Replies to comments by anonymous referee #1

We thank referee #1 for his/her comments. We completely agree with the general attitude behind these comments that complex measurements and data processing need substantial data validation and quality assurance efforts in order to produce robust and reliable results. As detailed below, we performed a large range of data validation efforts during the processing of our measurement data. Much of this is described in the submitted manuscript; detailed information on the other efforts could have been included as well. However, to avoid an overly lengthy manuscript, we only presented statistical summaries of many validation results. If the editor feels that this would improve the paper, we are more than happy to provide a supplement with graphical information and detailed description on the data validation tests.

Comment: The manuscript by Struckmeier et al. analyzed four datasets that were collected at two sites in different seasons in Rome (suburban vs. urban). This study contains various real-time online measurements including aerosol chemical composition, gaseous species, particle number concentrations, and meteorological parameters. The sources of organic aerosols (OA) were also analyzed with positive matrix factorization. While rich chemical information was provided in this work to address the sources, dynamics, and spatial variations, the discussions e.g., composition, dust event, new particle formation, OA, and CSOA are scattered and lack of focus.

Reply:

The intention and focus of our manuscript is to provide an assessment of the sub-micron aerosol and its potential sources at an urban and a suburban location in the Rome area during different measurement periods. This includes a general overview (the “rich chemical information” mentioned by the reviewer), but also deeper discussion on specific areas, which need to be addressed in order to characterize a complex urban environment like Rome. In particular with respect to the very different sources it would have been incomplete if for example the Saharan dust or the NPF, or other aspects had been left out. Thus, the focus of our work is on the description and, if possible, explanation of aerosols from the various sources, similar to approaches in previous publications from different groups (e.g., Kostenidou et al., 2015;Crippa et al., 2013b) which show that there is a general interest in this kind of analysis.

Comment: Also, I have several major concerns on data analysis and the interpretations: (1) each campaign lasted less than two weeks, and most importantly, the measurements at the suburban and urban sites were not simultaneous. This clearly increases the uncertainties in comparing aerosol chemistry and sources between the two sites. In addition, it is difficult to see the dynamic variations of aerosol species in Rome if the authors didn’t present time series data.

Reply:

The durations of the data acquisition periods are in detail:

DIAPASON2013: 16 days of measurements (including 14 full days)
POPE2013: 8 days of measurements (including 6 full days)
DIAPASON2014: 16 days of measurements (including 14 full days)
POPE2014: 14 days of measurements (including 12 full days)

This shows that only POPE2013 was shorter than two weeks. The measurements were performed subsequently and not simultaneously as stressed in the manuscript, e.g., in the first sentence of the abstract. Obviously this results in a larger uncertainty when comparing the observations from the urban and suburban site, as the reviewer correctly states. This is why we do not generalise observations or differences in observations at different locations or during different seasons, but rather present our findings considering potentially different weather conditions etc., as clearly indicated several times in the manuscript, e.g.:

- Page 12, line 5: "Regarding absolute PM_1 concentrations […] neither any general conclusion whether aerosol mass concentrations are higher at the city centre or in the suburb, nor whether PM_1 concentrations are elevated during any of the two different seasons, can be drawn."
- Page 12, line 12: "As discussed above, changes in meteorological conditions are likely one explanation for this result …"
- Page 12, line 18: "In addition to meteorological conditions (e.g. solar radiation, BLH, TKE, air mass origin, etc.) local air quality can be strongly influenced by local emission from various sources (traffic, cooking, biomass burning)."

Nevertheless, each of the four measurement intervals provides valuable information on properties and dynamics of various aerosol types in the city centre and at the suburban location, which are found to be sufficiently robust within the available measurement time.

Of course, we could provide time series of all measured parameters for each campaign. However, we decided not to focus on detailed temporal evolution or individual events but on typical aerosol properties and dynamics (e.g., diurnal cycles). In our case, where measurements were not performed simultaneously at both locations, this seems more appropriate and meaningful.

