

## RC1

This paper describes the analysis of a year long dataset acquired with a TOF-ACSM in Athens, Greece. The paper is well-written and the comparison of two different PMF approaches is interesting and worth publishing. There were a few sections that were confusing. Addressing the following comments should clear those up.

We genuinely thank the reviewer for the insightful comments and for considering the manuscript well-written and worth publishing. We present here our response to each comment (blue font) and we quote the respective part of the revised manuscript (grey font).

### 10 Specific comments:

**Comment 1. Lines 119-123: This is not how CDCE is applied. It's not the ammonium to nitrate fraction that matters, but the fraction of ammonium nitrate to total mass loading. Fraction of ammonium nitrate is clearly below 0.4 (based on the time-series in Figure S1 and Table S2), but the particles are also not neutralized, so you need to consider the second part of CDCE for acidic aerosols. Based on Table S2, CE=0.5 is fine for winter and spring, but a bit low for summer (CE=0.55) and fall (CE=0.56). It will only be a 10% error or so to apply CE=0.5 for all seasons, but you should explain why you are doing that.**

The reviewer emphasizes an extremely important point that needed to be changed and clarified. We thank the reviewer for the comment.

The ANMF was calculated and not the ammonium to nitrate fraction as was incorrectly mentioned in the manuscript. This paragraph was revised as follows:

“The collection efficiency chosen depends on three parameters; firstly, on the particulate water content. To account for it, a Nafion drier was placed in the inlet line. CE also depends on the ammonium nitrate fraction of the aerosol (ANMF), which was calculated to be higher than 0.4 for 99.9 % of the data indicating that a constant CE value of 0.5 should be optimum. Finally it depends on the acidity of the aerosol. Based on that, the CE was calculated 0.52 for NDJF, 0.49 for MAM, 0.55 for JJA and 0.56 for SO, while for the yearlong period it was 0.52. Therefore, the constant value of 0.5 was selected and this small variability should not affect much the solution given that the overall uncertainty for CE is 30 % (Bahreini et al., 2009).”

**Comment 2. Lines 250-256: Interquartile to median is a measure of spread or variability, not error so I would not call it an error. Isn't the variability in the mass concentration a reflection of atmospheric variability? It's not clear to me that lower variability necessarily means the PMF factors are a better representation of atmospheric sources. It also seems like a disconnect with the previous paragraph where the combined matrix had higher residuals (worse PMF) but lower spread (better PMF?).**

We really thank the reviewer for this comment. The reviewer is right pointing out that this should not be called an error, thus we name this value of the interquartile to median as uncertainties of the modelled factor (Canonaco et al., 2021, Chen et al., 2021). Since me-2 does not provide one unique solution (and thus there is no true answer),

we always need to consider how many possible solutions there are within the acceptable limits and how variant they are from each other. The variability in this part refers to the variability of the many repeats of the model, which in turn can be translated as the uncertainty of the solution.

40 Additionally, variability arises from the many repeats for each data point due to the technique of random a-values and the bootstrap resampling strategy and also from the different solutions in different rolling windows. Moreover, larger uncertainty, or more spread, is not necessarily indicative of worse PMF, but since all solutions within the spread are mathematically equivalent, higher spread indicates the variation of possible solutions. Since we do not know the true answer this can be translated to uncertainty. On the other hand, higher residuals by definition means worse modelling results.

45 This paragraph that was moved to the last section (4.4) was changed as follows:

Line 886: "Since PMF provides a range of possible solutions, there is the need to determine how many of these solutions are within the acceptable limits and how much they vary from each other. The variability in this part refers to the variability of the many repeats of the model that can be translated as uncertainty. Moreover, uncertainty is created by the generation of each time point many times after the application of the random a-values constraints, the resampling technique of bootstrapping and the technique of the rolling window. Thus, the ratio of the interquartile to the median concentration is used as a measure of this uncertainty (Canonaco et al., 2021)."

55 **Comment 3. Lines 436-451. This paragraph is very confusing. What is a subtracted f44-f43 plot? You are plotting f44 vs f43 for OOA factors so why do you need to subtract HOA? Or do you mean you subtracted an HOA factor for the raw data points in the background of the Figure S8? In Figure S8, the markers are color coded by month, not concentration. There is a shading scale for concentration in the legend, but it is impossible to see in the figure. Maybe use size for concentration? The triangle plot does not evaluate the goodness of the PMF fit. It shows if the PMF profiles obtained here are consistent with typical ambient measurements. The description of the trends as vertical or horizontal is not very helpful. Please describe in terms of chemistry, i.e., as more or less oxygenated.**

65 The authors thank the reviewer for the comment. This kind of plots is widely used in relevant studies (Canonaco et al., 2015, Chen et al., 2021) for understanding how OOA factors adapt to the variations of f44 vs f43 using rolling PMF. The equation that this is based upon, as also found in the supplement of Chen et al (2021), is the following:

$$\text{Subtracted } f_{44} = \frac{\text{mass concentration of OOA at } \frac{m}{z} 44}{\text{mass concentration of OOA at } \frac{m}{z} 44 + \text{residual of total OOA}}$$

$$\text{Subtracted } f_{43} = \frac{\text{mass concentration of OOA at } \frac{m}{z} 43}{\text{mass concentration of OOA at } \frac{m}{z} 43 + \text{residual of total OOA}}$$

70 The reason for the subtraction of the primary factors is that the fractions at  $m/z$  44 and  $m/z$  43 are usually the dominating ions in OOA factors. Nevertheless, the authors decided that this plot was more confusing than adding value to the description of the dataset and fell outside of the scope of this study and therefore it was removed.

**Specific minor comments:**

75 **Line 30: This methodology has been published before, so rather than saying this “work presents a new methodology,” say “this work applies a new methodology to a year-long dataset.”**

The authors thank the reviewer for the comment. This sentence was rephrased as:

This work applies a new methodology to a year-long ACSM dataset.

**Line 49-50: Do you mean IVOCs? VOCs are typically emitted already in the gas-phase.**

80 We thank the reviewer for this comment. This part of the sentence was deleted, since the authors agree that VOCs are already in the gas phase.

85 **Figure 1: I don't find pictures of instrument containers particularly useful and the contrast in the upper left panel is poor. I would suggest making this a 2-panel figure, one panel with a map that shows a scale between the upper left and upper right panels and one panel with the lower right photo. You could put the prevailing winds on the map, at least for winter and spring. In the lower right photo, label the yellow dot and indicate which direction is north.**

The authors thank the reviewer for the suggestion and agree that this adaptations will be helpful. This figure was replaced with a 2-panel and a compass was added to indicate north. The prevailing winds for each season appear in the supplement (Fig. S3) and the authors think it would not fit to insert the winds in this figure:



**Line 107: What was the detection limit for your instrument? Which species is this detection limit for?**

We thank the reviewer for the comment. The detection limit for each species was added in a sentence:

The 10 min detection limit for each species measured with the ToF-ACSM is 0.062 for organics, 0.006 for  $\text{SO}_4^{2-}$ , 0.007 for  $\text{NO}_3^-$ , 0.058 for  $\text{NH}_4^+$  and 0.003 for  $\text{Cl}^-$  (Fröhlich et al., 2013).

95 **Line 127: Please describe the approach rather than requiring someone to read the Supplement. Maybe replace “as described in the Supplement (Sect. S1).” with “from the wavelength dependence of the absorption (Sect. S1).”**

The paragraph of Section S1 was moved to the manuscript to avoid referring the reader to the supplement to check the approach followed.

100 **Line 168-171: This is a very long sentence. Replace “technique application a technique that” with “technique that” and put a period after “size.” Then start a new sentence with “Calculations are repeated...”**

We thank the reviewer for this comment. The two sentences were separated as follows:

105 “SoFi Pro includes the rolling window technique that allows the user to track the variability of the factors by applying a window with selected length (usually 7, 14 or 28 days, depending on the size of the studied dataset) that moves with a chosen step. Calculations are repeated in that moving span providing the temporal changes in both profile and time series of the factors (Canonaco, 2021).”

**Line 174: Since the previous sentence mentions both wind and air mass analysis, indicate which one you are applying CPF to. Maybe start this sentence with “The wind analysis used the” and delete “was used”**

110 The authors thank the reviewer for the comment. The sentence was reshaped as follows:

“The wind analysis used the conditional probability function (CPF) to provide...”

**Line 182: 1000 m seems really high for back trajectory analysis of ground level measurements. Can you explain why you chose this height?**

115 The reviewer is right to point this out. The reason why the height of 1000 m AGL was chosen for the HYSPLIT runs was the relatively high altitude of the station (270 m ASL). The uncertainty due to the ground effects would be much if a lower height was to be chosen. Moreover, the trajectories were plotted for three different starting heights (500, 1000 and 1500 m) and the results were resembling.

120 **Line 191: The terminology in PMF can be confusing and I would define the terms in this introductory paragraph. Maybe something like “In the following, profile refers to the mass spectrum of a given factor and variable refers to an individual m/z.”**

We find this comment helpful. The following sentence was added in order to explain better the PMF terms:

“In the following, profile refers to the mass spectrum of a given factor and variable refers to an individual mass to charge ratio ( $m/z$ ).”

125 **Lines 192-202: The sentence about the mass concentration should go with the next paragraph that describes the mass loading calculation.**

We thank the reviewer for this comment. The sentence was moved to the end of the following paragraph.

**Line 200: You downweight the errors for the variables, not the whole species.**

The reviewer is correct to point out this fact. This statement was phrased as:

“The error values for each inorganic variable were downweighted...”

130 **Line 212: I’m not sure what “for each matrix” is referring to here. Maybe end the sentence after “number of factors.”**

We thank the reviewer for this comment. This sentence was ended after “number of factors”:

“The first step for source apportionment was to perform PMF analysis on the winter months (November–February) in order to identify the number of factors.”

135 **Line 243: Maybe “subjective” or “qualitative” is better than “user-dependent” as in “the interpretation of PMF results is qualitative”**

We agree with the reviewer’s statement. The word user-dependent was changed to “subjective”.

**Line 247: Aren’t OOAs and oxidized aerosols the same thing?**

140 We thank the reviewer for this comment. As oxidized aerosols are referred here the MOA and LOA factors that contain both organic and inorganic species. The sentence was rephrased to be clearer:

“The points at which the scaled residuals exceeded these thresholds were associated with peaks in SOAs in the OA PMF analysis and in oxidized aerosols (MOA and LOA) in the combined PMF analysis...”

145 **Lines 273-276: A step is missing in this description. Hysplit does not track species, only air masses. Do you mean that the Hysplit back trajectories are colored by the sulfate concentration at the end point? Also, the red blob looks more diffuse in winter, spring and summer than fall so I’m not sure about your conclusion that fall sulfate is more regional.**

The reviewer is right to point out that Hysplit does not track species. Having said that, we have not used the back trajectories independently, but as part of a trajectory statistical model (TSM), that makes it possible to identify source locations. The following part was added in the text:

150 “The basis of PSCF is that if a source is located at (i, j), an air parcel back trajectory passing through that location indicates that material from the source can be collected and transported along the trajectory to the receptor site. The PSCF is calculated as:

$$\text{PSCF} = n_{ij}/m_{ij} \quad (8)$$

155 Where  $n_{ij}$  is the number of times that the trajectories passed through the cell (i, j) and  $m_{ij}$  is the number of times that a source concentration was high when the trajectories passed through the cell (i, j). The criterion for determining  $m_{ij}$  is based on the distribution of the measured values (e.g., upper quartile).”

Moreover, concerning the concentration of sulphate, we claim that it is a combination of regional transport, local formation and meteorology and the higher concentrations in spring, summer and autumn are due to local photochemical activity and less precipitation compared to winter:

160 “Simultaneously, sulfate levels were the result of regional transport, photochemical activity and local meteorology. The regional character of sulfate for all seasons is indicated by the HYSPLIT back trajectories in Fig. S2. In winter, sulfate values are lower due to enhanced precipitation, although regional sulfate was being transported to the station, while in the other seasons regional transport combined with local photochemical activity and less precipitation results in higher sulfate values (Stavroulas et al., 2019, Theodosi et al., 2018; 165 Cusack et al., 2012, Dayan et al., 2017).”

**Lines 294-296: Since the sulfate is not neutralized with ammonia that suggests more local than regional sources. It would be more accurate to say that the flat diurnal in winter is consistent with regional sources. The afternoon peak in spring suggests local photochemical activity. The increase at night in summer and fall is due to larger changes in boundary layer height compared to other seasons. Make sure that your 170 conclusions from the diurnals are consistent with your conclusions from the Hysplit back trajectories.**

The authors thank the reviewer and agree with the suggestions on the explanation of the diurnal behavior of sulphate, thus it was changed to:

175 “. . .the diurnal profile of sulfate was flat in winter, consistent with regional sources and meteorological conditions that do not favor local photochemical activity. In spring, summer and early autumn sulfate presents a diurnal structure that is related to local photochemical activity and boundary layer height”

**Lines 297-299: The formation of NH<sub>4</sub>Cl would be higher at night when the temperature is lower. How does that explain an afternoon peak?**

180 We thank the reviewer for the comment. The term used was wrong, the second peak mentioned is an evening peak and not an afternoon peak since it is observed at 20:00. Thus it is due to NH<sub>4</sub>Cl formation when the temperature drops. Therefore, the sentence was rephrased as follows:

“Chloride presented two distinct peaks (i.e. morning and evening) for all the seasons, related to temperature-dependent gas-particle partitioning of chlorine (i.e. chloride is primarily detected as ammonium chloride), biomass burning emissions and prevailing atmospheric conditions.”

185 **Line 339: Change the section heading to make it clear that this section is about the OA PMF analysis, not organic aerosols in general.**

The authors thank the reviewer for this comment. The heading was changed to:

“PMF analysis of organic aerosols”

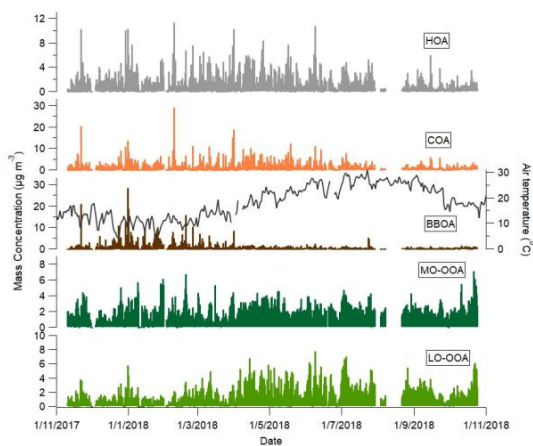
**Line 341:** Be more specific, e.g., “the mass spectrum from  $m/z$  100 to 200 is depicted”

We thank the reviewer for this comment. This sentence was rephrased as:

190 “The profiles of the five factors for  $m/z$  10 to 100 are presented...”

