Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-619-RC2, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric Evolution of Emissions from a Boreal Forest Fire: The Formation of Highly-Functionalized Oxygen-, Nitrogen-, and Sulfur-Containing Compounds" *by* Jenna C. Ditto et al.

Anonymous Referee #2

Received and published: 16 September 2020

ACP manuscript 2020-619 reports on the detailed chemical composition of gas- and particle-phase samples collected from a boreal forest fire under ambient conditions. Samples were analyzed using gas and liquid chromatography (GC, LC) with detection by high-resolution and tandem mass spectrometry (MS, MS/MS). The focus of the analysis was on organic compounds, particularly those containing carbon, hydrogen, oxygen, nitrogen, and/or sulfate functionalities ("CHONS"); including as a function of plume age. Targeted and non-targeted approaches were used. Using both GC and LC allowed analysis of less polar (GC) and more polar/more functionalized compounds

(LC) than could be achieved using a single method. Results are largely discussed in the context of elemental composition, with less focus on compound identification. It was observed that during aging particle-phase CHO compounds became less abundant, while particle-phase CHON(S) became significantly more abundant. The paper also presents precursors and pathways leading to the formation of observed sulfides included among the CHONS compounds. The paper is well written and presents interesting analysis and results that have not been presented before. The results, implications, and approach should be of interest to ACP readers. The methods are generally well described and could be reproduced based on the information provided in the SI. A few comments are provided below, both technical and editorial in content. The most significant comment on the technical side is that there are places in the manuscript where it is not clear if the compound volatility classes are being appropriately defined (i.e., based on published saturation vapor concentration ranges) based on the observed gas- and particle- phase distributions.

Technical Comments:

line 96: Is the uncertainty on the MCE values really +/- 0.4? That seems very large, given the typical range of ambient MCE values.

Starting on line 104, the description of the volatility range of compounds sampled is a little unclear. It seems that compounds that are largely in the gas phase at OA mass loadings of 10-30 ug/m3 would be classified as I/VOCs and not SVOCs. On the other end of the spectrum, C10-20 compounds that are largely in the gas phase may be in the VOC range (and not necessarily in the I/SVOC range). This continues in 204-205, with discussion of "particle-phase" IVOCs; it isn't clear why at mass loadings of 10-30 ug/m3 of OA, particle-phase IVCOs would be above detection limits. By definition, such compounds are largely in the gas phase except at high OA loadings. In lines 241-243, it is suggested that compound types that have widely been observed in gas-phase smoke samples, evaporated with dilution. While a fraction of the directly emitted gas-phase compounds may partition to the particles, many of the compounds in the classes listed

are not expected to contribute directly to the particle phase. Such compounds first undergo chemical transformation to create lower volatility products and then condense to the particle phase. It is not clear whether the parent compounds and their products would be observed as the same mass fragments using the techniques described. The discussion of volatility and partitioning needs to be carefully reviewed throughout the manuscript, and revised for accuracy, consistency, and clarity.

line 134: What were the “strict” QC/QA guidelines for peak retention? These are not defined in the manuscript or SI.

line 198: Is quantification of filter species affected at all by compound volatility? Or is the extraction process sufficient to extract the presumed ELVOCs with reasonable recovery?

SI line 48: How was the collection efficiency of the AMS determined? Lim et al. 2019 ACP demonstrated the significant impact of CE on

SI line 83: I’m assuming that the field blanks were used to correct for background, and not to reduce background as stated here.

Editorial Comments: line 62: In this context, what is meant by “unprecedented”? Is it in reference to the analytical techniques used? Or the extent of chemical composition data obtained? Other?

line 113: No hyphen is needed between “gas” and “phase” (also in line 224 in the SI). SI line 75: remove one of the “s” on “VOCss”

line 129: “mode” should be plural

SI line 295: suggest to move the Kroll et al reference as it suggests the values themselves (rather than the approach) are from Kroll et al.

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