9-year trends of PM_{10} sources and oxidative potential in a rural background site in France

Authors' response

We would like to thank the referees for their time to evaluate our manuscript and for their positive and constructive feedbacks, which helped improve the quality of the paper. Our response to the comments are presented below (in blue):

General revisions: All grammatical and cross-referencing errors in the text were corrected (listed below). Thank you very much to our referees.

- Line 17: Change "from" to "analysed on".
- Line 25: Change "However, this" to "even though this"
- Line 26: Change "signal" to "indicate"
- Line 30: Change "on chemical characterization and sources of PM" to "PM chemical characterization and sources" and "is concerned" to "focuses"
- Line 31: Delete "as they are the places"
- Line 33: Change "done" to "carried out" and delete "to try"
- Line 34: Change "could" to "can"
- Lines 43-44: Please rephrase as "However, only few sites provide long-term in-depth series of PM chemical speciation data."
- Line 46: Delete "would"
- Lines 47-48: Change "the case of the oxidative potential (OP) of PM" to "the case of PM oxidative potential (OP)"
- Line 52: Change "see" to "analyse" or "investigate"
- Line 53: Add "the" before "efficiency"
- Line 55: Change "measurement" to "measurements"
- Line 56: Change "large filter" to "long-term filter"
- Line 66: Change "a good" to "considered representative"
- Line 67: Add "at this site" after "chemistry"
- Line 93: Define MSA
- Line 109: Change "includes" to "including"
- Line 139: Change "PMF 5.0" to "EPA PMF 5.0"
- Line 159: Change "in" to "with"
- Line 164: Change "difference" to "differences"
- Line 182: Add "used" after "that". It is not clear if there are any differences with that methodology or not. Response: The sentence was revised as follows: "This methodology is based on the procedure proposed in Weber et al. (2018)."
- Line 201: Change "discusses" to "discuss" (twice)
- Line 210: Delete comma after "although"
- Line 226: Remove 100 out of 100
- Line 249: Change "lead" to "have led". Response: The sentence was revised as follows: "As OC in a rural site can undergo multiple re-transformations in the atmosphere from the emissions sources, this has led to a wide range of OC-to-EC ratios as similarly found in Weber et al. (2019), hence this constraint was excluded."
- Line 281: Change "were" to "was"
- Line 305: Change "typologies" to "sites"
- Line 332: Change "dissimilarity" to "dissimilarities"

- Line 457 and 458: Delete “as much as”
- Line 476: Add “in” before “Figure”
- Line 482: Change “confident” to “confidence”
- Line 484: Change “follow” to “follows”
- Line 546: Change “this” to “the”

Response to anonymous referee #1:

Referee comment: First of all, the analysis of the variability of PM10 concentration (Section 3.1) focuses on just reconstructed PM10, and it is not clear how much of the measured mass is efficiently reconstructed. In addition, the analysis covers only yearly averages and therefore interannual variability, while a focus on seasonal and perhaps subseasonal time scales could be interesting as well.

Response: Thank you for the feedback. We have improved Figure 2 by adding the portion of unknown species in PM_{10}. It should be noted that only 69% (n=299) of the collected filters were paired with TEOM-FDMS measurements. Overall, the average reconstructed mass of non-volatile species measured on the filter, at about a grand average of 10% over the sampling period, is in the range of results from other studies in rural areas (e.g., Pey et al., 2009).

The authors acknowledge that our very large dataset could be worked in many different directions, including investigations of daily and seasonal evolution, and that all of these would give interesting information. However, this would also lead to a much longer paper, and we chose here to concentrate on 3 directions (sources of PM studied with PMF, sources of oxidative potential, and trends in the sources contributions), which covers already a large scope of investigation.

However, some information in the SI, like Figure S10, presents the STL deconvolution of PM_{10} concentrations in terms of monthly and seasonal averages. The STL deconvolution (Seasonal and Trend decomposition using Loess) presented in this manuscript is a versatile and robust method for decomposing time series developed by Cleveland et al. (1990).

A paragraph in section 2.2 was also added and now reads as:

The PM10 measurements from the tapered element oscillating microbalance (TEOM-FDMS) are all in a daily (24-hour, 09:00 to 09:00) resolution, while the reconstructed PM10 were obtained from chemical analysis performed on filters collected on a weekly (7 days, 09:00 to 09:00) or daily (24-hour, 09:00 to 09:00) basis. A total of 299 out of 434 (69%) TEOM-FDMS measurements were paired with reconstructed PM10 data, due to many interruptions in the TEOM-FDMS functioning, in order to evaluate the semi volatile mass missing in the mass reconstruction with filter chemistry.

A paragraph in section 3.1 was also added and now reads as:

The yearly average volatile mass (i.e., unaccounted by chemical analysis), deduced from the difference between TEOM-FDMS measurements and reconstructed PM_{10}, ranges from 9% to 44% with an average of 22% (of the yearly median) and is well within range generally found in a rural environment (Pey et al., 2009).

Referee comment: Secondly, the information reported on the choice of the PMF solution is not complete, and as such it is not possible to judge if the choice was done appropriately.

Response: We revised section 2.4.2 (Criteria for a valid solution) to elaborate more on the specific conditions evaluated. This paragraph now reads as:

Solutions with a total number of factors from 6 to 11 were tested for the baseline models. Following the recommendations of the European guide on air pollution source apportionment with receptor models (Belis, 2019), the Q/Q_{exp} ratio (<1.5), the geochemical interpretation of the factors, the weighted residual distribution, and the total reconstructed mass were evaluated during factor selection.
Moreover, the bootstrapping method (BS) was used on the final solution to estimate errors and ensure the stability and accuracy of the solutions. The BS method was applied with 100 iterations of the model and contribution uncertainties are presented in the SI (S3) as mean±std of the 100 BS runs. The contribution uncertainties were estimated based on the method presented in Weber et al. (2019) and presented in Figures S2 to S10. The daily specie contributions are estimated using:

$$X_{BSi} = G_{ref} \times F_{BSi}$$

where F_{BSi} is the profile of the bootstrap i, and X_{BSi} is the time series of each species according the reference contribution G_{ref} and the bootstrap run F_{BSi}.

Finally, the factor chemical profiles obtained during this study were compared with those from previous studies in France, using the PD-SID method (Belis, 2019; Weber et al., 2019), in order to validate their proper similarity.