**Figure 3:** It is difficult to see what is going on in the panel with both BBOA and temperature. I would suggest a separate y-axis for temperature. Or, alternatively, you could average the temperature to daily values since it is the seasonal trend that matters.

195 We thank the reviewer and agree with this point, thus the figure was changed; the temperature wave was replaced with the daily averaged temperature as shown below:



**Lines 377-382:** Make it clear that these previous studies are high resolution analysis that gives specific ion fragments at  $m/z$  55 and 57. Also, not clear why you are giving chemical names of gas-phase species for ions from particles. I would delete the chemical names.

200 The authors thank the reviewer and highly agree with this point. Although, upon closer examination this sentence was not considered as very useful and was removed from the manuscript by the authors.

**Line 387:** Why surprising? It is the same site.

We thank the reviewer and agree that the use of this word was incorrect and was therefore removed.

205 **Line 394:** What does “with a total duration of 8 h” mean? Are you comparing only 8 hours of data? If so, specify which 8 hours.

We thank the reviewer for this comment. The loading is referred to the hours that cooking or traffic emissions are observed compared to the hours of the day when the concentration of COA and HOA drops. It means the duration of the loading effect of this emission.

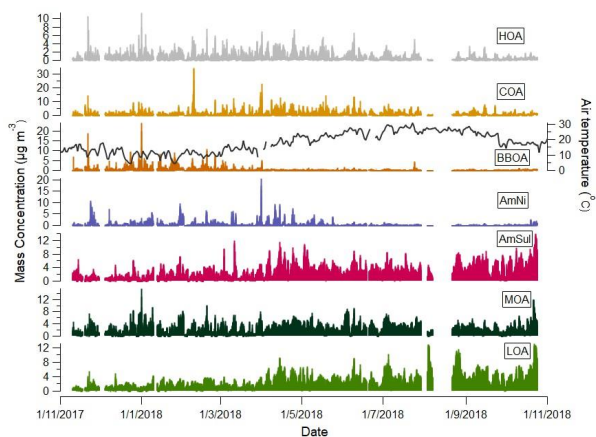
210 **Line 452: Change the section heading to make it clear that this section is about the combined PMF analysis, not submicron aerosols in general.**

The authors thank the reviewer for this comment. The heading was changed to:

“PMF analysis of submicron aerosol”

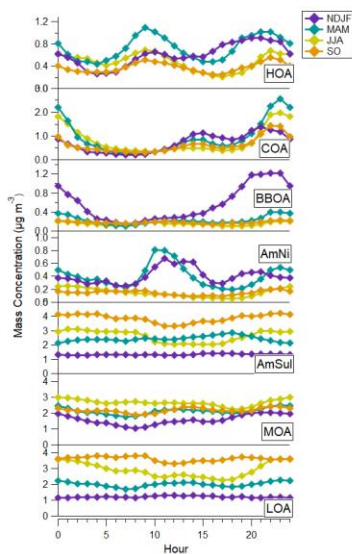
215 **Figure 4. Would suggest averaging the temperature data to make the panel with both T and BBOA clearer. It's very hard to see RH and T in the panel with AN. I would make a separate panel. The caption should say “aerosol factors” not “sources.”**

The authors thank the reviewer for this helpful suggestion. Figure 4b was changed after averaging temperature with daily resolution. Nevertheless, the part of the manuscript about the dependence of ammonium nitrate on temperature was removed, therefore the plot 4c was replaced by the diurnals of the factors without the interference of temperature and relative humidity:



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The caption was changed to:

“Figure 4. Mass spectra (a), time series (b) and diurnal plots (c) of the seven submicron factors and (d) diurnal plot of AmNi with Relative Humidity and Air Temperature.”

225 **Lines 472-474: Many of these changed by 0.01. Is that significant? Maybe point out one or two cases where there was a significant improvement.**

We thank the reviewer for the comment and agree that this changes were not all significant. This sentence was moved to the new section (4.4) and replaced by the following:

230 “Finally, the correlation between the factors obtained and external tracers appears in Table S6, from which a slight improvement can be seen for spring. For the other seasons the correlations are stable between the factors from the two analyses and their respective external tracers.”

**Line 507: Insert “The CPF polar plot in” before “Figure S10” so the reader does not have to go to the SI to find out what S10 is.**

The authors thank the reviewer for the comment. The phrase “The CPF polar plot in” was added before Fig. 10:

235 “The CPF polar plot in Fig. S10 further confirms that ammonium nitrate was locally formed.”

Line 522: You need something to transition between these two sentences. Maybe “As noted above for the OA PMF analysis,”

The authors thank the reviewer for the comment. The phrase “As noted above for OA PMF analysis” was added in the beginning of the sentence.

240 “As noted before for the OA PMF analysis, LO-OOA and MO-OOA, retrieved by PMF analysis on the organic fraction, were well correlated with...”

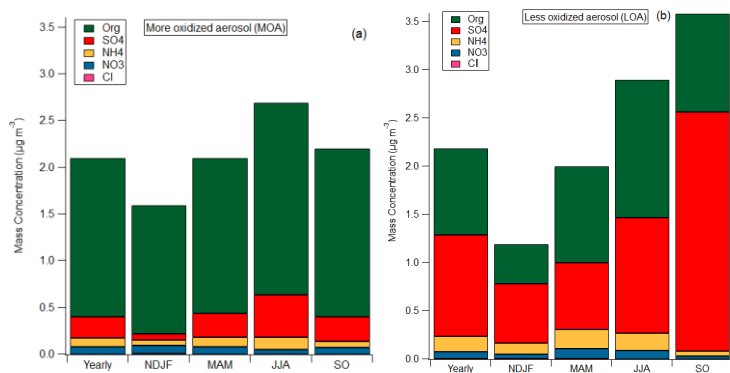
Line 536: I think you mean the “attribution of organics” rather than the “contribution of organics.” This sentence should end in a comma, not a period, because the next sentence is not a complete sentence.

245 We thank the reviewer for this comment. The word “contribution” was replaced with the word “attribution” and the following sentence was added:

“Overall, the attribution of organics to MOA and LOA followed the same trend as that of MO-OOA and LO-OOA, while the difference in absolute values between MO-OOA/MOA and LO-OOA/LOA concentrations was mainly driven by the sulfate apportioned to the combined secondary factors.”

250 **Figure 5. Use the same y-axis scaling for both panels so that it is easier to interpret the discussion in the text.**

The authors thank the reviewer for this suggestion. The same y-axis was used for the two panels and the figure was replaced:



255 Lines 557-568: This whole paragraph seems like it should go earlier in this section since it is more of an overview of the results. Also, some of it repeats information that you have already discussed in more detail.

**And the phrase “will be discussed below” doesn’t make any sense since this is the last paragraph of the results.**

260 The authors thank the reviewer for this comment and highly agree that the repositioning of this paragraph will benefit the manuscript. Moreover, some parts that were already discussed in previous sections needed to be deleted. Thus, the first part of this paragraph was moved at the beginning of the Section 4.3. The rest of it, that referred to Fig. S10 was deleted, because it was also present in the factors description above and the reader was referred to Fig. S10 when it was needed in the above paragraphs of the Section 4.3:

Lines 701: ...small contribution of inorganic species in this traffic-related factor (Fig. S10).

Line 706: As also shown in Fig.S10, this factor consisted mainly of organics...

265 Line 712: In this factor the inorganics presented lower contribution than on the other two POA factors (Fig. S10).

Line 717: The ammonium nitrate factor resolved in this study was composed of 55 %  $\text{NO}_3^-$  and 18 %  $\text{NH}_4^+$  (Fig. S10)

Line 804: A factor predominantly composed of sulfate and ammonium was retrieved in this study. 64 % of the mass of this factor was attributed to  $\text{SO}_4^{2-}$  and 19.5 %  $\text{NH}_4^+$  (Fig. S10).

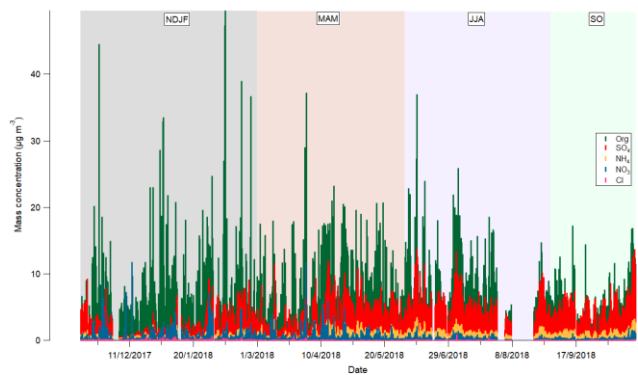
270 The last part discussing Fig. S11 was left as the last paragraph of the section 4.3.

**Table S1: Why is SFBOA in this table? It is not discussed in the paper.**

The authors thank the reviewer for pointing this out. SFBOA was a typing mistake and it was replaced by BBOA.

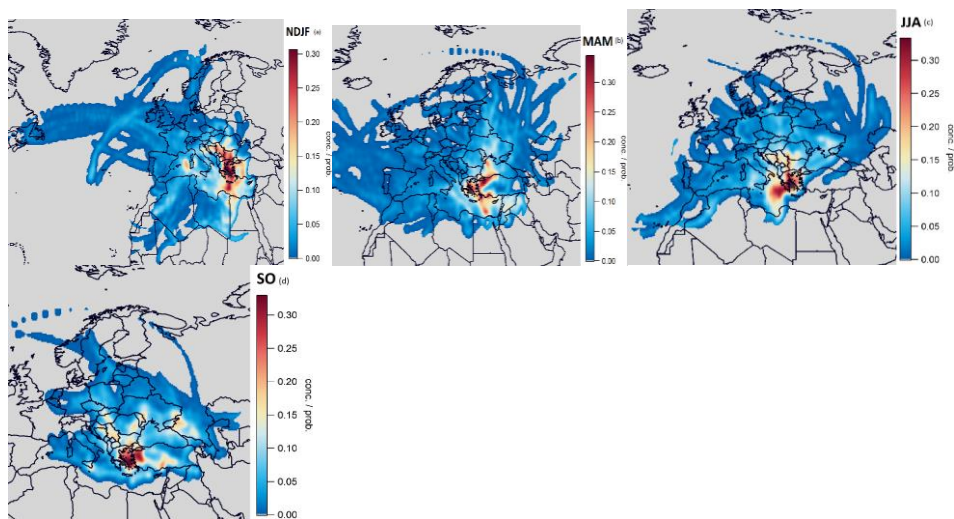
**Figure S1: It would be helpful to indicate the seasons with vertical bars.**

275 We thank the reviewer and agree that it would be helpful to revise this plot in the way proposed. The seasons were added as shaded vertical bars in this figure:



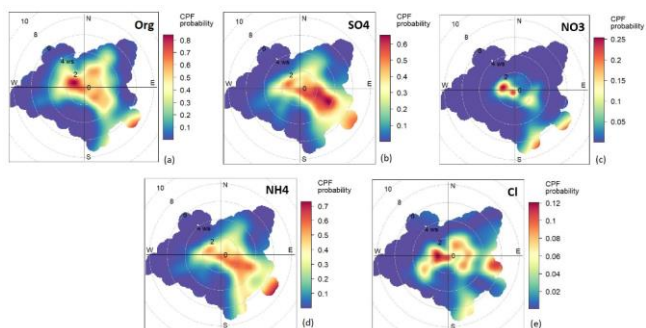
**Figure S2.** I would expand the maps so the detail is clearer. Asia and Africa are not relevant to the discussion. Also, it would be nice to have the season label on each panel.

280 We thank the reviewer and agree with this suggestion. The maps were expanded to show more clearly the scale that is relevant for the discussion and also seasons were labeled on each panel:



**Figure S4.** It would help to have species labels on each panel. Same comment for Figure S7.

285 The authors thank the reviewer for this comment. Species labels were added in Figures S4 and S7 as recommended:



**Table S4:** Since NH4 is a linear combination of SO4 and NO3, and in this data dominated by SO4, correlations with NH4 do not add any new information. I would delete the two NH4 rows.

290 We thank the reviewer for the comment. The NH4 rows of the table were deleted, because as stated by the reviewer and agreed by the authors they didn't add any new information.

**Figure S8:** Explain what the black dots are – is this the subtracted data? The shading for size is not visible. Maybe use marker size instead? Not clear what “on the upper size,” “on the lower size,” and “in the middle” mean. I would delete.

295 The authors thank the reviewer for the comment. The black dots were the subtracted data, but as discussed before it was decided that this plot be removed.

**Table S5.** Make sure that the tables are in the same order as mentioned in the text.

We thank the reviewer for this helpful suggestion. The order that the tables are mentioned in the text was corrected.

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**Technical corrections:**

We deeply thank the reviewer for the thorough revision of the manuscript and the truly helpful technical revisions proposed below.

All the technical corrections were made following the reviewer's comments:

- 305 **Line 28: No “s” at the end of “aerosols”**
- Line 37: “causes of” is better than “reasons for”**
- Line 44: No “s” at the end of “clouds”**
- Line 45: Start the sentence with “The”**
- Line 58: No “s” at the end of “vehicles”**
- 310 **Line 64: Start the sentence with “The”**
- Lines 64-67: This sentence would be easier to understand if you delete “by real-time measurements” at the end and insert “real-time” before “quantification”**
- Line 66, 68, 93: Define all acronyms: PM1, PMF, GAW, ACTRIS, PANACEA**
- Line 78: “fingerprint” not “footprint”**
- 315 **Line 96: replace “North east from” with “northeast of”**
- Line 113: Particles are focused into a “narrow beam” not a “narrow airbeam”**
- Line 115: Delete “in a tungsten filament” The electrons come from a tungsten filament, but the ionization doesn’t occur in the filament.**
- Line 115: Replace “following” with “according to”**
- 320 **Line 118: Should be a comma before “while” rather than a period before “While”**
- Lines 146-149: I would put Eq 1 after the sentence that ends “G and F (Eq.1).”**
- Line 201: Add “s” to “variable”**
- Line 211: Add “the” before “winter”**
- Line 214: Delete “s” at the end of “factors”**
- 325 **Line 226: Do you mean “lunchtime” or “mealtime”? It’s not “noon” if it’s 14:00.**
- Line 228: Insert “of” between “fractions” and “m/z”**
- Line 246: Replace “was well-fitted” with “fit the data well”**

Line 265: Replace “at” with “in”

Line 278: Replace “portioning” with “partitioning”

330 Line 285-287: The end of this sentence is confusing. Do you mean “except for sulfate, for which concentrations were more similar.”

