

Answer to referee #2

In this manuscript, the authors presented source apportionment results of OP-DTT and OP-AA measured on PM₁₀ filter samples collected at 14 different locations in France using PMF and multiple linear regression models. The authors mainly focus on discussing the intrinsic OP, the variability of different sources, and the daily mean and median contribution of sources to OP. The limitation of the study is well discussed. This study has a unique dataset. However, in my opinion, the authors did not fully utilize their dataset. One of the uniqueness of this study is that the dataset spans 15 years and covers a wide range of environments. Seasonal variations of OP-DTT and OP-AA are discussed but the authors may consider looking into other aspects that are more interesting, for example, the spatial homogeneity or the historical changes of OP. How do the OP sources and source contributions change over the 15-year period? Are there differences in the historical trends of OP-DTT and OP-AA and how does it compare to PM mass? What chemical components are the most important drivers to the changes of OP and PM mass? It is well known that biomass burning, traffic emissions, secondary processing are important OP sources. Presenting something other than sources would enhance the scientific significance of this manuscript. Below are my comments:

We thank the reviewer for its positive feedback and numerous propositions!

Most of them are highly interesting and were considered in the revised version of the manuscript. However, some of them are impossible to achieve with the datasets used in the present study.

The spatial homogeneity of OP was already studied in a previous paper (Calas et al. 2019) using 7 sites in France. We agree that this temporal and spatial variability of OP could be further emphasized, but we chose in this article to focus on the source-apportionment of OP, that already raises lots of questions and discussions.

We do not think, however, that the current dataset could be used to investigate the temporal trend of OP over the region of interest. Indeed, many parameters are changing together (site location, sources identification and contribution, meteorology, etc). We here want to stress that the dataset does not cover a 15-year period, but 14 sampling sites with 1 to 2 years of sample collection. To clarify, we added figure in the supplementary information to better highlight the sampling period per site.

Major comments:

1. Please provide detailed protocols for both the DTT and AA assays. Multiple versions of DTT assays are currently used in the community. It is important to show which DTT protocol was used in this work. Perhaps the most important is the initial concentration of DTT as studies have shown that the initial DTT concentrations can have a large impact on the DTT consumption rates e.g. (Lin and Yu 2019).

The OP assays conducted at IGE have been deeply investigated and published as methodological papers (Calas et al, 2017, 2018).

For OP DTT, we use an initial concentration of 12.5 nmol of DTT (50 μ L of 0.25 mM DTT solution in phosphate buffer) to react with 205 μ L of phosphate buffer and 40 μ L of PM suspension.

For OPAA, we mix 80 μ L of PM suspension with 24 nmol of AA (100 μ L of 0.24 mM AA solution in Milli-Q water) and follow the AA depletion within 30 min.

This has been added in the revised manuscript.

- Line 110, particles removed from the filters were added to 96-well plates for DTT analyses, and the authors claimed that this included “soluble and insoluble” particles. What is the extraction efficiency? Could there be particles that are not extractable and attached to the filters. Other studies that measured total DTT run the extract along with the filter in DTT solutions. E.g. (Gao, Fang et al. 2017). A note should be added to emphasize the differences in the protocol and state that the DTT activities may not be “total”.

We thank the referee for this remark. We already investigated this issue in the methodological paper of Calas et al. 2017: “The importance of simulated lung fluid (SLF) extractions for a more relevant evaluation of the oxidative potential of particulate matter”. The efficiency of the extraction is quantified according to different protocols for extraction and according to the particle extraction media. Of course, it may vary according to the nature of particles. Then the supernatant (to avoid filter in the well) without filtration is injected in the wells leading to soluble and insoluble (visible) particles being in contact with DTT. We don't think this methodology can strongly differ from (Gao, Fang et al, 2017), and this previous extraction of particles from the filter is justified by the use of the microplate reader that prevent to put the filter directly into the well (interfering with light source of the reader that would prevent from the online monitoring of the reaction).

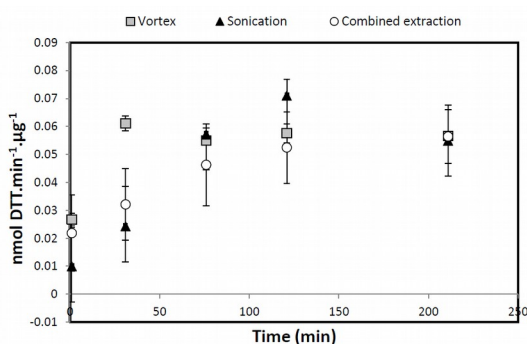


Figure 5 11: Kinetics of DTT depletion (normalized per μ g of PM) when comparing three techniques of extractions: vortex, sonication and a combined extraction (sonication followed by vortex). (Bars correspond to standard deviation (SD) of triplicate).

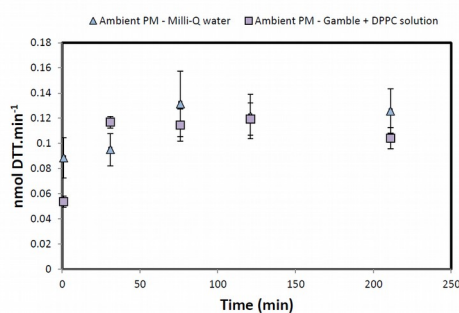


Figure 5 12: Kinetics of DTT depletion when comparing the same sample extracted in Milli-Q water or Gamble + DPPC solution. (Bars correspond to SD of triplicate).

- In Figure 3, OP-AA from road traffic, biomass burning, dust and OP-DTT from biomass burning and dust sources are bi-modal distributions. Why? It would be interesting to look into details in chemical components to figure out the observed distributions.