Comment: (2) the data quality was not validated adequately, particularly the AMS measurements. A simple comparison between PM1 measured by EDM and that measured by AMS and MAAP (NR-PM1 + BC) will help.

Reply:

We agree that assuring data quality is good practice. During the analysis of the AMS (and other instrument's) data all standard procedures, checks, calibrations, corrections, intercomparisons, etc. have been performed (see statements in Sections 3.1 and 3.2). Besides other necessary quality checks, also comparison of AMS plus BC data with independent PM_1 data (EDM, but also PM_1 calculated from size distribution measurements) was performed as well as many other comparisons. All comparisons showed reasonable

agreement (e.g., for PM_1 from AMS+BC versus EDM, R^2=0.69-0.85, Slopes: 0.73-1.37). We will add this kind of detailed information in our revised manuscript.

Comment: (3) the AMS data analysis needed to be expanded. For example, which approach (Aiken et al., 2008 or Canagaratna et al., 2015) was used to calculate the elemental ratios the calculation of elemental ratios? If there are elemental ratios, why did the authors still use f43 and f44 to discuss the oxidation states?

Reply:

The results from AMS measurements were inspected for relationships among these data and relationships with data from other instruments. For the data obtained with the AMS and the other instruments temporal evolution, diurnal patterns and individual events were analysed (see Section 4). The relevant results of the various quality assurance tests can be provided in a supplement to our revised manuscript.

Elemental ratios were calculated based on the current state of the art method (Canagaratna et al., 2015). We thank the reviewer for pointing out this missing information, and will add it to the revised manuscript.

Our discussion using f43 and f44 focused on the aerosol aging levels, for which the "triangle" introduced by Ng et al. (2010) is commonly used (e.g., Zhang et al., 2015;Ortega et al., 2016;Xu et al., 2016). We also calculated elemental ratios for the various factors, but didn't include them in the discussion on aerosol aging levels since they show equivalent behaviour as the f44/f43 data. We can add this information to Figure 7.

Comment: (4) the PMF analysis is a big weakness of this study. The authors didn't have a full evaluation of the PMF results. At least, the authors need to present the mass spectral profiles and times series of all OA factors, and also the comparisons with collocated measurements.

Reply:

The performed PMF analysis and corresponding tests are subject of Section 3.2. All typical and many other tests to validate the results were applied, amongst others those according to the guidelines by Zhang et al. (2011), Table 1. All relevant information (e.g. m/z-range used for PMF, method of error and data matrix preparation, treatment of isotopes, treatment of low S/N data, treatment of CO_2-related ions, range of factors, fPeak and seed investigated) is detailed in the text.

Furthermore, each PMF factor was inspected for reasonability and validated by comparing factor time series with external species and mass spectral profiles with such from literature. Details are given in the text, e.g., page 8, lines 17-19; page 19, lines 13-17; page 20, lines 1-7; page 21, lines 17-21; page 22, lines 19-22; page 24, lines 5-12.
So far we did not present all individual correlation plots and mass spectra in graphs, but presented this information in the form of R^2 values to save journal space and keep the length of the manuscript at a reasonable level without losing information. We could include this information in a supplement.

Comment: The diurnal correlations the authors mentioned in page 21 did not mean much.

Reply:

Such correlations are commonly used to show potential relationships between variables (e.g., Sun et al., 2016;Zhang et al., 2014), and to validate PMF factors (Zhang et al., 2011). In page 21 we discuss that the diurnal patterns of HOA correlate well with those of other typically traffic-related species (BC, NOx, PAH). As stated in page 21, line 21, not only the diurnal cycles, but also the time series correlate well.

Comment: Figure 2 also showed substantial differences in HOA/BC ratios at the two sites in different seasons, and surprising BC contributions, which should be well interpreted.

