

Author Response

We would like to thank both anonymous reviewers as well as the editor for their comments. All these comments have been taken into consideration. Below, in blue and italics, a point by point response.

REVIEWER #2

The revised manuscript is of much better quality, and the authors should be acknowledged for that. They have done an accurate revision work, following the recommendations of all reviewers. I am therefore favorable to publication.

Response: We would like to thank the Reviewer for his/her comments in every step of the peer review procedure. We feel that this constructive review provided significant aid in the improvement of the manuscript. The technical corrections proposed have been taken into account.

Going through the manuscript, I noted few technical corrections:

- p2 l49 : "ED" is not defined

Response: "ED" has now been changed to "emergency department"

- p2 l52 : replace "particle" by "particulate"

Response: Amended.

- p3 l85 : replace "emerge" by "has become"

Response: Amended.

- p6 l174 : delete space character in "capt ure"

Response: Amended.

- p6 l185 : PSI is not defined

Response: PSI is now defined.

REVIEWER #3

The manuscript of Stavroulas et al. has been improved significantly after the revision. The interpretation of PMF factors is more solid now and all the details on the PMF analysis have been given in the supplemental material. I think that this manuscript merits publication after the minor comments listed below are taken into consideration.

Response: We would like to thank the Reviewer for the detailed and thorough comments, which undoubtedly acted as a valuable guide towards the improvement of this manuscript.

Minor comments:

1. Manuscript needs careful proofreading, please double check figure numbers and abbreviations (they are spelled out several times or zero times at the moment)

Response: The manuscript has gone through a thorough examination and proofreading. We believe all the mentioned accidental mistakes have been corrected in the revised version.

2. Abstract, “These results, based on the combined contribution of BBOA and SV-OOA, highlight the rising importance of biomass burning in urban environments during wintertime, as revealed through this characteristic example of Athens, Greece, where the economic recessions led to an abrupt shift to biomass burning for heating purposes in winter.” This statement should be removed or toned down as this topic (increase in BB in last years) is not discussed in the manuscript anymore

Response: The statement is toned down in the revised version of the manuscript.

3. Introduction is fragmented (short paragraphs on different topics), consider modifying

Response: The introduction has been modified in the revised version taking into account the Reviewer’s comment

4. Introduction; “to study the year-to-year changes of aerosol sources during winter time, with special emphasis on wood burning”. This should be removed or modified as wood burning has not been investigated more extensively than other factors in the manuscript

Response: This sentence has been modified in the revised version of the manuscript.

5. Page 18, line 550-551; COA concentration rising from (from?) 30% to 60% of the daily average during lunch hours (12:-15:00 LT). Please check these numbers, based on figures 5 and 6 these numbers can’t be that large

Response: The average daily concentration of COA during wintertime is $0.98 \mu\text{g m}^{-3}$. When calculating the average diurnal variability, we find that at 12:00 that the concentration is $0.3 \mu\text{g m}^{-3}$, while at 15:00 it rises to $0.6 \mu\text{g m}^{-3}$. These numbers correspond to the 30% and 60% respectively of the average daily concentration and have been added to the manuscript. Unfortunately, the steep rise in COA concentrations during night-time, creates a scale issue in the Figures.

Editor’s comments on the revised version of ms. acp-2018-356 by I. Stavroulas et al., entitled “Identification of sources and processes that control submicron organic aerosol content at an urban Mediterranean environment using high temporal resolution chemical composition measurements”

François Dulac, 16 Nov. 2018

I thank you for revision of your manuscript submitted to the ChArMEx special issue in ACP. I agree with both reviewers to acknowledge a great improvement in the manuscript. I invite you to follow their last recommendations for technical corrections and minor revisions. In the following, you will find a list of additional technical corrections. Line numbers refer to the version of the manuscript with visible corrections included in your Authors’ response. Changes are in red.

Response: All the editor's additional technical corrections, reported in the following list, have been incorporated in the revised version of the manuscript. We would like to thank the editor for his thorough reading of the manuscript.

- Abstract, line 30: round up to "22%".
- Introduction, line 86: not clear to me what you mean by "precursor emissions emerge altered".
- Instruments and Methods, line 126: add a comma after "Practically".
- Instruments and Methods, line 135: Budisulistiorini et al. (2014) is absent from the reference list; do you refer to doi:10.5194/amt-7-1929-2014?
- Instruments and Methods, line 181: "were used".
- Instruments and Methods, line 188: "were also calculated".
- Instruments and Methods, line 192: "to capture".
- Source Apportionment, line 207: "of factor profiles".
- Source Apportionment, line 225: I think you should explain what is α here, by reintroducing the sentence that has been erased from lines 235-236 ("The α value ranges between 0 and 1 and is a measure of" [...]).
- Source Apportionment, line 226: "Initial" or "Initially,".
- Choosing the optimal configuration, line 274: "On the other hand, constraining two factors during the warm period, namely".
- Choosing the optimal configuration, line 276: "previous".
- Choosing the optimal configuration, line 277: "during the warm periods".
- Chemical composition and characteristics, line 352: "while maxima".
- Chemical composition and characteristics, line 354: do you mean "(up to around 100"?
- Diurnal variability, line 403: "rush hours".
- Diurnal variability, line 423: "the organics variation also follows".
- Source apportionment of organic aerosol/Warm period, l.466: "solution stems from a two factor constrained run".
- Source apportionment of organic aerosol/Warm period, l.482: "can be attributed".
- Source apportionment of organic aerosol/Warm period, l.509: remove the comma before "(2005)".
- Source apportionment of organic aerosol/Warm period, l.517: "provide some".
- Source apportionment of organic aerosol/Warm period, l.551: "when concentrations".
- Source apportionment of organic aerosol/Warm period, l.559: "night-time".
- Source apportionment of organic aerosol/Warm period, lines 575-576: "and thus exhibits".
- Source apportionment of organic aerosol/Cold period, l.578: "solution stems from a three factor constrained run".

- Source apportionment of organic aerosol/Cold period, lines 607-608: “compared to BBOA in Bologna, Athens and Patras”; provide references.
- Source apportionment of organic aerosol/Cold period, l.621: by “extended area”, do you rather mean “region”?
- Source apportionment of organic aerosol/Cold period, l.622: “The identification of BBOA [...] as biomass burning tracers. Indeed, BBOA exhibits excellent correlation”.
- Source apportionment of organic aerosol/Cold period, l.625: “and as reported”.
- Source apportionment of organic aerosol/Cold period, l.630: do you mean “and exhibits” referring to BBOA, or “which exhibits” referring to BC_{wb}?
- Source apportionment of organic aerosol/Cold period, lines 636-637: decapitalize “northern and eastern Europe”.
- Source apportionment of organic aerosol/Cold period, l.643: remove “who “ and make a new sentence after “the basin”: “. They found”.
- Source apportionment of organic aerosol/Cold period, l.646: change “locality”; do you mean “ ”?
- Source apportionment of organic aerosol/Cold period, l.650: add a comma before “respectively”.
- Source apportionment of organic aerosol/Cold period, l.661: “product fraction seems” (or “products seem” but pay attention to the following “Its” and “part of it”).
- Source apportionment of organic aerosol/Cold period, l.661: do you mean oxidation of “combustion emissions” rather than “combustion sources”?
- Source apportionment of organic aerosol/Cold period, l.684: “SV-OOA”.
- Source apportionment of organic aerosol/Cold period, l.691: check “1-hr lag the morning traffic.”
- Source apportionment of organic aerosol/Cold period, l.692: do you mean oxidation of “combustion emissions” rather than “combustion source”?
- Summary and conclusions, l.720: “in addition to routine”.
- Summary and conclusions, l.743: “peak values” or “values peaking”.
- Summary and conclusions, l.755: “rush hours”.
- Summary and conclusions, l.773: “contribution to air quality degradation”?
- References, l.802: year at the end.
- References, lines 808-809: “Meteor. Atmos. Phys.”; remove issue number “(1-3)”.
- References, lines 813-814: “Environ. Sci. Technol.”; remove issue number “(15)”; final dot missing.
- References, l.841: “Meas. Tech.”.
- References, lines 885-886: “Atmos. Environ.”.
- References, lines 893-894: “emissions, Proc. Nat. Acad. Sci., 113, 10013”; add missing doi.
- References, lines 920 and 110: remove spare lines.
- References, lines 925-926: decapitalize a number of words in the article title; “Aerosol Sci. Technol.”.
- References, l.1022: “Anal. Chim. Acta”; remove issue number “(1-2)”.
- References, l.1026: “data values, Environmetrics”; remove issue number “(2)”.
- References, lines 1067-1069: decapitalize a number of words in the article title; “Environ. Sci. Technol., 47, 13313-13320”.

- References, l.1108: "Metorol., 124, 61-79" (no italic).
- References, lines 1112-1113: "Atmos. Environ." (dots).
- References, lines 1126-1128: "Fine particulate"; "Environ. Health, 8".
- Figure 6: put the left plot above and enlarge plots as in the previous version.
- Figure 7: put the left plot above and enlarge plots.
- Figure SF.21: if possible, use a different colour or lighter green for the land background in the map, to have more contrast with the green used for SV-OOA; enlarge the text boxes associated to each pie, and the numbers within the pies, or possibly turn the figure by 90° (landscape format) and enlarge.

Sources and processes that control the submicron organic aerosol in an urban Mediterranean environment (Athens) using high temporal resolution chemical composition measurements.

5 Iasonas Stavroulas^{1,2,3}, Aikaterini Bougiatioti^{1,3}, Georgios Grivas³, Despina Paraskevopoulou^{3,4}, Maria Tsagkaraki¹, Pavlos Zampas¹, Eleni Liakakou³, Evangelos Gerasopoulos³ and Nikolaos Mihalopoulos^{1,3}

¹Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, 71003 Crete, Greece

10 ²Energy Environment and Water Research Center, The Cyprus Institute, Nicosia 2121, Cyprus

³Institute for Environmental Research and Sustainable Development, National Observatory of Athens, Lofos Koufou, P. Penteli, 15236, Athens, Greece

⁴[School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A](#)

15 *Correspondence to:* A. Bougiatioti (kbougiatioti@gmail.com) and N. Mihalopoulos (nmihalo@noa.gr)

Abstract. Submicron aerosol chemical composition has been studied during a year-long period (26/07/2016-31/07/2017) and two winter-time intensive campaigns (18/12/2013 – 21/02/2014 and 23/12/2015 – 17/02/2016), at a central site in Athens, Greece, using an Aerosol Chemical Speciation Monitor (ACSM). Concurrent measurements include a Particle-Into-Liquid Sampler (PILS-IC), a Scanning Mobility Particle Sizer (SMPS), an AE-33 Aethalometer and Ion Chromatography analysis on 24 or 12-hour filter samples. The aim of the study was to characterize the seasonal variability of the main submicron aerosol constituents and decipher the sources of organic aerosol (OA). Organics were found to contribute almost half of the submicron mass, with 30-min resolution concentrations during wintertime reaching up to 200 $\mu\text{g m}^{-3}$. During winter (all three campaigns combined), the primary sources contribute about 33% of the organic fraction, comprising of biomass burning (10%), fossil fuel combustion (13%) and cooking (10%), while the remaining 67% is attributed to secondary aerosol. The semi-volatile component of the oxidized organic aerosol (SV-OOA; ~~21.822~~%) was found to be clearly linked to combustion sources and in particular biomass burning, and even a part of the very oxidized, low-volatility component (LV-

20
25
30

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States), Pattern: Clear

Formatted: Font: 12 pt

OOA; 44%) could also be attributed to the oxidation of emissions from these primary combustion sources.

~~These results, based on the combined contribution of biomass burning organic aerosol (BBOA) and SV-OOA, indicate the importance of increased biomass burning in the urban environment of Athens as a result of the recession. These results, based on the combined contribution of BBOA and SV-OOA, highlight the rising importance of biomass burning in urban environments during wintertime, as revealed through this characteristic example of Athens, Greece, where the economic recessions led to an abrupt shift to biomass burning for heating purposes in winter.~~ During summer, when concentrations of fine aerosols are considerably lower, more than 80% of the organic fraction is attributed to secondary aerosol (SV-OOA 31% and LV-OOA 53%). In contrast to winter, SV-OOA appears to result from a well-mixed type of aerosol, linked to fast photochemical processes and the oxidation of primary traffic and biogenic emissions. Finally, LV-OOA presents a more regional character in summer, owing to the oxidation, within a few days, of organic aerosol.

1. Introduction ~~(This sections has been rewritten)~~

Exposure to fine particulate matter is recognized as a leading cause of premature mortality in Europe. Even if the annual limit value is not exceeded at the majority of regulatory monitoring stations in European countries, health effects are expected to appear at lower levels as well, even below the WHO guideline values (EEA, 2017).

Organic carbon (OC) is among the key PM components which record the strongest associations with short-term mortality (Ito et al., 2011; Klemm et al., 2011). Moreover, short-term exposure to OC has also been linked to respiratory and cardiovascular hospital admissions (Levy et al., 2012; Zanobetti et al., 2009) and pediatric asthma ED-emergency department visits (Strickland et al., 2010).

~~In view of the health significance of fine aerosols, It appears that~~ the characterization of ~~their~~ fine aerosol_chemical properties and ~~their~~ short term variability is critical, especially at the urban background level which is more relevant for the average population exposure. ~~And W~~while the majority of transformations related to ~~partiele-particulate~~ sulfate and nitrate have been well described, there is much progress to be made regarding the understanding of mechanisms that govern—and characteristics of secondary organic aerosol (SOA) formation from precursors products.

Formatted: Indent: First line: 0"

In this direction, ~~the~~ development of the Aerosol Mass Spectrometer (AMS) technology has been an important breakthrough, ~~facilitating~~ ~~in~~ the study of aerosol chemical composition, in high temporal resolution. The ability to ~~further~~ differentiate between primary and secondary components, based on specific markers, introduces an important advancement to organic aerosol (OA) source apportionment (Jimenez et al., 2009), which otherwise mainly relied on a statistical approach using elemental and organic carbon thermal-optical data (EC tracer method and variants; Turpin and Huntzicker, 1995). Capitalizing on abundant spectroscopic data, PMF (Positive Matrix Factorization) source apportionment (SA) is used to discern between various primary sources like traffic and biomass burning, and to categorize secondary aerosols depending on their degree of oxidation.

The ACSM (Aerosol Chemical Speciation Monitor) ~~has been developed as~~ an instrument relying on AMS technology ~~while enabling~~ ~~and is specifically designed for~~ long-term routine monitoring (Ng et al., 2011).

While many ~~relevant~~ studies have focused at regional and rural background areas, ~~long-term~~ ACSM results from large European urban centers are relatively scarce. Canonaco et al. (2013) have performed one year of measurements at an urban background site in the center of Zurich. Aurela et al. (2015) have deployed an ACSM at residential, traffic and highway sites within the Metropolitan Area of Helsinki, for a total of five months. Findings from 10 months of measurements at the North Kensington urban background site in London are reported by Reyes-Villegas et al. (2016).

