

Answer to comment of **Referee#2**

on “*Speciation of organic aerosols in the Saharan Air Layer and in the free troposphere westerlies*” by M.I. García et al.

Reviewer Comment - OVERVIEW:

This manuscript presents a substantial and comprehensive speciation of organic aerosols transported in the SAL and in the North Atlantic free troposphere westerlies. The sampling methods and analysis methods are valid. The Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) model was applied to present sources of organic aerosol. The scientific results are presented in a well-organized way. Atmospheric particulate matter on secondary inorganic species, organic species, elemental composition, chemical composition and 40 organic tracer species were analyzed, which provides possible sources of organic aerosol. Source apportionment method also gives the contributions of total organic aerosol from different sources, such as biomass burning (BB), combustion POA, and organic dust. Overall, this manuscript is publishable in Atmospheric Chemistry and Physics with the following minor comments are addressed.

REPLY:

Thanks to Referee #2 for the useful comments that contribute to improve the original manuscript. Please, find below a point-by-point reply to each question and suggestion.

Minor comments

1. What is “ddmmm” in Figure 1?

REPLY:

"ddmmm" refer to day and month of sampling. with “ddmmm” referred to ending sampling day.

CHANGES IN THE MANUSCRIPT [R2#C1]:

Sentence

“with “ddmmm” referred to ending sampling day”

reworded as

“the dates refer to the day of completion of the sampling”.

2. A large fraction of OM was not determined under FT-SAL, BL-SAL and BBE in Figure 4 or Figure 7. Can authors explain the difference of undetermined fraction between FT-SAL and FT-WES? Is this due to method limitation or the size cut-off of collected particles for dust-associated compounds?

REPLY:

It not due to the size cut-off, since the samples in the FT-SAL and FT-WES airflows were collected in PM_T fraction (i.e. total suspended particles). The organic aerosols comprise thousands of organic species from which only ~10 to 30% has been identified by the scientific community (see details in Andreae, 2009) and the analysis of the samples by means of gas chromatography–mass spectrometry (GC-MS) covers a very small fraction (often < 5 % of the organic matter; Alier et al., 2013, included in the reference list of the ACPD manuscript). The fact that undetermined fraction is higher in the FT-SAL than in the FT-WES indicate that the number of unknown organic species is higher in the SAL than in the WES, so these differences are actually a method limitation. Although the number of identified species is in general low with these techniques, the correlation between the score factors and the organic matter (Table S1) indicates that the selected organic tracers can be representative of the potential sources contributing to the composition of the organic aerosols.

Reference:

Andreae, M. O.: A new look at aging aerosols, *Science*, 326, 1493–1494, doi:10.1126/science.1183158, 2009.

CHANGES IN THE MANUSCRIPT [R2#C2]:

An explanation of the above mentioned difference of undetermined fraction between FT-SAL and FT-WES has been introduced in “3.2.9 Determined fraction of OM”. We have added to the main text: “*Differences in the determined fraction of the samples collected under the FT-SAL and FT-WES influence – as observed in Fig. 4 – is a result of the method limitation as the analysis of the samples by means of gas chromatography–mass spectrometry (GC-MS) covers a very small fraction (often < 5 %; Alier et al., 2013) of the organic matter*”.

3. P.4 Line 25: Please define “SIM” mode.

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C3]:

We have replaced “SIM mode” by “*selected ion monitoring (SIM) mode*”.

4. Can authors explain the “score factor” in the method or in Figure 5?

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C4]:

A description of “loadings” and “scores” has been provided in “3.3 Sources of OM”. We have added to the main text: “*The data matrix was decomposed in two factors: loadings (i.e. the relative amount of the chemical compounds in the source) and scores (i.e. the relative contribution of the potential sources to the organic aerosol) (Tauler et al., 2009)*”.

The following reference has been added:

Tauler, R., Viana, M., Querol, X., Alastuey, A., Flight, R. M., Wentzell, P. D. and Hopke, P. K.: Comparison of the results obtained by four receptor modelling methods in aerosol source apportionment studies, *Atmos. Environ.*, 43(26), 3989–3997, doi:10.1016/j.atmosenv.2009.05.018, 2009.

5. The author wrote the correlations of total concentration of SOA ISO and total concentration of SOA PIN exhibits two distinct trends in Figure 2, and the correlation between SOA ISO and NO₃⁻ presents three tendencies. The explanation for these biogenic SOA sources is not clearly discussed and supported by significant evidence. The ratio of isoprene to NO_x, and the daytime photooxidation process and nighttime nitrate chemistry can be discussed.

REPLY:

Thank you very much for your suggestion, which will definitively enrich the manuscript. The back-trajectories analysis allows identifying air masses from North Africa and North America, but the methodology does not allow a deeper differentiation of potential source regions within North Africa. We do not see differences in the back-trajectories of dusty days associated with high and with low concentrations of nitrate, SOA ISO or SOA PIN, they mostly show the regular circulation associated with the Saharan Air Layer (discussed by Rodríguez et al., 2015, included in the reference list of the ACPD manuscript). The lack of association of a trajectory type with a certain amount of nitrate (or SOA ISO or SOA PIN) is due to the fact that (i) an air mass may have a difference amount of a secondary aerosol depending on the emissions in the source region days backward and (ii) these emissions in the source region change along time.

In section <3.2.8 Tracers of isoprene oxidation (SOA ISO)> we suggest the correlation between SOA-ISO and SOA-PIN “might be” due to “different global sources of the precursor volatile compounds” as “global estimations of isoprene and α -pinene emissions and sources show they are diverse and not equally distributed in the globe (Luo et al., 2010; Guenther et al., 2012; Sindelarova et al., 2014)”. Further studies are needed on this topic.

