Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1053-RC1, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "An apportionment method for the Oxydative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France" *by* Samuël Weber et al.

Anonymous Referee #1

Received and published: 24 January 2018

This paper uses a PMF analysis to determine the sources of PM10 OP measured with two assays, ascorbic acid (AA) and dithiothreitol (DTT). A multiple regression analysis is then used to derive a linear model to predict the OP for each assay with sources as the independent variable. This model provides the intrinsic OP (OP/mass) for each source. Relative contributions of the sources to PM10 mass and the OP for each assay are contrasted. The results are interesting and add more general insight into these assays. However, there are a number of issues. 1) The PMF/multiple regression analysis approach on OP has been done before (Bates et al). This should be recognized and

more comparisons between this and the Bates method provided. This is not a novel idea, as seems to be indicated in the Abstract. 2) After noting that a current issue with various studies investigating OP of aerosols is the lack of a standard method, the authors utilize a non-standard method for the OP assay. This makes comparisons with other reported studies difficult. 3) The authors use PM10 in the analysis, which leads to further difficulties in comparing with other studies (many are PM2.5) and makes the source apportionment much more complicated. Furthermore, it raises the possibility of greater artifacts arising in the OP analysis due to interactions between aerosol chemical species that are not mixed in the ambient aerosol, or likely to be mixed when deposited in the respiratory system. Although this adds to the confusion when comparting OP results, the results are of sufficient interest for publication in this journal. Specific comments follow.

Specific Comments:

Pg 2 Line 1. Specifically explain how OP measurements relies on surface area and particle size

Pg 2 lines 17 to 25: Issues with PMF. This paragraph is rather opaque and possibly unnecessary. First, PMF analysis of aerosol data sets is now very common practice, so many of the issues have been addressed. Thus it is not clear why such detailed discussions are included. It would be better to refer to some of the original papers. Furthermore, a number of investigators have reported using PMF on OP data. These should also be cited. A better literature review by the authors is warranted.

Pg 4 lines 19 to 21. Explain specifically how meteorology and inversions increase correlations between measured species. Take inversions, for example, how is covariability affected by a factor that changes concentrations of all independent variables by roughly the same amount?

Pg 4 line 32, what does geochemically sounded mean?

Pg 5, what does pulled up maximally mean?

Was the DTT assay performed in simulated lung fluid (SLF)? If so, this deviates from the standard DTT protocol as described by Cho et al, 2005. This means the DTT activities reported in this work cannot necessarily be compared to most other published work, which follow the Cho method. This issue is important since it potentially adds confusion to the public literature on OP. This should be made very clear in the Abstract, Conclusions etc. Optimally, a conversion factor comparing this SLF_DTT to the standard method DTT activities would be included in the paper to help in interpreting the results. It is rather surprising these authors have done this given statements in the paper on limitations with no standard method used in practice (ie, the statement is made, then a non-standard practice is utilized).

Pg 5 Section 2.4 Does the filter extraction method include only water soluble species or both water and water insoluble species. For example, does the method extract BC? It is later stated that BC is correlated with the measured OP, but it is unclear if the assays are actually exposed to BC. More details on the extraction method are needed.

No discussion given on blanks, which are critical in OP measurements. Is the OP data blank corrected?

Pg 5 line 26, the unit nmol min-1 m-1 is incorrect.

Pg 6 line 19, typo, has shows. . .

Pg 6 line 20 and 21. What does the following line mean? . . . This underlines that the assays are sensitive to different ROS. . .. Is it being asserted that the assays are measuring ROS on the particle? This is not what these assays are designed to measure. I think the line gives a false impression, versus what the authors really mean.

Fig 10. The vehicular source does not appear constant throughout the year. The mean is very likely higher during cold seasons versus warm seasons, contrary to what is stated in the paper. Any explanation?

How is the multiple regression analysis performed in this paper novel relative to the published results of Bates et al (which is cited)? A detailed contrast would be valuable since it appears this paper is following, in general, the same approach as Bates et al. Or maybe it differs?

Pg 8, line 35. Why does the OP never display negative values? Is it because they were thrown out in the data set, ie samples with low masses where not included. These would be cases where the measurements would be near the detection limits and negative values possible. This needs more explanation as it can bias the results.

Pg 9, line 1. A non-zero intercept is also possible due to sampling artifacts associated with the filter sampling. Un-denuded sampling onto quartz filters are known to have positive artifacts. Add a discussion on possible effects of filter artifacts on this analysis.

Pg 10 line 13 and 14. These assays do not measure the ability to generate ROS, they measure the depletion of the antioxidant. There is a big difference.

Pg 10 Regarding the discussion comparing the intrinsic OP levels. Why not compare to other reported intrinsic values? For DTT, see for example, Shiraiwa et al (Shiraiwa, M., K. Ueda, A. Pozzer, G. Lammel, C. J. Kampf, A. Fushimi, S. Enami, A. M. Arangio, J. Frohlich-Nowoisky, Y. Fujitani, A. Furuyama, P. S. J. Lakey, J. Lelieveld, K. Lucas, Y. Morino, U. Poschl, S. Takahama, A. Takami, H. Tong, B. Weber, A. Yoshino, and K. Sato (2017), Aerosol health effects from molecular to global scales, Envir. Sci Technol. , 51, 13545-13567). Keep in mind that much data is likely PM2.5.

Pg 10. When comparing the results of this study to others, eg, Bates, et al., Fang et al., Verma et al., Charrier et al., keep in mind that those studies were PM2.5 not PM10, which could have a significant effect. Furthermore, the assay was performed differently in this study.

Pg 13 line 17. In what sense are the results very good. This is an opinion. Are the results very good because the models could reproduce the total observed OPs?

Uncertainties. A large uncertainty not considered is mixing aerosols over a broad size range into a single liquid sample and testing the OP of that mixture. These particles are definitely not internally mixed in the ambient atmosphere, nor in contact when deposited in the lung. Using PM10 makes this situation much worse as it mixes aerosol of widely different sources (secondary and mechanically generated primary, for fine and coarse, respectively). A number of papers show that there are both antagonistic and synergistic interactions possible between species that will affect the OP measurement (eg, see: Xiong, Q., H. Yu, R. Wang, J. Wei, and V. Verma (2017), Rethinking The Dithiothreitol (DTT) Based PM Oxidative Potential: Measuring DTT Consumption versus ROS Generation, Envir. Sci. Technol, 51, 6507-6514)

The last line of the paper needs to be edited.

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