Dear Dr. Russell,

Thank you very much for your observations on the manuscript <acp-2017-108>. We have already replied to each of your questions following the structure (1) comments from Editor, (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 your comments. In addition, the manuscript has been reviewed by a professional translator, that you can contact if you think is necessary (Elaine Ann Barbour, elaineannbarbour@gmail.com).

Please, find attached (i) the "Authors Response Report", which includes the answer to Editor, with a reply to each question and the description of the changes in the manuscript as a consequence of each comment, (ii) the "Revised Manuscript" and (iii) the "Revised Supplement", where the changes performed (with respect to the version uploaded after the reviewers comments) are highlighted, so changes can easily be tracked.

This revised version includes the Editor minor comments and correction of language/spelling problems.

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 EDITOR Dr. Russell

Please, find below a point-by-point reply to each question and suggestion.

1. The following partial list of the Language/spelling problems that remain in the revised manuscript and serve to obfuscate the science intended:

    Aerosol cocktail
    The determined organic
    At daytime
    Can suffers
    Mounts
    As is >> and is
    The arriving
    Meet cooking
    Up whirling
    Guenter
    Monoterpenes reacts
    Than this found >> than that found
    A same origin thought the same
    Is pointed as
    Arriving to
    Could also contributes with
    Concentration determine
    Associated to
    Implication on
    "a" 15%, 84%, etc.
    "This determined fraction" means a fraction that has made up its mind not a fraction that has been determined.
    Accounted by
    Significantly representative of
    Predominant presence
    Those form fungi
    Because of
    Highly significant
    Undermined >> undetermined???
    Determined OM

Since the above list of syntax issues is not complete, I ask that you provide a signed certification by a native English speaker (or equivalent) that the revised paper has been corrected. Alternatively you hire ACP to do language editing, since this job should not fall either to reviewers or associate editors.

REPLY:
Thank you very much for your deep revision. We really apologize for all this language/spelling problems, which we will avoid in future submitted articles. The changes you have suggested have been specifically pointed as [Ed#C1]. All manuscript has been revised by a professional translator (highlighted in green).

CHANGES IN THE MANUSCRIPT [Ed#C1]**:**

"Aerosol cocktail"	>>	Aerosols
"The determined organic"	>>	The organic fraction determined
"At daytime"	>>	In daytime
"Can suffers"	>>	Can suffer
"Mounts"	>>	Mountains
"As is"	>>	and is
"The arriving"	>>	the arriving of "the air mass started moving towards.."
"Meet cooking"	>>	Meat cooking
"Up whirling"	>>	Up-lifted
"Guenter"	>>	Guenther
"Monoterpenes reacts"	>>	Monoterpenes react
"Than this found"	>>	than that found
"A same origin thought the same	>>	Sentence: "…indicates a same origin thought the same …" Reworded as: "…would seem to indicate they formed through the same…"
"Is pointed as"	>>	Sentence: "…Europe is pointed as a potential source …" Reworded as: "…Europe is a potential source …"
"Arriving to"	>>	"Arriving at"
"Could also contributes with"	>>	"may also contribute with"
"Concentration determine"	>>	Concentration determines
"Associated to"	>>	Associated with
"Implication on"	>>	Implications for
"a" 15%, 84%, etc.	>>	"a" deleted from list in <3.2.9 Determined fraction of OM> and other %
"This determined fraction" means a fraction that has made up its mind not a fraction that has been determined.	>>	"determined fraction" changed by "the fraction determined" inthe manuscript
"Accounted by"	>>	Accounted for
"Significantly representative of"	>>	representative of
"Predominant presence"	>>	Major presence
"Those form fungi"	>>	Those related to fungi
"Because of"	>>	because
"Highly significant"	>>	statistically significant
"Undermined"	>>	undetermined
"Determined OM"	>>	"Fraction determined of OM"

2. Also, claims for significance and correlation should be related to a standard benchmark; specify yours and apply it consistently throughout, defining all phrases such as "significantly", "highly representative", etc.

REPLY:
Thanks for your suggestion, which definitively will improve the final revised manuscript. We have specified in <3.2 Organic molecular tracers> that (i) the correlations among the organic groups and the major species are evaluated by means of the Pearson correlation coefficient (r) and that (ii) the significance levels are determined according to the p-value. We have replaced the coefficient of correlation (R^2) by the Pearson correlation coefficient (r) thought the text and apply this coefficient it consistently throughout phrases such as "statistically significant correlation".

CHANGES IN THE MANUSCRIPT [Ed#C2]**:**

1. Sect. <3.2 Organic molecular tracers>
Sentence:
"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)."
Reworded as:
"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 by means of the Pearson correlation coefficient (r) (Table 3); significance levels are determined according to the p-value (p). This coefficient is applied for all correlation thought the manuscript. "

2. Sect. <3.2.3 Saccharides>
Sentence:
"…both isomers showed a good correlation (R^2= 0.998)…"
Reworded as:
"…both isomers showed a statistically significant correlation (r = 0.99, p<0.01)…"

3. Sect. <3.2.4 n-Alkanes>
Sentence:
"…is a significant correlation between…"
Reworded as:
"…is a statistically significant correlation between…"

4. Sect. <3.2.5 Hopanes>
Sentence:
"The quantified hopane and norhopane showed very good linear correlations (R2= 0.95), pointing to the same emission sources."
Reworded as:
"The quantified hopane and norhopane showed a statistically significant correlation (r = 0.97, p<0.01), implying the same emission sources."

Sentence:
"A strong correlation is observed in the FT…"
Reworded as:
"A statistically significant correlation is observed in the FT…"

5. Sect. <3.2.6 Polycyclic aromatic hydrocarbons>
Sentence:
"In the FT there is a strong correlation between PAHs and EC (r = 0.7, p<0.01…"
Reworded as:
"In the FT there is a statistically significant correlation between PAHs and EC (r = 0.7, p<0.01…"

6. Sect. <3.2.7 Tracers of α-pinene oxidation (SOA PIN)>
Sentence:
"…with a significant correlation (R^2 = 0.81) that points…"
Reworded as:
"…with a statistically significant correlation (r = 0.90, p<0.01) pointing…"

7. Sect. <3.2.8 Tracers of isoprene oxidation (SOA ISO)>
Sentence:
"A significant correlation among 2-MT1 and 2-MT2 was found for individual values (R2 = 0.94)…"
Reworded as:
"A statistically significant correlation among 2-MT1 and 2-MT2 was found for individual values (r = 0.90, p<0.01)…"

Sentence:
"This significant correlation between …"
Reworded as:
"This statistically significant correlation between …"

Sentence:
"…the same temporal trend (FT-SAL 2-MTs us 2-MGA-r2: 0.1), which…"
Reworded as:
"…the same temporal trend (r = 0.4, p<0.05 within the FT-SAL), which…"

Sentence:
"Significant…"
Reworded as:
"Statistically significant…"

8. Sect. <3.3.1 Biomass Burning (BB)>
    Sentence:
    "…significantly associated to…"
    Reworded as:
    "… significantly correlated to…"

9. Sect. <3.3.2 Combustion POA>
    Sentence:
    "…and highly representative for the BL, as shown by its Pearson correlation coefficient…"
    Reworded as:
    "…and representative for the BL, as shown by its statistically significant correlation…"

10. Sect. <3.3.3 Organic dust>
    Sentence:
    "The scores of this component display the highest correlation with dust…"
    Reworded as:
    "The scores of this component display the highest statistically significant correlation with dust…"

11. Sect. <3.3.4 Source apportionment of OM in the SAL and the westerlies>
    Sentence:
    "The correlation between the sum of the three components scores and the OM within the FT (OM r-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 (OM r-BL = 0.33; Table S1)…"
    Reworded as:
    "The statistically significant correlation between the sum of the three components scores and the OM within the FT (OM r-FT = 0.63, p < 0.05; 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 (OM r-BL = 0.33, p < 0.05; Table S1)…"

3. Recommend Cite Garrett et al. 2003 JGR

REPLY:
Thank you very much for recommending us this valuable study. We have added a reference to the study of Garrett et al. (2003) in section <3.2.8 Tracers of isoprene oxidation (SOA ISO)>

CHANGES IN THE MANUSCRIPT [Ed#C3]**:**

Sentence added:
"; this is supported by a previous study (Garrett et al., 2003) in which it was suggested that carbonaceous, sulphate, and nitrate particles – in aerosol plumes transported from North Africa over the North Atlantic Ocean within the FT – were anthropogenic pollution from Europe."

Reference added:
Garrett, T. J., Russell, L. M., Ramaswamy, V., Maria, S. F., and Huebert, B. J.: Microphysical and radiative evolution of aerosol plumes over the tropical North Atlantic Ocean, J. Geophys. Res. Atmos., 108, 4022–4038, doi: 10.1029/2002JD002228, 2003.

Revised Manuscript

Changes are highlighted in <mark>yellow</mark> (based on Editor comments) and <mark>green</mark> (language corrections). Brackets indicate the comment that prompts the change.