We agree that the correlation in Fig.3 needs more theoretical support. Changes have been introduced in the manuscript.

CHANGES IN THE MANUSCRIPT [R2#C5]:

We have added the following description to the introduction (*italic*):

"Some [R2#C9] important factors influencing SOA formation are reactive nitrogen species (NO_x) (Presto et al., 2005; Ng et al., 2007, 2008), which are further oxidized to the highly reactive nitrate radical (NO_3). NO_3 interacts with VOCs in gas-phase, likely having an impact in global OA levels as indicated by modelling (Pye et al., 2010) and experimental work (Surratt et al., 2006). *At daytime, NO_x can react with organic peroxy radicals (RO_2) resulting in peroxy nitrates (RO_2NO_2) and alkyl and multifunctional nitrates ($RONO_2$) (O'Brien et al., 1995); the formation of organic nitrates provisionally sequesters NO_x , which can suffer long-range transport to more remote environments (Horowitz et al., 1998; Mao et al., 2013). At nighttime, the interaction VOCs- NO_3 dominates, with SOA yields greater than that for OH or O_3 oxidation (Ng et al., 2016 and references there in). Previous modeling studies carried by Hoyle et al. (2007) suggested that, during twilight conditions, ~ 21% of the global average SOA may be due to oxidation of SOA precursors by NO_3 , and measurements performed by Brown et al. (2009) found that, during nighttime, 1-17% of SOA was the result of NO_3 initiated isoprene oxidation."*

We have extended the discussion in section <3.2.8 Tracers of isoprene oxidation (SOA ISO)> (*italic*):

"SOA ISO seems to depend strongly on the conditions (aerosol acidity, NO_x concentrations and pre-existing aerosol) used to oxidize isoprene (Surratt et al., 2006, 2007; Marais et al., 2016). NO_x concentration determine the pathway (low- NO_x and high- NO_x) followed by the isoprene oxidation, leading to different secondary organic species (Paulot et al., 2009a, b); the low- NO_x pathway is ~5 times more efficient than the high- NO_x pathway (Marais et al., 2016). Experiments carried out by Kroll et al. (2006) evidence how the isoprene SOA yield varies depending on NO_x concentration, increasing from no injected NO_x , to a plateau between 100 and 300 ppb NO_x , and decreasing at higher NO_x concentrations.

We found the relation among SOA ISO and NO_3^- within the FT-SAL (Fig.3) present three tendencies which might be associated to the ratio isoprene: NO_x in the source. *The different correlation are supported by the fact that the SOA ISO markers (2-MTs and 2-MGA) do not exhibit the same temporal trend (FT-SAL 2-MTs vs 2-MGA- r^2 : 0.1), which has been suggested to be linked to the NO_x concentration influence on this SOA ISO markers formation pathways (El Haddad et al., 2011). The high- NO_x pathway leads to the reaction of isoprene peroxy radicals (iRO_2) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low- NO_x pathway leads to the reaction of iRO_2 with hydroperoxy radicals (HO_2) resulting in hydroxyhydroperoxides ($iROOH$), and carbonyls production to a lesser extent (Carlton et al., 2009; Paulot et al., 2009). This has implication on the abundance of the secondary organic markers from isoprene photo-oxidation (2-MT and 2-MGA): high- NO_x pathway results in the major product 2-MGA and low- NO_x pathway is associated to the major products 2-MTs (El Haddad., 2011)."*

The following references have been included in the manuscript:

- Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dubé, W.P., Atlas, E., Weber, R. J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S. A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 3027–3042, doi:10.5194/acp-9-3027-2009, 2009.
- Horowitz, L. W., Liang, J., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, *J. Geophys. Res.-Atmos.*, 103, 13451–13476, 1998.
- Hoyle, C. R., Berntsen, T., Myhre, G., and Isaksen, I. S. A.: Secondary organic aerosol in the global aerosol – chemical transport model Oslo CTM2, *Atmos. Chem. Phys.*, 7, 5675–5694, doi:10.5194/acp-7-5675-2007, 2007.

- Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.
- Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crouse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, *J. Geophys. Res.-Atmos.*, 118, 11256–11268, doi:10.1002/jgrd.50817, 2013
- Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO₂ emission controls, *Atmos. Chem. Phys.*, 16, 1603-1618, doi:10.5194/acp-16-1603-2016, 2016.
- Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, 17, 2103-2162, doi:10.5194/acp-17-2103-2017, 2017.
- O'Brien, J., Shepson, P., Muthuramu, K., Hao, C., Niki, H., Hastie, D., Taylor, R., and Roussel, P.: Measurements of alkyl and multifunctional organic nitrates at a rural site in Ontario, *J. Geophys. Res.*, 100, 22795–22804, 1995.
- Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009a.
- Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kürten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxideformation in the gas-phase photooxidation of isoprene, *Science*, 325, 730–733, doi:10.1126/science.1172910, 2009b.

Technical correction

6. P.16 Line 18: “wad” should be “was”.

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C6]:

We have replaced “wad” by “was”.

7. P.6 line 21: Some species “shows” should be “show”.

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C7]:

We have replaced “shows” by “show”.

8. P.13 line 9: “represents” should be “represent”.

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C8]:

We have replaced “represents” by “represent”.

9. P.2 line 14”: “An important factor” should be “Some important factors”.

REPLY:

Thank you very much for your observation.

CHANGES IN THE MANUSCRIPT [R2#C9]:

We have replaced “An important factor” by “*Some important factors*”.