~~Focusing on~~ ~~Regarding~~ Southern European cities, ~~long-term~~ results ~~are provided~~ ~~have been presented~~ ~~from by~~ the intensive ACSM campaign of Minguillon et al. (2016), at an urban background site in Barcelona. ~~Shorter-term~~ ~~--~~ up to one month - studies ~~in Southern Europe~~ using the AMS have ~~also~~ been conducted in Barcelona (Mohr et al., 2012), Bologna (Gilardoni et al., 2016) and Marseille (El Haddad et al., 2013). In urban Athens, a one-month AMS campaign during winter 2013 has been carried out for chemical composition and OA sources (Florou et al., 2017).

The Greater Athens Area (GAA) appears as a challenging urban milieu for the study of aerosol dynamics, as it combines a large population (about 4 million) and intense primary emissions, with complex topography and meteorology, that lead to high levels of atmospheric pollutants and significantly deteriorate air quality (Kanakidou et al., 2011; Pateraki et al., 2014). ~~However,~~ ~~The~~

characteristics and related processes of secondary organic aerosols, in the long-term, have received up to this point limited attention (Grivas et al., 2012; Paraskevopoulou et al., 2014).

Moreover, since 2013, due to the economic recession in Greece, primary and secondary precursor emissions ~~emerge-have become~~ altered and intensified, as the residents have switched from fossil fuel combustion to uncontrolled burning of wood and biomass for space heating (Saffari et al., 2013, Fourtziou et al., 2017, Gratsea et al., 2017). Existing measurements of aerosol chemical composition in Athens have ~~been~~ mainly ~~been~~ performed using filter sampling (Theodosi et al., 2011, 2018; Paraskevopoulou et al., 2014) and have indicated the ~~dominant role~~importance of fine organic aerosols, ~~in the fine particle fraction~~.

In this study we present, for the first time, long-term results on the sources of submicron organic aerosols in Athens from high temporal resolution ~~measurements~~ during a year-long period, complemented by two intensive winter campaigns. For the collection of data, we deployed an Aerosol Chemical Speciation Monitor (ACSM) and in addition a Particle Into Liquid Sampler (PILS) coupled with ion chromatography, an AE-33 Aethalometer, while also conducting auxiliary aerosol (filter-based) and gas phase measurements.

The main objectives ~~of this~~ are (i) to characterize the submicron aerosol and its variability using high temporal resolution, (ii) to quantify the sources of the organic aerosol and their seasonal variability (via PMF analysis) and (iii) to study the year-to-year changes of aerosol sources during winter time, ~~with special emphasis on wood burning~~.

2. Experimental Methods

2.1 Sampling site and period

The measurements exploited in this study were conducted, at the urban background site of the National Observatory of Athens (NOA) at Thissio (37.97N, 23.72E), as representative of the mean population exposure over Athens metropolitan area (Fourtziou et al., 2017). The site stands at an elevation of 105 m above sea level, in a moderately populated area, where the influence of direct local emissions is limited.

The measurement period lasted for an entire year, from July 2016 to July 2017. Additionally, two intensive winter campaigns took place at the same site, the first from mid-December 2013 to mid-February 2014 and the second from 23 December 2015 to 17 February 2016. These intensive

Formatted: Indent: First line: 0"

campaigns aimed at studying the year-to-year variability and impact of biomass burning on the air quality of the city of Athens during wintertime.

125 2.2 Instruments and Methods

Measurements were performed with an Aerosol Chemical Speciation Monitor (ACSM) by Aerodyne Research Inc. (Ng et al. 2011a), measuring the non-refractory PM₁ (NR-PM₁) chemical composition in near real-time (30-minute temporal resolution). The instrument was sampling through a BGI Inc. SCC 1.197 Sharp Cut Cyclone operated at 3 L min⁻¹, yielding a cut off diameter of approximately 2 μm. Practically, the ACSM operates following a similar principle as the
130 Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000) where ambient air is drawn through a critical orifice to a particle focusing aerodynamic lens; the resulting particle beam is flash-vaporized at 600°C, ionized via electron impact ionization and guided through a quadrupole mass spectrometer. Ammonium nitrate and ammonium sulfate calibrations were performed prior to the ACSM's deployment on the site for the period of 2016 – 2017 and the response factor (RF) for
135 nitrate along to the Relative Ionization Efficiencies (RIEs) for ammonium and sulfate were determined. For the 2013 – 2014 and 2015 – 2016 intensive winter campaigns ammonium nitrate calibration were performed and the RIE for sulfate was determined according to the fitting approach proposed by Budisulistiorini et al. (2014). Values are presented in Table ST_1 of the
140 supplementary material. The detection limits for the ACSM provided by Ng et al. (2011a) are: 0.284 μg m⁻³ for ammonium, 0.148 μg m⁻³ for organics, 0.024 μg m⁻³ for sulfate, 0.012 μg m⁻³ for nitrate, and 0.011 μg m⁻³ for chloride. Mass concentrations are calculated using a chemical composition dependent collection efficiency (Middlebrook et al., 2012) (Fig. SF.1).

Parallel measurements were performed for biomass burning identification, but also for quality
145 control purposes. In this context, a Metrohm ADI 2081 Particle Into Liquid Sampler (PILS; Orsini et al., 2003) coupled with ~~Ion-ion Chromatography chromatography~~ (Dionex ICS-1500) was used, which was sampling ambient air from a different, but adjacent to the ACSM's, PM₁ inlet. Two denuders were placed inline, upstream of the instrument in order to remove gas phase species (e.g. NH₃, HNO₃, SO₂) The ion ~~Chromatograph chromatograph~~ was set to measure cations such as
150 ammonium and potassium at a time resolution of 15 minutes. The resulting concentrations from the ACSM were tested against filter measurements and the concentrations provided by the PILS. For the PILS, the detection limit was calculated at 1 ppb for Na⁺, NH₄⁺ and 2 ppb for K⁺. Non sea

~~salt~~ K^+ (nss- K^+) concentrations were calculated using the Na^+ concentrations and the Na^+/K^+ ratio in seawater as a reference (Sciare et al., 2005). Reported concentrations were blank corrected.

Formatted: Not Superscript/ Subscript

155 Furthermore, filter sampling was also conducted in parallel at the Thissio station. $PM_{2.5}$ aerosol samples ~~were collected~~ on Quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47mm, PALL), ~~were collected~~ on a daily basis, while during the winter periods the sampling frequency was set to 12h. A Dichotomous Partisol Sampler 2025 (Ruprecht & Patashnick) was used at a flow rate of 16.7 L min^{-1} . The samples were analyzed for organic and elemental carbon (OC, EC) with the 160 Thermal-Optical Transmission technique, using a Sunset Laboratories OC/EC Analyzer and applying the EUSAAR-2 protocol (Cavalli et al., 2010). Filters were also analyzed for determination of the main ionic species using ion chromatography as described in Paraskevopoulou et al. (2014).

Two different absorption photometers were monitoring Black Carbon (BC) concentrations. A 165 7-wavelength Magee Scientific AE-42 portable aethalometer was used for the 2013-14 and 2015-16 winter campaigns, providing 5-min resolution measurements. For the year-long period a dual spot, 7-wavelength Magee Scientific AE-33 aethalometer (Drinovec et al., 2015) was used, operating at 1-min resolution ~~and a 5 L min^{-1} flow rate~~. Standard gas analyzers for O_3 (Thermo Electron Co., model: 49i), CO, SO_2 and NO_x (HORIBA, 360 series) and a Scanning Mobility 170 Particle Sizer for PM_1 size distributions (SMPS 3034, TSI Inc.) measuring in the ~~size~~ range of 10.4 – 469.8 nm, were also operating at the sampling site. Wavelength dependent source apportionment of the BC load was performed by the AE-33 Aethalometer, based on the approach of Sandradewi et al. (2008) providing a fossil fuel (BC_{ff}) and a wood combustion (BC_{wb}) component. The default absorption ~~Ångström~~ exponents of 1 for fossil fuel combustion and 2 for pure wood burning, as 175 incorporated in the AE-33 software, ~~was-were~~ used, very close to the respective values of 0.9 and 2, used in a suburban site in Athens (Kalogridis et al., 2017). Meteorological parameters for the study were taken from the actinometric meteorological station of NOA, at Thissio (Kazadzis et al., 2018) (Fig. SF.2). All measurements were averaged to 1-hour intervals in order to synchronize the different data sets.

180 The bivariate wind speed-direction plotting methodology developed by Carslaw and Ropkins (2012) in the Openair R-package, was used for the identification of source areas, as incorporated in the Zefir Igor Pro-based tool (Petit et al., 2017). Four-day back trajectories were ~~also~~ calculated using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT_4) model

(Draxler and Hess, 1998) developed by the [Air Resources Laboratory \(ARL/NOAA\)](#), and 1-degree GDAS (NCEP) meteorological data. Trajectories were computed every 3-h, for air masses arriving at Athens at a height of 1000 m. The selected height is considered suitable to capture transport at a representative upper limit of the boundary layer in Athens (Markou and Kassomenos, 2010). Trajectory clustering was performed using the TrajStat plugin (Sirois and Bottenheim, 1995; Wang et al., 2009) of the MeteoInfo GIS software. The change of the total space variance for decreasing number of clusters was examined as a criterion for cluster number selection. The analysis was performed separately for summer and winter, resulting in 5 clusters for each period.

2.3 Source apportionment of the submicron organic fraction using PMF analysis.

2.3.1 PMF strategy.

Positive Matrix Factorization (PMF; Paatero and Tapper, 1994) was performed on the organic mass spectra obtained by the ACSM. The graphic interface SoFi (Source Finder) version 6.1, developed at [the Paul Scherrer Institute \(PSI\)](#), Zurich (Canonaco et al., 2013) was used. SoFi implements the multilinear engine algorithm ME-2 (Paatero and Hopke, 2003), analyzing the acquired mass spectral timeseries matrix into a linear combination of factor profiles (FP) and time series sub-matrices. Detailed description of the method can be found in the above referenced studies.

For our datasets only $m/z \leq 125$ were used in order to avoid interferences from the naphthalene signal (m/z 127, 128 and 129). Weak signals, with signal-to-noise ratio (S/N) below 0.2 were downweighted by a factor of 10, and those with S/N between 0.2 and 1 were downweighted by a factor of 2 (Ulbrich et al., 2009), using [the](#) built in utilities of the SoFi toolkit.

The input organics and organics' error matrices are derived automatically from the ACSM data analysis software. Several model runs were performed, with and without applying constraints to the derived FPs, using the α value approach (Canonaco et al., 2013; 2015) and following the methodology proposed by Crippa et al. (2014). [The \$\alpha\$ value ranges between 0 and 1 and is a measure of how much the resulting FPs are allowed to vary from the constraints.](#) Initially, unconstrained PMF runs provided insight on the potential number and type of factors. For the following steps, reference factor profiles (RFPs) were introduced in order to constrain primary OA factors, (i) first for the Hydrocarbon – like organic aerosol (HOA), (ii) then for both HOA and BBOA and (iii) finally for HOA, BBOA plus cooking – like organic aerosol (COA). Potential FPs

Formatted: Indent: First line: 0.5"

Formatted: English (United States)

215 for secondary organic aerosols were left unconstrained. A thorough discussion on the choice and
representativeness of the RFPs used can be found in section SI.4.1 of the supplementary material.
Each factor was constrained using different α values within the limits suggested by Crippa et al.
(2014). Next, the model's residuals, for each different model setup, were analyzed in search of
structures that could indicate underestimation or overestimation of the number of separated factors.
220 Stability of factors for different model seeds and correlations of the obtained FP spectra with FPs
reported in similar environments and conditions were examined (Section SI.4.8). Finally,
correlations of the time series of the selected optimal solutions to both gas phase and particulate
independent measurements such as BC, BC_{ff}, BC_{wb}, CO, nss-K⁺, NO₃⁻, SO₄²⁻ and NH₄⁺ was
examined to solidify the selection (Section SI.4.9).

225 The year-long data series was divided into a cold period, from November 2016 to March 2017
and warm period consisting of two sub-periods from August to September 2016 and from May to
July 2017 which were treated separately. According to studies on the climatology of Southern
Greece, the transient period (spring and fall seasons) in Athens doesn't exceed 60 days on average
(Argyriou et al., 2004), covering mainly the months of April and October - which were excluded
230 from the seasonal analysis (Figure SF.1). The two wintertime campaigns of 2013-2014 and 2015-
2016 were also treated separately.

The coefficient of determination r^2 for simple linear regression is used as a metric for all
comparisons, e.g. both affinity of obtained FPs with literature spectra and correlation of the
235 respective factor time series with independent measurements.

2.3.2 Choosing the optimal configuration

240 Presentation of, and discussion on the optimal configuration chosen for the ME-2 model, as
well as results from each step of the implemented strategy described above, followed by a
sensitivity analysis on the α value influence on the obtained factors, can be found in section SI.4.
In brief, for the cold period and the two winter – time intensive campaigns, constraining three
factors, namely HOA, BBOA and COA, and leaving two unconstrained SOA factors, produces a
solution that is characterized by minimal seed variability and model residual structures, while FPs,
time-series, relative contribution and diurnal variability of the factors appear to be environmentally
245 relevant, resembling solutions proposed earlier for the region (Kostenidou et al., 2015; Florou et

Formatted: Indent: First line: 0.5"

al., 2017). Leaving factors unconstrained leads to an unstable model behavior such as diurnal residual structures for key variables (e.g. alkyl fragments like $m/z=55$ or 57) and large FP variability for different model seed runs. Furthermore, deconvolved spectra were missing expected variable contributions in profiles such as BBOA (very low $m/z=41$ and 43 relative contributions), while the COA—like factor was dominated by the CO_2^+ fragment at $m/z=44$. Configuring less or more than five factor solutions, resulted either in an even more pronounced residual diurnal cycle, pointing to poor factor separation or in splitting behavior and resulting factors which were environmentally irrelevant.

On the other hand, ~~for the warm period~~ constraining two factors ~~during the warm period~~, namely HOA and COA, and leaving two unconstrained SOA factors was found to be the solution exhibiting higher relevance while being robust and close to previous knowledge related to OA in the Greater Athens Area. A BBOA factor could not be identified ~~for during~~ the warm periods, since contribution of the marker fragments for biomass burning $m/z=60$ and $m/z=73$ are almost absent in these periods dataset. The COA factor is present in all the studied periods, validated following the approach of Mohr et al. (2012) (Fig. SF.9), and emerged in all the steps (unconstrained and constrained runs) of the implemented strategy (Figures ~~SISF.4-5~~ through ~~SISF.7-8~~ and related discussion in section SI.4).

