Manuscript ID: acp-2014-548 10/09/2014

Dr. Dr. Yinon Rudich
Editor
Atmospheric Chemistry and Physics

Dear Dr. Rudich,

Along with this letter, we have submitted our revised manuscript titled “**Reactive Oxygen Species Associated with Water-Soluble PM2.5 in the Southeastern United States: Spatiotemporal Trends and Source Apportionment”** (Manuscript ID: acp-2014-548) for your consideration to publish in Atmospheric Chemistry and Physics.

All comments raised by the reviewers have been addressed on a point-by-point basis in the attached response document along with the marked-up manuscript version (track-changes mode). The manuscript has been substantially updated and revised to incorporate most of the reviewers’ suggestions.

The co-authors and I thank you and the reviewers for the useful comments and help in improving this work.

Sincerely,

Vishal Verma, Ph.D.
Research Scientist,
School of Earth and Atmospheric Sciences
Georgia Institute of Technology
311 Ferst Dr NW, Room 2128
Atlanta, GA 30332
213 590 9213

Reviewer: Michal Pardo

The paper “Reactive oxygen species associated with water soluble PM2.5 in the southeastern united states: spatiotemporal trends and source apportionment” by Verma et al. assessed the potential of the water-soluble fraction of atmospheric fine aerosols in the southeastern US to generate ROS and identify major ROS associated emission sources. The study used a very large data set, after a year of sampling in several different sites and seasons. PM chemical components indicated diverse ROS reaction at these sites in different seasons. Biomass burning and secondary aerosol formation were quantified as the strongest sources of DTT activity. Several correlations were used to identify ROS activity by DTT and WSOC in summer.

The article is well written, it uses a large amount of samples which could explain variations seen in other small scale studies. Sampling was performed in several different locations, with different aerosol content. Analysis and correlations were performed comprehensively. Minor revisions: 1. Graphs of the same figures should be at the same panel nominated a. b. etc. there is no need for: "Figure 2. Continued" 2. Since paragraphs are long, please add the number of graphs you refer to, in parenthesis, as a reminder to which figure you are referring to.

Response

We thank the reviewer. Figure 2 is merged in one panel, labeled as a, b and c. We have added the figure number as much as possible in each paragraph as a reminder to the reader.

Reviewer: Anonymous Reviewer #2

This manuscript is a companion paper of Fang et al., “A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE)” Atmos.Meas.Tech.Discuss. 7,7245-7279,2014. This paper focus more precisely on the relationship between the composition of water extracts from filters and their redox activity toward DTT. A very large number of filters (23 h integrated samples) have been collected during one year around Atlanta and Birming- ham. The water extracts of these filters have been analysed for components like OC, “brown carbon”, metals, inorganic ions as well as for their oxidative potential toward DTT. Seasonal and spatial variability of different aerosols characteristics are described. Identification and apportioning the sources potentially explaining the oxidative activity is reported. The important results are that secondary oxidation processes are the dom- inant contributor in summer to the DTT activity whereas biomass burning is the most important one in winter.

This paper is worth to be published in ACPD as it integrates a large number of data on DTT activity of ambient PM2.5, which is not common in this field. As the DTT activity may be an integrative PM characteristic related to health effects, the identification of relevant compounds explaining this redox activity is an important scientific and regulatory question. In addition, the paper is well structured and clear.

Response:

We thank the reviewer for their recommendation on the acceptance.

For discussion purpose, I have the following specific comments/question:

§2.3: How long were the filters stored at -18◦ before analysis? Did the author observed any reduction/increase of the DTT activity during this storage process?

Response: The sampling began in June, 2012 and continued till September, 2013. The analysis of the stored filters started in March, 2013 and completed in January, 2014. Thus, the filters were stored in freezer (-18 ^oC) on an average for about 6 -12 months. The decay of DTT activity during storage might be a valid concern, however, this has not yet been assessed through a systematic study. For example, a study where DTT activity of stored filters is measured at various time intervals (e.g. after 10, 20, 30, 50, 80….days) is planned. Additionally, our lab is developing an online system for measuring the DTT activity of ambient PM in real-time, to help address the concerns related with chemical alteration of collected particles in the stored samples. Following reviewer's comment, we have explicitly noted in the revised manuscript that the samples have been stored for up to a year prior to analyses and therefore the DTT activity measured on these samples represents only the activity associated with stable PM compounds.

§2.6: The measured DTT activity in this study corresponds to a sub-fraction of the total PM2.5 (water extractable fraction). For consistency reasons, the expression of the DTT reactivity should be based on the amount of the water extracted mass and not based on the total PM2.5 mass. This last calculation could be done only if the insoluble mass fraction is negligible compared to the water soluble fraction. Is it the case in this study?

Response: What normalizing mass should be used to determine the intrinsic DTT activity is a complex question. As the reviewer notes, water-soluble PM mass seems more appropriate when focusing on water-soluble DTT activity. However, we couldn't measure this mass in the present study, given the particles were collected on quartz filters. But, it could be argued that even the water-soluble mass is not perfect since many water soluble components are not likely to be DTT active, such as inorganic species, yet they comprise a large fraction of the water-soluble mass. In a subsequent paper (Verma et al., 2014, submitted to ES&T) we report the intrinsic activity for specific organic sub-fractions, determined with an aerosol mass spectrometer, which provides more insights than normalizing by total mass or even water-soluble mass. We believe the main issue is that the normalizing parameter be explicitly stated, which should then remove all ambiguity. In this paper, we have normalized the DTT activity by total $PM_{2.5}$ *mass, which was determined from the parallel TEOM measurement.*

§3.2, line 6-8: Regarding the daily variability of the DTTv activity, the authors attribute it to different and general factors. Do the authors have access to meteorological data collected during this sampling period and could they identify variables such as temperature, solar irradiation, wind, ozone level, which may contribute to such variability?

Response: In our companion paper (Fang et al., 2014), we showed that the volume-normalized DTT activity is well correlated with $PM_{2.5}$ *mass concentrations. Therefore, the factors (including the meteorological parameters in addition to the daily variations in emission sources) that affect* $PM_{2.5}$ *concentrations at a site similarly affect the DTT activity. Thus, in the context of present study which focuses on the emission sources of DTT activity, assessing the role of meteorology is not important given the daily variability of DTT activity can be explained by the similar variability in* $PM_{2.5}$ *mass concentrations.*

§3.3.1: As EC and OC have been determined on the total particle (insoluble + soluble part), their correlation with the DTT activity should be done with the total collected particle only and not with the soluble sub-fraction as it is done in this study. It is possible that the insoluble part contribute to some extent to the DTT activity (see for example McWhinney et al., "Filtrable redox cycling activity: A comparison between diesel exhaust particles and secondary organic aerosol constituents", Environ. Sci. Tecnol.,2013, 47, 3362-3369). Do the authors have some information about the contribution of the insoluble part to the DTT activity?

Response: The reviewer is correct that the insoluble fraction of ambient PM contributes significantly to the DTT activity, as shown in McWhinney et al., 2013 and also our previous paper (Verma et al., 2012; about 20-50 %), however, the present manuscript is focused only on the water-soluble fraction of DTT activity. The correlation of EC and OC *with the water-soluble DTT activity as shown in this study is not to imply that these components are participating in the DTT reaction, but to indicate their sources (e.g. as source tracers - vehicular emissions for EC, and secondary sources and biomass burning for OC), which also probably emit the water-soluble species contributing to the measured DTT activity. Thus, EC and OC should be considered as the surrogate for those unknown DTT-active water-soluble PM species.*

References Cited:

Fang, T., Verma, V., Guo, H., King, L. E., Edgerton, E. S., and Weber, R. J.: A Semi-automated System for Quantifying the Oxidative Potential of Ambient Particles in Aqueous Extracts Using the dithiothreitol (DTT) assay: Results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE), Atmospheric Measurement Techniques Discussion, 7, 7245-7279, 2014.

