

Review of “Oxidative potential of ambient water-soluble PM<sub>2.5</sub> measured by Dithiothreitol (DTT) and Ascorbic Acid (AA) assays in the southeastern United States: contrasts in sources and health associations”

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### **Introduction.**

Fang and co-authors describe results from two different measurements of oxidative potential – DTT (dithiothreitol) and AA (ascorbic acid) – for ambient particles collected in the southeast U.S. as part of the SCAPE center. The DTT and AA data sets are analyzed in three different ways: (1) linear regressions between oxidative potential and various chemicals in an attempt to identify the responsible chemical species; (2) positive matrix factorization (PMF) and chemical mass balance (CMB) modeling to identify important sources of ROS-generating PM; and (3) epidemiological modeling on approximately a decade-long time series of estimated DTT and AA results to assess if either measure of oxidative potential is associated with health effects.

The AA results are novel and, though not fully explored, form the core of a good manuscript. With some additional pieces, this could be a very nice piece of work. On the other hand, the DTT results have all been presented previously and there is nothing that warrants spending half the manuscript on these past results. There are some new (and better) ways in which the DTT data could be treated; if this is done, it could be an important contribution to our understanding of DTT and would significantly improve the manuscript.

### **Major Points.**

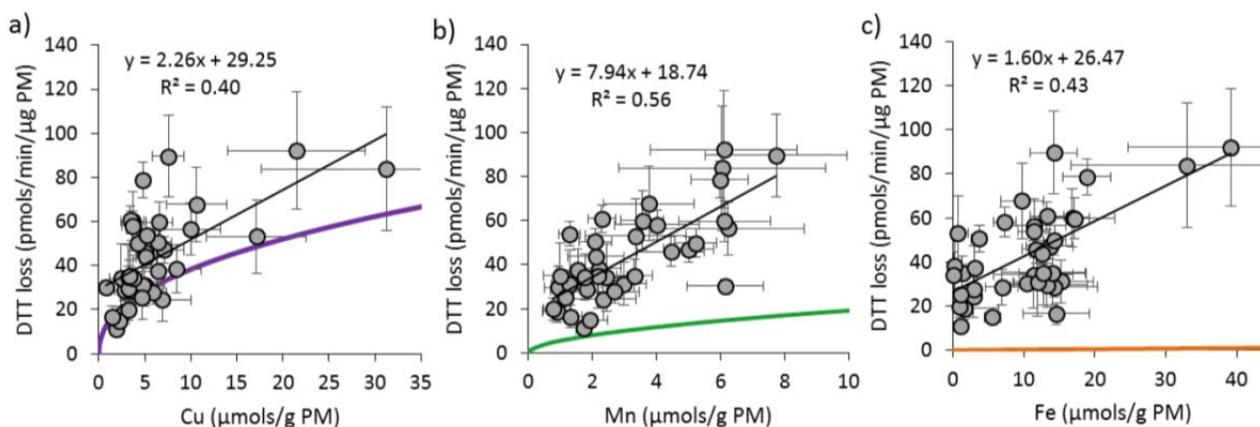
**1.** The DTT figures in the manuscript have all been shown (and discussed) previously: Figure 1b, the DTT results in Figure 2, and Figures 3c and c are all from Verma et al. (2014), while the DTT data in Figure 4 is from Bates et al. (2014). This previously published work represents approximately half of the data in the manuscript. I appreciate that the authors want to compare their new AA results with their old DTT results, but giving the two sets of data equal weight in the manuscript takes away from the ascorbate findings. It also makes for a repetitious experience for readers of Verma et al. (2014). My recommendation is to minimize the presentation of the previous DTT figures and the discussion of the DTT results. The comparison of the DTT and AA results is useful but could be done with a brief text discussion after each AA figure. Beyond comparisons with AA, if the authors want to present significant amounts of DTT results in the manuscript, they should be new; see the point #2 below for some suggestions on this.

The authors should more thoroughly present and discuss the AA results, as their treatment in the manuscript is often weak. For example, the authors measured hundreds of samples, but only 17 monthly averages are presented. Is there anything interesting to show from the time series data? Is there anything interesting in the mass-normalized data? What do correlation plots of DTT and AA rates at the various sites show? What is the average value of the (DTT rate) / (AA rate) for each site/season; does this ratio say anything useful?

**2.** The authors have used linear regressions to assess the significance of metals and other components in the two assays. For DTT this analysis (e.g., Figure 2) is inappropriate because (1) two of the major

contributors (Cu and Mn) have non-linear responses and (2) many of the components are correlated with each other. I ranted to the authors about this in my comments to Verma et al. (2014); see <http://www.atmos-chem-phys-discuss.net/14/19625/2014/acpd-14-19625-2014-discussion.html>. Since these past comments were largely ignored, allow me rant again, both for the purposes of the current manuscript and more broadly as a statement to DTT/ROS users.

