Author response to anonymous referee #1

We thank the reviewers and editor for their critical reading and important input. In the following we address the questions point by point (reviewer comments in italic, our replies in normal font, changes in the manuscript marked in blue).

General comments

This manuscript presents chemical characterization and source apportionment of the organic fraction performed on PM1, PM2:5 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.

We thank the reviewer for providing a better suited reference. We included it instead of Braun-Fahrländer (1997).

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.

The comment is considered: at *P8615 L22:*

In the selected 5-factor solution, the non-constrained factors extracted by ME-2 were related to BBOA, a highly oxygenated (OOA1) and moderately oxygenated (OOA2) organic aerosol; the sum of OOA1 and OOA2 will be henceforth considered as a proxy for secondary organic aerosol (referred to as OOA) which can though be mixed with aged primary organic aerosol.

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

The AMS allows particle sizing but the size of the particles is determined by the nebulizer and thus not interpretable in an environmental sense. Therefore, we prefer for clarity not to mention PToF as an advantage of offline AMS compared to ACSM. However, we agree with the reviewer that with the offline AMS methodology we can analyze size segregated particle samples (e.g. PM1, PM2.5 and PM10) and draw some conclusions on OA sources in the different particle fractions. As stated in the manuscript:

These results are expected to significantly broaden the spatial, temporal, and particle size ranges accessible to AMS measurements of organic aerosol.

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.

This information was added as:

Field blanks were collected using the same method as for the exposed filters. The filters were stored in sealed bags at -18°C and only transported cooled. Before handling the filters, they were left for 15 minutes at room temperature in the sealed bags in order to avoid condensation of volatile compounds on the cold surface. The offline AMS analysis of the filters collected in April 2011 in Zurich were conducted in October 2011. The other filters were analyzed between April and October 2012. While samples were collected at different seasons at 16 sites including urban, suburban and rural sites (Table 1), we will mainly focus on the Zurich datasets (filters evenly distributed in the years 2011-2012) because of the extensive supporting measurements performed there. Measurements on the remaining samples are used for the assessment of the bulk OA water-solubility.

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).

The comment was included as:

The resulting particles are dried by a silica gel diffusion dryer, and subsequently analyzed by the HR-ToF-AMS (V-mode).

…

The particles generated with this nebulizer have a mode diameter of ~200 nm (dV/dlogDp).

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

No variables had to be discarded because of low S/N. It was not mentioned in the manuscript but there were 19 variables excluded from the PMF matrix since they were not present in the reference spectra used.

The text was adapted as following:

For offline AMS analyses, both sample and blank uncertainties are incorporated. Following the recommendation of Paatero and Hopke (2009), variables with low signal-to-noise (SNR < 0.2) are removed (no variables affected), whereas "weak" variables (0.2 < SNR < 2) are downweighted by a factor of 3 (26 variables in the PMF input affected). Further, 19 variables were not considered in PMF because they were not present in the reference spectra used.

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?!

PMF on ACSM data is mainly based on the diurnal variability. Distributing the data in shorter periods allows a better adaptation of the PMF solution to the variability.

As the reviewer mentions, sorting the data chronologically is a good option. Canonaco et al., 2015 showed for Zurich (same data as used for the online ACSM source apportionment in this manuscript) a strong temperature dependence of f44 in SOA. Therefore, we decided to sort the data with respect to the daily average temperature before PMF. This way, days are grouped in the same window if they have similar daily average temperatures which reflects similar conditions for SOA formation. Furthermore, BBOA is typically anticorrelated with temperature.

Accordingly the manuscript was altered as following:

The PMF window was rolled over the temperature-sorted Zurich data (by daily average temperature). By sorting the data with respect to temperature, days with similar conditions in terms of SOA formation and dominant primary sources (e.g. BBOA at lower temperature) are grouped together. For every window the solution was optimized using criteria based on correlations between the time series and the diurnal cycles of the factors and those of the markers.

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.

Indeed, we agree that sulfate has to be inorganic and bonded to ammonium so that we can accurately detect it in the AMS. A word of caution is added in the text about this. The sulfate was used in our case to estimate the OA recovery, when other data was not available (e.g. direct measurement of WSOC). However, we show that for our conditions the recovery estimates based on the WSOC/OC and those based on the sulfate are comparable within our uncertainty, which support the use of sulfate as quantitatively extractable and measureable specie.

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.

The fitted R_{bulk} shows no seasonality and captures the measured recoveries within the experimental errors (Figure 4). Note that these measured recoveries are based on the extraction efficiency using water as a solvent, while other parameters (e.g. gas/particle equilibration upon nebulization) can come into play influencing the recoveries. The measured R_{bulk} is noisy and shows values up to 1.3 during winter 2012 which might indicate an error of up to 30%. The fitted R_{bulk} does not track extreme events well because PMF does not represent them accurately (e.g. low outlier corresponding to heavily cooking influenced day in summer). Given these uncertainties, we think that there is also no visible seasonality in the measured R_{bulk}. Throughout the year OOA is dominant and thus also no strong seasonality of R_{bulk} is expected.