McWhinney, R. D.; Badali, K.; Liggio, J.; Li, S. M.; Abbatt, J. P. D., Filterable Redox Cycling Activity: A Comparison between Diesel Exhaust Particles and Secondary Organic Aerosol Constituents. Environmental Science & Technology, 47, (7), 3362-3369, 2013.

Verma, V., Rico-Martinez, R., Kotra, N., King, L., Liu, J., Snell, T. W., and Weber, R. J.: Contribution of water-soluble and insoluble components and their hydrophobic/hydrophilic sub-fractions to the reactive oxygen species-generating potential of fine ambient aerosols Environmental Science & Technology, 46, 11384-11392, 2012.

Verma, V., Fang, T., Lu, X., Nga, N. L., Peltier, R., Russell, A.J., Weber, R.J., Organic aerosols associated with Reactive Oxygen Species (ROS) generation, submitted to Environmental Science and Technology.

Reviewer: Cort Anastasio

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 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.

Response
We thank the reviewer for the very interesting comments and have addressed them point-by-point in the following discussion. We would like to point out that many of the issues may relate to applying results from the reviewer's own research, but conducted at a single location, to our sampling regions, where there is a very different mix of aerosol sources. This fact could explain many of the discrepancies.

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.

Response:
Addressing reviewer's 1st point about the correlation analysis, we agree that correlation doesn't mean causation. But causation implies correlation, i.e. if an independent variable is making a substantial contribution to the dependent variable; it will have some positive correlation. Now, as per the reviewer's comment, if Cu and Mn are making the largest contribution to DTT activity in all our SCAPE samples, then they should be at least

somewhat correlated with DTT at all of the sites and during all seasons. Looking at Table 2 of the paper doesn't reveal that. In fact, even negative correlations for Cu (the largest contributor to DTT as per the reviewer; R= -0.09 at RS-September, 2013 and -0.12 at CTR-June) have been observed.

We agree with the reviewer's 2nd point about the possibility of a non-linear association of Cu and Mn with DTT activity and we understand that the linear regression is not perfect to capture their power-law relationships. However, we believe that this difference cannot result in some of the very poor correlations reported in Table 2 (e.g. R<0.30 for both Cu and Mn). To further test this argument, we tried the correlations on logarithms of both DTT and metals (Cu and Mn), which should convert their relationships back to linear (See Table R1 below). The R values for both log(DTT)-log(Cu) and log(DTT)-log(Mn) correlations are only marginally improved in some cases, compared to their direct correlations. We believe this implies that the poor correlation of DTT and metals in our study is not only due to the non-linear behavior of these metals, but there is also lack of causation, i.e. other species also contribute substantially to the observed DTT activity in our study locations. In fact, if Cu and Mn are the only major contributors to DTT activity, then given their non-linear associations, we would not expect the linear regression to yield the excellent correlation of any species (e.g. OC and PM mass in our study) with the observed DTT activity.

Regarding the reviewer's third point, we are also aware of the problem of collinearity in the correlations due to PM mass. But as stated in the paper, there is little day-to-variability in the mass normalized DTT activity, and therefore, volume normalized levels provide more dynamic range useful for identifying DTT sources. This collinearity of the variables has both disadvantages and advantages. For example, although it confounds the relationship of the actual drivers of the DTT activity, in the source apportionment models such as PMF, this collinearity plays a vital role in identifying the major factors or the emission sources. For example, the collinearity of BrnC, WSOC and K leads to the identification of biomass burning factor in winter. Converting all these species to their mass fractions would loose the collinearity and thus making it difficult to conduct the source apportionment.

We should point out here that correlation is used in our analysis only to roughly identify the major groups of species appearing to contribute to the DTT activity or are associated with the emission sources that contribute to DTT activity. And as described in the paper, this analysis actually supports our PMF and CMB analysis, which is then used to quantify the contribution of each source to the measured DTT activity. We didn't attribute the DTT activity to any specific component purely based on the statistical single species correlation.

Table R1: Correlations of Mn and Cu with DTT activity

Site_season	linear correlations (DTT vs Mn and Cu)		log correlations (log (DTT) vs. log (Mn) and log (Cu)	
	Mn	**Cu**	**Mn**	**Cu**
JST-GT_Summer	0.72	0.71	0.68	0.71
YRK_Summer	0.63	0.09	0.58	0.26
JST_Fall	0.37	0.20	0.26	0.16
RS_Fall	0.27	0.61	0.31	0.59
JST-GT_Winter	0.46	0.63	0.47	0.68
YRK_Winter	0.68	0.43	0.69	0.52
RS_Winter	0.49	0.35	0.45	0.56
CTR_Summer	0.36	-0.12	0.44	-0.17
BHM_Summer	0.75	0.23	0.67	0.39
GT_Fall	0.58	0.46	0.50	0.44
RS_Fall	0.84	-0.09	0.83	0.00

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 agreement 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.

Response

Based on the reviewer's suggestion, we used the same mechanistic approach developed by Charrier and Anastasio, (2012) and the results are shown below (Figure R1). As can be seen, the summed DTT activity estimated by Cu, Mn and Fe (all Fe assumed as Fe(II)), over predicts the measured DTT activity in most sites by 10-100 %. This suggests that only Cu and Mn contribute to the DTT activity of ambient PM. This is in contradiction to the previous mechanistic studies both from our and other groups, which show that there are organic compounds like HULIS (Humic-like substances), which drives a substantial fraction of the DTT activity (Verma et al., 2012; Lin and Yu, 2011). In fact, in our previous publication, we showed that separating the HULIS fraction of the ambient samples, which is free from Cu, removes at least 60 % of the DTT activity of ambient $PM_{2.5}$ in Atlanta during the winter season (Verma et al., 2012).

To further test the validity of these results showing a dominant contribution of metals in our SCAPE samples, we tested the correlation between the estimated DTT activity (from metals) and measured DTT and found almost no correlation (Figure R2; R^2=0.01). Note, that this correlation shouldn't be affected by the non-linear behavior of the metals *towards DTT since the DTT activity is estimated from the equations derived by the reviewer's group (Charrier and Anastasio, 2012).*

One possible explanation for this overestimation is that the reviewer's approach assumes that all the measured metals are in their free forms and available to oxidize DTT, which might not be true. Although, metals-organic complexes are highly prevalent in natural water (Fujii et al., 2014; Christensen and Christensen, 2000), much less is known on this issue in aerosol samples. We believe that there is more work needed to quantify the fraction of metals which are available for chemical and biological reactions, and translating the results from pure metals solution to the ambient PM samples may be problematic when apply to all sampling regions, or at least in our SCAPE samples.