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

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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 flow<mark>s</mark> from North America <mark>~~through~~ over</mark> 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.. <mark>on ~~in~~</mark> 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 $\mu g \cdot m^{-3}$. 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 α-pinene and isoprene, determined by gas-chromatography coupled <mark>with ~~to~~</mark> mass-spectrometry) accounted for <mark>a</mark> 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 <mark>~~the~~</mark> organic matter accounted for ~28% of the bulk mass <mark>of aerosols [Ed#C1]</mark>. In the westerlies, the <mark>~~determined~~</mark> organic aerosol species <mark>determined</mark>

[Ed#C1] accounted for 64% of the bulk organic matter, ~~being~~ with SOA ISO and dicarboxylic acids being the most abundant; the highest concentration of organic matter (3.6 μg·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 of the formation rate of secondary organic aerosols due to interaction with anthropogenic NO_x emissions.

1 Introduction

Atmospheric aerosols, or particulate matter, ~~influence on~~ have an 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 of organic species constituting the so-called organic aerosols (OA) (IPCC, 2013). OA accounts for an important fraction of particulate matter, ranging from ~20% (continental mid-latitudes) to ~90% (tropical forested areas) (Kanakidou et al., 2005). As with 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 significantly to the global budget of SOA (Guenther [Ed#C1] et al., 2012). Some 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 on ~~in~~ global OA levels as indicated by modelling (Pye et al., 2010) and experimental work (Surratt et al., 2006). In daytime [Ed#C1], 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 [Ed#C1] long-range transport to more remote environments (Horowitz et al., 1998; Mao et al., 2013). At nighttime, the ~~interaction~~ VOCs-NO_3 interaction dominates, with SOA yields greater than ~~that~~ those for OH or O_3 oxidation (Ng et al., 2017 and references therein). 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 NO3 initiated isoprene oxidation. In remote environments, VOCs enhance condensational growth of new particles, which can enter ~~to~~ the free troposphere (FT) by means of elevated mountains [Ed#C1] (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, and is [Ed#C1] spatially representative of the remote background conditions having important implications for global air quality and climate.

The most extended technique used 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 with ~~to~~ mass-spectrometry analysis of aerosol samples allows the speciation of the organic compounds and the quantification of many of those identified as tracers used to ~~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 less common ~~searce~~ (Simoneit et al. 2004b; Fu et al., 2008, 2014; Wang et al., 2009; van Drooge et al., 2010; Meng et al., 2014), in spite of the fact that ~~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 the 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 blow~~s~~ in the marine boundary layer. This results in the development of the SAL – a warm, dry and stable air stream that expands from the 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 transports 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 the Western Sahara to the Caribbean within the SAL (Garrison et al., 2013). Viruses, bacteria, fungal fungi and pollens also travel mixed with dust across the Atlantic (Griffin et al., 2007; Izquierdo et al., 2011). Field measurements in the SAL at Izaña Observatory found dust to be being the major ice nuclei at temperatures colder than -30ºC (Boose et al., 2016), whereas the observed ice nuclei at -8ºC 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 ~2400 m a.s.l. on 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 on in Tenerife Island (Fig. 1; 16º29'58"W, 28º18'32"N). The site is located on a mountaintop (2373 m a.s.l), surrounded by a pine forest (whose limits lied between ~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 activates 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 Izaña Observatory annual aerosols summer campaign of the Izaña Observatory in August 2013. Particulate Matter (PM) was collected on pre-heated (at

205ºC) quartz filters (Pall Science 150 mm diameter) on high volume air samplers (Hi-Vol; MCZ) at a flow rate of 30 m^3·h^{-1}. 30 samples of total particulate matter (PM$_T$) were collected daily during night-time (22:00–6:00 GMT; FT) and 12 samples of particulate matter smaller than 2.5 μm (PM$_{2.5}$) on ~~in~~ non-consecutive days during daytime (10:00–16:00 GMT; BL). Field

5   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

A ~~One~~ quarter of the filter sample was used for the organic compounds speciation by gas-

10   chromatography coupled with ~~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), and extracted ultrasonically in a mixture of dichloromethane and methanol. Extracts were filtered and concentrated to ~~until~~ 0.5 ml. For the

15   analysis of polar compounds, i,e. acids and saccharides, a 25 μL aliquot of the extract was evaporated to ~~until~~ dryness, and 25 μL of bis-(trimethylsilyl)-trifluoroacetamide (BSFTA) + trimethylchlorosilane (99:1) (Supelco, Bellefonte, PA, USA) and 10 μl of pyridine (Merck, Darmstadt, Germany) were added and left overnight to derivatize the polar compounds to their trimethylsilyl esters and ethers for analysis ~~in order to analyse them~~ by GC-MS. The remaining

20   extract was used for the analysis of PAHs, n-alkanes and hopanes, and was cleaned up by adsorption column chromatography, packed with 1 g of aluminium oxide (Merck, Germany). The analytes were eluded 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 μl under a gentle nitrogen stream for quantification by GC-MS (Thermo Trace GC Ultra – DSQ II). The MS detector was

25   operated in full scan (m/z from 50 to 650) and electron impact (70 eV) ionization mode for the polar compounds. The sample extracts for the analysis of non-polar species were ~~was~~ performed in selected ion monitoring (SIM) 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).

30   ### 2.3.2 OC and EC

Organic and elemental carbon (OC and EC) were analysed by thermal-optical transmittance (TOT, Sunset Laboratory Inc. ™) 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 of which 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

The methodology used for the inorganic speciation is described in detail in Rodríguez et al. (2015). Briefly, soluble species were determined by ion chromatography ($SO_4^=$, NO_3^-, Cl^-) and selective electrode (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™) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, X Series II, THERMO™) after acid digestion of the sample. Mineral dust was calculated as the sum of $Al_2O_3 + SiO_2 + Fe + CaCO_3 + K + Na + Mg + P + Ti + Sr$ (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 et al., 2016). $SO_4^=$ was split into non-sea salt sulphate (nss-$SO_4^=$) and sea salt sulphate (nss-$SO_4^= = SO_4^= - ss-SO_4^=$) ~~through~~ based on the relation between marine Na and $SO_4^=$. Blank field filters were subject to gravimetric and chemical analysis and mean values subtracted to the PM_x samples.

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 National Centre for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS, 1 degree) data set. Ten-day 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 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 organic aerosol in urban and rural areas (Alier et al. 2013; Van Drooge and Grimalt 2015). The ~~explained~~ variance explained 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. Multi-linear regression tools were applied to quantify the contribution of the identified sources to the total OM.

3 Results and Discussion

5 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

10 Izaña after circulation around the Azores High in summer (see back-trajectories of the samples collected from 26 Aug to 30 Aug – with "ddmmm" referringed to ending sampling day – in Fig.1A). The SAL expands from North Africa to the Americas at subtropical latitudes in summertime (see back-trajectories associated during the study period in Fig. 1B), the season in which the Izaña Observatory is mostly within this dusty airstream and the presence of the WES

15 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 warming of the terrain, which typically results in increases of primary gaseous pollutants and new particle

20 formation at Izaña (García et al, 2014; Rodríguez et al., 2009).

Thus, in this study we differentiate between 4 scenarios: PM_T (FT, night-time) 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

25 Table 1 shows the composition of the aerosol samples collected at Izaña. Concentrations of aerosol major components are the same as 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.

30 ### 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 into ~~on~~ the origin and sources of some FT organic aerosols, correlations among the organic groups and the major species are evaluated by means of the Pearson correlation coefficient (r) (Table 3); significance levels are determined according to the p-value (p). This coefficient is applied for all correlation throughout the manuscript [Ed#C2].

3.2.1 Levoglucosan

Levoglucosan (1,6-anhydro-β-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~~ due to 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 ng·m^{-3} for all samples, except on 28 Aug when ~9 ng·m^{-3} was measured. Hysplit back-trajectories and the Atmospheric Infrared Sounder (AIRS) satellite images (NASA) indicate the North American origin of the air masses, where several wildfires – such as the Rim Fire – were affecting western USA 10 days before ~~the arrival of~~ [Ed#C1] the air mass started moving 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~~ lend support to the atmospheric stability of levoglucosan, ~~for~~ under the specific atmospheric conditions of ~~the atmospheric~~ this 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 westerlies conditions ~~of the westerlies~~ (FT-WES; Table 2). Levoglucosan concentration, measured at Izaña during the BBE (9.3 ng·m^{-3}), is similar to the average levels detected in the marine BL ~~on~~ over the Azores in the North Atlantic (5.2 ng·m^{-3}) or at a free tropospheric site in the European continent (7.8 ng·m^{-3}), but much lower than those found ~~in~~ at sites under the influence of local BB or continental sites in winter (653–1290 ng·m^{-3}) (Puxbaum et al. 2007).

