

Interactive comment on “Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris” by M. Crippa et al.

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This manuscript summarizes wintertime observations of aerosol composition in downtown Paris and two suburban areas. Factor analysis has been performed on the aerosol mass spectrometer data to assess contribution of different sources to the submicron aerosol mass at these sites. The results are sound and consistent with the summer-time measurements, indicating a significant regional contribution to the aerosol mass in the area. However, there are few points that need clarification or a better explanation. I suggest publishing this work after authors respond to the following comments:

Technical comments:

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1. Regarding the CE in AMS: for the data obtained at the LHVP site a CE=0.4 applied at all times. This is lower than what is typically applied for ambient data and it contradicts the data shown in figure SI-2e. Based on the SI data, there's definitely a NO₃-effect apparent in the dataset, so applying a constant, low CE factor appears to not be justified. If the DMPS data are valid, authors should revisit the CE determination. Note also that the explanation that's given in terms of the higher density particles affecting AMS CE doesn't apply here- with higher densities, particles appear larger in the vacuum aerodynamic sense and it's more likely that they fall out of the 'good' transmission region of the AMS lens; in such case AMS mass decreases compared to other instruments whereas the data in SI-2e at high NO₃ fraction times indicate that the apparent AMS mass is actually higher compared to the other times. In general, I believe now that parameterization of composition dependent CE is available, it makes sense to apply such parameterizations and then evaluate the closure between estimated AMS mass and other measurements; if this is not done in this order, the estimated CE appears to be more of a 'fudge' factor to make sure 'consistent' results (but may be low or high depending on errors in the other measurements) are obtained.

While a CE of 0.5 is frequently assumed for ambient measurements, the CE of 0.4 proposed here for the LHVP falls within the range of CEs typically found when this estimation is attempted with ambient data. For example, Takegawa et al. (2005) reported AMS/PILS ratios of 0.81 to 1.26 for inorganic species after assuming CE = 0.5. We further note that the CE = 0.4 value does not come from the comparison of the AMS with a single instrument (in which case errors in the other measurement might be expected to play a large role), but is rather selected to for consistency with a suite of instruments (SMPS, PILS, ATOFMS, FDMS-TEOM). A detailed analysis of these intercomparisons will be presented in a forthcoming paper (Poulain et al., in preparation), and the results are briefly summarized as follows: - AMS+MAAP vs. SMPS: slope of 1.06 R² 0.77 - PILS SO₄ (slope 0.68 R² = 0.84) - PILS NH₄ (slope 0.53 R² = 0.65) - PILS NO₃ (slope 0.81 R² 0.79)

Moreover, LHVP used an aerosol dryer in the inlet line, that might result in a reduced CE. Publication of the CE analysis for the LHVP dataset (Healy et al., 2012) predates the publication of the CE parameterization by Middlebrook et al. (2012) paper. Therefore, while an assessment of the NO₃ dependence of the CE was performed, we retain the constant CE = 0.4 in this paper to maintain consistency with the previous publication. The Middlebrook calculation for this dataset provided differences between ~10-15% for the different AMS species quantification compared to the application of a CE=0.4.

After applying a CE = 0.4, remaining discrepancies between AMS and PILS inorganics are believed to mainly result from the instrument size cuts (~PM₁ of the AMS and PM_{2.5} of the PILS). We observed an increase in the coarse mode concentration when AMS underestimated the PILS concentrations (Poulain et al., in preparation).

Concerning the density explanation shown in Fig. SI-2c, we want to underline that it is referred to the SIRTAs case and not to the LHVP one as mentioned by the reviewer.

2. Discussion on angstrom exponent values for traffic and biomass burning BC is circular- in section 2.3.2 it's mentioned that the choice of the parameters is discussed in section 3.3 while in sec. 3.3 it's referred back to 2.3.2! It appears these values come directly from another study. Maybe the best is to explain a bit in Section 2.3.2 how these factors were determined. Related to the BC mass- the concentrations reported here are awfully high! Are there any wintertime direct BC mass measurements (e.g., by SP2) to confirm such high concentrations in Paris or could this be due to the choice of mass absorption efficiencies used to estimate BC mass? Also, in the apportionment of BC only biomass burning and traffic related BC are considered. Isn't cooking also a source of BC? Do we know how small this source is to justify the assumptions here?

The discussion on the choice of the angstrom exponent is now entirely reported in section 2.3.2 as suggested by the Reviewer.

