Answer to referee#1

This manuscript is focused on the source apportionment of the oxidative potential (OP) of atmospheric PM_{10} from a long-term large-scale sampling campaign in France. More than 1700 samples from 14 sites and 15 years sampling period were analyzed for OP in two endpoints (OP^{AA} and OP^{DTT}) and various chemical species. The authors implemented a positive matrix factorization (PMF) coupled with multiple linear regression (MLR) protocol for identifying the sources from individual sites contributed to measured OP. The importance of different sources was discussed based on both intrinsic OP (OPm) and their contributions to the total OPv. The authors also attempted to explain the seasonality of certain sources in the context of OP. Overall, the manuscript presented very interesting and significant results of PM_{10} OP in West Europe area, and strongly supported the health effect study and legislation of air quality control in France. However, it lacks a discussion on OP's spatial distribution and the linkages of chemical composition to OP. Following are my specific comments.

We are thankful to the referee for their constructive feedback and the different comments and questions raised. Hereafter you will find our answer in blue.

Specific comments:

1. Generally, fine particles (PM_5) have been linked to the adverse effect caused to human respiratory and cardiovascular system, since these particles have highest penetration efficiency in lower respiratory tract. However, the PM samples collected in this manuscript have involved larger sized particles which have shown lower oxidative potential (Hu et al., 2008;Ntziachristos et al., 2007) and somewhat lesser relevance to human health. Thus, a justification should be provided for using PM_{10} in this health-related study, i.e. source apportionment of PM OP.

We, indeed, agree with the reviewer that a difference exists between PM_{10} and $PM_{2.5}$, both in terms of processes and of particle size prone to deposition in the lungs. However, studies also point out the role of the coarse fraction of PM for health impact (Keet et al. 2018 ; Chen et al. 2019 ; Wang et al. 2018). Finally, in EU and France, daily limit values are set for PM_{10} only and used as alert tool for health issues. PM_{10} need to be investigated with this respect.

It should also be noted that the 2.5 µm threshold commonly used to differentiated fine and coarse aerosols - is mainly based on technical considerations, but do not always reflect properly the bimodal size distribution actually observed in ambient air. Various studies, including those mentioned by the Reviewer, showed clear differences both for deposition of OP in respiratory tracts and in OP activity depending on the size of PM; but with size threshold varying between 1.18 and 3.2 µm, which can already make great differences in the composition of the PM compared to the $PM_{2.5}$ fraction. For instance, in the study by Fang et al (2017), Cu^{2+} mass concentrations are equally distributed between $PM_{2.5}$ and $PM_{2.5-10}$ fractions.

However, we added this remark as a limitation and edited the text as follows in the method section:

Even if it has been shown that mainly $PM_{2.5}$ deposit in lung alveoli (Fang et al., 2017), PM_{10} are still a public health concern and under regulation in EU and France (Directive 2008/50/CE). Moreover, recent studies also highlight the role of the coarse fraction of PM for heatlh impact (Keet et al. 2018, Chen et al. 2019; Wang et al. 2018). PM_{10} has the advantage to encompass all parts of PM potentially reaching the lower respiratory track.

2. Lines 85 – 89: Please provide more details on the geographical information of all sites, e.g. distance to local highways, industries and/or coast, wind direction and relative location in the valley/peak of Alpine area etc. This can help to directly identify some potential sources.

We agree that a detailed view of the site would help to better understand the different specificities of the sites. However, in this study, we do not want to focus on given sites. Instead, we want to elucidate common features, thanks to a large dataset, in order to extract the main impacts of sources to the OPs at a larger scale.

We extended the description of the Table S1 to give sufficient metadata information on the sites, classifying by typology (i.e Urban Background, Urban traffic (i.e. near an in-city highway), Traffic (near a main highway), Urban valley (surrounded by mountain) and Industrial (located in one of the most important France refinery area). Short paragraphs were also added in the supplementary information to picture each site in brief descriptions.

3. Line 119: Why 1,4-naphthoquinone was chosen as the positive control for AA? Does it have a consistent and high AA activity?