Formatted: Indent: First line: 0.2"

Formatted: English (United States)

3. Results and Discussion

3.1 Comparison of ACSM data with ancillary measurements

As a first quality control/quality assurance of the ACSM data, the ammonium concentrations are compared to the respective ones derived from the PILS, on an hourly basis for winter 2016-17. A good agreement is found ($r^2=0.80$, slope of 0.82). The sulfate and nitrate concentrations for the winter 2016-2017 period are compared to the respective ones from the ion chromatography analysis ($\text{PM}_{2.5}$ filters), on a daily basis ($r^2=0.75$, slope of 0.81 and $r^2=0.78$, slope of 0.95, respectively). The organics concentrations are compared to the organic carbon concentrations of the $\text{PM}_{2.5}$ filters. An excellent agreement is found ($r^2=0.93$, slope of 1.59) with the slope being close to values reported for urban areas (Petit et al., 2015) and OM:OC calculations from AMS measurements in polluted environments (Saarikoski et al., 2012). The results from the aforementioned comparisons are provided in the Supplementary material (SF.3).

During the intensive winter 2015-2016 campaign, the concentrations of the ACSM components are compared to those determined from the ion chromatography, based on concurrent filter samples collected at the same site, twice per day, (06:00 - 18:00 pm and t 18:00 - 06:00 local time). Results indicate an excellent agreement for sulfate ($r^2=0.88$, slope of 1.0), ammonium ($r^2=0.82$, slope of 1.06), and nitrate ($r^2=0.88$, slope of 1.12) (Figure SF.4). During the intensive winter 2013-2014 campaign, the ammonium concentrations from the ACSM showed significant correlation with the respective ones from the PILS ($r^2=0.80$, slope of 0.81).

Finally, the sum of the ACSM component concentrations plus BC, measured with the 7-wavelength aethalometer, was compared with the mass concentrations determined by the SMPS since February 2017 at Thissio. The density used to convert volume distributions and consequently volume concentrations of spherical particles to mass concentrations, was obtained by applying the methodology of Bougiatioti et al. (2014) assuming that the aerosol PM₁ population was dominated by ammonium sulfate and organics and calculating the respective mass fractions time series based on the ACSM measurements. A density of 1.77 g cm⁻³ was used for ammonium sulfate and 1.3 g cm⁻³ for organics (Florou et al., 2017). The results obtained using a chemical dependent collection efficiency to determine the ACSM derived mass concentrations, are portrayed in Figure 1 and indicate excellent correlation ($r^2=0.89$) a slope of 0.96 and an intercept of 0.60.

3.2 PM₁ average chemical composition and temporal variability

3.2.1 Chemical composition and characteristics

The time series of the main submicron aerosol components measured by the ACSM and the black carbon concentrations are presented in the upper panel of Figure 2 (one complete year period). The period's average cumulative concentration of the ACSM components and BC was 12.4±12.5 µg m⁻³. The highest concentrations were measured during winter (average 16.1±19.5 µg m⁻³) and the lowest during summer (average 10.3±5.6 µg m⁻³). On an annual basis, the most abundant component was organic aerosol, followed by sulfate, contributing 44.5% and 27.8% to the total submicron mass, respectively, while BC contribution was calculated at 15.1%, ammonium at 7.9% and nitrate at 4.3%. In the middle and bottom panels of Figure 2 the respective time series of the main submicron aerosol components during the two intensive 2-month winter campaigns are presented. During winter 2013-14 the average mass concentration of the ACSM components (plus BC concentrations) was 24.5±24.7 µg m⁻³, with organics and BC contributing 55.6 and 14.6%

to the total submicron mass, respectively, followed by sulfate (13.6%). During winter 2015-16 the average concentration was $21.2 \pm 27.4 \mu\text{g m}^{-3}$, with organics and BC contributing 51.6 and 15.2% to the total submicron mass, respectively, followed by sulfate (14.8%), nitrate (6.5%) and ammonium (6.7%). It is clearly deduced that during the last winters, organics constitute half or even more of the total PM_{10} mass, sulfate around 20% and BC around 14%.

The other striking feature is that during wintertime, PM_{10} concentration spikes can reach up to $220 \mu\text{g m}^{-3}$ hourly values, with organics taking up most of the mass. Maxima are recorded during night-time and mostly during meteorological conditions favoring pollutants emission and accumulation, such as low wind speed and low temperature (Fourtziou et al., 2017). There are on average 8 such incidents occurring during each winter (10 in 2013-14, 7 in 2015-16 and 7 in 2016-17), with organic levels being higher than $100 \mu\text{g m}^{-3}$. To our knowledge, such levels are the highest reported for Europe during wintertime and highlight the strong impact of local emissions and especially those related to heating/wood burning (see below), on the levels of organics and consequently PM_{10} . Similar maxima to the ones observed in this study are also reported by Florou et al. (2017, same site from 10 January until 9 February 2013), where organics concentration alone reached up to $125 \mu\text{g m}^{-3}$ and while maxima of $8 \mu\text{g m}^{-3}$ for BC and up to $5 \mu\text{g m}^{-3}$ for nitrate, were recorded. Similarly, wintertime pollution events with increased local character and elevated organics concentrations (up to around $100 \mu\text{g m}^{-3}$, average of $22.6 \mu\text{g m}^{-3}$) have been reported at a regional background site, just outside of Paris, during February 2012 (Petit et al., 2015).

3.2.2 Seasonal variability

The seasonal variability of the main measured species, along with the average PM_{10} concentration ($\mu\text{g m}^{-3}$), as calculated from the ACSM+BC measurements is shown in Figure 3 and the basic statistics are included in Table 1. Organics contribute 46% to the total submicron aerosol mass in summer, followed by sulfate (30.5%), BC (12.6%), ammonium (8.3%) and nitrate (2.6%), while in winter, organics and sulfate contribute 48.1% and 23.2%, respectively, followed by BC (14.7%), ammonium (6.9%) and nitrate (6.3%).

The mass concentrations of organics, nitrate, chloride and BC exhibit a clear annual cycle, with minimum during summer and maximum in winter. This pattern seems to be due to a combination of three simultaneous processes. At first, the additional primary emissions from domestic heating play an important role, as is evident by the largely elevated concentration levels of organics and

BC, which during winter are also emitted by central heating systems and fireplaces. A second reason could be the decreased boundary layer depth during winter. According to Kassomenos et al., 1995 and Alexiou et al., 2018, daytime PBL depth shows a clear annual cycle, with maxima during the warm months (June to September) and exhibiting a two-fold decrease during wintertime. Finally, the effect of temperature to the partitioning of the semi-volatile inorganics and organics can also contribute to the processes leading to the observed pattern. In support of the above, larger standard deviation is found in winter, demonstrating the frequency and magnitude of the observed pollution events due to the increased need for heating purposes (Fourtziou et al., 2017). Independently of the year, it can be seen that winter concentrations of organics, nitrate, chloride and BC are very similar and more than twice the respective ones during the rest of the seasons (Table 1).

Organics concentrations are consistently high during all studied winters (from December to February), while the higher nitrate values, exhibiting similar trend with organics and BC can be attributed to the combination of lower temperatures during night-time along with the increased combustion sources which lead to reduced acidity, resulting at the favorable partitioning of nitrate in the aerosol phase- (Park et al., 2005; Mariani and de MelloMello, 2007; Guo et al., 2016). Ammonium and sulfate exhibit the opposite seasonal cycle, with maximum values in summer and minimum during winter and spring. The higher summer sulfate levels are the result of enhanced photochemistry associated with more intense insolation, combined with less precipitation, favoring the regional transport of polluted air masses (Cusack et al., 2012). The seasonal variation of concentrations is in agreement with that observed in Athens, during prior long-term measurement campaigns based on analysis of daily filter samples (Theodosi et al. 2011, Paraskevopoulou et al., 2014; 2015).

3.2.3 Diurnal variability

When investigating the diurnal patterns of the measured species (Figure 4), it is observed that during wintertime, ammonium and sulfate do not exhibit any significant variability, which is due to the regional character of ammonium sulfate. In order to quantify the extent of this variability we calculated the normalized diurnal pattern by dividing each hourly value with the respective species daily mean concentration. More specifically, sulfate varies by 13% around the mean value while ammonium varies by 40%. On the other hand, organics, BC and nitrate vary significantly

370 during the day (183%, 79.8% and 110% respectively). These species clearly double their
concentrations during night-time, caused by the additional primary emissions. Furthermore, BC
also exhibits a second maximum during early morning hours, which should be attributed to the
primary emissions during the morning traffic rush-hours.

During summer, all concentrations are significantly lower, especially organics (note scale
change) which exhibit a 5-fold decrease of their mean maximum concentration during night-time.

375 Normalizing the diurnal cycles, as mentioned above, reveals a much less pronounced variability
for organics (65%), implying a more regional character, while BC and nitrate exhibit the highest
variability (67.7% and 77% respectively) in accordance to their local nature. The night-time
maxima of BC ~~vanishes~~vanish, while nitrate shows much lower concentrations, due to nitrate
partitioning between gas and aerosol phase, favoring the vaporization of ammonium nitrate. BC
380 still exhibits only one maximum during early morning hours owing to traffic emissions.
Ammonium and sulfate diurnal profile follows expected photochemistry patterns, with peaking
concentrations around 14:00 LT (UTC+02:00), consistent with secondary aerosol formation and
increased vertical mixing with regional aerosol from aloft due to the evolution of the convective
boundary layer which exhibits a bell shaped diurnal structure ranging from a few hundred meters
385 to above one kilometer, with maximum heights during early afternoon (Asimakopoulos et al.,
2004; Tombrou et al., 2007). Finally, organics concentrations are somewhat higher during early
night which could possibly be associated with biogenic/vegetation sources either local or regional
that produce volatile compounds and condense on the particulate phase during night when
temperatures are lower, as is further elaborated during the source apportionment results discussion
390 in section 3.3. Furthermore, the organics variation also follows the late afternoon peak also
observed for ammonium and sulfate. Condensation of the particulate phase could apply for nitrate
as well, which also exhibits higher concentrations during night-time (almost double).

3.3 Source apportionment of organic aerosol

395 **Warm period:** In this period, the selected solution ~~is stems from~~ a two factor constrained run
(HOA using $\alpha = 0.05$ and COA using $\alpha = 0.1$) and consists of four factors: HOA, COA-like, SV-
OOA (~~semi-volatile oxygenated-OA~~) and LV-OOA (~~low-volatility oxygenated-OA~~). As already
mentioned, the two summer periods have been treated separately, but the derived spectra were

400 almost identical (r^2 ranging from 0.98-0.99). The time series of the four identified sources during
summer 2017 is shown in Figure 5 along with their diurnal variability and the respective average
~~daily-hourly~~ contribution. The mass spectra of the selected solution are also provided in the
supplementary material (Fig SF.12). No primary biomass burning aerosol could be identified,
which is justified by the absence of fresh emissions over the city center during the warm period.
405 In the summer periods HOA makes up 4.3% of the total organic fraction, ~~while~~ COA around 10%
on average (7.3 and 11.3% for 2016 and 2017, respectively). In summer 2016 SV-OOA made up
32% and the rest 56% is LV-OOA. In summer 2017, SV-OOA contributes 34.6% to the total
organic fraction while LV-OOA 49.7%. The dominance of secondary influence (SV-OOA & LV-
OOA) is apparent, and accounts for the majority of the organic aerosol. This finding is in
410 accordance with Kostenidou et al. (2015), who reported that 65% of the sampled aerosol during
summer can ~~be~~ attributed to SOA (SV-OOA & LV-OOA), at a suburban site in Athens.

A comparison of the derived FPs with mass spectra in literature is shown in ~~Figures~~ SF.15-
~~through SF.19~~ in the supplement. COA FP exhibits excellent correlation with spectra obtained in
previous studies in the city (Florou et al., 2017; Kostenidou et al., 2015) as well as with spectra
415 obtained in laboratory experiments investigating fresh OA emissions from meat charbroiling
(Kaltsonoudis et al., 2017). When calculating the O:C ratio in COA following the study of
Canagaratna et al. (2015) we find a ratio of 0.19, which is comparable to the value of 0.24 obtained
for COA during summer at a suburban site in Athens (Kostenidou et al., 2015).

The HOA FP exhibits excellent correlation with literature spectra measured in cities located
420 in the Mediterranean environment (Florou et al., 2017; Kostenidou et al., 2015; Gilardoni et al.,
2016) as well as in other environmental and socioeconomical settings (Crippa et al., 2013; Lanz et
al., 2009). According to Figure SF.18, where the affinity of SV-OOA with literature spectra is
assessed, some assumptions could be made regarding the origin of the factor in this study.
Similarity with ~~Isoprene-Epoxydiol organic aerosol (IEPOX – OA)~~, which is the oxidation product
425 of isoprene, could denote a possible link of SV-OOA with biogenic aerosol. This association is
further strengthened by considering the excellent correlation with SOA from biogenic precursors,
such as a- and b-pinene reported by Bahreini et al.; (2005) (r^2 of 0.86 and 0.89, respectively). These
precursors are found to exhibit maxima during- night-time (Harrison et al., 2001; Li et al., 2018;
Hatch et al., 2011) coinciding with the diurnal behavior of SV-OOA in this study. On the other
430 hand, comparison of the derived SV-OOA with SOA from diesel exhaust after 4 h of

photochemical ageing (Sage et al. 2008) yields an r^2 of 0.89. Finally, SV-OOA exhibits the lowest correlations with the mass spectrum from aged organic aerosol emissions from meat charbroiling (Kaltsonoudis et al., 2017). The above mentioned comparisons with literature FPs_s provides some indication that during summer, SV-OOA could be linked to SOA formation from the oxidation of
435 volatile organic compounds (VOCs) from both biogenic and traffic sources and is not linked to the oxidation of primary COA. The low volatility component derived, exhibits excellent correlation to the very oxidized regional OOA found in the area (Bougiatioti et al., 2014) and good correlation with deconvolved OOA factors from previous studies in Athens (Florou et al., 2017; Kostenidou et al., 2015). When calculating the elemental ratios based on the study of Canagaratna et al. (2015),
440 the O:C ratio for LV-OOA is 1.2, which is identical to the value of OOA obtained at Finokalia (Bougiatioti et al. 2014).

In terms of comparison with independent measurements, HOA exhibits good correlation with nitrate ($r^2=0.62$) as well as with BC_{ff} ($r^2=0.63$), while COA, as expected, shows poor correlation with CO ($r^2=0.33$) and nitrate ($r^2=0.36$). SV-OOA is highly correlated with nitrate ($r^2=0.86$),
445 implying common mechanisms in their variability, possibly linked with the partitioning between the gas and particulate phases. The poor correlation with CO ($r^2=0.4$) and BC ($r^2=0.35$) implies that SV-OOA may, to some extent, partially originate from a combustion source. LV-OOA shows good correlation with sulfate ($r^2=0.62$) and ammonium ($r^2=0.63$), consistent with the regional character of this factor. Results from the trajectory cluster analysis (Figure-Fig. SF.21) show that
450 enhanced LV-OOA levels are related to air masses originating from Eastern Europe and the Black Sea region, which have both been identified as the main areas of influence for secondary aerosols that are regionally processed and transported to Athens (Gerasopoulos et al., 2011; Grivas et al., 2018). The regional character of LV-OOA is confirmed by high concentrations associated with increased wind speeds (Figure-Fig. SF.20), especially those that originate from the Northern sector.
455 These results (presented in the Figure-Fig. SF.20 for the full dataset) are contrasted with HOA which displays a much less diffuse spread, due to the intensity of local emissions (mainly traffic in the center of Athens). The distant signal for LV-OOA to the SE direction could possibly be associated to processed aerosol deriving from shipping activity (Petit et al., 2014) in the Aegean Sea.

