

Dear Dr. Russell,

I contact you because of the end of the discussion period of the ms <acp-2017-108>. As you can see in the web site, we have already replied to each of the question of the two reviewers. In the reply we have followed the structure (1) comments from Referees, (2) author's response, (3) author's changes in manuscript, recommended by ACP.

We have now prepared a revised version of the manuscript. For preparing this version we have taken into account the comments of both reviewers. As you can see in the reports, both referees have arisen minor and technical comments and agree publication of this manuscript in ACP. The questions and suggestions of the reviewers have definitively contributed to improve the manuscript.

Please, find attached to this letter (i) the “Authors Response Report”, which includes the answers to reviewers 1 and 2, with a reply to each question and the description of the changes in the manuscript as a consequence of each referee comment, and (ii) the “Revised Manuscript and Supplement”, where the changes performed (with respect to the ACPD version) are highlighted. We have also followed the structure (1) comments from Referees, (2) author's response, (3) author's changes in manuscript, recommended by ACP, so changes can easily be tracked.

This revised version includes the minor comments and technical changes were introduced to include the comments of the referees.

The latex file of the manuscript and the pdf of the supplement will be uploaded in a further step.

Thanks,  
Sergio Rodríguez

# Authors Response Report

## **REPLY TO REVIEWER#1:**

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  $\alpha$ -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 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<sub>x</sub>, to a plateau between 100 and 300 ppb NO<sub>x</sub>, and decreasing at higher NO<sub>x</sub> concentrations.

We found the relation among SOA ISO and NO<sub>3</sub><sup>-</sup> within the FT-SAL (Fig.3) present three tendencies which might be associated to the ratio isoprene:NO<sub>x</sub> 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<sup>2</sup>: 0.1), which has been suggested to be linked to the NO<sub>x</sub> concentration influence on this SOA ISO markers formation pathways (El Haddad et al., 2011). The high-NO<sub>x</sub> pathway leads to the reaction of isoprene peroxy radicals (iRO<sub>2</sub>) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low-NO<sub>x</sub> pathway leads to the reaction of iRO<sub>2</sub> with hydroperoxy radicals (HO<sub>2</sub>) 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<sub>x</sub> pathway results in the major product 2-MGA and low-NO<sub>x</sub> pathway is associated to the major products 2-MTs (El Haddad., 2011)."*

The following references have been included in the manuscript:

- Brown, S. S., de Gouw, 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., Crounse, 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 SO<sub>2</sub> 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., Crounse, 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., Crounse, 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.

## **REPLY TO REVIEWER#2:**

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<sub>T</sub> 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  $\text{NO}_3^-$  presents three tendencies. The explanation for these biogenic SOA sources is not clearly discussed and supported by significant evidence. The ratio of isoprene to  $\text{NO}_x$ , 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  $\alpha$ -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 ( $\text{NO}_x$ ) (Presto et al., 2005; Ng et al., 2007, 2008), which are further oxidized to the highly reactive nitrate radical ( $\text{NO}_3$ ).  $\text{NO}_3$  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,  $\text{NO}_x$  can react with organic peroxy radicals ( $\text{RO}_2$ ) resulting in peroxy nitrates ( $\text{RO}_2\text{NO}_2$ ) and alkyl and multifunctional nitrates ( $\text{RONO}_2$ ) (O'Brien et al., 1995); the formation of organic nitrates provisionally sequesters  $\text{NO}_x$  which can suffer long-range transport to more remote environments (Horowitz et al., 1998; Mao et al., 2013). At nighttime, the interaction VOCs- $\text{NO}_3$  dominates, with SOA yields greater than that for OH or  $\text{O}_3$  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  $\text{NO}_3$ , and measurements performed by Brown et al. (2009) found that, during nighttime, 1-17% of SOA was the result of  $\text{NO}_3$  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,  $\text{NO}_x$  concentrations and *pre-existing aerosol*) used to oxidize isoprene (Surratt et al., 2006, 2007; Marais et al., 2016).  $\text{NO}_x$  concentration determine the pathway (low- $\text{NO}_x$  and high- $\text{NO}_x$ ) followed by the isoprene oxidation,

leading to different secondary organic species (Paulot et al., 2009a, b); the low-NO<sub>x</sub> pathway is ~5 times more efficient than the high-NO<sub>x</sub> pathway (Marais et al., 2016). Experiments carried out by Kroll et al. (2006) evidence how the isoprene SOA yield varies depending on NO<sub>x</sub> concentration, increasing from no injected NO<sub>x</sub>, to a plateau between 100 and 300 ppb NO<sub>x</sub>, and decreasing at higher NO<sub>x</sub> concentrations.

We found the relation among SOA ISO and NO<sub>3</sub><sup>-</sup> within the FT-SAL (Fig.3) present three tendencies which might be associated to the ratio isoprene:NO<sub>x</sub> 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<sup>2</sup>: 0.1), which has been suggested to be linked to the NO<sub>x</sub> concentration influence on this SOA ISO markers formation pathways (El Haddad et al., 2011). The high-NO<sub>x</sub> pathway leads to the reaction of isoprene peroxy radicals (iRO<sub>2</sub>) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low-NO<sub>x</sub> pathway leads to the reaction of iRO<sub>2</sub> with hydroperoxy radicals (HO<sub>2</sub>) 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<sub>x</sub> pathway results in the major product 2-MGA and low-NO<sub>x</sub> 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 SO<sub>2</sub> 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”.

# Revised Manuscript

Changes are highlighted in **green** for reviewer#1, in **yellow** for reviewer#2 and in **blue** for authors. Brackets indicate the reviewer and comment that prompt the change.



# Speciation of organic aerosols in the Saharan Air Layer and in the free troposphere westerlies

M. Isabel García<sup>1,2</sup>, Barend L. van Drooge<sup>3</sup>, Sergio Rodríguez<sup>1</sup> and Andrés Alastuey<sup>3</sup>

<sup>1</sup> Izaña Atmospheric Research Centre, AEMET, Joint Research Unit [Authors] to CSIC “Studies on Atmospheric Pollution”, Santa Cruz de Tenerife, 38001, Spain

<sup>2</sup> Department of Chemistry (T.U. Analytical Chemistry), Faculty of Science, University of La Laguna, La Laguna, 38206, Spain

<sup>3</sup> Institute of Environmental Assessment and Water Research, CSIC, Barcelona, 08034, Spain

*Correspondence to:* Sergio Rodríguez (srodriguez@aemet.es)

**Abstract.** We focused this research on the composition of the organic aerosols transported in the two main airflows of the subtropical North Atlantic free troposphere: (i) the Saharan Air Layer – the warm, dry and dusty airstream that expands from North Africa to the Americas at subtropical and tropical latitudes – and (ii) the westerlies – which flows from North America through the North Atlantic at mid and subtropical latitudes –. We determined the inorganic compounds (secondary inorganic species and elemental composition), elemental carbon and the organic fraction (bulk organic carbon and organic speciation) present in the aerosol collected at Izaña Observatory, ~2400 m a.s.l. in Tenerife Island. The concentrations of all inorganic and almost all organic compounds were higher in the Saharan Air Layer than in the westerlies, with bulk organic matter concentrations within the range 0.02–4.0  $\mu\text{g}\cdot\text{m}^{-3}$ . In the Saharan Air Layer, the total aerosol population was by far dominated by dust (93% of bulk mass), which was mixed with secondary inorganic pollutants (<5%) and organic matter (~1.5%). The chemical speciation of the organic aerosols (levoglucosan, dicarboxylic acids, saccharides, n-alkanes, hopanes, polycyclic aromatic hydrocarbons and those formed after oxidation of  $\alpha$ -pinene and isoprene, determined by gas-chromatography coupled to mass-spectrometry) accounted for a 15% of the bulk organic matter (determined by the thermo-optical transmission technique); the most abundant organic compounds were saccharides (associated with surface soils), secondary organic aerosols linked to oxidation of biogenic isoprene (SOA ISO) and dicarboxylic acids (linked to several primary sources and SOA). When the Saharan Air Layer shifted southward, Izaña was within the westerlies stream and the organic matter accounted for ~28% of bulk mass of the aerosol cocktail. In the westerlies, the determined organic aerosol species accounted for 64% of the bulk organic matter, being SOA ISO and dicarboxylic acids the most abundant; the highest concentration of organic matter (3.6  $\mu\text{g}\cdot\text{m}^{-3}$ ) and of some organic species (e.g. levoglucosan and some dicarboxylic acids) were associated with biomass burning linked to a fire in North America. In the Saharan Air Layer, the correlation found between SOA ISO and nitrate suggests a large-scale impact of the enhancement in the formation of secondary organic aerosols due to interaction with anthropogenic  $\text{NO}_x$  emissions.

## 1 Introduction

Atmospheric aerosols, or particulate matter, influence on processes affecting climate, on continental and marine ecosystems, and on human health. The magnitude of these effects depends on the aerosols composition, which may include secondary inorganic species (e.g. sulphate, nitrate, ammonium and sea salt), mineral dust, elemental carbon and a number organic species constituting the so-called organic aerosols (OA) (IPCC, 2013). OA account for an important fraction of particulate matter, ranging from ~20% (continental mid-latitudes) to ~90% (tropical forested areas) (Kanakidou et al., 2005). As other aerosol components, OA also contributes to (i) light scattering and absorption (Kirchstetter and Novakov, 2004), (ii) cloud formation providing cloud condensation and ice nuclei (Sun and Ariya, 2005), and (iii) heterogeneous chemical reactions in the atmosphere (Kanakidou et al., 2005).

Principal sources of Primary OA (POA) include vegetation, fossil fuel combustion, biomass burning, biological aerosols and particles from soils. Precursors of Secondary OA (SOA) include natural and anthropogenic sources (Volkamer, et al., 2006; Gouw and Jimenez, 2009); emissions of biogenic volatile organic compounds (VOCs) significantly contribute to the global budget of SOA (Guenter et al., 2012). Some [R2#C9] important factors influencing SOA formation are reactive nitrogen species ( $\text{NO}_x$ ) (Presto et al., 2005; Ng et al., 2007, 2008), which are further oxidized to the highly reactive nitrate radical ( $\text{NO}_3$ ).  $\text{NO}_3$  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,  $\text{NO}_x$  can react with organic peroxy radicals ( $\text{RO}_2$ ) resulting in peroxy nitrates ( $\text{RO}_2\text{NO}_2$ ) and alkyl and multifunctional nitrates ( $\text{RONO}_2$ ) (O'Brien et al., 1995); the formation of organic nitrates provisionally sequesters  $\text{NO}_x$ , which can suffer long-range transport to more remote environments (Horowitz et al., 1998; Mao et al., 2013). At nighttime, the interaction VOCs- $\text{NO}_3$  dominates, with SOA yields greater than that for OH or  $\text{O}_3$  oxidation (Ng et al., 2017 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  $\text{NO}_3$ , and measurements performed by Brown et al. (2009) found that, during nighttime, 1-17% of SOA was the result of  $\text{NO}_3$  initiated isoprene oxidation [R2#C5 and R1#C1]. In remote environments, VOCs enhance condensational growth of new particles which can enter to the free troposphere (FT) by means of elevated mounts (García et al., 2014). These tropospheric aerosols are subject to much greater lifetimes and wind speed than in the planetary boundary layer (BL), favouring long-range atmospheric transport and aerosol impacts (Winker et al., 2013). The aged and processed long-range transported OA is of particular interest, as is spatially representative of the remote background conditions having important implications for global air quality and climate.