3.2.2 Dicarboxylic acids

Dicarboxylic acids can be emitted in small quantities from several natural and anthropogenic primary sources such as vegetation, meat [Ed#C1] 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 ∑dicarboxylic acids concentrations within the FT (SAL: 14.4 ng·m^{-3}; WES: 16.7 ng·m^{-3}) and the BL (SAL: 11.1 ng·m^{-3}; WES: 12.9 ng·m^{-3}) 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^{-3} for the FT-BL) much lower than those [Ed#C1] found for PM$_{2.5}$ in the FT Mount Tai (suc: 30 ng·m^{-3} ; Wang et al., 2009), similar to those observed in PM$_T$ in the Himalayas (4276 m a.s.l.) (suc: 13.7 and pth: 9.5 ng·m^{-3}; Cong et al., 2015), but higher than those detected for PM$_T$ in the North Pacific remote marine (suc: 2.8 and pth: 0.66 ng·m^{-3}; Kawamura and Sakaguchi., 1999). Malic acid within the BL (the third most abundant poly-acid at Izaña; Table 2) might ~~have a photochemical~~ be photochemical in origin via OH oxidation of the surrounding biogenic compounds transported by the daytime 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 measured at Izaña. Oxidation of these biogenic precursors may also provide important amounts of C$_7$–C$_9$ 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 line ~~agreement~~ with the observed values for the long-range transport BBE (82 ng·m^{-3}). Concentrations of succinic, glutaric and malic acids were high (~33 ng·m^{-3}, ~7 ng·m^{-3} and ~32 ng·m^{-3}, respectively; Table 2), compared to the rest of the period, ~~surely~~ most likely 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 (α, β), 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~~ up-lifted 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$_T$ (23.5 ng·m^{-3}) and the BL-PM$_{2.5}$ (3.5 ng·m^{-3}). Previous studies have shown that some organic compounds are strongly particle-size dependent (Mochida et al., 2003; Van Drooge and Grimalt, 2015), with special emphasis ~~in~~ on sugars and sugar alcohols, which are present mostly in very large particles (Graham et al., 2003; Yttri et al., 2007). This size-segregation is clearly seen for the PM$_{2.5}$ samples collected within the BL, that cuts 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^{-3}; BL-WES = 4.0 ng·m^{-3}). A different scenario takes place with the PM$_T$ samples, for which concentrations rise one order of magnitude from SAL influence to clean conditions (FT-SAL = 27 ng·m^{-3}; FT-WES = 2.5 ng·m^{-3}) linked to Saharan dust contribution. The average saccharides levels in the FT-SAL are higher than ~~these~~ those observed in a natural forest area in tropical India (12.78 ng·m^{-3}; Fu et al., 2010) and a rural background in Norway (10.4 ng·m^{-3}; Yttri et al., 2007), but very similar to the average concentrations measured in the FT over central China (28.1 ng·m^{-3}; Fu et al., 2014).

Glucose (α+β) was the predominant saccharide within the SAL, with a mean FT concentration of ~10 ng·m^{-3} (Table 2); both isomers showed a ~~good~~ statistically significant correlation (r = 0.99, p<0.01 ~~R^2 = 0.998~~) [Ed#C2] consistent with their relation in the soil (Simoneit et al. 2004a). Under the WES airflows, glucose (α+β), 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. This load is more evident in the sucrose (FT-WES = 0.3 ng·m^{-3}; BL-WES = 1.3 ng·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

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 nC$_{24}$ to nC$_{34}$ were quantified, with total n-alkanes mean concentrations (~8 ng·m^{-3} in the FT and in the BL) much lower than ~~this~~ those measured in the tropical Indian summer (126 ng·m^{-3}; Fu et al., 2010), but similar to ~~this~~ those found in rural Spain during the warm period (12 ng·m^{-3}; Van Drooge and Grimalt, 2015).

Information about the possible source may ~~can~~ be provided by the carbon number maximum (C$_{max}$). In general, nC$_{27}$, nC$_{29}$ and nC$_{31}$ are related to waxes from terrestrial higher plants,

whereas low-molecular-weight alkanes (C_{22}–C_{25}) are more associated with ~~to~~ combustion sources (Mazurek et al. 1989). At Izaña, the most abundant n-alkanes within the FT-SAL were nC_{27}, nC_{29} and nC_{31} (~1.0 ng·m^{-3}, ~1.4 ng·m^3 and ~1.8 ng·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 nC_{24}–nC_{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 type is the carbon preference index (CPI = ∑odd n-alkanes / ∑even n-alkanes) with CPI > 1 related to biogenic origin and CPI ≈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 (~2) higher than those for the BL (~1.7) and the FT-WES (~1.2), reflecting the ~~larger~~ greater 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 statistically [Ed#C2] significant correlation between n-alkanes and NO_3^- (r = 0.8, p<0.01; Table 3), mostly due to its anthropogenic fraction (C_{24}–C_{25}).

3.2.5 Hopanes

Hopanes (17α(H),21β(H)-29-norhopane and 17α(H),21β(H)-hopane) are linked to mineral oil and related to unburned lubricating residues from primary vehicle~~s~~ emissions (Rogge et al., 1993; Schauer et al., 1996, 2002). ∑Hopanes mean concentrations were 0.13 and 0.08 ng·m^{-3} within the FT and BL respectively, values much higher than the $7 \cdot 10^{-4}$ ng·m^{-3} measured by von Schneidemesser 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 an influence of pollution transported within the BL, related to motorized vehicle emissions. ~~The~~ Quantified hopane and norhopane showed a statistically significant correlation (r = 0.97, p<0.01) ~~very good linear correlations (R^2 = 0.95),~~ implying [Ed#C2] the same emission sources.

A statistically significant ~~strong~~ [Ed#C2] correlation is observed in the FT between hopanes and NO_3^- (r = 0.8, p<0.01; Table 3) suggesting that the origin of most ~~of~~ NO_3^- in the FT ~~has its origin~~ lies in on-road vehicle emissions ~~instead of the~~ rather than industry. Anthropogenic sources of NO_x (the major NO_3^- precursor) include fossil fuel emitted from agriculture, power plants, industry and transport. The latter ~~one covers~~ accounts for almost ~~a~~ 50% of ~~the~~ nitrogen oxide~~s~~ 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 Tg·year^{-1}) compared to non-road (10.1 Tg·year^{-1}), shipping (16.2 Tg·year^{-1}), aviation (3.0 Tg·year^{-1}) or rail (1.6 Tg·year^{-1}) (Yan et al., 2014).

3.2.6 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are organic pollutants generated during incomplete combustion of organic natural material ~~natural~~ (e.g. forest fires, volcanic activity) and anthropogenic (e.g. fossil fuels combustion, coke production) sources (Howsam and Jones

5 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 are potentially endocrine disruptive~~ness~~, affecting human health. At Izaña mean values of the total PAHs exhibited higher values in the BL (24 pg·m^{-3}) than in the FT (16.3 pg·m^{-3}), reflecting the contribution of the upslope winds as described for other organic compounds.

10 Similar PAHs concentrations were previously found by van Drooge et al. (2010) who measured an average PAHs concentration of 33.1 pg·m^{-3} at Izaña. In general, all individual PAHs decreased ~~in its~~ concentration ~~excep~~ with the exception of benz(a)anthracene ~~that~~ which 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

15 such as Mt. Tai (1534 m a.s.l.) where ~9 ng·m^{-3} were measured (Fu et al., 2008). In the FT there is a ~~strong~~ statistically significant [Ed#C2] 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 (28 Aug), PAHs concentration was 9.4 pg·m^{-3}, which is much lower than levels measured in Thailand for PM$_T$ samples during BBEs in the

20 dry season (1150 to 4140 pg·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 α-pinene oxidation (SOA PIN)

25 Vegetation emits large quantities of biogenic volatile organic compounds (BVOCs) into the atmosphere compared to anthropogenic VOCs (Guenther [Ed#C1] 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 α-pinene (Andreani-Aksoyoglu and Keller, 1995; Rinne et al., 2009; Smolander et al., 2014) and the tracers related to its

30 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 few ~~couple of~~ extreme points that increased their average concentration. SOA PIN exhibited the lowest concentration in the FT-WES (1.2 ng·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

5 concentrations of 3-HGA (8.5 ng·m^{-3}) and MBTCA (1.9 ng·m^{-3}) than those measured in the present study (Table 2). Further generation oxidation products (3-HGA and MBTCA) were higher in the BL (0.51 and 0.24 ng·m^{-3} correspondingly; Table 2), with a statistically significant correlation (r = 0.90, p<0.01) ~~(R^2 = 0.81)~~ [Ed#C2] ~~that points~~ pointing to a same precursor. Monoterpenes react [Ed#C1] relatively ~~fast~~ rapidly, with atmospheric lifetimes ranging from

10 minutes to hours (Saxton et al., 2007), resulting in α-pinene emitted in the ~~ring~~ forest ring that reacts along its upward transport to the Observatory. Daytime emissions of gaseous α-pinene at Izaña were measured by Fisher at al. (1998) with concentration in the range of 0.011–0.102 ppbv (mean: 0.028 ppbv), supporting ~~the~~ evidence of its origin being close to the Observatory during the day.

15 **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 Tg·y^{-1}; Guenther [Ed#C1] et al., 2012), making it the largest BVOC emitted from land vegetation (Guenther [Ed#C1] 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 (Guenther [Ed#C1]

20 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^{-3}; Table 2) and over the central China FT (8

25 and 17 ng·m^{-3}; 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^{-3} respectively) revealing the emission and ~~following~~ subsequent ascending transport of biogenic or anthropogenic compounds, as found in previous studies performed at Izaña, which observed emissions of

30 isoprene during daytime associated with ~~to~~ anthropogenic compounds (Salisbury et al., 2006). A statistically [Ed#C2] significant correlation among 2-MT1 and 2-MT2 was found for individual values (r = 0.90, p<0.01) ~~(R^2 = 0.94)~~ [Ed#C2] 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 that [Ed#C1] found by El Haddad et al. (2011).