Line 287: Replace “rest” with “other”

Lines 292-293: This is a run on sentence. Replace “night, however” with “night. However,”

335 Line 352: Not clear what “distinctly recognized” means. Do you mean “identified based on its distinctive mass spectrum”

Line 355: Delete the chemical formulas since you have them in parentheses later in the sentence.

Line 357: Replace “most” with “quite”

Line 360: Insert “with the” after “correlated”

Line 363: Insert “The” at the beginning of the sentence.

340 Line 365: Insert “the” before “HOA factor”

Line 385: Replace “in” with “at”

Line 392: Replace “configuring right” with “separating”

Line 394: Replace “respective” with “loading”

Line 406: Replace “to” with “with”

345 Line 412: Replace “were very relevant to” with “was highly correlated with”

Line 416: Replace “at” with “in”

Line 417: Insert “the” before “BBOA”

Line 424: Insert “The” before “MO-OOA”

Line 427: Do you mean Figure 3c?

350 Line 428: Replace “on” with “to”

**Lines 455-456: Replace “daily trends...concentration” with “diurnal trends (Fig. 4c) of each factor”**

**Line 471: Replace “resembles significantly to” with “is similar to”**

**Line 472: Replace “configuration of this factor with” with “agreement of this factor between”**

**Line 476: Add “s” to “contribution”**

355 **Line 478: Delete “highly” before “agreed” and “’s” on “COA”**

**Line 502: “the ammonium nitrate peak” sounds better than “ammonium nitrate’s peak”**

**Line 505: Replace “leaded” with “led”**

**Line 506: Delete “’s” on “nitrate”**

**Line 510: “predominantly” not “dominantly”**

360 **Lines 530-531: Delete “highly” Delete “s” on “SOAs” Delete “particles” after “sulfate”**

**Line 534: “and higher” might be better than “while peaked”**

**Line 573: Replace “sources” with “factors”**

**Line 577: Open parenthesis missing.**

**Line 586: Replace “simulations” with “sources”**

365 **Line 591: Replace “errors” with “variability” or “spread”**

**Line 598: Replace “on ambient aerosols...best of information that can be obtained by” with “of ambient...best information from”**

**Line 605: Replace “finding” with “funding”**

## 370 **References**

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, 10, 2015.

Canonaco, F., Tobler, A., Chen, G., Sosedova, Y., Slowik, J. G., Bozzetti, C., Daellenbach, K. R., El Haddad, I., Crippa, M., Huang, R.-J., Furger, M., Baltensperger, U. and Prévôt, A. S. H.: A new method for long-term source apportionment with



375 time-dependent factor profiles and uncertainty assessment using SoFi Pro: application to 1 year of organic aerosol data,  
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submicron organic aerosol for a rural site in an alpine valley using a rolling positive matrix factorisation (PMF) window,  
380 Atmos. Chem. Phys., 21, 15081–15101, <https://doi.org/10.5194/acp-21-15081-2021>, 2021.

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## RC2

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**This work presents a valuable yearlong ToFACSM dataset for organic and inorganic source apportionment in Athens. It provide valuable information for the source of organic and inorganic source in Athens. The manuscript is generally well written, and falls well within the scope of AMT. Thus, it is of value to be published. After said that, some modifications are necessary to clarify what values the work add.**

415

**We sincerely thank the reviewer for the helpful comments on our manuscript and for deeming it as well written and of value to be published. Below, we reply to each comment (blue font) and we cite the changed parts as appear in the revised manuscript (grey font).**

### Major comments

420 **This manuscript exhibits valuable measurements for organic and inorganic source apportionment, while it lacks focus. It may be helpful to strengthen how this dataset is useful for environmental studies or climate studies. Besides, it would be better to provide some implications on what values this dataset adds compared to previous studies. In summary, the authors should provide more discussions to strengthen the values of the dataset. Besides just providing values, it is also valuable to clarify why these values are valuable.**

425 The reviewer has focused on some points which can be extremely beneficial for the manuscript. We thank the reviewer for the recommendations. We refer here to the parts of the manuscript where the strength of this methodology is pointed out.

430 Line 27-30: “This work applies a new methodology to a year-long ACSM dataset, provides insights on the sources of the non–refractory species of ambient aerosol and using innovative tools for applying PMF (Rolling window) enables the study of the temporal variation of these sources and also the variability of their composition.”

Line 114-116: “Nevertheless, a long period of combined organic and inorganic source apportionment study spanning over a period of a year has not yet been published, leaving a gap in the comprehensive understanding of ambient aerosol sources, formation processes and mixing.”

435 Line 701-703: “The peaks of the previously resolved HOA (Sect. 4.2) that were attributed to poor separation of the OA factors were not present in the combined matrix analysis, highlighting the improvement of the solution.”

440 Line 957-962: “As regards the significance of the combined PMF analysis over organics PMF, it was shown that incorporating the inorganics in the PMF analysis valuable information regarding the mixing of organics and inorganics over time and the sources of total non-refractory species of PM1 can be obtained, while at the same time maintaining the quality of the solution obtained.”

Although, we understand the point of the reviewer and therefore a new section (4.4) was added that compared the two analyses and stated more the value added by this work:

Line 872-909: “Integrating the inorganics in the PMF analysis adds valuable information concerning the mixing characteristics of organic and inorganic species over time, while rendering results that are qualitatively comparable to the widely-used organic aerosol PMF. Obtaining a better understanding on the sources and evolution processes of the total NRS, instead of merely OA, by applying source apportionment methods in combined organic and inorganic datasets for various site locations and for long-term datasets can be proven beneficial for atmospheric studies and climate models. The two analyses applied in the present study provided acceptable solutions both in terms of uncertainty (spread) of the factors and in terms of residuals, as explained in the paragraphs below.

...

Moreover, the primary factors obtained by both analyses were highly correlated with each other in terms of temporal variation, suggesting that the inclusion of the inorganics in the PMF scheme did not adversely affect the quality of the initial solution. More specifically, the time series of the HOA factor obtained from the combined matrix presented good correlation with the organic matrix resolved HOA factor (R–Pearson = 0.87). Combined COA time series agreed with the previously resolved COA time series (R–Pearson = 0.92). The BBOAs resolved from the two different analyses were highly correlated with each other (R–Pearson = 0.88). Finally, the correlation between the factors obtained and external tracers appears in Table S6, from which a slight improvement can be seen for spring. For the other seasons the correlations are stable between the factors from the two analyses and their respective external tracers, which confirms the successful deconvolution of the primary factors by both analyses.”

#### **Minor comments.**

**Abstract, The method has been proposed in previous studies, but you applied it in a yearlong investigation in Athens. Thus, “new methodology” is not proper.**

We thank the reviewer for the comment. Indeed, in this work we apply this new methodology, we do not present a new one. This sentence was rephrased as:

This work applies a new methodology to a year-long ACSM dataset.

**Line 41. Brown carbon is also organic aerosol, while it absorbs light from ultraviolet to visible region.**

We agree with the reviewer and the sentence was revised:

“For example, black carbon can absorb light at all wavelengths, brown carbon absorbs ultraviolet and visible radiation (Moosmüller et al., 2009), while organic aerosol (except for brown carbon), nitrate and sulfate particles are responsible mainly for light scattering (Cabada et al., 2004).”

**Line 46. “Organic fraction usually comprises the greatest fraction of ambient aerosol”, is it correct for all the regions?**

475 We thank the reviewer for the comment. The sentence was altered as follows:

“The organic fraction comprises 20-90 % of ambient fine aerosols (Kanakidou et al., 2005, Chen et al., 2022).”

**Line 48 “Secondary” should be “Secondary organic aerosols”.**

We agree with the reviewer that this phrase was incomplete and he revised it:

“Secondary organic aerosols are the organic aerosols that are...”

480 **Line 51 -52 “aerosol forming” should be “aerosol-forming”.**

We thank the reviewer for the comment. The revision of the phrase follows:

“...which then condense onto pre-existing aerosol-forming secondary organic aerosols (SOAs).”

**Line 53. “SOAs are the dominant form of organic aerosols”, is it really correct? Please provide the references.**

485 We appreciate the reviewer’s comment. The sentence was removed, since it is not a globally valid point.

**Line 54 – 58, please provide references to verify your clarifications.**

We thank the reviewer for the comment and agree that references are important here to verify our clarifications. The paragraph was revised:

490 “Secondary sulfates are found in the atmosphere mainly in the forms of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ , after the neutralization of sulfuric acid by ammonia (Biggins and Harrison., 1979). Ambient ammonium nitrate is formed through the oxidation of anthropogenic NOx emissions (NO and  $\text{NO}_2$ ) to nitric acid ( $\text{HNO}_3$ ), which eventually reacts with ammonia ( $\text{NH}_3$ ) (Stelson et al., 1979).”

**Please check the English grammar. Some examples are shown in the following.**

We thank the reviewer for pointing out some grammatical infelicities of the manuscript.

495 **Line 58 “in agriculture etc” should be “in agriculture, etc”**

The reviewer is correct and the sentence was revised:

“...pesticides in agriculture, etc.”

**Line 60 “are also released in” should be “are also released into”.**

We thank the reviewer for the comment.

500 “Chloride containing particles are also released into the atmosphere...”

**Line 82** you said “Although source apportionment studies on organic aerosols for long periods have been prevailing in recent years covering a wide range of different sites, a long period of combined organic and inorganic source apportionment has not yet been published.”, but in line 70 you also say “Previous studies on particulate matter source apportionment in Greece have mainly focused on inorganic datasets”. I know you mean that the aims of this work is to combine organic and inorganic source apportionment for a yearlong investigation. However, the logic of the sentence should be re-arranged.

We thank the reviewer for the comment. It needs to be clarified that the sentence “Previous studies on particulate matter source apportionment in Greece have mainly focused on inorganic datasets” refers to the classical SA approaches on sample collection analysis and not in inorganic species measured by high time resolution instruments like the ACSM. The species included in this case are elemental component of PM and possibly ionic component and carbonaceous species as total EC, OC.

**Line 82 – 84: This sentence is too long.**

The reviewer brings up a helpful comment for this sentence which was split into two sentences as follows:

“Long period source apportionment studies on organic aerosols in recent years have covered a wide range of sites. Nevertheless, a long period of combined organic and inorganic source apportionment study spanning over a period of a year has not yet been published, leaving a gap in the comprehensive understanding of ambient aerosol sources, formation processes and mixing.”

**Line 85 – 86: It would be better to re-write this sentence as two sentences. “one on the combined” should be “another on the combined”**

We thank the reviewer for the helpful comment.

“This study is the first one to present the results of two PMF analyses, one on the organic fraction and another on the combined organic and inorganic dataset of a ToF-ACSM for one year. The technique of the rolling window was also enabled in order to examine the temporal variability and the varying composition of the combined factors.”

**Line 93 “member of” should be “a member of”.**

We thank the reviewer for the comment.

“... (DEM), a member of the...”

**Line 96 “North east” should be “Northeast”.**

The reviewer is correct for pointing that out.

530 "...8 km to the Northeast of Athens city..."

**Line 107 "afterwards" should be "afterward".**

We thank the reviewer for the comment.

"...the data were afterward averaged..."

**Line 108 "principle of" should be "the principle of".**

535 We appreciate the reviewer's comment.

"...and the principle of operation is given..."

**Figure 3: the axis of different subfigures are too close.**

We thank the reviewer for this comment, the figure was replotted.

**Line 576: is "OA" "OOA"?**

540 We thank the reviewer for this comment, we meant to say oxidized oxygenated OA. The sentence was altered to:

"...one more oxidized (MO-OOA) and one less oxidized OOA..."

**Line 596 – 599: This sentence is too long. In addition, in the discussion, some specific discussions on how the dataset adds should be added.**

545 We thank the reviewer for the comment. The sentence was rearranges and the added value of this study is highlighted in the added last section (4.4):

550 "Integrating the inorganics in the PMF analysis adds valuable information concerning the mixing characteristics of organic and inorganic species over time, while rendering results that are qualitatively comparable to the widely-used organic aerosol PMF. Obtaining a better understanding on the sources and evolution processes of the total NRS, instead of merely OA, by applying source apportionment methods in combined organic and inorganic datasets for various site locations and for long-term datasets can be proven beneficial for atmospheric studies and climate models. The two analyses applied in the present study provided acceptable solutions both in terms of uncertainty (spread) of the factors and in terms of residuals, as explained in the paragraphs below."

# 555 **Combined organic and inorganic source apportionment on yearlong ToF-ACSM dataset at a suburban station in Athens**

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565 **Abstract.** The current improvements in aerosol mass spectrometers in resolution and sensitivity, and the analytical tools for mass spectra deconvolution, have enabled the in depth analysis of ambient organic aerosol (OA) properties. Although OA constitutes a major fraction of ambient aerosol, the overall aerosol properties are determined by the mixing characteristics of both organic and inorganic contents of ambient aerosol. In the present study, the mass spectra of both organic and inorganic aerosol were obtained by a time-of-flight aerosol mass spectrometer (ToF-ACSM) and further merged into one input matrix for Positive Matrix Factorization (PMF) analysis. The scope of this work was to assess the sources of organic aerosol and total non-refractory species in the suburbs of Athens, check their temporal variation and the interactions between organic and inorganic species. The results revealed five factors in the case of the organic aerosol analysis. Three of them were primary OA factors: hydrocarbon-like (HOA), cooking related (COA) and biomass burning (BBOA), and the remaining two were secondary, less and more oxidized oxygenated organic aerosol (LO-OOA and MO-OOA, respectively). The relative contributions of these factors were HOA 15 %, COA 18 %, BBOA 9 %, MO-OOA 34 % and LO-OOA 24 % (yearly averaged). In the case of the combined aerosol matrix, two additional factors were identified that were mainly composed of ammonium sulfate (83.5 %) and ammonium nitrate (73 %). Moreover, the two secondary factors contained both organics and inorganics and were named as more (MOA) and less oxidized aerosols (LOA). The relative contributions on a yearly average of these factors were HOA 7 %, COA 9 %, BBOA 3 %, Ammonium Nitrate 3 %, Ammonium Sulfate 28 %, MOA 580 24 % and LOA 26 %. This work applies a new methodology to a year-long ACSM dataset, provides insights on the sources of the non-refractory species of ambient aerosol and using innovative tools for applying PMF (Rolling window) enables the study of the temporal variation of these sources and also the variability of their composition.

