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Interactive comment on "Reactive oxygen species associated with water-soluble PM2.5 in the southeastern United States: spatiotemporal trends and source apportionment" *by* V. Verma et al.

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The authors report results from nearly a year of DTT "oxidative potential" measurements at several sites in the southeast U.S. using a new, semi-automated DTT assay system that they developed. This is, by far, the most extensive set of DTT measurements reported, both in terms of the number of samples (nearly 500) as well as in the seasonal and site coverage. This is a major advance compared to past DTT studies.

The data set is analyzed using three different techniques: (1) linear regressions

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between DTT response and the concentration of numerous chemical species (e.g., water-soluble organic carbon, WSOC) to identify which species are responsible for DTT loss; (2) positive matrix factorization (PMF) to identify the different sources, their PM composition, and their DTT reactivity; and (3) chemical mass balance (CMB) modeling to identify the DTT reactivity of different PM sources. As described below, the linear regressions analysis has very little value in identifying DTT-active species and should be replaced with a mechanism-based analysis of the contributions of transition metals. There are a few other issues that should also be addressed.

Major Points.

In Section 3.3.1 the authors use correlations to identify the chemical species responsible for DTT loss in their PM extracts, but this approach has three major problems. First, correlation, of course, does not mean causation. For example, Zn has a number of very good correlations in Table 2, but it cannot oxidize DTT (Charrier and Anastasio, 2012) and thus is not responsible for any of the measured DTT loss. Second, the concentration-response curves for Cu and Mn (e.g., the rate of DTT loss versus Cu concentration) are strongly non-linear, so we don't expect linear regression to identify these two, likely dominant, DTT-active species. A third problem is that the authors are using the volume-normalized DTT response (DTTv) for their correlations, which introduces another confounder: PM mass. DTTv is equal to the intrinsic (i.e., mass-normalized) DTT activity (DTTm) times the PM mass concentration for a given sample. Thus any PM component that is correlated with PM mass likely gives a good correlation with DTTv, whether the PM component can oxidize DTT or not.

In light of these fundamental problems with correlations as a tool to identify the major DTT-active species in PM, we developed an alternative, mechanistic approach (Charrier and Anastasio, 2012). We recently applied this approach to particle extracts from Fresno, California and found that Cu and Mn were the dominant contributors to DTT loss (Charrier et al., Atmos. Chem. Phys. Discuss., 14, 24149-24181, 2014), in agree-

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ment with our 2012 work. The authors should apply this approach to their data to determine the contributions of Cu, Mn, and other metals in their DTT responses. This would be relatively simple since they know their metal concentrations. This approach would definitively assess the importance of the transition metals and show the extent to which other species (including WSOC) contribute to the DTT loss. Based on its appreciable concentrations (Figure 3), it seems likely that copper is a major oxidant of DTT in the SCAPE samples. While the authors assert that transition metals are a minor source of DTT activity in their samples, this assertion is based on very weak evidence.

The use of PMF (and CMB) to identify particle sources is interesting and is made possible by the large number of samples that the authors were able to analyze. But since they are using DTTv as their response variable the results might be driven by PM mass concentration rather than intrinsic PM reactivity. The extent to which the PMF (and CMB) results are driven by the relationship between DTTv and PM mass concentration needs to be addressed. Why does this matter? Fundamentally, it is a question of whether PM mass is a useful proxy for the redox-active species in particles. There are (at least) two areas where this issue of mass should be addressed:

(1) p. 19647, lines 10 – 18. Are the PMF assignments of source contributions to the DTT response primarily driven by estimated contributions of the factors to PM mass? Figure 9a shows the campaign-averaged contributions of the different sources to DTT. What does the equivalent pie chart for PM2.5 mass contributions look like?

(2) p. 19647. To what extent are the CMB results driven by PM mass? What does the equivalent pie chart for PM2.5 mass contributions from CMB look like? Does this distribution look very similar to Figure 9b? To compare with equation 1, what is the equivalent equation for PM2.5 mass? After normalizing the coefficients so that the PM2.5 mass and DTTv equations can be compared, what does this comparison say about how strongly PM mass drives equation 1?