Reply:

We thank the reviewer for this valuable comment, and will add some more discussion on this topic. We agree that there are differences in the HOA/BC ratios observed during the fall 2013 campaigns and during the spring 2014 campaigns (fall 2013: 0.26-0.33; spring 2014: 0.46-0.53). We attribute this to the fact that both, biomass burning and traffic contribute to total BC, as mentioned on page 10, lines 20-21. Biomass burning is more predominant in fall, leading to higher BC mass concentrations, and therefore lower HOA/BC ratios during this season. The fact that larger ratios were found in the city centre in both seasons reflects the lower contribution of biomass burning emissions at this site. The contribution of different sources (traffic and biomass burning) also explains why the ratio of HOA/BC from our study is different to such ratios found in source measurements of pure traffic-related emissions. Separation of BC related to the two sources unfortunately is not possible with the instrument used (MAAP), but measurements in other cities with the aethalometer instrument (e.g., Crippa et al., 2013a) have shown that BC contributions from biomass burning to total BC can be non-negligible. We will include this discussion in the revised manuscript.

Comment: The PMF uncertainties lead to another major concern of the cigarette smoking factor. Although the authors concluded this as a major finding and presented a long discussion on it, it is still not convincing due to the limited resolution of V-mode (C5H10N+) and the absence of the measurements of molecular markers for cigarette smoking. I am also suspicious that the diurnal profile of CSOA did not reflect cigarette smoking that is expected less affected by boundary layer dynamics (if the authors claimed it as a point source). Showing the times series of CSOA factor will help.

Reply:

PMF analysis is always associated with uncertainties. As described in the manuscript we have taken all care in order to minimize these uncertainties and we have made multiple tests and comparisons with other data (e.g. mass spectra of previously identified CSOA, as described in the manuscript) in order to obtain results as robust as possible. While the CSOA factor was first obtained from the PMF analysis of the whole mass spectra, afterwards the $C_5H_{10}N^+$ marker was identified and found to have time series that correlate very well with those of

CSOA. Indeed, as discussed in the manuscript, CSOA has been identified before from AMS data in which the newly found marker fragment at m/z 84 was not fitted at all (Faber et al., 2013) and yielded a very similar factor mass spectrum with correlation coefficients $0.65<R^2<0.96$ (page 24, line 6). (Re-analysis later showed that the marker fragment indeed was present also in these data, as discussed in the manuscript.) Therefore, and from other tests we performed in the data evaluation and quality assurance of the PMF-results, the retrieval of CSOA seems robust to us.

We agree that V-mode has a limited resolution, and we would not generally use it for determination of N-containing ion fragments. In the particular instance of m/z 84, contributions of C,H,O-containing fragments are rather small, which makes it possible to distinguish the N-containing marker fragment with reasonable certainty even in V-mode. Figure 1 below shows a typical fit on m/z 84, based on a 30 s run. As can be seen, the N-containing fragment can be clearly distinguished. We can add this or a similar figure to the revised manuscript or a supplementary information, if desired.

