

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

### **Anonymous Referee #2**

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The manuscript describes size-segregated measurements of chemical composition and redox activity from particles collected in the Los Angeles - Long Beach Harbor area of Southern California. The chemical speciation information is highly aggregated, in part because it is apparently the subject of a separate recently submitted manuscript. There are two measures of PM redox activity: a fluorescence assay that uses aqueous extracts of PM in the presence of rat alveolar macrophages (ROS) and the dithiothreitol (DTT) oxidation assay used on particle suspensions. The redox activity measures are also highly aggregated, but there appears to be no reason for this.

There are some interesting observations in the manuscript, mainly the regressions be-

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tween the redox measures and the chemical composition. But there is an outstanding question as to why the seven weeks of data were apparently combined to give one result for each endpoint in each PM size at each site. I can understand the need to combine daily samples to give weekly averages; but there is no apparent need to combine all of the weekly averages for a given parameter to give one 7-week average. This issue is not discussed in the manuscript, suggesting that the averages over the entire data set are hiding large amounts of variability from week to week.

The manuscript should be reworked so that the data analyses use the larger data set with weekly averages (and with explicitly stated measures of variability on the averages). In addition to this, I recommend that the points below be addressed before the manuscript is published in ACP.

### Major Comments

1. Supporting information. I cannot find the supporting information on the web: the address given in the text does not point to the supporting information and I cannot find it on the general ACPD web site. This is probably an oversight of the journal, but regardless of the cause, it makes it difficult to evaluate some of the statements in the manuscript.
2. Introduction. There is a large amount of literature on ROS generation by ambient and source particles, but most of the ROS references cited in the introduction are work of the USC/UCLA authors. It would be more reflective of the field to include some of the important papers from other groups, both for organics and metals as sources of ROS.
3. Experimental methods. (a) More details are needed to describe the sampling and analysis frequencies. My understanding is that: (i) PM samples were collected each weekday for seven weeks. (ii) Each week's five days of PM samples were combined into a single weekly sample for chemical composition and redox activity measurements. Beyond this, it is difficult to determine what was done.

(b) Were ROS/DTT measurements made on the weekly site/size composites? If so, why are there not 7 results for ROS and DTT for each PM size at each site? This would give 7 times more data than is presented in the paper, which presents 1 ROS and 1 DTT result for each PM size at each site. Are the ROS and DTT results averages of the 7 weeks of results? If so, why and how? It would be much better to have the additional data. More information is needed to explain what was done with the samples.

(c) Measures of the variability for the chemical and redox endpoints (e.g., standard deviations) should be given.

(d) Some additional information about the ROS technique would be useful, since the Landreman paper is submitted but currently unavailable. For example, what was the composition of the cell medium? How long were cells exposed? How was fluorescence measured?

(e) Some basic information about the DTT assay would be helpful. For example, how were PM suspensions prepared?

(f) There needs to be some discussion of the blank filters for the two redox activity assays. Were blank filters used for both the ROS and DTT assays? What were the average blank/sample ratios for the different size fractions for the two assays? Were blank values subtracted from the sample results? Similarly, what were the blank data and blank treatment for the chemical composition measurements?

(g) Section 2.5 (Regressions). How were the data binned before doing the regressions? It appears that regressions were done on values averaged over the entire 7 weeks of collection. Why weren't weekly average values used? If the data is available, regressions with weekly average values should be done.

Table 1. (a) Need more details on what these data represent. Are these averages over the entire sampling campaign? How many samples went into each site/size average?

(b) Some statistical description of each data point needs to be given: e.g., relative

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standard deviation (i.e., CV) for each average value, minimum and maximum values

Table 2. (a) It's somewhat surprising (and certainly interesting) that the correlation with Fe didn't meet the minimum threshold of significance. Given the wealth of literature on Fe-mediated ROS formation, including the Fe results in the text, and discussing them in the text, would be useful, even if there's no significant correlation with the ROS or DTT results. (b) Similarly, Cu and Mn are two other redox-active transition metals that have been linked to ROS generation by PM. Even though they are not significantly correlated with the two ROS measures here, it would be useful to include their results in the table.

Figure 3. It's surprising that there's no measure of uncertainty/variability on these values. Does each bar represent the average of the weekly composite samples? Should show error bars reflecting the standard deviation (or SE) for each bar. With these levels of variability, are the differences between sites significant?

