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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of anthropogenic and biogenic sources on the seasonal variation of the molecular composition of urban organic aerosols: a field and laboratory study using ultra-high resolution mass spectrometry" *by* Kaspar R. Daellenbach et al.

Anonymous Referee #1

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Daellenbach et al. propose a comprehensive characterization of the molecular composition of aerosols sampled at an urban site in Central Europe (Zurich, Switzerland). Chemical composition is retrieved using an ultra-high resolution mass spectrometry (Orbitrap) and further compare with aerosols sampled during wood burning emissions from Alpine valleys and chamber investigations of wood smoke. Finally, samples from the boreal forest were also used to evaluate the influence of biogenic emission in aerosol formation in Zurich. The results presented in this work are interesting and

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provide important information on source apportionment of aerosol in Central Europe. The comparison lab and field data is particularly valuable. Overall, the interpretation and the results are well sustained. Therefore, I think the paper should be publishable after some comments are addressed.

General comments: page 2, lines 31-33: the authors mentioned that ESI coupled to a UHR-MS is a promising technique. It is now an established technique and cannot be classified as promising. Indeed many studies in atmospheric sciences and analytical chemistry have demonstrated the capabilities of the UHR-MS including the Orbitrap technology (commercialized by Thermo $\sim$ 15 years ago).

page 3, 1-3: Another major limitation of any offline technique compare to the AMS is the time resolution, which is worth mentioning.

page 3, 27-30: How many samples were analyzed? Different sizes (e.g., PM10, PM1,...) were chemically characterized and compared. However, the authors never mentioned the influence of the size, how would that impact the interpretation?

page 4, analytical procedure: The authors decided to use the Orbitrap in negative mode. Why didn't they explore the positive mode as well? As recently highlighted by e.g., Lin et al. (Anal Chem, 2018 10.1021/acs.analchem.8b02177) the positive mode can provide additional valuable information. The positive mode is generally less selective than the negative mode. Therefore for a global screening, both modes should be used.

page 4, lines 20-21. While replicate/triplicate measurements were performed the authors never mentioned the variability of their measurements. Screening analysis might bring large variability. Therefore, the authors should provide some statistical analysis in order to better validate their results/findings.

page 7, lines 21-23: As it is presented it is hard to see any correlation. Please provide the r or r2 for the different species to support the discussion (e.g., a table showing all

the r2 should be added). The authors mentioned that they measured the concentration of CO. How does CO correlate with other anthropogenic pollutants?

page 8, lines 4-15: It was already acknowledged by the authors that the relative contribution of a compound cannot be directly linked to its concentration(lines 1-3, page 3). However, it would be worth mentioning this point in this paragraph as it is an important aspect. Indeed, nitroaromatics are highly sensitive using ESI (-) but their large contribution to the MS doesn't imply that they are the most abundant species.

page 9, lines 18-19: Are the ratios (e.g., H/C or O/C) weighted by the area of the individual peak?

page 9, line 22: Accretion products imply aerosol processes (i.e., IUPAC definition). However, the chemistry describes by Berndt et al is a gas phase process. In addition, it is unlikely that these compounds arise from isoprene-RO2 + monoterpene-RO2 as isoprene concentration is very low in the Boreal forest and contributes overall to a small fraction of the OH and O3 reactivities (e.g., Hakola et al., 2012).

page 10, lines 1-5: Those products were also formed from the oxidation of isoprene (e.g., Surratt's group). Please check the literature and provide some information on the concentration of isoprene within the studied areas.

page 10, 3.4.2: The discussion of this paragraph is not consistent with the previous section. For instance, as it is written the authors suggest that the C4 & C5 compounds are formed from the aging of monoterpene-derived SOA but in the paragraph 3.4.2 they mention that the isoprene emissions are larger in Zurich than in Hyytiala, implying that isoprene chemistry plays a bigger role in Zurich. Please clarify and make the discussion more consistent.

page 13, lines 33-34: Based on the molecular signature of this group, can the authors propose a potential source? Could it be the VCP recently highlighted by McDonald et al. (2018, science)?

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Figure 3b: Why is the dendrogram not symmetric? For instance, hyytiala 2011 vs hyytiala 2014 is different than hyytiala 2014 vs hyytiala 2011. It should not be like that, or should it be (if so, please explain)? In addition, the axes are not consistent compare to Figure 3a. Please revise Figure 3b to be consistent with Figure 3a.

Figure 5 (and S3) is hard to read. Please make all the graphs bigger. Another option would be to split the figure and have one figure for biogenic conditions with Zurich summer, Hyytiala 2011/2014 and possibly Zurich winter. Another figure will include wood burning experiments and episodes as well as Zurich winter.

Figure 7a is really hard to read and does not bring much information, as it is. It can be one separate figure and once again split between biogenic and wood burning SOA.

Figure 9 (and S4) doesn't include Zurich winter. Why?

technical comments: page 1, line 19: define OA page 2, line 22: Marseilles should be Marseille

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