Figure R1:

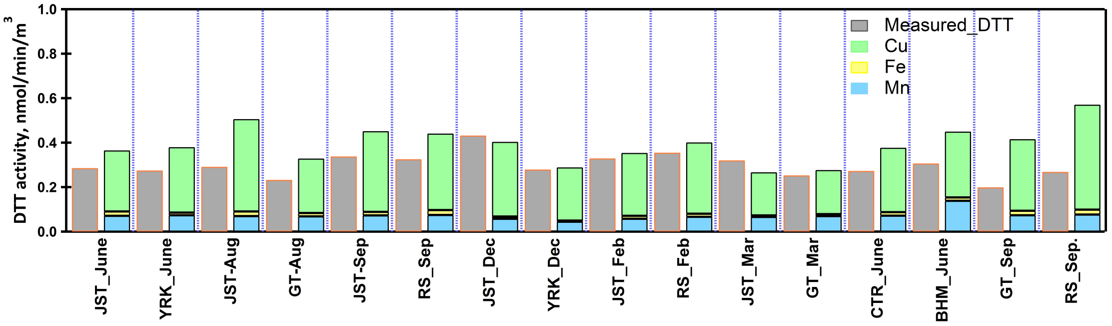
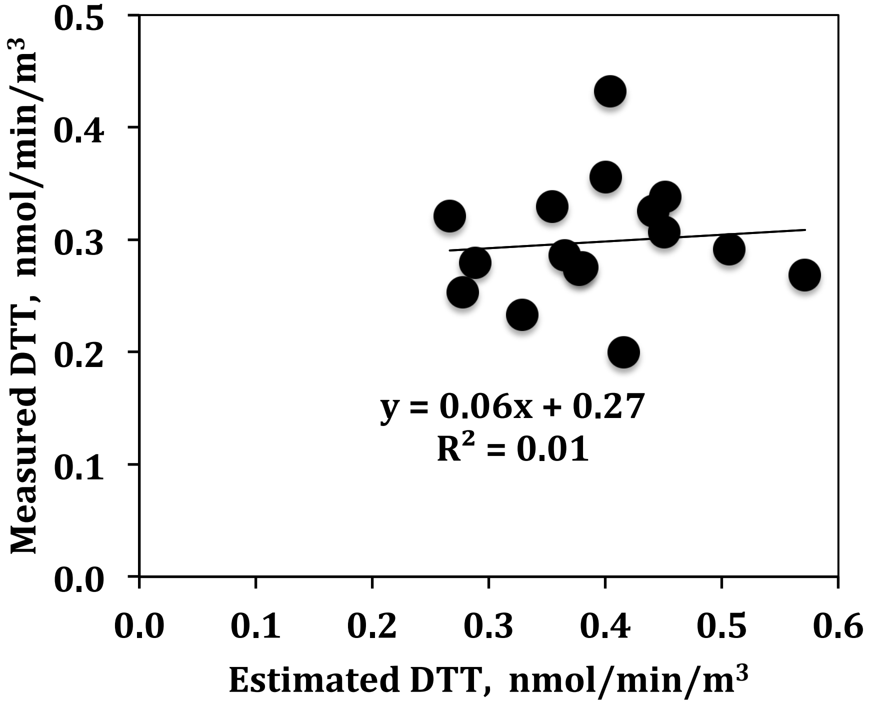


Figure R2:



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?

Response

Based on the reviewer's suggestion, we ran both of the source apportionment models, i.e. PMF and CMB on $PM_{2.5}$ *and the results are shown in Figure R3. As evident, the drivers of* $PM_{2.5}$ *mass and the DTT activity are different. The major sources of* $PM_{2.5}$ *mass in Southeast US are secondary oxidation processes (58 % from PMF and 52 % from CMB), while biomass burning (14 % from PMF and 19 % from CMB) and vehicles (19 % from PMF and 12 % from CMB) contribute much less than that. In contrast, biomass burning was the strongest source of DTT activity (35 % from PMF and 33 % from CMB), while slightly lower contribution from secondary sources (31 % from PMF and 29 % from CMB). This difference in the contribution of various sources in the PM mass and DTT activity clearly shows that the results of both PMF and CMB are not driven by the PM mass concentrations. It can be noted that these source apportionment results are consistent to the previous studies conducted in the same region, which shows the highest contribution of secondary process and very little contribution from biomass burning in* $PM_{2.5}$ *mass (Zhang et al., 2010; Zhang et al., 2012).*

Equation 1 was derived for modeling the DTT activity by multiple linear regressions using these CMB- $PM_{2.5}$ *source apportionment results. Thus the equivalent equation for* $PM_{2.5}$ *mass is basically the same mathematical representation of the results shown in Figure R3b.*

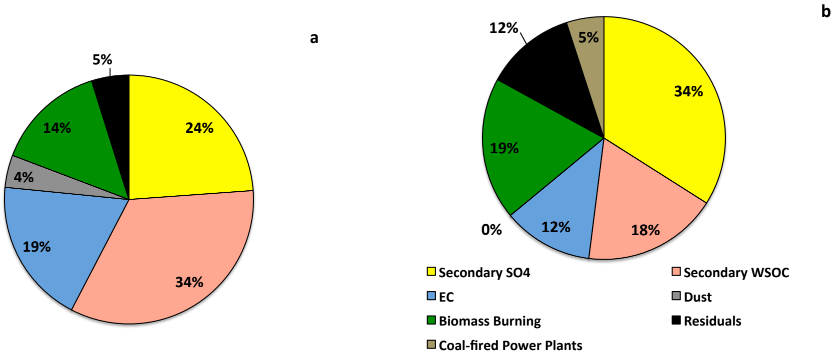


Figure R3: $PM_{2.5}$ source apportionment using a) PMF; b) CMB

Section 3.2. The general lack of a difference in DTT responses between the urban and rural sites is surprising. Quantifying the contributions from transition metals should help clarify why this is the case.

Response

In light of our present results showing that secondary oxidation drives the DTT activity in summer while biomass burning in winter, we do not think that the spatial homogeneity of DTT response is actually surprising. Note, the WSOC- a marker of secondary processes is similar at both JST and YRK sites in summer. In winter, BrnC – a marker of biomass burning is slightly higher at JST than YRK and so is the DTT activity.

We have quantified the contribution from transition metals based on the reviewer's approach and we do not believe it helps to clarify this issue further.

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.

Response

Based on the reviewer's suggestion, we have calculated the enrichment factors (EFs) relative to both Ca and K, for these four metals (Mn, Cu, Fe and Zn; Table R2). We agree that EFs for Cu and Zn are well above 1, but not for Mn and Fe. It suggests that Cu and Zn at our sampling sites also have anthropogenic sources. These metals are generally emitted from the wearing of tires and brake pads (Greenwald et al., 2014); however very little EC in factor 3 suggests that their emissions might not directly correspond to the engine exhausts.

The very high concentration of Ca in this factor suggests that these metals are more associated with dust, which might also have been altered from vehicular sources. It is possible that after emissions from vehicular sources, these metals get deposited in the *road dust, which is then enriched in these elements relative to other crustal metals (e.g. Ca). Considering this and following reviewer's suggestion, we re-labeled this factor as the "road dust" instead of "mineral dust".*

Table R2: EFs for transition metals relative to Ca and K

EF relative to Ca	**JST_June**	**YRK_June**	**JST-Aug**	**GT-Aug**	**JST-Sep**	**RS_Sep**	**JST_Dec**	**YRK_Dec**	**JST_Feb**	**RS_Feb**	**JST_Mar**	**GT_Mar**	**CTR_June**	**BHM_June**	**GT_Sep**	**RS_Sep.**
Mn	0.83	0.79	0.34	0.34	0.50	0.40	0.96	0.51	0.83	0.67	0.80	0.46	0.89	1.17	0.94	0.46
Fe	0.17	0.09	0.08	0.05	0.08	0.08	0.15	0.06	0.17	0.11	0.06	0.04	0.15	0.05	0.18	0.09
Cu	56.24	57.35	60.59	18.86	60.80	41.42	148.10	59.00	88.72	71.96	28.68	15.27	66.53	26.89	84.85	92.41
Zn	51.83	39.35	30.16	22.47	34.57	34.58	102.43	61.56	117.38	99.60	57.06	38.50	36.26	80.89	83.77	48.49
EF relative to K																
Mn	0.55	0.61	0.70	0.84	0.68	0.65	0.35	0.30	0.39	0.55	0.66	0.70	0.53	1.89	0.61	0.76
Fe	0.11	0.07	0.16	0.14	0.11	0.13	0.05	0.04	0.08	0.09	0.05	0.07	0.09	0.08	0.12	0.15
Cu	37.22	44.39	125.03	47.03	83.60	66.17	54.12	35.41	41.45	58.96	23.72	22.92	39.92	43.46	55.60	152.34
Zn	34.30	30.46	62.23	56.04	47.54	55.23	37.43	36.95	54.85	81.60	47.18	57.77	21.76	130.75	54.89	79.94

Note: The EFs are calculated based on the approach described in Ntziachristos et al., (2007)

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?