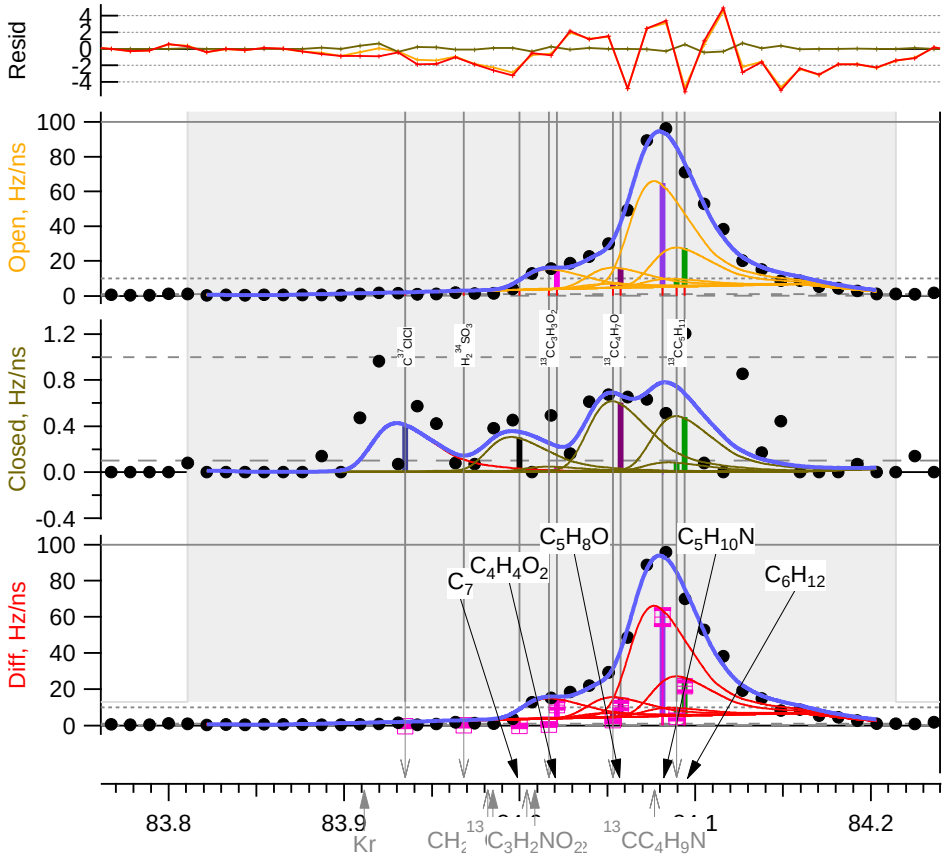

Figure 1: m/z 84 of a raw spectrum for a 30 s run during a period of increased CSOA concentrations during POPE2014.

Of course the fitting of $C_5H_{10}N^+$ only works as long as CSOA contributes sufficiently to the total m/z 84 signal with respect to contributions from POA_{noCSOA} (primary organic aerosol excluding cigarette smoke), as we discuss in the manuscript (page 25, lines 15-25). We also discussed the limitations of identification and quantification of CSOA using this marker, taking into account the limited resolution of the V-mode (page 25, line 26 to page 26, line 5).

Concerning "the absence of the measurements of molecular markers for cigarette smoking" we identified the fragment ion $C_5H_{10}N^+$ as an indication of nicotine, which is a molecular marker. While we do not have independent measurements of the same marker using

different methods, we used the very good correlation of the time series of this marker ion and the CSOA factor to associate this marker ion with cigarette smoke. The fact that the marker ion was also found in laboratory measurements of cigarette smoke (see discussion on page 24, lines 16-19) gives us confidence in its applicability.

Concerning the referee's comment on the time series: If the time series are affected by boundary layer dynamics (we won't speculate on whether this is the case or not), the "true" diurnal patterns would have an even larger amplitude since boundary layer dynamics would result in inverse structures to the observed patterns. Since the observed diurnal (and weekly) patterns of the CSOA factor agree very well with our observations of smoking activities in the vicinity of the sampling site, we are very confident that the patterns presented in Figure 13 reflect the concentrations of smoking-related aerosol well. For this reason we stated in the text:

> Page 24: "The diurnal cycle of the CSOA factor strongly correlates with typical working hours at the measurement location…" and "show distinct differences between working days and weekend, when the administration of the hospital where the measurements took place was closed, supporting the attribution of this PMF factor to locally emitted CSOA."

Time series of CSOA concentrations show the same as the information summarized in Figure 13, and therefore was omitted in the original manuscript in order to avoid duplicate information. However, we can include the time series in a supplement to our revised submission, as part of a discussion of the factor analysis results.

Comment: (5) the new particle formation in this study appears to have problems too. At least from the average diurnal cycles in Figure 5, we didn't see "banana" shape. On the other hand, the diurnal cycles appears to indicate strong local sources at both sites.