The most extended technique to quantify the amount of bulk organic and elemental carbon in the atmospheric aerosols is the thermo-oxidant combustion and optical detection (Birch and Cary, 1996; Cavalli et al., 2010; Karanasiou et al., 2015). This is a useful method for mass closure, but does not provide information on OA speciation and consequently on OA sources and properties related to impacts. Alternatively, gas-chromatography coupled to mass-spectrometry analysis of aerosol samples allows the speciation of the organic compounds and the quantification of many of those identified as tracers for distinguish sources and processes contributing to the budget of OA (Bauer et al. 2008; Mazurek et al. 1989; Claeys et al., 2007; Hallquist et al., 2009; Howsam and Jones 1998; Iinuma et al., 2007; Kawamura and Kaplan, 1987; Medeiros and Simoneit 2007; Narukawa et al., 1999; Rogge et al., 1993; Shauer et al. 2002; Simoneit et al. 1991; Simoneit et al. 2004a; Simoneit, 2002; Szmigielski et al., 2007). A number of studies have focused on OA speciation in urban areas (Alier et al., 2013; Kawamura and Kaplan, 1987; Puxbaum et al., 2007; Schauer et al., 1996; Simoneit et al., 1991; Van Drooge and Grimald, 2015) compared to remote environments. Studies in the free troposphere are scarce (Simoneit et al. 2004b; Fu et al., 2008, 2014; Wang et al., 2009; van Drooge et al., 2010; Meng et al., 2014), even if they are of interest due to the long-range transport potential linked to the high wind speeds above the boundary layer.

In this study we focused on the OA transported from inner Sahara over the North Atlantic in the so-called Saharan Air Layer (SAL; Prospero and Carlson, 1972). In summertime, the continental BL depth grows up to 5 km a.s.l. over the Sahara (Cuesta et al., 2009) and the prevailing easterly winds prompt the export of the warm Saharan air to the North Atlantic above the cool NNE trade winds that blows in the marine boundary layer. This results in the development of the SAL – a warm, dry and stable air stream that expands from North African coast, at altitudes 2 to 5 km a.s.l., to the Americas (Prospero and Carlson, 1972; Tsamalis et al., 2013) –. Because of the high stability associated with the warm air above the cool marine air, the SAL acts as a band conveyor that transport continental Saharan dusty air – originally placed near ground – over the North Atlantic; in addition to dust, other substances such as pollutants, vegetation debris or microorganisms are carried mixed with dust.

OA in the SAL has received little attention, even if its impacts are of interest. Anthropogenic bioaccumulative and toxic organic compounds (including organochlorine and organophosphate pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyl) are transported from Western Sahara to the Caribbean within the SAL (Garrison et al., 2013). Viruses, bacteria, fungal and pollens also travels mixed with dust across the Atlantic (Griffin et al., 2007; Izquierdo et al., 2011). Field measurements in the SAL at Izaña Observatory found dust

being the major ice nuclei at temperatures colder than  $-30^{\circ}\text{C}$  (Boose et al., 2016), whereas the observed ice nuclei at  $-8^{\circ}\text{C}$  points to a role of OA as ice nuclei at warm temperatures (Conen et al., 2015).

In this study we primarily focused on the origin of OA in the SAL. We collected in-situ aerosol samples directly into the high-altitude SAL at Izaña Observatory, located at  $\sim 2400$  m a.s.l. in Tenerife Island. The profile of the organic species was used for a source apportionment of the bulk organic matter. The results were compared with a similar data set obtained during the same campaign under the westerlies (WES) airflow that regularly brings air from North America across the North Atlantic. The observed differences illustrate the diversity of OA sources over the North Atlantic free troposphere.

## 2 Methodology

### 2.1 Sampling site

Sample collection was performed at the Izaña Global Atmospheric Watch (GAW) Observatory in Tenerife island (Fig. 1;  $16^{\circ}29'58''\text{W}$ ,  $28^{\circ}18'32''\text{N}$ ). The site is located on a mountaintop (2373 m a.s.l), surrounded by a pine forest (limited between  $\sim 500$ – $2300$  m). The Observatory remains almost permanently above the temperature inversion layer associated to the trade winds, which separates the moist marine BL from the dry FT avoiding vertical mixing before sunrise. Sunlight during daytime activate thermal convection, developing an orographic thermal-buoyant upslope winds, that transport species emitted in the BL by biogenic and anthropogenic sources (see details in Rodríguez et al., 2009).

### 2.2 Sampling

Samples were collected within the annual aerosols summer campaign of the Izaña Observatory in August 2013. Particulate Matter (PM) was collected on pre-heated (at  $205^{\circ}\text{C}$ ) quartz filters (Pall Science 150 mm diameter) on high volume air samplers (Hi-Vol; MCZ) at a flow rate of  $30\text{ m}^3\cdot\text{h}^{-1}$ . 30 samples of total particulate matter ( $\text{PM}_{\text{T}}$ ) were collected daily during nighttime (22:00–6:00 GMT; FT) and 12 samples of particulate matter smaller than  $2.5\text{ }\mu\text{m}$  ( $\text{PM}_{2.5}$ ) in non-consecutive days during daytime (10:00–16:00 GMT; BL). Field blanks were collected weekly and treated like the samples regarding preparation, transport and storage, as part of the quality assurance / quality control (QA/QC) protocol.

### 2.3 Chemical Analysis

#### 2.3.1 Organics

One quarter of the filter sample was used for the organic compounds speciation by gas-chromatography coupled to mass-spectrometry (GC-MS). A detailed description of the analytical method is given elsewhere (Fontal et al. 2015, van Drooge and Grimalt 2015). Briefly, filters were spiked with deuterated standards of acids, anhydro-saccharides, alkanes, and polycyclic aromatic hydrocarbons (PAHs) [Authors], and extracted ultrasonically in a mixture of dichloromethane and methanol. Extracts were filtered and concentrated until 0.5 mL. For the analysis of polar compounds, i.e. acids and saccharides, a  $25\text{ }\mu\text{L}$  aliquot of the extract was evaporated until dryness, and  $25\text{ }\mu\text{L}$  of bis-(trimethylsilyl)-trifluoroacetamide (BSFTA) + trimethylchlorosilane (99:1) (Supelco, Bellefonte, PA, USA) and  $10\text{ }\mu\text{L}$  of pyridine (Merck, Darmstadt, Germany) were added and left overnight to derivatize the polar compounds to their trimethylsilyl esters and ethers in order to analyse them by GC-MS. The remaining extract was used for the analysis of polycyclic aromatic hydrocarbons (PAHs) [Authors], n-alkanes and hopanes, and was clean-up by adsorption column chromatography, packed with 1 g of aluminium oxide (Merck, Germany). The analytes were eluted with 10 ml of hexane: dichloromethane (1:2 (v/v), Merck, Germany), which was collected and concentrated to 1 ml by rotovap and to  $25\text{ }\mu\text{L}$  under a gentle nitrogen stream for quantification by GC-MS (Thermo Trace GC Ultra – DSQ II). The MS detector was operated in full scan (m/z from 50 to 650) and electron impact ( $70\text{ eV}$ ) ionization mode for the polar compounds. The sample extracts for the analysis of non-polar species was performed in selected ion monitoring (SIM) [R2#C3] mode for the

corresponding ions of the compounds. Organic species were identified by their GC retention time and characteristic ions in the MS (see section S1 of the supplement).

### 2.3.2 OC and EC

5 Organic and elemental carbon (OC and EC) were analysed by thermal-optical transmittance (TOT, Sunset Laboratory Inc. <sup>TM</sup>) by using the EUSAAR2 protocol (Cavalli et al., 2010). The method provided four OC fractions (OC1, OC2, OC3 and OC4), from which the more volatile were discarded based on the results of the field blank filters analysis. Organic Matter (OM) was determined by using the ratio OM/OC = 1.8 for remote places (Pitchford et al. 2007; Dzepina et al. 2015).

### 2.3.3 Inorganics

10 The methodology used for the inorganic speciation is described in detail in Rodríguez et al. (2015). Briefly, soluble species were determined by ion chromatography ( $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) and selective electrode ( $\text{NH}_4^+$ ) after water leaching a fraction of filter. Elemental composition was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, IRIS Advantage TJA Solutions, THERMO<sup>TM</sup>) and Inductively  
15 Coupled Plasma Mass Spectrometry (ICP-MS, X Series II, THERMO<sup>TM</sup>) after acid digestion of the sample. Mineral dust was calculated as the sum of  $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{Fe} + \text{CaCO}_3 + \text{K} + \text{Na} + \text{Mg} + \text{P} + \text{Ti} + \text{Sr}$  (see details in Rodríguez et al., 2011, 2015) and normalized so Al accounts for 8% of the dust mass (see details in Pérez  
García-Pando [Authors] et al., 2016).  $\text{SO}_4^-$  was split in non-sea salt sulphate (nss- $\text{SO}_4^-$ ) and sea salt sulphate (nss- $\text{SO}_4^- = \text{SO}_4^- - \text{ss-}\text{SO}_4^-$ ) through the relation between marine Na and  $\text{SO}_4^-$ . Blank field filters were subject to gravimetric and chemical analysis and mean values subtracted to the  $\text{PM}_x$  samples.

### 20 2.4 Meteorology

The air mass origin and transport was tracked by means of backward trajectory analysis. Calculations were performed with the HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT, <http://ready.arl.noaa.gov/HYSPLIT.php>; Draxler and Rolph, 2003; Draxler and Hess, 1998; Stein et al., 2015) developed by the National Oceanic and Atmospheric Administration (NOAA). HYSPLIT was run with the  
25 National Centre for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS, 1 degree) data set. Ten days back-trajectories arriving at 2400 m a.s.l were computed daily (00 UTC) for August 2013.

### 2.5 Data treatment

In order to observe the similarities and differences among the chemical composition of the samples, the experimental organic compound data were merged for evaluation with Multivariate Curve Resolution  
30 Alternating Least Squares (MCR-ALS). The joint dataset was imported into MATLAB 7.4 (The Mathworks, Natick, USA) for subsequent calculations using MATLAB PLS 5.8 Toolbox (Eigenvector Research Inc, Masson WA, USA) (Jaumot et al. 2005). The MCR-ALS method decomposes the data matrix using an Alternating Least Squares algorithm under a set of constraints such as non-negativity, unimodality, closure, trilinearity or selectivity (Tauler et al., 1995a, b). The MCR-ALS method had been applied successfully in a previous study on  
35 organic aerosol in urban and rural areas (Alier et al. 2013; Van Drooge and Grimalt 2015). The explained variance by the different components is similar to a PCA, but not orthogonal. Since the natural sources in the environment are rarely orthogonal, the MCR-ALS method provides more realistic descriptions of the components than the orthogonal database decomposition methods. Multilinear regression tools were applied to quantify the contribution of the identified sources to the total OM.

### 40 3 Results and Discussion

We collected aerosol samples in four different airflows: 2 FT airflows and other 2 airstreams potentially mixed with BL air. Samples collected at night ( $PM_T$ ) are representative of the two FT airflows that prevail in this region: the WES and the SAL. As already described, the WES flow from North America across the North Atlantic at mid-latitudes, with their southern edge shifting to the subtropics in winter, and flow over Canada (Merry and Moody, 1996) reaching Izaña after circulation around the Azores high in summer (see backtrajectories of the samples collected from 26Aug to 30Aug – with "ddmmm" referred to ending sampling day – in Fig.1A). The SAL expands from North Africa to the Americas at subtropical latitudes in summertime (see backtrajectories associated during the study period in Fig. 1B), season in which the Izaña Observatory is mostly within this dusty airstream and the presence of the WES is associated with southern shifts of the SAL.