Response
In this particular study, we didn't measure the concentration of quinones and therefore, cannot address this comment of the reviewer. The loss of semi-volatiles is a common phenomenon during sampling and also storage in the freezer, and this statement is generalized based on the losses of these compounds reported in previous studies (Ashbaugh and Eldred, 2004; Chang et al., 2000; Warner et al., 2001).
About the reviewer's concern on the importance of PQN, we have performed a mechanistic study resolving the different components of DTT-active ambient HULIS, which suggests a very small contribution from major quinones. Detailed results will be published soon.

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)?

Response:
We agree with reviewer's comment and have made the following changes.

1) *The rate of DTT consumption for both blanks and positive control as reported in the concentration units are 0.38 ± 0.1 µM/min for blank and 1.27± 0.19 µM /min for PQN.*
2) *The concentration of PQN in the positive control was 0.095 µM*
3) *The blank values are slightly higher than the values reported in Charrier and Anastasio (2012) (0.24 ± 0.09 µM/min). As pointed out in the text (Page 19639, Lines 25-27), our measurements of the samples are in the typical range observed for ambient particles 0.1–1.5 nmol min^{-1} m^{-3} for DTTv and 0.005–0.1 nmol min^{-1} µg^{-1} for DTTm), as reported in other studies including 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.

Response:
We do not agree to the reviewer's suggestion and we believe that the site pair correlations reveal important information about the spatiotemporal trends of DTT activity in the region. Not only the uniform levels of DTT activity (as shown in Figures 5) but the somewhat similar temporal changes as revealed in site-to-site correlations (R^2), indicate that their emission sources at different sites are not drastically different. Given, the title of the paper (spatiotemporal trends), we would like to keep these plots. Moreover, this section does not significantly lengthen the paper (412 words+1 figure).

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.

Response:
We are not entirely clear what the reviewer implies by "unappreciated complication with the PMF results". Like all source apportionment models, PMF analysis also has limitations and is subjective to the input parameters and their respective uncertainties. However, given their limitations, these models are extensively used by the research community in investigating the aerosol emission sources in a region and have been found to yield comparable results within an acceptable range (for example, see Pachon et al., (2010) paper on estimating SOC in Atlanta from four different methods – EC tracer,

regression, CMB, and PMF). Considering these limitations and issues of model validation, we have used two source apportionment methods, which use intrinsically different statistical modules. The consistent results obtained by both methods provide sufficient confidence in our estimate of the contributions from different sources to the DTT activity. Moreover, following the reviewer's suggestion, we have also conducted the source apportionment on $PM_{2.5}$ *using both models, and they yield similar results which are also consistent with the previous source apportionment studies conducted in the region (Zhang et al., 2010; Zhang et al., 2012). The contrasting results from source apportionment conducted on the DTT activity vs.* $PM_{2.5}$ *further shows that the PMF results are not driven by PM mass and therefore view the source apportionment as a valuable tool for identifying DTT sources.*

The reviewer's mechanistic approach of applying the results of pure metals solution to ambient PM, doesn't seem to fit in these results as discussed before (Figure R1). In fact, there is not enough evidence to prove that the metals in ambient PM occur in free form and as such are all-available to oxidize DTT. If they are bound to organic compounds, the translation of DTT activity results measured from pure metal compounds to the ambient PM is not appropriate.

We would like to stress this main point in our overall response to the reviewer that this manuscript is mainly focused on investigating the sources contributing to the DTT activity of ambient PM, and not on pinpointing the specific DTT-active components in those sources. We by no means imply to say that the metals do not contribute to the DTT activity of ambient PM. And, we agree if their behavior is non-linear, then their contribution to DTT is more difficult to quantify. The reviewer's approach by testing their pure salts in laboratory seems a viable option but we believe it also has some complications associated with the complexity of metals' behavior in mixture vs. pure solutions. It is plausible that metals emitted from different sources (e.g. direct and indirect vehicular emissions, biomass burning) are in different forms (e.g. different oxidation and complexation states), which could be a major determining factor in their contribution to the DTT activity of ambient PM. In light of these points, we agreed to remove the lines 19 (page 19646)- 9 (page 19647) and would like to keep the focus in this manuscript on the sources. The low activity associated with factor 3 suggests to us that the road dust, although rich in metals, but probably inactive forms, has overall a low contribution to the DTT activity. We have also indicated the possibility that metals present in other sources might be contributing to the DTT activity, but it is difficult to differentiate from organic compounds given our statistical approach. Clearly, more mechanistic studies (possibly separating organic compounds and metals in ambient PM) need to be done to deconstruct their exact role. This is actually a topic of another manuscript currently in review.

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.

Response:
We agree with the reviewer's suggestion and we have moved figures 4 a and b to the supplemental information. We believe that Figure 8 is the most important figure of the manuscript and it has been described in details (Page 19646) and cannot move it 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"?

Response:
The term "analytical efficacy" here was used to denote the lack of sufficient evidence from translating the results of tests done on pure compounds to the ambient PM. We do question the accuracy of the tests conducted to measure the DTT activity of pure compounds as summarized in Charrier and Anastasio (2012); however, the evidences suggesting that these compounds would behave similarly in ambient PM, which is a mixture of multiple unknown compounds, as they behave in their pure form, are not analytically sufficient. Considering the reviewer's concern, we have modified this sentence and removed the term "analytical efficacy" in the revised manuscript. The modified sentence reads as "However, evidences showing that any of these chemicals play a substantial role in the DTT activity of ambient PM in a range of environments (locations) are limited."

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?

Response:
Although we have not done experiment to test this specific aspect of the extraction method, we would note this point in our future experiments. The fact that our DTT levels are in agreement with those reported by other investigators using different methods, it is not likely a significant issue.

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.

Response:
Yes, all measured inorganic ions ammonium, sulfate and nitrate, were included in the equation to estimate the PM mass. We have modified the equation to reflect this change.

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)?

Response:
We are not aware of such work for extracting the filters in DTT solution. As described in the text, we extracted our filters in deionized water and analyzed DTT activity and metals from the same extract, except that before metals analysis, we added 0.2 % HNO_3 to keep the metals solubilized during conveyance in XRF system. There might be an issue of the extraction efficiency for metals but since our methodology is consistent for both DTT and metals, it should not be a concern for the underestimation of their contribution in the measured water-soluble DTT activity. Moreover, as noted above, when following the reviewers' method we over predict the role of metals, inconsistent with an under-measurement of metals due to extraction methods.

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?

