**Atmospheric
Chemistry
and Physics**
Discussions

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Interactive comment on "Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona, Spain" *by* M. Alier et al.

M. Alier et al.

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Anonymous Referee #1 Received and published: 29 June 2013

Overall Comment and Recommendation:

This manuscript examines the potential sources of organic aerosol contributing to the PM1 fraction at two sites in Barcelona, Spain, during September-October 2010 using the Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method. I think the authors do a nice job outlining the similarities and differences of this source apportionment method compared to the more commonly used PCA and PMF ap-

proaches in our field. This is a well-written manuscript that will certainly add to the current literature about sources of organic aerosol at various locations. I should state here that the use of the GC/MS technique with prior derivatization was properly used and well described. Before publication, I would like to ask the authors to address my specific comments below. Due to the nature of these comments, I would like to recommend that this paper be accepted with major revisions noted below.

Specific Comments:

1.) I was surprised to see that the mass concentrations of the known (and typically abundant) isoprene SOA tracers (e.g., 2-methyltetrols, C5-alkene triols, and 2- methyl-glyceric acid) were really low in this study (i.e., only 1-2 ng/m3), but the overall contributions of the SOA ISO source were estimated as high as 400 ng/m3 and 300 ng/m3 for the UB and RS sites, respectively, based on their source apportionment method. Even though the authors don't measure the organosulfates produced from isoprene-derived epoxides, such as the isoprene epoxydiols (IEPOX) [Paulot et al., 2009, Science; Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T] and methacrylic acid epoxide (MAE) [Lin et al., 2013, PNAS], the major constituents that are typically abundant are so small in this present study. Thus, it is hard to describe the 400 and 300 ng/m3 estimated by the source apportionment method. The reason I point this out is due to recent work by the Surratt group at UNC. They showed in recent field measurements in the southeastern U.S. [Lin et al., 2013, ACPD] that isoprene SOA, especially those derived from reactive uptake of IEPOX [Lin et al., 2013, ES&T] can explain upwards of 20% of the OM mass when only measuring 6-8 tracers. The 2-methyltetrols measured in that study were measured as high as 573 ng/m3 and the C5-alkene triols were measured as high as 524 ng/m3. All other constituents, like the organosulfate derivatives, were typically much lower (i.e., less than or equal to 100 ng/m3) than these major constituents. How do the authors reconcile that their method estimates 400 and 300 ng/m3 for these sites but the major constituents are around 1-2 ng/m3? If you look at your profile in Figure 2, it seems you have a lot of non-isoprene derived constituents contributing to this profile.

How do you know you have fully resolved the isoprene SOA from other OM sources with your method? I'm slightly worried here that you haven't fully resolved this source from some other source. The concentrations of the isoprene SOA tracers seem to range between large gradient, as mentioned in the manuscript (11184, last paragraph; page20 line12 word document). The ones observed in this study are lower than those observed in other studies (as mentioned in the manuscript and by the reviewer), but in range of those in a similar area in the Mediterranean Basin. Part of the variation between concentrations could be the quantification of the analytes. Since we did not use any isoprene SOA tracers for calibration, but instead quantified by using the response factor of succinic acid (m/z 247) vs. the responses (areas) of 2-MGA (m/z 219), C5-alkene triols (m/z 231) and 2-MTs (m/z 231), this may lead to differences when the results are compared to results from other studies. However, application of different calibration curves of other standards leads to a maximum variation of factor of 3, and results in even lower concentrations. Therefore, the applied quantification method does not explain the large variance in concentrations between the different studies. We can confirm that the concentration variation of isoprene SOA tracers in the urban area of Barcelona is a fact. In a new study collecting samples throughout the year (manuscript in preparation) we observe individual isoprene SOA concentrations ranging between 1 and 200 ng/m3, using the same analytical method that was used for the presented results. These new results will be discussed in the next manuscript, but we can already say that seasonality is important for the isoprene SOA tracers analyzed here. As mentioned by the reviewer, despite the low concentrations, the contribution to the isoprene SOA component was estimated to be around 11%, which was about 0.3 μg OC/m3. This component is composed of mainly isoprene SOA tracers, although some of the biogenic pinene SOA tracers and phthalic acid are represented as well. Therefore, the component may not be completely resolved; however, we believe that the dominance of the isoprene SOA tracers in this component is strong enough to call this component the isoprene SOA component.

