over the sample years.

In order to further clarify and support our hypotheses, we have taken the following measures:

- *Discussion points from our first paper, where these storage studies were initially reported, have been moved to the Discussion section of this paper (Section 3.2; page 13-14). Specifically, we have expanded upon the variability of re-analyzed filters and differences between shorter- and longer-term storage. We have additionally highlighted changes in COOH and oxOCO in particular, since these two FGs were observed to*

decline over time in the present work.

- *The observation that the 2009-2010 FG and OM concentrations were actually increasing (due to the 2008 recession) also supports the lack of OM loss during storage; this has been further highlighted in Section 3.2 (page 13-14).*
- *The cold storage of filters (< 4 °C) to minimize loss of volatile species is now mentioned in the Methods section (Section 2.1, page 5) and within the Discussion section (Section 3.2, pages 13-14).*

Further, the authors attempt to make links to temporal trends among NO_x or O₃ with specific FTIR-derived functional groups almost exclusively with literature concerning ambient data. It's my opinion that links to laboratory literature with reference to specific spectra wavenumbers help make their arguments stronger.

There have only been limited studies of laboratory (chamber) experiments published thus far using infrared spectrometry, and studies quantifying specific molecules (for which FG composition is known) explain only a small fraction of the overall OM mass. Due to aging times, specific fuels or precursor molecules, and photooxidation conditions, the resonances of functional groups in condensed molecules may vary according to a variety of intramolecular and intermolecular interactions. Therefore, broad ranges rather than specific wavenumbers are used to interpret the FG composition in this study. However, biogenic secondary organic aerosols observed in various ambient environments are consistent with reported FG composition and spectral profiles due to oxidation of biogenic precursors in chamber experiments (for example, Corrigan et al., 2013; Liu et al., 2018).

*Corrigan, A. L., Russell, L. M., Takahama, S., Aijälä, M., Ehn, M., Junninen, H., Rinne, J., Petäjä, T., Kulmala, M., Vogel, A. L., Hoffmann, T., Ebben, C. J., Geiger, F. M., Chhabra, P., Seinfeld, J. H., Worsnop, D. R., Song, W., Auld, J., and Williams, J.: Biogenic and biomass burning organic aerosol in a boreal forest at Hyytiälä, Finland, during HUMPPA-COPEC 2010, *Atmospheric Chemistry and Physics*, 13, 12 233–12 256, doi:10.5194/acp-13-12233-2013, 2013.*

*Liu, J., Russell, L. M., Ruggeri, G., Takahama, S., Claffin, M. S., Ziemann, P. J., Pye, H. O. T., Murphy, B. N., Xu, L., Ng, N. L., McKinney, K. A., Budisulistiorini, S. H., Bertram, T. H., Nenes, A., and Surratt, J. D.: Regional Similarities and NO_x-Related Increases in Biogenic Secondary Organic Aerosol in Summertime Southeastern United States, *Journal of Geophysical Research: Atmospheres*, 123, 10,620–10,636, doi:10.1029/2018JD028491, 2018.*

In response to the reviewer's concern, we have simplified and moved much of the material in this literature-based discussion to the Supplement. The discussion in the manuscript highlights the findings of other FT-IR spectrometry studies, including the work cited above, and particularly work done using samples from the SE U.S. However, as mentioned above, the FT-IR spectrometry literature is still somewhat limited, so we hope to only suggest probable links to atmospheric sources or processes in other discussions.

I found Table 2 very confusing. It appears the aCH trend is driven by 'just' BHM summer, COOH 'just' in the summer, but many other values are presented. I understand how this would be value for careful readers. However there are more compelling plots in the SI that I think would make better use of the main text space.

We appreciate the reviewer's precise suggestions for improving the clarity of our paper. We have moved Table 2 from the main text to the Supplement and have embedded important values from that table within the text. In an effort to keep our manuscript succinct, we have decided not to move additional figures from the Supplement.

Page 4, Line 16: The authors state fossil fuel combustion may contribute substantially to

OM in the SE U.S. I think the authors here are referring to the carbon component specifically. It is well established that fossil fuel combustion aids OM formation, e.g., impacts on the NO_x/oxidants and POA are known for over a decade...work by Lane, Griffin, Carlton.

Upon considering the literature suggested by the reviewer, we have altered the text here to specify known effects of fossil fuel combustion on OC and OM concentrations. The text now reads (Section 1.2, page 4):

"Fossil fuel combustion contributes substantially to OC in the SE U.S., especially at urban sites: ~50 % of primary and secondary OC at urban BHM was estimated to be from fossil sources, but at rural CTR, >80 % of primary and all of secondary OC was from modern sources such as trees (in the early 2000s; Blanchard et al., 2008). In addition, other emissions from fossil fuel combustion, including NO_x, SO₂, and primary OM, also affect OM concentrations by modulating aerosol surface area, aerosol water content, aerosol acidity, and oxidant concentrations (Nguyen et al., 2015; Carlton et al., 2010; Al-Naiema et al., 2018)."

Al-Naiema, I. M., Hettiyadura, A. P. S., Wallace, H. W., Sanchez, N. P., Madler, C. J., Cevik, B. K., Bui, A. A. T., Kettler, J., Griffin, R. J., and Stone, E. A.: Source apportionment of fine particulate matter in Houston, Texas: insights to secondary organic aerosols, Atmos. Chem. Phys., 18, 15601–15622, <https://doi.org/10.5194/acp-18-15601-2018>, 2018.

Carlton, A. G., Pinder, R. W., Bhave, P. V., and Pouliot, G. A.: To What Extent Can Biogenic SOA be Controlled?, Environ. Sci. Technol., 44, 3376–3380, <https://doi.org/10.1021/es903506b>, 2010.

Nguyen, T. K. V., Capps, S. L., and Carlton, A. G.: Decreasing Aerosol Water Is Consistent with OC Trends in the Southeast U.S., Environ. Sci. Technol., 49, 7843–7850, <https://doi.org/10.1021/acs.est.5b00828>, 2015.

Page 11, Line 6/7: I do not follow the logic behind the statement that OM trends are unrelated to changing PM_{2.5} concentrations due to lack of trend in Si and K. These species

We have removed this sentence from the manuscript; it was unnecessary.