

Answer to comment of **Referee#1**

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 study focused on organic aerosol composition in the free troposphere from airflows transported by westerlies over the north Atlantic as well as airflows from the Saharan Air Layer. Organic tracers were used to identify possible atmospheric particulate matter sources. Saharan Air was dominated by dust and only contained about 1.5% organic mass. The Westerlies had significantly higher amounts of organic mass fraction, most of which was dicarboxylic acids and isoprene SOA. These measurements highlight the importance of atmospheric transport as an aerosol source.

REPLY:

Thanks to Referee #1 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. In figure 2 and 3 you claim that there are multiple tendencies that can reasonably be explained to be from different source locations, however the argument is weak if you do not have some further evidence to support that there are multiple tendencies rather than no correlation when fitting all the data. This is especially important since there are such a few amount of samples. Did you actually find evidence for this in back trajectories or any other analysis?

REPLY:

Thank you very much for highlighting this point. 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 the correlation in Fig.3 need more theoretical support. Changes have been introduced in the manuscript.

CHANGES IN THE MANUSCRIPT [R2#C1]:

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 suffers 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 NO₃, and measurements performed by Brown et al. (2009) found that, during nighttime, 1-17% of SOA was the result of NO₃ 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 Kröll 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 NO₃⁻ 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-r²: 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 (iRO₂) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low-NO_x pathway leads to the reaction of iRO₂ with hydroperoxy radicals (HO₂) 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:

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