## 1 Introduction

585 The adverse effects of atmospheric aerosols on human health and the environment have been addressed by many studies (Ramanathan et al., 2009; Wilson and Suh., 1997; Pope et al., 2000; Jacobson et al., 2001). Particulate air pollution is one of

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the most important causes of respiratory diseases (Dominici et al., 2006; Medina-Ramón et al., 2006). Apart from the negative consequences on human health, atmospheric aerosol may also be considered responsible for direct and indirect effects on climate. Ambient aerosols are mixtures of different chemical components that may cause both light absorption and scattering (U.S.A EPA, 2012). For example, black carbon can absorb light at all wavelengths, brown carbon absorbs ultraviolet and visible radiation (Moosmüller et al., 2009), while organic aerosol (except for brown carbon), nitrate and sulfate particles are responsible mainly for light scattering (Cabada et al., 2004). Additionally, aerosol particles can act as cloud condensation nuclei (CCN) particles affecting cloud microstructure and lifetime (Rosenfeld et al., 2008). The overall effect of aerosols on climate and the aerosol–cloud interaction remain highly uncertain. Therefore, it has become essential to study ambient aerosol’s physical and chemical properties thoroughly.

The organic fraction comprises 20-90 % of ambient fine aerosols (Kanakidou et al., 2005, Chen et al., 2022). Depending on their origin and formation process, they can be categorized either as primary (POA) or secondary (SOA) organic aerosols. They are considered as primary when they are directly emitted from a source, either anthropogenic or natural. Secondary organic aerosols are the organic aerosols that are generally formed through the oxidation of Volatile Organic Compounds (VOCs). VOCs quickly react with oxidants, such as hydroxyl radical (OH), ozone (O<sub>3</sub>) and NO<sub>3</sub><sup>-</sup> radical, to form semi-volatile and low-volatility organic vapours (Robinson et al., 2007), which then condense onto pre-existing aerosol-forming secondary organic aerosols (SOAs). SOAs can stay in the atmosphere long enough to undergo continuous oxidation and growth via coagulation and gas to particle condensation.

Inorganic species also comprise a significant fraction of atmospheric particulate matter. Secondary sulfates are found in the atmosphere mainly in the forms of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>3</sub>, after the neutralization of sulfuric acid by ammonia (Biggins and Harrison., 1979). Ambient ammonium nitrate is formed through the oxidation of anthropogenic NOx emissions (NO and NO<sub>2</sub>) to nitric acid (HNO<sub>3</sub>), which eventually reacts with ammonia (NH<sub>3</sub>) (Stelson et al., 1979). Ammonia is emitted into the atmosphere from different sources and processes, such as biomass burning, vehicle emissions, livestock emissions, the use of NH<sub>3</sub> based fertilizers and pesticides in agriculture, etc. (Behera et al., 2013; Schlesinger and Harley, 1992). Chloride containing particles are also released into the atmosphere during biomass combustion or are found in the form of NH<sub>4</sub>Cl (Lobert et al., 1999).

Over the years, mass spectrometry instruments have gained more reliability since their time resolution, sensitivity and selectiveness have improved, making them a powerful tool for chemical on–line and real–time characterization of ambient particulate matter. The time of Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) is a descendant instrument of the Aerosol Mass Spectrometer (AMS), which enables the real-time quantification and chemical characterization of the non-refractory PM<sub>1</sub> (Particulate Matter <1µm) species (species that rapidly vaporize at 600 °C under vacuum conditions): organic, sulfate, nitrate, ammonium and chloride (Fröhlich et al., 2013). The application of different source apportionment (SA) techniques (e.g. Positive Matrix Factorization) on the derived mass spectra has enabled the in depth investigation of the sources and formation processes of organic aerosols (Ulbrich et al., 2009; Crippa et al., 2014; Zhang et al., 2019).

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655 Previous studies on particulate matter source apportionment in Greece have mainly focused on inorganic datasets (Karanasiou et al., 2009; Argyropoulos et al., 2017; Diapouli et al., 2017; Manousakas et al., 2017; Manousakas et al., 2020; Manousakas et al., 2021), while only a few of them centred on measurements of the organic fraction measured by aerosol mass spectrometers (AMS/ACSM) (Stavroulas et al., 2019; Florou et al., 2017; Kostenidou et al., 2015). SA of organic aerosol is typically performed using the PMF algorithm. One of the latest advances in source apportionment modelling is the rolling window technique (Parworth et al., 2015; Canonaco et al., 2021; Chen et al., 2021; Tobler et al., 2021) that is based on the modelling of a moving period of the initial dataset at each iteration. This technique has been found useful in order to examine the temporal variation of the identified factors and especially for the oxygenated organic aerosols, whose chemical fingerprint can vary in time. A few studies have included in source apportionment schemes both the organic fraction and the inorganics from mass spectrometric instruments (Sun et al., 2012; McGuire et al., 2014; Hao et al., 2014; Äijälä et al., 2019).

660 All of these studies revealed that the inclusion of inorganics in SA studies improves both the solution obtained and the understanding of atmospheric processes and mixing between species. Long term source apportionment studies on organic aerosols in recent years have covered a wide range of sites. Nevertheless, a long period of combined organic and inorganic source apportionment study spanning over a period of a year has not yet been published, leaving a gap in the comprehensive understanding of ambient aerosol sources, formation processes and mixing.

670 This study is the first one to present the results of two PMF analyses, one on the organic fraction and another on the combined organic and inorganic dataset of a ToF-ACSM, for one year. A comparison between the two solutions was performed and the mixing of organics and inorganics in different seasons was investigated. The validity of the retrieved factors from both analyses was assessed based on the model residuals, the statistical uncertainty of each one of the retrieved solutions and their correlation with specific external data.

## 675 2 Methods and Instrumentation

### 2.1 Measurement site

Measurements were performed at the Demokritos station (DEM), a member of the Global Atmosphere Watch program (GAW) and part of the Aerosol, Clouds, and Trace Gases Research Infrastructure (ACTRIS) and the PANhellenic infrastructure for Atmospheric Composition and climate change (PANACEA) (37.995° N, 23.816° E), at 270 m above sea level (a.s.l.) (Eleftheriadis et al., 2021). The station is located within the National Centre for Scientific Research (NCSR) “Demokritos” campus, a vegetated area at the foot of Mount Hymettus, about 8 km to the Northeast of Athens city centre (Figure 1). The measurement site can be considered representative of the atmospheric aerosol in the suburbs of the Athens Metropolitan Area, since during the day it is exposed to pollution transported from the urban area of Athens under most atmospheric conditions (western wind direction), whereas it is also occasionally influenced by incoming regional aerosol.

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**Figure 1.** The Demokritos Atmospheric Aerosol Measurement station in Ag. Paraskevi, Athens, Greece, DEM (GAW, ACTRIS). The maps were obtained from © Google Maps (maps.google.com) Imagery 2021 Terrametrics, Mapdata 2021 and modified by the authors.

## 2.2 Instrumentation

Measurements of mass concentrations of non-refractory species (NRS) of PM<sub>1</sub> (i.e. organic; sulfate, SO<sub>4</sub><sup>2-</sup>; nitrate, NO<sub>3</sub><sup>-</sup>; ammonium, NH<sub>4</sub><sup>+</sup>; chloride, Cl<sup>-</sup>) were performed from November 2017 to October 2018 by a Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) (Aerodyne Research Inc., Billerica, MA, USA). The ToF-ACSM was operated with a time resolution of 10 min and the data were afterward averaged to 30 min. The 10 min detection limit for each species measured with the ToF-ACSM is 0.062 for organics, 0.006 for SO<sub>4</sub><sup>2-</sup>, 0.007 for NO<sub>3</sub><sup>-</sup>, 0.058 for NH<sub>4</sub><sup>+</sup> and 0.003 for Cl<sup>-</sup> (Fröhlich et al., 2013). A detailed description of the instrument's main components and the principle of operation is given by Fröhlich et al. (2013). In short, the instrument sampled dried (RH < 40 % with a Nafion drier) ambient aerosol through a PM<sub>2.5</sub> virtual impactor. The aerosol entered the instrument through the inlet system which consists of an automatic three way valve switching system (i.e. a filter was interposed, every 20 sec, into the flow of ambient air to the instrument to measure the background signal), a critical orifice (i.e. sample flow 85 mL min<sup>-1</sup>), and the aerodynamic lens. The aerodynamic lens focuses the submicron aerosol particles in a narrow beam into the vacuum chamber, at the end of which the particles impact on a heated (600 °C) tungsten plate. There, the non-refractory species are flash vaporized and subsequently ionized by electron impact (EI) at 70 eV and detected, according to their mass-to-charge ratios, by the Tofwerk time-of-flight mass analyser (ETOF).

The Relative Ionization Efficiencies (RIEs) used for organics, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> were 1.4, 1.1 and 1.3, respectively (Fröhlich et al., 2013), while the RIE values for SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were calibrated during the campaign and were found to be 1.2 and 3.4, respectively. Additionally, a collection efficiency (CE) correction factor was applied to all ACSM data, to compensate for particle losses during their collection. The collection efficiency chosen depends on three parameters (Middlebrook et al., 2009); firstly, on the particulate water content. To account for that, a Nafion drier was placed in the inlet line. CE also



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depends on the ammonium nitrate fraction of the aerosol (ANMF), which was calculated to be higher than 0.4 for 99.9 % of the data indicating that a constant CE value of 0.5 should be optimum. Finally, it depends on the acidity of the aerosol. Based on that, the CE was calculated 0.52 for NDJF, 0.49 for MAM, 0.55 for JJA and 0.56 for SO, while for the yearlong period it was 0.52. Therefore, the constant value of 0.5 was selected and this small variability should not affect the solution given also that the overall uncertainty for CE is 30 % (Bahreini et al., 2009).

The equivalent black carbon (eBC) mass concentrations were also measured by an aethalometer AE33 (Magee Scientific Corp., Berkeley, CA 94703, USA). The AE33 provides a real-time compensation for multiple scattering in the filter matrix and loading effects using the DualSpot Technology (Drinovec et al., 2015). The light absorption coefficients and the respective eBC concentrations (using an appropriate Mass Absorption Cross section number, MAC) at seven wavelengths (370, 470, 520, 590, 660, 880 and 950 nm) are provided by the instrument. In this study, the eBC concentrations are reported at  $\lambda=880$  nm (Petzold et al., 2013), considering a MAC number to convert absorption coefficient to eBC concentration equal to  $4.6 \text{ m}^2\text{g}^{-1}$  (Kalogridis et al., 2018). Additionally, the contribution of wood burning and fossil fuel to the total eBC mass concentrations can be found with application of the Aethalometer model as described by Sandradewi et al. (2008) and shown in Eq.(1)-Eq.(3):

$$\frac{b_{abs}(\lambda_{UV})_{ff}}{b_{abs}(\lambda_{IR})_{ff}} = \left(\frac{\lambda_{UV}}{\lambda_{IR}}\right)^{-\alpha_{ff}} \quad (1)$$

$$\frac{b_{abs}(\lambda_{UV})_{wb}}{b_{abs}(\lambda_{IR})_{wb}} = \left(\frac{\lambda_{UV}}{\lambda_{IR}}\right)^{-\alpha_{wb}} \quad (2)$$

$$b_{abs}(\lambda_{UV})_{wb} = \left(\frac{1}{1 - \left(\frac{\lambda_{UV}}{\lambda_{IR}}\right)^{-\alpha_{ff}} \left(\frac{\lambda_{UV}}{\lambda_{IR}}\right)^{\alpha_{wb}}}\right) (b_{abs}(\lambda_{UV}) - \left(\frac{\lambda_{UV}}{\lambda_{IR}}\right)^{-\alpha_{ff}} b_{abs}(\lambda_{IR})) \quad (3)$$

where  $\alpha_{ff}$  and  $\alpha_{wb}$  are the absorption Ångström exponents for pure fossil fuel combustion and pure wood burning aerosol, respectively;  $b_{abs}(\lambda_{UV})$  and  $b_{abs}(\lambda_{IR})$  are the absorption coefficients measured at the UV (470 nm) and IR (950 nm) wavelengths, respectively, with the blue (470 nm) channel found to perform better than the traditionally formulated UV channel (370 nm) in the aethalometer model  $b_{abs}(\lambda_{UV})_{wb}$  &  $b_{abs}(\lambda_{IR})_{wb}$  and  $b_{abs}(\lambda_{UV})_{ff}$  &  $b_{abs}(\lambda_{IR})_{ff}$  are the corresponding absorption coefficients at these two wavelengths that are related to wood burning (wb) and fossil fuel combustion (ff). According to the earlier sensitivity study for our area  $\alpha_{ff}$  and  $\alpha_{wb}$  values was found equal to 0.9 and 2 respectively (Diapouli et al., 2017; Kalogridis et al., 2018).

In addition, the elemental carbon (EC) and organic carbon (OC) mass concentrations were measured by the thermo-optical transmittance method (OC/EC Semi-Continuous Field Analyzer, Sunset Lab, Inc.). The instrument collected aerosol samples on a 3 h basis from a  $\text{PM}_{2.5}$  cut-off inlet and a flow rate of  $8 \text{ l m}^{-1}$ . The sampling inlet was equipped with an activated carbon denuder for the removal of organic gases from the air stream (Diapouli et al., 2017). The sample analysis was performed applying the EUSAAR2 thermal protocol (Panteliadis et al., 2015). Moreover, a high energy, polarization geometry energy-dispersive XRF spectrometer (Epsilon 5 by PANAnalytical, Almelo) was used for analysis on  $\text{PM}_{2.5}$  filters, which measured the following elements: Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr and Pb (Manousakas et al., 2017). Nitrogen oxides (NOx) and ozone ( $\text{O}_3$ ) measurements with a 1 hour time resolution were obtained from the air quality

**Deleted:** Generally, CE varies with chemical composition, acidity and water content of the particles (Matthew et al., 2008). However, in the present study we applied a constant CE value of 0.5 to account for the particle losses, given that the ammonium to nitrate fraction was found below 0.4 for the majority (99.9 %) of the data points (Middlebrook et al., 2012).¶

**Deleted:** Afterwards, the fraction of fossil fuel and wood burning eBC (eBCff and eBCwb, respectively) was determined as described in the Supplement (Sect. S1).

monitoring station of the Greek Ministry of Environment and Energy air quality network located at the grounds of NCSR Demokritos campus. Standard meteorological parameters (T, Solar radiation, RH, wind speed and wind direction) were recorded at an hourly time interval. The meteorological sensors were installed on a meteorological mast, at 10 m height above ground.