“Literature values of the BC absorption Ångstrom exponent vary between 1.9 and 2.2

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for wood burning (Sandradewi et al., 2008) and 1 ± 0.1 for traffic (Bond and Bergstrom, 2006; Bond et al., 2004). In the present study absorption Ångström exponent values for traffic and wood burning were chosen as $\alpha_{tr}=1$ and $\alpha_{wb}=2$ coherently with Sciare et al. (2011). The choice of such α values is in agreement with previous sensitivity analyses performed in the Paris region in order to evaluate the influence of different absorption exponent values on the aethalometer model (Sciare et al., 2011).”

Below are some additional comments on the choice of angstrom exponent and the BC mass concentration measured in Paris.

In Sciare et al. (2011), α_{wb} was taken equal to 2, based on values previously reported for wood burning aerosols (Lewis et al., 2008; Clarke et al., 2007) and used by Favez et al. (2010). This value is also close to the highest a value of 1.92 obtained by Sciare et al. (2011) for a suburban site of Paris.

The BC mass concentrations are obtained from a constant mass absorption efficiency (MAE = $5.78 \text{ m}^2 \text{ gC}^{-1}$ at 880 nm) that has been calculated from on-line EC measurements performed with a Sunset Field instrument. Quality control of EC measurements were performed using off-line EC measurements performed in parallel during the campaign. Comparison of EC measurements between the LHVP site and another background urban site located at 3-4km are very consistent (Bressi et al., ACP, 2012 submitted), suggesting that the site is not particularly impacted by high local traffic emissions. For these reasons, there is no reason to believe that BC measurements are awfully high (considering that the French car fleet is mainly composed of diesel cars). We applied a similar MAE for biomass burning and traffic because of the poor influence of biomass burning on the MAE as observed in Sciare et al. (2011), whose MAE is mainly driven by coating.

We do not expect cooking to be a source of BC since BC is produced mainly from combustion processes, which do not typically occur during cooking. Recent smog chamber studies performed in our laboratory showed also the absence of BC from

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cooking emissions. Allan et al. (Allan et al., 2010) also found very bad correlation between their PMF cooking factor and BC measurements.

3. P. 22551: Comparison of MAAP and aethalometer results in a slope of 1.16- is this considered a good closure? In this case, reasoning of instrument differences for different BC mass estimates is not valid; I suggest removing that sentence.

We do consider that 1.16 agreement between MAAP and aethalometer being quite good; however in agreement with the Reviewer's suggestion we removed that sentence.

4. P. 22555: indicate what the correlation coefficients are when comparing PMF BBOA related factors and filter-based levoglucosan measurements.

The corresponding R2 values are added to the manuscript.

5. P. 22559: Sciare (2010) analysis indicated OM/OC =0.9- does this OM include only HOA or other PMF factors as well? If it included other factors then it's not surprising that HOA/BC(tr) is lower than 0.9. However some explanation is needed as to why compared to Chirico (2010) work a factor of two higher HOA/BC is obtained in this work.

In the manuscript we referred to the OM/EC and not to the OM/OC ratio being equal to 0.9. However the reported OM/EC value was wrong (the correct value was OC/EC=0.7), so the sentence was reformulated as following:

"The average ratios of HOA to BC_{tr} found from the slopes in Figure 11 are 0.37 (intercept=0.33) and 0.61 (intercept=-0.12) for the two sites, and the BBOA to BC_{wb} ratios are 3.16 (intercept=0.11) and 3.62 (intercept=-0.12) both ratios are thus quite consistent between the two stations. Considering the SIRTA case, a positive intercept is found both for the HOA vs. BC_{tr} and BBOA vs. BC_{bb} comparison (0.33 and 0.106, respectively), representing an underestimation of BC_{tr} and BC_{bb} for this site. For the LHVP case the opposite situation is observed: negative intercepts are found for the HOA and BBOA vs. the corresponding BC fractions (-0.12 for both sources), meaning that the BC

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associated to these two sources is slightly overestimated. The observed HOA to BCtr ratio is smaller than values reported for tunnel measurements at low OA concentrations (Chirico et al., 2011) because of different measurement conditions (lower temperatures during wintertime), different vehicles fleets and in urban areas stop-and-go traffic might be different than constant speed driving in a tunnel.”

6. Why isn't OOA compared to sulfate? Since NH_4 can be associated with SO_4 and NO_3 and so it can have a diurnal temperature-dependent variation, it's better to compare the regionally influenced OOA factor with SO_4 .

For completeness, in the manuscript the R^2 values for all the secondary inorganic species with the respect of OOA are now reported.

“The R^2 values for NH_4^+ , NO_3^- and SO_4^{2-} with the respect of OOA component are 0.64, 0.53 and 0.65 for the LHVP site, 0.36, 0.32 and 0.21 for the GOLF site and 0.67, 0.53 and 0.63 for the SIRTA site, respectively.”