460 Primary fossil fuel emissions (HOA) are very low during summer exhibiting a fivefold decrease compared to the cold season, as in July and August most of the Athenians leave for their

summer vacations, thus reducing local traffic. Concentrations peak around 7:00 and after 19:00 LT that corresponds to the early morning and evening rush hours in downtown Athens. COA exhibits a slight hump during lunch hours (13:00-15:00 LT) ~~where-when~~ concentrations rise to 465 65% of the daily COA average after the morning minimum of around 50%, also seen in the relative contribution of the factor, while a large night-time peak is present at around 22:00 LT. This late peak, three times higher than the daily average value, is consistent with the late dinner hours and operation of grill houses and restaurants in central Athens. SV-OOA exhibits 40% higher concentrations during night-time compared to the SV-OOA daily average, which apart from 470 boundary layer dynamics may also be attributed to the condensation of semi-volatile compounds, as also implied by the excellent correlation of the factor with nitrate. During daytime, following the sharp decrease from the night time maxima, concentrations remain for some hours (10:00 to 14:00) close to 80% of the daily average before declining further in the afternoon. Finally, LV-OOA exhibits a peak during mid-day, consistent with increased photochemical processes during 475 the peak of solar radiation intensity (~~Figure-Fig.~~ SF.24) that lead to further organic aerosol oxidation.

In summary, during the warm period, the vast majority (more than 80%) of organic aerosol in the area is linked to secondary organic aerosol formation. The semi-volatile product is of mixed origin, linked to quick atmospheric processes, within a few hours, such as photochemistry of 480 primary sources, like biogenic emissions from vegetation, traffic emissions, or probably to a lesser extent regional biomass burning. This last assumption could be supported by the fact that OOA linked to aged BBOA has been reported in regional background sites in Greece (Bougiatioti et al., 2014) and elsewhere (Minguillon et al., 2015), as well as by the fact that during the warm season, air masses which mostly originate from the north, northeastern sector, carry pollutants from the 485 Balkans and around the Black Sea, areas heavily impacted by wildfires from July to September (Sciare et al., 2008) (Fig. SF.21). On the contrary, the low-volatility product is the result of more extensive oxidation of organic aerosol in the area, within a few days, ~~and has, and~~ thus, exhibits a more regional character.

490 **Cold period:** In this period, the selected solution ~~is stems from~~ a three factor constrained run (HOA using $\alpha = 0.1$, COA using $\alpha = 0.2$, BBOA using $\alpha = 0.4$) and consists of five factors: BBOA (~~biomass burning OOA~~), HOA, COA, SV-OOA and LV-OOA. The solution for winter 2016-17 is

presented (Fig. 6), while the respective solutions for winter 2013-14 and 2015-16 are provided in the supplementary material (Fig. SF.13). The time series of the five PMF factors for winter 2016-17 are shown in Figure 6 along with their diurnal variability and the hourly contribution of each factor.

In terms of affinity with RFPs found in the literature, HOA for the cold season in this study is found to exhibit excellent correlations with spectra obtained during the same season in earlier studies in Athens as well as other Greek cities (e.g. Patras) (Florou et al., 2017) and also with HOA factors obtained in different environments, a fact also observed for the warm season obtained spectrum (Fig. SF.15). COA is excellently correlated with COA from Florou et al. (2017) in both Athens and Patras as well as with COA measured by Kaltsonoudis et al. (2017) (Fig. SF.16). When calculating the elemental ratios based on the study of Canagaratna et al. (2015) the O:C ratio for COA is 0.18, which is in accordance with the value of 0.11 derived for COA at the same site by Florou et al. (2017). BBOA exhibits high correlation with factors from Zurich, Paris and Finokalia as summarized in Figure SF.17, while excellent correlation is found when compared to BBOA found in Bologna, earlier studies in Athens and in Patras (Gilardoni et al., 2016; Florou et al., 2017). Once more, the calculated O:C ratio for BBOA is 0.25, which is in accordance with the value of 0.27 derived for BBOA at the same site by Florou et al. (2017). The SV-OOA spectrum exhibits high correlation with the average SV-OOA from Ng et al. (2011b), as well as with the IEPOX-OA from Budisulistiorini et al. (2013) ($r^2=0.80$ in both cases), as isoprene main oxidation products such as methyl vinyl ketone and methacrolein are often used as biomass burning tracers (Santos et al., 2017). Similar correlation is also found with IEPOX-OA and SV-OOA during the winter 2015-16 campaign. The factor exhibits high correlation with SV-OOA from wintertime in Paris (Crippa et al., 2013) and SV-OOA from Hyytiälä (Äijälä et al., 2017) (Fig. SF.18). Finally, LV-OOA records an excellent correlation with the LV-OOA from Crippa et al. (2014), the average LV-OOA from Ng et al. (2011b), LV-OOA from Zurich during winter (Lanz et al., 2008) as well as with the oxidized OOA found in the ~~extended area~~ region (Finokalia) (Bougiatioti et al., 2014) (Fig. SF.19).

~~Since~~ The identification of BBOA is mainly based on the two fragments of m/z 60 and 73, considered as the “fingerprint” fragments of levoglucosan and biomass burning tracers. ~~Indeed~~, BBOA exhibits ~~indeed~~ excellent correlation with these two fragments ($r^2=0.94$ and 0.9, respectively). Nss-K^+ is also proposed as a very good tracer for biomass burning and as ~~is~~ reported

by Fourtziou et al. (2017), it shows a significant correlation with BC coming from wood burning (BC_{wb}), during wintertime in Athens. Consequently, the time series of nss-K⁺ provided by the PILS-IC and m/z 60 are studied together. It appears that during both winters (2013-14 and 2016-17) for which nss-K⁺ data is available, m/z 60 is in very good agreement with nss-K⁺ ($r^2=0.85$) (Figure 7a). Furthermore, BBOA is highly correlated with BC_{wb} ($r^2=0.77$), and exhibits good correlation with nss-K⁺ ($r^2=0.55$) and with CO ($r^2=0.51$). SV-OOA correlates excellently with both wood burning “fingerprint” fragments of m/z 60 and 73 ($r^2=0.99$ for both), highly with BC_{wb} ($r^2=0.90$) and CO ($r^2=0.73$) (Figure 7b) while exhibiting good correlation with nss-K⁺ ($r^2=0.55$), demonstrating the direct link between SV-OOA and primary combustion sources (mainly biomass burning) (Table ST.2). It can be seen in Figure SF.21, that increased concentrations of both BBOA and SV-OOA are linked to air masses originating from Northern-northern and Eastern-eastern Europe. During wintertime, these flow categories are associated with the prevalence of synoptic-scale northern winds and a decline in temperature in the area, leading to the appearance of PM episodes due to local combustion for residential heating (Paschalidou et al., 2015). The input of local sources confined in the Athens basin and in the vicinity of the sampling site is indicated by results of the wind analysis presented in Figure SF.20. Markedly enhanced levels are associated with weak or stagnant conditions. Results are contrasted with those of Grivas et al. (2018)-who at a moderately populated area in the eastern part of the basin. They found that local biomass burning emissions played a less important role than advections from the northern part of the area. In the present case, in the densely populated center of Athens this effect is less apparent. The locality local character of wood burning aerosols in dense residential areas in Athens has also been indicated by Argyropoulos et al. (2017).

Comparison of the HOA time series with BC and CO yields a good correlation ($r^2=0.65$ and $r^2=0.65$ respectively). The factor correlates consistently better with BC_{ff} than with BC_{wb} (e.g. for the 2016 – 2017 r^2 is 0.60 versus 0.52, respectively). Correlation of COA with nss-K⁺ and chloride ($0.3 < r^2 < 0.4$) could indicate a minor influence from emissions derived from biomass burning in meat-cooking (Akagi et al. 2011; Kaltsonoudis et al., 2017). Finally, LV-OOA showed a good correlation with ammonium ($r^2=0.58$), nitrate ($r^2=0.61$), nss- K⁺ ($r^2=0.4$) and m/z 73 ($r^2=0.51$), demonstrating that part of the very oxidized OA during wintertime may also originate from combustion sources as well.

Formatted: English (United States)

Therefore, during the cold period, the organic aerosol in the area linked to secondary organic
555 aerosol formation contributes around 65% to the total organic fraction. In contrast to summer, the
semi-volatile products seems to be linked to the fast oxidation of primary combustion ~~sources~~
~~emissions~~ (e.g. BBOA), which is also reflected on its diurnal variability (Fig. 6) and also on the
strong correlations with external tracers of primary combustion (see Table ST.2). ~~Its a~~Affinity to
560 biomass burning tracers points out that the largest part of ~~it-SV-OOA~~ originates from the fast
oxidation of BBOA. The low-volatility product is, in this case, likely of more local than long-range
transport nature, as also highlighted by the almost two-fold higher values during night-time.

The diurnal cycles of the five factors are shown in Figure 6. HOA, originating from fossil fuel
combustion, exhibits maximum values during night, associated with combustion from central
heating, and presents a secondary peak at 09:00 coinciding with the early morning traffic rush
565 hour. The association of the factor to local primary emissions is also corroborated by the wind
analysis plots (Figure SF.20). The dependence of HOA on wind speed and direction is similar
between cold and warm seasons. The concentration vs. wind speed distribution, displays a wind
dilution effect and is characteristic for traffic-related fine particles in Athens (Chaloulakou et al.,
2003; Kassomenos et al., 2012).

COA has similar winter and summer diurnal profiles with a moderate hump, with
570 concentrations rising ~~form from~~ 30% ($0.3 \mu\text{g m}^{-3}$) to 60% ($0.6 \mu\text{g m}^{-3}$) of the daily average (0.98
 $\mu\text{g m}^{-3}$) during lunch hours (12:00-15:00 LT) and a large night-time peak (approx. 22:00 LT),
partly controlled by the decrease of the planetary boundary layer, but also owing to the expected
increase in the activity of numerous restaurants in the area. A similar diurnal cycle for COA has
575 been reported by Florou et al. (2017). BBOA is characterized by a pronounced diurnal cycle with
peaking values during night-time, associated with the production of this component in the evening
by combustion for heating purposes. SV-OOA exhibits the largest diurnal amplitude, with night-
time values being almost 6-fold higher compared to daytime. A plateau, with concentrations of
SV-OOA being around 50% of the daily average value, following the sharp decline after midnight,
580 is observed during the morning traffic rush hour, before another decline occurs until the daily
minimum is reached at 14:00, demonstrating the possibility of the factor's provenance from the
oxidation of freshly-emitted primary combustion organic aerosol. Finally, LV-OOA also exhibits
2-fold higher values during night-time compared to daytime. It has a, similar to the SV-OOA factor
behavior, with a secondary peak at 10:00, ~~followed exhibiting by~~ a 1 – hour lag ~~after~~ the morning

Formatted: Font: 12 pt, Not Italic, Font color: Auto, English (United States)

Formatted: Font: 12 pt, Not Italic, Font color: Auto

Formatted: Font: 12 pt, Not Italic, Font color: Auto, English (United States)

Formatted: Font: 12 pt, Not Italic, Font color: Auto

585 traffic rush hour, showing once more that part of the low volatility OA may also originate from
the fast oxidation of primary combustion ~~source~~emissions, as also implied by its correlation with
combustion tracers.

Table 2 sums up the contribution of each one of the 5 identified factors during the three studied
winters. Overall, during wintertime BBOA constitutes around 10% of the total organic fraction.
590 Based on the diurnal variability of this factor, its contribution is more pronounced during night-
time, when concentrations are 4-fold or higher than the daytime ones, matching emissions from
fossil fuel combustion represented by the HOA factor incorporating both traffic and heating oil
combustion. Even though an exact mechanism has yet to be established, our assumption that the
larger part of the ~~semi-volatile OOA (SV-OOA)~~ comes from the rapid oxidation of freshly emitted
595 BBOA through processes which involve nitrate radicals and/or heterogeneous reactions, appears
justified via the excellent correlations with biomass burning tracers as well as when-by considering
similar assessments found in other studies (Latham et al., 2013; Cubison et al., 20011; Bougiatioti
et al., 2014). In this manner the overall contribution of biomass burning becomes even more
significant. Given that SV-OOA contributes around 30% to the organic mass, it is evident that
600 during wintertime, biomass burning may contribute almost half of the total organic aerosol, with
this contribution maximizing during night-time. More specifically, for BBOA the lowest
contribution during daytime is 5.5% reaching a maximum of 27.5% during night (Figure 6). The
same applies to SV-OOA with daytime minimum contribution of 13.8% and night-time maximum
of 34.9%. What is also very important is the fact that even though the winter and summer mass
605 spectra of SV-OOA have some similarities ($r^2=0.83$), there are also differences, especially in the
origin of this component, as during winter the majority is linked to the oxidation of primary
combustion sources, while during summer the absence of a significant correlation with BC or nss-
K⁺ implies the presence of different sources, both anthropogenic (but not biomass burning) and
possibly biogenic.

610

4. Summary and conclusions

High temporal-resolution measurements were conducted for an entire year (plus two, two-
month duration, intensive measurement campaigns during wintertime) at an urban background site
in Athens, using an ACSM, a PILS-IC system and an aethalometer, in excess addition to routine
615 pollution measurements. During the 16 – month measurement period, several pollution events with

PM₁ concentrations reaching as high as 220 µg m⁻³ were recorded, all encountered during wintertime nights. In these cases, organics contributed the largest fraction to the submicron particulate mass, with overall contribution during wintertime reaching 50%, followed by sulfate (~20%) and BC (~14%). Within a typical winter day, organics, BC and nitrate double their concentrations during night-time. The increase of the first two can be attributed to emissions linked with domestic heating while nitrate exhibits higher concentrations due to the combined effect of decreased temperature and aerosol acidity, favoring partitioning in the aerosol phase. During summer, organics, BC and nitrate concentrations are significantly lower while sulfate and ammonium levels are increased. Organics are once more the main aerosol constituent contributing by 46%, followed by sulfate (30.5%), ammonium (8.3%) and BC (8%). Within a typical summer day, ammonium and sulfate concentrations peak at about 14:00 LT (UTC+2), consistent with secondary aerosol formation.

Organics, nitrate, chloride and BC exhibited a clear seasonal cycle with maximum during winter and minimum during summer. Sulfate and ammonium exhibited the opposite cycle, as a result of enhanced photochemistry, limited precipitation and higher regional transport.