Response:
We have added a brief overview of the semi-automated system in the revised manuscript. As addressed in our response to another reviewer, the filters were stored in freezer (-18 °C) on an average for about 6 -12 months. The sampling began in June, 2012 and continued till September, 2013, while the analysis of the stored filters started in March, 2013 and completed in January, 2014.
The filters (about 18) were extracted everyday and the extracts kept immediately in a freezer (-18 °C). About 2/3rd (~12) of these samples' extracts were kept for the DTT activity measurement overnight and the remaining 1/3rd (~6) were analyzed the next morning. Typical range of PM mass concentrations in the extracts for DTT assay were 10-25 µg/mL. These details have been added in the revised manuscript.

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.

Response:
We agree, we have eliminated this sentence in the revised manuscript.

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.

Response
We agree that modeling the non-linear behavior of metals with linear regression model, whether simple or multiple, is inappropriate. However, in that manuscript, we have used multiple regressions only to estimate the intrinsic DTT activity of organic aerosols. The contribution of organics and metals to the DTT activity was estimated based on a different mechanistic approach by separating these components through a solid phase extraction column, which exclusively removes the organic compounds and does not substantially affect the metals. We have eliminated this sentence in the revised manuscript.

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

Response
We thank the reviewer's recommendation for acceptance. However for the reasons given above, we feel that linear regressions support our observed spatial and temporal distributions of DTT and the source apportionment results and so should remain in the manuscript. As noted above, the reviewer's mechanistic approach was tested and neither it appears to explain our observed DTT levels, nor it's spatial or temporal variability. Extrapolating results from the reviewer's relatively small sample size, made at a specific location, to another region with a different mix of emissions may also partly explain the discrepancies. Clearly more research is needed to test the reviewer's method, but all the evidence we have so far points to the significant contributions from both organic species and metals to DTT activity. This includes the results presented in this manuscript.

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Reviewer: Anonymous Reviewer # 4

Although it is not yet known which chemical species drive the correlation observed between particulate (PM) levels and negative health outcomes, there are a number of PM assays that are thought to relate in some way to these effects. The DTT assay is one, where the assay measures the ease by which PM can transfer electrons from electron-rich substrates to oxygen under physiologic conditions. While this assay has been used in controlled laboratory and short-campaign style investigations, this is the first study which reports the DTT response across a coupled spatially and temporally resolved study. In particular, measurements were conducted over several seasons in both urban and rural locations close to Atlanta. It is found through both PMF and CMB approaches that a variety of sources contribute to the response and that there is a relatively uniform response across the study dimensions of time and space. This is significant because it indicates that this intrinsic property of the particles is relatively uniform, at least for the extent of conditions sampled. As well, this sub field has been focussed on either a metals-based or organic (usually quinone) based interpretation of significance. I like this paper because it highlights that it is both metals and organic components that are important, depending on the source of the PM.
I recommend publication of the paper. It is well written, it is a significant step forward in terms of scope of DTT field measurements, and it is very much strengthened by the extent of (a lot of) simultaneous PM chemical measurements performed.

Response:
We thank the reviewer for their recommendation of acceptance.

A slight weakness in the paper is that the PMF analysis is not described in detail, in particular to the choice of the number of factors chosen. Can the different factors chosen be shown to be independent of each (perhaps by including R2 values for their relative correlations)? I also wonder how the uncertainties of each chemical species included in the PMF are handled, and whether there is any need to down-weight the importance of one input variable or another, if their uncertainties are unusually low compared to others?

Response:
We have added more details on the PMF analysis. A different number of factors, i.e. 4, 5 and 6 were tested, but among all, five factors made the most sense, i.e. lowest object function (Q-value). With fewer factors, the individual tracer species started merging (e.g. dust and WSOC came in the same factor in four factor solution). For more than five factors, a converged solution was not obtained.
The correlation among individual factors was tested by G-space plots. The solution space of these plots was filled by the contribution values indicating the independence of different factors.
The uncertainties for each chemical species used in PMF were the overall uncertainties obtained by propagating the uncertainties at each step starting from filter collection to analysis. The analytical uncertainties were obtained by analyzing the standards (e.g. 9, 10-Phenanthrenequinone for DTT, sucrose solution for OC and WSOC, copper sulfate for Cu, iron sulfate for Fe, etc.) or the same ambient sample (e.g. for brown carbon)

multiple times (N>6) and calculating the standard deviation from the measurement. The uncertainties calculated in this way come out to be within 20-30 % for most species and thus there was no need to down-weight the importance of any variable.

Also, although this is perhaps in the references, I would like more information on how the DTT analysis was actually done, e.g. temperature, buffer solutions, how DTT loss is analyzed, extraction of species from the filters, sample handling, etc. There are many ways to do this assay and so it is important to add these details.

Response

As mentioned in the manuscript, we used an automated system for measuring the DTT activity of these samples. The automated system was built on the protocol developed by Cho et al., (2005) and is described in complete details in our companion paper (Fang et al., 2014). Some of the description is reproduced in this paper.

The procedure for filters extraction has been described in the paper but we have added more details in addition to that about the storage of filters and extracts before analysis.

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Reactive Oxygen Species Associated with Water-Soluble $PM_{2.5}$ in the Southeastern United States: Spatiotemporal Trends and Source Apportionment

Vishal Verma[1], Ting Fang[1], Hongyu Guo[1], Laura King[1], Josephine T. Bates[1], Richard E Peltier[2], Eric Edgerton[3], Armistead G. Russell[1], Rodney J. Weber[1*]

[1]Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30328
[2]University of Massachusetts Amherst, 686 North Pleasant Street
Amherst, MA 01003
[3]Atmospheric Research & Analysis, 410 Midenhall Way, Cary, NC 27513

*Corresponding author
Professor Rodney J. Weber, Ph.D.
Georgia Institute of Technology
School of Earth and Atmospheric Sciences
311 Ferst Drive Atlanta GA 30332
office phone 404.894.1750
Email: rodney.weber@eas.gatech.edu

Abstract

We assess the potential of the water-soluble fraction of atmospheric fine aerosols in the southeastern United States to generate reactive oxygen species (ROS) and identify major ROS-associated emission sources. ROS-generation potential of particles was quantified by the dithiothreitol (DTT) assay and involved analysis of fine particulate matter (PM) extracted from high-volume quartz filters (23-hour integrated samples) collected at various sites in different environmental settings in the southeast, including three urban Atlanta sites, in addition to a rural site. Paired sampling was conducted with one fixed site in Atlanta (Jefferson Street), representative of the urban environment, with the others rotating among different sites, for ~250 days between June 2012 and September 2013 (N = 483). A simple linear regression between the DTT activity and aerosol chemical components revealed strong associations between PM ROS generation potential and secondary organic aerosol (WSOC) in summer, and biomass burning markers in winter. Redox-active metals were also somewhat correlated with the DTT activity, but mostly at urban and roadside sites. Positive matrix factorization (PMF) was applied to apportion the relative contribution of various sources to the ROS generation potential of water-soluble $PM_{2.5}$ in urban Atlanta. PMF showed that vehicular emissions contribute uniformly throughout the year (12 to 25 %), while secondary oxidation processes dominated the DTT activity in summer (46 %) and biomass burning in winter (47 %). ~~Mineral~~ Road dust was significant only during drier periods (~12 % in summer and fall). Source apportionment by chemical mass balance (CMB) was reasonably consistent with PMF, but with higher contribution from vehicular emissions (32 %). Given the spatially large data set of PM sampled over an extended period, the study reconciles the results from previous work that showed only region- or season-specific aerosol components or sources contributing to PM ROS activity, possibly due to

smaller sample sizes. ~~Our results indicate that the ability to generate ROS is a generic property of fine PM to which almost all major emission sources contribute to variable extents.~~ The ubiquitous nature of the major sources of PM-associated ROS ~~generation property of ambient particulate matter~~ suggests widespread population exposures to aerosol components that have the ability to catalyze the production of oxidants in vivo.

