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Comment on acp-2021-1033

Anonymous Referee #1

Referee comment on "Highly time-resolved chemical speciation and source apportionment of organic aerosol components in Delhi, India, using extractive electrospray ionization mass spectrometry" by Varun Kumar et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1033-RC1, 2022

The study by Kumar et al., investigates sources contributing to SOA in Delhi (India) via source apportionment of data from EESI-TOF and AMS. In general, this paper is well structured and presents interesting results to aerosol community. I have a few comments below, which I think need to be addressed before publishing this work at ACP.

The authors inform a reader about disadvantages of widely used analytical instrumentation for aerosol characterisation and apply EESI and AMS for their study. I agree that EESI technique certainly has some advantages (which the authors briefly listed in the introductory section); however, as any other techniques, it has numerous limitations (e.g. sensitivity), which, I believe (to avoid any biases) need to be reflected in the introductory section. I believe for this reason, off-line organic analysis techniques are still widely applied for aerosol characterisation (Noziere et al., 2015). Another disadvantage of the later technique is that it employs electrospray ionisation which suffers from competitive ionisation and lead to signal enhancment or supression. This is affected by a compound's functional group (-OH, -COOH) and presence of inorganic salts in the matrix that are important constituents of atmospheric aerosols (Noziere et al., 2015).

The authors need to be more specific what they mean by atmospherically relevant compounds when stating detection limit ''*in order of 1-10 ng m-3 for atmospherically relevant compounds* '' especially in light with the comments regarding competitive ionisation, selectivity and specificity of the applied technique. For example, PAHs (oxidised PAHs), sugar alcohols and carboxylic acids are atmospherically relevant compounds but have critically different ionisation efficiencies in ESI (and thus in EESI). Do you expect this technique to have the same ''in order of 1-10 ng m-3'' detection limit for all of these atmospherically relevant compounds? If yes, please provide a reference or data to support this statement.

Including a reference for the following statement would be beneficial or support this by

showing data: ‘’ In the configuration of the mass spectrometer and ionization scheme used in this study, one can detect a wide range of molecules present in the organic aerosols, including sugars, alcohols, acids, and organo-nitrates.’’

The authors report a range of molecular formula detected by the technique and relate them to specific compounds, e.g., levoglucosan. I failed to find the mass accuracy and resolving power of the applied EESI technique to support their molecular assignments. Please add this to the paper and consider how this will impact on the presented results (molecular assignments).

The authors associate $C_2H_4O_2^+$ (*m/z* 60) and $C_3H_5O_2^+$ (*m/z* 73) to levoglucosan. It is worth mentioning that other anhydrosugars (levoglucosan isomers) can lead to this fragmentation. These include galactosan and mannosan, which are isomeric compounds of levoglucosan and cannot be distinguished/separated by the applied technique. Again, this caveat needs to be stated in the manuscript.

Line 10 (page 12) ‘’*The mass spectra of BBOA-1 and BBOA-2 both have strong signals from $C_2H_4O_2^+$ (m/z 60) and $C_3H_5O_2$ + (m/z73) fragments, which are characteristic of anyhdrosugars like levoglucosan, a product of cellulose pyrolysis (Simoneit et al., 1999).*’’ needs revising. The work by Simoneit et al., 1999 reports data for TMS esters so the reference to levoglucosan fragments is invalid. If this reference was used to support the second part of the statement i.e., ‘’*a product of cellulose pyrolysis*’’, then the sentence needs revising as well.

Reference: Nozière B, Kalberer M, Claeys M, Allan J, D'Anna B, Decesari S, Finessi E, Glasius M, GrgiÄ I, Hamilton JF, Hoffmann T, Iinuma Y, Jaoui M, Kahnt A, Kampf CJ, Kourtchev I, Maenhaut W, Marsden N, Saarikoski S, Schnelle-Kreis J, Surratt JD, Szidat S, Szmigielski R, Wisthaler A. The molecular identification of organic compounds in the atmosphere: state of the art and challenges. Chem Rev. 2015 May 27;115(10):3919-83. doi: 10.1021/cr5003485.