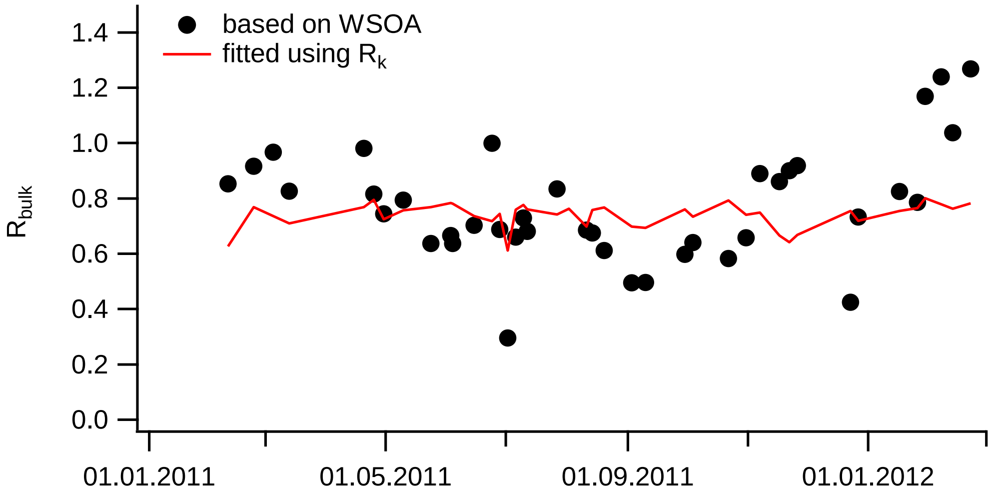

Figure 4: R_{bulk} estimated based on WSOA used in Figure 3.c in the manuscript and fitted using R_k shown as a time series.

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 PM2.5 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.

The deployed aethalometer model (AE 31, Magee Scientific Inc.) allows the separation of eBC into eBC_{wb} and eBC_{tr}. Besides using eBC as an HOA marker, the quality of the solution was also checked using eBC_{tr}. For both markers, the same a-value combination was considered best according to the overall criterion. Both eBC_{wb} and CO are good BBOA tracers. Since eBC_{wb} in this dataset is noisy, we chose to use CO.

We added the following sentence:

… Besides using eBC as an HOA marker, the quality of the solution was also checked using eBC_{tr}. For both markers, the same a-value combination was considered best according the overall criterion. …

90 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 RBBOA 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?

We agree in principle with the reviewer that a BBOA profile generated from analysis of Zürich data is more likely to be appropriate for Zürich than is a generic profile. However, the aim of the current study is to evaluate and validate the offline method. Because the offline method has not been tested, we cannot *a priori* be certain that the retrieved offline BBOA profile is without problems or biases. Using such a (hypothetically) faulty profile could lead to good agreement between offline and online solutions for the wrong reasons, thereby underestimating the uncertainties/biases inherent in the offline method. We therefore prefer to conduct the online PMF analysis such that it is a true reference and completely independent of the offline dataset. That said, the results of this analysis do indicate that the offline and online BBOA profiles are similar, and the method suggested by the reviewer could be a productive approach in future analyses (i.e. investigations not aimed at method validation).

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) - http://www.atmos-chem-phys.net/14/3325/2014/acp-14-3325-2014.html***

Technical corrections

P8604 L4: "source apportionment" (missing word?)

The text was adapted.

P8604 L5: please specify the aethalometer model

The aethalometer model was added.

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

The version was added (PIKA v1.10C).

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

It is a metrohm system. The main text is adapted.

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)

The SoFi version was added (SoFi 4.7)

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

This part was removed from the text.

P8608 L14: "concentrations" ("t" missing)

The word was corrected.

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

The extra verb is removed.

P8611 L4: "aerosol" (no "s")

The text was adapted.

P8612 L22: rather "PM<2:5"?

This was wrong and was corrected.

P8614 L26: "apportionment"

The text is adjusted.

P8614 L27: "those", not "these"

These was replaced by those.

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

The extra bracket was removed.

P8616 L5-6: "additional"

The text was adapted.

P8616 L16: move the comma before "and", not after

The text was corrected.

P8618 L14: "5-factor"

The text was corrected.

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

The text was corrected.

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

The text was corrected.

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

The text was corrected.

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

This information is now also mentioned at the suggested place in the manuscript.

P8633 Figure 1a: why no number 8?

It was a mistake. The figure was corrected.

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

This information is specified now in the figure caption.

P8637 Figure 5: What do the error bars represent? Are the Rfrag values mean recoveries?

The figure caption was changed accordingly:

Median recovery of single organic fragments, and chemical families for the Zurich spring campaign (offline vs. online PM2:5 AMS). The first and third quartiles of the inter-sample variability are shown as error bars. A ratio of 1 indicates a recovery of 100 %. The fragments are color-coded with the family (CH (hydrocarbon fragments, split into saturated and unsaturated), CHOz=1 and CHOz>1 (oxygenated fragments) and CHN (nitrogen-containing hydrocarbon fragments)). Numbers across the top of the plot indicate the fragments' nominal mass. Families include all respective fragments weighted by their mass contribution.

Besides the technical corrections, we also found an inconsistency between the formula in Figure 8.a and the main text on page 8617 line 22. In Figure 8.a, the formula of the overall quality criterion is displayed as:

$$|\mathrm{sum}(\log(\sigma_g(x))/\log(\mu_g(x))|)$$

On page 8617 line 22 the formula is displayed as:

$$\mathrm{sum}(\log(\sigma_g\ (x))/\log(\mu_g(x)))$$

Both formulas were changed to the correct version:

$$\mathrm{sum}(|\log(\sigma_g\ (x))/\log(\mu_g(x))|)$$

Reference:

Canonaco, F., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: Seasonal differences in oxygenated organic aerosol composition: implications for emissions sources and factor analysis, Atmos. Chem. Phys., 15, 6993–7002, doi:10.5194/acp-15-6993-2015, 2015a