

***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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General Comments:

This is a very comprehensive study aiming at providing detailed insights into the secondary fraction of the organic aerosol in Marseille, a Mediterranean urban area, during a 2008 summer period. The primary OC was found to correspond on average to 22% of the OC, implying that 78% of the OC is secondary. In addition, radiocarbon measurements revealed that more of 70% of this fraction is modern or of biogenic origin. However, it was found using the tracer-based approach that the contribution from tra-

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ditional biogenic secondary organic carbon (SOC) originating from isoprene, α -pinene and β -caryophyllene was only 4.2% and was dominated by α -pinene SOC (3.4%). It appears that the tracer-based approach shows shortcomings in estimating the fraction of the OC that is due to biogenic SOC. The authors provide possible reasons for this discrepancy and conclude that several issues remain unanswered and warrant further investigation. Especially the isoprene SOC appears to be quite low compared to other field studies, suggesting that the available source profiles may not be applicable for inferring the isoprene SOC in Marseille. It is puzzling to me why the concentrations of the isoprene SOA markers (i.e., 2-methyltetrols and 2-methylglyceric acid) are that low; it is likely that the 2-methyltetrols are present as organosulfates and nitrooxy organosulfates, but even in this case these derivatives would be measured as 2-methyltetrols with the trimethylsilylation GC/MS technique. It is also quite puzzling that the concentrations of 2-methylglyceric acid are higher than those of the sum of the 2-methyltetrols.

Specific comments:

Page 25498 – lines 5-10: several meteorological conditions were encountered during the campaign, including conditions where clean air masses were advected from the Mediterranean Sea: could it be that during these episodes a substantial fraction of the SOC had a marine origin? SOC with a marine origin has not been considered in this study.

Page 25509 – line 19: as already stated, the 2-methyltetrol concentrations (average 1.9 ng/m³) are quite low in my opinion, although low (but higher) 2-methyltetrol concentrations have been found for a coastal site in the USA, i.e. 6.1 ng/m³ for Pensacola, FL (Clements and Seinfeld, Atmos. Environ. 41, 1825-1830, 2007).

Page 25510 – line 13: it is also surprising that the isoprene SOC markers do not display a diel (day/night) variation; in field studies where we have taken 12-h samples, a diel variation has been noted for the 2-methyltetrol concentrations, for example, at K-pusztá, Hungary (Ion et al., 2005) and in Rondonia, Brazil (Claeys et al., ACP 10,

9319-9331, 2010).

Page 25511 – lines 21-27: here, the authors discuss the impact of the NO_x regime on the 2-MT/2-MGA ratios. As expected, a decrease is observed at high-NO_x. I wonder whether it was also possible to observe the C₅-alkene triols in low-NO_x episodes, considering that these tracers are characteristic for low-NO_x conditions (Surratt et al., 2006).

Page 25511 – line 28 – page 25512 – 6: for more recent insights in the formation mechanism of 2-MGA and the 2-MTs, see the article by Surratt et al. in Proc. Natl. Acad. Sci. U.S.A. 107, 6640–6645, 2010.

Pages 25513 – 25516 (Part 4.1.3 Sensitivity of isoprene SOC estimates): in this section the authors discuss possible sources of biases with the tracer-based approach developed by Kleindienst et al. (2007) for estimating the isoprene SOC, namely:

- use of different surrogate standards for the quantification of 2-MGA and the 2-MTs;
- use of marker-to-SOC ratios from chamber experiments conducted under different conditions; and
- differences in profiles obtained in ambient and chamber conditions.

It is concluded that the main biases arise from the choice of isoprene SOC markers; greater differences in the estimation of isoprene SOC exist when 2-MT is severely depleted against 2-MGA. In our experience, however, 2-MT/2-MGA ratios as low as in the present study (0.3) have not been encountered in the field studies we have conducted. In this respect, it would be worthwhile that more certainty is obtained about the 2-MT measurements and to consider an intercomparison exercise. Again, even in the case the 2-MTs were in the form of organosulfates or nitrooxy organosulfates, they should have been captured by the trimethylsilylation GC/MS technique.

Technical corrections:

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Page 25492 – line 15: β -caryophyllene

Page 25493 – line 9: anthropogenic sources

Page 25493 – line 20: model predictions

Page 25494 – line 20: β -caryophyllene

Page 25495 – line 9: in the particle phase

Page 25500 – line 7: Electron Ionisation

Page 25500 – line 16: acetonitrile

Page 25500 – line 19: which converted hydroxyl groups to trimethylsilyl groups (TMS).

Page 25501 – line 11: abundant fragment ions at ...

Page 25501 – line 19: However, the TMS-derivatisation technique does not allow to distinguish between alcoholic and carboxylic hydroxyl groups in the same molecule

Page 25501 – line 24: through five- to eight-membered ...

Page 25502 – line 5: the two 2-methyltetrol diastereoisomers:

Page 25502 – line 15: the C₈-tricarboxylic acid (with the 8 written in subscript as it indicates the number of carbon atoms in the molecule and not a position)

Page 25502 – line 29: d-limonene

Page 25505 – line 17: we discuss

Page 25506 – line 27: fossil origin

Page 25507 – line 11: is of primary origin and 47% is of secondary origin.

Page 25507 – line 28: biogenic origin

Page 25508 – line 15: β -caryophyllinic acid

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Page 25509 – line 9: 2-methylthreitol (without capital)

Page 25509 – line 10: 2-methylerythritol (without capital)

Page 25511 – line 21: has a significant impact

Page 25517 – line 12: β -caryophyllinic acid

Page 25518 – line 14 and 25: d-limonene

Page 25519 – line 5: C7-tricarboxylic acids or C8-hydroxydicarboxylic acids (with 7 and 8 written in subscript to denote the number of carbon atoms in the molecule)

Page 25522 – line 4: sensitivity

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