1,4-NQ is used as positive control due to its constant and predicted high OP. We use 25 µM 1,4NQ as positive control (6.6 µM final concentration in the well) and observe a constant two to three fold higher AA activity in comparison to ambient PM samples.

4. The apportionment of SOA factors in this paper is ambiguous. The authors did not explain the contributions of OC in three highlighted SOA-related factors, i.e. nitrate-rich SIA, sulfate-rich SIA and MSA-rich. We suggest a better explanation should be provided on their formation and the differences of their contributions to OP and mass of PM_5.

We agree with the reviewer that SOA fractions are very difficult to clearly identify and quantify in such source apportionment studies. Some developments were recently undertaken to address this issue, notably in France (e.g., Srivastava et al. 2018a, 2018b, 2019 ; Petit et al. 2019 ; Borlaza et al. 2021). However, such methodologies could not be used for the sites/datasets used in the present study, and we do not see the need for having an extensive discussion on his topic here, which would also add a lot of content to this manuscript. Such a discussion has already been proposed in previous papers (e.g., Waked et al., 2014; Weber et al., 2019 ; Favez et al, 2021). In particular, the details of the chemical profiles obtained for each of the PMF factors at each site used in the present study can be found at http://getopstandop.u-ga.fr/results?component=pmf_profiles and are discussed in Weber et al. (2019).

Thanks to this remark of the reviewer, we notice a typo in the manuscript where the OC apportioned by the **sulfate-rich** should read **nitrate-rich** factor line 375:

In fact, the sulfate rich one accounts for around 14% of the total OC, with some important variability between sites (from 5 to 33%). Nevertheless, this full section has been eventually re-written, and now presents a deeper discussion on the chemical component of the different factors, also considering our answer to the next comment raised by the Reviewer.

5. The subsections in Section 3.3 are confusing. I suggest combining Sections 3.3.2 – 3.3.5 to a single subsection "Intrinsic OP of main PMF sources", and create a new subsection for Sections 3.3.6 – 3.3.12 (like Section 3.4), "Profiles of OPm sources".

We thank the reviewer for this suggestion. Due to a formatting issue, the heading level was missing. A similar concern was raised by reviewer #2, so we reworked this section to account for it. We also discussed more in depth the different factors here, following the comments of both reviewers.

6. Lines 367 – 370: The authors tend to tone down the intrinsic OP of MSA-rich factor. In fact, I found very high $OP^{DTT}m$ for this factor at GRE-cb, NGT and STG-cle with reasonable CV (<0.6), while $OP^{AA}m$ at these sites were near 0. I would suggest the authors to further explore the redox-active components and explore the reasons for different activities between two endpoints for this factor at these sites.

Indeed, the MSA-rich factor may be considered as associated with an important intrinsic OP in some sites, but the inter-site variability is very high. Moreover, this PMF factor is identify thanks to a single marker (MSA) and very few studies only have reported it so far. The exact primary sources or processes leading to this factor are still under discussion for non-arctic regions (Golly et al. 2018). We wanted to tone down the impact of MSA-rich factor mainly due to the important uncertainties and variabilities of the chemical component of the factor, and the inter-site variability of intrinsic OP. For instance, GRE-cb and VIF are within 15 kilometers with similar sampling periods, but present respectively the highest and lower intrinsic OP^{DTT} for this factor. It is indeed of great interest that for the AA assays, however, the MSA-rich factor appears more similar at all sites.

For now, it is not clear if the uncertainties are mainly due to the sources' chemical component variabilities or to the inversion method used. The low amount of PM mass and its important uncertainties apportioned by the different PMF for this factor (between 0.7 to 5.5% of total PM_{10} mass) could also be an explanation of the variability of the intrinsic OP of this factor. Hence, we prefer not to conclude to a clear effect of this source on the OP.

This discussion has been added in the manuscript.

7. Lines 391 – 395: Please specify the factors with low variability of OPm and explain why the other factors show large variability.

We reworked the section 3.4 and subsequent ones, to clarify this discussion. We now present the variability thanks to the interquartile range of intrinsic OP, and discuss the variability in the text.