Referee comment: As a third point, the STL analysis is applied to all factors, but Figure 6 focuses only on the traffic factor: however, it is interesting to note that papers analysing long term trends at high-altitude or regional background sites (in some cases even less impacted by anthropogenic sources than this particular site) have indicated an important role of changes in meteorology for the observed decrease in PM10 in the last decades. This would be very interesting to analyse here as well, because it could indicate that the role of control policies in driving PM10 decreases was sustained by meteorological changes. As such, this investigation could complement nicely the findings presented here.

Response: We appreciate this comment. We agree that meteorological data can provide very interesting findings, however we would like to focus mainly on the sources of PM_{10} and its oxidative potential. We have added a statement in section 3.5 to clarify that meteorological influence cannot be ruled out in the trends observed in this study. Please see a detailed answer for the comment on lines 371- 382 and a corresponding improvement in section 3.5. We also provided an answer to a similar question by reviewer 2. We would also like to point out that, in fact, the STL deconvolution used in section 3.5 (methodology explained in section 2.6) decomposes the PM10 time series into three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology on the long-term trend of PM10. This is now included in section 2.6, with the sentence :

The STL (Season-trend deconvolution using locally estimated scatterplot smoothing) model decomposes the PM10 time series into three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology

on the long-term trend of PM10.

Referee comment: Line 15: A specification of the name/location of the site could be given in addition.

Response: Thank you for the suggestion. We revised this sentence as:

In this study, a 9-year sampling of PM_{10} (particles with an aerodynamic diameter below 10 µm) was performed in a rural background site in France (Observatoire Pérenne de l'Environnement or OPE) from February 28, 2012 to December 22, 2020.

Referee comment: Lines 19-22: The difference between the two sentences is not straightforward and clear. Could you please rephrase and make the difference clearer?

Response: To address the referee's comment, we improved the sentence as:

The sources of OP were also estimated using multiple linear regression (MLR) analysis. In terms of mass contribution, the dominant sources are secondary aerosols (nitrate- and sulphate-rich) associated with long-range transport (LRT).

Referee comment: Line 24: But this is not a result of this study, since you did not analyse urban areas.

Response: We appreciate the feedback. The authors would like to note that all OP measurements, including those in Figure 7, were analysed by our group at Institut des Géosciences de l'Environnement (University Grenoble Alpes) and published in different publications (Borlaza et al., 2021; Weber et al., 2021). References were added to make it clearer, and we feel that with this, the comparison and discussion of OPE results compared to OP values from other sites are therefore fully a result from this publication, and should as such be included in the main text.

Referee comment: Line 29: This sentence is not clear: revise.

Response: We appreciate the feedback. We revised the sentence as:

Particulate matter (PM) pollution is a key factor in various environmental concerns affecting public health and climate.

Referee comment: Line 35: "geochemical" may be not the most appropriate term in this context. In addition, the pollutants are transported, not the sources. Please revise.

Response: Thank you for the suggestions, we improved the sentence as:

Rural sites are of great interest as well because they can represent the regional background of the atmosphere and potential influence from long-range transport (LRT) of pollutants.

Referee comment: Lines 36-37: Well, not only large-scale processes, but also mesoscale

processes are needed for chemical transport models. Revise.

Response: Thank you for the suggestion, we improved the sentence as:

Studies at such sites enable the understanding of large-scale and mesoscale processes (Anenberg et al., 2010; Mues et al., 2013; Konovalov et al., 2009), which is necessary to elaborate chemical transport models.

Referee comment: Line 38: Again, "geochemical" is not the appropriate term in this context.

Response: Thank you for the suggestion, we improved the sentence as:

The continuing observations in background sites can lead to the identification of long-term trends and the effect of recent changes in the source emissions.

Referee comment: Lines 55-60: I would suggest presenting the structure of the work rather than summarizing the results and conclusions.

Response: We appreciate the feedback. To address the referee's comment, we improved Lines 55-60 as:

The OPE site (Observatoire Pérenne de l'Environnement) is located in a rural site in Houdelaincourt, north-eastern France, well-representing the French national background PM. The long-term monitoring of PM_{10} (particles with diameter $\leq$ 10 µm) over a 9-year period (n = 434) in the OPE site allowed an extensive characterization of the chemical and OP of PM_{10}. The objectives of this work are, first, to achieve for the very first time a study of the main sources of PM in a rural environment in Europe, using a long-term database including several specific organic tracers in the carbonaceous fraction. The PMF methodology includes a unique validation with comparison of the chemical profiles of the factors with those obtained in many other studies in France. The second objective is to quantify the temporal evolution of the contributions of these sources over the period of the study, particularly focusing for the first time on the vehicular emission that have already been shown to decrease in urban environments in Europe during the last decades. Finally, another major objective is to perform the deconvolution of the contribution of the PM sources to the OP measured with AA and DDT assays, and to determine the most important sources for the oxidizing capabilities of PM influencing human health in such an environment.

Referee comment: Line 63: The acronym was introduced previously without explanation: better move this explanation to the first time it is cited.

Response: The acronym is now defined in Line 55:

The OPE site (Observatoire Pérenne de l'Environnement) is located in a rural site in Houdelaincourt, north-eastern France, well-representing the French national background PM.

Referee comment: Lines 63-68: Any additional description of the typical local climate? This

can affect PM concentrations and may be relevant for the rest of the discussion.

Response: Thank you for this suggestion. We added some information about the local climate in section 2.1 and reads as:

The mean annual temperature between 2011 and 2018 in the area was 10.5°C [minimum, maximum: -15.2°C, 36.4°C], average cumulated yearly precipitation was 829 mm, and the predominant local wind regimes are south-westerly and east-north-easterly winds (Conil et al., 2019).

Referee comment: Lines 75-78: This means that you analysed only field blanks and not blank filters? With which frequency did you analyse these field blanks?

Response: Field blank filters (filters subjected to all the same steps of preparation and sampler loading, but not exposed to sample flow) were collected and analysed regularly, with about 2 to 3 field blanks per month. This amounting to 15% field blanks compared to real samples, which is a high standard for field collection.

Referee comment: Line 89: What is this "range of ratio"? Please explain better.

Response: Apologies for this typographical error. We clarified this by revising the sentence as:

Yazdani et al. (2021) showed that this is consistent with the range estimated for rural samples from the IMPROVE network, that are generally higher than for urban samples.

Referee comment: Lines 83-111: Any specifications of the Limits of Detection, and other experimental parameters?

