

Review of “Characterizing the impact of urban emissions on regional aerosol particles; airborne measurements during the MEGAPOLI experiment” by Freney et al.

This paper describes the evolution of organic matter in the outflow from the city of Paris; it involves airborne measurements and contributes to the general knowledge in the secondary aerosol formation field. Correctly capturing changes in organic mass concentration and its evolution remains a challenge for regional models, which highlights the importance of this study.

The paper is generally well written, but some questions concerning the PMF solutions and methodology should be answered before this manuscript is suitable for publication.

General comments:

A comparison with ground based measurements (Freutel et al., 2013) would add more value to the study, differences and similarities should be discussed. PMF solutions and especially HOA seems different from this study and much more comparable with previous HOA's found in the literature. I guess it is expected result as airborne measurements are by default further from the source, but then it should be clearly discussed in the text. Actually, I have doubts that authors separated a clear HOA factor in this study (see specific comments), maybe it is not justified to push for HOA if it isn't exist. Otherwise, more convincing evidence should be provided for HOA separation. PMF, in general, raises many questions: time trends of different factors doesn't show significant difference and seems correlating quite well between each other, is there really a reason to separate 3 factors? Correlations with reference spectrums or external tracers are not so unambiguous as well...

In addition, one would expect HOA to increase within the plume, but it is not obvious in the current Fig. 2 or S2. Moreover, $\Delta\text{HOA}/\Delta\text{BC}$ would likely to decrease with photochemical aging (Fig.6) due to evaporation of volatile compounds or at least remain constant, but not increase as stated in text. This could also indicate problems in resolving HOA factor.

Concept of scaling ΔOA to ΔBC needs more rezoning, if one assumes that ΔOA is constant and ΔBC is decreasing with going further from the source, which is very reasonable as BC would eventually go to the background level, then the ratio of ΔOA to ΔBC would increase as you have in the paper, but it won't be resulted from an increase in OA mass, it would be rather due to decrease in BC. Plausibility for OA to remain constant vs. increase with decreasing BC should be elaborated and explained in more details.

Specific comments:

Page 24891 lines 17-20: mass, not volume, was compared in Figure S1. Why constant densities were selected for SO_4 , NH_4 , NO_3 ? Ammonium nitrate density differs from that of sulphate or sulphuric acid. Correlation or slope or line 1:1 or all of them should be presented in Figure S1. Why only two flights were selected (although, text states that all flights were compared), single graph on all flights with all statistical parameters would be much more informative. How neutralization of sulphate affected CE, did authors exclude that for a reason, if yes, it should be explained in the manuscript as original algorithm by Middlebrook et al. (2011) includes that.

Page 24892 lines 22-23: Separate Fig. S3 into a b c d and refer accordingly in the text, otherwise, it takes some time to understand to which graph authors are referring.

Page 24894 line 4: update HYSPLIT citation to the newest one.

Figure 2: BC time trends overlap and hide Organic's and PMF factor's trends; authors should work on that figure a bit more. Periods of “in” and “out” of the plume referred in table 2, figure 3 and elsewhere, have to be identified in figure 2. As it is presented now, the difference between organics in the plume and organics out of the plume seems to be within the variations, could you present averages with standard deviations or maximums, minimums in table 2.

Page 24896 line 25: oceanic source rather than oceanographic (oceanography is a marine science).

Page 24897 lines 16-21: SO₂ or NO₂ reactions with OH will result in sulphuric or nitric acid, which further be neutralized by existing ammonia and form ammonium sulphate or nitrate. In fact, sulphuric acid is a stronger acid; therefore, it would be neutralized first and preferably form ammonium sulphate particles. Degree of aerosol neutralization by ammonium would give more information. If aerosol was acidic or fully neutralized, one can estimate from AMS data. Maybe, another explanation could be included as well: sulphate formation through secondary processes from anthropogenic SO₂, which would result in higher background SO₄ concentrations if compared to the plume ones. The latter would add up to marine sulphate and form elevated background sulphate concentrations. Reduction of sulphate in the plume due to competition is not so convincing if considered remote and not local (marine) source of SO₂.

Page 24898 line 16: figure S5 not S6?

Page 24899 lines 17-19: Sentence is not clear.

Page 24899 lines 20-22: Only for the 3 factor solution not 4. Reasoning of why 0.2 was selected instead of 0 should be provided, not only stated.

Tables S2 and S3: references for the reference mass spectra should be provided in the captions.

Page 24899 line 25- page 24900 line 6: HOA mass spectrum is quite different from the reference HOA or other HOA's presented in the literature. Correlation of 0.86 is not so good and not so different from the 0.82 or 0.8 correlations with ref BBAO and SV_OOA. It should be addressed and explained in the text. I'm not convinced that the factor, which authors identify as HOA is really HOA, more evidence should be provided. Do correlations provided in tables S2-4 correspond to one flight (which?) or all flights? As for some flights HOA could be more real (N29) than for others (N21). Did you do separate PMF on all flights or combined?

Figure S2. Why SO₄ didn't drop to 0 during filter periods? (Assuming that concentration drop ~14:30 is the filter period).

Page 24901 lines 24-25: Provide R² and slope for $\Delta\text{NO}_3/\Delta\text{BC}$ as well, now it is not obvious if it is really insignificant or scaling problem in the graph S2.

Page 24902 lines 14-16: Discussion why CO doesn't increase over the background is needed.

Page 24904 line 14: correct figure numbers, I assume it is only S2d, which is relevant.

Page 24905 lines 6-7: "Higher values in N21 may be related to the sparse data points available for N21 (Fig. S2)." Elaborate more as significant difference in data point availability from N29 (figure 2) is not really obvious.

Figure 1. Color scale is not clear, should be elaborated more in the caption.

Figure 4. SO₄ (b,d) not (b,c)

Figure 5. Consistency with the text should be maintained in the legend: flights should be named according to classification (N16, N21 and so on) instead of the real flight number.

Figure S2: $\Delta\text{OA}/\Delta\text{BC}$ is nondimensional in d.

Figure S6: correct a or d caption, now it is both SV-OOA1