

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

**I. El. Haddad et al.**

imad.el-haddad@etu.univ-provence.fr

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We want to thank Pr. Magda Clayes for raising these really relevant comments.

**Concentrations of isoprene oxidation products and analytical issues:**

Major concerns of the review regard the relatively low concentrations of isoprene oxidation products, 2-methyltetrols (2-MT) and 2-methylglyceric acid (2-MGA), measured in our study. Indeed, these concentrations can be considered

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at the bottom end of the range of concentrations reported in previous studies. For instance, the 2-methyltetrol concentrations found here (average  $1.9 \text{ ng m}^{-3}$ ) are lower than those reported at a coastal site in the US, i.e.  $6.1 \text{ ng m}^{-3}$  for Pensacola, FL (Clements and Seinfeld, 2007). We also found such result a little bit puzzling; however we think that a direct comparison of our results with those reported in previous studies cannot be considered totally relevant giving the particularity of Marseille environment (long range transport, severe photochemical conditions, industrial, high  $\text{NO}_x$  inputs ...).

As discussed in the article and mentioned in the review the analytical determination of these markers is a critical issue. We totally agree that an intercomparison exercise is needed for these compounds. We have compared levoglucosan concentrations obtained with the analytical approach used here, i.e. GC/MS coupled to BSTFA derivatization, with those determined using a LC/MS<sup>2</sup> method (Figure 1). We observe an excellent agreement between the two independent methods, which support our analytical determinations at least for levoglucosan. As levoglucosan (anhydrous sugar having three hydroxyl moieties) bears similar functional groups as 2-MT and 2-MGA, one would expect that the latter products can be also determined accurately using this method.

Another puzzling observation that can be made regarding the concentrations of isoprene oxidation products is the relatively low ratios of 2-MT-to-2-MGA found during this study, ranging from 0.3 to  $3.7 \text{ g g}^{-1}$ , whereas this ratio encountered in previous studies is higher. This issue is discussed in the supporting information (Figure S3). According to recent and state of the art literature a wide range of ratios are found in ambient measurements, spanning more than three orders of magnitude [ $0.05\text{-}100 \text{ g g}^{-1}$ ]. This wide range of ratios encompasses the one found in our study. In addition if we use the same quantification procedure as used in Kleindienst et al. (2007) our 2-MT-to-2-MGA ratios would increase by a

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systematic factor of about 2 (indicated in Figure S3 by the term “This study”). In such conditions, the range of ratios that we have found matches the range measured by Kleindienst et al. (2007) at an urban site. On the other hand, the range of ratios found in this study is lower than those reported at forested sites, which is not surprising owing most likely to inputs of  $\text{NO}_x$  or the decay of these markers in our case. Consequently, MT-to-MGA ratios determined in our study cannot be considered as low in view of the wide range already reported in Kleindienst et al. (2007) or in other studies.

## Marine impact:

Estimating the marine direct (primary, POA) and indirect (secondary, SOA) impact on the aerosol components is a very relevant topic. The contribution of primary sea-salt can be roughly estimated using the sodium  $\text{Na}^+$  as a tracer. This was done in the companion paper and the result suggests that on average 1.3% of the  $\text{PM}_{2.5}$  mass can be assigned to sea-salt. However, the assessment of secondary marine inputs is more delicate; all that we can say is that we did not observe significant increases in the % contributions of the secondary indicators, i.e. %WSOC, %BSOA, %HULIS, when the site was downwind of the Mediterranean. On the other hand, the concentrations of Methyl-Sulfonic Acid (a tracer of marine SOA) were very, during the 15-day campaign, suggesting that marine SOA did not constitute the predominant fraction in our case.

Indeed, longer dataset can be most useful to make quantitative conclusions regarding this issue. A specific work on Mediterranean POA and SOA will be conducted in a near future in order to better quantify marine inputs.

## Diurnal variation:

Unlike previous studies (e.g. Ion et al., 2005), secondary components, such as WSOC, BSOA, HULIS, BSOA markers did not exhibit any diurnal variation.

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Only POA originating from vehicular emissions display a slight diurnal variation with higher daytime concentrations ( $0.9 \mu\text{g m}^{-3}$  during day and  $0.6 \mu\text{g m}^{-3}$  during night). It seems that the regional transport and the variability of the sources and the air mass origins overwhelm the local photochemistry. This regional impact is especially clear in the case of industrial emissions (see companion paper), but can also be noticed from the isoprene gas phase concentrations (Figure 3) as there are periods when the concentrations of this component are much higher. These periods can be related probably to air masses highly impacted by biogenic emissions. This none typical variability of air mass origins and its impact on biogenic inputs can explain the fact that these markers did not exhibit a typical diurnal variation. More details will be added in the corrected version of this paper regarding this issue.

We will take into consideration the minor corrections of the reviewer in the corrected version.

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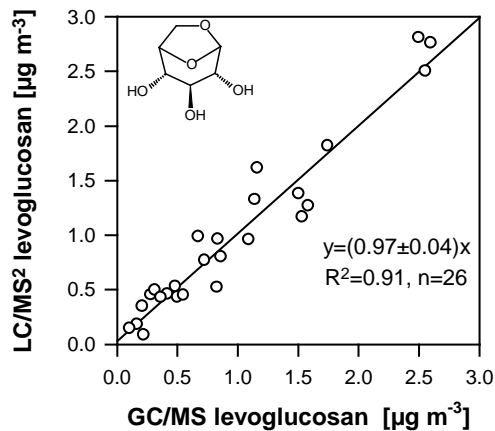
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**Fig. 1.** Comparison between levoglucosan concentrations determined by GC/MS analysis coupled to BSTFA derivatization and those determined by a LC/MS2 method (Piot et al., in prep).

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