Keywords: ROS generation, DTT activity, Secondary organic aerosol, Biomass burning, Source apportionment, Positive matrix factorization, Chemical mass balance

1. Introduction

Substantial research has been dedicated to understand the mechanisms by which ambient particulate matter (PM) causes adverse health effects in humans (Hoek et al., 2002; Samet et al., 2000; Gauderman et al., 2007; Stayner et al., 1998; Riediker et al., 2004; Sun et al., 1984; Sagai et al., 1993; Donaldson et al., 1996; Donaldson et al., 1997; Donaldson et al., 2003; Li et al., 2003; Li et al., 2009a; Delfino et al., 2013). In many of these studies, a large number of PM health effects have been attributed to the oxidative or oxidant generating properties of ambient particles (Donaldson et al., 2003; Donaldson et al., 1996; Li et al., 2003; Li et al., 2009a; Delfino et al., 2013). It has been hypothesized that several oxidative mechanisms can arise simultaneously, leading to a cascade of events that results in high concentrations of reactive oxygen species (ROS) in vivo (Tao et al., 2003; Castro and Freeman, 2001; Donaldson et al., 2003). ROS concentrations in excess of the anti-oxidant capacity to neutralize them leads to oxidizing other cellular components, which eventually translates into numerous health outcomes (Delfino et al., 2005; Li et al., 2009a; Peters et al., 2006).

Based on this possible mechanistic route linking aerosol chemistry to health, numerous studies have been initiated in the past several years focused on measuring the oxidative properties of ambient particles. A variety of probes have been developed to quantify different aspects of PM induced oxidative stress. These include chemical systems that mimic the loss of antioxidants, such as oxidation of dithiothreitol [(DTT assay) (Cho et al., 2005)], glutathione (GSH (Godri et al., 2011), and ascorbic acid [(AA) (DiStefano et al., 2009; Mudway et al., 2004)], covalent bonding with glyceraldehyde-3-phosphate dehydrogenase [(GAPDH) (Rodrigueza et al., 2005)], and hydroxyl radical generation in the presence of H_2O_2 (Shi et al., 2003). Other probes measure cellular responses when exposed to aerosols; such as macrophage ROS generation (Landreman et al., 2008), the induction of hemeoxygenase-1 (HO-1) and other stress protein expression (Li et al., 2003), and cytokine activation (Wilson et al., 2010). Each of these assays represents a plausible mode of PM toxicity and collectively they should be considered as the toolkit for deconstructing the complex mechanisms of PM ROS generation. One advantage of these assays, is that they are integrative of various aerosol chemical properties, and as pointed out by several researchers (Ayres et al., 2008; Venkatachari and Hopke, 2008; Kuenzli et al., 2004), many of them can serve as a screening step for assessing the PM samples/emission scenarios for more detailed chemical analysis and downstream health studies.

The DTT assay was devised to simulate the in-vivo generation of superoxide radicals, wherein DTT was used as a surrogate of the biological reducing agents (NADH and NADPH) (Kumagai et al., 1997; Kumagai et al., 2002). When incubated at 37°C with a test PM sample, a decreasing DTT concentration over time is inferred as a measure of the ROS generating capability of the particles. A number of pure chemicals have been found to be associated with the response of this assay, e.g. quinones have been known to catalyze the transfer of electrons from DTT to oxygen (Kumagai et al., 2002). In a recent study, certain transition metals (e.g. Fe, Cu and Mn) have also been shown to be active in this assay (Charrier and Anastasio, 2012). However, evidences showing that any of these chemicals play a ~~significant~~ substantial role in the DTT activity of ambient PM in a range of environments (locations) are ~~sparse and~~ limited ~~in terms of their analytical efficacy.~~ . The major components of the ambient PM identified so far to be associated with the DTT activity are often bulk groups of species such as organic carbon [OC, both water-soluble (WSOC) and insoluble (WIOC)] and water-soluble HULIS (Humic-like-substances) compounds [a class of WSOC characterized by strong hydrophobicity]. However, most of these associations have been inferred based on statistical correlations (Ntziachristos et al., 2007; Verma et al., 2009a; Verma et al., 2009b; Hu et al., 2008; Biswas et al., 2009b), which do not necessarily establish causation, while very few have used semi-mechanistic approaches such as physical separation of the organic compounds and metals (Verma et al., 2011; Lin and Yu, 2011; Charrier and Anastasio, 2012).

Both approaches have merits, however, a major concern with the studies solely based on regression analysis of DTT activity vs. chemical components is related to the sample size (N); most are based on N<30 with very few exceeding 100 [e.g. Delfino et. al., (2013); N = 111], which limits the statistical significance of the inferred associations. This is partly due to analytical complexity of the DTT assay, which entails a laborious and time intensive protocol. To address this problem, we developed a semi-automated instrument involving minimal manual operation. The instrument, which has been described in detail in Fang et al., (2014), allowed us to conduct the DTT assay on a large number of aqueous samples (~1200) as part of the Southeastern Center for Air Pollution and Epidemiology (SCAPE) study.

SCAPE is a collaborative center – combining five multi-disciplinary studies from Georgia Tech and Emory University, aimed at achieving a better understanding of the ambient PM health effects. Along with describing the automated DTT analytical method in our previous paper from the Center studies, Fang et al., (2014) showed that the DTT activity of ambient fine aerosols collected from various sites and seasons in the southeast US is generally correlated with PM mass, however the strength and slope of the correlation varied (R^2 = 0.40 - 0.90; slope = 0.01-0.05 nmol/min/μg) among different sites and seasons. Here we discuss the detailed spatial and temporal profiles of the PM ROS generation potential measured by the DTT assay on these samples. The bulk and specific chemical components, i.e. OC, elemental carbon (EC), WSOC, inorganic ions, water-soluble brown carbon (BrnC), and various water-soluble transition metals, were also measured. Both univariate linear regression and receptor modeling techniques were used to identify and apportion the contribution of major emission sources to the ROS generating potential of ambient particles in the southeastern US. This analysis focuses only on the water-soluble extracts from filter samples, while other reports will present results involving water-insoluble components and isolated chemical fractions of both water-soluble and insoluble species. The paper presents a unique and possibly the largest dataset on PM ROS generation potential (N, the number of filter samples = 483), linked to a range of aerosol sources that varies over seasons of the year, ~~. These results may help to explain some of the differences reported previously on the association of DTT activity with chemical components in studies based on~~

~~smaller sample sizes~~ and thus provides a broader regional view of fine particle ROS characteristics.

2. Experimental Methods

2.1 Sampling plan

The sampling plan for SCAPE involved paired simultaneous measurements using two instrumented sites, one of which was fixed at the Jefferson Street SEARCH (Southeastern Aerosol Research and Characterization) site (Edgerton et al., 2005, 2006; Hansen et al., 2003), the other was rotated among three different satellite sites, i.e. Yorkville, Roadside Atlanta, and Georgia Tech, all in Georgia. The sampling covered the period from June, 2012 to September, 2013; details of the sampling dates at each site are provided in Table 1. Each paired deployment lasted roughly one month, and was repeated in different seasons. Based on the temperature profile in Atlanta during the sampling period, shown in Figure S1, data are classified into three seasons – summer (June-August, 2012), fall (September, 2012 and 2013), and winter (November, 2012-March, 2013). To provide a broader perspective, additional measurements (summer, June-July 2013) were made in Alabama, at the SEARCH rural-urban pair; Centreville (rural) and Birmingham (urban).