Based on the source apportionment of the organic aerosol, four factors were identified during summer, namely ~~hydrocarbon-like-OA (HOA)~~, ~~cooking-like-OA (COA)~~, ~~semi-volatile oxygenated-OA (SV-OOA)~~ and ~~low-volatility-OA (LV-OOA)~~, and five factors during winter, the same as in summer with the addition of primary biomass burning emissions (BBOA). During summer, HOA makes up 4.3% of the total organic fraction, COA around 10%, and the rest is linked to secondary organics (SV-OOA and LV-OOA). HOA has peaking values during the morning traffic rush hour, and COA mainly during night-time. SV-OOA exhibits two-fold higher concentrations during night-time while LV-OOA exhibits a peak during mid-day, consistent with photochemical processes. The semi-volatile product is clearly of mixed origin, linked to quick atmospheric processing within a few hours, of VOCs emitted from primary sources like vegetation, traffic and to some limited extent to processed regional biomass burning. The low-volatility product, on the other hand, is the result of more excessive oxidation, in the order of several days, having thus a more regional character.

Combining the results from the three different winter campaigns, HOA accounts for almost 13% of the organic fraction, COA around 10%, BBOA 10%, SV-OOA 22% and LV-OOA 45%. All constituents exhibit significantly higher concentrations during night-time, with HOA being

also linked to primary emissions by heating oil combustion from central heating units and presenting a secondary peak during the morning traffic rush hours. COA has a similar diurnal profile to the one observed during summer. BBOA is also characterized by a pronounced diurnal cycle with peaking values during night from combustion for heating. SV-OOA has almost 6-fold higher concentrations during night, consistent with its link to the oxidation of primary combustion sources, while even LV-OOA exhibits almost 2-fold higher concentrations during night. In contrast to summer, the semi-volatile product during winter has a very clear origin, linked to the fast oxidation of primary combustion sources (HOA and BBOA) with BBOA being the major source, due to the affinity of SV-OOA with biomass burning tracers. Part of the LV-OOA, as well, could originate from the extensive oxidation of the local primary combustion sources, showing that LV-OOA during winter is of more local than regional character.

Concluding, it is clear that organic aerosol constitutes a large fraction of submicron aerosol throughout the year, in the urban environment of Athens. During wintertime, a large part of this OA, as high as 50%, originates from combustion sources for heating purposes, such as biomass burning and diesel oil fueled central heating-, causing significant air quality deterioration. Night-time contribution of BBOA is 7-fold higher than the one during day, while the respective contribution of SV-OOA is increased by a factor of 2.6. Given that during wintertime, fine PM concentrations reach up to $220 \mu\text{g m}^{-3}$, the significance of these sources contribution [to air quality degradation](#) becomes even more striking, demonstrating the necessity for strategic, long-term mitigation actions.

Acknowledgments

I. Stavroulas and N. Mihalopoulos acknowledge support by the State Scholarship Foundation (“IKY Fellowships of Excellence for Postgraduate Studies in Greece -Siemens Programme, 2016-2017”), in the framework of the Hellenic Republic-Siemens Settlement Agreement. The authors would also like to acknowledge support from Francesco Canonaco and Andre Prévôt from PSI, who developed SoFi and provided valuable input related to Positive Matrix Factorization. This study contributes to ChArMEx work package 1 on emissions and sources.

References

- 680 Äijälä, M., Heikkinen, L., Fröhlich, R., Canonaco, F., Prévôt, A. S. H., Junninen, H., Petäjä, T.,
Kulmala, M., Worsnop, D., and Ehn, M.: Resolving anthropogenic aerosol pollution types –
deconvolution and exploratory classification of pollution events, *Atmos. Chem. Phys.*, 17,
3165-3197, doi:10.5194/acp-17-3165-2017, 2017.
- Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J.
D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in
atmospheric models, *Atmos. Chem. Phys.*, 11, 4039-4072, [https://doi.org/10.5194/acp-11-](https://doi.org/10.5194/acp-11-4039-2011)
685 4039-2011, 2011.
- Alexiou, D., Kokkalis, P., Papayannis, A., Rocadenbosch, F., Argyrouli, A., Tsaknakis, G. and
Tzani, C.G.: Planetary boundary layer height variability over athens, greece, based on the
synergy of raman lidar and radiosonde data: Application of the kalman filter and other
techniques (2011-2016), *EPJ Web of Conferences*, - Vol. 176, p. 06007, EDP Sciences, 2018.
- 690 Aurela, M., Saarikoski, S., Niemi, J.V., Canonaco, F., Prevot, A.S.H., Frey, A., Carbone, S.,
Kousa, A., and Hillamo, R.: Chemical and source characterization of submicron particles at
residential and traffic sites in the Helsinki Metropolitan Area, Finland, *Aerosol Air Qual. Res.*,
15, 1213-1226, doi: 10.4209/aaqr.2014.11.0279, 2015.
- Argyriou A, Kassomenos P, Lykoudis S. On the methods for the delimitation of seasons. *Water*
695 *Air Soil Pollut Focus*, ~~2004~~;4:65–74, 2004.
- Argyropoulos, G., Samara, C., Diapouli, E., Eleftheriadis, K., Papaikonomou, K., and Kungolos,
A.: Source apportionment of PM₁₀ and PM_{2.5} in major urban Greek agglomerations using a
hybrid source-receptor modeling process, *Sci. Total Environ.*, 601-602, 906-917,
doi:10.1016/j.scitotenv.2017.05.088, 2017.
- 700 Asimakopoulos, D.N., Helmis, C.G. and Michopoulos, J.: Evaluation of SODAR methods for the
determination of the atmospheric boundary layer mixing height, ~~*Meteorology-Meteor. and*~~
~~*Atmospheric-Atmos. PhysicsPhys.*~~, 85(1-3), 85-92, doi:10.1007/s00703-003-0036-9, 2004.
- Bahreini, R., Keywood, M.D., Ng, N.L., Varutbangkul, V., Gao, S., Flagan, R.C., Seinfeld, J.H.,
Worsnop, D.R. and Jimenez, J.L. Measurements of secondary organic aerosol from oxidation
705 of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass
spectrometer, ~~*Environmental-Environ. science-Sci. & Technology*~~, 39(15), 5674-5688.,
doi:10.1021/es048061a, 2005.

- 710 Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zampas, P., Theodosi, C., Kouvarakis, G.,
Canonaco, F., Prevot, A.S.H., Nenes, A., Pandis, S.N., Mihalopoulos, N.: Processing of
biomass-burning aerosol in the eastern Mediterranean during summertime, *Atmos. Chem.*
Phys. 14 (9), 4793-4807, doi:10.5194/acp-14-4793-2014, 2014.
- Budisulistiorini, S.H., Canagaratna, M.R., Croteau, P.L., Marth, W.J., Baumann, K., Edgerton,
E.S., Shaw, S.L., Knipping, E.M., Worsnop, D.R., Jayne, J.T., Gold, A., and Surratt, J.D.:
715 Real-time continuous characterization of secondary organic aerosol derived from isoprene
epoxydiols in downtown Atlanta, Georgia using the Aerodyne Aerosol Chemical Speciation
Monitor, *Environ. Sci. Technol.*, 47 (11), 5686-5694, doi:10.1021/es400023n, 2013.
- Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Baumann, K., Edgerton, E. S., Kollman,
720 M. S., Ng, N. L., Verma, V., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T.,
Weber, R. J., and Surratt, J. D.: Intercomparison of an Aerosol Chemical Speciation Monitor
(ACSM) with ambient fine aerosol measurements in downtown Atlanta, Georgia, *Atmos.*
Meas. Tech., 7, 1929-1941, <https://doi.org/10.5194/amt-7-1929-2014>, 2014.
- Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt
Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J.
T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol
725 mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem.*
Phys., 15, 253-272, doi:10.5194/acp-15-253-2015, 2015.
- Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: SoFi, an IGOR-
based interface for the efficient use of the generalized multilinear engine (ME-2) for the source
apportionment: ME-2 application to aerosol mass spectrometer data, *Atmos. Meas. Tech.*, 6,
730 3649-3661, doi:10.5194/amt-6-3649-2013, 2013.
- Canonaco, F., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: Seasonal differences in
oxygenated organic aerosol composition: implications for emissions sources and factor
analysis, *Atmos. Chem. Phys.*, 15, 6993-7002, <https://doi.org/10.5194/acp-15-6993-2015>,
2015.
- 735 Carslaw, D.C., and Ropkins, K.: Openair - an R package for air quality data analysis, *Environ.*
Model. Softw., 27-28, 52-61, doi:10.1016/j.envsoft.2011.09.008, 2012.

Formatted: Font: (Default) Times New Roman, 12 pt,
Font color: Auto, English (United States), Pattern: Clear

- Cavalli F., Viana M., Yttri K.E., Genberg J., Putaud J.P.: Toward a standardised thermal–optical protocol for measuring atmospheric organic and elemental carbon: The EUSAAR protocol, *Atmos. Meas. Techniques*, 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.
- 740 Chaloulakou, A., Kassomenos, P., Spyrellis, N., Demokritou, P., and Koutrakis, P.: Measurements of PM₁₀ and PM_{2.5} particle concentrations in Athens, Greece, *Atmos. Environ.*, 37, 649–660, doi: 10.1016/S1352-2310(02)00898-1, 2003.
- Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N.,
745 Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, *Atmos. Chem. Phys.*, 13, 961–981, doi: 10.5194/acp-13-961-2013, 2013.
- Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis,
750 D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived
755 from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, *Atmos. Chem. Phys.*, 14, 6159–6176, doi:10.5194/acp-14-6159-2014, 2014.
- Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A.,
760 and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11, 12049–12064, doi:10.5194/acp-11-12049-2011, 2011.
- Cusack M, Alastuey A, Pérez N, Pey J, Querol X.: Trends of particulate matter (PM_{2.5}) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010), *Atmos. Chem. Phys.*, 12, 8341–8357, doi:10.5194/acp-12-8341-2012, 2012.

- 770 Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M.,
Sciare, J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The "dual-spot" Aethalometer:
an improved measurement of aerosol black carbon with real-time loading compensation,
Atmos. Meas. Tech., 8, 1965-1979, doi: 10.5194/amt-8-1965-2015, 2015.
- EEA, 2017. Air quality in Europe — 2017 report, No 13/2017. European Environment Agency.
ISSN 1725-917.El Haddad, I., D'Anna, B., Temime-Roussel, B., Nicolas, M., Boreave, A.,
Favez, O., Voisin, D., Sciare, J., George, C., Jaffrezo, J.-L., Wortham, H., and Marchand, N.:
Towards a better understanding of the origins, chemical composition and aging of oxygenated
775 organic aerosols: case study of a Mediterranean industrialized environment, Marseille, Atmos.
Chem. Phys., 13, 7875-7894, 2013.
- Florou, K., Papanastasiou, D. K., Pikridas, M., Kaltsonoudis, C., Louvaris, E., Gkatzelis, G. I.,
Patoulas, D., Mihalopoulos, N., and Pandis, S. N.: The contribution of wood burning and other
pollution sources to wintertime organic aerosol levels in two Greek cities, Atmos. Chem. Phys.,
780 17, 3145-3163, doi: 10.5194/acp-17-3145-2017, 2017.
- Fourtziou, L., Liakakou, E., Stavroulas, I., Theodosi, C., Zampas, P., Psiloglou, B., Sciare, J.,
Maggos, T., Bairachtari, K., Bougiatioti, A. and Gerasopoulos, E.: Multi-tracer approach to
characterize domestic wood burning in Athens (Greece) during wintertime. Atmospheric
785 Atmos. Environment Environ., 148, 89-101, doi:10.1016/j.atmosenv.2016.10.011, 2017.
- Gerasopoulos, E., Amiridis, V., Kazadzis, S., Kokkalis, P., Eleftheratos, K., Andreae, M.O.,
Andreae, T.W., El-Askary, H., Zerefos, C.S.: Three-year ground based measurements of
aerosol optical depth over the Eastern Mediterranean: The urban environment of Athens,
Atmos. Chem. Phys. 11, 2145-2159, doi:10.5194/acp-11-2145-2011 2011.
- Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S.,
790 Sandrini, S., Costabile, F., Gobbi, G.P. and Pietrogrande, M.C.: Direct observation of aqueous
secondary organic aerosol from biomass-burning emissions. Proceedings Proc. of the National
Nat. Academy — Acad. of Sciences Sci., 113(36), pp.10013-10018,
doi:10.1073/pnas.1602212113 2016.
- Gratsea, M., Liakakou, E., Mihalopoulos, N., Adamopoulos, A., Tsilibari, E., and Gerasopoulos,
795 E.: The combined effect of reduced fossil fuel consumption and increasing biomass
combustion on Athens' air quality, as inferred from long term CO measurements, Sci. Tot.
Environ., 592, 115-123, doi:10.1016/j.scitotenv.2017.03.045, 2017.

Formatted: Font: (Default) Times New Roman, 12 pt,
English (United States)

Grivas, G., Cheristanidis, S., and Chaloulakou, A.: Elemental and organic carbon in the urban environment of Athens. Seasonal and diurnal variations and estimates of secondary organic carbon, *Sci. Tot. Environ.*, 414, 535-545, doi:10.1016/j.scitotenv.2011.10.058, 2012.

800 Grivas, G., Cheristanidis, S., Chaloulakou, A., Koutrakis, P., and Mihalopoulos, N.: Elemental composition and source apportionment of fine and coarse particles at traffic and urban background locations in Athens, Greece, *Aerosol and Air Qual. Res.*, 18, 1642-1659, doi: 10.4209/aaqr.2017.12.0567, 2018.

805 Guo, H., Sullivan, A.P., Campuzano-Jost, P., Schroder, J.C., Lopez-Kilfiker, F.D., Dibb, J.E., Jimenez, J.L., Thornton, J.A., Brown, S.S., Nenes, A., and Weber, R.J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, *J. Geophys. R. Atmos.*, 121, 10355-10376, doi:10.1002/2016JD025311, 2016.

Harrison, D.; Hunter, M. C.; Lewis, A. C.; Seakins, P. W.; Bonsang, B.; Gros, V.; Kanakidou, M
810 ; Touaty, M.; Kavouras, I.; Mihalopoulos, N.; Stephanou, E.; Alves, C.; Nunes, T.; Pio, C.: Ambient isoprene and monoterpene concentrations in a Greek fir (*Abies Borisii-regis*) forest. Reconciliation with emissions measurements and effects on measured OH concentrations, *Atmos. Environ.*, Vol. 35, Issue 27, p. 4699-4711, 2001.

Hatch, L.E., Jessie M. Creamean, Andrew P. Ault, Jason D. Surratt, Man Nin Chan, John H.
815 Seinfeld, Eric S. Edgerton, Yongxuan Su, and Kimberly A. Prather: Measurements of Isoprene-Derived Organosulfates in Ambient Aerosols by Aerosol Time-of-Flight Mass Spectrometry—Part 2: Temporal Variability and Formation Mechanisms, *Environ. Sci. Technol.*, 45 (20), 8648-8655, doi: 10.1021/es2011836, 2011.