2.) Can the authors provide and refer to a SI table that clearly outlines which stan-

dards were used to quantify their tracers, especially since many (like the isoprene SOA tracers), do not have commercially available standards? How do the authors think the lack of authentic standards affect their results here? As mentioned in page 11176; the studied compounds were quantified with authentic standards, except in the case of 3-hydroxyglutaric acid, MBTCA, 2-methylglyceric acid, C5 alkene triols, 2-methylthreitol and 2-methylerythritol. These compounds were quantified with succinic acid. As mentioned in 1), this method may affect the concentration of the analytes, however it will be maximum a factor of 3. In the part on the methodology this methodology is mentioned now in more detail.

The new text is (page10, line 23 word document): "Besides comparison of retention times, levoglucosan and mannosan were identified with ion m/z 204, galactosan with ion m/z 217 and nicotine with ion m/z 84. Acids, polyols and 2-methyltetrols were identified with the following ions: malonic acid (m/z 233), succinic acid (m/z 247), glutaric acid (m/z 261), pimelic acid (m/z 289), suberic acid (m/z 303), azelaic acid (m/z 317), glyceric acid (m/z 292), malic acid (m/z 233), tartaric acid (m/z 292), phthalic acid (m/z 295), tricarballytic acid (m/z 377), cis-pinonic acid (m/z 171), 3-hydroxyglutaric acid (m/z 349), 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (m/z 405), 2-methylglyceric acid (m/z 219), C5-alkene triols (m/z 231), 2-methylthreitol and 2-methylerythritol (m/z 219). Quantification was performed with the external standard calibration curves. All concentrations were corrected by the recoveries of the surrogate standard succinic acid (m/z 251) and levoglucosan-d7 (m/z 206). No standards were available for 3-hydroxyglutaric acid, MBTCA, 2-methylglyceric acid, C5 alkene triols, 2-methylthreitol and 2-methylerythritol. Their chromatographic peaks were identified by comparison of their mass spectra to literature and library data (Claeys et al., 2007; Kourtchev et al., 2005; Cleemens et al., 2007) and they were quantified with the calibration curve of succinic acid. Application of the calibration curves of other standards leads lower concentrations with a maximum variation of factor of 3. Therefore, caution should be taken when comparing these results with those from other studies".

3.) Section 3.1.7: The authors should be made aware of recently published work by the Surratt group, especially since more developments have been made in our understanding of how high-NOx levels affect isoprene SOA formation. The authors accurately describe in this section that 2-MGA can be produced from the oxidation of MPAN. However, recent work described in Lin et al. (2013, PNAS) shows that MPAN oxidation produces methacrylic acid epoxide (MAE) in the gas phase that subsequently produces SOA. MAE is now considered the direct precursor to 2-MGA in the aerosol phase. Interestingly, MAE seems to be produced more in high-NOx conditions where as IEPOX is more favorably produced under low-NO conditions. IEPOX is considered the direct precursor to 2-methyltetrols, C5-alkene triols, and 3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols) [Lin et al., 2012, ES&T]. Just curious, did the authors see 3-MeTHF-3,4-diols in their samples when using GC/MS? The authors are aware of the recent developments in the formation of isoprene SOA and the mentioned work of Lin et al. (2013) is now introduced to section 3.1.7 (page page 21, line 9 word document). The reference is also added to the list. "Recent work by Lin et al. (2013) found that 2-MGA is directly formed from methacrylic acid epoxide (MAE), which is a gas-phase oxidation product of MPAN."

3-methyltetrahydrofuran-3,4-diols (using m/z 262) were not identified in these samples.

4.) Did the authors observe day-night differences in the SOA ISO source profile? I couldn't really tell from Figure 2 since it is so small and hard to read. There was no day/night difference in the ISO SOA profile. This is in agreement with the individual isoprene SOA tracers that did not show any day/night or week/weekend fluctuations (mentioned on page 11185, page 20 line 23 word document).

5.) Table 1: The heading of the table seems to be mislabeled. The authors say the concentrations are in ug/m3. Don't they mean ng/m3? There was a mistake in the heading of the table. The concentrations were in ng/m3 and not μg/m3. This mistake is corrected in the new version.