Samples collected during daylight ( $PM_{2.5}$ ) are representative of the FT potentially mixed with BL air, more specifically the BL-SAL mixing and BL-WES mixing. The presence of BL air is associated with the development of buoyant upslope winds caused by the heating of terrain, which typically results in increases of primary gaseous pollutants and new particle formation at Izaña (García et al, 2014; Rodríguez et al., 2009).

Thus, in this study we differentiate between 4 scenarios:  $PM_T$  (FT, nighttime) within (i) the SAL (FT-SAL) and (ii) the WES (FT-WES), and  $PM_{2.5}$  (BL, daytime) within (iii) the SAL (BL-SAL) and (iv) the WES (BL-WES).

### 3.1 Major Components

Table 1 shows the composition of the aerosol samples collected at Izaña. Concentrations of aerosol major components are the same order to those found in previous studies (Maring et al., 2000; Rodríguez et al., 2011). All species present much higher concentrations within the SAL than within the WES. Some species **show** slightly higher concentrations during the day linked to the upslope winds and boundary layer air.

### 3.2 Organic molecular tracers

In the next sections, organic speciation results are described. Table 2 shows the average concentrations of the 40 organic compounds analysed in this study under the different scenarios (SAL and WES) for  $PM_T$  and  $PM_{2.5}$ . In order to improve the insight on the origin and sources of some FT organic aerosol, correlations among the organic groups and the major species are evaluated (Table 3).

#### 3.2.1 Levoglucosan

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is emitted during biomass burning as a consequence of the thermal alteration of cellulose and hemi-cellulose present in vegetation (Simoneit, 2002). It is considered a particle-phase marker for the identification of wood combustion because of its source specific emission, but its atmospheric stability is still a matter of discussion. Experiments carried out by Hennigan et al. (2010) and Hoffmann et al. (2010) showed that levoglucosan reacts with gas-phase hydroxyl radicals (OH), especially under high relative humidity conditions. However, studies performed by Fraser and Lakshmanan (2000) demonstrated no degradation of levoglucosan under acidic conditions over a period of 10 days.

Levoglucosan daily values measured at Izaña within the FT and the BL were  $< 1.5 \text{ ng}\cdot\text{m}^{-3}$  for all samples, except on 28Aug when  $\sim 9 \text{ ng}\cdot\text{m}^{-3}$  was measured. Hysplit back-trajectories and the Atmospheric Infrared Sounder (AIRS) satellite images (NASA) indicate the North America origin of the air masses, where several wildfires – as the Rim Fire – were affecting western USA 10 days before the arriving of the air mass towards Izaña (detailed information not provided for sake of brevity). We detected a long-range transport biomass burning plume within the FT from the fires originated in North America. Other studies performed at Pico Mountain Observatory (Azores, 2225 m a.s.l.) have also detected the impact of other biomass burning plumes by means of the levoglucosan detection (Dzepina et al, 2015). These results give support to the atmospheric stability of levoglucosan, for the specific conditions of the atmospheric long-range transport. Due to the particular composition of this biomass burning event (BBE), we will discuss this sample separately (Table 2) and the sample will not be included when describing the general composition of the samples collected at night under

conditions of the westerlies (FT-WES; Table 2). Levoglucosan concentration, measured at Izaña during the BBE (9.3 ng·m<sup>-3</sup>), is similar to the average levels detected in the marine BL on the Azores in the North Atlantic (5.2 ng·m<sup>-3</sup>) or at free tropospheric site in the European continent (7.8 ng·m<sup>-3</sup>), but much lower than those found in sites under influence of local BB or continental sites in winter (653–1290 ng·m<sup>-3</sup>) (Puxbaum et al. 2007).

### 5 3.2.2 Dicarboxylic acids

Dicarboxylic acids can be emitted in small quantities from several natural and anthropogenic primary sources such as vegetation, meat cooking and motor exhaust emissions (Kawamura and Kaplan, 1987, Narukawa et al., 1999), although atmospheric photochemical transformation of volatile and semi-volatile organic compounds is considered to be an important source for the presence of these aged compounds in the atmosphere (Alier et al. 2013, Jang and McDow, 1997; Kleindienst et al. 2012; Paulot et al. 2011). This oxidative degradation of VOCs by tropospheric oxidants may be responsible for the similar mean  $\Sigma$ dicarboxylic acids concentrations within the FT (SAL: 14.4 ng·m<sup>-3</sup>; WES: 16.7 ng·m<sup>-3</sup>) and the BL (SAL: 11.1 ng·m<sup>-3</sup>; WES: 12.9 ng·m<sup>-3</sup>) at Izaña.

Succinic (suc) and phthalic (pth) acids were the most abundant dicarboxylic acids (Table 2) with FT and BL average values (suc: 6.5–3.7 and pth: 3.2–2.8 ng·m<sup>-3</sup> for the FT-BL) much lower than this found for PM<sub>2.5</sub> in the FT Mount Tai (suc: 30 ng·m<sup>-3</sup> [Authors]; Wang et al., 2009), similar to those observed in PM<sub>T</sub> in the Himalayas (4276 m a.s.l.) (suc: 13.7 and pth: 9.5 ng·m<sup>-3</sup>; Cong et al., 2015), but higher than those detected for PM<sub>T</sub> in the North Pacific remote marine (suc: 2.8 and pth: 0.66 ng·m<sup>-3</sup>; Kawamura and Sakaguchi., 1999). Malic acid within the BL (the third most abundant poly-acid at Izaña; Table 2) might have a photochemical origin via OH oxidation of the surrounding biogenic compounds transported by the day-time upslope winds. The Izaña Observatory is surrounded downhill by a forest ring – an important source of biogenic volatile organic compounds (BVOCs) – which contributes significantly to the measured concentrations at Izaña. Oxidation of these biogenic precursors may also provide important amounts of C<sub>7</sub>–C<sub>9</sub> dicarboxylic acids.

High concentrations of dicarboxylic acids have been reported in plumes from BB (Narukawa et al., 1999; Gao et al., 2003), which is in agreement with the observed values for the long-range transport BBE (82 ng·m<sup>-3</sup>). Concentrations of succinic, glutaric and malic acids were high (~33 ng·m<sup>-3</sup>, ~7 ng·m<sup>-3</sup> and ~32 ng·m<sup>-3</sup>, respectively; Table 2), compared to the rest of the period, surely as a consequence of the lofted concentration emitted in the open fire and long-range transport photochemical aging processes.

### 3.2.3 Saccharides

Primary saccharides and polyols are tracer compounds of surface soils (Medeiros and Simoneit 2007; Simoneit et al. 2004a), related to plant tissue and microorganisms. Glucose ( $\alpha$ ,  $\beta$ ), fructose and sucrose are important constituents of OM in soils (Simoneit et al. 2004a), whereas mannitol is related to airborne fungal spores (Bauer et al. 2008). They are completely water-soluble, contributing to water soluble organic carbon (WSOC) in aerosols (Simoneit et al. 2004a). Wind erosion and up whirling of soil dust emit these compounds to the atmosphere (Simoneit et al. 2004a).

The average concentration of the saccharides exhibits a marked difference within the FT-PM<sub>T</sub> (23.5 ng·m<sup>-3</sup>) and the BL-PM<sub>2.5</sub> (3.5 ng·m<sup>-3</sup>). Previous studies have shown that some organic compounds are strongly particle size dependent (Yttri et al., 2007; Mochida et al., 2003 [Authors]; Van Drooge and Grimalt, 2015), with special emphasis in sugars and sugar alcohols which are present mostly in very large particles (Graham et al., 2003; Mochida et al., 2003; Yttri et al., 2007 [Authors]). This size-segregation is clearly seen for the PM<sub>2.5</sub> samples collected within the BL, that cut off an important fraction of the coarse organic soil dust aerosol, showing similar concentrations under SAL and WES influence (BL-SAL = 3.3 ng·m<sup>-3</sup>; BL-WES = 4.0 ng·m<sup>-3</sup>). A different scenario takes place with the PM<sub>T</sub> samples, for which concentrations rise one order of magnitude from SAL influence to clean conditions (FT-SAL = 27 ng·m<sup>-3</sup>; FT-WES = 2.5 ng·m<sup>-3</sup>) linked to Saharan dust contribution. The average saccharides levels in the FT-SAL are higher than these observed in a natural forest area in tropical India (12.78 ng·m<sup>-3</sup>; Fu et al., 2010) and a rural background in Norway (10.4 ng·m<sup>-3</sup>; Yttri et al., 2007), but very similar to the average concentrations measured in the FT over central china (28.1 ng·m<sup>-3</sup>; Fu et al., 2014).

Glucose ( $\alpha+\beta$ ) was the predominant saccharide within the SAL, with mean FT concentration of  $\sim 10 \text{ ng}\cdot\text{m}^{-3}$  (Table 2); both isomers showed a good correlation ( $R^2=0.998$ ) consistent with their relation in the soil (Simoneit et al. 2004a). Under the WES airflows, glucose ( $\alpha+\beta$ ), sucrose and mannitol were slightly higher during the day (BL; Table 2), suggesting that there might be some soil contribution of transported terrestrial OM by land breeze.

5 This load is more evident in the sucrose (FT-WES =  $0.3 \text{ ng}\cdot\text{m}^{-3}$ ; BL-WES =  $1.3 \text{ ng}\cdot\text{m}^{-3}$ ; Table 2), which is a predominant sugar in the phloem of plants playing a key role in developing flowers (Bieleski et al., 1995) and has been suggested as a tracer for airborne pollen grains (Fu et al., 2012).

### 3.2.4 n-Alkanes

10 n-Alkanes, or aliphatic hydrocarbons, are a result of biogenic and anthropogenic emissions such as plant waxes and fossil fuel combustion products (Mazurek et al. 1989; Simoneit et al. 1991; Shauer et al. 2002). In the present study n-alkanes from  $n\text{C}_{24}$  to  $n\text{C}_{34}$  were quantified, with total n-alkanes mean concentrations ( $\sim 8 \text{ ng}\cdot\text{m}^{-3}$  in the FT and in the BL) much lower than this measured in the tropical Indian summer ( $126 \text{ ng}\cdot\text{m}^{-3}$ ; Fu et al., 2010), but similar to this found in rural Spain during the warm period ( $12 \text{ ng}\cdot\text{m}^{-3}$ ; Van Drooge and Grimalt, 2015).

15 Information about the possible source can be provided by the carbon number maximum ( $C_{\text{max}}$ ). In general,  $n\text{C}_{27}$ ,  $n\text{C}_{29}$  and  $n\text{C}_{31}$  are related to waxes from terrestrial higher plants, whereas low-molecular-weight alkanes ( $\text{C}_{22}$ – $\text{C}_{25}$ ) are more associated to combustion sources (Mazurek et al. 1989). At Izaña, the most abundant n-alkanes within the FT-SAL were  $n\text{C}_{27}$ ,  $n\text{C}_{29}$  and  $n\text{C}_{31}$  ( $\sim 1.0 \text{ ng}\cdot\text{m}^{-3}$ ,  $\sim 1.4 \text{ ng}\cdot\text{m}^{-3}$  and  $\sim 1.8 \text{ ng}\cdot\text{m}^{-3}$  respectively; Table 2) reflecting a vegetative source as previously described for Saharan dust samples measured in the North Atlantic (Simoneit et al., 1977), whereas within the BL  $n\text{C}_{24}$ – $n\text{C}_{25}$  presented the higher concentrations (Table 2) linked to anthropogenic emissions carried by the upslope winds. Another indicator that can be used to show the type of source is the carbon preference index ( $\text{CPI} = \sum \text{odd n-alkanes} / \sum \text{even n-alkanes}$ ) with  $\text{CPI} > 1$  related to biogenic origin and  $\text{CPI} \approx 1$  to combustion processes (Mazurek et al. 1989; Simoneit, 2002). In this study, CPI values ranged from 0.9 to 6.3 with average values for the FT-SAL ( $\sim 2$ ) higher than for the BL ( $\sim 1.7$ ) and the FT-WES ( $\sim 1.2$ ), reflecting the larger influence of vegetation within the FT-SAL and the predominance of combustion contribution within the BL and FT-WES samples. Although the vegetative source dominates in the FT, there is a significant correlation between n-alkanes and  $\text{NO}_3^-$  ( $r = 0.8$ ,  $p < 0.01$ ; Table 3), mostly due to its anthropogenic fraction ( $\text{C}_{24}$ – $\text{C}_{25}$ ).

