

Interactive comment on “Oxidant production from source-oriented particulate matter – Part 1: Oxidative potential using the dithiothreitol (DTT) assay” by J. G. Charrier et al.

Anonymous Referee #2

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Review of Charrier et al

This manuscript discusses the measurement of oxidative potential of ambient particulate matter using DTT assay in the Central Valley of California. The paper applies a novel approach for the source-apportionment of oxidative potential by Chem-Vol sampling, which segregates the different samples by using on-line single particle mass spectrometry. Furthermore, the authors measure the concentration of metals in their samples, which was then used to estimate the contribution of metals in the measured DTT activity. The later was performed based on the mechanistic equations derived by the authors in their previous publication (Charrier and Anastasio, 2012)

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Identifying the sources of oxidative potential of ambient PM is very important from the point-of view of emission related policies. The author's approach of conducting the source apportionment based on the single particle spectrophotometry seems interesting in terms of that it does not require a large sample size like conventional models, but from the actual results shown in the paper, it does not seem to work out practically. This is evident from the large fraction of PM (40-60 %) attributed to the unknown sources. This is one of the major concerns in this study and it is somewhat awkward to call it a source-apportionment analysis, if more than 50 % of sources are unidentified.

Another fundamental concern in the study is related with the mechanistic approach used by the authors to estimate the contribution of transition metals based on the empirical equations derived in their previous publication – Charrier and Anastasio, 2012. If this mechanistic method actually explains the dependence of the DTT activity measured in aerosol sample extracts (as the authors are claiming) it has major implications on the use of this assay. Note that the equations that describe the DTT response are in the form of liquid concentrations (i.e. μM), and since these are based on the non-linear relationship between DTT and metals, it implies that the translation of DTT loss results from the extracts to ambient atmosphere (i.e. in terms of $\text{nmol/min}/\mu\text{g}$ of PM or $\text{nmol/min}/\text{m}^3$ of air) will be dependent on the concentration of metals in the extracts used for DTT assay. If Cu and Mn are the biggest contributors to the DTT activity as concluded by the authors, then the relationship between DTT activity and PM mass will also be non-linear. It follows then by this method the calculated DTT activity of the ambient PM ($\text{nmol/min}/\mu\text{g}$ of PM) is dependent on the liquid concentration of the PM mass in the extract used for DTT assay.

This is an important point as it raises the following fundamental concerns on the use of this assay in measuring the oxidative potential of PM:

1. The different methodologies used for extraction of PM (i.e. different volumes of extraction liquid) would yield different results of the calculated DTT activity of PM and different estimates of contribution from Cu and Mn.

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2. It means that the mass normalized DTT activity of the ambient PM has no meaning, as this would be a function of the mass of the PM extracted in the solution for DTT assay (a function of the method).

3. It also means that any comparison of the DTT activity among different ambient samples (as they have different PM masses) or even among different ambient studies is meaningless.

Thus, essentially it all comes down to the question of assessing the actual contribution of Cu and Mn in the DTT activity of ambient PM. A relatively simple approach to test this could be to extract a given sample of known PM mass in different volumes of liquid (or in a fixed volume of liquid and make serial dilutions to obtain different samples of varying PM liquid concentrations) and measure their DTT activity. If Cu and Mn, are really the major contributors of DTT activity in ambient PM, then these samples would yield different mass normalized DTT activities and there should not be any linear correlation between the DTT loss ($\mu\text{M}/\text{min}$) vs. PM mass concentration ($\mu\text{g}/\text{mL}$). I believe the authors can easily do this experiment. If it comes out true, then it is not clear how to interpret the analysis conducted on the mass and volume normalized oxidative potential in the present study (i.e. Figure 2, 3 and 4).

Another concern of the study is that the authors highly generalize the results obtained from a single site and from a very limited number of samples ($n < 40$). Even if it turns out that metals make a substantially large contribution to the DTT activity of these samples, extrapolation of the results to the linkages between epidemiological results and metals concentration in California in general (e.g. most of the discussion on Page 24167; "Vehicular emissions", and Page 24169, Line 15-17) seems exaggerated.