Figure 3 presents the distribution of the 15 independent MLR model runs (one model analysis per site). Each series of model runs has been associated with uncertainty estimation using

bootstrap, leading to a Gaussian distribution of the regression coefficient (i.e. intrinsic OP of the sources). The multi-modal distribution observed in the Figure 3 reflect the individual Gaussian distribution obtained for each site.

Since this section has been re-written according to comments raised by reviewer#1 and next comment, some discussion is now provided for this variability. However, former Figure 3 has also been replaced by a more concise and general view of the intrinsic OP. We want here to emphasize the generalities of intrinsic OP, thanks to the extensive dataset, and not to discuss the details of each site (that could be done one by one potentially in a more specific study of each site). Former Figure 3 is now in SI alongside the table of intrinsic OP per site.

Some hypothesis concerning the multimodal distribution of intrinsic OP is now better described in the revised manuscript as well (difference in chemical compound or aging). See revised manuscript for the details since the multimodal reason doesn't seem to be unique but factor and site dependant.

4. Section 3.3.6-3.3.11, I appreciate the authors' efforts in discussing the variability of the intrinsic OP. However, it is not clear to me what do variabilities of different OP sources really bring about. It seems more interesting to compare the intrinsic OP or the contribution of different sources to OP with those from other studies or those from other regions of the world. These subsections lack in-depth discussion on each source. For example, for road traffic, transition metals (non-exhaust) and quinones from PAHs or soot (exhaust) can contribute to OP-DTT and OP-AA. How does your source profile from road traffic differ from others? What are the linkages of traffic-related chemical components to measured OP? What new insights does this work bring? One interesting questions is whether you can differentiate the contribution of exhaust and non-exhaust emissions to OP.

It would be, indeed, of great interest to compare this source-apportionment of OP to other studies. However, due to the differences in methodology to measure the OP or to estimate source contribution to PM mass, it is still difficult to directly compare intrinsic OP between studies using different protocols (use of gamble+DPPC, iso-mass, PMF-filter, CMB, PMF-AMS, PCA, etc). This study, however, presents a method of inter-comparison for homogeneous datasets and a national synthesis that could be useful for inter-study comparisons (i.e., other regions in the world) in the future.

Regarding the road traffic factor(s), we actually do not have a single factor here, but 15 different ones, determined by 15 different PMF (one for each studied site). They do present some variabilities in terms of chemical compound and are now discussed in the text and in the SI (with the similarity assessment) and in Weber et. al (2019). Comparing these factors with previous studies would be indeed of great interest. However, this goes far beyond the scope of this study (non-homogeneous dataset comparison, methodology of source apportionment, etc). For your interest, the chemical profiles used in this study aims to be uploaded to the SPECIEUROPE database, notably for comparison exercise. We were not able to differentiate the exhaust and non-exhaust of traffic-related emission in our current dataset. Hence, we cannot discuss their respective impact on OP.

We purposely did not discuss in depth the link between the chemical component of factor profile and the OP, because the whole point of doing the apportionment of OP by sources and not by species is to get rid of the issue of the all array of un-measured chemical species. For instance, doing inversion by species would lead to a high impact of levoglucosan, although this species has no effect on OP, simply due to the co-emission of other organic species with levoglucosan, or even due to formation of SOA (quinone-containing for instance) due to the aging of biomass burning emissions (see the recent paper of Campbell et al. 2021 for instance). « Hiding » everything into source categories allow to have only few molecular proxies of sources but still being able to identify important source contributors, even without knowing the exact source composition and responsible species.

5. It would be useful to present how are metals (especially Fe and Cu) apportioned into each factor. Atmospheric metals can be found in biomass burning, road traffic, dust, or sulfate particles by acid processing. Discussions on how metals are distributed in these factors may help to interpret the contribution of different sources to OP.

The full description of the source profiles is given in the interactive SI (http://getopstandop.u-ga.fr/results?component=pmf_profiles). We also extensively revised section 3.3 to discuss more in-depth the different profiles, with regards to both their chemical compound and variability across sites.

6. It is not clear that what are the new findings in this manuscript compared to previous work from the same group, e.g. (Weber, Uzu et al. 2018).

Weber et al, 2018, implemented the first OP apportionment with PMF tool in Chamonix as a proof of concept. In the present paper, we now expand this unified methodology to 15 sites datasets. The main point here is to investigate if what was previously established held at a larger geographical scale or rather if each site would present very different ranking of intrinsic OP per source. Since each site present similar ranking and order of magnitude for the intrinsic OP, what we presented earlier is not a singular case but present a “global approach” that synthesizes the geochemistry and OP of PM₁₀ in France.

In the present study, we also proposed different statistical tools used to quantify population exposure (the mean vs. median discussion). We highlighted that a drastic difference can be observed in this regard. With previously « limited » datasets, such an investigation could not be conducted due to low number of samples and poor statistical analysis possibility. Documenting the mean and median in this work is then an important step towards closing the gap between atmospheric science and epidemiological.

Other comments:

1. Line 257, “organic specie” should be “organic species”
2. Line 258, define “HULIS”
3. Use the same font type throughout, for example, line 464, numbers seem to be a different font than other contents

We thank the reviewer for their careful reading. For the font type, it is unfortunately due to the latex template of ACPD of unit formatting.

References:

Gao, D., T. Fang, V. Verma, L. Zeng and R. Weber (2017). "A method for measuring total aerosol oxidative potential (OP) with the dithiothreitol (DTT) assay and comparisons between an urban and roadside site of water-soluble and total OP." *Atmos. Meas. Tech. Discuss.* **2017**: 1-25.

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