2.2 Sampling sites

A map showing the locations of all sites is shown in Figure 1. Jefferson Street is located roughly 4 km northwest of downtown Atlanta and is representative of urban-Atlanta. The site is surrounded by commercial and residential buildings, with nearby street traffic patterns consistent with a mixed-use urban environment. The site has extensively been used in past studies characterizing urban Atlanta air quality (Hansen et al., 2006; Marmur et al., 2005) and the data used in epidemiological studies (Sarnat et al., 2008; Strickland et al., 2010). In this study, Jefferson Street is again used as representative of urban Atlanta, to which the other three satellite measurements (discussed next) are compared.

The Roadside site is located on the Georgia Tech campus adjacent (i.e., within a few meters) to the interstate highway I-75/85. The degree to which the site is under direct influence of emissions from approximately 280,000 vehicles per day on a 14-lane freeway depends on wind direction and wind speed. The traffic fleet is mostly (97 %) light-duty gasoline vehicles. Slow-moving traffic is typical during the morning and evening rush-hour periods. Jefferson Street is located roughly 2 km from this highway.

Georgia Tech site is situated between the Roadside and Jefferson Street sites on the Ford Environment Sciences and Technology building top floor, ~600 m from the interstate. This site is an intermediate location between the Roadside (direct freeway emissions) and urban background (Jefferson Street) that could moderately be impacted by the roadway emissions.

Yorkville, also a SEARCH site, is located in a rural environment approximately 70 km west of Atlanta, which is generally up-wind. The site is surrounded by agricultural land (e.g., pastures) and forests, with the nearest residences at least 1 km away. There are no major roadways in the vicinity of the site and nearby traffic emissions are negligible.

As a contrast to Atlanta, measurements were also made in an additional southeastern US city. The urban Birmingham Alabama SEARCH site has several coking ovens within 10 km and a cast iron pipe foundry located approximately 400m east. The site also receives emissions from nearby (<4km) freeways (I-65, US-31and I-20).

Centreville is the SEARCH rural pair to Birmingham, located approximately 85 km south-southwest of Birmingham. The site is heavily wooded and is surrounded by the Talladega National Forest with a high density of oak and pine trees. Measurements were conducted simultaneously at Birmingham and Centreville and overlapped with the Southern Oxidant and Aerosol Study (SOAS).

Detailed descriptions of all of the SEARCH sites used in this study can be found elsewhere (Hansen et al., 2003). The Jefferson Street, Roadside, Georgia Tech, Yorkville, Birmingham and Centreville sites are referred to as JST, RS, GT, YRK, BHM and CTR respectively.

2.3 Filter collection and extraction protocol

A high-volume sampler (HiVol, Thermo Anderson, non-denuded, nominal flow rate 1.13 m^3/min, $PM_{2.5}$ impactor) was setup at each site and fine particles were collected onto pre-baked 8x10" quartz filters (Pallflex® Tissuquartz™, Pall Life Sciences). 23-hour integrated samples (12:00 noon-11:00 am next day) were collected daily during the sampling periods (Table 1) at each site, along with periodic field blanks (at least 3 per site per month). The number of samples collected from each site, approximately 30 per site per season (total = 483) is given in Table 1. After collection, the filters were wrapped in pre-baked aluminum foil and immediately stored in a freezer (-18 °C). The chemical and ROS-generation analysis of the filters was started in March 2013. Prior to the ~~chemical and oxidative potential~~ analysis, the filters were cut using a 1"

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diameter metallic punch. For the DTT activity, WSOC and BrnC analysis, three filter sections (1” diameter each) were extracted in 15 mL of deionized water (DI, Milli-Q; >18 MΩ) via sonication in a water bath for 30 minutes, while additional punches were extracted separately in the same manner (15 mL of DI for 30 minutes of sonication time) for the metals (4 punches) and inorganic ions (1 punch) analysis. These extracts were then filtered using PTFE 0.45-µm pore syringe filters (Fisher brand). The filtered extracts for metals were acidified by adding nitric acid (high purity trace metal grade; 2 % w/v final solution), consistent with current protocols (Henshaw et al., 1989; Talbot and Weiss, 1994).

2.4 Online instruments

$PM_{2.5}$ mass concentrations were monitored by a tapered element oscillating microbalance (Thermo Scientific TEOM 1400a), operating continuously at JST, BHM, YRK and CTR throughout the sampling period (Atmospheric Research Analysis Inc. data). At other sites (RS and GT), summed concentrations from measured chemical components [EC + 1.6 ~~–~~OC + ions (SO_4^{-2} + NH_4^+ + NO_3^-) + ~~–~~water-soluble metals], were used as a proxy for the PM mass ~~concentrations~~concentrations. This method has been found to agree well with the TEOM concentrations at JST and YRK sites, where co-located measurements were available (Fang et al., 2014).

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2.5 Chemical analysis on PM filters

Water soluble organic carbon (WSOC) and the WSOC light absorption properties (Brown Carbon, BrnC, used as a source tracer) were measured on HiVol extracts via an automated system using an autosampler (Dionex 40AS), spectrophotometer and total organic carbon (TOC) analyzer. BrnC was measured on an aliquot (300 µL) of the extracts via a liquid waveguide capillary cell (LWCC-2100, World Precision Instruments, Sarasota, FL), which was coupled to a UV/VIS spectrophotometer (USB4000 spectrometer, Ocean Optics, Dunedin, FL) (Hecobian et al., 2010). Following the waveguide, the aliquot was conducted to a Sievers TOC analyzer (Model 900, GE Analytical Instruments; Boulder, CO) for determination of WSOC concentration.

The automated system was also used to measure water-soluble metals, which involved nebulizing the water extracts and directing the aerosol stream to an XRF (X-ray fluorescence) instrument (Xact™ 625 Monitoring System), capable of online measurements of a range of elements. Details of the nebulizer-XRF system would be published in a subsequent publication. Briefly, 5 mL of the acidified PM water-extracts was aerosolized using a continuous flow ultrasonic nebulizer (CETAC, U5000 AT^+). The resulting fine aerosol was conducted by a flow of clean filtered air through a drying system (a 136°C heated section followed by a cooled section at -5°C). The dried aerosol stream was neutralized by a Kr-85 source and mixed with clean filtered (Pall HEPA Capsule, Part No. 12144) air to obtain the instrument sample flow rate of 16.7 lpm. A wide range of elements were measured by the instrument, however we present only the relevant species which are either used as specific emission markers [Ca (dust; (Coz et al., 2010), K (biomass burning; (Artaxo et al., 1994),] or possibly play a role in ROS generation [Fe, Cu, Mn, Zn; (Schoonen et al., 2006)].

Elemental and organic carbon content of the PM was measured on a small section (1.45 cm^2) of the HiVol filters using a thermal/optical transmittance (TOT) analyzer (Sunset Laboratory) by NIOSH (The National Institute for Occupational Safety and Health) method (Birch and Cary, 1996). For the measurement of inorganic ions (SO_4^{-2}, NH_4^+, NO_3^-, etc.) at JST and GT, ion-chromatography (IC) (LC30 chromatography oven, and Dionex CD20 conductivity detector, with IonPac® CS12A carboxylate-functionalized cation-exchange and IonPac® AS12A carbonate eluent anion-exchange columns) was performed on the aerosol extracts of HiVol filters collected from those sites.