### 3.2.5 Hopanes

30 Hopanes ( $17\alpha(\text{H}),21\beta(\text{H})$ -29-norhopane and  $17\alpha(\text{H}),21\beta(\text{H})$ -hopane) are linked to mineral oil and related to unburned lubricating residues from primary vehicles emissions (Rogge et al., 1993; Schauer et al., 1996, 2002).  $\sum$ Hopanes mean concentrations were  $0.13$  and  $0.08 \text{ ng}\cdot\text{m}^{-3}$  within the FT and BL respectively, values much higher than the  $7 \cdot 10^{-4} \text{ ng}\cdot\text{m}^{-3}$  measured by von Schneidmesser et al. (2009) in remote Greenland (3200 m a.s.l.) where anthropogenic emissions in the surrounding region are minimal. Under the WES airflows, hopanes concentrations were slightly higher during the day, suggesting influence of pollution transported within the BL, related to motorized vehicle emissions. The quantified hopane and norhopane showed very good linear correlations ( $R^2=0.95$ ), pointing to the same emission sources.

A strong correlation is observed in the FT between hopanes and  $\text{NO}_3^-$  ( $r = 0.8$ ,  $p < 0.01$ ; Table 3) suggesting that most of  $\text{NO}_3^-$  in the FT has its origin in on-road vehicle emissions instead of the industry. Anthropogenic sources of  $\text{NO}_x$  (the major  $\text{NO}_3^-$  precursor) include fossil fuel emitted from agriculture, power plants, industry and transport. The latter one covers almost a 50% of the nitrogen oxides emissions (<http://www.eea.europa.eu/data-and-maps/indicators/eea-32-nitrogen-oxides-nox-emissions-1/assessment.2010-08-19.0140149032-3>), with on-road transport in 2010 being the highest ( $25.2 \text{ Tg}\cdot\text{year}^{-1}$ ) compared to non-road ( $10.1 \text{ Tg}\cdot\text{year}^{-1}$ ), shipping ( $16.2 \text{ Tg}\cdot\text{year}^{-1}$ ), aviation ( $3.0 \text{ Tg}\cdot\text{year}^{-1}$ ) or rail ( $1.6 \text{ Tg}\cdot\text{year}^{-1}$ ) (Yan et al., 2014).

### 45 3.2.6 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are organic pollutants generated during incomplete combustion of organic material natural (e.g. forest fires, volcanic activity) and anthropogenic (e.g. fossil fuels combustion, coke production) sources (Howsam and Jones 1998; Iinuma et al., 2007; Rogge et al., 1993; Schauer et al., 1996, 2002). PAHs are composed of two or more fused aromatic rings and some of them have carcinogenicity, genotoxicity, and potential endocrine disruptiveness, affecting human health. At Izaña mean values of the total PAHs exhibited higher values in the BL ( $24 \text{ pg}\cdot\text{m}^{-3}$ ) than in the FT ( $16.3 \text{ pg}\cdot\text{m}^{-3}$ ), reflecting the contribution of the upslope winds as described for other organic compounds.

Similar PAHs concentrations were previously found by van Drooge et al. (2010) who measured an average PAHs concentration of  $33.1 \text{ pg}\cdot\text{m}^{-3}$  at Izaña. In general, all individual PAHs decreased its concentration except benz(a)anthracene that increased by a factor of 1.5 and 1.35 with respect to the mean concentrations of the FT and BL correspondingly. Much higher concentrations have been reported in other remote FT locations as Mt. Tai (1534 m a.s.l.) where  $\sim 9 \text{ ng}\cdot\text{m}^{-3}$  were measured (Fu et al., 2008). In the FT there is a strong correlation between PAHs and EC ( $r = 0.7$ ,  $p < 0.01$ ; Table 3), which points to the incomplete combustion of fossil fuels (Frenklach., 2000).

During the detected North America wildfire event (28Aug), PAHs concentration was  $9.4 \text{ pg}\cdot\text{m}^{-3}$ , which is much lower than levels measured in Thailand for  $\text{PM}_{\text{T}}$  samples during BBEs in the dry season (1150 to  $4140 \text{ pg}\cdot\text{m}^{-3}$ ; Chuesaard et al., 2014). The concentrations of PAHs measured in the sample corresponding to the fire event were not higher than those observed in the other samples, which may be due to photochemical transformations of PAH in the atmosphere during long-range transport.

### 3.2.7 Tracers of $\alpha$ -pinene oxidation (SOA PIN)

Vegetation emit large quantities of biogenic volatile organic compounds (BVOCs) into the atmosphere compared to anthropogenic VOCs (Guenter et al., 2006, 2012; Lamarque et al., 2010), particularly monoterpenes and isoprene. The most abundant volatile monoterpene, emitted mainly by coniferous trees (i.e. *Pinus canariensis*) is  $\alpha$ -pinene (Andreani-Aksoyoglu and Keller, 1995; Rinne et al., 2009; Smolander et al., 2014) and the tracers related to its photochemical oxidation (SOA PIN) are *cis*-pinonic acid, 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Claeys et al., 2007; Szmigielski et al., 2007).

SOA PIN organic tracers were not detected in all samples, with values in the FT influenced by a couple of extreme points that increased their average concentration. SOA PIN exhibited the lowest concentration in the FT-WES ( $1.2 \text{ ng}\cdot\text{m}^{-3}$ ) with a predominance of *cis*-pinonic acid (Table 2). Aircraft measurements in the FT over central China (Fu et al., 2014) recorded higher concentrations of 3-HGA ( $8.5 \text{ ng}\cdot\text{m}^{-3}$ ) and MBTCA ( $1.9 \text{ ng}\cdot\text{m}^{-3}$ ) than measure in the present study (Table 2). Further generation oxidation products (3-HGA and MBTCA) were higher in the BL ( $0.51$  and  $0.24 \text{ ng}\cdot\text{m}^{-3}$  correspondingly; Table 2), with a significant correlation ( $R^2 = 0.81$ ) that points to a same precursor. Monoterpenes reacts relatively fast, with atmospheric lifetimes ranging from minutes to hours (Saxton et al., 2007), resulting in  $\alpha$ -pinene emitted in the ring forest that reacts along its upward transport to the Observatory. Daytime emissions of gaseous  $\alpha$ -pinene at Izaña were measured by Fisher et al. (1998) with concentration in the range of 0.011–0.102 ppbv (mean: 0.028 ppbv), supporting the evidence of its origin close to the Observatory during the day.

### 3.2.8 Tracers of isoprene oxidation (SOA ISO)

It is estimated that about a half of the total global BVOCs emission is due to isoprene ( $535 \text{ Tg}\cdot\text{y}^{-1}$ ; Guenter et al., 2012), making it the largest BVOC emitted from land vegetation (Guenter et al., 2006). Isoprene emission is limited to a number of species in the plant kingdom, contrary to many other BVOCs that are emitted from most plants (Guenter et al., 2012). Secondary products of isoprene oxidation (SOA ISO) evaluated in the present study are 2-methylglyceric acid (2-MGA), 2-methylthreitol (2-MT1) and 2-methylerythritol (2-MT2) (Claeys et al., 2004; Hallquist et al., 2009).



Analogous FT concentrations of 2-methylthreitol and 2-methylerythritol were measured in the present study under the SAL (7.3 and 16.8 ng·m<sup>-3</sup>; Table 2) and over the central China FT (8 and 17 ng·m<sup>-3</sup>; Fu et al., 2014), one of the most important source regions of isoprene emission in the world during summertime (Guenther et al., 1995). Similar SOA ISO concentrations were found in the BL within the SAL and the WES (~17 and ~16 ng·m<sup>-3</sup> respectively) revealing the emission and following ascending transport of biogenic or anthropogenic compounds, as found in previous studies performed at Izaña, which observed emissions of isoprene during daytime associated to anthropogenic compounds (Salisbury et al., 2006). A significant correlation among 2-MT1 and 2-MT2 was found for individual values ( $R^2 = 0.94$ ) as previously observed in other studies (Ion et al., 2005; El Haddad et al., 2011), but with a mass concentration ratio 2-MT1 vs. 2-MT2 (slope from linear regression=2.3) slightly lower than this found by El Haddad et al. (2011). This correlation between the two diastereoisomers indicates a same origin thought the same photo-oxidation process.

The highest concentration of SOA ISO was measured under the FT-SAL (~28 ng·m<sup>-3</sup>), associated to Saharan dust, as was observed for SOA PIN (~33 ng·m<sup>-3</sup>). However, global estimations of isoprene and  $\alpha$ -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). Correlation between total concentration of SOA ISO and total concentration of SOA PIN (Fig. 2) exhibits two distinct trends in the FT that might be associated to different global sources of the precursor volatile compounds, although the trajectories of the sampled air mass does not distinguish clearly between different origins. Some species with a high isoprene emission potential have been identified in central and western Africa, but quantification of isoprene emissions are largely unverified for West Africa (Saxton et al., 2007). Several evaluations of isoprene and  $\alpha$ -pinene global emissions (Luo et al., 2010; Guenther et al., 2012; Sindelarova et al., 2014) confine the North Africa sources to a small belt over the northern part of Morocco, Algeria and Tunes, whereas Europe is pointed as a potential source. Some episodes, for which SOA PIN and SOA ISO were measured, do not have a trajectory over this African belt – based on the Hysplit model – , suggesting that air masses from Europe can also incorporate gaseous precursors and oxidized species previous to its pass over Africa and Izaña in the Atlantic Ocean.

Rodríguez et al. (2011) previously reported high concentrations of  $\text{SO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for air masses arriving to Izaña from the Atlantic coast of Morocco, Eastern Algeria, Northern Algeria and Tunisia. Industrial states with sources of gaseous precursors ( $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{NH}_3$ ) of these aerosol compounds were identified. Although African emissions seem to be responsible of the pollutants arriving to the North Atlantic FT, Europe could also contributes with an amount of pollutants that should not be neglected as evidenced by the concentration of SOA PIN and SOA ISO arriving to Izaña. These species could play a key role in secondary organic aerosol formation, as some studies point to the influence of anthropogenic emission on secondary organic aerosol formation (El Haddad et al., 2011; Hoyle et al., 2011). SOA ISO seems to depend strongly on the conditions (aerosol acidity,  $\text{NO}_x$  concentrations and pre-existing aerosol) used to oxidize isoprene (Surratt et al., 2006, 2007; Marais et al., 2016).  $\text{NO}_x$  concentration determine the pathway (low- $\text{NO}_x$  and high- $\text{NO}_x$ ) followed by the isoprene oxidation, leading to different secondary organic species (Paulot et al., 2009a, b); the low- $\text{NO}_x$  pathway is ~ 5 times more efficient than the high- $\text{NO}_x$  pathway (Marais et al., 2016). Experiments carried out by Kroll et al. (2006) evidence how the isoprene SOA yield varies depending on  $\text{NO}_x$  concentration, increasing from no injected  $\text{NO}_x$ , to a plateau between 100 and 300 ppb  $\text{NO}_x$ , and decreasing at higher  $\text{NO}_x$  concentrations [R2#C5 and R1#C1].

