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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.

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The manuscript of Weber et al. represents the OP results obtained by analyzing a series of filter PM10 samples collected during a year-long period at an urban location in France, using two different assays, namely the dithiothreitol assay (DTT) and the ascorbic acid assay (AA). Combining results obtained by different analyses of the collected filters, including soluble ions, metals, PAHs and combining these results with

PMF and linear regressions analyses for the identification of different sources and the subsequent attribution of redox-activity to different PM sources. It occurs that a large part of the observed OP is linked to biomass burning and vehicular sources for both assays. The paper is well written and easy to follow, though there are some issues and more thorough discussion should be made in specific sections. A very interesting point of the study is that the used assays appear to be sensitive to different ROS. Other than that the paper can be recommended for publication after addressing the issues listed below.

The authors would like to thank the second referee for his/her review and very useful comments that helps us to improve the paper. We tried to answer his/her question point by point in the following discussion.

1) Samples consist of PM10 while PM2.5 is most commonly used as being able to penetrate inside the respiratory system. Although the used range (PM10) surely covers the totality of the OP distribution, the difference of acidity between fine and coarse fraction surely plays a key role in the aerosol OP, influencing the solubility of metals (e.g. Fang et al. 2017). Authors should comment on this.

We indeed agree with the reviewer that a difference exist between PM10 and PM2.5, both in term of processes influencing the OP values (like changing pH values, hence solubility of some species, according to the size), and of particle size prone to deposition in the lungs. However, in EU and France, PM10 are under regulation, –not PM2,5, and are used as alert tool for health issues. Therefore, they need to be investigated with this respect. Further, as we answered to the first reviewer, the distinctions in PM10, PM2.5 etc, are norms and are generally not be fully physically based considering the large variability of the modal size distributions observed in actual environments. Fang et al. (2017) indeed showed clear differences both for deposition of OP in respiratory tracks and in OP activity depending on the size of PM; but the threshold vary between PM1.18 and PM3.2, which can already make great differences in the composition of the PM compared to the PM2.5 population. For instance, in the study by Fang et al

(2017), Cu2+ presents its mean mass distribution value for Dp = 2.5 μm, therefore half of Cu2+ is in the PM2,5 fraction, but half of it is in larger sizes. However, we added this remark as a limitation and edited the text as follows, including also our answer to the first reviewer' comment (p14):

Even if it has been shown that mainly PM2.5 deposit in lung alveoli (Fang et al., 2017), PM10 are still a public health concern and under regulation in EU and France. PM10 has the advantage to encompass all parts of PM potentially reaching the lower respiratory track. However, in doing so, a source of uncertainty probably arises from the mixing, in our measurements systems, of PM populations with different chemical characteristics (i.e. acidity), that can influence the OP (i.e. changing solubility of trace metal, for example).This potential artifact, already existing for PM2.5, may be reinforced with PM10.

Ting Fang, Hongyu Guo, Linghan Zeng, Vishal Verma, Athanasios Nenes, and Rodney J. Weber: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environmental Science & Technology 2017 51 (5), 2611-2620, DOI: 10.1021/acs.est.6b06151

2) It is stated that the current study uses simulated lung fluid (SLF) solution, complicating the direct comparison with other studies. It should be clearly stated in the abstract and conclusions section that a method different than the standard DTT protocol is used in order to avoid confusion. Furthermore, as seen in Calas et al. (2017), the OPDTT measured in Milli-Q water and three different SLF extracts does not present statistically significant differences. Authors should comment on the choice of extract. Finally, in the extraction phase (P5,L13) is different extraction volume used for different samples or only a different area of the used filter? This is not clear.

We agree that we should keep in mind the difference for the extraction protocol when trying to compare studies. This comment is also shared with the first reviewer and text modification is given in our answer. We clarified the extraction protocol in the method-

ology part and added a paragraph in the discussion concerning the comparativeness of our solution.

