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

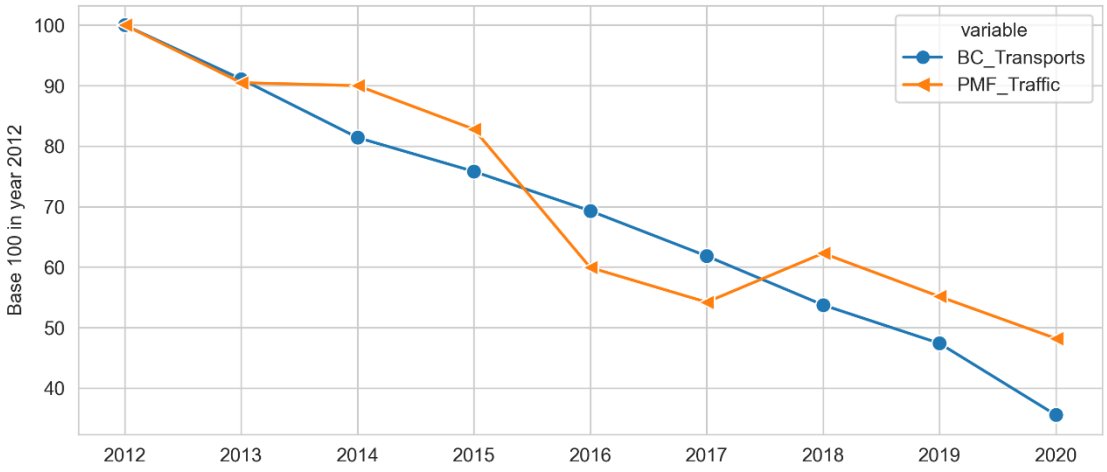
Authors' response

We would like to thank the referees for their time to re-evaluate our manuscript and the improvements made during the first and second rounds of review. Our point-by-point response to the third round of comments are presented below (in blue).

Anonymous Referee #2 nominated 25 May 2022, accepted 30 May 2022, report 30 May 2022 (Report #1):

- Thanks for addressing my concerns, especially the introduction-related ones. The research questions and goals of the paper are outlined much better now, and I do think that the authors are addressing an interesting question. The only suggestion that I have is to improve the quality of Figure 7, as I noted in the previous round of review (tick marks, y-axis is missing, low-resolution, etc.) -- Scientific papers should also have good quality in presenting the data.

RESPONSE: We appreciate the feedback of the referee. We have improved Figure 7 as:



Anonymous Referee #1 nominated 25 May 2022, accepted 01 Jun 2022, report 06 Jun 2022 (Report #2):

- Lines 431: Regarding the added sentence, it is not clear what the authors mean by "further exacerbate PM mass concentration" and specifically how this is connected to the revealed (decreasing) trends.

RESPONSE: Line 429 to 436 is a paragraph discussing the interplay between meteorological conditions and PM. To make it clearer, the specific sentence mentioned above was improved and now the paragraph reads as:

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. In most cases, there is a complex interplay between

PM and meteorological conditions that could increase or decrease PM mass concentration (Chen et al., 2020). Indeed, there are some studies at high-altitude or regional background sites that highlighted a concurrent role of changing large scale 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 concentrations.

- General comment #2 from second round of review: I would suggest to include part of the response in the revision.

RESPONSE: Accordingly, a paragraph was added in section 3.5 that reads as:

"These findings allowed the unravelling of the decreasing trend in terms of source contributions by the STL model. The STL deconvolution was applied on all the identified sources, which clearly showed that the traffic source has the highest tendency with a decreasing trend. The other major sources of PM, such as biomass burning, mineral dust, nitrate-rich sources, do not have as much decreasing tendency as the traffic factor. The internal annual variabilities of weather/climate conditions might not be the leading factors explaining these trends, as they would have affected PM sources in the same way."

- Line 34 to 35: "Particulate matter (PM) pollution causes various environmental concerns affecting public health and climate.": Still not clear, in particular related with the climate effect of PM (since the dominant effect should be a cooling so compensating for global warming.

RESPONSE: We understand the concern of the reviewer. PM is composed of a wide range of species that can have either warming or cooling effects on the climate, nevertheless air pollution and climate influence each other through complex interactions in the atmosphere—which the authors deem unnecessary to elaborate on the first sentence of the introduction.

- You can then provide a reference to the Supplementary Material for such description.

RESPONSE: Please refer to Line 237 that reads: "The reconstructed mass of PM_{10} in the OPE site was calculated following Eq. S1 in the SI and is presented in Figure 2."

- Section 2.4.2: The guide does not have a specific value for the added extra uncertainty (to the whole dataset) and in any case it provides general guidelines on how the uncertainty can be determined but many details (e.g., evaluation of the S/N ratio, calculation of the uncertainty for missing data and for data below detection limits, etc.) are absolutely not fixed. I would suggest to include more details on this on the revised version of the manuscript.

RESPONSE: We appreciate the feedback of the reviewer. We have further improved section S3 in the supplementary information which now includes more information about the PMF methodology, that reads as:

"For some species, it was necessary to use an expanded uncertainty that takes into account analytical error and sampling error, which can be used instead of the methodology proposed by (Gianini et al., 2012). An uncertainty of $\frac{5}{6} \times DL$ was used for values <DL and the uncertainties that are four times the specie concentration geometric mean were attributed to missing or replaced values.