We found the relation among SOA ISO and  $\text{NO}_3^-$  within the FT-SAL (Fig.3) present three tendencies which might be associated to the ratio isoprene: $\text{NO}_x$  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  $\text{NO}_x$  concentration influence on this SOA ISO markers formation pathways (El Haddad et al., 2011). The high- $\text{NO}_x$  pathway leads to the reaction of isoprene peroxy radicals ( $i\text{RO}_2$ ) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low- $\text{NO}_x$  pathway leads to the reaction of  $i\text{RO}_2$  with hydroperoxy radicals ( $\text{HO}_2$ ) resulting in hydroxyhydroperoxides ( $i\text{ROOH}$ ), 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- $\text{NO}_x$  pathway results in the major product 2-MGA and low- $\text{NO}_x$  is associated to the major products 2-MTs (El Haddad., 2011) [R2#C5 and R1#C1].

Significant correlations in the FT between biogenic secondary organic compounds and  $\text{NO}_3^-$  ( $r$  SOA PIN– $\text{NO}_3^- = 0.6$ ,  $p < 0.01$ ; Table 3) and  $\text{nss-SO}_4^{2-}$  ( $r$  SOA ISO– $\text{nss-SO}_4^{2-} = 0.6$ ,  $p < 0.01$ ; Table 3), point to its formation from the oxidation of their gaseous precursors  $\text{NO}_x$  and  $\text{SO}_2$  respectively. Dust transformation in the FT is also evidenced by its highly significant correlation with SOA PIN ( $r = 0.7$ ,  $p < 0.01$ ; Table 3) as well as both saccharides ( $r = 0.6$ ,  $p < 0.01$ ) and hopanes ( $r = 0.9$ ,  $p < 0.01$ ) showing that natural and anthropogenic substances might be mixed after aging processes.

### 3.2.9 Determined fraction of OM

Bulk organic carbon (OC) determined for every single day (thermo-optical transmittance method) at Izaña during this study was within the range  $0.01\text{--}2.20 \mu\text{g}\cdot\text{m}^{-3}$ , which is of the order to that found in other FT studies (e.g.  $1.4 \mu\text{g}\cdot\text{m}^{-3}$  at Qomolangma, Mt. Everest, 4276 m a.s.l. by Cong et al., 2015 and  $4 \mu\text{g}\cdot\text{m}^{-3}$  at NW Pacific, 2–6.5 km column by Heald et al., 2005). FT- $\text{PM}_{10}$  OC under SAL conditions ( $0.77 \mu\text{g}\cdot\text{m}^{-3}$ ) was higher than under WES ( $0.52 \mu\text{g}\cdot\text{m}^{-3}$ , including the BBE) events. Figure 4 shows the mass closure (sum of the organic species determined by speciation) of bulk organic matter OM (determined as  $\text{OC}\cdot 1.8$ ); this mass closure accounts for 2 to 100 % of the OM for every single day, depending on the sample and the airflows.

Concentrations of OM were much higher in the FT-SAL ( $1.39 \mu\text{g}\cdot\text{m}^{-3}$ ) than under FT-WES ( $0.04 \mu\text{g}\cdot\text{m}^{-3}$  without the BBE;  $0.94 \mu\text{g}\cdot\text{m}^{-3}$  including the BBE) conditions. The selected tracers (levoglucosan, SOA ISO, SOA PIN, n-Alkanes, saccharides, dicarboxylic acids, hopanes and PAHs) represent [R2#C8] as average:

- (i) a 15% of the OM (Fig. 4), under FT-SAL conditions (when mean OM was  $1.39 \mu\text{g}\cdot\text{m}^{-3}$ ). This determined fraction is mainly composed by SOA ISO (30%), saccharides (27%) and dicarboxylic acids (18%).
- (ii) a 84% of the OM (Fig. 4), in the FT-WES airflows without the BBE (when mean OM was  $0.04 \mu\text{g}\cdot\text{m}^{-3}$ ). This determined fraction is constituted by dicarboxylic acids (44%; mainly succinic and phthalic, indicating aged aerosols after the long-range atmospheric transport), and SOA ISO (34%) with a minor presence of saccharides (8%). Biogenic SOA represent an important fraction of the OM at Izaña (~40%), as seen in other remote high altitude regions (Xu et al. 2015).
- (iii) a 3% of the OM (Fig. 4) in the FT-WES during the BBE (when mean OM was  $3.64 \mu\text{g}\cdot\text{m}^{-3}$ ). The determined fraction of OM for 28Aug (3%) contained a 68% of dicarboxylic acids (mostly succinic and malic acids) and an 8% of the BB tracer levoglucosan. This sample has the OM profile with the highest contribution of aged SOA (di-acids), formed during the long-range atmospheric transport, and the lowest contributions of SOA PIN (4%) and SOA ISO (12%), which could indicate the further oxidation of these products under the BBE air masses conditions.
- (iv) a 64% of the OM in the FT-WES including the BBE (when mean OM was  $0.94 \mu\text{g}\cdot\text{m}^{-3}$ ). This determined fraction is constituted mainly by dicarboxylic acids (50%), and SOA ISO (28%).

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 [R2#C4]. The determined OM composition within the BL ( $\text{PM}_{2.5}$ ; BL-FT: 9% of the OM and BL-WES: 77% of the OM; Fig. 4) remains almost the same under both airflows, but with higher concentrations of SOA ISO and n-alkanes under the SAL. However, due to the  $\text{PM}_{2.5}$  cut-off of the collected particles, the influence of the dust-associated organic compound is probably not well represented since these products are situated in the coarse fraction of the PM.

### 3.3 Sources of OM

We used receptor modelling for apportioning OM between the OA sources traced by the species included in the speciation performed in this study. This analysis is complementary to the mass closure performed above (Fig.4). 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) [R2#C4]. The loading factors obtained in the MCR-ALS were used to identify OA sources (Fig.5A1–5C1), whereas the score factors were used as independent variables in the Multilinear Regression Analysis (MLRA) to apportion the determined fraction of OM between the identified sources. Three components (sources) were identified (Fig. 5), which accounted by 81% of the total variance. MCR-ALS method was also applied only to PM<sub>T</sub> samples to verify the influence of PM<sub>2.5</sub> in the final results; no significant differences were observed as shown in Fig. S1 of the supplement.

### 3.3.1 Biomass Burning (BB)

The major component (accounting for 63% of the total variance) is associated with levoglucosan, dicarboxylic acids, phthalic acid, SOA PIN, C<sub>24</sub>–C<sub>28</sub> alkanes and hopanes and PAHs to a lesser extent (Fig. 5A). This factor represents biomass burning aerosols (BB). The peak event in the score factor observed the 28Aug (Fig. 5A2) is associated with the episode of levoglucosan linked to the long-range transport of BB from North America. SOA PIN indicates photochemical oxidation of biogenic volatile organic compounds during the wild fire. The presence of short-chain dicarboxylic acids, along with important amounts of malic acid, suggests the effective oxidation of organic species to shorter di-acids chains during long-range atmospheric transport. PAH contribution in this component is low, despite potential emissions of PAHs during biomass burning. The low PAH contributions could be the result of photochemical degradation during long-range transport, which on their term could be related to the presence of higher contributions of phthalic acid in this component. BB in the FT is significantly associated to the OM (r-FT = 0.40, p < 0.05; Table S1) and EC (r-FT = 0.65, p < 0.01; Table S1) concentrations.

### 3.3.2 Combustion POA

The second component (accounting for 21% of the total variance) is associated with long-chain dicarboxylic acids, SOA ISO, C<sub>24</sub> – C<sub>29</sub> n-alkanes and PAHs (Fig. 5B). This factor is related to the primary organic aerosols linked to combustion sources. This is the component that best represents the variability of PM<sub>2.5</sub> samples collected during daylight, when the BL may reach Izaña under the slope wind regime. High loadings of suberic (C<sub>8</sub>) and azelaic acids (C<sub>9</sub>) indicate the presence of oxidized compounds in the early stage of photochemical transformation processes, such as the ozonolysis of oleic acid (Moise and Rudich, 2002). Organic species supporting the anthropogenic contribution are lower-molecular-weight n-alkanes (C<sub>24</sub> – C<sub>25</sub>) and PAHs (from incomplete combustion processes). FT aerosol is also described by this component with the exception of low-molecular-weight alkanes (C<sub>24</sub>–C<sub>25</sub>) which is the main feature of the BL samples. The component is significantly representative of the measured EC for all samples, and highly representative for the BL, as shown by its Pearson correlation coefficient (r-All = 0.36 and r-BL = 0.71, p < 0.05; Table S1).

### 3.3.3 Organic dust

The third component, accounting for 16% of the total variance, is composed by short-chain dicarboxylic acids, SOA ISO, saccharides, C<sub>26</sub>–C<sub>34</sub> alkanes, hopanes, and PAHs to a lesser extent (Fig. 5C). This component, identified as organic dust, is associated with soil re-suspension as evidenced by the saccharides and mannitol high loadings. The predominant presence of the soil OM related compounds, those from fungi and terrestrial higher plants (C<sub>27</sub>, C<sub>29</sub> and C<sub>31</sub>), suggest fresh and primary OA. Notwithstanding, glutaric, adipic and pimelic acids indicate oxidation products, suggesting the aging of the samples. As a consequence of this aging, natural and anthropogenic markers are mixed in this component. The biogenic influence is indicated by the presence of soil related markers and oxidation products from isoprene (2MGA, 2MT-1 and 2MT-2), whereas the anthropogenic influence is well defined by the presence of hopanes (primary vehicle emissions) and high molecular weight PAH (products of incomplete combustion). The scores of this component display the highest correlation with dust (r-All = 0.84, p < 0.01; Table S1) and OM (r-All = 0.64, p < 0.01; Table S1) concentrations

for all samples. Although this component is not relevant for the BL-PM<sub>2.5</sub> samples – because of part of the compounds are present in the larger particle size fractions – the correlation with dust ( $r_{\text{BL}} = 0.73$ ,  $p < 0.01$ ; Table S1) and OM ( $r_{\text{BL}} = 0.75$ ,  $p < 0.01$ ; Table S1) are highly significant due to the mixing of dust with the anthropogenic compounds.

### 5 3.3.4 Source apportionment of OM in the SAL and the westerlies

The source apportionment of OM was performed by the multilinear regression technique described above. The difference between the bulk OM (determined by thermo-optical method) and the sum of the organic species (determined with the speciation) was labelled as undetermined fraction. Figure 6 shows the time series of the daily contribution of each source to the determined OM and Fig. 7 shows the average source contribution to total OM in the aerosol samples collected in the different airstreams. The correlation between the sum of the three components scores and the OM within the FT ( $r_{\text{FT}} = 0.63$ ; Table S1) indicates that the identified sources might describe, not only the determined fraction of the OM but also the total OM. This significant correlation is not seen for the BL ( $r_{\text{BL}} = 0.33$ ; Table S1), where there could be additional sources.