### 2.3 Positive Matrix Factorization (PMF)

The data derived from the ToF-ACSM were analysed using the Aerodyne software Tofware version 3.2. The concentration in nitrate-equivalent mass and the error matrices of each species were exported from Tofware for further assessment via the PMF model. The method was implemented within the Source Finder Pro software package (SoFi Pro, Datalystica Ltd, Villigen, Switzerland) that uses the multilinear engine ME-2 (Paatero 1999) as a PMF solver (Canonaco et al., 2021). PMF is a bilinear model used to describe a non-negative matrix X using two factors (G and F), while there is also a residual matrix (E) containing the data that could not be described with G and F (Eq. (4)):

$$X = GF + E, \quad (4)$$

For our data, the matrix X is the mass spectra of organics or total NRS through time, G is the time series of each factor and F is the matrix of the factors profile as described by Eq. (4):

The aim of this model is to find the minimum of the quantity Q which is the sum of the square of the ratio of the residuals (e) to the uncertainties ( $\sigma$ ) of all the X matrix data as given by Eq. (5):

$$Q^m = \sum_{i=1}^m \sum_{j=1}^n \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2, \quad (5)$$

Where m is the number of rows of F and n is the number of columns of the matrix G. The minimization of this quantity ensures that data points with low signal-to-noise ratio ( $\frac{e_{ij}}{\sigma_{ij}} \ll 1$ ) are taken less into consideration.

Partially constrained G and/or F matrix, or a-value approach, is one of the techniques used in order to cope with the model's rotational ambiguity, which is the potential of F and G matrices to rotate, giving thus a very high number of solutions. The a-value represents the value to which the solution is supposed to vary from a reference value as shown in Eq. (6) and Eq. (7):

$$f_{j,solution} = f_j \pm a \cdot f_j, \quad (6)$$

$$g_{i,solution} = g_i \pm a \cdot g_i, \quad (7)$$

Where  $f_j$  and  $g_i$  are rows and columns of the matrices F and G respectively.

An important feature of the SoFi Pro software is that it enables the user to apply specific or random a-values to constrain the input profiles and/or time series with auxiliary reference data (Canonaco et al., 2013). Moreover, SoFi supports the downweighting of the data for which the signal to noise ratio is low, in order to minimize their effect on the solution. To assess the statistical uncertainty resulting from the changes in factor profiles, a resampling strategy is usually applied in PMF modelling, called bootstrapping (Efron, 2000). This uncertainty is estimated based on variations of the obtained factor

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profiles coming after the rearrangement of the original input that generates a new set of initial matrices at each iteration. SoFi Pro includes the rolling window technique that allows the user to track the variability of the factors by applying a window with selected length (usually 7, 14 or 28 days, depending on the size of the studied dataset) that moves with a chosen step. Calculations are repeated in that moving span, providing the temporal changes in both profile and time series of the factors (Canonaco, 2021).

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## 2.4 Wind air mass trajectory analysis

To investigate the potential location of NRS emission sources, wind and air mass backward trajectory analysis was performed. The wind analysis used the conditional probability function (CPF) to provide directional information concerning the major sources of NRS species. The CPF calculates the probability that in a particular wind sector and wind speed interval, the concentration of a species is greater than some specified value, which is usually expressed as a high percentile of the species of interest (e.g. 75<sup>th</sup> percentile). In the present study, CPF analysis was performed by using the OpenAir software (Carslaw and Ropkins, 2012). A wide range of percentile values was examined to get a more complete insight into the sources of each species and each factor.

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To assess the potential influence of long range transport events to NRS concentrations, the air mass backward trajectories were calculated using the NOAA Hybrid Single-Particle Lagrangian Intergrated Trajectory (HYSPLIT-4) model (Draxler and Hess, 2004; Stein et al., 2015). The 120 h backward trajectories were computed every 1 hour, at a height level of 1000 m Above Ground Level (AGL), and then further analyzed using ZeFir v3.7 (Petit et al., 2017) for the identification of the potential aerosol sources from the Potential Source Contribution Function (PSCF). The PSCF values can be interpreted as a conditional probability describing the potential contribution of a grid cell to the high air pollutant loadings at the receptor site. Specifically, the basis of PSCF is that if a source is located at (i, j), an air parcel back trajectory passing through that location indicates that material from the source can be collected and transported along the trajectory to the receptor site. The PSCF is calculated as shown in Eq. (8):

$$PSCF = n_{ij}/m_{ij} \quad (8)$$

Where  $n_{ij}$  is the number of times that the trajectories passed through the cell (i, j) and  $m_{ij}$  is the number of times that a source concentration was high when the trajectories passed through the cell (i, j). The criterion for determining  $m_{ij}$  is based on the distribution of the measured values (i.e. 90<sup>th</sup> percentile).

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The trajectories were computed using the Global Data Assimilation System (GDAS) meteorological dataset.

## 3 Source apportionment

### 3.1 Data analysis

In the present study, two different PMF analyses were performed to apportion the sources of organic and inorganic aerosol. The first analysis included only the mass spectra of the organic aerosol (organic aerosol matrix), whereas in the second

analysis the mass spectra of organic and inorganic aerosol (combined matrix) were combined ~~for~~ PMF analysis, in order to investigate the sources and dynamic processes of non-refractory PM<sub>1</sub> aerosol. In the following, profile refers to the mass spectrum of a given factor and variable refers to an individual mass to charge ratio (m/z).

For the deconvolution of the sources of the total NRS, the organic and inorganic variables and error time series matrices were exported from Tofware for each species separately (org, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>) without applying RIEs or the CE correction, with a time resolution of 10 min, which was then averaged to 30 min. In order to create the combined matrix, the variables of the inorganics that are characteristic for each species were added to the organics matrix; that is m/z 18, 32, 48, 64, 80, 81 and 98 for SO<sub>4</sub><sup>2-</sup>, m/z 30 and 46 for NO<sub>3</sub><sup>-</sup>, m/z 16 and 17 for NH<sub>4</sub><sup>+</sup> and m/z 35 and 36 for Cl<sup>-</sup>. The variables of inorganic species selected as representative of each species, were perfectly correlated with the respective species (R<sup>2</sup>≈1) and accounted for the major fraction of their total mass concentration (> 76 %). ~~The error values for each inorganic variable were~~ downweighted before PMF analysis by a factor of sqrt(N) (Ulbrich et al., 2009), where N is the number of ions of each species that are duplicate according to the fragmentation table (Allan et al., 2004).

In order to correct the results from nitrate-equivalent to real mass concentrations the RIEs and CE needed to be applied. This took place easily in the case of the organic matrix, by dividing the respective variables with the CE (0.5) and RIE of organics (1.4). In the case of the combined matrix though, the factors contained more than one species, so the application of the RIEs became more complicated. The time series of each factor were decomposed to the time series of all the variables that constitute each factor using the SoFi interface. Then, at each variable, the RIE of the respective species that this variable belongs to is applied, as is also the CE and afterwards, the time series of these variables are added to form the initial factor time series. After applying PMF analysis, the mass concentration of each species was calculated based on the contribution of the variables included in the initial matrix to the total mass concentration of each species.

### 3.2 PMF analysis and factor identification

The first step for source apportionment was to perform PMF analysis on the winter months (November–February) in order to identify the number of factors. ~~For this purpose,~~ unconstrained winter simulations took place examining a broad number of sources (3–12 factors). To identify the optimum number of factors, the slope of the Q/Qexp plot was examined, as well as the residuals of the diurnals and of the factor ~~profiles~~. This resulted in a five factors solution for the organic aerosol matrix and a seven factors solution for the combined matrix. As previously mentioned, the OA matrix was described by a hydrocarbon-related factor (HOA), a cooking aerosol (COA), a biomass burning OA (BBOA) and two secondary OA (MO-OA and LO-OA). The combined organic–inorganic matrix was best described with the same primary factors, ~~two~~ secondary inorganic factors (ammonium sulfate and ammonium nitrate) and two secondary aerosols (MOA and LOA). The next step for both analyses was to study each season separately, applying random a-values from 0 to 0.5 to the constant profiles of the primary factors and enabling the bootstrap technique for one hundred simulations in order to assess the uncertainties and check the stability of the solution obtained. Specific criteria were applied to the organic matrix to select the environmentally reasonable solutions (Chen et al., 2021), which are summarized in Table S1. Specifically, the correlation

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900 between HOA and eBCff was used as a criterion for this factor and for BBOA its correlation with eBCwb was used as well as the variation of  $m/z$  60, 73 and 115 explained by this factor. A t-test was also used for these criteria and a p-value lower than 0.05 was chosen; more details of the t-test were introduced in the Supplement of Chen et al. (2021). In the case of COA factor, the ratio of COA concentration at lunchtime (14:00 local time) over COA mass concentrations in the morning (average COA concentration between 09:00 and 10:00 local time) was chosen to be larger than 1. Concerning the SOAs, the fractions  $m/z$  of 43 and 44 were monitored and should be higher than 0.

905 PMF analysis was then conducted on a subset of data defined by a small window of 14 days that is moved in 1 day increments across the entire dataset and as such allows capturing variations of the factor profiles (Canonaco et al., 2021). This resulted in a total of 17200 runs. The mass spectra of the three primary factors obtained through the seasonal PMF simulations were used afterwards as reference profiles for the rolling window runs. In order to select the best solutions, the same criteria for selection were used as described before (Table S1). The averaged solution for both organic aerosol and combined matrix analyses are further discussed in Sect. 4.

It needs to be mentioned that in the combined matrix analysis, for the deconvolution of organic and inorganic sources, the primary OA factors and the two inorganic factors (ammonium sulfate and ammonium nitrate) were constrained with the respective factors identified in winter under the unconstrained simulations, for both seasonal and rolling PMF simulations.

915 Overall, tighter constraints than those applied in the OA modelling were used, allowing for a maximum variability from the anchor profiles of up to  $\pm 20$  % (random a-value 0–0.2). The criteria used in this case were the same as that of the OA interpretation that appears in Table S1.

## 4 Results and Discussion

### 4.1 Fine aerosol chemical characterization

#### 920 4.1.1 Seasonal and diel variability

In Fig. S1 the time series of the NRS derived from the ToF-ACSM are presented. All time-related plots are in local time. The time series imply strong temporal variation of the NRS mass concentration. The maximum 30 min average total NRS concentration recorded during this campaign was  $61.6 \mu\text{g m}^{-3}$ , while, overall, the total NRS concentration was higher than  $5 \mu\text{g m}^{-3}$  for 74 % of the period studied. As highlighted in Table S2, the organic fraction, as well as the total NRS concentration, presented higher values in spring and summer rather than winter at our site. This was probably connected to the location characteristics of our site, which is located at the suburbs of Athens. In winter, higher contribution of the anthropogenic emissions (e.g. BBOA) to the total organic mass concentration was observed compared to spring and summer. In the latter case, the absence of precipitation and the increased production of biogenic volatile organic compounds in the forest near our station (Lappalainen et al., 2009) combined with enhanced photochemical activity may have led to higher formation of SOA, consequently resulting in higher organics concentrations (Table S2). Simultaneously, sulfate levels were

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The assessment of the uncertainty and the errors of the OA factors retrieved is a key for evaluating the solution obtained, since PMF is considered as a technique. One way to assess the uncertainty of the retrieved solution is through the evaluation of the scaled residuals. For 99 % of the data the scaled residuals of the organic fraction PMF analysis were in the range of  $\pm 3$ , which is the suggested reasonable range (Paatero and Hopke., 2003). This percentage was reduced to 91 % for the combined analysis, although it remained high enough to assume the model was well fitted. The points at which the scaled residuals exceed these thresholds ( $\pm 3$ ) were associated with peaks at OAs and oxidized aerosols in OA and combined PMF analysis respectively, which was expected since these factors are linked to higher uncertainties due to being unconstrained.¶ Additionally, the PMF errors modelled for the retrieved factors, which were represented as the slope of the linear fit of the interquartile to median mass concentration values for each factor, were studied. Overall, higher error values were observed for SOA than POA factors, given their profiles perform higher variability. The combined PMF analysis was in general associated with lower PMF errors than the OA matrix analysis for all factors (e.g. 9.5 % for combined HOA instead of 10 % for OA HOA, 5 % for combined COA instead of 7 % for OA COA, 3 % for combined matrix BBOA instead of 5 % and 13 % on average for oxidized aerosols rather than 19 % for SOAs). In both cases, however, the errors were low enough to claim that we have arrived at optimal solutions.¶

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960 the result of regional transport, photochemical activity and local meteorology. The regional character of sulfate for all seasons is indicated by the HYSPLIT back trajectories in Fig. S2. In winter, sulfate values are lower due to enhanced precipitation, although regional sulfate was being transported to the station, while in the other seasons regional transport combined with local photochemical activity and less precipitation results in higher sulfate values (Stavroulas et al., 2019, Theodosi et al., 2018; Cusack et al., 2012, Dayan et al., 2017). Nitrate, which is semivolatile, presented, as expected, higher concentrations in the cold months when the lower temperature favours the formation of ammonium nitrate and partitioning nitrate into the particle phase, instead of the gas phase in which it appears when temperature rises and nitrate is predominantly in the HNO<sub>3</sub> form (Lin and Cheng., 2007). Ammonium presented higher concentrations in warmer months, following a similar pattern as that of sulfate. Chloride exhibited its highest concentration in winter correlating its emission to biomass burning, as was also resolved by the unified matrix PMF analysis discussed in Sect. 4.2.2.

970 In comparison to the results reported in a previous study conducted in the centre of Athens (Stavroulas et al., 2019) by the National Observatory of Athens (NOA), the suburban site presented lower concentrations for all NRS in wintertime, which is mainly attributed to the higher anthropogenic emissions generally occur in the urban area of Athens. Specifically, we observed that all NRS presented concentration levels 3 to 4 times lower than those at the centre of Athens in winter except for sulfate for which concentrations were more similar. For the other seasons, the inorganic species presented similar concentration levels at both sites (i.e. higher contribution of secondary aerosol than primary emissions to the observed NRS levels), while organics were higher at the suburban site in spring and autumn. This is probably related to the enhanced SOA formation at the suburban area which is dominated by pine tree vegetation. Black carbon exhibits lower concentrations in the suburbs, in agreement with the comparison study conducted by Kalogridis et al (2018).