35 This statistically significant [Ed#C1] correlation between the two diastereoisomers ~~indicates a~~

same origin would seem to indicate they formed [Ed#C1] through the same photo-oxidation process.

The highest concentration of SOA ISO was measured under the FT-SAL (~28 ng·m^{-3}), associated with Saharan dust, as was observed for SOA PIN (~33 ng·m^{-3}). However, global estimations of isoprene and α-pinene emissions and sources show they are diverse and not equally distributed around the globe (Luo et al., 2010; Guenther et al., 2012; Sindelarova et al., 2014). The 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 with different global sources of the precursor volatile compounds, although the trajectories of the sampled air mass do not clearly distinguish between different origins. Some species with 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 α-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 Tunisia, whereas Europe is [Ed#C1] 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 their passing over Africa and Izaña in the Atlantic Ocean.

Rodríguez et al. (2011) previously reported high concentrations of SO$_4^=$, NO$_3^-$ and NH$_4^+$ for air masses arriving at [Ed#C1] Izaña from the Atlantic coast of Morocco, Eastern Algeria, Northern Algeria and Tunisia. Industrial states with sources of gaseous precursors (SO$_x$, NO$_x$ and NH$_3$) of these aerosol compounds were identified. Although African emissions seem to be responsible for the pollutants reaching the North Atlantic FT, Europe may also contribute [Ed#C1] with amounts of pollutants that should not be neglected as evidenced by the concentration of SOA PIN and SOA ISO arriving at [Ed#C1] Izaña; this is supported by a previous study (Garrett et al., 2003) in which it was suggested that carbonaceous, sulphate, and nitrate particles – in aerosol plumes transported from North Africa over the North Atlantic Ocean within the FT – were anthropogenic pollution from Europe [Ed#C3]. These species may 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 heavily 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 determines the pathway (low-NO$_x$ and high-NO$_x$) followed by the isoprene oxidation, leading to different secondary organic species

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

5   We found the relation among SOA ISO and NO$_3^-$ within the FT-SAL (Fig.3) presents three tendencies which might be associated with [Ed#C1] the ratio isoprene:NO$_x$ in the source. The different correlations are supported by the fact that the SOA ISO markers (2-MTs and 2-MGA) do not exhibit the same temporal trend (r = 0.4, p<0.05 within the FT-SAL) (FT-SAL 2-MTs us 2-MGA-r^2: 0.1) [Ed#C2], which has been suggested to be linked to the NO$_x$ concentration

10   influence on~~this~~ these SOA ISO markers formation pathways (El Haddad et al., 2011). The high-NO$_x$ pathway leads to the reaction of isoprene peroxy radicals (iRO$_2$) with NO resulting in carbonyls and hydroxynitrates production (Surratt et al., 2006), whereas the low-NO$_x$ pathway leads to the reaction of iRO$_2$ with hydroperoxy radicals (HO$_2$) resulting in hydroxyhydroperoxides (iROOH), and carbonyls production to a lesser extent (Carlton et al.,

15   2009; Paulot et al., 2009). This has implications for [Ed#C1] the abundance of the secondary organic markers from isoprene photo-oxidation (2-MT and 2-MGA): high-NO$_x$ pathway results in the major product 2-MGA and low-NO$_x$ pathway in major products 2-MTs (El Haddad., 2011).

Statistically [Ed#C2] significant correlations in the FT between biogenic secondary organic
20   compounds and NO$_3^-$ (r SOA PIN–NO$_3^-$ = 0.6, p<0.01; Table 3) and nss-SO$_4^=$ (r SOA ISO–nss-SO$_4^=$ = 0.6, p<0.01; Table 3), point to its formation from the oxidation of their gaseous precursors NO$_x$ and SO$_2$ respectively. Dust transformation in the FT is also evidenced by its ~~highly~~ statistically [Ed#C1] significant correlation with SOA PIN (r = 0.7, p<0.01; Table 3) ~~as well as~~ in addition to both saccharides (r = 0.6, p<0.01) and hopanes (r = 0.9, p<0.01) showing
25   that natural and anthropogenic substances might be mixed after aging processes.

3.2.9 ~~Determined~~ [Ed#C1] Fraction determined of OM

Bulk organic carbon (OC) determined for every single day (thermo-optical transmittance method) at Izaña during this study was within the range 0.01–2.20 µg·m^{-3}, which is in line with ~~of the order to~~ that found in other FT studies (e.g. 1.4 µg·m^{-3} at Qomolangma, Mt. Everest, 4276
30   m a.s.l. by Cong et al., 2015 and 4 µg·m^{-3} at NW Pacific, 2–6.5 km column by Heald et al., 2005). FT-PM$_T$ OC under SAL conditions (0.77 µg·m^{-3}) was higher than under WES (0.52 µg·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 OC·1.8); this mass closure accounts for 2-100 % 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 µg·m^{-3}) than under FT-WES (0.04 µg·m^{-3} without the BBE; 0.94 µg·m^{-3} including the BBE) conditions. The selected tracers (levoglucosan, SOA ISO, SOA PIN, n-Alkanes, saccharides, dicarboxylic acids, hopanes and PAHs) represent on ~~as~~ average:

5   (i)   [Ed#C1] 15% of the OM (Fig. 4), under FT-SAL conditions (when mean OM was 1.39 µg·m^{-3}). This ~~determined~~ fraction determined [Ed#C1] is mainly composed of ~~by~~ SOA ISO (30%), saccharides (27%) and dicarboxylic acids (18%).

    (ii)   [Ed#C1] 84% of the OM (Fig. 4), in the FT-WES airflows without the BBE (when mean OM was 0.04 µg·m^{-3}). This ~~determined~~ fraction determined [Ed#C1] is

10   comprised of ~~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).

15   (iii)   [Ed#C1] 3% of the OM (Fig. 4) in the FT-WES during the BBE (when mean OM was 3.64 µg·m^{-3}). The ~~determined~~ fraction determined [Ed#C1] of OM for 28 Aug (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 of this sample has ~~with~~ the highest contribution of aged SOA (di-acids), formed during the

20   long-range atmospheric transport, and the lowest contributions of SOA PIN (4%) and SOA ISO (12%), which ~~could~~ may indicate the further oxidation of these products under ~~the~~ BBE air masses conditions.

    (iv)   [Ed#C1] 64% of the OM in the FT-WES including the BBE (when mean OM was 0.94 µg·m^{-3}). This ~~determined~~ fraction determined [Ed#C1] is comprised

25   ~~constituted~~ mainly of ~~by~~ dicarboxylic acids (50%), and SOA ISO (28%).

Differences in the ~~determined~~ fraction determined [Ed#C1] 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. The

30 ~~determined~~ OM composition determined [Ed#C1] within the BL (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 PM$_{2.5}$ cut-off of the collected particles, the influence of the dust-associated organic compound is likely ~~probably~~ not well represented as ~~since~~ these products are situated in the coarse fraction of the

35 PM.

3.3 Sources of OM

We used receptor modelling for apportionment of 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). 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 Multi-linear Regression Analysis (MLRA) to apportion the ~~determined~~ fraction determined [Ed#C1] of OM between the identified sources. Three components (sources) were identified (Fig. 5), which accounted for [Ed#C1] 81% of the total variance. MCR-ALS method was also applied only to PM_T samples to verify the influence of $PM_{2.5}$ 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_{24}–C_{28} 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 on ~~the~~ 28 Aug (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~~ large 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~~ may 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 correlated ~~associated~~ [Ed#C2] 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_{24} – C_{29} 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 $PM_{2.5}$ samples collected during daylight, when the BL may reach Izaña under the slope wind regime. High loadings of suberic (C_8) and azelaic acids (C_9) 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 ($C_{24} - C_{25}$) and PAHs (from incomplete combustion processes). FT aerosol is also described by this component

5   with the exception of low-molecular-weight alkanes (C_{24}–C_{25}), which is the main feature of the BL samples. ~~The~~ This component is ~~significantly~~ [Ed#C1] representative of the measured EC for all samples, and ~~highly~~ [Ed#C2] representative for the BL, as shown by its statistically significant correlation ~~Pearson correlation coefficient~~ [Ed#C2] (r-All = 0.36 and r-BL = 0.71, p < 0.05; Table S1).

10   **3.3.3 Organic dust**

The third component, accounting for 16% of the total variance, is comprised of ~~composed by~~ short-chain dicarboxylic acids, SOA ISO, saccharides, C_{26}–C_{34} 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~~ A ~~predominant~~

15   major [Ed#C1] presence of the soil OM related compounds, those ~~form~~ related to fungi [Ed#C1] and terrestrial higher plants (C_{27}, C_{29} and C_{31}), suggests 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

20   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 statistically significant [Ed#C2] 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

25   this component is not relevant for the BL-$PM_{2.5}$ samples – because ~~of~~ part of the compounds are present in the larger particle size fractions – the correlation with dust (r-BL = 0.73, p < 0.01; Table S1) and OM (r-BL = 0.75, p < 0.01; Table S1) are ~~highly~~ statistically [Ed#C1] significant due to the mixing of dust with the anthropogenic compounds.

   3.3.4 Source apportionment of OM in the SAL and the westerlies

30   The source apportionment of OM was performed by the multi-linear 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 determined [Ed#C1] and Fig. 7 shows the average source contribution to

total OM in the aerosol samples collected in the different airstreams. The statistically significant [Ed#C2] correlation between the sum of the three components scores and the OM within the FT (OM r-FT = 0.63, p < 0.05 [Ed#C2]; Table S1) indicates that the identified sources might describe, not only the ~~determined~~ fraction determined [Ed#C1] of the OM but also the total OM.