In the FT-SAL airflow, most of OM was undermined (~85, Fig.7). The three identified sources, i.e. the organic dust, combustion POA and biomass burning, accounts for 8%, 6% and 1% of the bulk OM, respectively (62%, 34% and 4% of the determined OM, respectively). The presence of biogenic SOA products mixed with combustion POA was also found in previous studies which suggested that biogenic SOA formation may be more efficient in polluted atmospheres (Gouw and Jiménez., 2009 and references therein).

In the FT-WES, the undermined fraction accounts for ~36% of the OM (Fig.7). The contribution of the three identified sources, i.e. the organic dust, combustion POA and biomass burning, is 22%, 19% and 23% to the bulk OM, respectively (28%, 23% and 49% to the determined OM, respectively). Yttri et al. (2007) proposed biomass burning as a source of saccharides in the OA and Fraser and Lakshmanan (2000) found that some saccharides resist degradation in the atmosphere over a period of 10 days, being able to be transported over long distances; this may be the source of the organic fraction of dust we detected in the FT-WES.

For the BL samples, the dust related component is not well represented (Fig. 6), because the coarse fraction was not sampled here. On the other hand, combustion POA explains a 6 and 41 % (Table S2) of the bulk OM for the SAL and WES, respectively. Background regional fires also affect the BL as described by the BB component, which represent a 2 and 36 % (Table S2) of the bulk OM for the SAL and WES, respectively.

## 4 Conclusions

The present study is focused on the organic aerosol composition within the two main airflows of the subtropical North Atlantic free troposphere: (i) the Saharan Air Layer – the warm, dry and dusty airstream that expands from North Africa to the Americas at subtropical and tropical latitudes – and (ii) the westerlies – which flows from North America through the North Atlantic at mid and subtropical latitudes –. Atmospheric particulate matter was analysed on secondary inorganic species, elemental composition, elemental and organic carbon and 40 organic tracer species (levoglucosan, dicarboxylic acids, saccharides, n-alkanes, hopanes, polycyclic aromatic hydrocarbons and those formed after oxidation of  $\alpha$ -pinene and isoprene) in order to distinguish possible sources for the organic aerosol. The organic particulate aerosol speciation and its subsequent source apportionment was [R2#C9] performed for 42 filter samples collected in summer at the Izaña Observatory (~2400 m a.s.l.) in Tenerife, Spain.

The levels of all inorganic and almost all organic tracers were generally higher under the Saharan Air Layer influence in comparison to the pristine conditions of the Westerlies and the differences in the composition of the determined organic matter under these two air masses were important.

In the Saharan Air Layer, the aerosol composition was dominated by dust (93%), secondary inorganic pollutants (<5%) and organic matter (~1.5%). The organic compounds (determined by gas-chromatography coupled to

mass-spectrometry) accounted for a 15% of the bulk organic matter and were related to soils (saccharides), biogenic secondary organic aerosols linked to isoprene oxidation (SOA ISO) and natural and anthropogenic primary sources such as vegetation and motor exhaust emissions (dicarboxylic acids).

5 In the Westerlies, the organic matter represented a higher fraction of the total aerosol bulk (~28%) and the determined organic compounds accounted for an 64% of the organic matter with dicarboxylic acids and SOA ISO being the most abundant. In this airstream, a long-range atmospheric transport of a biomass burning plume from North America was detected (with organic matter representing a 53% of the total aerosol bulk), supporting the atmospheric stability of levoglucosan over transport and time under certain conditions.

10 Three sources of organic aerosol, which contribute to the organic matter composition in this part of the North Atlantic, could be resolved in multivariate analysis: one biomass burning-related, one primary combustion-related and one organic dust-related. In the Saharan Air Layer, the organic matter comes from organic dust (8% of the bulk OM; 63% of the determined OM) and combustion (6% of the bulk OM; 34% of the determined OM) sources, whereas under the westerlies comes from organic dust (22% of the bulk OM; 28% of the determined OM), biomass burning (23% of the bulk OM; 49% of the determined OM) and combustion (19% of the bulk OM; 23% of the determined OM) sources, showing that the free troposphere is highly influenced by combustion and biomass burning compounds.

20 A comprehensive knowledge of the organic aerosol chemistry is of high importance for assessing anthropogenic influences and evaluating the effect of radiative forcing. The work presented here offers new insights into the organic composition of the North Atlantic free troposphere as well as the trans-boundary origin of some compounds. Further studies are needed to understand the main mechanisms by which the aerosol is lofted into the free troposphere and transported over long distances.

25 *Acknowledgements:* This study was performed within the context of the projects AEROATLAN (CGL2015-66299-P; MINECO/FEDER) and TEAPARTICLE (CGL2011-29621), supported by the Ministry of Economy and Competitiveness of Spain and the European Regional Development Fund (ERDF). The authors acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT back-trajectories used in this publication. The excellent work performed by the staff of the Atmospheric Research Centre (C. Bayo, C. Hernández, F. de Ory, V. Carreño, R. del Campo and SIELTEC Canarias) and of the Institute of Environmental Assessment and Water Research (R. Chalder, D. Fanjul, and B. Hortelano) is appreciated. M. I. García acknowledges the grant of the Canarian Agency for Research, Innovation and Information Society (ACIISI) co-funded by the European Social Funds. Measurements at Izaña observatory are performed within the context 30 Global Atmospheric Watch networks with the financial support of the State Meteorological Agency of Spain (AEMET).

*Competing interests:* The authors declare that they have no conflict of interest.



European Regional  
Development Fund



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Agencia Canaria  
de Investigación, Innovación  
y Sociedad de la Información



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**Table 1.** Average concentration of the chemical major compounds for (i) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> having into account all samples, (ii) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> collected within the Saharan air layer (SAL), (iii) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> collected within the Westerlies (WES) without the FT-PM<sub>T</sub> biomass burning event and (iv) FT-PM<sub>T</sub> biomass burning event (BBE).

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	FT-PM <sub>T</sub> ALL	BL-PM <sub>2.5</sub> ALL	FT-PM <sub>T</sub> SAL	FT-PM <sub>T</sub> WES	BL-PM <sub>2.5</sub> SAL	BL-PM <sub>2.5</sub> WES	FT-PM <sub>T</sub> BBE
∑ CC, μg·m <sup>-3</sup>	78.98	13.70	92.74	2.16	17.07	4.70	6.84
Dust, μg·m <sup>-3</sup>	73.61	11.18	86.71	1.51	14.10	3.39	1.66
Sea Salt, μg·m <sup>-3</sup>	0.53	0.36	0.59	0.27	0.25	0.66	< 0.01
OM, μg·m <sup>-3</sup>	1.32	0.47	1.39	0.04	0.61	0.09	3.64
EC, μg·m <sup>-3</sup>	0.04	0.07	0.03	< 0.01	0.08	0.05	0.29
NO <sub>3</sub> <sup>-</sup> , μg·m <sup>-3</sup>	0.73	0.08	0.87	< 0.01	0.11	< 0.01	< 0.01
NH <sub>4</sub> <sup>+</sup> , μg·m <sup>-3</sup>	0.33	0.25	0.35	0.14	0.32	0.07	0.54
nss-SO <sub>4</sub> <sup>=</sup> , μg·m <sup>-3</sup>	2.42	1.28	2.80	0.19	1.61	0.43	0.71
ss-SO <sub>4</sub> <sup>=</sup> , μg·m <sup>-3</sup>	0.02	0.01	0.02	0.01	0.01	0.03	< 0.01

∑CC: sum chemical composition; OM: organic matter; EC: elemental carbon; nss-SO<sub>4</sub><sup>=</sup>: non sea salt sulphate; ss-SO<sub>4</sub><sup>=</sup>: sea salt sulphate.

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**Table 2.** Average concentration of the selected organic species for (i) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> having into account all samples, (ii) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> collected within the Saharan air layer (SAL), (iii) FT-PM<sub>T</sub> and BL-PM<sub>2.5</sub> collected within the Westerlies (WES) without the FT-PM<sub>T</sub> biomass burning event and (iv) FT-PM<sub>T</sub> biomass burning event (BBE).

	FT-PM <sub>T</sub> ALL	BL-PM <sub>2.5</sub> ALL	FT-PM <sub>T</sub> SAL	FT-PM <sub>T</sub> WES	BL-PM <sub>2.5</sub> SAL	BL-PM <sub>2.5</sub> WES	FT-PM <sub>T</sub> BBE
<b>Levogluconan</b>							
Levogluconan, ng·m <sup>-3</sup>	0.75	0.53	0.41	0.40	0.34	1.04	9.33
<b>Dicarboxylic acids</b>							
Succinic, ng·m <sup>-3</sup>	6.51	3.70	5.70	3.52	4.03	2.80	33.35
Glutaric, ng·m <sup>-3</sup>	1.97	0.83	1.90	0.74	0.85	0.77	7.23
Adipic, ng·m <sup>-3</sup>	1.43	0.69	1.53	0.62	0.72	0.60	1.71
Pimelic, ng·m <sup>-3</sup>	0.83	0.35	0.92	0.37	0.33	0.39	0.17
Suberic, ng·m <sup>-3</sup>	0.48	0.30	0.50	0.29	0.29	0.31	0.39
Azelaic, ng·m <sup>-3</sup>	0.88	0.79	0.93	0.57	0.78	0.82	0.71
Malic, ng·m <sup>-3</sup>	2.01	2.15	0.75	1.20	1.67	3.43	32.21
Phthalic, ng·m <sup>-3</sup>	3.18	2.77	2.19	9.43	2.38	3.80	6.21
<b>Saccharides</b>							
α-glucose, ng·m <sup>-3</sup>	9.26	0.90	10.79	0.62	0.90	0.89	1.65
β-glucose, ng·m <sup>-3</sup>	9.13	1.00	10.63	0.61	1.01	0.98	1.65
Fructose, ng·m <sup>-3</sup>	2.02	1.01	2.23	0.95	1.10	0.76	0.69
Sucrose, ng·m <sup>-3</sup>	2.72	0.47	3.18	0.27	0.18	1.26	0.01
Mannitol, ng·m <sup>-3</sup>	0.35	0.12	0.40	0.08	0.12	0.12	0.07
<b>n-Alkanes</b>							
nC24, ng·m <sup>-3</sup>	0.72	1.63	0.75	0.48	1.87	0.97	1.01
nC25, ng·m <sup>-3</sup>	0.93	2.93	0.95	0.40	3.26	2.05	2.09
nC26, ng·m <sup>-3</sup>	0.60	0.64	0.65	0.26	0.69	0.49	0.54
nC27, ng·m <sup>-3</sup>	0.89	0.95	0.98	0.24	0.94	0.98	0.76
nC28, ng·m <sup>-3</sup>	0.37	0.32	0.39	0.17	0.38	0.17	0.36
nC29, ng·m <sup>-3</sup>	1.18	0.42	1.34	0.25	0.48	0.25	0.63
nC30, ng·m <sup>-3</sup>	0.45	0.14	0.51	0.07	0.16	0.10	0.18
nC31, ng·m <sup>-3</sup>	1.55	0.31	1.77	0.37	0.33	0.25	0.29
nC32, ng·m <sup>-3</sup>	0.39	0.10	0.45	0.05	0.11	0.06	0.08
nC33, ng·m <sup>-3</sup>	0.48	0.10	0.55	0.06	0.12	0.06	0.13
nC34, ng·m <sup>-3</sup>	0.29	0.05	0.34	0.02	0.05	0.04	0.01
<b>Hopanes</b>							
Hopane, ng·m <sup>-3</sup>	0.06	0.02	0.07	0.01	0.03	0.01	0.03
nor-Hopane, ng·m <sup>-3</sup>	0.07	0.05	0.08	0.02	0.07	0.02	0.03
<b>PAHs</b>							
B [a] A, pg·m <sup>-3</sup>	1.48	1.48	1.58	0.80	1.61	1.13	1.37
Chr, pg·m <sup>-3</sup>	4.27	4.37	4.63	1.92	5.12	2.39	3.38
B [b+j+k] F, pg·m <sup>-3</sup>	3.67	5.74	4.20	0.66	6.69	3.21	1.13
B [e] P, pg·m <sup>-3</sup>	1.36	1.94	1.50	0.47	2.22	1.20	0.83
B [a] P, pg·m <sup>-3</sup>	0.78	1.21	0.89	0.18	1.25	1.08	0.29
In[123cd] P, pg·m <sup>-3</sup>	1.47	2.33	1.65	0.46	2.18	2.74	0.56
B [ghi] Per, pg·m <sup>-3</sup>	3.29	6.94	3.56	1.73	6.37	8.46	1.84
<b>SOA PIN</b>							
Cis-Pinonic, ng·m <sup>-3</sup>	27.83	15.24	32.72	0.89	13.23	20.59	1.00
3-HGA, ng·m <sup>-3</sup>	0.21	0.51	0.09	0.24	0.39	0.81	2.88
MBTCA, ng·m <sup>-3</sup>	0.03	0.24	0.01	0.05	0.13	0.54	0.27
<b>SOA ISO</b>							
2MGA, ng·m <sup>-3</sup>	4.22	2.38	4.46	1.63	2.65	1.65	6.56
2MT-1, ng·m <sup>-3</sup>	6.64	4.94	7.27	3.40	5.16	4.33	2.40
2MT-2, ng·m <sup>-3</sup>	15.45	9.53	16.79	8.95	9.24	10.31	5.53