Ito, K., Mathes, R., Ross, Z., Nádas, A., Thurston, G., and Matte, T.: Fine particulate matter
820 constituents associated with cardiovascular hospitalizations and mortality in New York City, *Environ. Health Perspect.*, 119, 467-473, doi:10.1289.ehp.1002667, 2011.

Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an Aerosol Mass Spectrometer for ~~s~~Size and ~~Composition~~composition. Analysis of ~~Submicron—submicron~~ Particlesparticles, *Aerosol Science—and*
825 ~~Technology~~Technol., 33, 49-70, doi:10.1080/027868200410840, 2000.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S.H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. D., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A.,

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

- 830 Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara,
P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J.,
Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y.,
Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell,
L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y.
835 M., Dzepina, K., Kimmel, J.R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M.,
Williams, L. R., Wood, E. C., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution
of organic aerosol in the atmosphere, *Science*, 326, 1525–1529, doi:10.1126/science.1180353,
2009.
- Kalogridis, A.-C., Vratolis, S., Liakakou, E., Gerasopoulos, E., Mihalopoulos, N., and
Eleftheriadis, K.: Assessment of wood burning versus fossil fuel contribution to wintertime
840 black carbon and carbon monoxide concentrations in Athens, Greece, *Atmos. Chem. Phys.*
Discuss., <https://doi.org/10.5194/acp-2017-854>, in review, 2017.
- Kaltsonoudis, C., Kostenidou, E., Louvaris, E., Psichoudaki, M., Tsiligiannis, E., Florou, K.,
Liangou, A., and Pandis, S. N.: Characterization of fresh and aged organic aerosol emissions
from meat charbroiling, *Atmos. Chem. Phys.*, 17, 7143-7155, doi: 10.5194/acp-17-7143-2017,
845 2017.
- Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E.,
Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A.F.,
Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., Von Savigny, C.,
Burrows, J.P., Ladstaetter-Weissenmayer, A., Moubasher, H.: Megacities as hot spots of air
850 pollution in the East Mediterranean, *Atmos. Environ.* 45, 1223-1235, doi:
10.1016/j.atmosenv.2010.11.048, 2011.
- Kassomenos, P., Kotroni, V., and Kallos, G.: Analysis of climatological and air quality
observations from Greater Athens Area, *Atmos. Environ.*, 29, 3671-3688, doi:10.1016/1352-
2310(94)00358-R, 1995.
- 855 Kassomenos, P., Vardoulakis, S., Chaloulakou, A., Grivas, G., Borge, R., and Lumbreras, J:
Levels, sources and seasonality 30 of coarse particles (PM₁₀-PM_{2.5}) in three European capitals
- Implications for particulate pollution control, *Atmos. Environ.*, 54, 337-347,
10.1016/j.atmosenv.2012.02.051, 2012.

- Kazadzis, S., Founda, D., Psiloglou, B. E., Kambezidis, H., Mihalopoulos, N., Sanchez-Lorenzo, A., Meleti, C., Raptis, P. I., Pierros, F., and Nabat, P.: Long-term series and trends in surface solar radiation in Athens, Greece, *Atmos. Chem. Phys.*, 18, 2395-2411, doi: 10.5194/acp-18-2395-2018, 2018.
- Klemm, R.J., Thomas, E.L., and Wyzga, R.E.: The impact of frequency and duration of air quality monitoring: Atlanta, GA, data modeling of air pollution and mortality, *J. Air Waste Manage. Assoc.*, 61, 1281-1291, doi:10.1080/10473289.2011.617648, 2011.
- Kostenidou, E., Florou, K., Kaltsonoudis, C., Tsiflikiotou, M., Vratolis, S., Eleftheriadis, K., and Pandis, S. N.: Sources and chemical characterization of organic aerosol during the summer in the eastern Mediterranean, *Atmos. Chem. Phys.*, 15, 11355-11371, doi:10.5194/acp-15-11355-2015, 2015.
- Lanz, V. A., Alfara, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S., Wehrli, M. N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., and Prevot, A. S. H.: Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra, *Environ. Sci. Technol.*, 42 (1), 214–220, doi:10.1021/es0707207, 2008.
- Latham, T. L., Beyersdorf, A. J., Thornhill, K. L., Winstead, E. L., Cubison, M. J., Hecobian, A., Jimenez, J. L., Weber, R. J., Anderson, B. E., and Nenes, A.: Analysis of CCN activity of Arctic aerosol and Canadian biomass burning during summer 2008, *Atmos. Chem. Phys.*, 13, 2735–2756, doi:10.5194/acp-13-2735-2013, 2013.
- Levy, J.I., Diez, D., Dou, Y., Barr, C.D., and Dominici, F.: A meta-analysis and multisite time-series analysis of the differential toxicity of major fine particulate matter constituents, *Am. J. Epidemiol.*, 175, 1091-1099, doi:10.1093/aje/kwr457, 2012.
- Li, J., Gehui Wang, Can Wu, Cong Cao, Yanqin Ren, Jiayuan Wang, Jin Li, Junji Cao, Limin Zeng & Tong Zhu, 2018. Characterization of isoprene-derived secondary organic aerosol at a rural site in North China Plain with implications for anthropogenic pollution effects, *Scientific Reports*, 8, Article number 535, 2018.
- Mariani, R.L. and de Mello, W.Z.: PM_{2.5-10}, PM_{2.5} and associated water-soluble inorganic species at a coastal urban site in the metropolitan region of Rio de Janeiro, *Atmos. Environ.*, 41, 2887-2892, doi:10.1016/j.atmosenv.2006.12.009, 2007.
- Markou, M.T., and Kassomenos, P.: Cluster analysis of five years of back trajectories arriving in Athens, Greece, *Atmos. Res.*, 98, 438-457, doi:10.1016/j.atmosres.2010.08.006, 2010.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

- 890 Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of
Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer
using Field Data, *Aerosol Sci. Technol.*, 46, 258–271, doi: 10.1080/02786826.2011.620041,
2012.
- Minguillón, M.C., Pérez, N., Marchand, N., Bertrand, A., Temime-Roussel, B., Agrios, K., Szidat,
895 S., Van Drooge, B., Sylvestre, A., Alastuey, A., Reche, C., Ripoll, A., Marco, E., Grimalt, J.O.,
and Querol, X.: Secondary organic aerosol origin in an urban environment: Influence of
biogenic and fuel combustion precursors, *Faraday Discuss.*, 189, 337-359,
doi:10.1039/c5fd00182j, 2016.
- Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C.,
900 Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R.,
Baltensperger, U. and Prévôt, A. S. H.: Identification and quantification of organic aerosol
from cooking and other sources in Barcelona using aerosol mass spectrometer data, *Atmos.*
Chem. Phys., 12, 1649–1665, doi:10.5194/acp-12-1649-2012, 2012. Ng, N. L., Herndon, S. C.,
Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R.,
905 Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for
routine monitoring of the composition and mass concentration of ambient aerosol, *Aerosol Sci.*
Technol., 45, 780–794, doi:10.1080/02786826.2011.560211, 2011a.
- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.:
Real-time methods for estimating organic component mass concentrations from aerosol mass
910 spectrometer data, *Environ. Sci. Technol.*, 45, 910–916, doi:10.1021/es102951k, 2011b.
- Orsini, D.A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K., Weber, R.J.: Refinements to the
particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble
aerosol composition, *Atmos. Environ.* 37 (9-10), 1243-1259, doi:10.1016/S1352-
2310(02)01015-4, 2003.
- 915 Ostro, B., Lipsett, M., Reynolds, P., Goldberg, D., Hertz, A., Garcia, C., Henderson, K.D. and
Bernstein, L.: Long-term exposure to constituents of fine particulate air pollution and
mortality: Results from the California teachers study, *Environ. Health Perspect.*, 118, 363-369,
doi:10.1289/ehp.0901181, 2010.

- 920 Paatero, P. and Hopke, P.K.: Discarding or downweighting high-noise variables in factor analytic models, *Analytica—Anal. Chimica—Chim. Acta*, 490(1-2), 277-289, doi:10.1016/S0003-2670(02)01643-4, 2003.
- Paatero, P. and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 5(2), 111-126, doi:10.1002/env.3170050203, 1994.
- 925 Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E., Theodosi, C., Mihalopoulos, N.: Long-term characterization of organic and elemental carbon in the PM_{2.5} fraction: the case of Athens Greece, *Atmos. Chem. Phys.* 14, 13313-13325, doi:10.5194/acp-14-13313-2014, 2014.
- Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E., and Mihalopoulos, N.: Sources of atmospheric aerosol from long-term measurements (5years) of chemical composition in 930 Athens, Greece, *Sci. Tot. Environ.*, 527-528, 165-178, doi:10.1016/j.scitotenv.2015.04.022, 2015.
- Park, S.S., Ondov, J.M., Harrison, D., and Nair, N.P.: Seasonal and short-term variations in particulate atmospheric nitrate in Baltimore, *Atmos. Environ.*, 39, 2011-2020, doi:10.1016/j.atmosenv.2004.12.032, 2005.
- 935 Paschalidou, A.K., Kassomenos, P., Karanikola, P.: Disaggregating the contribution of local dispersion and long-range transport to the high PM₁₀ values measured in a Mediterranean urban environment, *Sci. Total Environ.*, 527-528, 119-125, doi: 10.1016/j.scitotenv.2015.04.094, 2015.
- Pateraki, St, Asimakopoulos, D.N., Bougiatioti, A., Maggos, Th, Vasilakos, Ch, and 940 Mihalopoulos, N.: Assessment of PM_{2.5} and PM₁ chemical profile in a multiple-impacted Mediterranean urban area: origin, sources and meteorological dependence, *Sci. Total Environ.* 479, 210-220, doi:10.1016/j.scitotenv.2014.02.008, 2014.
- Petit, J.-E., Favez, O., Sciare, J., Canonaco, F., Croteau, P., Močnik, G., Jayne, J., Worsnop, D., and Leoz-Garziandia, E.: Submicron aerosol source apportionment of wintertime pollution in 945 Paris, France by double positive matrix factorization (PMF₂) using an aerosol chemical speciation monitor (ACSM) and a multi-wavelength Aethalometer, *Atmos. Chem. Phys.*, 14, 13773-13787, doi:10.5194/acp-14-13773-2014, 2014.
- Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haeffelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical

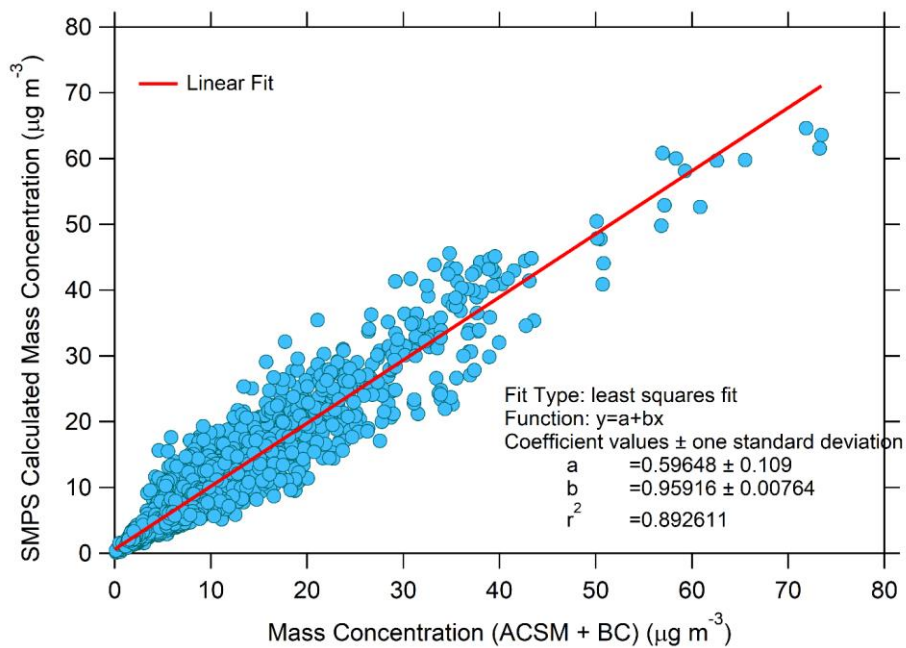
- 950 composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, *Atmos. Chem. Phys.*, 15, 2985-3005, doi: 10.5194/acp-15-2985-2015, 2015.
- Petit, J.-E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: wind and trajectory analyses, *Environ. Model. Soft.*, 88, 183-187, doi: 10.1016/j.envsoft.2016.11.022, 2017.
- 955 Reyes-Villegas, E., Green, D. C., Priestman, M., Canonaco, F., Coe, H., Prévôt, A. S. H. and Allan, J. D.: Organic aerosol source apportionment in London 2013 with ME-2: exploring the solution space with annual and seasonal analysis, *Atmos. Chem. Phys.*, 16, 15545–15559, doi:10.5194/acp-16-15545-2016, 2016.
- 960 Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L., Trimborn, A., Facchini, M. C., Fuzzi, S., Hillamo, R., and Worsnop, D.: Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy, *Atmos. Chem. Phys.*, 12, 8401-8421, doi:10.5194/acp-12-8401-2012, 2012.
- Saffari, A., Daher, N., Samara, C., Voutsas, D., Kouras, A., Manoli, E., Karagiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M.M., Schauer, J.J., and Sioutas, C.: Increased ~~b~~Biomass Burning ~~burning~~ ~~Due~~ ~~due~~ to the ~~Economic~~ ~~economic~~ ~~Crisis~~ ~~crisis~~ in Greece and ~~Its~~ its ~~Adverse~~ ~~adverse~~ ~~Impact~~ ~~impact~~ on ~~Wintertime~~ ~~wintertime~~ ~~Air~~ ~~air~~ ~~Quality~~ ~~quality~~ in Thessaloniki. ~~Environmental-Environ. Science-Sci.& TechnologyTechnol.~~, 47-(23), 13313-13320, doi:10.1021/es403847h, 2013.
- 965
- 970 Sage, A. M., Weitkamp, E. A., Robinson, A. L., and Donahue, N. M.: Evolving mass spectra of the oxidized component of organic aerosol: results from aerosol mass spectrometer analyses of aged diesel emissions, *Atmos. Chem. Phys.*, 8, 1139-1152, doi:10.5194/acp-8-1139-2008, 2008.
- Sandradewi, J., Prevot, A. S. H., Szidat, S., Perron, N., Lanz, V. A., Weingartner, E., and Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, *Environ. Sci. Technol.*, 42, 3316–3323, doi:10.1021/es702253m, 2008.
- 975 Santos, F. C., Longo, K. M., Guenther, A. B., Kim, S., Gu, D., Oram, D. E., Forster, G. L., Lee, J., Hopkins, J. R., Brito, J. F., and Freitas, S. R.: Biomass burning emissions disturbances on