In addition to these serious concerns, I have some additional comments as discussed below:

Page 24150: Line 7: This sentence is somewhat arbitrary. What is meant by the source's ability to generate ROS? Are the authors talking about ROS on the particles

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itself? If yes, then how is it related with transition metals? If not, then this sentence doesn't mean anything.

Page 24151: "true toxicity of PM": What does it mean? What is false toxicity?

Page 24152, Line 25-26: The authors in this study measured only metals, which constitutes less than 5 % of the PM mass. Can the authors really refer to it as chemical composition when they didn't measure the major chemical components such as carbonaceous species, which generally constitutes more than 50 % of the PM mass?

Page 24153, Line 26: word is repeated. ... "time", "times"

Page 24154, Line 1: Dates of sample collection: 9 November 2008 to 21 October 2008?

Page 24154, Lines 7-10: The SMF and UF fraction of the particles were collected on different substrates? Have the authors investigated the effects of substrate type on the oxidative potential of PM in any of their or others previous study?

Page 24156, line 18: "After 1.5 or 24 h of incubation"- Why there is a time-range? Was the extraction time different for different filters?

Page 24159, 8-12: There is some problem in the structure of this sentence.

Page 24159, Line 27-28: The fact that authors themselves accept that the differences in the mass normalized activity of UF and SMF fractions compared to the previously reported studies might be due to different chemical composition at different sites demonstrates that the author's results based on a single site cannot be generalized, as has been done in this study.

Page 24160: Equation 3: Mass Weighted Oxidative Potential: I am unable to understand the physical significance of this parameter. If I understand correctly, the mass normalized activity of PM in itself is a complete parameter no matter how low or high the PM mass. Now if you multiply the mass normalized oxidative potential by its mass

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fraction, I do not understand what additional information you get. It does not represent the total exposure from this fraction, which is obtained by multiplying the mass normalized oxidative potential with mass concentration. The authors need to state its significance.

Page 24161, Line 28: "are contribute"- wrong sentence structure.

Page 24162, Line 2-6: As the authors themselves admit that the agreement between measured and estimated DTT is due to large error bars, I see it in almost all samples, particularly in the estimated DTT activity from metals. The authors seem to ignore this issue and discussed it only to explain the higher estimated activity than measured for a few samples. This explanation is clearly biased towards showing the dominant contribution of metals and I wonder if the authors should explicitly address it.

Page 24162, Line 24: Ca or Cu?

Page 24162, Line 27-28: Do the authors believe that dust would contribute to the SMF and UF sampled in their study? Can they provide any reference to it?

Page 24162, Line 24: Expand VMT

Page 24164, Line 2: How did the authors calculate the concentration of quinones in liquid extract based on their atmospheric concentration? Did they assume quinones are all soluble in water?

Page 24164, Line 22: From the figure S5, the correlation between measured DTT and metals seem to somewhat fit the mechanistic curve (green and purple line) derived for Cu, but it is far-off for Mn. Do authors have any explanation for this?

Page 24166, Line 1-4: As mentioned before, these appear quite strong statements attributing all DTT activity to Mn and Cu, based on a single site and limited sample size? Also, wrong spelling – "Speces".

Page 24168, Line 16-17: The authors need to give rain data in the supplemental infor-

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mation to substantiate their argument.

Page 24168, Line 24-26: This statement is inconsistent with the authors' conclusion as it implies that Fe is one of the major components of DTT activity, which doesn't seem to fit with their results.

Final Recommendation

This paper is an important effort in the direction of identifying different chemical species contributing to the oxidative potential of PM, and thus I recommend the acceptance but only after assessing the author's approach in light of the comments raised in this review. Specifically, if the DTT activity being measured is due mainly to a nonlinear dependence on the liquid extract Mn and Cu concentration, as proposed by these authors, the DTT activity is a function of the analytical method. Thus one would expect little consistency between any of the DTT data reported in the literature (unless all samples were collected and analyzed the same way, which is not true) and suggests the DTT assay is not a valid measure of aerosol oxidative potential. If the authors cannot reconcile this issue, their analysis is fundamentally flawed. As a final point, the source apportionment analysis conducted in the study does not seem valid as more than 50 % of the PM mass is unaccounted and thus should be removed from the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 24149, 2014.

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