5   This significant correlation is not seen for the BL (OM r-BL = 0.33, p < 0.05 [Ed#C2]; Table S1), where there could be additional sources.

In the FT-SAL airflow, most ~~of~~ OM was undetermined [Ed#C1] (~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

10   determined [Ed#C1], 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 undetermined [Ed#C1] fraction accounts for ~36% of the OM (Fig.7). The

15   contribution of the three identified sources, i.e. ~~the~~ organic dust, combustion POA and biomass burning, is 22%, 19% and 23% of ~~to~~ the bulk OM, respectively (28%, 23% and 49% of ~~to~~ the ~~determined~~ OM determined [Ed#C1], 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

20   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

25   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~~ focuses on the organic aerosol composition within the two main airflows of the subtropical North Atlantic free troposphere: (i) the Saharan Air Layer – the

30   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 α-pinene and isoprene) in order to distinguish possible sources for the organic aerosol. The organic particulate aerosol speciation and its subsequent source apportionment was performed for 42 filter samples collected in summer at the Izaña Observatory (~2400 m a.s.l.) ~~in~~ on Tenerife, Spain.

5   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 determined [Ed#C1] under these two air masses were ~~important~~ substantial.

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

15   In the Westerlies, ~~the~~ organic matter represented a higher fraction of the total aerosol bulk (~28%) and the ~~determined~~ organic compounds determined [Ed#C1] 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
20   atmospheric stability of levoglucosan over transport and time under certain conditions.

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
25   determined [Ed#C1]) and combustion (6% of the bulk OM; 34% of the ~~determined~~ OM determined [Ed#C1]) sources, whereas under the westerlies it comes from organic dust (22% of the bulk OM; 28% of the ~~determined~~ OM determined [Ed#C1]), biomass burning (23% of the bulk OM; 49% of the ~~determined~~ OM determined [Ed#C1]) and combustion (19% of the bulk OM; 23% of the ~~determined~~ OM determined [Ed#C1]) sources, showing that the free
30   troposphere is highly influenced by combustion and biomass burning compounds.

A Comprehensive knowledge of the organic aerosol chemistry is of great ~~high~~ importance in ~~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.

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Table 1. Average concentration of the chemical major compounds for (i) FT-PM$_T$ and BL-PM$_{2.5}$ taking ~~having~~ into account all samples, (ii) FT-PM$_T$ and BL-PM$_{2.5}$ collected within the Saharan Air Layer (SAL)‚ (iii) FT-PM$_T$ and BL-PM$_{2.5}$ collected within the Westerlies (WES) without the FT-PM$_T$ biomass burning event and (iv) FT-PM$_T$ biomass burning event (BBE).

	FT-PM$_T$	BL-PM$_{2.5}$	FT-PM$_T$	FT-PM$_T$	BL-PM$_{2.5}$	BL-PM$_{2.5}$	FT-PM$_T$
	ALL	ALL	SAL	WES	SAL	WES	BBE
$\sum$ CC, µg·m^{-3}	78.98	13.70	92.74	2.16	17.07	4.70	6.84
Dust, µg·m^{-3}	73.61	11.18	86.71	1.51	14.10	3.39	1.66
Sea Salt, µg·m^{-3}	0.53	0.36	0.59	0.27	0.25	0.66	< 0.01
OM, µg·m^{-3}	1.32	0.47	1.39	0.04	0.61	0.09	3.64
EC, µg·m^{-3}	0.04	0.07	0.03	< 0.01	0.08	0.05	0.29
NO$_3^-$, µg·m^{-3}	0.73	0.08	0.87	< 0.01	0.11	< 0.01	< 0.01
NH$_4^+$, µg·m^{-3}	0.33	0.25	0.35	0.14	0.32	0.07	0.54
nss-SO$_4^=$, µg·m^{-3}	2.42	1.28	2.80	0.19	1.61	0.43	0.71
ss-SO$_4^=$, µg·m^{-3}	0.02	0.01	0.02	0.01	0.01	0.03	< 0.01

$\sum$**CC**: sum chemical composition; **OM**: organic matter; **EC**: elemental carbon; **nss-SO$_4^=$**: non sea salt sulphate; **ss-SO$_4^=$**: sea salt sulphate.

Table 2. Average concentration of the selected organic species for (i) FT-PM$_T$ and BL-PM$_{2.5}$ <mark>taking</mark> ~~having~~ into account all samples, (ii) FT-PM$_T$ and BL-PM$_{2.5}$ collected within the Saharan Air Layer (SAL), (iii) FT-PM$_T$ and BL-PM$_{2.5}$ collected within the Westerlies (WES) without the FT-PM$_T$ biomass burning event and (iv) FT-PM$_T$ biomass burning event (BBE).

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	FT-PM$_T$ ALL	BL-PM$_{2.5}$ ALL	FT-PM$_T$ SAL	FT-PM$_T$ WES	BL-PM$_{2.5}$ SAL	BL-PM$_{2.5}$ WES	FT-PM$_T$ BBE
Levoglucosan							
Levoglucosan, ng·m^{-3}	0.75	0.53	0.41	0.40	0.34	1.04	9.33
Dicarboxylic acids							
Succinic, ng·m^{-3}	6.51	3.70	5.70	3.52	4.03	2.80	33.35
Glutaric, ng·m^{-3}	1.97	0.83	1.90	0.74	0.85	0.77	7.23
Adipic, ng·m^{-3}	1.43	0.69	1.53	0.62	0.72	0.60	1.71
Pimelic, ng·m^{-3}	0.83	0.35	0.92	0.37	0.33	0.39	0.17
Suberic, ng·m^{-3}	0.48	0.30	0.50	0.29	0.29	0.31	0.39
Azelaic, ng·m^{-3}	0.88	0.79	0.93	0.57	0.78	0.82	0.71
Malic, ng·m^{-3}	2.01	2.15	0.75	1.20	1.67	3.43	32.21
Phthalic, ng·m^{-3}	3.18	2.77	2.19	9.43	2.38	3.80	6.21
Saccharides							
α-glucose, ng·m^{-3}	9.26	0.90	10.79	0.62	0.90	0.89	1.65
β-glucose, ng·m^{-3}	9.13	1.00	10.63	0.61	1.01	0.98	1.65
Fructose, ng·m^{-3}	2.02	1.01	2.23	0.95	1.10	0.76	0.69
Sucrose, ng·m^{-3}	2.72	0.47	3.18	0.27	0.18	1.26	0.01
Mannitol, ng·m^{-3}	0.35	0.12	0.40	0.08	0.12	0.12	0.07
n-Alkanes							
nC24, ng·m^{-3}	0.72	1.63	0.75	0.48	1.87	0.97	1.01
nC25, ng·m^{-3}	0.93	2.93	0.95	0.40	3.26	2.05	2.09
nC26, ng·m^{-3}	0.60	0.64	0.65	0.26	0.69	0.49	0.54
nC27, ng·m^{-3}	0.89	0.95	0.98	0.24	0.94	0.98	0.76
nC28, ng·m^{-3}	0.37	0.32	0.39	0.17	0.38	0.17	0.36
nC29, ng·m^{-3}	1.18	0.42	1.34	0.25	0.48	0.25	0.63
nC30, ng·m^{-3}	0.45	0.14	0.51	0.07	0.16	0.10	0.18
nC31, ng·m^{-3}	1.55	0.31	1.77	0.37	0.33	0.25	0.29
nC32, ng·m^{-3}	0.39	0.10	0.45	0.05	0.11	0.06	0.08
nC33, ng·m^{-3}	0.48	0.10	0.55	0.06	0.12	0.06	0.13
nC34, ng·m^{-3}	0.29	0.05	0.34	0.02	0.05	0.04	0.01
Hopanes							
Hopane, ng·m^{-3}	0.06	0.02	0.07	0.01	0.03	0.01	0.03
nor-Hopane, ng·m^{-3}	0.07	0.05	0.08	0.02	0.07	0.02	0.03
PAHs							
B [a] A, pg·m^{-3}	1.48	1.48	1.58	0.80	1.61	1.13	1.37
Chr, pg·m^{-3}	4.27	4.37	4.63	1.92	5.12	2.39	3.38
B [b+j+k] F, pg·m^{-3}	3.67	5.74	4.20	0.66	6.69	3.21	1.13
B [e] P, pg·m^{-3}	1.36	1.94	1.50	0.47	2.22	1.20	0.83
B [a] P, pg·m^{-3}	0.78	1.21	0.89	0.18	1.25	1.08	0.29
In[123cd] P, pg·m^{-3}	1.47	2.33	1.65	0.46	2.18	2.74	0.56
B [ghi] Per, pg·m^{-3}	3.29	6.94	3.56	1.73	6.37	8.46	1.84
SOA PIN							
Cis-Pinonic, ng·m^{-3}	27.83	15.24	32.72	0.89	13.23	20.59	1.00
3-HGA, ng·m^{-3}	0.21	0.51	0.09	0.24	0.39	0.81	2.88
MBTCA, ng·m^{-3}	0.03	0.24	0.01	0.05	0.13	0.54	0.27
SOA ISO							
2MGA, ng·m^{-3}	4.22	2.38	4.46	1.63	2.65	1.65	6.56
2MT-1, ng·m^{-3}	6.64	4.94	7.27	3.40	5.16	4.33	2.40
2MT-2, ng·m^{-3}	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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Table 3. Pearson correlation coefficients matrix of the organic and inorganic compounds within the free troposphere (PM$_T$). ~~Highly~~ Statistically [Ed#C1] significant correlations (p-value < 0.01) are highlighted. BBE was excluded in this analysis.

