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Journal: Atmospheric Measurement Techniques Discussions**Title:** Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry**Authors:** K. Daellenbach et al.**General comments:**

This manuscript presents chemical characterization and source apportionment of the organic fraction performed on PM₁, PM_{2.5} or PM₁₀ filter samples using offline aerosol mass spectrometry (Aerodyne HR-ToF-AMS) and compares the obtained results with those more classically determined by concomitant online AMS(ACSM) measurements. Although the offline chemical analysis method is not new but scarcely used with this type of instrument (as mentioned by the authors themselves), the extended datasets used here (16 rural and urban sites for a total of 256 samples but limited to Switzerland and Paris, France) allows for a more robust interpretation of source apportionment modeling. The conclusions should probably emphasize more the fact that most conclusions are drawn from the detailed analysis of one particular dataset from Zürich. Nevertheless, the main interest of this method is to better characterize the supermicronic fraction, especially for coarse primary organic sources, where continuous ACSM measurements are limited to submicron particles, as highlighted in the conclusion. This opens a promising way to test this methodology in other types of environments and better utilize filter samples collected worldwide for source apportionment studies.

Specific comments:

P8601 L25: The reference of Braun-Fahrländer et al. (1997) is more linked to indoor air quality. The authors could eventually cite the more recent review from Kelly and Fussell (2012) that deals specifically with health impact of fine particles.

P8602 L20: The authors state that the oxygenated organic aerosol factor (OOA) is generally considered as a proxy for secondary organic aerosol (SOA), classically defined as aerosol coming from gas-to-particle conversion processes. Although this is true in areas close to biogenic sources, it should be mentioned that OOA is probably a mixture of SOA and aging of primary organic aerosol (POA) in urban areas. This comment can also be considered P8615 L22.

P8602 L27: Another important drawback of ACSM compared to AMS is the absence of particle sizing.

P8603 section 2.1: Important information is missing in the text: sampling time (found in Table 1), seasonal distribution of the filters over the yearly campaigns (are they evenly distributed?), storage conditions of the filters (particularly of importance when dealing with possibly semi-volatile organic matter), time between collection and analysis of the filters.

P8605 L5-7: It would be interesting to know if the AMS spectra have been recorded in both V and W modes, or just in the high resolution one. If V-mode (and PToF) information is available, was the size distribution of nebulized particles assessed and what particle size is

generated by this custom-built setup? (for instance Mihara and Mochida obtained size distributions centered around 300 nm mobility diameter).

P8607 L9: Please give an indication of the percentage of variables with low S/N ratios that have been excluded.

P8609 L12: Why did the authors choose to apply a rolling window using temperature-sorted data? This choice is not explained although using chronological data would seem a more obvious approach and should be able to distinguish seasonal variations as well?!

P8611 L7: It should be mentioned that sulfate is mostly bonded to ammonium because of the absence of any known major SO₂ source at this specific site. This assumption may not always be true and should be checked at other locations.

P8612 L13: Did the authors observe any time trend in the recoveries of the organic fraction? In particular, it could be expected that primary biogenic particles or SOA formation would be more important in summer (as observed by Waked et al. (2014) at a Northern French site where primary biogenic emissions represented up to 40% OC in summer), with organic species more hydrophilic than in winter when major combustion sources (traffic, heating) are expected to contribute to the organic fraction.

P8617 L9: Authors have decided to use Equivalent Black Carbon (EBC) as a marker for HOA. However Black Carbon can be emitted both from vehicle exhaust and biomass burning so could be partially correlated with BBOA as well. Depending on the type of aethalometer used (see technical comment on P8604 L5), the contribution of fossil fuel (FF) and wood burning (WB) to BC concentrations may be investigated using the well-known approach of Sandradewi et al. (2008). Although Herich et al. (2011) confirm that FF is the major contributor to BC in summer for PM_{2.5} sampled at the same site in Zürich (90%), WB contribution was estimated at 25% in winter. Similar observations were made for the Paris site with an average contribution of 20% in winter (Favez et al., 2009). So, if possible, the authors should comment on that point.

P8618 L16-17: Due to the impossibility to separate the BBOA factor using ME-2 on the online ACSM dataset, a known BBOA profile from the literature was used. I was wondering why the BBOA profile from the offline solution was not chosen as a constraint. One could think it would better represent the type of wood burning from the Zürich area. In my opinion, it should also improve the correlation plotted Figure 11c and finally lead to a R_{BBOA} recovery value (P8621 L5-6) only due to the difference in the size fraction collected, or at least not biased by possible site-dependent BBOA ... or am I mistaken somewhere?

References:

* Favez et al. (2009)

<http://www.sciencedirect.com/science/article/pii/S1352231009003690>

* Kelly and Fussell (2012)

<http://www.sciencedirect.com/science/article/pii/S1352231012006024>

* Herich et al. (2011)

<http://www.atmos-meas-tech.net/4/1409/2011/amt-4-1409-2011.html>

* Sandradewi et al. (2008)

<http://pubs.acs.org/doi/abs/10.1021/es702253m>

* Waked et al. (2014)

Technical corrections:

P8604 L4: “source apportionment” (missing word?)

P8604 L5: please specify the aethalometer model

P8605 L21: please check the Pika version (not the same as the Squirrel one)

P8605 L26: please indicate the column supplier (Metrohm, etc.)

P8607 L12: please indicate the SoFi version (especially important since new features such as time-dependent S/N ratios are implemented in the most recent one and do not seem to have been used here – see comment about L9)

P8608 L11: delete “added in quadrature” – already in the sentence L9

P8608 L14: “concentrations” (“t” missing)

P8609 L10: delete “contains” (two verbs in the same sentence)

P8611 L4: “aerosol” (no “s”)

P8612 L22: rather “PM_{<2.5}”?

P8614 L26: “apportionment”

P8614 L27: “those”, not “these”

P8616 L1-3: revise the sentence structure (one extra closing bracket at the end)

P8616 L5-6: “additional”

P8616 L16: move the comma before “and”, not after

P8618 L14: “5-factor”

P8621 L1-5-6-7: four occurrences of “quartiles” (should be plural)

P8622 L10: shouldn't the two “/EBC” on this line be no subscripts?

P8622 L10-11-12-22: six occurrences of “quartiles” (should be plural)

P8623 L3-4: information on Quartz-Pall filters should probably be better located in the 2.1 section (e.g. P8603 L16)

P8633 Figure 1a: why no number 8?

P8636 Figure 4: Please specify if the mass spectra for online analyses correspond to a single record or if they have been averaged over the same period as the offline analyses.

P8637 Figure 5: What do the error bars represent? Are the R_{frag} values mean recoveries?