Response: We appreciate the suggestion. The authors added specifications on the quantification limits (QL) of each chemical specie measured in the OPE site, please see Table S1 and a sentence in section 2.2 that reads as:

A summary of the quantification limits (QL) on each chemical specie measured in the OPE site is also provided in Table S1.

Referee comment: Lines 115-116: If the analysis was started on samples collected from June 13, 2017 to December 22, 2020, it means that then you analysed also the rest of the samples. Is this true? If not, please revise.

Response: Thank you for the suggestion, we appreciate it. To clarify the statement, the authors revised the sentence as:

The OP analysis only started on samples collected from June 13, 2017 to December 22, 2020, amounting to a total of 191 samples.

Referee comment: Line 139: Change "PMF 5.0" to "EPA PMF 5.0".

Response: To address the referee's comment, we improved the sentence as:

The United States Environmental Protection Agency Positive Matrix Factorization (EPA PMF

5.0) software (Norris et al., 2014) was used to identify and quantify the major sources of PM_{10}.

Referee comment: Line 140: This definition is not correct: please revise.

Response: We appreciate the feedback. We have revised the definition as:

PMF is a receptor model fully described by Paatero and Tapper (1994) and is now widely used for source apportionment around the world.

Referee comment: Lines 147-148: Which paper did you follow for this step? And do you know that this is not complete to characterize the strength of the variables? The analysis of the residuals should be also made. In addition, how did you treat the additional uncertainty? Please revise.

Response: Thank you for the feedback. In the supplementary information (S2), the authors have provided a detailed PMF methodology. The uncertainties were estimated following the method proposed by Gianini et al. (2012). To make it clearer, the authors improved section 2.4.2 as follows:

Solutions with a total number of factors from 6 to 11 were tested for the baseline models. Following the recommendations of the European guide on air pollution source apportionment with receptor models (Belis, 2019), the Q/Q_{exp} ratio (<1.5), the geochemical interpretation of the factors, the weighted residual distribution, and the total reconstructed mass were evaluated during factor selection.

Gianini, M., Fischer, A., Gehrig, R., Ulrich, A., Wichser, A., Piot, C., Besombes, J.-L., and Hueglin, C.: Comparative Source Apportionment of PM_{10} in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation, Atmos. Environ., 54, 149–158, https://doi.org/10.1016/j.atmosenv.2012.02.036, 2012.

Referee comment: Lines 150-152: How did you analyse weighted residuals? Please provide additional details.

Response: Please refer to the supplementary information (S2) in Eq. S4.

Referee comment: Lines 164-171: Did you use any particular software for this calculation?

Response: The equations used for the PD-SID metric are mentioned in the supplementary information (S2) closely following a previous work by our group (Weber et al., 2019, 2021) and were calculated using Python. See also the answer to reviewer 3 on a similar question.

Referee comment: Line 204: What does it mean “reconstructed”? How far is this reconstruction from the measured value?

Response: Thank you for the clarification. Reconstructed PM mass is the mass calculated from chemical characterization (i.e. total PM reconstructed from all chemical analysis performed). We have improved Figure 2 to estimate the amount of unknown species (e.g. the semi volatile fraction) in the total measured PM_{10}.

Referee comment: Lines 211-212: A decrease during this period is quite evident, while the change in composition is less evident.

Response: Apologies for the confusion, we have revised the sentence as:

Some changes in the concentration may arise in the PM10 mass concentration, but changes in the major chemical components at the OPE site are less visible, even with the lockdown restrictions during year 2020.

Referee comment: Line 215: Is this a mean value? From Figure 2 this value does not seem constant.

Response: Yes, this is the mean percentage contribution of OM to total PM_{10}. To clarify, the sentence was improved as:

Accounting for 37% to 45% (based on year) of the reconstructed PM_{10} mass concentrations, organic matter (OM) is the largest contributor.

Referee comment: Lines 219-220: This example does not explain much. Please revise.

Response: We appreciate the feedback. However, the example serves as a general comment about expected species in vehicular emissions and road dust. These were further clarified in section 3.3, where both factors were discussed in detail.

Referee comment: Lines 220-221: This sentence is not well linked with the previous results shown. Please revise.

Response: Thank you for the feedback. The authors deem that the sentence could be useful in linking the composition of PM (section 3.1) and the sources identified by PMF (section 3.2 and 3.3), and then consequently should be an essential step for efficient air quality policies.

Referee comment: Lines 223-225: Please provide additional details on how this solution was selected. The signs of instability are worrying.

Response: We appreciate the feedback. In section 2.4.2 and 2.4.3, the criteria for a valid solution and the appropriate constraints in the PMF model were discussed. Additionally, the authors have allotted section 3.2 to discuss the statistical stability of the PMF solution. Finally, Figures S2 to S10 presents the chemical profile and temporal evolution with error estimates of the PMF-resolved factors. Please refer to the improved version of section 2.4.2.

Referee comment: Lines 233-235: Couldn’t you use a value more appropriate for a rural site?

Response: We have tried a range of values, but none has led to better PMF solutions. Hence, the decision of not applying such constraints.

Referee comment: Lines 263-265: But local sources cannot be excluded: if not, we would have always higher nitrate and sulphate concentrations at rural sites than at urban ones, which is not

the case.

Response: The authors agree with the referee that local sources should not be excluded. However, the OPE site is located in a remote area in the north-eastern part of France (48.5°N, 5.5°E) and without any residential areas within several kilometres (see Figure 1). The density is about or less than 5 inhabitants per km^2 within a radius of 10 km around the site. The sentence in Line 263 to 265 mentioned that sulphates and nitrates are mainly formed through secondary processes with long atmospheric lifetimes and can originate from regional sources or LRT. With the *a priori* knowledge of the site description, the authors deemed it was appropriate.

Referee comment: Line 270-271: Can you explain the reasons of this seasonality in these 2 factors?

Response: In France, biomass burning emissions are expected to be more prominent in the winter due to residential wood burning, while the seasonality in the nitrate-rich factor can due to greater photochemical activities in spring associated with agricultural spreading of manure and fertilizers. The general characteristics of the PM over France are presented in Favez et al., 2021).

Referee comment: Lines 296-297: Couldn't this be due to the fact that Na+ and Mg2+ are primary seasalt particles while MSA particles are secondary? What about the correlation with nss-SO42-? See for instance papers from the group of Silvia Becagli and Roberto Udisti (e.g., Udisti et al., 2016; Becagli et al., 2019, 2021). Did you try to analyse the source (with wind or back-trajectories)?