7. Figure 5- in COA factor, m/z 43, 55, 57 seemed to have been mis-marked. Please double check.

Figures 3 and 5 are now corrected

8. Figure 9- please clarify 'avg' lines are the 'reference' lines.

The caption of Fig.9 includes now the definition of COAavg and HOAavg as reference lines:

Figure 9. Mass fraction of m/z 55 and 57 (f_{55} and f_{57}) for primary organics at the LHVP site. Reference lines for pure COA and HOA (defined as COAavg and HOAavg, respectively) are shown.

9. Figure 11- These fitted lines shouldn't be forced to go through zero. I believe the nonzero intercepts actually are an indication for the extent that the 'factorization' doesn't work. For example, at SIRTA, the positive intercept of HOA may indicate that

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BC(tr) is underestimated and that is consistent by getting a positive intercept for BC(BB) when looking at BBOA vs. BC(BB).

We accepted the Reviewer's suggestion and we did not force the fit through zero. The new fitting parameters are now shown in Fig. 11 and reported in the manuscript.

The following sentence was added to the manuscript:

“Considering the SIRTA case, a positive intercept is found both for the HOA vs. BCtr and BBOA vs. BCbb comparison (0.33 and 0.106, respectively), representing an underestimation of BCtr and BCbb for this site. For the LHVP case the opposite situation is observed: negative intercepts are found for the HOA and BBOA vs. the corresponding BC fractions (-0.12 for both sources), meaning that the BC associated to these two sources is slightly overestimated.”

10. Figure SI-2d: is there an explanation of why comparison of SO₄ and NO₃ between AMS and PILS is so off during the 'high' period while NH₄ looks ok? Is this good agreement for the wrong reason (wrong RIE(NH₄)).

During the high concentration periods the agreement between the AMS and the PILS is not so good because of the different size cut of the two instruments (PM₁ vs. PM_{2.5}), as shown also in Fig. SI-2f for the LHVP case. In fact, we observed an increase in the coarse mode concentration when AMS overestimated the PILS concentrations. However we agree with the Reviewer that in Fig. SI-2d the good agreement of NH₄ between AMS and PILS and the discrepancy observed for NO₃ and SO₄ might be partially associated with wrong RIE values.

11. Figure SI- 3a-b: again- you shouldn't force the lines to go through zero. There are enough data points close to (0,0) that the line should be fitted freely.

We agree with the Reviewer that there might be still small errors in the zero of the instruments (air corrections), therefore we allowed the intercept of the fit to vary to check the quality of the data. New graphs are now reported in Figs. SI-3a, SI-3b, SI-3c

and SI-3d.

12. Figure SI-4: how is OC calculated from AMS measurements? There was no reference to what OM/OC was assumed; this of course will change the comparison shown here!

The OM/OC ratio is this figure was calculated from high resolution AMS analysis performed at the LHVP and SIRTA sites. The HR- analysis provided an average OM/OC ratio equal to 1.58 ± 0.11 for LHVP and to 1.79 ± 0.10 for SIRTA. This was stated in the text accompanying SI-4 and the OM/OC values will be added.

13. Figure SI-5: there was no reference to this plot in the main text. I suggest either adding a ref. to it or removing it.

In the main text the following sentences have been added:

“In addition, Fig. SI-5.1 shows that the identified organic sources at the three sites are grouped in different regions of the triangular space defined by Ng et al. (2010). Some of the differences within each group of sources are probably due to the deployment of different types of instruments (e.g. C-ToF vs HR-ToF-AMS), different ion transmission and fragmentation etc.”

14. Figure SI 6.6.2- what is the explanation for not having high f_{55}/f_{57} at peaks of COA time series at SIRTA?

The SIRTA site is considered an urban background location since not directly exposed to primary emission sources and 20 km far from the core of Paris. The diurnal pattern retrieved at this had a much less distinct diurnal pattern than at other locations. This is consistent with the strongest cooking emissions being located near the city center rather than near SIRTA. While Figure SI-6.6.2 shows some high COA events yielded high f_{55}/f_{57} ratios, the proportionally stronger contributions of non-COA factors to m/z 55 and 57 was proportionally stronger at SIRTA.

The following sentence was added in the supplementary information:

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“The relative fraction of cooking is never reaching as high values at SIRTAs compared to LHVP. In rural areas, the f_{55}/f_{57} approach will be much more uncertain as also OOA contributes to a higher degree to these mass fragments compared to urban areas.”

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/12/C10529/2012/acpd-12-C10529-2012-supplement.pdf>

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