Reply:

Banana-like shapes in particle size distributions are only expected when observing the evolution of the particle size distribution of freshly nucleated particles over time. This can only be done if either the measurement follows the air mass in a Lagrangian experiment or the nucleation occurs over a sufficiently large area simultaneously (like in the boreal forest) and the air masses passing by the measurement site all have the same history. Both are not the case in our measurements, and in similar measurements in urban environments. Therefore it is not surprising that we do not see banana-like shapes in Figure 5 and in the raw data. Also the studies performed by Brines et al. (2015) in the cities of Barcelona, Brisbane, Los Angeles, Madrid, and Rome showed nucleation bursts without strong subsequent growth (depicted in Fig. 5 Brines et al., 2015), different from the typical "banana-like" nucleation episodes usually described in regional background environments. Minguillon et al. (2015) reported the restriction of nucleation events in Barcelona to midday and early afternoon, when condensation sinks are low due to decreased traffic emissions. Therefore, nucleation events found in urban environments are often similar to those found in our study, and do not necessarily exhibit a "banana shape".

Our measurements were performed stationary in a suburban/urban area, which is why we observe a strong contribution of small particles during the rush hour times in the morning

and the evening (of course there are strong local sources at both sites), as discussed in the manuscript (page 15, lines 9-10). During midday, when concentrations of particles from traffic are typically at their minimum, we observe different patterns in the diurnal cycles of particle number concentrations between late fall and late spring. Only during the warmer season we observed increased particle number concentrations during midday. The connection of the increased particle number concentrations during midday with new particle formation events is supported by mean particle number size distributions measured with the FMPS. These indicate increased concentrations of rather small particles during this time of the day, as discussed in the manuscript (pages 15-17).

Comment: (6) the classifications of "home-made" and "advected" might also have large uncertainties. For example, OOA can be from both sources since SV-OOA and LV-OOA cannot be separated. Although nitrate has a shorter life time than sulfate and LV-OOA, many studies have shown that regional transport can be important. I understand the authors can judge this based on the polar plots in Figure 8. In fact, I suggest that the authors re-analyze the polar plots by considering the influences of the number points in each cell. For example, the wind rose plots in Figure 1b shows a small frequency from the northeast, the polar plots in this direction can be significantly biased by sporadic spikes.

Reply:

We agree that this classification has large uncertainties. Therefore we described the comparison of "home-made" and "advected" submicron aerosol as a "rough estimate" in the first sentence of the related paragraph (page 11, line 14). We agree that OOA (not separated into LV- and SV-OOA during Oct/Nov 2013) can be from both, local and remote sources. However, as shown in Figure 7, OOA was found to be rather aged and therefore was assumed to preferentially be associated with the "advected" type. This assumption has some uncertainties and will lead to a small additional uncertainty in the final result of this analysis. However, this small uncertainty is much smaller than the uncertainty implicitly claimed in the text by expressions such as "rough estimate" and "approximately half of the locally measured PM_1 was home-made" (page 27, line 26). The same is true for potential small fractions of transported nitrate, which also could contribute a slight additional uncertainty to the overall analysis.

The referee is right that for the northeast wind direction a relatively low number of data points is available due to the low frequency of wind from this direction. However, an estimation shows that this is not a real problem for our interpretation of the data: According to Figure 1b about 5% of the data are associated with wind from this direction. For ca. 15 days of measurement and 1-minute data this corresponds to about 1080 data points (15 x 24 x 60 x 0.05) for this wind direction. These data points distribute over approximately 90 pixels of the polar plots, resulting in an average of ~12 data points per pixel. Furthermore, in the analysis of the polar plots only the general trends were investigated and not individual "hot spots" of single pixels with extraordinarily high numbers (outliers). Therefore we conclude that even for such wind directions a reasonable data base is available to avoid significant biases by sporadic spikes.

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