Atmos. Chem. Phys. Discuss., 12, C8448–C8453, 2012
www.atmos-chem-phys-discuss.net/12/C8448/2012/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "On the chemical nature of the oxygenated organic aerosol: implication in the formation and aging of α-pinene SOA in a Mediterranean environment, Marseille" *by* I. El Haddad et al.

I. El Haddad et al.

imad.el-haddad@psi.ch

Received and published: 20 October 2012

We acknowledge both reviewers for their relevant comments that we address separately below.

Reviewer 1

1/Comment A

Comment: *The apportionment of fossil vs. non-fossil sources of OOA as a tracer for SOA is a creative strategy but has seldom been applied yet, so that this investigation will be very helpful for the general understanding of SOA formation and the interpretation of AMS data. A discussion with the few previous studies of that kind should be included.*

Response: In the corrected manuscript we have added some comparisons with previous studies, namely Minguillón et al., 2011 and Hodzic et al., 2010.

2/Comment B

Comment: *Although the comparison of PMF with CMB doesn't seem to provide new aspects at first view, both techniques should be regarded as independent approaches so that their similarity points towards sound results for both. However, the drawback of both approaches (e.g. the too small variability of sources for PMF for the Marseille campaign and dependence on literature emission factors for CMB) should be kept in mind and presented in a clearer way. The same should be done for the limitations of the independency of both approaches from each other. In general, a discussion of uncertainties of the results needs to be included in the main paper. This was thoroughly done in the supplementary material and deserves a summary chapter in the main part.*

Response: This is a very relevant comment taken into consideration in the corrected manuscript.

Reviewer 3

1/Major comment and minor comment 1

Comment: *The authors present a third paper in what appears to be a four part series on the aerosol measurements made in Marseille in summer 2008. Detailed measurements of this nature are very valuable and the quality of the work appears high. The manuscript is well written and clearly makes the point that the main contributor to organic aerosol at this time was long-range transport of biogenic organic aerosol. As far as I can tell, the only new results presented in this work are the four factors of OA identified by PMF2 on the AMS measurements. While this would have been a better fit in the previous paper–since the methods and sampling site are identical–the authors do provide additional evidence that biogenic organic aerosol predominates the OA in Marseille. In addition, AMS measurements are made across many research groups and having this type of data is valuable for comparison. It is clear that authors have put a great deal of thought into these factors and their interpretation, but whether or not this new information merits an entire new manuscript is unclear to me. Aside from this issue, the manuscript itself is very close to being ready for publication. I have only minor comments.*

AMS/PMF2 measurements provide more insight into the organic aerosol makeup than the CMB model. However, it is unclear that we understand any more about the system from the PMF results. Figure S9 shows just how similar the results were for the PMF and CMB results. In the previous paper (El Haddad et al., 2011b) the authors showed that "Radiocarbon measurements suggest that more than 70% of this fraction is of non-fossil origin, assigned predominantly to biogenic secondary organic carbon (BSOC)" and that "Using the marker-based approach, the aggregate contribution from traditional BSOC was estimated at only 4.2% of total OC and was dominated by α-pinene SOC accounting on average for 3.4% of OC." It seems like the conclusion in the new manuscript do not differ from the previous results or even improve upon them substantially. The only new finding I see is the correlation of each factor with other metrics. Given that the PMF analysis was constrained by these external factors in the first place, it is not surprising that they correlate. In order to justify this paper, I would need to see something substantial from the PMF results that could not have been discovered without them.

Response: In principle, we agree with Referee 3 that the new data we present in the current paper could have been included in our previous papers. However, the analysis made for this paper was not completed when we published the previous twin papers, and we believe that the new results obtained here are very relevant and worth sharing with the atmospheric science community even if this would require an additional paper. The reviewer mentioned that the only new results presented in this work are the four factors of OA identified by AMS/PMF2 that compares with our CMB/markers results. Indeed this paper shares some conclusions with the previous ones, but we believe that the AMS/PMF2 results and their comparison with filter based metrics (14C, CMB analysis, HULIS, α-pinene oxidation products) have offered three substantial novel findings:

i/ Source apportionment methodologies: Currently, different techniques are applied to apportion OA sources, each of which is able to deconvolve different OA fractions and each of which has its drawbacks and underlying uncertainties. As mentioned by referee 1, comparing these techniques is rarely done, although this clearly enhances the understanding of SOA sources and offers a better assessment of the uncertainties related to these techniques. In this study, we showed that two independent source apportionment techniques (AMS/PMF and CMB/tracers) applied to independent measurements agree very well. We also demonstrated for the first time to the best of our knowledge, the ability of AMS/PMF to predict the contribution from industrial emissions to total OA. Such emissions remain one of the most complicated to apportion using a CMB methodology in conjunction with elements and organic markers, given the great number of industrial processes with highly variable profiles. AMS/PMF can then constitute an alternative approach. The industrial OA MS profile shall be also shared with the AMS community.

ii/ Source and chemical composition of OOAs: Over the past 7 years, AMS/PMF showed the predominance of OOA in urban areas. This fraction is separated according to volatility and oxidation degree into SV-OOA and LV-OOA. Currently, there is an increasing need to identify and characterize the precursors and the chemical composition of these two fractions and to elucidate their formation mechanism (see point number 3, below) in order to properly represent them in models. We provided in this work a methodology for combining AMS/PMF and 14C results to investigate the fossil and non fossil origin of OOAs with a thorough uncertainty assessment. We also showed that LV-OOA and SV-OOA present the same features as HULIS and a-pinene SOA, respectively, both arising from biogenic precursors but having different photochemical ages. These findings could not be obtained without applying AMS/PMF separating the CMB SOA into two fractions (for example in the previous papers we could not observe any correlation between the oxidation products of biogenic precursors with the total SOA, although the later is dominated by non-fossil carbon).

iii/ Impact of aging on OOA composition: We have clearly showed the reactive nature of OOA and OOA components. Our results suggest that the aging of SV-OOA into LV-OOA lead to the formation of HULIS, the decay of SOA first generation products and the formation of the latter generation products. These results are important for future studies using these markers to estimate biogenic SOA contribution, assuming that these are stable. In the corrected manuscript we estimated that the observed aging occurs within 3.7 days (considering an average OH concentration of 10^6 molecule cm^{-3}); i.e. in 3.7 days half of SV-OOA would be transformed into LV-OOA. As this transformation strongly influence OA physico-chemical properties and its interaction with clouds and its wet removal, our results have a direct implication for modeling climate impact of OA.

2/minor comment 2

Comment: *Table 1 is a bit confusing because I am looking for the groups of compounds which correlate to one another but it's hard to see how they are grouped when they are listed in order. Numerical order makes some sense, but it would be better to highlight the compounds that are somehow connected more clearly.*

Response: done in the corrected manuscript.

3/minor comment 3

Comment: *Figure 2. The absolute concentration of all the factors follows the same general trend (as do many of the tracers). The traces do seem to line up as assigned, but it should be noted that when the levels of OA increase, all the factors should increase to some extent. It may be more useful and more meaningful to show the factors as fractions of OA instead.*

Response: We added in the new version of the supplementary information the times series of the factors

---