Response: We appreciate the comment. The OPE site is 340 km away from the closest sea, making it difficult to assume that these are, essentially, primary sea salt particles. Road salting in the winter could potentially be an origin of salt particles. The discussion on seasonal variability and sources of MSA (together with a PSCF analysis) in the OPE site (together with 4 other rural sites in France) can be found in Golly et al., 2019 (already in the list of references, doi.org/10.1016/j.atmosenv.2018.10.027). Our group is also currently working on a synthesis paper discussing MSA concentrations and its sources across France, using about 20 yearly sampling campaigns from different sites, in order to discuss the links with marine source and transport.
The mentioned articles by Silvia Becagli and Roberto Udisti were studies performed in marine areas in the Arctic or Antarctic, which is not totally relevant for our conditions. However, another publication by Becagli (http://dx.doi.org/10.3189/172756405781813384) says: "The spatial distribution of nssSO42− and MSA is discussed as a function of distance from the sea, altitude and accumulation rate. Depositional fluxes of nssSO42− and MSA decrease as a function of distance from the sea, with a higher gradient in the first 200 km step." It follows that concentrations further away from coastline should be quite low.

Referee comment: Figure 6: Check the y-scale (measurement unit).

Response: To clarify the measurement unit, the figure caption was revised as follows:

Figure 6: The Season-trend (STL) deconvolution of contributions in µg m^{-3} from the traffic factor to PM_{10} from year 2012 to 2020.

Referee comment: Lines 371-382: There are also studies at high-altitude or regional background

sites, some of which highlighted a concurrent role of a changing meteorology and of a change in the frequency of Saharan dust advections to Europe. Please look at: Tsyro et al., 2018; Colette et al., 2011, 2017; Brattich et al., 2012, 2020 and references therein). Thus this discussion may be improved.

Response: We appreciate the suggestion. We can remark that most of the literature quote is from modelling work, with all the questioning related to the capabilities of models to clearly reproduce the local concentrations in the boundary layer. We note also that Collette et al. (2011) clearly state that the decreasing emissions during the last decades largely dominate any impact of the meteorological conditions for species of anthropogenic origins. The work of Brattich et al. (2020) is quite interesting with a thorough comparison of regional circulation patterns with local measurements, but is performed for Mont Cimone, an altitude site in the free troposphere where the large-scale circulation is much more important than the local (a few hundred km) one. For example, average winter PM10 concentration of less than 3-4 μg m^{-3} at this site cannot be said representative of boundary layer rural concentrations in Europe, but much more related to large scale transport only.

However, we have improved this section and now reads as:

The downward trends found in our study are well consistent with other existing studies in Europe (Li et al., 2018; Sun et al., 2020; Salvador et al., 2012; Pandolfi et al., 2016; Gama et al., 2018; Amato et al., 2014), nearly all of them conducted in urban areas. Pandolfi et al. (2016) found a significant long-term decrease of the contributions from anthropogenic emissions (specifically a mixed industrial/traffic factor, -0.11 μg m^{-3} $year^{-1}$, 56% total reduction) in a regional background site in altitude in northeast of Spain (Montseny, Spain) from 2004 to 2014. This is also consistent with a similar study in the metropolitan area of Madrid, Spain (Salvador et al., 2012) which showed a reduction of 32.7% attributed to traffic emissions, alongside the decrease of the carbonaceous and SO_4^{2-} in PM. In a southern Spain area (Andalusia), the same group also found a consistent decreasing trend of PM at some traffic and urban sites in the region (Amato et al., 2014).
Another long-term study in Central Europe (Sun et al., 2020) focusing on eBC concentrations found decreasing trends in high-altitude Alpine sites located in Germany (-3.88% $year^{-1}$, [-10.15%, 0.56%]) and Switzerland (-3.36% $year^{-1}$, [-8.71%, -0.28%]). These findings are also consistent with results from other parts of Europe, with the largest decrease found in OC up to -48% (Cusack et al., 2012) and the decrease in PM has been associated to non-meteorological factors (Barmpadimos et al., 2012). Other studies with pluri-annual series of data on PM chemistry in rural environments in Europe includes Splindler et al. (2013) (Melpitz, Germany, including EC measurement for 2003-2011), and Grange et al., (2021) (Payern, Switzerland comparison of 3 periods every ten years since 1998, including EC and trace elements). Both are showing decrease of EC concentrations over time during the study. Finally, while these studies did not target specific chemical species solely linked to vehicular emissions, most of them attributed the decline to the efforts to reduce vehicular emissions and other mitigation policies in their respective areas.
It should be noted that the role of meteorology on the observed decrease in PM in these studies (including ours) cannot be totally ruled out (Hou and Wu, 2016; Czernecki et al., 2017; Kim, 2019) and is generally not fully considered. However, the complex interplay of all meteorological variables on PM concentrations would be difficult to delineate. Indeed, there are some studies at high-altitude or regional background sites that highlighted a concurrent role of changing meteorology and changes in frequency of Saharan dust advections to Europe (Brattich et al., 2020) in modulating the dust concentrations in the atmosphere. The study at

Melpitz (Spindler et al., 2013), despite an in-depth work on the wind sector classification, does not address the impact of possible changing in the air mass origin on long-term changing origins.

Referee comment: Figure 8: Please check the x-axis and add more ticks. There are some peaks in all series: did you analyse the presence of outliers and investigate their causes?

Response: Thank you for the suggestion. Figure 8 was updated accordingly. There are very few data points (n=3) where the PM_{10} mass concentration was higher than usual. These samples did not exhibit particularly high OP activities. However, we have observed elevated levels of contributions from the nitrate-rich factor for about 9 to 12 times as much as the over-all average contribution.

Referee comment: Lines 511-514: This is not clear: the problem with weekly samples should be that differences and transient events (e.g., Saharan dust, fires, …) are smoothed but I cannot understand what you mean by "the weekly collected samples may contain particles that are not fully captured in a daily sample".

Response: We appreciate the comment. Weekly samples contain both weekend and weekday samples as the duration of collection is 7 days. On the other hand, a daily sample can either fall on a weekday or a weekend as samples are collected on a 6-day interval. This implies that the weekly collected samples may contain particles that do not have the same representability than daily samples. The authors hope that this clarifies the confusion.