- 980 the isoprene oxidation in a tropical forest, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2017-1083, in review, 2017.
- Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M.O. and Kirchner, U.: Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles, *Int. J. Mass Spectrom.*, 258, 37–49, doi:10.1016/j.ijms.2006.07.008, 2006.
- 985 Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N., Andreae, M.O., Waenhaut, W., and Sarda-Estève, R.: Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign, *Atmos. Chem. Phys.*, 5, 2253-2265, doi:10.5194/acp-5-2253-2005, 2005.
- 990 Sciare, J., Oikonomou, K., Favez, O., Liakakou, E., Markaki, Z., Cachier, H. and Mihalopoulos, N.: Long-term measurements of carbonaceous aerosols in the Eastern Mediterranean: Evidence of long-range transport of biomass burning, *Atmos. Chem. Phys.*, 8, 5551-5563, doi:10.5194/acp-8-5551-2008, 2008.
- Sirois, A., and Bottenheim, J.W.: Use of backward trajectories to interpret the 5-year record of PAN and O₃ ambient air concentrations at Kejimikujik National Park, Nova Scotia, *J. Geophys. Res.*, 100, 2867-2881, doi:10.1029/94JD02951, 1995.
- 995 Strickland, M.J., Darrow, L.A., Klein, M., Flanders, W.D., Sarnat, J.A., Waller, L.A., Sarnat, S.E., Mulholland, J.A., and Tolbert, P.E.: Short-term associations between ambient air pollutants and pediatric asthma emergency department visits, *Am. J. Respir. Crit. Care Med.*, 182, 307-316, doi:10.1164/rccm.200908-1201OC, 2010.
- 1000 Theodosi, C., Grivas, G., Zarnpas, P., Chaloulakou, A., and Mihalopoulos, N.: Mass and chemical composition of size-segregated aerosols (PM₁, PM_{2.5}, PM₁₀) over Athens, Greece: local versus regional sources, *Atmos. Chem. Phys.*, 11, 11895-11911, doi:10.5194/acp-11-11895-2011, 2011.
- 1005 Tombrou, M., Dandou, A., Helmis, C., Akylas, E., Angelopoulos, G., Flocas, H., Assimakopoulos, V. and Soulakellis, N.: Model evaluation of the atmospheric boundary layer and mixed-layer evolution, *Boundary-layer meteorology*, 124(1), 61-79, doi:10.1007/s10546-006-9146-5, 2007.

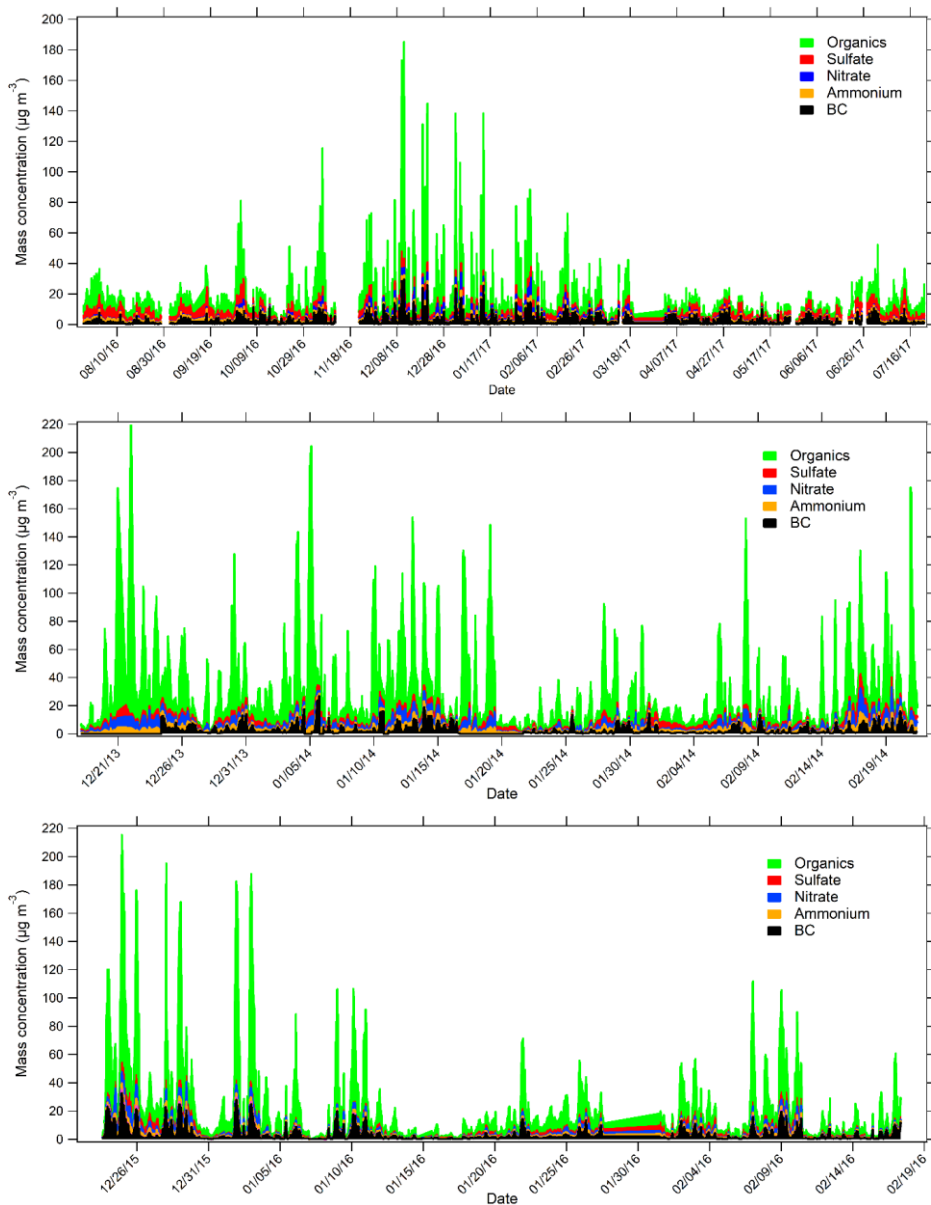
Formatted: Font: Not Italic

- 1010 Turpin, B.J., and Huntzicker, J.J.: Identification of secondary organic aerosol episodes and
quantification of primary and secondary organic aerosol concentrations during SCAQS,
Atmos. Environ., 29, 3527–3544, doi: 10.1016/1352-2310(94)00276-Q, 1995.
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation
of organic components from Positive Matrix Factorization of aerosol mass spectrometric data,
Atmos. Chem. Phys., 9, 2891-2918, doi:10.5194/acp-9-2891-2009, 2009.
- 1015 Ulbrich, I.M., Handschy, A., Lechner, M., and Jimenez, J.L. AMS Spectral Database. URL:
<http://cires.colorado.edu/jimenez-group/AMSsd/>, Database Version 5.2, Last Updated 2013.
- Wang, Y.Q., Zhang, X.Y., Draxler, R.: TrajStat: GIS-based software that uses various trajectory
statistical analysis methods to identify potential sources from long-term air pollution
measurement data, Environ. Mod. Softw., 24, 938–939, doi:10.1016/j.envsoft.2009.01.004,
1020 2009.
- Wilhelm, M., Ghosh, J.K., Su, J., Cockburn, M., Jerrett, M., and Ritz, B.: Traffic-related air toxics
and preterm birth: a population-based case-control study in Los Angeles county, California,
Environ. Health, 10, 89, doi:10.1186/1476-069X-10-89, 2011.
- 1025 Zanobetti, A., Franklin, M., Koutrakis, P., and Schwartz, J.: Fine particulate air pollution and its
components in association with cause-specific emergency admissions, Environ. Health ~~Global~~
~~Access. Sci.~~, 8, 58, doi:10.1186/1476-069X-8-58, 2009.

Field Code Changed



1030 **Figure 1:** Correlation between ACSM+BC vs. SMPS-derived 1 – hour averaged mass concentrations for the 2016-17 measurement period.

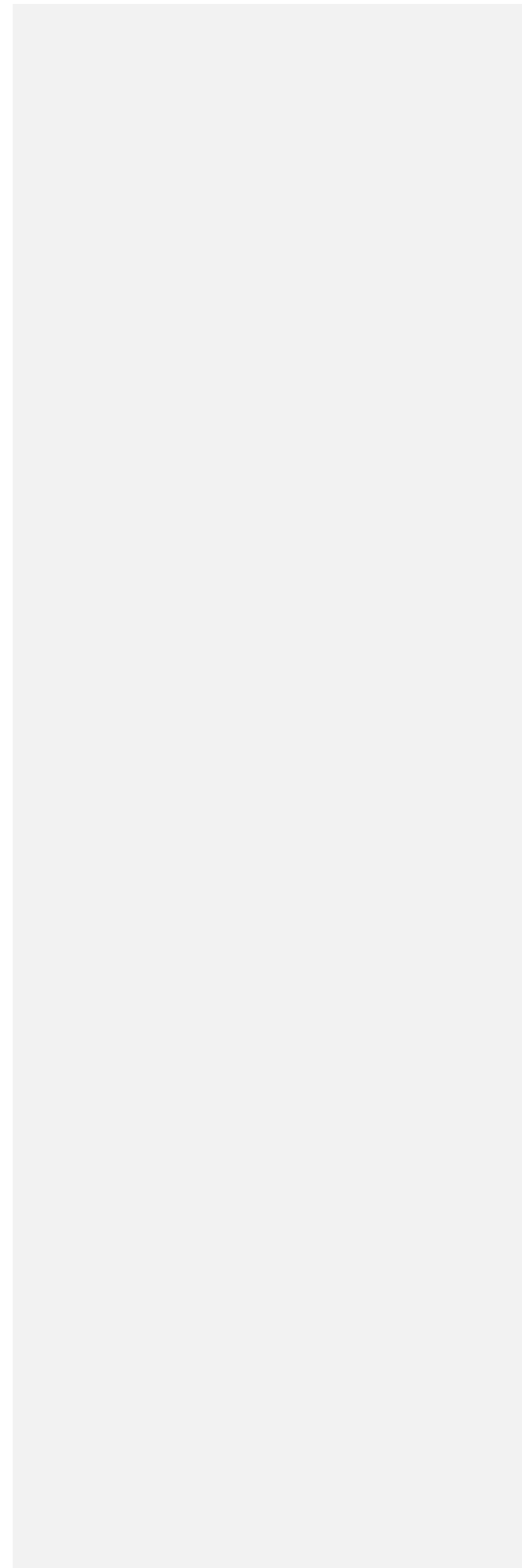


1035

Figure 2: Time series of the main submicron aerosol components. On the top panel the one-year period starting on 26 July 2016 and ending on 31 July 2017, on the middle panel the 2013-2014 winter campaign

(18 December-21 February), and on the bottom panel, the 2015-2016 winter campaign (23 December-17 February).

1040



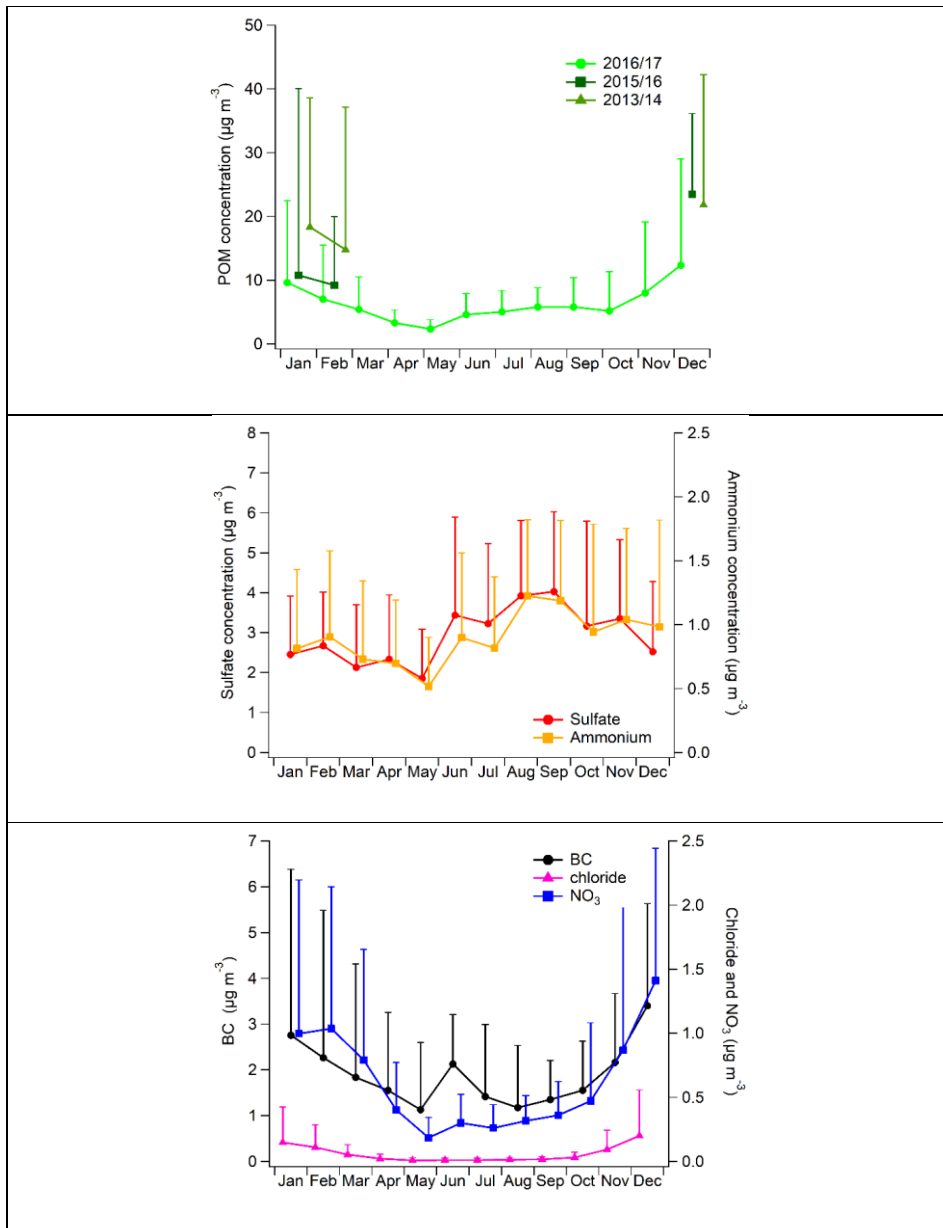
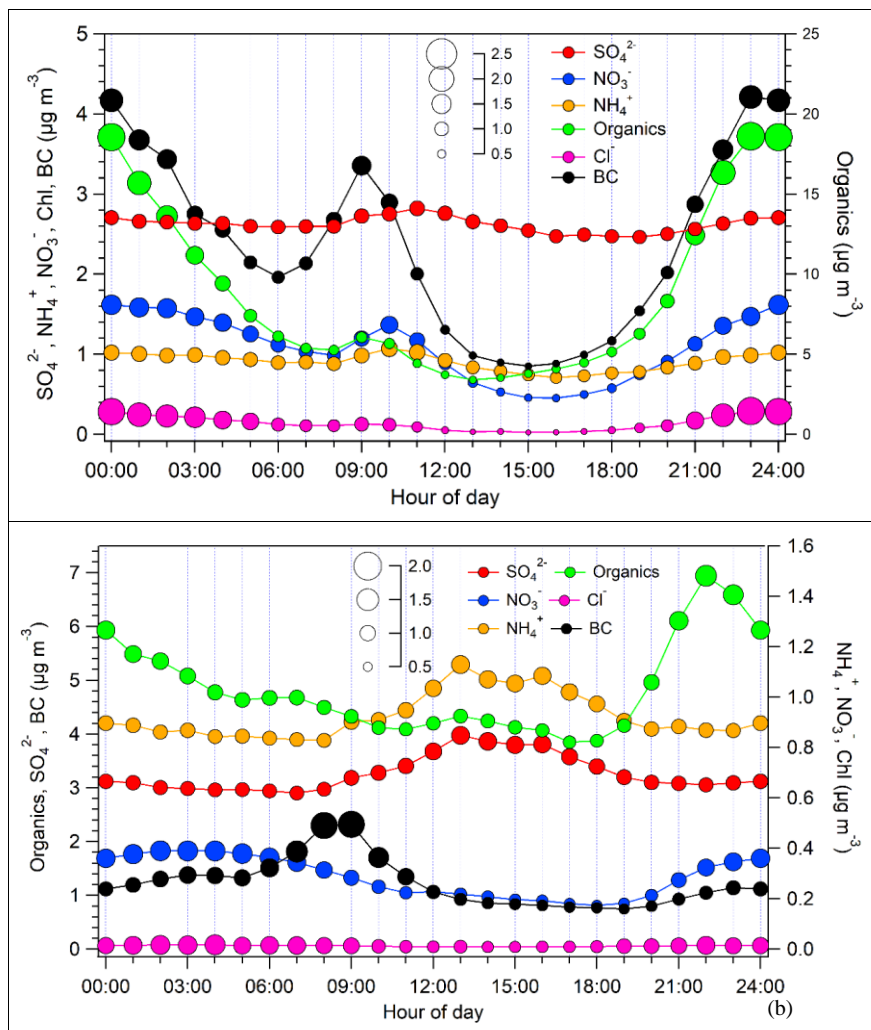