	Levoglucosan	Dicarboxylic acids	Saccharides	n-Alkanes	Hopanes	PAHs	SOA PIN	SOA ISO	Dust	Sea Salt	OM	EC	NO$_3^-$	NH$_4^+$	nss-SO$_4^=$	ss-SO$_4^=$
Levoglucosan	1.0															
Dicarboxylic acids	0.0	1.0														
Saccharides	0.0	0.4	1.0													
n-Alkanes	0.1	0.5	**0.5**	1.0												
Hopanes	0.0	**0.6**	**0.7**	**0.8**	1.0											
PAHs	0.3	0.3	0.2	0.3	0.3	1.0										
SOA PIN	-0.1	0.2	0.3	**0.6**	0.5	0.1	1.0									
SOA ISO	0.2	0.3	0.2	0.3	0.3	**0.6**	0.4	1.0								
Dust	0.0	**0.7**	**0.6**	**0.7**	**0.9**	0.2	**0.7**	0.2	1.0							
Sea Salt	**0.6**	-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	**0.7**	**0.8**	0.2	**0.8**	0.4	**0.9**	0.0	1.0					
EC	0.2	0.1	-0.1	-0.1	-0.2	**0.7**	-0.2	0.3	-0.3	0.3	-0.2	1.0				
NO$_3^-$	0.0	0.4	**0.7**	**0.8**	**0.8**	0.5	**0.6**	0.4	**0.8**	-0.1	**0.8**	0.0	1.0			
NH$_4^+$	0.1	0.1	0.2	0.2	0.3	**0.6**	-0.1	0.3	0.2	0.0	0.2	0.5	0.5	1.0		
nss-SO$_4^=$	0.1	0.2	**0.6**	0.5	**0.6**	0.5	0.5	**0.6**	0.5	0.1	**0.6**	0.1	**0.8**	**0.7**	1.0	
ss-SO$_4^=$	**0.6**	0.0	-0.2	0.0	-0.2	0.4	0.1	0.2	-0.2	**1.0**	0.0	0.3	0.0	0.0	0.0	1.0

OM: organic matter; **EC**: elemental carbon; **nss-SO$_4^=$**: non sea salt sulphate; **ss-SO$_4^=$**: sea salt sulphate.
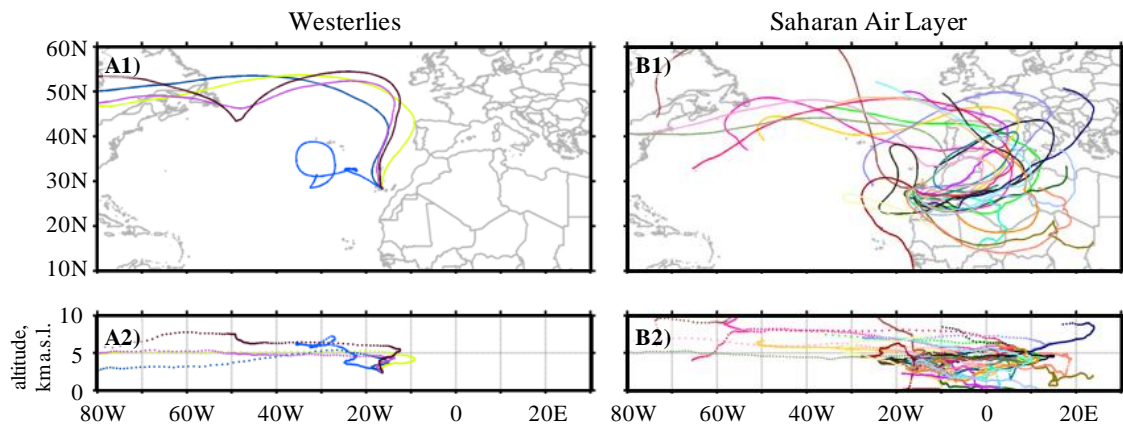
Figure 1: Ten-day back-trajectories based on HYSPLIT model for the samples collected within the **(A)** Westerlies (26 Aug–30 Aug) and (**B**) the Saharan Air Layer (01 Aug–25 Aug and 31 Aug–01 Sep); the dates refer to the day of completion of the sampling.
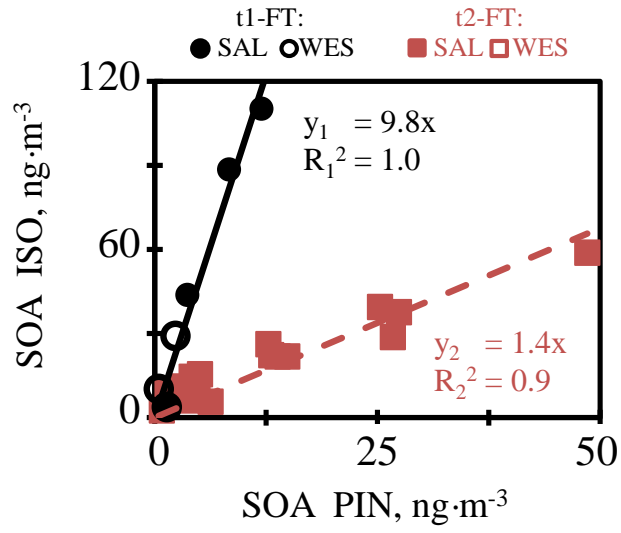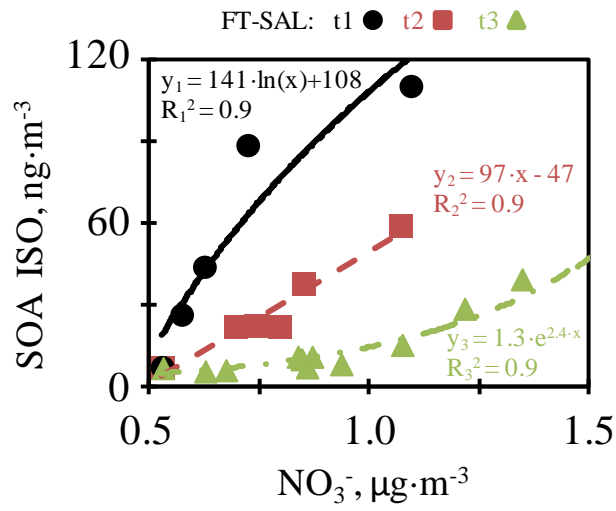
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Figure 2: Scatter plot between total concentration of SOA ISO and total concentration of SOA PIN within the FT (PM$_T$ collected during the night). Two tendencies can be distinguished: tendency-1 (t1; circles) and tendency-2 (t2; squares). Filled markers correspond to measurements within the SAL and open markers to measurements within the WES.