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This paper is an interesting paper that can contribute to the scope of ACP. The results are well discussed and well presented. Objectives of this paper study are to determine organic aerosols composition and apportion organic sources on two urban sites (Roadside and Urban background) in Barcelona during a fall intensive campaign (12-hours sampling in order to study daily evolutions). However, before the publication, authors must be more define or must make some corrections or provide additional information on these different points:

1. Title: maybe adding season and source apportionment method The authors would like to keep the title as short as possible. Adding the season of sampling and the MCR methodology would unnecessarily enlarge the title. The abstract mentions the sampling period and the source apportion methodology.

2. Abstract: - more nuanced some definitions of sources like it is detailed in the conclusions section - line 15: "local anthropogenic activities": what types of activities? Heating? Traffic? Industries? The sources behind the "local anthropogenic activities" in this study were mainly traffic related. However, nicotine as a tracer for cigarette smoke was also related to this component. This is now mentioned in the abstract.

The new sentence is (page 2 line 14 word document): "Primary organics from emissions of local anthropogenic activities (Urban primary organic aerosol, Urban POA), mainly traffic emissions but also cigarette smoke, contributed by 43% (1.5 μg OC m-3) and 18% (0.4 μg OC m-3) to OA at RS and UB, respectively".

3. Introduction: - Page 11169 line 27: "various atmospheric oxidants": which oxidants? The oxidants that were mentioned were OH radical, O3 and NOx. This is introduced in the text (page 4 line 10 word document).

The new sentence is: "Such primary particles can be modified in the presence of various atmospheric oxidants, such as OH radical, O3 and NOx, (Donahue et al., 2009),

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yielding more oxygenated products that change their original physico-chemical properties".

- Page 11170 line 7: input some more recent references The authors consider that the mentioned three references are enough to indicate that the amount of organic compounds in the atmosphere is very large.

- Page 11171 line 1: adding after "source apportionment techniques" the sentence "applied on off-line filter data" The suggested correction has been introduced in the manuscript. The new sentence is (page 5 line 13 word document): "The number of existing source apportionment techniques applied on off-line filter data is relatively large,. . .".

- Page 11171 line 11: MCR-ALS has previously applied for environmental source apportionment: in which types of environment? Urban? Rural? Traffic? MCR has been used for environmental source apportionment in atmospheric and water pollution data analysis. Pollution sources identified in these environmental studies were urban (including traffic), agricultural, industrial and others (see references).

- Page 11171 line 14: MCR-ALS produce analogous results to PMF: discussed this sentence, add a discussion on advantages and disadvantages of these 2 methods, notably in MCR-ALS uncertainties on data are not taken into account (what it means on source apportionment results?) A detailed comparison between PMF and MCR-ALS is given in reference Tauler et al., 2009. MCR-ALS and PMF are both based on a bilinear decomposition of the experimental data matrix using non-negativity constraints. They differ in the algorithm applied for the decomposition (ALS in MCR-ALS and a nonlinear conjugate gradient optimization in the case of PMF). PMF include uncertainties and error propagation estimations to achieve sounder estimates in case of noisy environmental data. MCR-ALS can also optionally incorporate data uncertainties using a weighted alternating least squares algorithm. Further discussion about similarities and differences of these approaches are given in reference Tauler et al., 2009. In this paper,

experimental uncertainties were not taken into account because they were considered to be rather low and also due to the difficulty in their accurate experimental estimation in practice. As shown also in previous cited reference, their effect on resolved scores and loading profiles is only significant in case their size is relatively high.

4. Analytical procedures: - Page 11176 line 18: why using an external standard calibration while you add deuterated internal standards before extraction? The external calibration with authentic standards allows the quantification of the studied compounds. The deuterated compounds act as surrogate standards to correct for any loss in the analytical procedure. The quantified concentrations were corrected for these losses.

- Page 11177 line 6: the calculation of LOQ do not take into account blank values and standard deviation of the measure, maybe you must use the term "Limit of Detection" than LOQ and calculate the LOD as the average concentration of 3 to 10 analysis of the low standard level plus standard deviation on these measures The authors consider the lowest level in the quantification curve valid for the LOQ. Below this level some compounds could still be detected, especially in the blanks.