Referee comment: Line 530: Figure 11 is not about PM concentrations, but on OP contributions. A decrease in PM concentration could instead be observed as previously noted.

Response: Figure 11 is part of the section that discuss the sources of OP of PM_{10}. The main take-away of the figure is that the available OP data only spans up to 4 years against 9 years for the PMF data. The shorter time range could be insufficient to reach significance and robustness in the trend assessment of OP levels compared to the trends analysis we have performed for PMF (Figure 6).

Referee comment: Lines 548-550: As previously noted, this discussion is limited since there are studies evidencing a simultaneous effect of the changing meteorology. This point should be improved.

Response: This paragraph has been improved and now reads as:

Thanks to the long-term dataset in the OPE site, it was observed that the traffic factor contribution to total PM_{10} has decreased over the years for this site that may well represent the French national background PM. This decrease is much larger than any change observed for the other PM sources and is in excellent agreement with estimations in the decrease in BC emissions from the transport sector all over France from the national inventory. This effect may be attributed to improvement of the exhaust emission of terrestrial transportation fleet, and/or to regulations restricting vehicular emissions in bigger cities and/or other regional-scale. However, persistent changes during the same period in some meteorological processes influencing the transport of air masses to OPE or formation of PM during this transport cannot be totally ruled out. We would also like to point out that, in fact, the STL deconvolution used in section 3.5 (methodology explained in section 2.6) decomposes the PM10 time series into

three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology on the long-term trend of PM10. This is now included in section 2.6, with the sentence :

The STL (Season-trend deconvolution using locally estimated scatterplot smoothing) model decomposes the PM10 time series into three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology on the long-term trend of PM10.

Referee comment: Code and data availability: Please check the statement for this: as on the ACP website https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html, "Authors are required to provide a statement on how their underlying research data can be accessed. … If the data are not publicly accessible, a detailed explanation of why this is the case is required. … Data do not comprise the only information which is important in the context of reproducibility. Therefore, Copernicus Publications encourages authors to also deposit software, algorithms, model code, video supplements, video abstracts, International Geo Sample Numbers, and other underlying material on suitable FAIR-aligned repositories/archives whenever possible"

Response: Thank you for this advice. We appreciate the reminder.

Response to anonymous referee #2:

Referee comment: The samples were collected in a 6-day sampling interval, but not weekly samples covering each year. The weakness should be discussed if any real-time measurements of PM10 are available

Response: Thank you for the suggestion. The authors would like to point out that a sampling interval of 1 every 3 days or 1 every 6 days has been reported as appropriate for meeting general monitoring objectives. An intensive sampling interval, however, is recommended for areas expected to exhibit higher ambient levels (Bortnick et al., 2002). The OPE site, being a rural background site, does not exhibit levels that require an intensive sampling interval.

Referee comment: Meteorological conditions would affect the long-term trends, and the issue should be quantified. This is particularly critical for semi-volatile species such as ammonium nitrate and organics when their interannual variations were analyzed.

Response: We appreciate the insight. We agree that meteorological conditions can have a wide range of impacts on PM concentrations. However, this is a really intricate issue, since both temperature, humidity, amount of rain, amount of radiation, wind, air mass origin, boundary layer height, amongst others can be at play, both locally but also during the few days during the transport to the site. Investigating the evolution over the last 10 years of all these parameters and the potential impact on PM is altogether a really large task, and most probably beyond the current state of the art. The authors are not sure that there is a single published study that investigated all these parameters (plus the PM sources of mass and OP) when studying a time series of observations.

We have added a statement to clarify that meteorological influence cannot be ruled out in the

trends observed in this study. Please refer to answers to reviewer #1's comments and associated changes in the text. We would also like to point out that, in fact, the STL deconvolution used in section 3.5 (methodology explained in section 2.6) decomposes the PM10 time series into three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology on the long-term trend of PM10. This is now included in section 2.6, with the sentence :

The STL (Season-trend deconvolution using locally estimated scatterplot smoothing) model decomposes the PM10 time series into three components: trend, season, and residual. With a free amplitude of the seasonal change, this method somehow takes into account the changes in seasonal cycles from year to year which could also delineate part of the effect of meteorology on the long-term trend of PM10.

Referee comment: Considering agriculture and natural emissions of ammonia, secondary aerosols could be formed before and during the long-range transport as well as formed locally. This may should be clarified.

Response: We appreciate this comment. We have incorporated this in the manuscript, see section 3.3. We have added a line that reads as:

Considering the agriculture and natural emissions of ammonia, especially expected in a rural site, secondary aerosols could also be formed locally in the OPE site.

Referee comment: Nacl could be derived from road salts or sea salts considering an inland site used in this study, please clarify.

Response: We appreciate this comment. We have incorporated this in the manuscript, see section 3.3. The paragraphs read as:

The **aged sea salt** factor is characterised by high loadings of Na^+ and Mg^{2+}, with a certain amount of species originating from potentially anthropogenic sources such as nitrates (6% of NO_3^- mass) and sulphates (19% of SO_4^{2-} mass) that can be attributed to mixing and transformation processes in the atmosphere. Interestingly, there are some contributions from EC (8% of EC mass), Cu (11% of Cu mass), Sb (13% of Sb mass), and Se (19% of Se mass). This could imply potential mixing of aged sea salt with other anthropogenic source linked to these species (e.g., traffic, shipping). The minimal loadings observed in the contributions of Cl^- in this factor can be a likely result of ageing processes occurring between sea salt and acidic particulate compounds such as nitric and sulfuric acid (Seinfeld and Pandis, 2016). This factor could also be associated to road salting in the winter, however there is no clear seasonality in the contributions to support this hypothesis. There was no added constraint in this factor as our solution shows a Mg^{2+} to Na^+ ratio at 0.06 while this ratio is usually found around 0.12 in sea-salt emissions (Henderson and Henderson, 2010).
The **fresh sea salt** factor is characterised by high loadings of Cl^- (91% of Cl^- mass) and some contributions from Na^+ (35% of Na^+ mass) and Mg^{2+} (25% of Mg^{2+} mass). This factor contributes 4% to total PM_{10} mass and, unlike the aged sea salt factor, it is less likely influenced by anthropogenic sources with extremely low contributions from carbonaceous and metal species.