975 Figure 2 presents the daily variability of NRS species for each period studied. Nitrate always increased during the night. However, in winter and spring a distinct morning peak also appeared which is probably linked to photochemical activity, meteorological conditions (gas-to-particle equilibrium) and ammonia availability. On the other hand, the diurnal profile of sulfate was flat in winter, consistent with regional sources and meteorological conditions that do not favor local photochemical activity. In spring, summer and early autumn sulfate presents a diurnal structure that is related to local photochemical activity and boundary layer height. Ammonium seasonal diurnal variability agreed quite well with that of sulfate. Chloride presented two distinct peaks (i.e. morning and evening) for all the seasons, related to temperature-dependent gas-particle partitioning of chlorine (i.e. chloride is primarily detected as ammonium chloride), biomass burning emissions and prevailing atmospheric conditions. The organic fraction showed a midday/early afternoon and an evening peak. Its diurnal cycle was most likely a combination of primary emissions from various sources, and secondary aerosol formation during the day. It has to be noted that all NRS species appeared to have increased concentrations during the night which may also be attributed to the increased atmospheric stability during the night (shallow nocturnal boundary layer).

980 On average, during the period of this campaign particulate matter consisted of 51.3 % organics, 34.7 % sulfate, 9.4 % ammonium, 4.4 % nitrate and 0.2 % chloride. In Fig. S3 the wind rose plots for each season appear, while Fig. S4 presents the seasonal bivariate CPF polar plots for all NRS to investigate the potential source regions of these species. The polar plots

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**Deleted:** This is in agreement with other studies performed in Athens (Theodosi et al., 2018; Stavroulas et al., 2019). HYSPLIT was used to track the different seasonal long-range origins of sulfate. As appears in Fig. S2, in spring, summer and early autumn sulfate originated mainly from central and eastern Europe and also Turkey, which are known to carry a significant amount of industrial emissions (Karagulian et al., 2015). This effect was observed as a maximum value of sulfate concentration for these seasons.

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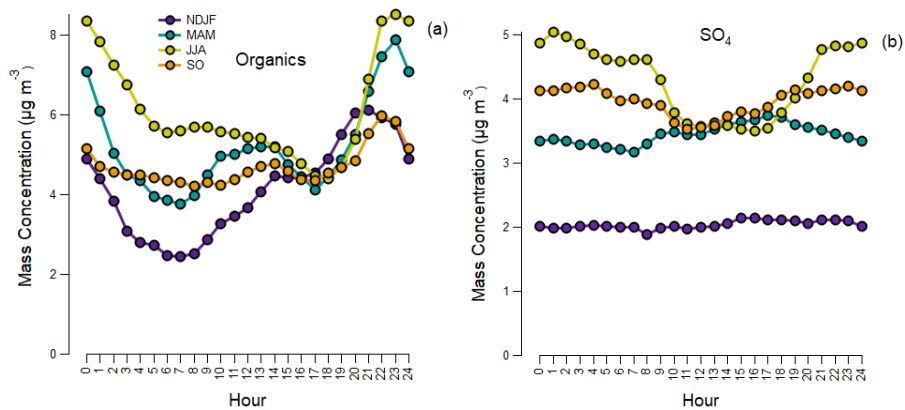
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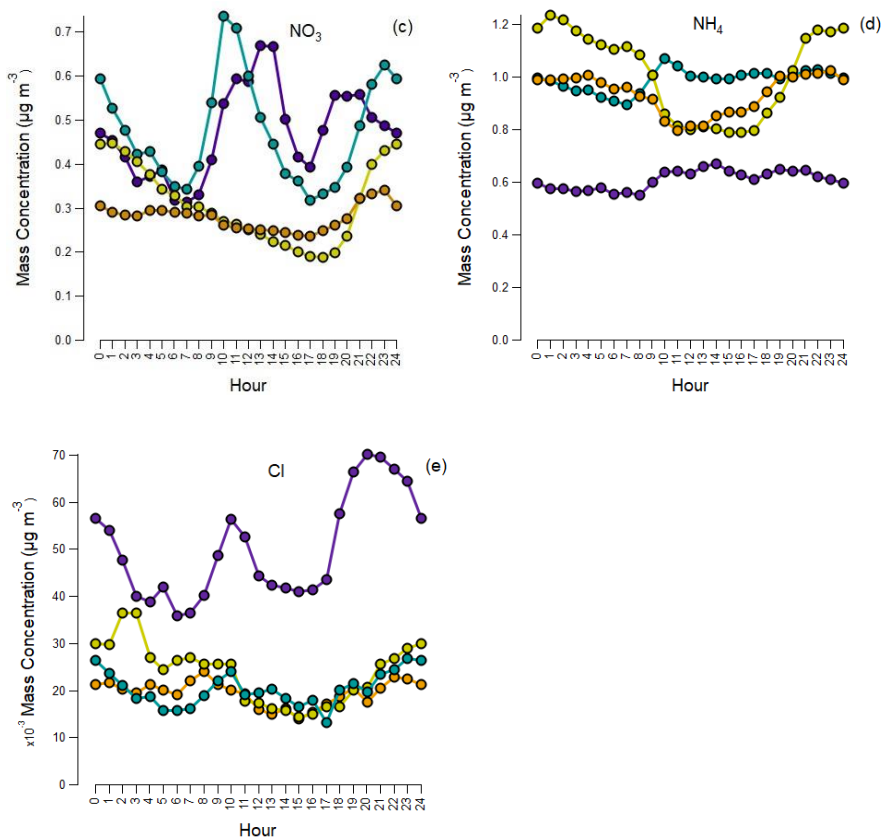


for organics showed highest concentrations for low and moderate wind speeds near the center area as well as in SE and NE directions indicative of both local emissions and regional transport. High concentrations of sulfate were observed for low, moderate and high wind speeds from the SE sector, suggesting that a combination of local emissions and regional and long-range transport may significantly contribute to the observed sulfate levels. This was also the case for ammonium, underlying the common origin of these species. Nitrate was primarily locally produced. The high potential source region of particulate nitrate coincided with the one observed for NO<sub>x</sub>, linking the particulate nitrate with the traffic-related NO<sub>x</sub> emissions (vehicle exhausts). High concentrations of chloride were observed at relative low wind speed implying that it was rather locally emitted, probably linked to local secondary aerosol formation and biomass burning emissions, as will also be discussed in Sect. 4.3.

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**Figure 2.** Mean diurnal variation of hourly concentrations of organics (a), sulfate (b), nitrate (c), ammonium (d) and chloride (e) for each period: November–February (NDJF), March–May (MAM), June–August (JJA), September–October (SO) in local time.

#### 4.1.2 Data from collocated instruments

Figure S5 depicts the time series of supplementary data from collocated instruments; that is eBC, NO<sub>x</sub>, O<sub>3</sub>, EC/OC, temperature, relative humidity, wind speed and wind direction. As shown, equivalent BC<sub>ff</sub> presented a quite stable contribution to ambient particulate matter throughout the year, while eBC<sub>wb</sub> had a stronger influence in winter as expected due to biomass burning emissions related to residential heating. During the study period, the cold months (October–March) were characterized by high humidity (74 % mean) and relatively low temperatures (12.7 °C mean), while the warm months

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(May–September) were characterized by moderate humidity (54 % mean) and temperature (24 °C mean) levels. The prevailing wind speed and direction are presented for each season. As highlighted also in Fig. S3, winter was influenced mainly by southwestern winds, implying a significant contribution from the emissions related to anthropogenic activities from the city centre. In spring the air masses originated mainly from southwest (urban city centre) and southeast (downslope wind) directions, possibly associated with Saharan dust events as well. In summer, the wind originated mainly from the southeast and northeast directions, underlying the role of regional transport along with the local aerosol emissions and formation processes, while in September and October the measurement site was mainly affected by north-western wind directions (regional and long–range transported aerosol).

#### 4.2 PMF analysis of organic aerosols

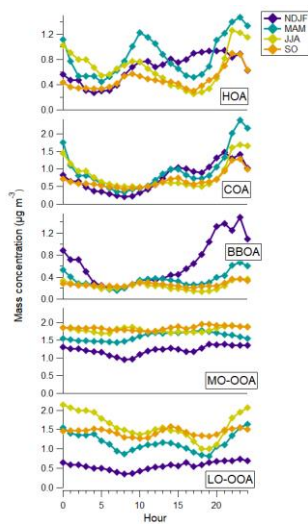
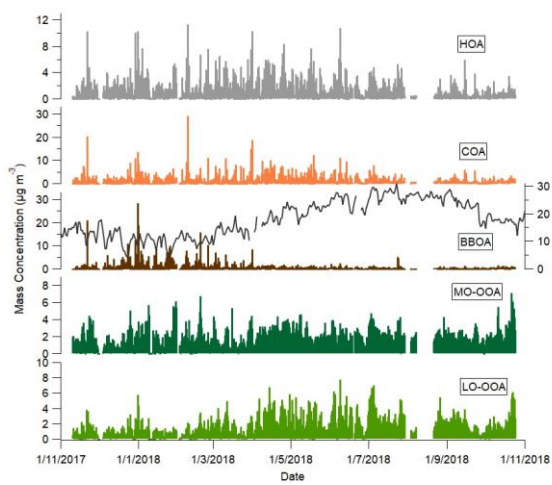
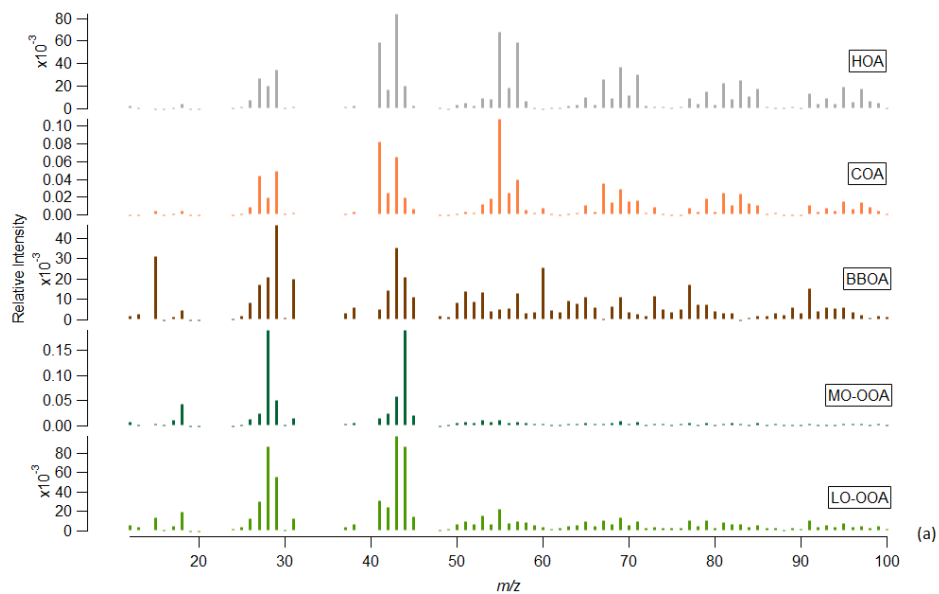
The profiles of the five factors for  $m/z$  10 to 100, are presented in Fig. 3a, along with the time series (Figure 3b) and the diurnal variation patterns (Figure 3c) of the respective mass concentrations. The remaining part of the mass spectrum is depicted in Fig. S6. In Fig. S7a, the polar plots present the spatial distribution for each factor, while in Fig. S7b the polar plots for external data (eBCff, eBCbb, NO<sub>x</sub> and O<sub>3</sub>) are depicted. The relative contribution and actual mass loadings for each factor and season are summarized in Table S3. The mass spectra, diurnal variations and potential sources of these factors will be discussed in detail in the following sections.

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**Figure 3.** Mass spectra (a), time series (b) and diurnal trends (c) of the five organic aerosol factors.

### Primary Organic Aerosols

The hydrocarbon-related (HOA) factor, linked to fossil fuel combustion emissions, was identified based on its distinctive mass spectrum, and attributed to the traffic-related emissions from the urban area of Athens, that are transported to the measurement site under westerly wind directions (Figure S7a). From the plots in Fig. S7b it can be seen that HOA shared the same emission origin with NO<sub>x</sub> and eBC<sub>ff</sub>. The HOA profile was dominated by peaks characteristic of the alkanes, with high contribution of  $m/z$  at 27, 41 and 55 ( $C_nH_{2n-1}^+$ ) and 29, 43 and 57 ( $C_nH_{2n+1}^+$ ) (Zhang et al., 2005). The fingerprint of the traffic-related factor profile has been identified to be quite stable over spatially different sites across Europe (Crippa et al., 2014). In the present study, the unconstrained HOA profile obtained was highly correlated with the HOA profile from Crippa et al (2013) ( $R^2 = 0.98$ ), which is typically used to constrain the HOA profile in urban environments. The HOA factor presented an overall good correlation with the time series of fossil-fuel combustion indicators like NO<sub>x</sub> ( $R$ -Pearson = 0.69), eBC<sub>ff</sub> ( $R$ -Pearson = 0.69) and EC ( $R$ -Pearson = 0.58) as shown in Table S4. The good agreement between the HOA and the traffic-related external parameters validated the correct identification of the HOA profile and the accurate separation of COA from HOA. In general, the peaks observed at the time series of this factor coincided with peaks also observed in the respective external data time series, eBC<sub>ff</sub> and NO<sub>x</sub>, except for the peaks observed on the 8<sup>th</sup> of February (connected to cooking emissions), and at the end of March, which both will be discussed in detail below. The diurnal variability of HOA's mass concentration presented two peaks, one morning peak at 9:00 and one evening peak at 21:00 (local times), coinciding with the morning rush hours and the evening traffic emissions and the shallow nocturnal boundary layer. As summarized in Table S3, HOA's average contribution to the total OA was 15 %, with its seasonal contribution at 18 % for winter and spring decreasing to 10–13 % in summer and early autumn. The latter decrease in HOA mass concentration and OA contribution was expected, since traffic-related emissions are reduced during the summer in Athens (Stavroulas et al., 2019), while SOA formation is enhanced.

The mass spectrum representative of cooking emissions was also identified in our study. The chemical fingerprint of the COA factor profile was similar to HOA's, in terms that the same variables that dominated the HOA profile were also present in the COA emissions profile, but the  $m/z$  at 55 was the prevailing one. On the 8<sup>th</sup> of February, a distinct peak in COA was observed that was related to the barbeque festival "Smokey Thursday". The simultaneous peak observed at that day in HOA time series was attributed to the enhanced organic aerosol emissions during this event that impedes the model from separating the two factors. The diurnal variability pattern of COA mass concentration presented a bimodal pattern (Figure 3c), with the two peaks coinciding with lunch and dinner time. The OA loading from cooking emissions over the day was lower than the loading from traffic, with a total duration of 8 h. COA's seasonal contribution to total OA followed the same trend as HOA, decreasing from 19% in colder months to 14–16 % in warmer months, while the average contribution of this

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In a study conducted in our station deploying an AMS for a short-term campaign in summer 2012, no cooking emissions were identified, instead two HOA factors were retrieved, one of which was interpreted as mixed traffic and cooking source (Kostenidou et al., 2015). In the present study, the identified COA factor had surprisingly similar characteristics both in terms of the mass spectrum profile as well as the diurnal pattern of COA mass concentration, with the fresh COA factor retrieved in a previous study conducted in Greece (Kaltsonoudis et al, 2017).