The robustness of the final PMF solution was evaluated using various statistical parameters based on the European guide on air pollution source apportionment with receptor models (Belis et al., 2014) and the geochemical soundness of the solution. In brief, the parameters are listed as follows:

- ✓ Evolution of the ratio Qtrue/Qrobust (<1.5)
- ✓ The weighted residuals are normally distributed for most of the species and between ±3 which should indicate good model results of most variables
- ✓ Evaluation of the statistical robustness of the optimal solution (sensitivity to noise and any random data point) using a bootstrap test (BS) for 100 successive iterations of the model and for a minimum correlation (r^2) of 0.6
- ✓ Evaluation of the geochemical soundness of the PMF-resolved factor profiles based on *a priori* knowledge of the chemical footprints of the sources, their specific tracers, the temporal variability (daily, weekly and seasonally), and the characteristics of the site studied
- ✓ Statistical evaluation and precision for constrained solutions using BS for 100 successive iterations of the model and for a minimum correlation (r^2) of 0.6
- ✓ There is no added extra uncertainty to the whole dataset"

- Ok, but perhaps a detail could be added in the revised version of the manuscript.

RESPONSE: Please refer to response above.

- Lines 266-268: I cannot understand this: meteorology does not have only a seasonal signal, and also how can the interannual variation in the seasonal signal be connected with the effect of meteorology? If you have references, please provide them, because this justification is not convincing. The response in the general comments does not address my specific comment above.

RESPONSE: In the second round of review, we have already addressed that the search for all the causes of the trends by internal annual variabilities of weather or climate conditions was not in the scope of our work, and it is still not in the direction that we want for this paper.

- Line 298: I still see this as confusing, and I would suggest to make the sentence clearer in this regard.

RESPONSE: Previously, the reviewer mentioned that NO_3^- and NH_4^+ should be among the main chemical species. Our response to that was to clarify that, indeed, these two species are

among the main chemical species (you can also refer to Figure 2 in the manuscript). For clarity, we have improved the sentence that now reads as:

"Some changes in the concentration can be observed in the PM10 mass concentration, but there are no drastic changes in the major chemical components at the OPE, even with the lockdown restrictions during year 2020".

- Detail on this should be added.

RESPONSE: The unaccounted portion of PM found in this study is well within range of other rural environments as supported by the reference that we have provided. The authors deem it unnecessary to elaborate further on fractions that are, as it is, unaccounted.

- Lines 384-386: And what about the sulphates to Na+ ratio? Did you observe if there is a particular wind direction for this factor? Or reasons to suspect collinearity? Or any other investigation on this factor which could be also a mixed source?: The response is incomplete since the absence of meteorological data does not justify the absence of the analysis of the sulphates (or other species) to Na+ ratio.

RESPONSE: We made it clear that we did not analyse meteorological data. This statement addresses the question, "Did you observe if there is a particular wind direction for this factor?". As discussed in Section 3.2, constraints were used in the final model (Table S3), which resulted to all factors being correctly mapped and all bootstrap runs converged, thereby showing overall statistical robustness of the model. The chemical profile and temporal evolution including the reference run, bootstrap and displacement error estimates of each identified factor were provided in the S3 in the supplementary information. The PMF solution description and factor contributions were also provided in Section 3.3. For example, 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). But even with the possible mixing with anthropogenic source, this factor is clearly aged sea salt based on its chemical profile and factor contributions (Figure S6).

Again, the authors would like to point out that it is really difficult to differentiate if species are indeed internally mixed in the PM because of interactions / modification during transport or if there are mixing issues in the PMF solution between sources. This is why it is important that the chemical profiles in the OPE site were compared with other existing chemical profiles in other sites in France as shown in Figure 5 (similarity plot (PD-SID metric) of the OPE site against all the French sites in the SOURCES programme). This is probably the best test on the robustness of the factor and it is very rarely considered in any PMF paper in the literature.

- Apart from the analysis of trends, could you explain more how to interpret the results of the STL analysis for example in terms of different importance of the three signal components? : This addition does not completely address my comment, since the information provided are generic for the STL analysis and does not refer explicitly to the results obtained here using this methodology. but perhaps a detail could be added in the revised version of the manuscript.

RESPONSE: We understand the reviewer's concern and have further improved section 2.6 which now reads as:

"The STL (Season-trend deconvolution using locally estimated scatterplot smoothing) model is a versatile and robust statistical method allowing the decomposition of a time-series dataset into three components including trend, seasonality, and residual. The trend provides a general direction of the over-all data; the seasonality is a repeating pattern that recur over a fixed period of time; finally, residual is the random fluctuation or unpredictable change in the dataset. The seasonal component allows to eliminate seasonal variation from the time series, resulting to a smoothed trend line that shows the tendency of the time-series dataset. 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 PM_{10}."

- I was referring to the image resolution and to units of the y-axis.

RESPONSE: The units are provided in the figure caption. The image resolution was increased to 300 dpi.