Figure 3: Monthly average concentrations of the main aerosol constituents. Organics are shown on the top panel for the one year 2016-2017 period as well as the 2013-2014 and 2015-2016 winter periods, while

1045 sulfate and ammonium on the middle panel, and BC, nitrate and chloride on the bottom panel shown for the one year 2016-2017 period. Standard deviation is also depicted (error bars; only the positive part is shown for plot's clarity issues).



1050 **Figure 4:** Average daily cycle of the main submicron aerosol constituents for the cold period 2016-17 on the top panel and the warm period of 2017 on the bottom panel. The size of the markers indicates the normalized values relative to each species' daily mean value.

1055

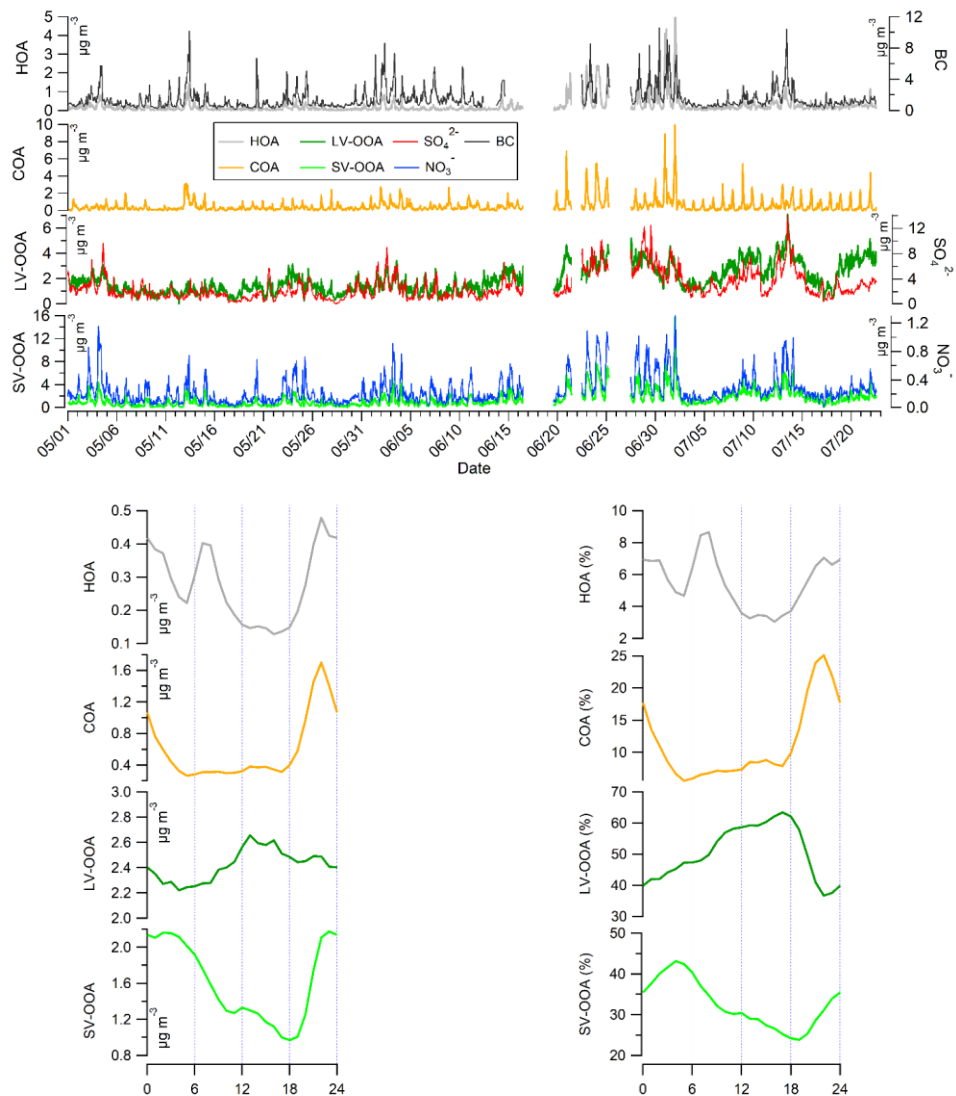


Figure 5: Time series of the contribution of the different factors identified by PMF between 1 May – 31 July 2017 (left top) along with their average diurnal cycles (middle bottom left) and the respective hourly average contributions (bottom right).

1060

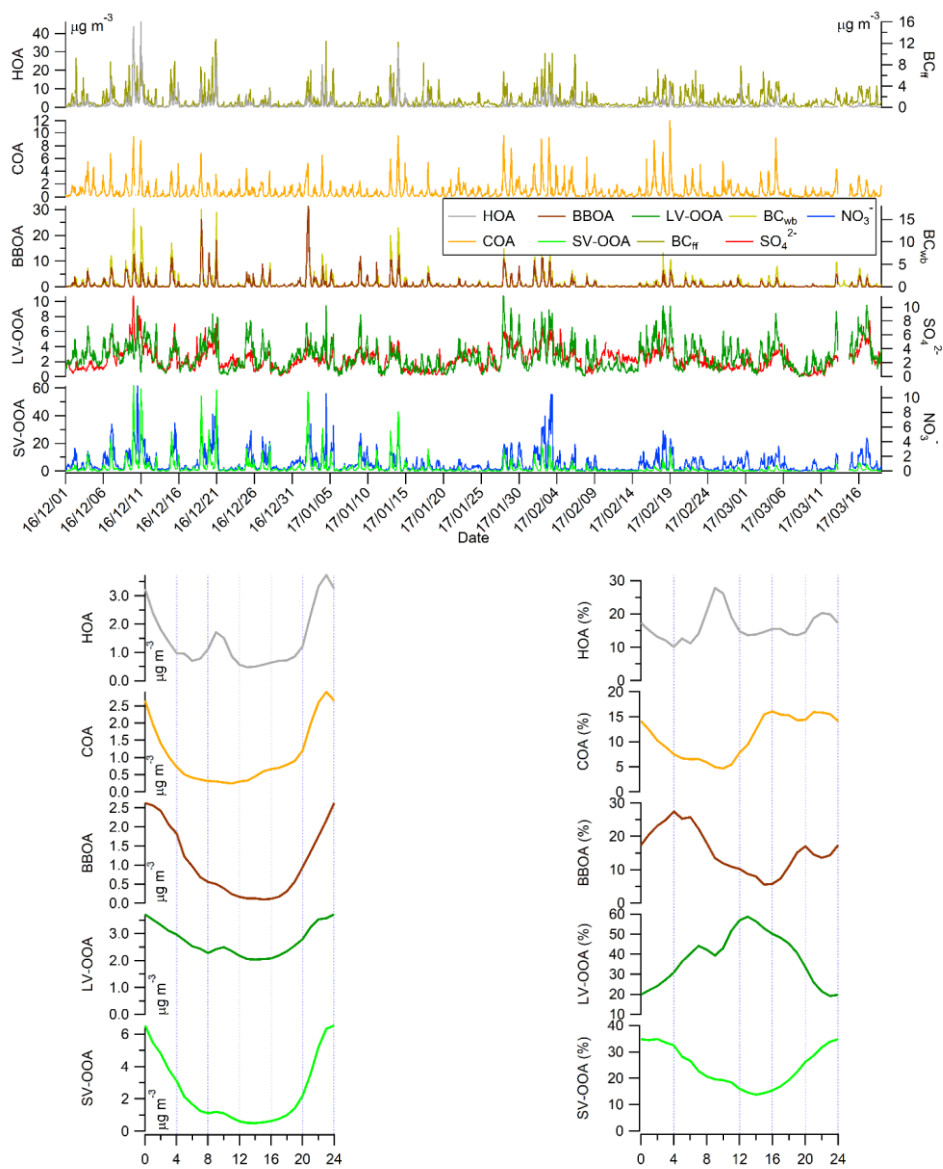


Figure 6: Time series of the contribution of the different factors identified by PMF between 21 Nov. 2016 – 1 March 2017 (**lefttop**) along with their average diurnal cycle (**middlebottom left**) and respective hourly contribution (**bottom right**).

1065

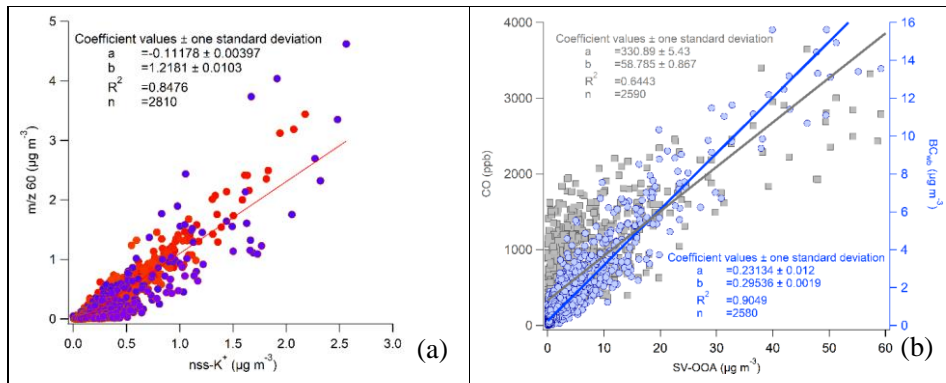


Figure 7: (a) Correlation of m/z 60 with nss-K⁺ for 2013-14 (red) and 2016-17 (blue), and (b) Correlation of SV-OOA with CO (grey) and BC (blue) for 2016-17.

	Mar – Apr – May 2017	Jul-Aug 2016 & Jun- Jul 2017	Sep – Oct – Nov 2016	Dec – Jan – Feb 2016- 2017	Dec – Jan – Feb 2013- 2014	Dec – Jan – Feb 2015- 2016
Organics	3.3 ± 3.0 (0.3-31.3)	5.4 ± 3.4 (0.3-41.9)	6.1 ± 7.5 (0.1-98.2)	9.0 ± 13.4 (0.2-153.9)	18 ± 24.4 (0.4-212.2)	12.4 ± 19.9 (0.7-1150.5)
Ammonium	0.6 ± 0.5 (0.4-3.1)	1.0 ± 0.6 (0.2-4.1)	1.0 ± 0.7 (0.4-5.7)	0.9 ± 0.7 (0.2-5.7)	1.8 ± 1.2 (0.2-9.1)	1.1 ± 1 (0.3-6.7)
Sulfate	2.1 ± 1.5 (0.2-10.1)	3.6 ± 2.1 (0.3-14.9)	3.5 ± 2.3 (0.1-17.1)	2.5 ± 1.5 (0.1-11.7)	2.6 ± 1.4 (0.4-13.9)	2.2 ± 1.7 (0.4-10.3)
Nitrate	0.4 ± 0.5 (0.05-5.4)	0.3 ± 0.2 (0.01-1.5)	0.5 ± 0.7 (0.1-6.9)	1.2 ± 1.5 (0.05-12.1)	2.6 ± 2.4 (0.09-18.3)	1.5 ± 1.4 (0.07-16)
Chloride	0.02 ± 0.05 (0-0.8)	0.02 ± 0.02 (0.04-0.2)	0.04 ± 0.09 (0.07-2.0)	0.15 ± 0.3 (0-3.5)	0.16 ± 0.24 (0.09-8.1)	0.12 ± 0.24 (0-2.6)
BC	1.5 ± 1.4 (0.1-14.6)	1.2 ± 0.8 (0.2-10.5)	1.7 ± 1.6 (0.1-12.4)	2.4 ± 3.4 (0.1-29.6)	2.7 ± 3.2 (0.2-26.8)	3.4 ± 4.6 (0.2-32.3)
PM1	8.9 ± 6.1 (0.6-42.4)	10.3 ± 5.6 (0.5-52.2)	13 ± 11.1 (0.9-115.5)	16.1 ± 19.5 (0.8-185.8)	24.5 ± 24.7(1.4- 227.2)	21.2 ± 27.4 (1.7-215.3)

1070 **Table 1:** Seasonal average concentrations \pm standard deviation (range) and total mass of the main submicron aerosol components for the one-year study period and the two winter campaigns.

	Winter 2013-14 18/12/13 – 21/02/14	Winter 2015-16 23/12/15 – 17/02/16	Cold 2016-17 01/11/16-18/03/17
BBOA	12.4%	8.9%	11.9%
HOA	12.2%	9.7%	16.4%
COA	10.4%	8.1%	11.7%
SV-OOA	19.8%	17.7%	28%
LV-OOA	45.2%	55.6%	32%

Table 2: Contribution of the five organic aerosol components to the total organic fraction during the three individual winter campaigns.

1075