

RC2

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.

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

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.

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.

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.”

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.”

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?

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...”

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.

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:

“Secondary sulfates are found in the atmosphere mainly in the forms of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , after the neutralization of sulfuric acid by ammonia (Biggins and Harrison., 1979). Ambient ammonium nitrate is formed through the oxidation of anthropogenic NO_x emissions (NO and NO_2) to nitric acid (HNO_3), which eventually reacts with ammonia (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.

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.

“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.

“...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”.

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”?

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.

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):

“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.”