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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.

S. Hu et al.

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We are thankful for the valuable comments from this reviewer. We have carefully considered the comments from the reviewer and incorporated them accordingly. Please find our response to the reviewer, which is given below in italic. We appreciate the reviewer's recommendation for the publication of this paper in ACP.

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

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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 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.

Response: This comment is is almost identical with the comment of reviewer 2. The weekly averaged values and their standard deviations are presented in Table S1 in the supporting information. The results showed that the week-to-week variability of the concentrations of the PM mass and major chemical species (EC/OC and inorganic ions) measured at each site was not significant, mostly because of the stable meteorological conditions and the constant influence of vehicular sources over the entire sampling campaign.

Due to the requirement to obtain sufficient mass, composited filters over the whole 7-week period were analyzed for organic species/tracers, elements, water Soluble OC (WSOC) and ROS/DTT.

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As described in Arhami et al., (2008) "Averaged meteorological data over the sampling period were similar across the other sites, with the average temperature, relative humidity and wind speed varying in the ranges of 16.6-19.1 °C, 52-63% and 0.8-2.3 m/s, respectively. These meteorological data reaffirm the overall climatological stability of Los Angeles and show that weather conditions did not have a considerable effect on differences of the PM and its components between the sampling sites."

In summary, we don't think that the week-to-week variability of the redox activity will be more informative than our current analysis.

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.

Response: The method section has been modified as following.

"Weekly samples, collected on both the Teflon (Zefluor) and quartz fiber filters, were sectioned into four equal parts that were analyzed at the Wisconsin State Lab of Hygiene (University of Wisconsin-Madison) for several important inorganic and organic species. Two sets of Quartz composites were analyzed by the following methods: a) Ion Chromatography (IC), b) Thermal Evolution/Optical Transmittance (TOT) to determine the concentrations of inorganic ions (Sheesley et al.,2000), OC and elemental carbon (EC) (Turpin et al.,2000; Schauer,2003). The third set of the quartz fiber filters was composited for the whole 7-week period at each site and they were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for organic species/tracers including PAHs, n- Alkanes, n-Alkanoic Acids, Resin Acids, Hopanes and Steranes (Zheng et al.,2002; Chowdhury et al.,2007), respectively. The fourth set of Quartz filters were archived for future analysis. Each set of the Zefluor filters were composited into one single sample, which represented the full 7-week sampling period at each site, and they were prepared for the following analysis: (a) Total Elements (b) Water Soluble Elements, and (c) Water Soluble OC (WSOC) and macrophage ROS, and (d)

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DTT assay. A magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS,Finnigan Element 2) was applied for the quantification of 52 trace elements (Herner et al.,2006) in the total digests and water extracts. Water extracts for TOC and ROS analysis were prepared by leaching the PM samples in 900 μL of Type 1 water for 16 hours with shaking[1]. A General Electric Instrument (Sievers Total Organic Carbon, TOC; GE, Inc.) was used to determine WSOC concentrations[1].”

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?

Response: The method section has been modified to clarify the analysis schedule for DTT/ROS assay.

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.

Response: correct. The cells are loaded with the ROS probe by incubating with the acetate form of DCFH (DCFH-DA) which is able to cross cell membranes, and this species is rapidly de-acetylated within the cells to generate the redox probe DCFH.

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 with the DTT assay.

Response: Agree. Modified as suggested:

“the rate is proportional to the concentration of the catalytically active redox-active species in the PM sample as well as their rate constants for the reaction with DTT.”

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 break-

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down 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.

Response: Please refer to the above response.

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.

Response: Weekly PM mass and its chemical compositions have been presented in Table S1 (supporting information). V and Ni concentration were reported in the main text. Selected water-soluble elements are presented in Table S6 in supporting information.

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.

Response: Please refer to the above response.

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.

Response: Agree. The following sentences are added in this paragraph to illustrate the difference.

"DCFH is a broad spectrum ROS probe, directly responsive to most common reactive oxygen species, including the hydroxyl radical, peroxide, superoxide radical, and

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peroxynitrite radical, and therefore provides a more comprehensive, less targeted, assessment of the redox activity of PM. For example; the ROS produced by many redox active metals, will be addressed by the DCFH, while the DTT assay is relatively insensitive to this mechanism. In many respects the two assays are quite complementary. The DTT method is strictly a chemical probe, especially sensitive to many organic functionalities (e.g. quinines), while the DCFH approach, fundamentally a cell-based method, probes the general oxidative stress imposed by PM on a living organism."

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 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 don8217;t get a sense from the discussion of how these components other than OC might change the predicted activities in these assays.

Response: Your understanding is correct. From the multiple linear regression models, we have found that the role of OC is different in contributing to the DTT and macrophage ROS. Since there is a significant influence of Vsoluble on ROS and lack of methodologies for near continuous measurements of particulate V, we are prevented from conducting a similar prediction of macrophage ROS as we did for DTT assay using OC. Therefore, we have removed Figure 5b and its description in the text.

Technical comments: 1) Introduction: p. 11645 line 21 should read "could be assay

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and/or" rather than "could be assays and/or".

Response: corrected as suggested.

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.

Response: The method section has been modified for clarification.

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.

Response: "Inorganic elements" is changed to "trace elements"

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

Response: changed as suggested.

5) Conclusions: (p. 11661, line 11) I8217;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.

Response: The final sentence was changed to "...suggesting that traffic emissions may increase the potential of airborne particles to induce oxidative stress on human cells."

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

Response: They are highlighted in the table.

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

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current axis settings.

Response: The Y axis has been scaled up to illustrate the values above 1. A sentence has been added in the text: "It should be noted that a few elements (such as Cd, Zn and Na) showed a relative high water-soluble fraction greater than 1 (<1.6), which could be due to the analytical uncertainty."

8) Figure 2: units appear to be incorrect on y-axis (mg/m3 instead of μg/m^3)

Response: corrected as suggested.

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