As an alternative to linear regressions we developed a mechanistic technique to quantify the contributions of chemical species to the measured DTT (or other ROS) rate. This involves measuring (1) concentration-response curves for each species (e.g., the rate of DTT loss as a function of copper concentration), (2) concentrations of Cu and Mn in each sample, and (3) the DTT rate of loss in each sample. We recently compared results from linear regressions and the mechanistic approach for a set of samples from Fresno, California (Charrier et al., 2015). Our mechanistic approach revealed that Cu, Mn, and unknown (likely organic) species account for an average of approximately 50%, 20%, and 30%, respectively, of the measured rates of DTT loss in these samples. These percentages are approximately

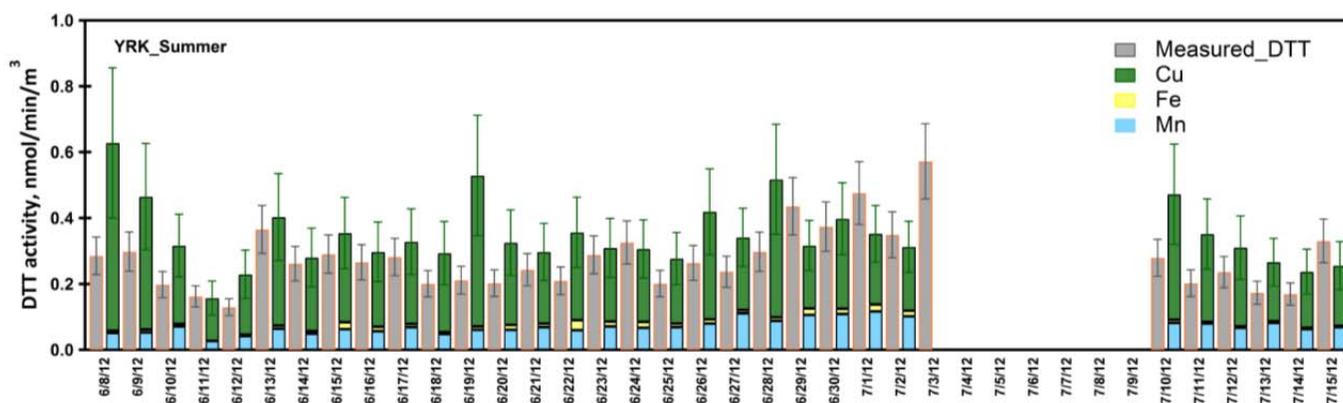


**Figure A.** Correlations between the measured rate of DTT loss and the concentrations of Cu, Mn, and Fe in samples from Fresno, California. Black lines represent the linear regressions. Each colored line represents the calculated rate of DTT loss from the metal based on our measured concentration-response curves (Charrier and Anastasio, 2012) and the typical PM mass loading of  $10 \mu\text{g mL}^{-1}$  that was used in the assay in this study. Reproduced from Figure S8 of Charrier et al. (2015).

shown by the colored lines in Figure A. In contrast, the corresponding linear regressions for Cu, Mn, and Fe show the weakest correlation for Cu ( $R^2 = 0.40$ ) and the strongest for Mn ( $R^2 = 0.56$ ). The Fe correlation ( $R^2 = 0.43$ ) is as strong as the copper correlation (and has a similar slope), despite the fact that copper accounts for half of DTT loss and Fe accounts for essentially none. Clearly regressions cannot be trusted to identify the species responsible for DTT loss.

Why does this matter for the Fang et al. manuscript? Because the authors have the opportunity to use the mechanistic approach to better assess the contributions of Cu and Mn in their samples. In response to my first review of Verma et al. (2014), the authors calculated the contributions of these metals for their DTT rates with the mechanistic approach. These figures show that Cu generally makes a major contribution to the SCAPE DTT; unfortunately, the figures can only be found in the authors' second response to my comments (<http://www.atmos-chem-phys-discuss.net/14/19625/2014/acpd-14-19625-2014-AR2.pdf>) as they were not included in the final version of Verma et al. (2014). In a subsequent paper, Verma et al. (2015), they assessed the contributions of transition metals towards DTT but did so using linear