5. Chemometrics: - Why do you not have applied CMB in order to apportion primary organic sources and to compare/validate your MCR-ALS results? There is no reason to assume that the total sum of the concentrations of the investigated organic compounds is equal to the total particulate matter taken for the analysis. Therefore, it has no sense to apply a CMB in this case. For this reason, for the purpose of analysis of organic compounds in PM1 filters, the total mass analyzed was not determined.

- The number of samples in matrices is 52 and 51: is sufficient for a good statistic validation? - Why do you not include OC or OM in the matrices? We consider that 103 independent samples is a good number of samples to resolve six different components (contaminant sources). OC was measured in the PM1 filters (see reference Dall'Osto et al., 2012a), but it was not used in the MCR-ALS as we wanted to observe correlations of the organic tracer compounds among eachother in relation to sources / processes.

Then, these sources / processes were used to build up the OC in the filter samples.

- In the matrices, concentrations are in different range: 0.01 to 4 ng.m-3, has it an impact on the decomposition by MCR-ALS and on results? Concentrations of the different analyzed organic compounds were scaled (divided by their respective standard deviations) to avoid differences among them in scale.

6. Results_Chemical analysis: - Page 11179 line 19: input comparisons with European sites data (same comment for hopanes) The results of PAH (and hopenes) are compared to those in Europe, using the recent publication of Křumal et al. (2013). The references of Ning et al., 2007; Subramanian et al., 2006 were used for the comparison of the hopane concentrations as well. The new sentences are:

For PAH (page 14 line 16 word document): "The observed concentrations in Barcelona were in the range of the ones observed in other urban areas in the USA (Ning et al., 2007; Subramanian et al., 2006) and Europe (Křumal et al. 2013 and references therein), although wintertime concentrations in those site are generally higher, due to enhanced fuel combustion for domestic heating."

For hopanes (page 15 line 10 word document): "The observed concentrations in BCN fit into the range of the concentrations observed in urban areas in the USA and Europe (Subramanian et al., 2006; Ning et al. 2007; Křumal et al. 2013)."

- Page 11180 Hopanes paragraph: input discussion on degradation of hopanes which could be observed at this season A observed in other studies, particle bounded hopanes are susceptible to oxidation. Nevertheless, this process seems to be important in regional atmospheres, at larger distance from the main emission source (traffic), while in urban atmospheres, close to the source, this is less relevant. This has been introduced to the manuscript and the mentioned references are added to the reference list. (page 15 line 13 word document)

"Although hopanes are susceptible to oxidation in the atmosphere (Robinson et al.

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2006a; Lambe et al. 2009), the depletion is probably small due to the very short distance between the sampling site and emission source."

7. Results_Multivariate data analysis: - Page 11186: the mass of selected organic components represents how many percent of OC mass? The percentage of OC mass that was chromatographically resolved in this study ranged between 2 and 6%. This information is now introduced into the manuscript (section 3.2 (page 22 line 6 word document).

"There was a very good correlation between the total OC concentrations of PM1 and of component for each sampled days ($r2 = 0.9$, $P < 0.05$), although between 2 and 6% of the total OC mass was chromatographically resolved."

- Page 11186: authors says "selected organic components can be representative for the contributions to the organic fraction": components analyzed explain some organic sources but maybe other sources could contribute to OC mass? In particular industrial emissions? Input a discussion on it.

The regression correlation of the score values from the MCR versus the OC concentrations on the PM1 was 0.9. This very good correlation indicates that multiple-day variation of the analyzed organic compounds explains for a very large part the OC fluctuations during the study. However, as mentioned by the reviewer, other sources than those mentioned in this manuscript could be of influence on few specific moments, or play a 'correlating'-role in the explained variation, although it was not interpreted in this study. The interpretation of the resolved components, however, discusses the uncertainties related to the sources behind these components, especially in the case of the "OOA urban" component (see section 3.2.6 and section 4).

- For POA Urban and BBOA results, add more comparisons of contributions of sources with other European sites More comparisons were added to the manuscript. POA Urban (section 3.2.1.(page 23 line 5 word document):

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"In the urban areas of Marseille along the Mediterranean coast a similar concentration of about 0.9 μg OC m-3 (17%) was attributed to primary urban emissions (El Hadded et al., 2011) based on organic tracer analysis, while the primary emissions in Paris ranged between 0.2 and 0.5 μg OC m-3, depending on the used method."

