Interactive comment on "Airborne Extractive Electrospray Mass Spectrometry Measurements of the Chemical Composition of Organic Aerosol" *by* Demetrios Pagonis et al.

Alexander Vogel (Referee)

vogel@iau.uni-frankfurt.de

Received and published: 12 November 2020

Pagonis et al. show airborne measurements with the extractive electrospray ionization mass spectrometer (EESI-MS) during the FIREX-AQ campaign. They describe quantitative measurements of the biomass burning markers levoglucosan and nitrocatechol in the condensed (aerosol) phase using the positive and negative EESI mode. A careful characterization of inlet losses and particle-size-dependencies of the EESI extraction is presented. A quantitative comparison to an AMS and a CHARON-PTR-MS dataset of levoglucosan (at 1 Hz acquisition) during BB plume intersects impressively demonstrates the agreement between the different techniques. An overestimation of

the levoglucosan AMS signal appears plausible, since oligomeric sugars in BB aerosol can fragment and contribute to m/z 60 in AMS spectra. Oligomeric sugars might appear as intact molecules in the soft-ionization instruments, and thus explain the bias.

The quality of the graphs is very good and the language is fluent and precise. Overall, I can recommend the paper to be published in AMT after addressing the following minor comments:

Minor comments:

Have you considered to check the negative spectra for other nitroaromatics in the BB plumes, e.g. nitrophenol and di-nitro-aromatics? To extract new information from the chemical composition of BB plumes through soft-ionization MS (in addition to what the AMS is already able to show), I think it is important to identify other organic markers that tell something about the origin, age, volatility or multiphase processing of fire plumes. It might be out of the scope of this technical paper, but some motivational words about why we need soft-ionization MS should appear in the introduction.

l. 110: Switching a valve –> low pressure transient –> loss of electrospray? Is this an issue?

l. 120 and throughout the manuscript: please use the minus sign instead of a hyphen in EESI($-$) and negative ions (e.g. ($C_2H_3O_2-$) in l.121.

l. 154: What is the maximum delta T between ambient and aircraft cabin during the campaign? Aren't higher losses expected for aerosols at higher altitudes (colder conditions), since intermediate-volatile compounds might expel levoglucosan into the gas phase when they evaporate during sampling? Can this be an issue?

l. 173: 100 ppm of NaI appears to me as a high concentration of a non-volatile salt, which mass spectrometrists usually like to avoid blowing into the MS. This working solution has been used in past EESI studies, but also caused to my knowledge trouble during field experiments. Can you please report how robust is the electrospray against

salt deposition on the tip of the EESI needle? Would a volatile ammonium salt (e.g. ammonium acetate) be an alternative to NaI?

l. 174: Doping the working solution with formic acid in negative ionization mode is questionable. Formic acid is a stronger acid than nitrocatechol (the analyte in the negative ionization mode). At low pH, there might be a suppression of the nitrocatechol ion formation due to a high proton concentration. In our lab we tested the sensitivity of Ibuprofen (organic acid) ionized with ESI($-$), and we found two orders of magnitude higher sensitivity when leaving formic acid (0.1 % v/v) out of the mobile phase solvents.

However, ESI and EESI are different ionization processes, and it might be correct that under EESI conditions the formation of FA-anions is occurring before collision with the sampled aerosol. Then the low pH of the working solution might not appear problematic. But, if the electrospray droplets hit the sampled aerosol before Coulomb explosion, a low pH of the EESI working solution might suppress the ionization. Please explain or comment.

l. 270: How well is the HR-fit during background measurements of levoglucosan? Can it be that the high LOD for levoglucosan can partly be explained by erroneous peak attribution to levoglucosan from the left shoulder of $C_8H_{18}O_3Na+$? Please provide a figure in the SI of the HR fit during a background measurement.

Figure S10 shows for EESI(+) that only a few compounds (<10) have signal-to-background ratios above one, indicating that background correction potentially can introduce a large bias on the signal intensity. I think the authors were very careful in determining the EESI background. However, no figure reports the variability of the background signal between subsequent HEPA-background measurements. I think that such a figure or a table (with the mean and SD of the grey area in Fig. S1 for a set of background measurements) would be beneficial in order to provide the reader an impression of the background variability.

l. 339: Having a larger overall OA sensitivity during BB-episodes has also been

demonstrated by other online soft-ionization methods than EESI: In Vogel, AMT, 2013 (https://doi.org/10.5194/amt-6-431-2013) we showed in figure 5 that during a biomass burning episode we observed an above-average of APCI OA signal compared to AMS OA.

Technical notes

l. 121: The acetate signal in Fig S2 exceeds 100 cps.

l. 144: SESI –> EESI

Figure 4: Numbers on the y-axis of panel B and D are missing.

Figure 4: I assume that the green spectra are the ones that are background-corrected? This should be clear from the legend.