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factor was 17.7 %. As shown in Fig. S7a, this factor had a local character, linked to the cooking emissions originating from the urban environment in close proximity to the measurement site.

We were able to resolve a factor dominated by wood burning ( $m/z$  60 and 73) and PAH ( $m/z$  77, 91, 115, 128, 165, 167) tracers. In order to ensure that the PAHs presented in the BBOA profile were attributed to biomass burning (Li et al., 2009), we conducted PMF runs constraining the profile of our BBOA factor with the BBOA profile retrieved from another study (Ng et al., 2011), trying to resolve a PAH-related factor in case it exists; no environmentally reasonable solution could be reached. Additionally, since PAHs can be also generated by gasoline car exhaust emissions (Okuda et al., 2010), we constrained our HOA and BBOA profiles up to the variables at  $m/z$  100 and conducted 100 simulations. Afterwards, using the criteria list, we eliminated the runs in which the PAH-related variables were attributed to HOA instead of BBOA and found out that for more than 70 % of the simulations these variables were associated to BBOA. Other PAH sources may include coal combustion (Okuda et al., 2010), but coal is generally not used in Greece for heating purposes, while the correlation of this factor with industry-related markers measured by XRF analysis on  $PM_{2.5}$  filters was very low (R-Pearson < 0.2 between BBOA and Pb, Cu, Mn, Zn, Sn, Cr, Cd, Rb, S, Fe, V, Ni). Moreover, polar plots revealed no connection between this factor and port emissions (Figure S7a). Thus, we concluded that this factor indeed originated primarily from biomass burning. The time series of this factor highly correlated with the time series of the wood burning fraction of eBC (eBCwb) obtained from the aethalometer (R-Pearson = 0.74), as illustrated in Table S4. The strong dependence of the concentration of biomass burning to the temperature is also depicted in Fig. 3b, where it is clear that the increased contribution of BBOA to OA concentrations generally occurred at low temperature (wintertime). However, the peaks in the time series of this factor were also connected to wild forest fires, like the one that occurred on the 23<sup>rd</sup> of July in the region of Attiki. In any case, all these peaks observed in the BBOA time series were also confirmed by peaks in the eBCwb time series. The winter contribution of BBOA to OA mass concentration was close to 18 % in winter and decreased to 5 % in summer (Table S3). BBOA's spatial distribution (Figure S7a) confirmed the strong local character of this factor, although long-range transport from the North sector may also have contributed to the increased BBOA levels.

#### Oxygenated organic aerosols

The oxygenated organic factors retrieved in the current study were of two types: one more oxidized oxygenated organic aerosol (MO-OOA) and one less oxidized (LO-OOA). Oxygenated organic aerosols (OOA) have as main tracers the  $m/z$  variables at 28, 29, 43 and 44. The MO-OOA profile was dominated by  $m/z$  44 (corresponding to the  $CO_2^+$  ion) instead of  $m/z$  43; the fraction at  $m/z$  44 ( $f_{44}$ ) provides information regarding the degree of oxygenation of the respective factor. On the other hand, LO-OOA mass spectrum was represented by almost equal contributions of  $m/z$  43 and  $m/z$  44 ( $C_2H_3O^+$ ) (Ulbrich et al., 2009). LO-OOA was significantly affected by temperature and presented a pronounced seasonal variation pattern (Figure 3b). LO-OOA's contribution to OA mass concentration in summer (31 %) was double that of winter (14 %) (Table S3). MO-OOA's contribution to the total OA was on average 34 % with no significant seasonal variability. LO-OOA exhibited similar correlation with the three inorganic ions ( $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$ ), except for summer when it was highly

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correlated with  $\text{NO}_3^-$ . MO-OOA showed good correlation with  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  in all seasons and with  $\text{NO}_3^-$  only in September–October. These relationships imply the complicated internal mixing of organic and inorganic species that will be further discussed in Sect. 4.3. From the polar plots presented in Fig. S7, it can be seen that the areas where the probability of SOAs being higher were similar to that of the oxidants  $\text{NO}_x$  and  $\text{O}_3$ . More specifically, MO-OOA originated from areas rich in both  $\text{NO}_x$  and  $\text{O}_3$  concentrations, while LO-OOA was mainly found on the NE and SE of our station, where  $\text{O}_3$  primarily appeared. This highlights possibly different oxidation mechanisms that take place to form the two types of SOAs in our site.

#### 4.3 PMF analysis of submicron aerosols

Figure 4 depicts the average profiles (Figure 4a) of the seven factors resolved from the combined input matrix PMF analysis for  $m/z$  up to 100. The profiles are the result of the average of 100 simulations, after applying the bootstrap technique and a rolling window of 14 days for the PMF runs. In the same figure, the time series (Figure 4b) and the diurnal trends (Figure 4c) of each factor are presented, while Table S5 shows the actual mass loadings of each factor and their relative contribution to the total NRS mass concentration for each season. Figure S8 presents the mass spectrum of NRS factors for  $m/z$  100–200 and Fig. S9 depicts the CPF polar plots of the seven sources identified. Figures S10 and S11 survey the contribution of each species in the NRS factors and the contribution of each NRS factor in the non-refractory species, respectively, in both relative (Figure S10a and Figure S11a) and absolute (Figure S10b and Figure S11b) terms.

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The subtracted  $f_{44}$ – $f_{43}$  triangle plot was used to evaluate the goodness of the fit of the retrieved PMF solution (Ng et al., 2011), emphasizing on the secondary OA factors which are more inclined to change in time, since their profiles were not constrained given that different SOA formation mechanisms may result in quite different mass spectrum profiles. As described in Sect. 3.2, the rolling window approach that was implemented here allows for the temporal evolution of the SOA factors to be further investigated through the subtracted  $f_{44}$ – $f_{43}$  plots. In Fig. S8 the fraction  $m/z$  44 to the fraction  $m/z$  43 plots, after the subtraction of the contribution of the primary factors (Canonaco et al., 2015), are shown for each season (markers are colour coded by concentration). The rectangular and circular markers (colour coded by date) represent the LO-OOA and MO-OOA concentrations, respectively. It can be seen that for all seasons the two SOA factors proposed could fully describe our data as most points fell inside the triangle area (Ng et al., 2011). However, a quite different seasonal pattern was revealed for both OOA factors, according to which, winter presented a vertical arrangement between the two SOA factors, while the shape became more horizontal and moved to the right side of the triangle in summer. During early spring (March) and October the data followed the trend of winter, while in April, May and September they followed a pattern closer to the one presented in warm months. This behaviour was indicative of the different prevailing SOA formation mechanisms for each season. ¶

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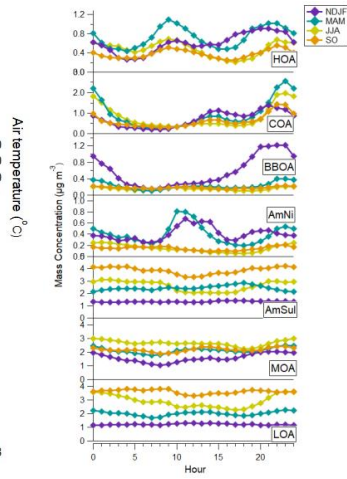
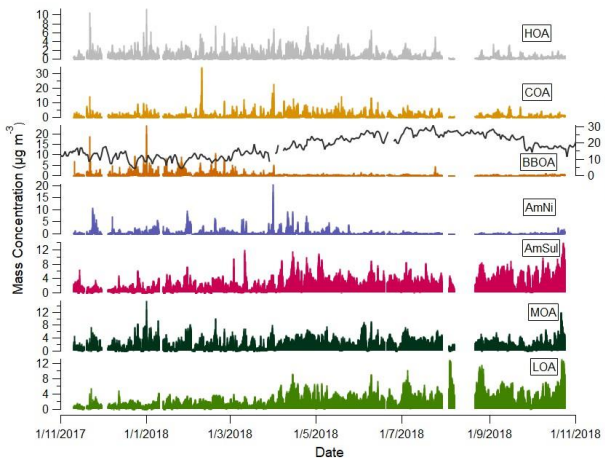
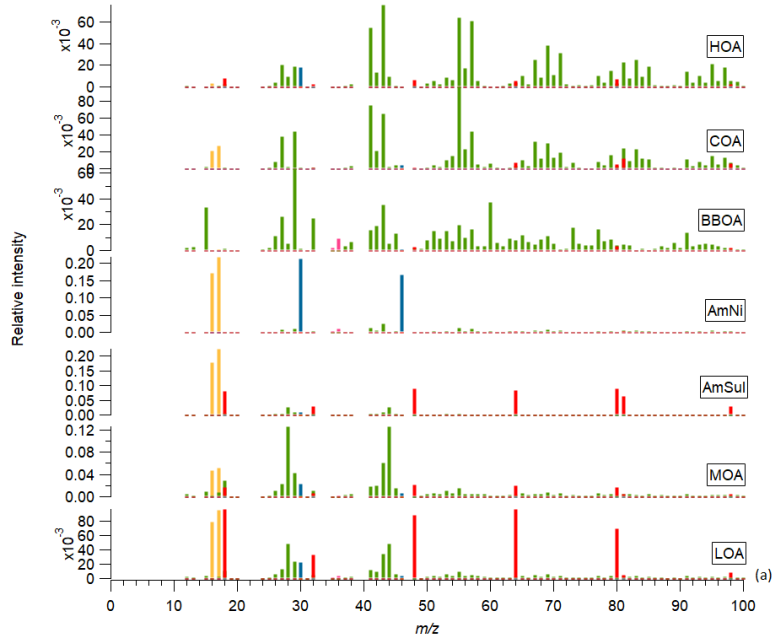
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**Figure 4.** Mass spectra (a), time series (b) and diurnal plots (c) of the seven submicron factors and (d) diurnal plot of AmNi with Relative Humidity and Air Temperature.

#### Primary Organic factors

The hydrocarbon-related factor that was retrieved with the combined matrix PMF method indicated the contribution of the same  $m/z$  variables to the mass spectral profile of organics as the previously described HOA factor. The deconvolution of the combined organic and inorganic dataset matrix revealed a small contribution of inorganic species in this traffic-related factor (Figure S10). More specifically, combined HOA contained 94 % organics, 3.6 %  $\text{SO}_4^{2-}$  and 2.3 %  $\text{NO}_3^-$ . The peaks of the previously resolved HOA (Sect. 4.2) that were attributed to poor separation of the OA factors were not present in the combined matrix analysis, highlighting the improvement of the solution. The polar plot of combined HOA is similar to the one from OA PMF analysis, as well as those of fossil-fuel markers (eBCff and  $\text{NO}_x$ ), implying the good agreement of this factor between both analyses (Figures S7 & S9).

Cooking-related emissions were again resolved as COA. As also shown in Fig. S10, this factor consisted mainly of organics (93.7 %) and presented low contributions of inorganic ions;  $\text{NH}_4^+$  (2 %),  $\text{SO}_4^{2-}$  (3.8 %) and  $\text{NO}_3^-$  (0.5 %). COA's mass spectral profile resolved from combined PMF analysis resembled the previously identified one. The diurnal pattern of this factor presented again two peaks that coincided with lunch and dinner time. Moreover, the polar plots of COA revealed again local emissions (Figure S9).

The factor connected to biomass burning was also identified through the combined PMF analysis. In this factor the inorganics presented lower contribution than on the other two POA factors (Figure S10). Combined BBOA was composed almost entirely of organics (97.8 % organics, 1 %  $\text{SO}_4^{2-}$  and 1 %  $\text{Cl}^-$ ). The two BBOAs presented similar diurnal patterns. Again, this factor's directionality (Figure S9) showed that it was a source affected by the city on the west and northwest of our site.

#### Ammonium Nitrate (AmNi)

The ammonium nitrate factor resolved in this study was composed of 55 %  $\text{NO}_3^-$  and 18 %  $\text{NH}_4^+$  (Figure S10). The remaining part of this factor is of organic nature and is linked to the condensation of organic vapours at the nitrate particles which takes place especially at night. The  $\text{NH}_4:\text{NO}_3$  ratio was 0.33, which is close to the theoretical ratio of 0.29 for pure ammonium nitrate. The respective ratio obtained by Sun et al (2012) was 0.36, while Äijälä et al (2019) reported a ratio of 0.46. In our study, nitrate was primarily present as ammonium nitrate; this factor accounted for 81.5 % of total nitrate. Ammonium nitrate's temporal variation agreed well with nitrate's ( $R$ -Pearson = 0.90). The diurnal variation of this factor showed enhanced concentration at noon (Figure 4c). Moreover, it was observed that the ammonium nitrate peak in cold months occurred three hours after the morning HOA peak, which further indicated the formation of ammonium nitrate through the reaction of traffic-related  $\text{NO}_x$  and ammonia (Figure 4c). In warm months, on the other hand, no morning peak existed, which combined with the lower particulate nitrate concentration levels during these months, led to the conclusion

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**Deleted:** Nevertheless, further insight into its diurnal trend in different seasons revealed that in summer an increase in temperature caused a decrease in the concentration of ammonium nitrate, while in winter ammonium nitrate's daily concentration followed the trend of RH. This was in agreement with the behaviour of  $\text{NH}_4\text{NO}_3$  in respect to the equilibrium constant value that controls the gas-particle partitioning of nitrate and depends on the temperature and the relative humidity of the atmosphere. More specifically, if the RH is higher than the deliquescence RH (DRH) of particulate  $\text{NH}_4\text{NO}_3$ , then the equilibrium constant for ammonium nitrate primarily depends on RH; the increase in RH favours particulate  $\text{NH}_4\text{NO}_3$  formation. Whereas, for RH levels lower than this critical point, the formation rate of  $\text{NH}_4\text{NO}_3$  is inversely proportional to the air temperature (Lin and Cheng, 2007). In our case, the winter RH was higher than the DRH of  $\text{NH}_4\text{NO}_3$  (62 %), thus the equilibrium constant value increased with increasing RH, as depicted in Fig. 4c. Fig. 4b highlights the effect of temperature on the equilibrium between particulate ammonium nitrate and gas phase  $\text{HNO}_3$  in summer; the increase in temperature was translated as a decrease in particulate ammonium nitrate's concentration, and consequently an increase in the formation rate of gaseous  $\text{HNO}_3$ .