**B[a]A:** benz[a]anthracene; **Chr:** chrysene; **B[b+j+k]F:** benzo[b+k]fluoranthene; **B[e]P:** benzo[e]pyrene; **B[a]P:** benzo[a]pyrene; **In[123cd]P:** indeno[1,2,3-cd]pyrene; **B[ghi]Per:** benzo[ghi]perylene; **3-HGA:** 3-hydroxyglutaric acid; **MBTCA:** 3-methyl-1,2,3-butanetricarboxylic acid; **2MGA:** 2-methylglyceric acid; **2MT-1:** 2-methylthreitol; **2MT-2:** 2-methylerythritol.

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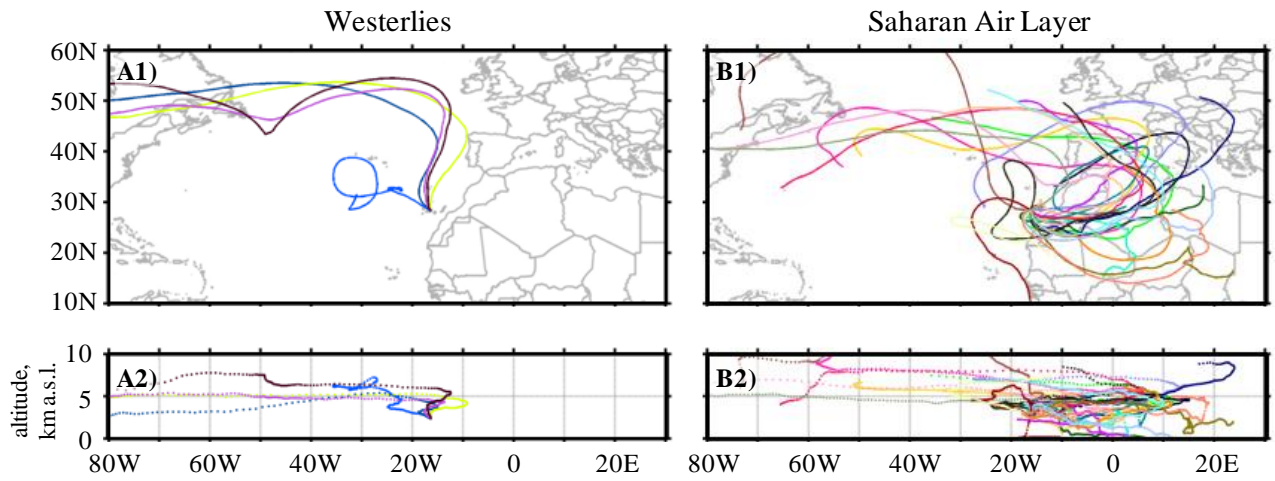
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**Table 3.** Pearson correlation coefficients matrix of the organic and inorganic compounds within the free troposphere (PM<sub>T</sub>). Highly statistically significant correlations (p-value < 0.01) are highlighted. BBE was excluded in this analysis.

	Levogluco san	Dicarboxy lic acids	Sacchari des	n-Alkane s	Hopane s	PAHs	SOA PIN	SOA ISO	Dust	Sea Salt	OM	EC	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	nss-SO <sub>4</sub> <sup>=</sup>	ss-SO <sub>4</sub> <sup>=</sup>	
Levogluco san	1.0																
Dicarboxy lic acids	0.0	1.0															
Sacchari des	0.0	0.4	1.0														
n-Alkane s	0.1	0.5	<b>0.5</b>	1.0													
Hopane s	0.0	<b>0.6</b>	<b>0.7</b>	<b>0.8</b>	1.0												
PAHs	0.3	0.3	0.2	0.3	0.3	1.0											
SOA PIN	-0.1	0.2	0.3	<b>0.6</b>	0.5	0.1	1.0										
SOA ISO	0.2	0.3	0.2	0.3	0.3	<b>0.6</b>	0.4	1.0									
Dust	0.0	<b>0.7</b>	<b>0.6</b>	<b>0.7</b>	<b>0.9</b>	0.2	<b>0.7</b>	0.2	1.0								
Sea Salt	<b>0.6</b>	-0.1	-0.2	-0.1	-0.3	0.4	0.1	0.2	-0.2	1.0							
OM	-0.1	0.3	0.3	<b>0.7</b>	<b>0.8</b>	0.2	<b>0.8</b>	0.4	<b>0.9</b>	0.0	1.0						
EC	0.2	0.1	-0.1	-0.1	-0.2	<b>0.7</b>	-0.2	0.3	-0.3	0.3	-0.2	1.0					
NO <sub>3</sub> <sup>-</sup>	0.0	0.4	<b>0.7</b>	<b>0.8</b>	<b>0.8</b>	0.5	<b>0.6</b>	0.4	<b>0.8</b>	-0.1	<b>0.8</b>	0.0	1.0				
NH <sub>4</sub> <sup>+</sup>	0.1	0.1	0.2	0.2	0.3	<b>0.6</b>	-0.1	0.3	0.2	0.0	0.2	0.5	0.5	1.0			
nss-SO <sub>4</sub> <sup>=</sup>	0.1	0.2	<b>0.6</b>	0.5	<b>0.6</b>	0.5	0.5	<b>0.6</b>	0.5	0.1	<b>0.6</b>	0.1	<b>0.8</b>	<b>0.7</b>	1.0		
ss-SO <sub>4</sub> <sup>=</sup>	<b>0.6</b>	0.0	-0.2	0.0	-0.2	0.4	0.1	0.2	-0.2	<b>1.0</b>	0.0	0.3	0.0	0.0	0.0	1.0	

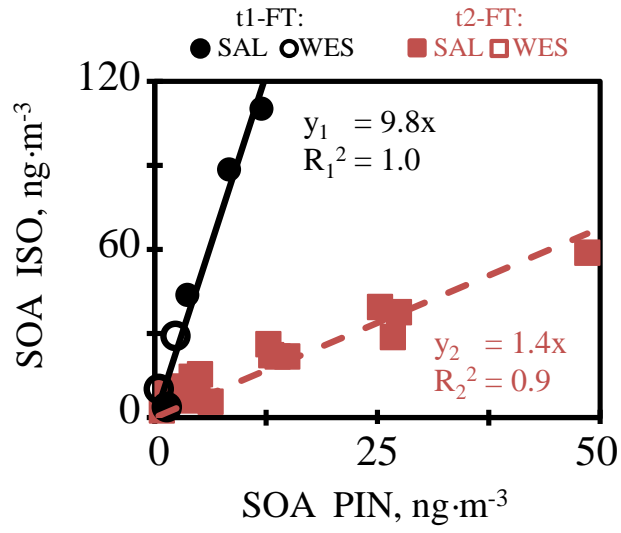
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OM: organic matter; EC: elemental carbon; nss-SO<sub>4</sub><sup>=</sup>: non sea salt sulphate; ss-SO<sub>4</sub><sup>=</sup>: sea salt sulphate.

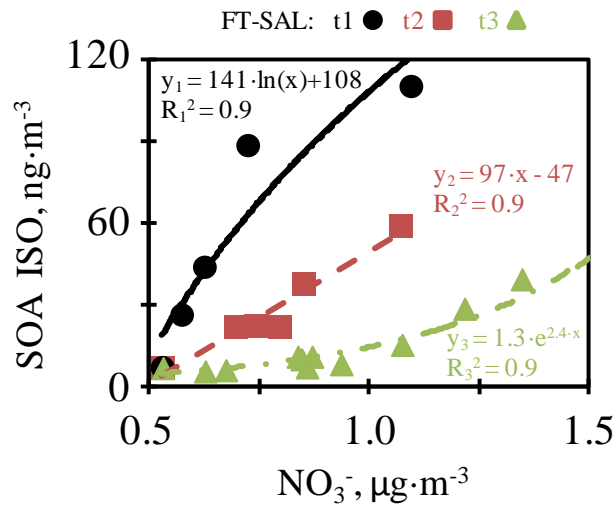


**Figure 1:** Ten-day back-trajectories based on HYSPLIT model for the samples collected within the (A) Westerlies (26Aug–30Aug) and (B) the Saharan Air Layer (01Aug–25Aug and 31Aug–01Sep); the dates refer to the day of completion of the sampling [R2#C1].