Figure 4. (a) This figure is too small to be legible. I suggest breaking it into 2 figures to make them larger. (b) The two outliers that were removed from the DTT and ROS regressions should be identified in the figure (e.g., by making them hollow symbols). (c) For both Al and Zn (and, to a lesser extent, Mo), the regressions (and high correlation coefficients) are driven by one point. Are these regressions still significant if this point is removed? Are there other regressions that are similarly driven by one (or two) points? I suggest that either Al or Zn be removed and replaced with Fe, since it has been identified as an important ROS-generating metal. Even though the Fe regression is not significant, it would be interesting to see the plot.

Figure 5a. (a) This figure would be more convincing (and valuable) if there were any actual measurements of DTT consumption during this period. As is, it's an unsubstantiated guess. (b) The final sentence "...traffic emissions can increase the redox potential of airborne PM substantially" is too definitive for this "data". Better to qualify this.

Figure 5b. (a) I cannot find the supporting information, but from the text it appears that

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while OC was chosen as a predictor variable, other variables had more explanatory power for the ROS endpoint. Is this true? If so, how to justify the choice of OC? Compared to V, OC explains very little of the ROS result, but the authors treat it as if it were as important as V. For example, stating that the ROS response from PM is a result of vehicular traffic, in addition to ship emissions/oil combustion, puts the traffic component at an equal level, something it doesn't appear to deserve. (b) Worse, Figure 5b uses an average V concentration and only varies OC to get differences in ROS throughout the day. With this exercise the authors appear to have elevated OC to the dominant factor affecting ROS generation. (c) I recommend deleting Fig 5b and its description in the text.

Miscellaneous points (a) Page 11647. It is difficult to assess what portion of the results described here are also included in the Arhami et al. manuscript submitted to AS&T (footnote 2). Since I don't have access to the AS&T submission, the editor should check to make sure that the overlap is minimal.

(b) It would be useful to have a correlation matrix in the supporting information (i.e., where the correlation coefficient between each pair of measured variables is given).

(c) Page 11657, lines 23 - 25. ('We hypothesize...'). If AI is just a surrogate for PAHs, why not use PAH instead as an independent variable in the regression? How good is the regression model with PAHs instead of AI? AI is not redox active and so is unlikely to itself be contributing to ROS generation in this system.

(d) Page 11658, lines 4-6 ('It is possible...'). This is an easily answered question: run the regression model with OC and PAHs (and perhaps other organic measures) as independent variables and see how well it does predicting DTT activity.

#### Minor Comments

1. Page 11648, line 3. What was the total air volume collected for each sample?
2. Page 11649, line 3. How were "water soluble elements" extracted?

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3. Page 11650, lines 4-6. The text states that 'The electron transfer is monitored by the rate at which DTT is consumed under a standardized set of conditions and the rate is proportional to the concentration of the catalytically active redox-active species in the PM sample.' This is likely not strictly true (that the rate is proportional to concentrations of redox-active species), since the DTT assay measures the sum of ROS generation from many different compounds, each likely with different efficiencies for electron transfer. For example, two separate samples with very different amounts of two redox-active species with very different efficiencies for DTT oxidation could give the same DTT result.

4. Page 11655, lines 16 - 19 ('The consumption of DTT...'). This statement implies that the biggest difference between the ROS and DTT assays is whether both soluble and insoluble components are included. But more important differences are that (1) the ROS method contains cells, which will affect redox cycling in the DCF method, and (2) it's likely that the mix of oxidants causing the response in the two methods are different (e.g., DTT is insensitive to metals, but the DCF/ROS method likely isn't).

5. Page 11656, lines 2-3 ('The species with...'). In contrast to this statement in the text, the significant correlations in Table 2 are not in bold.

6. Page 11656, lines 5 - 7 ('Nitrate and sulfate...'). But based on Table 1 it appears that in the Q-UF and accumulation modes that nitrate and sulfate are fully neutralized by ammonia. True?

7. Page 11656, lines 24-28 ('We hypothesize...'). To help the reader evaluate this claim, the V and Ni levels in this sample should be given in the text.

8. Figure 1. It appears that several of the averages are above 1. These numeric values should somehow be indicated in the figure or caption.

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