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that the background NO<sub>x</sub> mainly participated in ammonium nitrate formation in summertime. Generally, the pronounced peaks identified in AmNi time series coincided with peaks observed in NH<sub>4</sub> and NO<sub>3</sub> time series, as measured with the ToF-ACSM. The CPF polar plot in Fig. S9 further confirms that ammonium nitrate was locally formed.

#### Ammonium Sulfate (AmSul)

A factor predominantly composed of sulfate and ammonium was retrieved in this study. 64 % of the mass of this factor was attributed to SO<sub>4</sub><sup>2-</sup> and 19.5 % NH<sub>4</sub><sup>+</sup> (Figure S10). The theoretical ammonium to sulfate aerosol ratio typically ranges between 0.18 (NH<sub>4</sub>HSO<sub>4</sub>) and 0.36 ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). In our case, the respective NH<sub>4</sub>:SO<sub>4</sub> ratio was 0.31, indicating that the sulfate presented in this factor was almost neutralized as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and further supporting the successful deconvolution of this factor. This factor contained 53 % of the total sulfate and it highly correlated with ACSM SO<sub>4</sub><sup>2-</sup> (R-Pearson = 0.91) (Table S6). Sun et al (2012) also retrieved a SO<sub>4</sub>-OA factor, but in that study, 18 % of the mass of this factor was organic with a high degree of oxidation (O/C = 0.69), the highest among the other factors retrieved, while the NH<sub>4</sub>:SO<sub>4</sub> ratio was 0.34 which is close to the theoretical one for pure ammonium sulfate. Äijälä et al (2019) retrieved a factor of ammonium sulfate with NH<sub>4</sub>:SO<sub>4</sub> ratio between 0.2 and 0.24.

#### Secondary aerosols (MOA, LOA)

Two factors representative of secondary aerosols were identified, i.e. a less oxidized, LOA (less oxidized aerosol) and a more oxidized, MOA (more oxidized aerosol), categorized as more and less oxidized based on the oxidation state of the organic part of their mass spectra (*f<sub>44</sub>*). Inorganic components significantly contributed to these factors. As noted before for the OA PMF analysis, LO-OOA and MO-OOA, retrieved by PMF analysis on the organic fraction, were well correlated with the inorganic species (Table S4), implying that an intrinsic relationship between aged organic and inorganic species exists. The application of the combined organic and inorganic PMF analysis can shed light on the mixing characteristics between organics and inorganics. On a yearly average, MOA consisted of 81 % organics, 11 % SO<sub>4</sub><sup>2-</sup>, 4 % NH<sub>4</sub><sup>+</sup>, and 4 % NO<sub>3</sub><sup>-</sup>, while LOA included 41 % organics and mixed a high amount of SO<sub>4</sub><sup>2-</sup> (47.7 %), and also 3.3 % NO<sub>3</sub><sup>-</sup>, 7.4 % NH<sub>4</sub><sup>+</sup> and 0.6 % Cl<sup>-</sup>.

Figures 5 and S12 present the seasonal composition of the oxidized factors. As appears, LOA exhibited different composition in each season: in spring and summer organics and inorganics equally contributed to the LOA's mass concentration, while in winter and early autumn inorganics are seen to be higher than organics in LOA. The more oxidized aerosol presented a more stable composition throughout the year, with organics being the prevalent species accounting for 76 % (JJA) to 86 % (NDJF) of MOA concentration. The apportionment of inorganic species in these factors confirms the internal mixing of SOAs with inorganic species, as addressed by Zhang et al. (2005).

MOA presented a strong correlation with MO-OOA (R-Pearson = 0.86), whereas LOA showed a lower but still significant correlation with LO-OOA (R-Pearson = 0.68). LOA, as well as LO-OOA, presented a strong correlation with temperature (Figure 4b). LOA's seasonal contribution to total NRS was minimum in winter (19 %) and higher in summer (29 %) and September-October (33 %), whereas MOA's contribution to total NRS also peaked in summer to 27 % but dropped in

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September–October, to 20 %. The bivariate polar plots of MOA and LOA resembled the respective plots of MO-OOA and LO-OOA, respectively (Figure S7a and Figure S9). Specifically, higher concentrations of MOA and LOA for low and moderate wind speeds around the centre area as well as from NE and SE were observed, suggesting that a combination of local and regional sources may have contributed to the observed concentrations. These regions were also associated with increased concentrations of inorganics ( $\text{NO}_3$ ,  $\text{NH}_4$ , and  $\text{SO}_4$ ) and  $\text{O}_3$ .

An overview of the species that contributed to each factor is shown in Fig. S11. As demonstrated, the organics were present in all the factors, but they contributed less to the inorganic factors, AmNi and AmSul. Sulfate was mainly present in AmSul and in LOA. Ammonium was equally and mainly distributed in the two inorganic factors (AmNi and AmSul) while nitrate was primarily present in the AmNi factor. Chloride, although present in very low concentrations, was equally attributed to ammonium nitrate and BBOA, highlighting the two main sources of chloride: secondary formation of particulate ammonium chloride and biomass burning emissions.

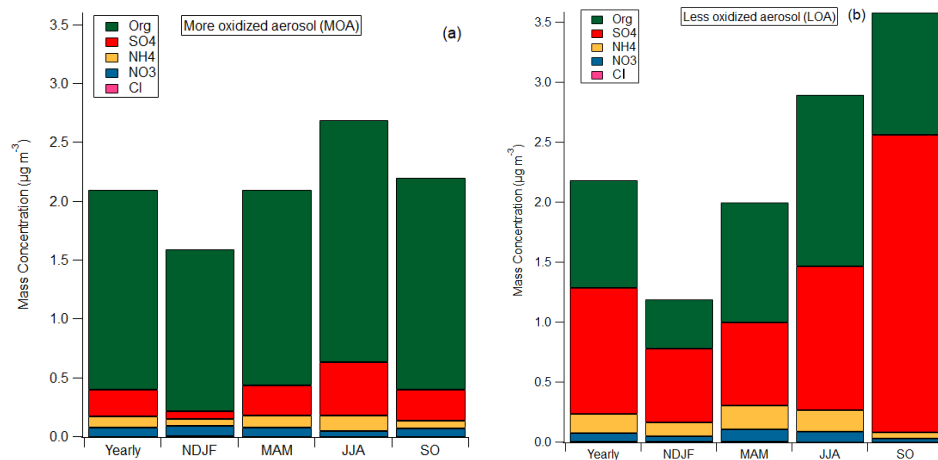


Figure 5. Mass concentration of each species in MOA (a) and LOA (b) in different seasons: Yearly, November–February (NDJF), March–May (MAM), June–August (JJA) and September–October (SO).

#### 4.4 Comparison of the two analyses

Integrating the inorganics in the PMF analysis adds valuable information concerning the mixing characteristics of organic and inorganic species over time, while rendering results that are qualitatively comparable to the widely-used organic aerosol PMF. Obtaining a better understanding on the sources and evolution processes of the total NRS, instead of merely OA, by applying source apportionment methods in combined organic and inorganic datasets for various site locations and for long-

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term datasets can be proven beneficial for atmospheric studies and climate models. The two analyses applied in the present study provided acceptable solutions both in terms of uncertainty (spread) of the factors and in terms of residuals, as explained in the paragraphs below.

1400 Since PMF provides a range of possible solutions, there is a need to determine how many of these solutions are within the acceptable limits and how much they vary from each other. The variability in this part refers to the variability of the many repeats of the model that can be translated as uncertainty. Moreover, uncertainty arises by the generation of each data point many times after the application of the random  $\alpha$ -values constraints, the resampling technique of bootstrapping and the technique of the rolling window. Thus, the ratio of the interquartile to the median concentration is used as a measure of this uncertainty (Canonaco et al., 2021). Overall, higher spread was observed for SOA than POA factors and all the factors of the combined PMF analysis were associated with lower spread than the OA factors (9.5 % for combined HOA instead of 10 % for OA HOA, 5 % for combined COA instead of 7 % for OA COA, 3 % for combined matrix BBOA instead of 5 % and 13 % on average for oxidized aerosols rather than 19 % for SOAs). The scaled residuals of the solutions were also evaluated in order to confirm that the modeling is mathematically correct. In the organics PMF analysis, 99 % of the scaled residuals were in the range of  $\pm 3$ , which is a reasonable range as suggested by Paatero and Hopke (2003). This percentage was reduced to 91 % for the combined analysis, although it remained high enough to assume the model fitted the data well. The points at which the scaled residuals exceeded these thresholds were associated with peaks in SOAs in the OA PMF analysis and in oxidized aerosols (MOA and LOA) in the combined PMF analysis, which was expected since these factors are linked to higher uncertainties due to the fact that they are unconstrained.

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1415 Moreover, the primary factors obtained by both analyses were highly correlated with each other in terms of temporal variation, suggesting that the inclusion of the inorganics in the PMF scheme did not adversely affect the quality of the initial solution. More specifically, the time series of the HOA factor obtained from the combined matrix presented good correlation with the organic matrix resolved HOA factor ( $R$ -Pearson = 0.87). Combined COA time series agreed with the previously resolved COA time series ( $R$ -Pearson = 0.92). The BBOAs resolved from the two different analyses were highly correlated with each other ( $R$ -Pearson = 0.88). Finally, the correlation between the factors obtained and external tracers appears in Table S6, from which a slight improvement can be seen for spring. For the other seasons the correlations are stable between the factors from the two analyses and their respective external tracers, which confirms the successful deconvolution of the primary factors by both analyses.

## 5 Conclusions

1425 The scope of this study was the characterization and source apportionment application to a yearly dataset of a ToF-ACSM at a suburban site in Athens. PMF was employed for two different analyses; one on the organic fraction and one combining the organic and the inorganic species ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$ ) of the ToF-ACSM dataset. From the first analysis, five organic aerosol factors were retrieved, while combined PMF analysis yielded seven factors. With both analyses three primary

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Figures S12 and S13 survey the contribution of each species in the NRS factors and the contribution of each NRS factor in the non-refractory species, respectively, in both relative (Fig. S12a and Fig. S13a) and absolute (Fig. S12b and Fig. S13b) terms. It appears that HOA, COA and BBOA consisted mainly of organics. Ammonium and sulfate together accounted for more than 80 % of the total mass of AmSul factor, while ammonium and nitrate accounted for more than 70 % of AmNi factor with 25 % of its mass being mixed with OA. Both organics and ammonium sulfate significantly contributed to the total LOA mass concentration; organic and sulfate accounted for about 41 and 48 % of the total mass respectively, but as will be discussed below its seasonal contribution significantly varied. MOA was primarily composed of OA with 15 % of its mass consisting of ammonium sulfate. Overall, organics were present in all the factors, but they contributed less to AmNi and AmSul. Sulfate was mainly present in AmSul factor and the secondary LOA factor. Ammonium was equally and mainly distributed in the two inorganic factors (AmNi and AmSul) while nitrate was primarily present in the AmNi factor. Chloride, although present in very low concentrations, it was equally attributed to ammonium nitrate and BBOA, highlighting the two main sources of chloride: secondary formation of particulate ammonium chloride and biomass burning emissions.¶

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organic aerosol factors were resolved; one hydrocarbon-related (HOA) from traffic emissions, one from cooking emissions (COA) and one related to biomass burning (BBOA). The organic aerosol interpretation produced two more factors; one more oxidized (MO-OOA) and one less oxidized OOA (LO-OOA), while these factors were mixed with inorganic species when resolved in the combined PMF analysis (named as MOA and LOA respectively). Two additional factors identified with the latter analysis were mostly inorganic: ammonium nitrate (AmNi) and ammonium sulfate (AmSul). The temporal composition of factors in combined PMF was investigated seasonally and higher variability in composition by seasons was observed for LOA.

As regards the significance of the combined PMF analysis over organics PMF, it was shown that incorporating the inorganics in the PMF analysis may lead to better a understanding of the sources and mixing characteristics of the non-refractory organic and inorganic species of PM<sub>1</sub>, while at the same time maintaining the quality of the solution obtained. A comparison of the two analyses in terms of residuals of the solution and errors of each factor, as well as the correlations between the factors from the two analyses and the factors with their respective external tracers took place and yielded motivating results in favor of the combined PMF analysis.

#### Data Availability

Data are available upon request to the author ([o.zografou@ipta.demokritos.gr](mailto:o.zografou@ipta.demokritos.gr)).

#### Competing Interest

The authors declare that they have no conflict of interest.

#### Author Contribution

OZ performed the formal analysis and writing the original draft; ACK, MG and KE helped with funding acquisition, project administration and resources; OZ, ACK and MG performed the investigation and data curation; MIM, GC and OZ provided the methodology and conceptualization; MIM and GC helped in running SoFi Pro and with discussions on the results; MG, MIM and GC provided supervision and validation; MG, MIM, GC, ACK, KE, ED and AP contributed in reviewing and editing the manuscript.

#### Acknowledgments

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Deleted: The absolute contribution of each primary factor obtained from the OA PMF analysis was 15 % HOA, 18 % COA and 9 % BBOA, while the SOAs contribute 34 % (MO-OOA) and 24 % (LO-OOA). The factors retrieved from the combined PMF analysis contribute to the total NRS as follows: HOA 7 %, COA 9 %, BBOA 3 %, AmNi 3 %, AmSul 28 %, MOA 24 % and LOA 26 %. The primary OA factors retrieved from the combined PMF analysis were mainly organic (95 % on average). MOA was also mainly composed of organics with 11 %, 4% and 4% of its mass attributed to SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, respectively, while LOA presented a seasonal variation in its composition with the average contribution of SO<sub>4</sub><sup>2-</sup> (47.4%) being slightly higher than that of organics (41%).

Deleted: External data from collocated instruments were used in order to identify the environmentally reasonable simulations. HOA presented in both cases significant correlation with traffic-related black carbon (eBC<sub>ff</sub>), while BBOA correlated well with wood burning black carbon (eBC<sub>wb</sub>). The time series of MO-OOA and LO-OOA showed a relationship with inorganic species, which was further elucidated by the combined PMF analysis. MOA and LOA both showed significant presence of ammonium and sulfate in the mass spectra, with both factors representing a prevailing class of ambient aerosols; that of mixed carbonaceous and ammonium sulfate particles. A better solution was achieved using the combined PMF analysis; the errors of the OA PMF solution were on average 12 % and they considerably improved for the combined PMF analysis (8 %). Furthermore, better correlation between the factors obtained by the latter analysis and the external data from collocated instruments was achieved, while the primary factors retrieved from the two analyses were highly correlated (R-Pearson = 0.89 on average). Overall, our study suggests that the combined matrix PMF analysis is an effective approach to gain more insights into the nature and origin of ambient aerosols while applying PMF over a long-term dataset of NRS.

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