8. Lines 410 – 415: the authors should highlight the high contribution of sulfate-rich SIA factor to OP^{DTT} In comparison to its marginal contribution to $OP^{AA}v$, it is also important to find out the ROS-active components in this factor for the difference between two OP endpoints.

We reworked this part and a full paragraph is now dealing with each factor, including Sulfate-rich.

9. Lines 421 – 425: The explanations on the mean and median values of contribution of sources are unclear. The authors should explain the meaning of these two values and justify why using them under different circumstances.

We clarified it at the beginning of the corresponding paragraph in the revised manuscript as follows:

Figure 5 reports the typical "mean" daily value, a parameter generally used in the atmospheric community while Figure 6 reports the "median" daily value, often used in epidemiological studies in order to discuss the chronical exposure of the population and avoid the high impact of unfrequent low or high events that highly influence the mean value.

Due to the non-normality of the contribution and the high contributions of some sources at some site (for instance, the biomass burning source in alpine valley), the results highly differ if considering the mean or the median contributions, and the two statistical indicators may not address the same questions (the mean is more related to the identification of the major sources contributors and the median to the exposure of population).

10. Lines 473 – 476: I suggest the authors further investigate the sensitive chemicals (like transition metals) to both OP endpoints at all the sites with the industrial factor, in order to explain the huge difference of OPm found among all six sites.

The industrial factor determined is only determined at 6 sites by PMF and is one of the most heterogenous factor (see Figure S1). According to the uncertainties (both estimated by the bootstrap and displacement method of the EPA PMF5 software), the exact loading of metals is highly variable. Some of the statistical solution even led to unrealistic industrial factor with contributions from some metals that are higher than the total mass of PM apportioned.

The full chemical profiles (with uncertainties) are available to the readers at http://getopstandop.u-ga.fr/results?component=pmf_profiles, and clearly indicate a huge contribution of metals (notably, As, Cr, Mn, Mo, Ni, Pb, Rb and Zn)

Then, we think that a detailed discussion of the link between OP and chemicals for this factor would not bring much information since this factor represents very different types of sources. To be able to discussed it into more details, efforts should first be focused on having a clearer and more stable industrial factor at each of the corresponding site (e.g., using additional markers that we unfortunately didn't have here).

<ol start="11">
Line 507: A considerable contribution from sulfate-rich factor has been noted in Figure 4 – 6. Hence, the author made a wrong statement here saying both SIA sources contribute barely to OP which should be corrected.

The reviewer is indeed right. We should have been clearer between the difference of OP^{DTT} and OP^{AA}. The sulfate-rich is still of importance with regard to the DTT, but not at all for the AA. We corrected the text and conclusion.

<ol start="12">
Line 512: The paper showed many sources with different spatial variability in intrinsic OP, which is not discussed. Therefore, caution should be exercised when making statements like "relatively stable intrinsic OP at a large geographical scale". The authors should discuss it in two types of sources – sources with low variability and stable intrinsic OP (e.g. road traffic), and sources with high variability and varied intrinsic OP (e.g. biomass burning).

We agree that we did not highlight enough the variabilities. Section 3.4 has been re-written with this comment in mind. We now set up an objective criterion to distinguish between a « variable » or « stable » intrinsic OP based on the interquartile value (Q25-Q75). We also stressed in the main text if the variability is related to spatial-variability (i.e. site presenting different intrinsic OP) or if it is due to important uncertainties for the results obtained by MLR model analyses.

Technical corrections :

1. Line 14: to prioritized – insert "be" between these two words.
2. Line 76: "multilinear" should be changed to "multiple linear" or "multivariate linear".
3. Line 115: the abbreviation in the parenthesis should be "RTLF".
4. Line 174, 237, 257: "specie" should be changed to "species".
5. Line 266, 459: The word "inversion" in the title is confusing. I suggest replacing "OP's inversion" with "intrinsic OP".
6. Line 431: I suggest moving "in Figure 5" to the end of the sentence or include it in parenthesis.
7. Legend of Figures 5 and 6: the error bars __ the 95% confidence level – insert "represent" at the underline.
8. Legend of Figure A2: "Searman" should be changed to "Spearman".

We thank the reviewer for its careful reading. Corrections were done accordingly in the revised manuscript.

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