However, we disagree with the term "standard DTT protocol". To the best of our knowledge, there is still no consensus toward a standardized DTT protocol. Indeed, even if Cho et al. (2005) is a general reference, several protocols have evolved from this starting one, including changes that can make large differences: removing EDTA considering its chelating effect (Charrier and Anastasio, 2012); changing the temperature of reaction and the times intervals of measurement of the kinetics ("under linear condition (DTT loss < 20%)" in Cho et al., (2005), "0, 4, 13, 23, 30 and 41 min" in Fang et al., (2015), "0, 10, 20, 30, 40 and 50 min" in Jedynska et al.,(2017), "0, 15 and 30 min" in Calas et al. (2017)) ; changing initial DTT concentrations: "160 μM" in Fujitani et al. (2017) ; "0.5 mM" in Calas et al. (2017), "1 mM" in Fang et al. (2015); "100 mM" in Jedynska et al. (2017)), etc. Moreover, it has been shown that the DTT response is not linear according to the amount of reacting species (i.e. the mass of PM) (Charrier et al., 2016), and it is definitively the main bias when comparing different studies using different PM mass extracted.

Calas et al (2018) showed that no statistical significant difference was found when using Gamble+DPPC or Milli-Q water as extraction fluids for the DTT the assay. However, in Calas et al (2018), only 5 samples were used and we clearly observed a small but constant higher OP in Milli-Q, that we explained by complexes that could take place between some species and the Gamble solution. Further, a significant difference was found between the extraction in Milli-Q water and in another lining fluid (the artificial lysosomal fluid); we did not selected this fluid for our standard protocol in our lab, since it is representative of inflammation in lung, and is therefore not relevant for all physiological conditions. As a result, we rather choose to keep the Gamble+DPPC protocol, as it is closer to biological conditions and may closely reflect the complexation occurring at the surface of lung epithelium when PM deposit.

Concerning the extraction phase, as all samples account for 24 h of sampling at con-

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stant flow rate (30 m^3/h), we adjust for each sample the surface of the filter needed in order to extract always the same mass of PM (selected in the range of linearity), has it has been shown that OPDTT and OPAA vary non-linearly with the mass of PM in assays. We clarify this in the text, as follows:

The extraction took place into SLF at iso-mass. All samples were analyzed at 10 μg.mL-1 of PM, by adjusting the area of filter extracted.

Calas, A., Uzu, G., Martins, J. M. F., Voisin, D., Spadini, L., Lacroix, T. and Jaffrezo, J.-L.: The importance of simulated lung fluid (SLF) extractions for a more relevant evaluation of the oxidative potential of particulate matter, Scientific Reports, 7(1), doi:10.1038/s41598-017-11979-3, 2017.

Fang, T., Verma, V., Guo, H., King, L. E., Edgerton, E. S. and Weber, R. J.: A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE), Atmospheric Measurement Techniques, 8(1), 471 482, doi:10.5194/amt-8-471-2015, 2015.

Fujitani, Y., Furuyama, A., Tanabe, K. and Hirano, S.: Comparison of Oxidative Abilities of PM2.5 Collected at Traffic and Residential Sites in Japan. Contribution of Transition Metals and Primary and Secondary Aerosols, Aerosol and Air Quality Research, 17(2), 574 587, doi:10.4209/aaqr.2016.07.0291, 2017.

Charrier, J. G., McFall, A. S., Vu, K. K.-T., Baroi, J., Olea, C., Hasson, A. and Anastasio, C.: A bias in the mass-normalized DTT response An effect of non-linear concentration-response curves for copper and manganese, Atmospheric Environment, 144, 325 334, doi:10.1016/j.atmosenv.2016.08.071, 2016.

Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals, Atmospheric Chemistry and Physics Discussions, 12(5), 11317 11350,

Jedynska, A., Hoek, G., Wang, M., Yang, A., Eeftens, M., Cyrys, J., Keuken, M., Ampe, C., Beelen, R., Cesaroni, G., Forastiere, F., Cirach, M., de Hoogh, K., De Nazelle, A., Nystad, W., Akhlaghi, H. M., Declercq, C., Stempfelet, M., Eriksen, K. T., Dimakopoulou, K., Lanki, T., Meliefste, K., Nieuwenhuijsen, M., Yli-Tuomi, T., Raaschou-Nielsen, O., Janssen, N. A. H., Brunekreef, B. and Kooter, I. M.: Spatial variations and development of land use regression models of oxidative potential in ten European study areas, Atmospheric Environment, 150, 24 32, doi:10.1016/j.atmosenv.2016.11.029, 2017.

3) There is no mention of the LOD for the specific assays using the SLF, nor blank/blank corrections.