BBOA (section 3.2.2 page 24 line 11 word document): "These contribution are in the lower range of those estimated for other European sites (0.04 – 3.1 μg OC m-3; Puxbaum et al., 2007), where the higher concentrations are observed in sites that are directly exposed to local biomass burning.

- Page 11189 line 1: "35% of the total hopanes signal": it is a high part, could you discuss this result, maybe it is an artifact of the model The MCR-ALS allows the distribution of the compounds among the different components. It is not an artifact, but indicates that components (sources) may be mixed for some part and that the resolution of the components is not perfect. The mixing of the resolved compounds is a reality when the aerosols in a complex urban atmosphere are being analyzed. However, the resolved six components give an insight on the influence of the potential sources / processes on the aerosol in the sampled period. This was stated in the manuscript (introduction in section 3.2 page 22 line 1 word document)

"Although many compounds were distributed between different MCR-ALS components for many of the chemical compounds, an insight of the contributions of the different OA sources can be seen in Fig. 2."

Further on in the presentation and discussion of the components we mention that there are relative contributions (in this case hopanes) in other components. This result is discussed in manuscript (page 25 line 10 word document).

"Hopanes were also found to contribute to this aerosol source (35% of the total hopanes signal) and could be related to biogenic hopanoid precursors produced by microbiota (Yan et al., 2008).".

- Page 11191: this component contains vehicular emissions, cooking, PAH, why the name OOA and not a name like "Urban aged" in opposition of the "POA Urban" source? And in order to estimate cooking, why other organic tracers like cholesterol were not analyzed? The discussion around the definition of Urban OOA is not conclusive at all. This was mentioned in the manuscript on page 11190; line 15 (see section 3.2.6. page 27 line 3 word document)

"Contrary to the previously described five OA sources, it is not known at this stage if this OOA Urban source has a primary and/or a secondary component, hence the name does not include any specification on this regard. The unique feature of this aerosol source is the strong association with pimelic (65%), suberic (61%) and azelaic (55%) acids (C7-C9 DCA)".

Therefore we do not want to call it "aged", but since there is a dominant contribution of C7-C9 diacids the component has an oxygenated character. It would have been better if this possible food cooking component could have been related to primary organic cooking tracers, such as cholesterol or oleic acid. Despite that these compounds were detected in all samples at concentrations around 1ng/m3, these levels were also observed in the field blanks. Therefore these tracers could not be used in the present study.

8. Implications and conclusions: - Page 11192 line 18: "in the same location during winter": atmospheric conditions were different than those from this study, notably conditions that can be influenced SOA formation, discuss it. The weather conditions in Barcelona during winter, with frequent anticyclonic conditions and relatively high solar radiation, allows that aged aerosols to accumulate in the PBL. This is the reason that SOA in winter contributes to the overall OA. This is mentioned now in the manuscript (section 4 page 29 line 10 word document). "The relatively high contribution of SOA in the urban background of Barcelona is related to the high frequency of anticyclonic weather conditions, allowing aged aerosols to accumulate.".

- Page 11193 lines 15-24: this paragraph must be more nuanced In the lines 3 to 14 (page 29 line 24 word document) more information on the issue is given in the manuscript. Similar to suppressed NPF in forested areas in the presence of isoprene, we have indications that this occurs as well in the urban area.

- Page 11194 line 26: some sources are not very well defined, so maybe give a range of percent of contributions The authors agree with the reviewer that it would be better to give the range of percentage of the OA that has an urban origin. This is then in accordance with the other paragraphs. The new sentence is (page 31 line 21 word document):

"This study reveals that between 43-66% and 18-28% of the OA detected at the RS and UB, respectively, has an urban origin,. . .".

9. Table 1: an error in the title, the unit is ng.m-3 and not μg.m-3 There was a mistake in the heading of the table. The concentrations were in ng/m3 and not μg/m3. This mistake is corrected in the new version.

10. Fig. 1: reference of figure? Google Earth? The Figure 1 is taken from Google Earth. This is now mentioned in the figure caption.

11. Fig. 2 and Fig. S1: add the unit of the column on the left We have not put units on the left because they are relative contributions.