

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.

Anonymous Referee #1

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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 approaches 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

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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-methylglyceric 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.

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

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-NO_x 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-NO_x 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?

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.

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?

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