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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Redox activity and chemical speciation of size fractioned PM in the communities of the Los Angeles – Long Beach Harbor" *by* S. Hu et al.

Anonymous Referee #3

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The discussion paper studies the relationship between the chemical composition of particulate matter and the corresponding activity in two oxidative stress related assays: one quantifying ROS generated by rat alveolar macrophages, and one quantifying redox activity with the dithiothreitol assay. Correlation between the assays indicates that there is some commonality in the chemical species that contribute to each assay. The use of multiple linear regression in an attempt to predict ROS and DTT activity as a basis of chemical composition of the aerosol is an interesting and potentially valuable way to better relate aerosol chemistry and toxicity.

The major drawback of the paper as it stands is that the data is summarised such

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that resolution within each site is lost. While it appears that there exist at least 7 data points for each analysis at each site, data is inexplicably averaged over the whole study without including an idea of variability within each site. At the very least, the variability of the chemical composition and the activities in the ROS and DTT assays within each sampling site should be included. In addition, the inclusion of each weekly data point rather than the 7-week averages within the statistical analyses would be valuable both in supporting the claims of the paper and providing a clearer picture of the aerosol chemistry for the reader.

While there are a few comments here, they should be easily addressed provided the weekly data is available as is suggested in the manuscript and should not change the conclusions reached by the authors. Overall, this is a well-written paper that represents novel ideas and is an interesting and valuable contribution to the current research on relating chemical composition of PM chemical composition and toxicity.

Specific comments:

1) Experimental methods: The methods section could use more detailed description of the sampling protocol and the chemical analyses, as the referenced paper is not currently available.

2) Gravimetric and chemical analyses: it is apparent that most analyses are performed using a weekly composite sample, however this is not clear for the DTT assay (p. 11649, line 1). Is this assay performed with daily or weekly samples?

3) Macrophage ROS and DTT assays: (p. 11649, line 16) It is my understanding that DCFH-DA is de-acetylated within the cell enzymatically to produce DCFH. This is then followed by oxidation by ROS to form the fluorescent analyte DCF.

4) Macrophage ROS and DTT assays: (p. 11650, line 4) The rate is proportional to both concentration of catalytically active constituents as well as their rate constants for the reaction with DTT. That is, not all catalytically active species are equally reactive

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with the DTT assay.

5) Results and Discussion: the methods section suggests that weekly composites are used for analysis, yet Table 1 implies a single data point for each site. A weekly breakdown of concentrations and redox activities should be included, or at the very least standard deviations, to give a better idea of week-to-week variability over the study.

6) Results and Discussion: given that a number of the specific inorganic elements (aluminium, cobalt, and vanadium in particular) are discussed in the paper, concentrations for these elements could be included either in the main paper or the supplementary information, rather than solely in figure 4.

7) Measured redox activities/DTT vs. macrophage ROS: Again, there seems to be a missed opportunity to describe the ROS results in more detail by summarizing the 7-week period into a single data point. I would be very interested in seeing the variability within the sampling sites themselves along with the variability between sites and how this variability compares.

8) DTT vs. Macrophage ROS: (p. 11655, line 16) This comparison of the two assays is somewhat awkward to read. It would be useful to address some of the bigger contrasts between the assays beyond the type of extract used. For example, that the DTT assay primarily measures ROS production potential by organic species, while the DCFH to DCF is sensitive to ROS themselves and thus can be sensitive to a number of species.

9) Multi-variance analysis/Figures 5a and b: I find this to be an very interesting take on predicting PM toxicity throughout the day. The predicted effect of changes in OC concentration is a valuable insight of this paper. However, while I understand that only OC has an hourly breakdown, the other aerosol components stated to be important have been somewhat neglected in this discussion. One particular question that comes to mind is: what might be the effect with a hypothetical change in soluble aluminium, cobalt or vanadium within the observed variance of these species during the study? For example, do week-to-week changes in concentration for these elements potentially

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outweigh the diurnal variation in OC observed, or is the diurnal variation more important in determining predicted redox activity? Considering that vanadium contributes particularly strongly to the ROS model, I don't get a sense from the discussion of how these components other than OC might change the predicted activities in these assays.

Technical comments:

1) Introduction: p. 11645 line 21 should read "could be assay and/or" rather than "could be assays and/or".

2) Site locations: (p. 11647, line 7) The sampling protocol is somewhat unclear from this description. Is the study over a continuous 7-week period? February through May encompasses more than 7 continuous weeks, which suggests some breaks in the sampling period.

3) Overview of the PM chemical speciation: (p. 11652, line 9) A more specific descriptor than "Inorganic elements" should be used since this chemical class is being differentiated from other inorganic aerosol components.

4) Multi-variance analysis: (p. 11658, line 23) this final sentence seems to have an extraneous comma (...redox active components, which are not included...).

5) Conclusions: (p. 11661, line 11) I'm not entirely sure that these results can "confirm" that traffic emissions can increase redox potential of PM, given that this is based on a model prediction rather than a direct measurement of vehicle emissions with an assay.

6) Table 2: lines dividing chemical classes appear to have been omitted, as have bold values referenced in the text.

7) Figure 1: Several values appear to be greater than 1 in the chart and are cut off with current axis settings.

8) Figure 2: units appear to be incorrect on y-axis (mg/m3 instead of ug/m3)

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