Referee comment: Lines 276-277, "The NH4+/NO3- mass ratio in this factor is 0.22, close to

the mass ratio (0.29) indicating the formation of NO3NH4 in the particulate phase." The statement does not sound scientific considering PM10 to be studies; the same comment is applied to lines 281-282" The NH4 + to SO4 2- molar ratio of 0.4 suggests that sulphates are mostly present as (NH4)HSO4 and only a small fraction as (NH4)2SO4.

Response: We removed these sentences, since they are not essential for the discussion of the paper.

Response to anonymous referee #3:

Referee comment: Many of the results related to the PM10 analysis are neither surprising nor original, i.e. traffic-related concentrations are decreasing (even in rural areas), SIA are large contributors to the total mass of PM10 in rural areas. What did we learn from your analysis that has general implications for atmospheric science, and was previously not known? Citing from the scope of ACP, "The journal scope is focused on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest.". In other words, I feel that a clear scientific hypothesis/research question is lacking in this manuscript, and perhaps the authors should elaborate more on what they are trying to uncover. The process of a scientific manuscript in a high-quality scientific journal (as ACP) should start with a clear question/hypothesis that authors should try to answer given some new observational data/new modeling experiments/new theoretical insights. Reading the manuscript, I felt that the focus of the paper is on the dataset itself, rather than using the dataset as a tool to answer a scientific question. As an example of this, the results from Pandolfi et al. (2016) also suggest that traffic concentrations in a rural background site (in Spain) have decreased in the last few years and secondary inorganics and organics are large contributors to PM10 in rural sites. For the PM10 results, what did we learn from your analysis that adds significant new knowledge with respect to Pandolfi et al. (2016) work (to cite one, but there are other similar works available in the literature)? This should exceed the simple time span differences considered in their work. With that said, I do acknowledge that there is some merit in analyzing OP contributions and show the differences with PM10 contributions (Sections 3.6-3.8), as OP is emerging as a promising endpoint-related metric to measure health impacts. However, in the introduction, you state that 'The characterization of PM sources and OP in a rural site will enable us to see the large-scale effects of mitigation policies that target reduction of PM mass concentrations. This will also provide knowledge of efficiency of current air quality guidelines in terms of other emerging health-based metrics of PM exposure.' (Lines 51-54). A similar statement is repeated at the end of the introduction (lines 58-60). What knowledge of efficiency of current air quality guidelines for OP did you find? This is not clearly reflected neither in the results nor in the conclusions, as the trends analysis for OP is not really revealing much given the relatively short (4 years) period available. Once again, I believe you should try to highlight the value of your analysis as it relates to a specific hypothesis/questions, rather than propose very general statements that confuse the reader.

Response: We really want to thank the reviewer for this strong comment that led us to think more about our work, and to read in more detail the work by Pandolfi's et al (2016) and some other pieces of work. All of these lead to several modifications in this present version of the paper that (according to us) fairly improved it.
Considering Pandolfi's work and what our work adds compared to it, as per referee's demand, we had a much deeper look at this seminal and interesting study conducted a while ago by excellent colleagues. In the end, we found out that our work is quite different from this paper, but also that the conclusions in Pandolfi et al. (2016) are not as strong as presented by the

reviewer. We think that some (we hope significant) aspects are somewhat innovative with our work, compared to Pandolfi's one, but also compared to all other papers dealing with long time series of sources of PM in rural environments in Europe.

- Our site is in a location that probably reflects more rural areas in Europe where people are living, compared to Montseny which is in altitude.
- Our work is including several innovative sources due to the inclusion of organic tracers that were not delineated in Pandolfi's work, nor in any previous study: biomass burning, MSA-rich, primary biogenic; the domestic biomass burning source is really important to evaluate for regulation purposes. Altogether, these "new sources" represent 24 % on average of the PM_{10} mass, and a much larger share of the organic matter mass. They were not investigated together previously in any published paper concerning long term trends in a rural area in Europe, and in itself, this makes our work innovative on a scientific point of view.
- The time series at Montseny in Pandolfi's work do not allow to detect any trends for EC nor OC. This is a clear sign that the source from traffic is, indeed, not likely to present a significant decrease, as observed from this site. The time series of EC at our site present a really clear decreasing trend, the most important of all chemical species measured. This is a huge difference.
- The PMF factor labelled industrial / traffic for Montseny in Pandolfi's the main text of the paper (and anthropogenic in its SI) does not include EC as a tracer but a global carbonaceous indicator (non-mineral C). The authors present this factor like much more influenced by industry than by traffic. Hence, EC is not decreasing, and there is no clear sign that a clearly identified traffic source is decreasing.
- The OP of PM has been gaining attention as an emerging health-based metric of PM exposure. The findings in this study, particularly the identified main drivers of OP of PM, could help validate the relative importance of some PM sources in terms of adverse health effects. For example, the nitrate-rich source is the highest contributor to PM mass but has minimal contributions in terms of OP (Figure 10 in the manuscript). So, setting a regulation targeting mass concentration during elevated ammonium nitrate events may have less adverse impacts on health than expected.

There are, of course, several other differences that makes our work innovative (according to us) on a scientific point of view, including the STL deconvolution that allows to precisely investigate tendencies, and of course the all section on OP measurements, as underlined by the reviewer. Even if we agree that 4 years of OP analysis is a bit short for trends analysis, we have not identified much studies that have published more than one or two years of OP time-series and, usually such publications rely heavily on reconstructed data (Fang et al. (2014), doi:10.5194/acp-14-12915-2014).

The comment by the reviewer led us to state the objectives of this work in a more explicit way at the end of the introduction, and we hope that it is now clearer to highlight the motivation of the study. This now reads as:

The OPE site (Observatoire Pérenne de l'Environnement) is located in a rural site in Houdelaincourt, north-eastern France, well-representing the French national background PM. The long-term monitoring of PM_{10} (particles with diameter ≤ 10 µm) over a 9-year period (n = 434) in the OPE site allowed an extensive characterization of the chemical and OP of PM_{10}. The objectives of this work are, first, to achieve for the very first time a study of the main sources of PM in a low altitude rural environment in Europe, using a long-term database including several specific organic tracers in the carbonaceous fraction. The PMF methodology

includes a validation step with the comparison of the chemical profiles of the factors with those obtained previously in many other studies in France. The second objective is to quantify the temporal evolution of the contributions of these sources over the period of the study, particularly focusing for the first time on the vehicular emission that have already been shown to decrease in urban environments in Europe during the last decades. Finally, another major objective is to perform the deconvolution of the contribution of the PM sources to the OP measured with AA and DDT assays, and to determine the more important sources for the oxidizing capabilities of the PM influencing human health.