Figure 3: Scatter plot between SOA ISO and nitrate within the SAL under FT conditions (FT-PM_T 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.
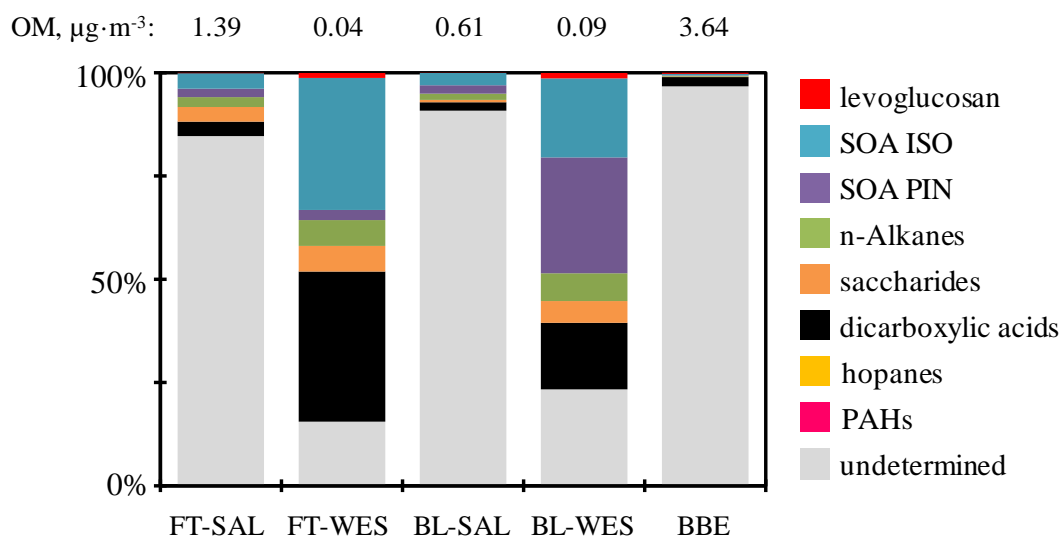
Figure 4: Contribution of the eight analysed organic groups to the Izaña OM composition within the FT and the BL under the SAL (FT-SAL and BL-SAL) and the WES (FT-WES, BL-WES, BBE). Average total OM for each air mass is at ~~on~~ top. FT-PM_T samples were collected during the night (22–6 GMT) and BL-$PM_{2.5}$ samples were collected during the day (10–16 GMT).
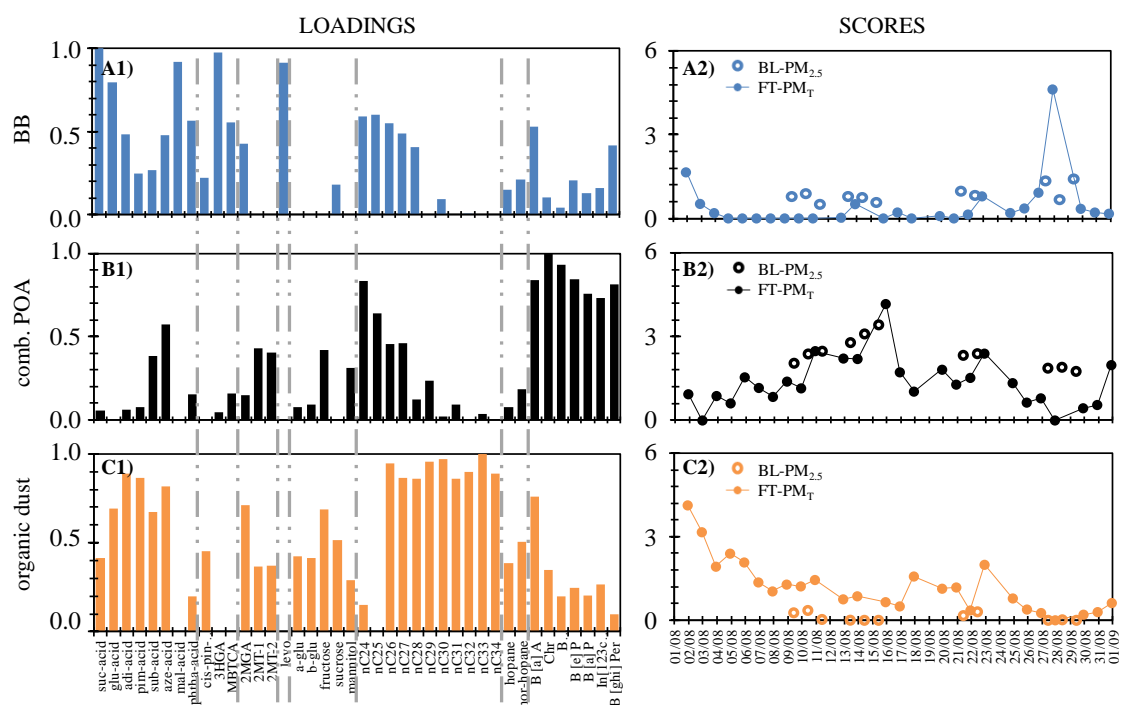
Figure 5: FT-PM$_T$ (night) and BL-PM$_{2.5}$ (day) loadings and scores of the three components from MCR-ALS resolved profiles. Filled markers correspond to FT-PM$_T$ and open markers to BL-PM$_{2.5}$. Grey lines separate the compounds belonging to the different organic groups: dicarboxylic acids, SOA PIN, SOA ISO, levoglucosan, saccharides, n-alkanes, hopanes and PAHs (from left to right).
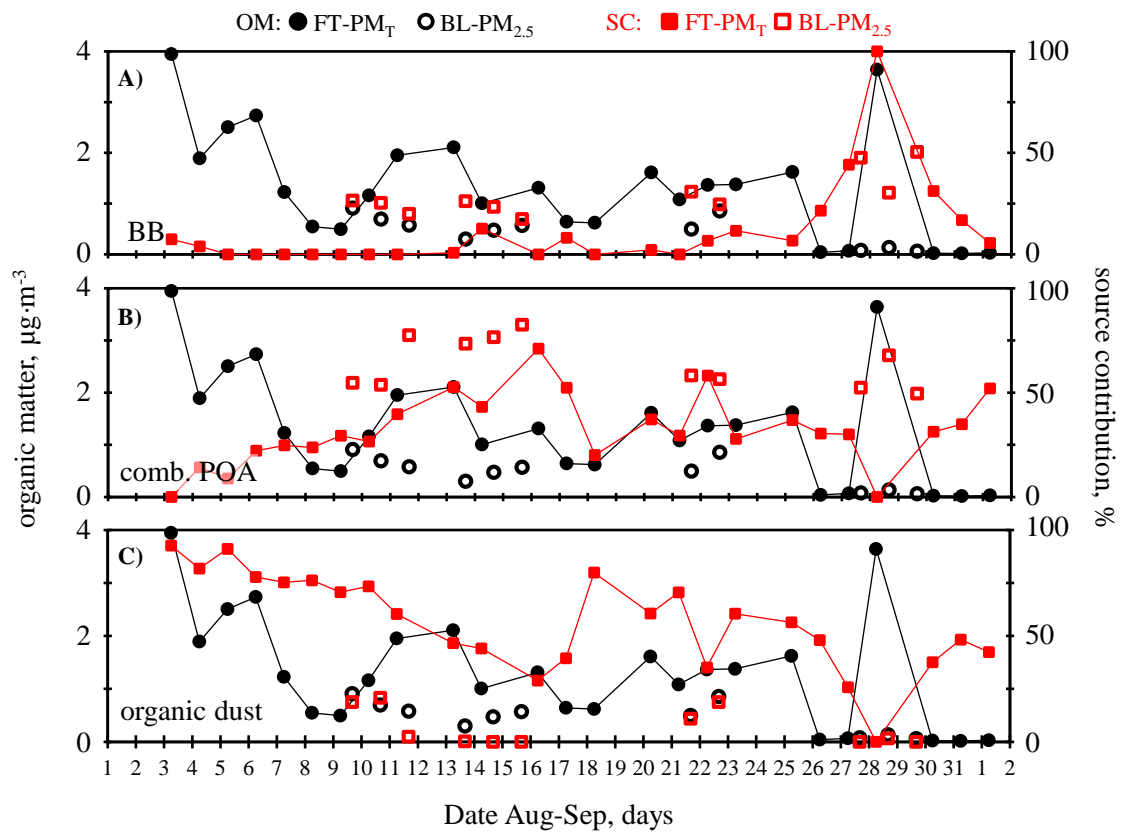
Figure 6: Time series of the total organic matter (OM; circle markers) and the source contribution (SC; square markers) to the ~~determined~~ organic matter determined [Ed#C1] for the FT-PM$_T$ (filled markets) and the BL-PM$_{2.5}$ samples (open markers). Sources: (**A**) biomass burning (BB), (**B**) combustion (comb.) POA and (**C**) organic dust.
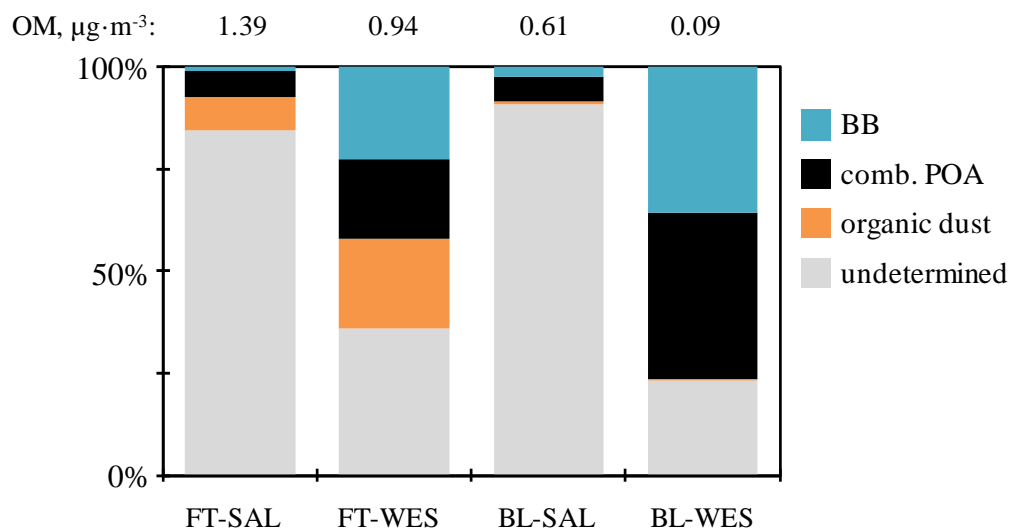
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Figure 7: Contribution of the identified organic aerosol sources to the total organic matter within the FT and the BL under the SAL (FT-SAL and BL-SAL) and the WES (FT-WES, BL-WES, BBE). Average total OM for each air mass is at ~~on~~ top. FT-PM$_T$ samples were collected during the night (22–6 GMT) and BL-PM$_{2.5}$ samples were collected during the day (10–16 GMT).

Revised Supplement

Minor changes are highlighted in ==yellow==.