regressions; these correlations suggest that Cu and Mn are each important in only 3 of the 7 SCAPE sample sets examined. In contrast, the mechanistic approach results show that Cu and Mn generally dominate the DTT response at every site/season, although there are some problematic samples. As an example, consider the YRK-June DTT data from Verma et al. (2015): linear regressions give  $R$  values of 0.64, 0.53, and 0.11 for Mn, Fe, and Cu, respectively. Since its regression fell below the  $R$  threshold, Cu was considered insignificant in these samples: the authors concluded that Mn and organics each accounted for approximately half of the DTT response, while Cu did not contribute. In contrast, the mechanistic approach for YRK-June (Figure B) shows that Cu generally dominates the DTT response, Mn is significant, and unknown components sometimes contribute. The measured and calculated rates for each sample in Figure B would likely agree better if the authors measured concentration-response curves on their automated system rather than used results from the manual runs in Charrier and Anastasio (2012). I encourage the authors to pursue this for the revised manuscript.



**Figure B.** Mechanistic assessment of the transition metal contributions to the DTT response in the YRK-June (and July) samples. From the Verma et al. response (29 October 2014) to my comments to Verma et al. (2014); see <http://www.atmos-chem-phys-discuss.net/14/19625/2014/acpd-14-19625-2014-AR2.pdf>

It is an open question whether Cu and Mn also have non-linear responses in the AA assay. If they do, then the linear regression assessment of which species contribute to the AA result in the manuscript might have problems. Since it would be a simple matter to measure the concentration-response curves for these metals in the authors' automated system, I recommend that they make these measurements. The authors should also use these curves to assess transition metal contributions to AA using a mechanistic approach and compare it to the regression results.

**3.** For AA, where it appears the response is dominated by Cu, one would expect that the source apportionment would be identifying the various sources of copper. Brake/tire wear, a large source of airborne Cu, accounts for approximately half of the identified sources in Figure 3; this result makes sense. But the Secondary Formation source, which also accounts for approximately half of the sources, doesn't fit. Unlike iron, one wouldn't expect secondary acids to make much of a contribution to copper availability since particulate Cu is generally soluble. Assuming the mechanistic species identification also shows that Cu is the dominant AA-active species, how can the authors explain the large contribution of this secondary source?

I suspect that one confounding factor in the source apportionment (for both AA and DTT) is that the mass- and volume-normalized results actually depend on the PM mass used for the extract. We have found that this is generally true for DTT, a consequence of the non-linear concentration-response curves for Cu and Mn. The authors should determine whether this is also true for these metals in the AA assay; if the concentration-response curves are non-linear, then the AA responses will depend on the PM mass concentration used in the extract. We discuss this issue for DTT in the supplemental material for Charrier et al. (2015) and are currently working on a manuscript describing the issue in detail. If the authors would like to potentially apply an analog of our DTT correction technique to their AA results I would be happy to discuss this with them.

#### 4. Backcast estimates of AA and DTT activities and the epidemiological analyses.

A discussion of the uncertainties in the backcast estimates of the AA response is needed. The uncertainties must be very large, as illustrated for DTT in Figure 1 of Bates et al. (2015). The equivalent figure for AA should be shown in the manuscript. As part of the discussion, how can the backcast uncertainties of AA (and DTT) activity be enormous, but the 95% confidence intervals around the RR data points in Figure 4 be quite small. Do the Figure 4 CIs include the full backcast uncertainties? How are these propagated?

Since AA is dominated by Cu, and there are enormous uncertainties in the backcast estimates of AA (and DTT) activity, it would be interesting to do the epidemiological modeling using measured particulate Cu rather than the predicted AA response. This might show a significant correlation with the health endpoints. Are there historical data in Atlanta that could be used for this? If this epidemiological analysis could be done relatively easily, I encourage the authors to include it in the current manuscript. If not, I hope to see it in a future manuscript.

#### **Minor Points.**

1. "AA" is used to represent the volume-normalized rate of AA loss, but of course it's also the name of AA itself, which is confusing. Better to use something like "AA<sub>v</sub>" for the rate, analogous to the DTT nomenclature of Verma et al. (2015). There is the same issue for DTT in the manuscript.
2. p.30630. The authors should include the results for the other health outcomes (COPD, pneumonia, IHD) in Table S4, as the comparison with asthma and CHF would be interesting.
3. p. 30631. The authors conclude that "For the region investigated in this study, the DTT assay was a more comprehensive multi-pollutant ROS (or oxidative potential) indicator than the AA assay making DTT a potentially valuable parameter to include in future PM health-related studies." Given the very small differences in the RRs for DTT and AA, and the very large uncertainties in their backcast estimates, this conclusion is far too strong.
4. Finally, I want to apologize to the authors for taking so long to complete this review.

## References.

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