Referee comment: In section 2.3, the difference between the two assays can be elaborated further. Are the large differences presented in Figure 9b and Figure 9c expected? Are the contributions to total OP completely different because the two assays are meant to look at different oxidative processes in the lungs? This can be discussed in more details either in the methodology (highlighting more clearly why the two assays are used) or in the results, when commenting on the differences between Figures 9b and 9c.

Response: Thank you for this comment. To address the referee's comment, we improved section 2.3 as follows:

DTT is used as a chemical surrogate to mimic *in vivo* interaction of PM with biological reducing agents, such as adenine dinucleotide (NADH) and nicotinamide adenine dinucleotide phosphate (NADPH), in the DTT assay. The consumption of DTT in the assay represents the ability of PM to generate ROS (i.e., superoxide radical formation) (Cho et al., 2005). The PM_{10} extract is mixed with the DTT solution. Afterwards, the remaining DTT that did not react with PM_{10} is titrated by 5,50-dithiobis-(2-nitrobenzoic acid) (DTNB). This reaction produces 5-mercapto-2-nitrobenzoic acid or TNB. The TNB is measured by absorbance at 412 nm wavelength using a plate-reader (TECAN spectrophotometer Infinite M200 Pro) with 96-well plates (CELLSTAR, Greiner-Bio) in a 10-minute time step interval for a total of 30 minutes of analysis time.
AA is a known lung antioxidant used in AA assays using a respiratory tract lining fluid (RTFL) (Kelly and Mudway, 2003). This antioxidant prevents the oxidation of lipids and proteins in the lung lining fluid (Valko et al., 2005). The consumption of AA also represents PM-induced depletion of a chemical proxy (i.e. cellular AA antioxidant). The mixture (PM_{10} extracts reacted with AA) is injected into a 96-well multiwall plate UV-transparent (CELLSTAR, Greiner-Bio) and measured at 265 nm absorbance using a plate-reader (TECAN spectrophotometer Infinite M200 Pro) in a 4-minute time step interval for a total of 30 minutes of analysis time.
Both DTT and AA assays measure OP by depletion of specific chemical proxies, cellular reductants (for DTT) and antioxidants (for AA). Studies have well-identified a large number of PM constituents that influence OP concentrations. At least, OP assays are known to be associated with some metals (Cu, Fe, Mn among others) and some organic species (especially photochemically sensitive species such as quinones) (Calas et al., 2017, 2019, Charrier et al., 2014, Pietrogrande et al., 2019). However, in ambient air, each assay reports its own associations that may vary according to the local context (emission sources, local transport leading to various ageing processes and spatiotemporal variations) (Gao et al., 2020). Hence, a synergetic approach using multiple OP assays, to capture the most complete information regarding PM reactivity, is commonly suggested. (Bates et al., 2019, Calas et al., 2017, Borlaza et al., 2021)).

Referee comment: I have some concerns about the MLR method presented in Section 2.5. One of the key assumption of linear regression is that the residuals ε are iid, but you're using the

MLR to model timeseries data, where the assumption is evidently violated (by definition the OP data are not independent, as there is a clear temporal dependence). Perhaps you should consider adding a temporal component to your model (e.g. ARMA) that takes care of the temporal dependence to avoid misinterpreting the results on the β coefficients. Adding a temporal component is somewhat equivalent to detrend the data and remove seasonality, as you seem to be doing for PM10 analyses but not for the MLR part.

Response: We appreciate the referee's feedback. The goal of MLR is to apportion observed OP to PMF-resolved sources allowing to determine the main drivers of OP. The β coefficients (intrinsic OP) in the MLR model represents the OP property of each PM_{10} source. The source-specific OP contribution is calculated by multiplying the intrinsic OP of each source by the mass contribution of the source to total PM_{10}. ARMA is a great model for forecasting and can be used both for seasonal and non-seasonal time series data, however forecasting is not the purpose of MLR in this study.

Referee comment: In the same section, I am not sure if I am interpreting Equation 1 correctly. Why is there a subscript to your and β matrices? In previous sections, referred to the total number of observations whereas the meaning of here is unclear. Shouldn't your model simply be:

$OP = G\beta + \varepsilon$

With my comment above, the model should be extended to something like:

$OP(t) = \alpha OP(t-1) + G\beta + \varepsilon$

To take care of the temporal dependence. Obviously the choice of AR(1) is very simple but different AR or ARMA models can be investigated. Also if G is a matrix, what does it mean the subscript ? I believe you should double check your notation to be consistent. If you decide to use matrix notation, you should be consistent throughout.

Response: Thank you for the clarification. Apologies for the confusion. The G matrix is the PMF-resolved source contributions and the subscript denotes the specific source (i.e., biomass burning, traffic, nitrate-rich, etc.). β is the regression coefficient representative of the intrinsic OP of each source as well.

Referee comment: At the end of the introduction (line 59), you mention long-term trends of emission sources. Please be sure to use the right words here, I do not believe you are discussing emission trends at all, but only the decomposition of PM10 concentrations in different PMF factors.