Indeed, this is perfectly right. The first reviewer also pointed it out. This was forgotten, and we added the following in the text :

Three filter blanks (laboratory blank) are included in every plate (OP AA and OP DTT) of the protocol. The average values of these blanks are then subtracted from the sample measurement of this plate. LOD value is defined as three times of the standard deviation of laboratory blanks measurements (blank filters in Gamble+DPPC solution).

4) When presenting the concentrations of the PMF sources, emphasis is only given for the correlation of OP solely with biomass burning and vehicular sources, even though it appears that "nitrate rich" source could also be correlated, as during winter enhanced nitrate concentrations are usually associated with biomass burning. Although mentioned further on (P12, L10) it should also be mentioned and commented on, here.

We choose to consider as "correlated" only the variables with r values above 0.6 (p<0,001 for n=85). Thus, the correlations between OP and the nitrate rich source (Fig. S3) are below this threshold of 0.6 (resp. 0.45 and 0.55 for OP AAv and OP DTTv). This is why we do not say that this factor is correlated with OP's. However, we agree

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that this is an arbitrary threshold. When we discuss it later in the text (page 10, line 11), we do not discuss about the correlation coefficient between PMF source and OP, but instead about the intrinsic OP of each source. This "low" correlation OP/PMF source but relatively high OP contribution is one of the key point of the multiple linear regression. We see that highly correlated source may have "low" intrinsic OP DTT (namely biomass burning/OP DTTv r=0.80 but intrinsic OP DTT_{BB}=0.07 nmol/min/μg) and poorly correlated source may have high intrinsic OP (namely Secondary biogenic/OP DTT r=0.40, but intrinsic OP DTT_{SOA}=0.18 nmol/min/μg). This emphasize the need of a more sophisticated statistical tool than simple univariate correlation when dealing with sources contribution to the OP.

We added the modified paragraph in the discussion: p7, l8:

Briefly, the vehicular and biomass burning sources appear to be strongly correlated to both OP (r > 0.8). The nitrate-rich factor presents a lower correlation, as well as the sea/road salt one (0.3 < r < 0.6 for both OP's), whereas the secondary biogenic, primary biogenic, and sulfate-rich factors are slightly anti correlated with both OP's (0.6 < r < 0.3). Crustal dust correlation is not significant with respect to the AA test but presents low correlation to the DTT test (r = 0.15 and r = 0.35, respectively).

P13 l3, we added this paragraph:

Nevertheless, all these results contrast with those from simple univariate correlations between OP and sources. Indeed, the secondary biogenic source which is slightly anti-correlated to both OP's is in fact the second most redox-active source when considering intrinsic OP_{DTT}. On the contrary, the sulfate-rich factor is slightly anti-correlated to the OP AAv but present an intrinsic OP_{AA} close to 0. The vehicular factor, which highly correlates with OP's is also the dominant source in terms of intrinsic OP's for both assays. Such results emphasize the real interest to go replace the simple univariate correlation by a more comprehensive statistical analysis when considering the contribution of the sources (or species) to the OP's.

5) A more thorough discussion should be made in the Intrinsic OP section, namely a comparison with other values found in the literature (even though the majority concerns PM2.5) and the use or not of an intercept in the linear regression model. Furthermore, it is stated that other studies also highlight the importance of the vehicular source to explain the OP. In Verma et al. (2015) even though HOA (representing traffic) correlates significantly with OP at some sites, the generated linear regression models do never include HOA, though in some cases the linear regression model include copper. It is known that copper may originate from brake wearing, but also it can be linked to other anthropogenic activities, such as industry and/or coal burning.

We agree that at some point a more in-depth discussion between our results and existing similar studies should be made. However, this was not the point of this paper which is focused on the methodology and only provides a case study for supporting it. An incoming study, applying this methodology to many other sites in France will be coming soon, and will compare our results to previous studies in much more details, and of course, Verma et al. (2015) will be discussed and compared in this paper.

Technical corrections: Title: "Oxydative" should be corrected to "Oxidative" Abstract, L1: ". . .induces cellular oxidative stress in vivo, leading to adverse. . ." P6, L19: ". . .DTTv shows larger values. . ." (delete "has") P7, L7: ". . .sources appear to be strongly correlated. . ." P14, L18: "...biomass burning and vehicular sources. . ."

We would like to thank again the reviewer for his/her careful review and corrections.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-1053/acp-2017-1053-AC2-supplement.pdf

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