

***Interactive comment on “Insights into the
secondary fraction of the organic aerosol in a
Mediterranean urban area: Marseille” by
I. El. Haddad et al.***

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First we want to thank reviewer 2 for raising these relevant comments and questions.

CMB model validation and BSOA domination:

The validation of CMB model results is indeed a crucial step be-

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fore drawing any conclusions regarding source contributions.

In the companion paper, we have shown the representativeness of source profiles included in CMB by examining the statistical performance measures provided. Moreover, when comparing CMB estimates for the fossil fraction with those computed using ^{14}C data, a good agreement between the two independent approaches was found, suggesting that our CMB analysis capture well the primary sources impacting the aerosol in Marseille (see companion paper for further information).

This validation procedure undertaken in the companion paper provides very reasonable bounds on our CMB results.

As suggested by Reviewer 2, factor analysis of AMS measurements (AMS/PMF) can also be another approach to confirm CMB modeling results. This analysis was performed in our case, but results will be thoroughly treated in a separate paper currently in preparation. Overall, a very good agreement between CMB estimates and those apportioned by AMS/PMF was observed. The latter approach revealed 4 factors: **HOA** (ascribed mainly to vehicular emissions), industrial emission factor (referred to as **F4**), and the two factors for SOA (**LV-OOA** and **SV-OOA**). The average contribution of HOA and F4 were estimated at 15% and 4% of the

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total OA, respectively. Accordingly, the foremost conclusion that can be drawn from both source apportionment approaches is the overwhelming domination of SOA.

As it was revealed by ^{14}C data analysis, more than 70% of the SOA is of biogenic origins (BSOA) although the main primary sources apportioned by the CMB or AMS/PMF emit fossil carbon in our case. Even though the domination of BSOA in such environment may seem unlikely, this result is in good agreement with ^{14}C measurements at urban sites like, for example, Mexico (MILARGO experiment, Hodzic et al., 2010) where fossil fuel combustion dominates primary sources (Hodzic et al., 2010).

The domination of BSOA in urban areas highly impacted by anthropogenic emissions naturally prompts the question about the impact of the primary emissions (NOX, SOX and primary organic aerosol) on the formation of BSOA (Carlton et al., 2010). In our opinion, this is a very relevant question that we intend to further investigate in future studies.

Correlations of MACR vs. isoprene and MVK vs. isoprene:

The measurements of gas phase volatile organic compounds (VOC; e.g. isoprene, MACR and MVK) were performed using a HS-PTRMS (High Sensitivity – Proton Transfer Reaction Mass

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Spectrometer) that cannot distinguish between isomers having the same molecular weight (de Gouw et al., 2003; de Gouw and Warneke, 2007). Therefore, only the aggregate concentration of MACR and MVK can be measured by the HS-PTRMS, preventing the comparison between the concentrations of each of these compounds with those of isoprene. However, these compounds display usually the same trends, being derived from the photo-oxidation of isoprene under high NOX conditions (Carlton et al., 2009). As a result, it can be expected that, when taken individually, MACR and MVK would display similar correlations with isoprene.

Isoprene SOA markers and atmospheric transport:

Circulation of air masses in the area of Marseille is complex (see companion paper), as local urban emissions are diffused into air masses from regional transport (Drobinski et al., 2007; Flaounas et al., 2009). This particular circulation heavily impacts the levels of the organic aerosol components, including isoprene SOA markers.

The first remark that has been raised by reviewer 2 is the high concentrations of isoprene SOA markers during some nights, which might result from dark O₃ oxidation or from regional transport.

Chamber experiments pertaining to investigate isoprene chem-

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istry shows that isoprene O₃ oxidation contributes little to SOA production (Carlton et al., 2009) and the formation of isoprene SOA markers (mainly 2-methyltetrols) only evolve photochemical reactions with OH radicals (Paulot et al., 2009). The results from chamber experiments are in agreement with ambient measurements conducted in forested areas where local photochemistry prevails, reporting substantially higher daytime concentrations. Accordingly, these high night time concentrations of isoprene SOA markers are most likely related to atmospheric transport, in our case. Thus, we strongly believe that these compounds are not formed locally, and the variability of their concentrations in Marseille is mostly dominated by regional transport.

The second remark pointed out by reviewer 2 is that our low NO_x concentrations (5-10 ppb) associated with high concentrations of isoprene SOA markers fall into the high NO_x regimes (> 1 ppb) generally considered in chamber experiments (Surratt et al., 2006).

This very relevant remark can also be explained by atmospheric transport. In general, in Marseille, low NO_x concentrations are observed when the area is subjected to synoptic clean air masses from the Mediterranean (Cros et al., 2004). During these

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episodes, higher concentrations of isoprene SOA markers were observed; these compounds are most likely produced during regional transport at low NOX regimes. However, once in Marseille, these clean air masses are mixed with the urban local emissions generally comprising high concentrations of NOX. This mixing may explain the fact that low NOX regimes observed in our case are generally higher than 5 ppb.

As suggested by reviewer 2, a more detailed discussion regarding the impact of atmospheric transport on concentrations of isoprene SOA markers will be presented in the corrected manuscript.

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