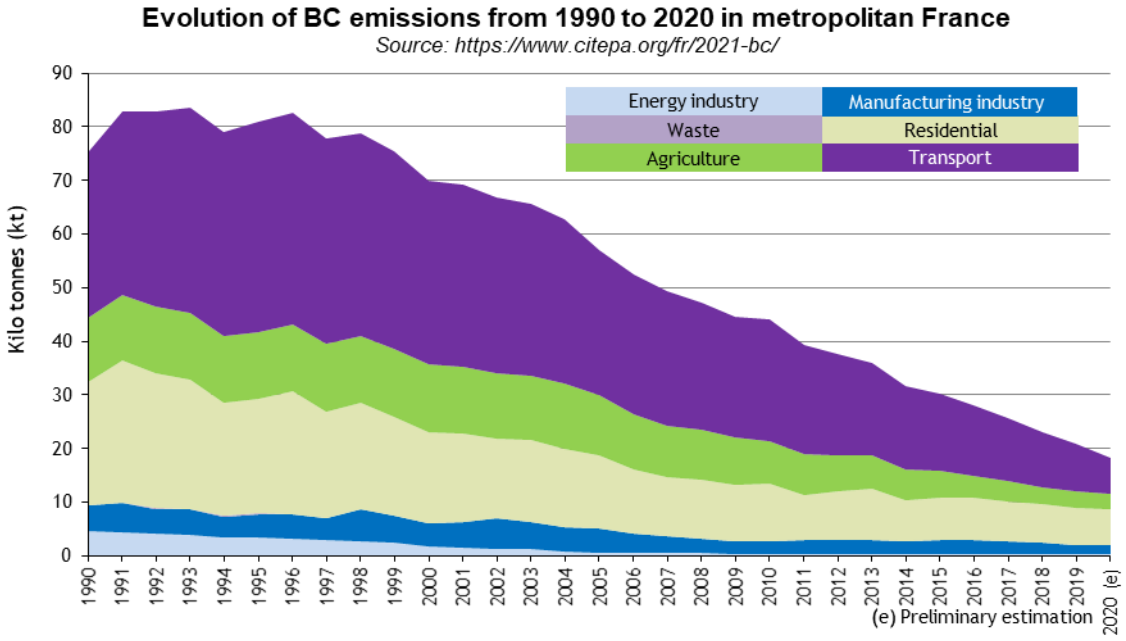
Response: We appreciate the feedback. The sentence was revised and now reads as:

Finally, another major objective is to perform the deconvolution of the contribution of the PM sources to the OP measured with AA and DDT assays, and to determine the more important sources for the oxidizing capabilities of the PM influencing human health in such an environment.

Referee comment: wonder if an effort could be made to actually show these emission data (aggregated at some level, for instance for the traffic category in a certain region), and see if there is some sort of correlation with the concentrations of the traffic factor that you showed from your analysis). A recurring theme of your manuscript is about analyzing the effect of recent changes in the source emissions (e.g. line 38-39), but I actually have not seen emission data at all. Can you make an effort to better substantiate that the reduced concentrations from

the traffic sector (Figure 6) are actually related to emissions rather than, say, changing meteorology?

Response: We appreciate the insight, that led us to effectively search for emissions data for comparison with our results. In fact, the Citepa is the official organization in France in charge of providing the emissions inventories at the national level. In their database, they have provided the evolution of black carbon (BC) emissions from 1990 to 2020 by different sectors (data available in https://www.citepa.org/fr/2021-bc/). The BC emissions by the transport sector decreased from 30.9 kt in 1990 to 6.8 kt in 2020 and is fully ascribed to the improvement of motorization and other traffic reductions.



In Figure 7 in the manuscript, we have provided a comparison of the evolution of the traffic factor source contribution at the OPE site obtained with our PMF study, and the BC emissions by the transport sector (source: CITEPA, https://www.citepa.org/fr/2021-bc/) for overall France. We have improved section 3.5 with an additional discussion about this that reads as:

The evolution of the absolute concentration of the traffic factor at the OPE site was also compared to an evaluation of black carbon (BC) emissions by the transport sector for overall France, provided by the CITEPA, the official agency in charge of the emissions inventory in France (https://www.citepa.org/fr/2021-bc/). Both series were converted in percentage change, using 2012 as the base 100 year (**Erreur ! Source du renvoi introuvable.**). This figure shows an excellent agreement in the trend and in the total decrease for estimated BC emissions from traffic (-64%) and the traffic source contributions observed at the OPE site (-52%), between the years 2012 to 2020.

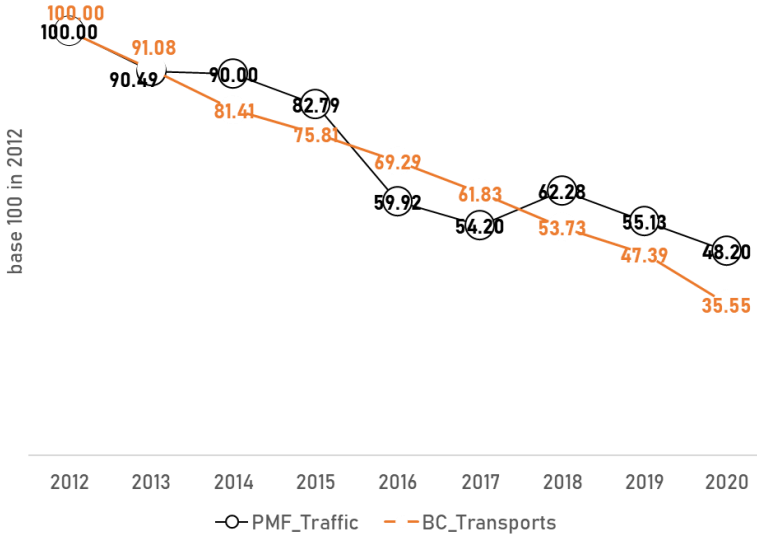


Figure 1: Comparison of the evolution of the traffic factor source contribution at the OPE site and the black carbon (BC) emissions by the transport sector (source: CITEPA, https://www.citepa.org/fr/2021-bc/) for overall France.

Referee comment: In Figure 2, it might be helpful to add error bars showing one or two standard deviations of your annual data. This would help interpreting how 'significant' (at least on a visual level) the differences between different years are.

Response: Thank you for the suggestion. However, Figure 2 mainly presents the average contribution of major components of PM_{10}. A better visualization of trends (monthly, seasonal, fit tendency) in terms of PM_{10} is presented in Figure S11.

Referee comment: Section 2.4.4 is quite unclear (or at least it's unclear until reading the results related to that section). I believe rephrasing the last couple of lines (166-170) and better defining what is implied by 'homogeneous' and 'heterogeneous' will help the reader in the interpretation of the associated results.

Response: Thank you for this comment. This section was revised as follows:

To investigate further any differences in the chemical profiles at the OPE site compared to those obtained at other French sites, a test of similarity was performed using the Pearson distance (PD) and standardized identity distance (SID) metric. This is calculated using Eq. S5 and Eq. S6 in the SI (S2) (Belis et al., 2015), closely following a previous work by our group (Weber et al., 2019). This comparison is based on the source relative mass composition, which allows the evaluation of the variability of PMF solutions across different sites. In this case, the chemical profiles obtained for the OPE site were compared against 15 different other sites over France. A "homogenous source" tends to have a similar profile over different site types and should have PD<0.4 and SID<1.0 (Pernigotti and Belis, 2018). Conversely, the sources with PD and SD values outside of this range are considered as "heterogeneous sources".