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Atmospheric Measurement Techniques Discussions
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Interactive comment on "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" *by* Dong Gao et al.

Anonymous Referee #1

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General comments: It is important to characterize and identify the components of PM contributing to its oxidation potential. Time-resolved and automated analysis systems are important to better assess exposure effects. The paper addresses the need for faster laboratory results and compares different methodologies to identify the relevant fractions contributing to PM oxidative potential. However, the methodology applied in some cases is not well thought and important points have not been addressed in the manuscript or considered by the authors. Thus, some of the conclusions are not correct, unless several assumptions are made.

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Main Comments: Line 53: authors note that water soluble OP is the common focus since it is the most straightforward. This reviewer disagrees as total DTT is most commonly reported and is a direct measurement, easier to conduct than water soluble OP, as no extraction, filtration or phase separation is required to conduct the analysis. Line 100: System comparison is important. Identifying the bias between collection systems is vital to identify and correct for differences in the results. However, as both systems are collecting PM in similar conditions, how can authors explain that there is no difference for WS-DTT but they have a considerable 10% for total DTT? The authors should indicate a possible explanation for this difference, is this due to the extraction? It is difficult to imagine a sampling difference that will only affect the non-water soluble components. Line 116. Authors indicate that the results from the comparison between extraction by sonication or shaking are similar; although the correlation is reasonable, the scattering is significant. This variation with extraction may indicate an effect of the extraction method depending on the chemical composition of the PM collected and extracted. Line 150. Method 1. After extraction with water and resuspension of the extracted solution, there is a considerable amount of sample removed from the filter. These particles are not then extracted with methanol which may lead to underestimating the OP of the methanol extract. Did the authors estimate the loss of particle mass during the first extraction? How much of the original sample remain in the vial for the consecutive extraction? It will be important to know how much is lost if corrections are to be made for more accurate comparison of the OP of the different fractions. Thus, the OP-Total DTT1 (line 164) obtained by adding the OP of each fraction is not accurate and already biased for comparison with the other extraction methods. To obtain a more accurate measurement of the OP of each fraction, and as result the total obtained using this method, the vial containing the extracted sample could be centrifuged and the supernatant removed. This way resuspended particles will remain in the vial for further extraction. Particles can be resuspended by short vortex mixing, and the sample ready for methanol extraction. Line 177. Method 2. Again, there is a bias in the method as a considerable fraction of the collected PM is removed with the filter.

Depending on the particle size, extraction efficiency varies. What was the extraction efficiency in this case? How much of the sample was removed with the filter? Ultrafine particles are not extracted from the filters easily and as many studies have shown, they are usually the main contributors to the OP of PM. As a result, the measurement is not accurate and comparison with other methods is not valid. Corrections could be made if the efficiency was known and OP measurements adjusted accordingly. Line 192. Automated system. In the description of the analytical method authors indicate that the system lines, valves and pump are only clean after a sample is run, have the authors considered interference in the results by cross contamination and sample interference between consecutive injections of the same sample? The solution remaining in the lines, ports and valves could interfere with the signal of the next injection. As the time between injections is considerable, reaction between DTT and solution can continue while in the lines and valves. Line 305. This sentence is speculation. Unless a comprehensive chemical analysis is conducted to identify the nature of the compounds associated with the sample, the statement is authors speculation. Line 311. Based on pervious comments made regarding the methods, this statement may not be correct. There is considerable amount of sample removed from the vial prior to the methanol extraction, which may lead to underestimation of the real potential of the insoluble components. If authors did not quantify the particle loses the methanol extract OP cannot be assumed accurate. Line 335. The OPsM-DTT is not a direct measure of the oxidation potential of water insoluble component. Components associated with PM present different solubility in different solvents. Many components are not extracted by methanol, and required other organic solvent for extraction. Extraction with hexane, dichloromethane, or acetonitrile, as examples, may result in different OP of the insoluble fraction. Thus, this reviewer disagrees with the statement made by the authors. It will be very difficult to directly measure the OP associated with the insoluble material. The more accurate measurement will be an estimation based on the difference between total OP and water-soluble (filtered) OP. Line 350. A contribution of 35 to 42% of the insoluble material to the total OP is not “some contribution”, it is a significant

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fraction of the total OP. Line 364. This sentence is again speculation. The authors do not present any results regarding the chemical composition to support the idea of secondary compounds as main contributors to the oxidative potential. Identification of primary and secondary compounds, as well as correlation between the different fractions, is required to validate this statement. Wind pattern, local emission sources and measurements at each location are needed to indicate the presence and contribution of primary and secondary compounds. Line 394. OP measurements for two points, GT and RS, are not representative of a wide area, so concluding the measured OP were largely spatially homogeneous is too broad of a statement. Line 395. Again, this is speculation by authors. Unless the correlation between primary and secondary compounds with OP is presented, there are no bases to make this statement.

Line 520. Table 2. Authors present correlation between OP measured under different methods and chemical speciation. Among the chemical compounds presented by the authors, K shows important correlation with OP. However, this compound has not been shown to be redox active or a chemical that can react with DTT. Why do the authors include this compound in their list and their correlations? If this is not a redox compound it does not contribute to the OP, and the correlation is not significant; unless the compound is used as a marker for sources that can contribute to other compounds that do contribute to the OP of the sample. A coherent explanation is needed regarding the inclusion of K in the table and results.

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