S1. Organic compounds

5   Organic species were identified by their GC retention time and characteristic ions in the ~~MS~~ mass spectrometer. Retention time was compared to those of the standards or with literature and NIST library and literature data (Claeys et al., 2007; Kourtchev et al., 2005; Clements and Seinfeld, 2007; Medeiros and Simoneit 2007; Fontal et al. 2015). The organic species analyzed and their characteristic ions are: succinic acid (m/z 247), glutaric acid (m/z 261), adipic acid (m/z 275), pimelic acid (m/z 289), suberic acid

10   (m/z 303), azelaic acid (m/z 317), malic acid (m/z 233), phthalic acid (m/z 295), cis-pinonic acid (m/z 171), 3-hydroxyglutaric acid (3-HGA; m/z 349), 3- methyl-1,2,3-butanetricarboxylic acid (MBTCA; m/z 405), 2-methylglyceric acid (2-MGA; m/z 219), 2-methylthreitol (2-MT1) and 2-methylerythritol (2-MT2; m/z 219); levoglucosan (m/z 204), α- and β-glucose (m/z 204), mannitol (m/z 319) and sucrose (m/z 361); benz[a]anthracene (m/z 228), chrysene (m/z 228), benzo[b+k]fluoranthene (m/z 252),

15   benzo[e]pyrene (m/z 252), benzo[a]pyrene (m/z 252), indeno[1,2,3-cd]pyrene (m/z 276), benzo[ghi]perylene (m/z 276); 17(H)α,21(H)β-29-Norhopane and 17(H)α,21(H)β-hopane (m/z 191); n-alkanes (m/z 71). The limits of quantification (LOQ) in the applied methodologies were 0.02 ng·m^{-3} for the saccharides, 0.01 ng·m^{-3} for the acids and 0.002 ng·m^{-3} for PAHs, hopanes and n-alkanes. The concentrations were corrected by the recoveries of the above mentioned surrogates. The recoveries of the

20   surrogate standards were higher than 60%. The field blanks concentrations of the reported compounds were between 1 and 30% of the sample concentration. Organic compounds, such as carboxylic acids are not reported due to higher blank concentrations. No corrections for the blank concentrations were applied on the sample concentrations.

25   S2. Sources of organic aerosol

Multivariate Curve Resolution (MCR-ALS) was applied to identify potential contribution sources to the OM. In order to evaluate possible changes in the sources profiles whether the method was applied to the free troposphere (FT-PM$_T$) and boundary layer (BL-PM$_{2.5}$) samples separately, we performed MCR-ALS only for the FT-PM$_T$ samples. Figure S1 shows the sources profiles, which did not vary greatly from

30   those obtain when ~~having~~ taking both sample sets (FT-PM$_T$ and BL-PM$_{2.5}$) into account. The main differences are seen in the n-alkanes and saccharides distributions, between combustion POA (fig. S1B1) and organic dust (fig. S1C1), as combustion POA is not affected by BL-PM$_{2.5}$.
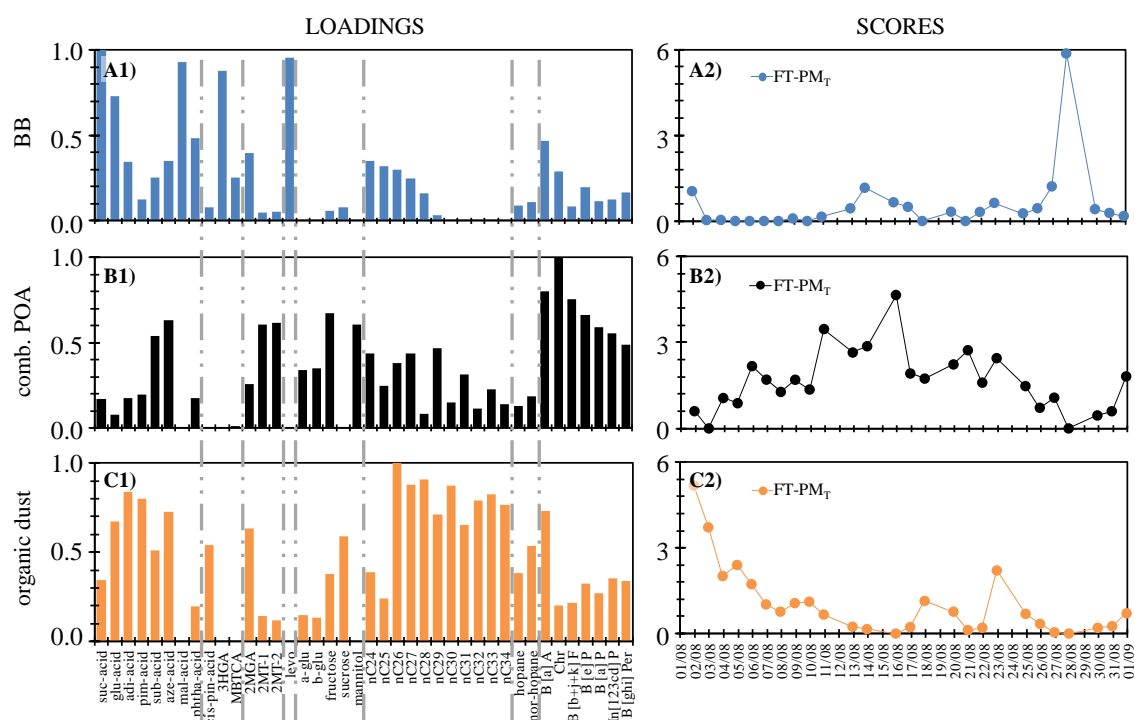
Figure S1. PM$_T$ samples loadings and scores of the three components from MCR-ALS resolved profiles. Grey lines separate the compounds belonging to the different organic groups: dicarboxylic acids, SOA PIN, SOA ISO, levoglucosan, saccharides, n-alkanes, hopanes and PAHs (from left to right). FT-PM$_T$ samples were collected during the night (22 to 06 GMT). **BB**: biomass burning; **comb. POA**: Primary organic aerosol from combustion.

S3. Evaluation of the MCR-ALS results

Scores obtained from the Multivariate Curve Resolution (MCR-ALS) applying non-negativity constraints, for both FT-PM$_T$ and BL-PM$_{2.5}$, were correlated with dust, organic matter (OM) and elemental carbon (EC). The correlation was done for all-samples, FT-samples and BL-samples, to verify there was a statistical relationship between the selected sources and the above mentioned variables. Overall, the correlation of the components sum with the total OM (r-All = 0.44, p < 0.01; table 1S) and EC (r-All = 0.51, p < 0.01; table 1S) concentrations is significant for all samples. The correlation holds for the FT (OM r-FT = 0.63 and EC r-FT = 0.49, p < 0.05; table 1S) and BL (EC r-BL = 0.67, p < 0.05; table S1) separately, revealing that the identified sources might describe, not only the ~~determined~~ fraction determined of the OM but also the total OM.

Table S1. Pearson correlation coefficients of the components scores and organic matter, elemental carbon and dust. Statistically significant correlations (p-value < 0.05) are highlighted. FT-PM$_T$ samples were collected during the night (22 to 06 GMT) and BL-PM$_{2.5}$ samples were collected during the day (10 to 16 GMT).

	BB	Com. POA	Organic dust	$\sum$SS
All				
dust	0.05	-0.27	**0.84**	**0.53**
OM	0.20	-0.28	**0.64**	**0.44**
EC	**0.57**	**0.36**	-0.38	**0.51**
FT-PM$_T$				
dust	0.14	-0.13	**0.84**	**0.63**
OM	**0.40**	-0.12	**0.55**	**0.63**
EC	**0.65**	0.24	-0.38	**0.49**
BL-PM$_{2.5}$				
dust	-0.08	-0.08	**0.73**	0.10
OM	-0.56	0.36	**0.75**	0.33
EC	-0.10	**0.71**	-0.50	**0.67**

BB: biomass burning; **comb. POA**: Primary organic aerosol from combustion; $\sum$ **SS**: sum scores of the three components; **OM**: organic matter; **EC**: elemental carbon;

S4. Sources contribution

To evaluate the contribution of each source to the ~~determined~~ OM determined, a multilinear regression analysis (r^2= 0.84) was performed with the scores - obtained in the MCR-ALS - as independent variables and the sum of the organic tracer compounds as the dependent variable. Average source contribution to the ~~determined~~ OM determined was calculated for the four studied air masses. The biomass burning event is enclosed in the free troposphere under the Westerlies influence (FT-WES).

5

Table S2. Contribution of the three identified sources to the OM fraction for the studied air masses: free troposphere under the SAL (FT-SAL) and WES (FT-WES) influence and BL under the SAL (BL-SAL) and the WES (BL-WES) influence. FT-PM$_T$ samples were collected during the night (22 to 06 GMT) and BL-PM$_{2.5}$ samples were collected during the day (10 to 16 GMT).

	BB, %	Com. POA, %	Organic dust, %	Undetermined, %
FT-SAL	1.1	6.1	8.2	84.6
FT-WES	22.5	19.4	22.2	35.8
BL-SAL	2.3	6.1	0.8	90.8
BL-WES	35.7	40.8	0.2	23.4

BB: biomass burning; **comb. POA**: Primary organic aerosol from combustion.

Supplement references

Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M. and Claeys, M.: Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland, Atmos. Chem. Phys. Discuss., 5(3), 2947–2971, doi:10.5194/acpd-5-2947-2005, 2005.

Clements, A. L. and Seinfeld, J. H.: Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States, Atmos. Environ., 41(9), 1825–1830, doi:10.1016/j.atmosenv.2006.10.056, 2007.