Section 3.2. The general lack of a difference in DTT responses between the urban and

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rural sites is surprising. Quantifying the contributions from transition metals should help clarify why this is the case.

p. 19645. I doubt that Factor 3 from the PMF analysis is primarily mineral dust since there are high concentrations of the redox-active transition metals. Assuming it is mineral dust, the authors should calculate enrichment factors of soluble Mn, Cu, and Zn relative to soluble Ca and K in this factor. I suspect EF values are well above 1, which would indicate the transition metals are not primarily from mineral dust and that this factor is mislabeled.

p. 19640, lines 22-25: "...the PM2.5 samples collected via HiVol filters in our study are not expected to contain a significant fraction of these [SVOCs] species due to losses associated with large flow-rate and long sampling duration..." This point needs to be explored more, especially for phenanthrenequinone (PQN), which is the most important of the identified quinones for DTT activity. Do the authors expect that all of the particulate PQN was lost? Can they give a semi-quantitative estimate of fractional losses? If you assume typical ambient PQN contributions, how much would this increase DTT response? In this case, what fraction of DTT response is from PQN?

p. 19634, lines 19 – 20. There is not enough detail to evaluate the stated values for the blank and positive control. (1) Both values should be given in concentration units (e.g., nM DTT/min). (2) The PQN concentration in the positive control needs to be given. (3) How do the blank and sample values compare to those listed in Charrier and Anastasio (2012)?

pp. 19641-42. The site pair correlations don't reveal much, especially for DTT, where the results are muddled and the interpretations are speculative. I suggest that the highlights of this section be kept in the main text but that the figure and details (e.g., most of the correlation coefficient comparisons) be moved to the Supplement.

p. 19646. In Figure 7 the metals-rich Factor 3 has one of the lowest DTT contributions. The authors interpret this to mean that metals make a minor contribution to the DTT responses, but mechanistically this does not make sense given that Cu and Mn are very active in the DTT assay. Rather, I suspect that this indicates either that there's some unappreciated complication with the PMF results or that the results are driven primarily by mass and that Factor 3 has a low mass concentration. Using the mechanistic approach will reveal the extent to which transition metals are responsible for the DTT results. If it is a small portion, then I would believe the PMF Factor 3 results. However, if metals are an important driver of the DTT response, then the PMF results are suspect.

Figure 4 (a and b) in the manuscript is the same as Figure 7 (a and b) in Fang et al. It's a very nice data set, but does ACP(D) allow the same figure in two manuscripts?

It appears that Figure 8 is never called out in the text. If it's not, it should be moved to the supplement.

Minor Points.

p. 19628, lines 17 – 19: After citing Charrier and Anastasio (2012) and our evidence that transition metals likely drive the DTT response in many aerosols, the text states "However, evidences showing that any of these chemicals play a significant role in the DTT activity of ambient PM are sparse and limited in terms of their analytical efficacy." What does this sentence mean? What is "analytical efficacy"?

p. 19631, line 15. Particles are extracted by sonication of the filters in Di water. Sonication can make ROS (e.g., OH), which likely oxidize particulate organics (e.g., PAHs) to quinones. Have the authors ever performed controls to examine the importance of such sonication-induced chemistry?

p. 19632, last sentence. Does the estimated PM mass equation also include the measured ammonium and sulfate mass concentrations? These terms are not included in the stated equation.

p. 19633. There is another issue with extracting filters with water. In other DTT work filters are extracted in DTT solution, which contains both DTT (generally 100 μM) and phosphate (generally 0.1 M). These ligands probably help solubilize particulate metals, so the water extract is likely less efficient at extracting metals from the particles. Based on literature, or any tests they've performed, can the authors estimate the difference in extraction efficiency between these approaches for the major DTT metals (Cu and Mn)?

Section 2.6. An overview of the automated system should be given so that the reader doesn't have to read Fang et al. (2014) to get a basic understanding of the system. In addition, there are some unanswered questions in the methods section. How, and for how long, are PM samples stored before extraction? How, and for how long, are extracts kept prior to being analyzed? What is the typical PM mass concentration in the DTT assay (micrograms/mL)? What is the range of mass concentrations?

p. 19639, lines 21-24. "While volume normalized activity is a function of strength of the emission source, and thus an extrinsic property, mass normalized levels represent an intrinsic property of PM, independent of its mass concentration and a characteristic of the specific source." This text describes each PM sample and its DTT response as if it was from a single source, which of course it's not.

p. 19647, lines 7 – 9. The authors indicate that they're working on a paper to use multiple linear regression to assess the contributions of organics and metals to DTT activity. For the reasons discussed above, this approach is unlikely to be any better than simple linear regression for identifying the DTT-active species.

Recommendation.

I recommend acceptance after major revisions, most notably by performing the mechanistic treatment of the DTT data in place of the linear regressions.

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