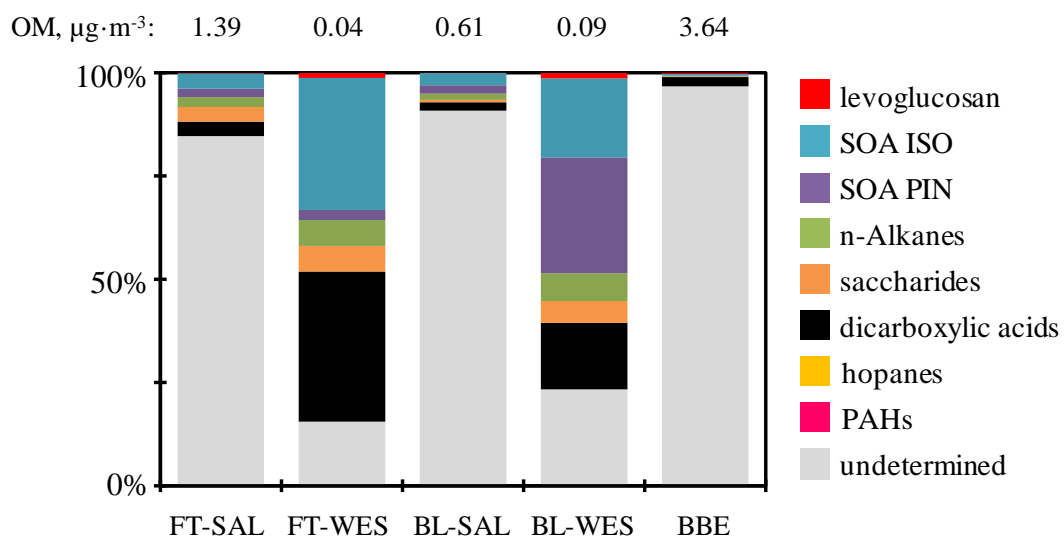




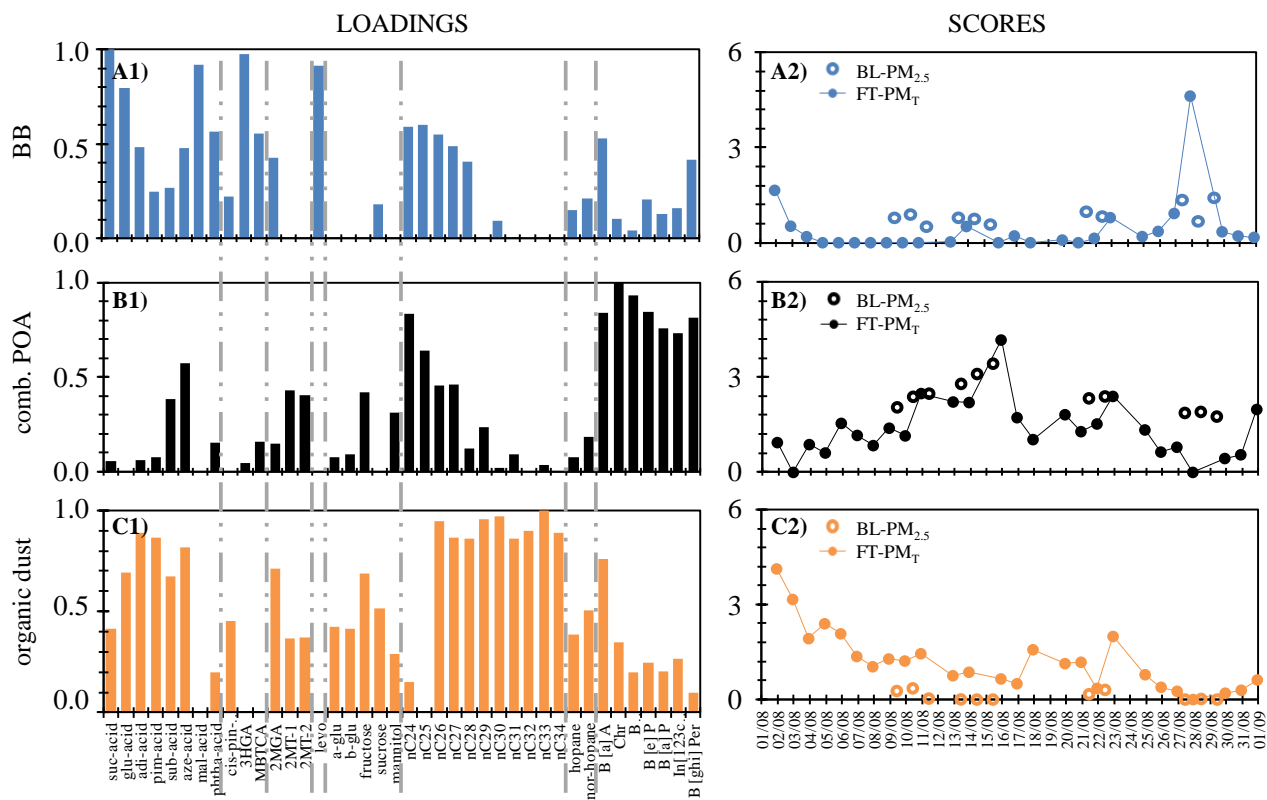
**Figure 2:** Scatter plot between total concentration of SOA ISO and total concentration of SOA PIN within the FT (PM<sub>T</sub> collected during the night). Two tendencies can be distinguished: tendency-1 (t1; circles) and tendency-2 (t2; squares). Filled markers correspond to measurements within the SAL and open markers to measurements within the WES.



5 **Figure 3:** Scatter plot between SOA ISO and nitrate within the SAL under FT conditions (FT-PM<sub>T</sub> samples collected during the night). Three tendencies can be distinguished: tendency-1 (t1; circles), tendency-2 (t2; squares) and tendency-3 (t3; triangles). Westerlies were excluded when calculating the regression coefficients as values were under the detection limit.

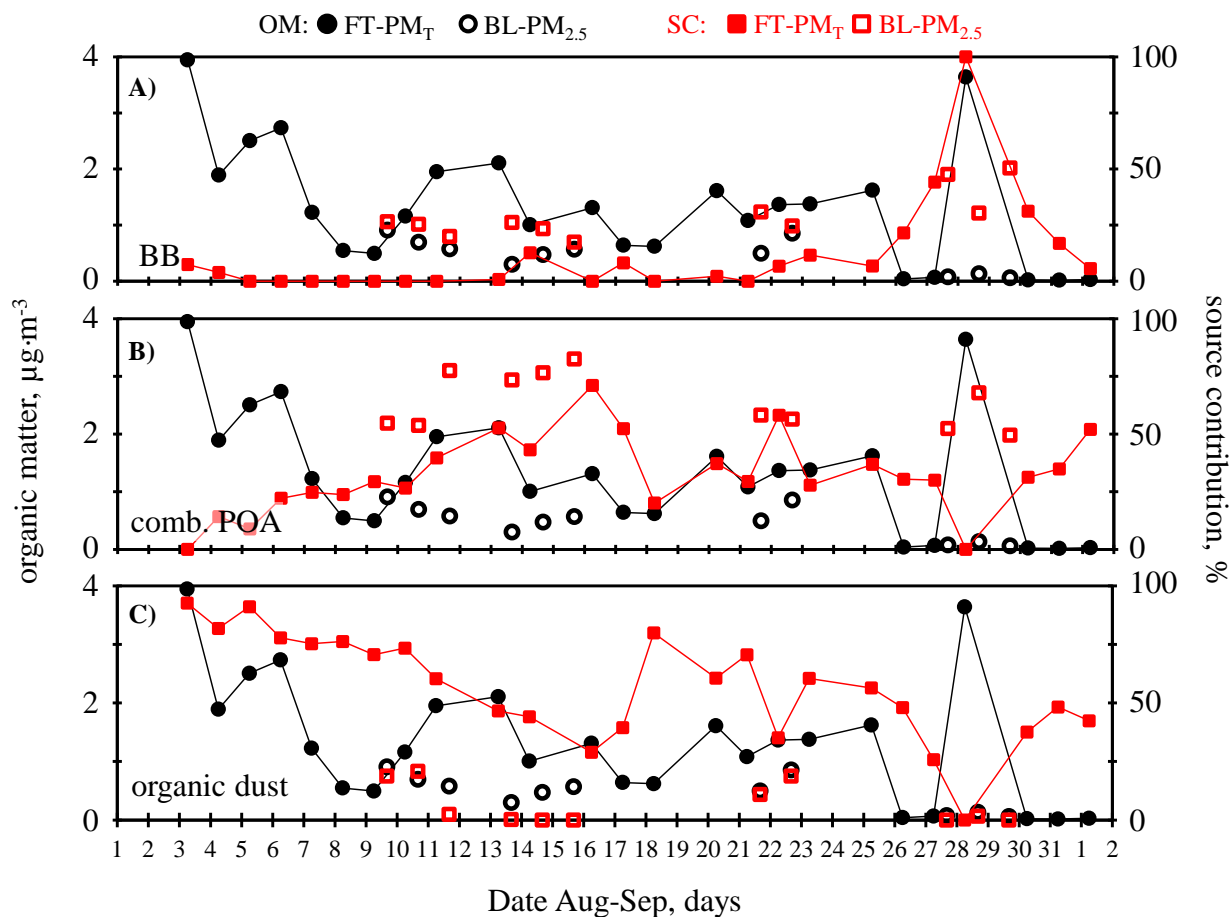


5 **Figure 4:** Contribution of the eight analysed organic groups to the Izaña OM composition within the FT and the BL under the SAL (FT-SAL and BL-SAL) and the WES (FT-WES, BL-WES, BBE). Average total OM for each air mass is on top. FT-PM<sub>T</sub> samples were collected during the night (22–6 GMT) and BL-PM<sub>2.5</sub> samples were collected during the day (10–16 GMT).



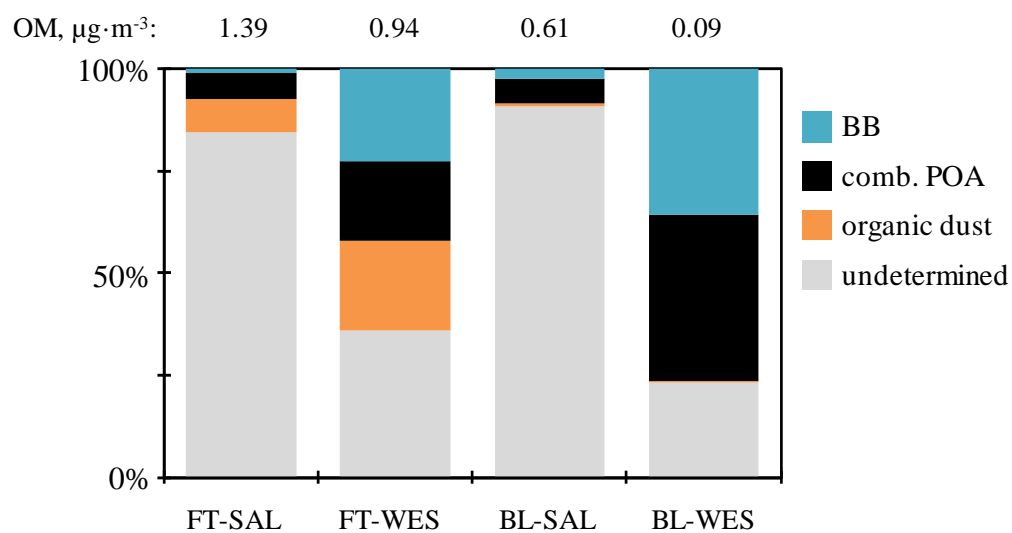
**Figure 5:** FT-PM<sub>T</sub> (night) and BL-PM<sub>2.5</sub> (day) loadings and scores of the three components from MCR-ALS resolved profiles. Filled markers correspond to FT-PM<sub>T</sub> and open markers to BL-PM<sub>2.5</sub>. Grey lines separate the compounds belonging to the different organic groups: dicarboxylic acids, SOA PIN, SOA ISO, levoglucosan, saccharides, n-alkanes, hopanes and PAHs (from left to right).

5



**Figure 6:** Time series of the total organic matter (OM; circle markers) and the source contribution (SC; square markers) to the determined organic matter for the FT- $\text{PM}_{\text{T}}$  (filled markets) and the BL- $\text{PM}_{2.5}$  samples (open markers). Sources: (A) biomass burning (BB), (B) combustion (comb.) POA and (C) organic dust.

5



5 **Figure 7:** Contribution of the identified organic aerosol sources to the total organic matter within the FT and the BL under the SAL (FT-SAL and BL-SAL) and the WES (FT-WES, BL-WES, BBE). Average total OM for each air mass is on top. FT- $\text{PM}_{\text{T}}$  samples were collected during the night (22–6 GMT) and BL- $\text{PM}_{2.5}$  samples were collected during the day (10–16 GMT).

# Revised Supplement

Changes are highlighted in **green** for reviewer#1, in **yellow** for reviewer#2 and in **blue** for authors. Brackets indicate the reviewer and comment that prompt the change.

Changes were not needed in the supplement.