2.6 ROS generation potential measurement

ROS generation potential of the ambient aerosols was measured by a semi-automated instrument (Fang et al., 2014) for measuring DTT activity of the PM extracts obtained from HiVol filters. The filters (about 18) for DTT assay were extracted everyday and the extracts ~~kept~~ immediately returned to ~~in~~the freezer (-18 °C). ~~About 2/3rd~~ Approximately two-thirds (~12) of these extracts were kept for the DTT activity measurement overnight and the remaining ~~1/3rd~~one-third (~6) were analyzed the next day morning. Typical range of PM mass concentrations in the extracts used in the ~~for~~ DTT assay were 10-25 µg/mL.

The semi-automated instrument is based on the protocol adopted from Cho et al. (2005) and uses two programmable syringe pumps (Kloehn, Inc., Las Vegas, NV, USA) for the mixing and transfer of reaction mixtures and reagents. The DTT oxidation in a mixture of DTT (1 mM; 0.5 mL), potassium phosphate buffer (0.5 M, pH =7.4, Chelex treated; 1 mL) and PM extract (3.5 mL) is carried out in a single vial (conical centrifuge polypropylene tube), continuously shaken and maintained at 37°C using a ThermoMixer (incubating accuracy: ±0.5 ◦C, Eppendorf North America, Inc., Hauppauge, NY, USA). A small aliquot (100 µL) of this reaction mixture is ~~withdrawn in~~ transferred to another vial at various time intervals (0, 4, 13, 23, 32 and 41 minutes) and mixed with tricholoroacetic acid (TCA, 1 % w/v; 1 mL), Tris buffer (0.08 M with 4

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Formatted: Font: (Default) Times New Roman, 12 pt mM EDTA; 2 mL) and 5,5'-dithiobis-(2- nitrobenzoic acid) (DTNB (0.2 mM; 0.5 mL). ~~Both these vials are continuously shaken and maintained at 37°C using a ?????give name of mixing device.~~The final reaction mixture is pushed through a liquid waveguide capillary cell (LWCC-M-100; World Precision Instruments, Inc., FL, USA), coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, FL, USA), to measure the absorption intensity at 412 nm. The rate of DTT consumption was calculated based on the linear regression slope of remaining DTT concentrations measured at various time intervals. ~~The method is conceptually identical to the manual procedure described by Cho et al. (2005). The initial DTT concentration was 100 µM and loss of DTT in the reaction vial at several time steps (0, 4, 13, 23, 32 and 41 minutes) was monitored and used to calculate the DTT consumption rate based on the linear regression slope.~~ The automated method provided a measurement of the DTT activity at a rate of 1 sample per hour. For each batch (consisting of either 7 or 14 samples), at least one field blank and one standard [(9,10-Phenanthraquinone; 0.095 µM) -used as a positive control~~)~~] were analyzed. Both blanks and standards were fairly consistent, with an average slope ± standard deviation of 0.38±0.10 (N=45) and 1.27±0.19 (N=55) µM/min~~nmol of DTT/min~~, respectively. The automated system was cleaned periodically (generally after every 15 days, or unless the slope of DTT reaction rate started to become non-linear) by rinsing thoroughly with methanol (at least 3 times) followed by DI (at least 6 times). The whole DTT analysis was completed by January 2014. Given the long storage period of the filters in freezer (varying from 6 -12 months), the DTT activities measured on these samples represent the ROS generation potential associated with only stable PM compounds.

2.7 Source apportionment analysis

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The emission sources contributing to ROS generation potential of the particles were investigated using regression and receptor modeling techniques. As typically done in these studies, a simple linear regression was conducted between the measured concentrations of various chemical components and DTT activity for each individual site and season. A rough indication of ROS sources was obtained based on the correlations between DTT activity and various species, and associating those species with sources. The large dataset from the combined JST and GT sites, which are representative of urban Atlanta air quality, allows a more quantitative source apportionment. Two receptor models were used - positive matrix factorization (EPA-PMF, version 3.0) and chemical mass balance (EPA-CMB, version 8.2).

Detailed description and procedural details of PMF are described elsewhere (Paatero, 1997; Norris and Vedantham, 2008). ~~In the present PMF analysis, WSOC, BrnC, NH_4^+, SO_4^{-2}, and EC were classified as strong [high signal-to-noise ratio) (S/N)] species, while metals K, Ca, Mn, Fe, Cu and Zn were categorized as weak (low S/N).~~ The uncertainties for each chemical species used in PMF and CMB were the overall uncertainties obtained by propagating the uncertainties at each step starting from filter collection to analysis. The analytical uncertainties were obtained by analyzing the standards (e.g. 9, 10-Phenanthrenequinone for DTT, sucrose solution for OC and WSOC, copper sulfate for Cu, and ammonium iron (II) sulfate hexahydrate ~~Iron Sulfate~~ for Fe, etc.) or the same ambient sample (e.g. for BrnC) multiple times (N>6) and calculating the standard deviation from the measurement. ~~In the present PMF analysis,~~ WSOC, BrnC, NH_4^+, SO_4^{-2}, and EC were classified as strong [high signal-to-noise ratio) (S/N)] species, while metals K, Ca, Mn, Fe, Cu and Zn were categorized as weak (low S/N). DTT activity was chosen as the "total variable" and thus by default assigned as weak species. Missing values in the data were

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replaced by the species median. For the base runs (N= 20), a seed of 25 was chosen and the model was executed for 4, 5 and 6 number of factors. The converged run with the highest goodness-of-fit parameter (lowest object function) was selected for five factors, which are identified as secondary WSOC, secondary SO_4^{-2}, vehicular emissions, ~~mineral~~ road dust and biomass burning. With ~~less number of~~fewer factors, the individual tracer species started merging (e.g. dust and WSOC came in the same factor~~,~~ in ~~if we use~~ four factor~~s~~ solution). ~~Using~~For more than five~~higher number of~~ factors, ~~than 5 didn't~~ a converged ~~to a~~ solution was not obtained. The correlation among individual factors was tested by ~~the~~ G-space plots. The solution space of these plots was ~~all~~ filled by the contribution values indicating the independence of different factors.

In the CMB approach (Coulter, 2004), source contributions to $PM_{2.5}$ at JST were first determined and then the sources most associated with DTT activity were identified through correlations. The model was run using eight yearly average source profiles, which were derived from JST in a previous study (Marmur et al., 2005). Profiles included primary sources from gasoline vehicles (LDGV), diesel vehicles (HDDV), soil dust (SDUST), biomass burning (BURN), and coal fired power plants (CFPP). Secondary source profiles included ammonium sulfate (AMSULF), ammonium bisulfate (AMBSULF) and other OC (OTHROC), which is taken to be secondary OC (SOC). Using the JST-GT-combined HiVol concentration data, which includes inorganic ions, water-soluble metals, OC and EC, contributions of each source to the measured concentration of various species were predicted at JST on a daily basis. DTT activity was then related to these CMB-identified $PM_{2.5}$ source contributions through a stepwise regression analysis using Akaike Information Criterion (AIC) approach (Akaike, 1974), with DTT activity as the dependent

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variable and sources contributions as the independent variables. Note, the source profiles used total metals, whereas the fitting data were water-soluble metals; however, using total metals data from the SEARCH data archive for the sampling period showed little effect on the final DTT source apportionment. More detailed analysis based on the improved source profiles recently developed by an ensemble approach (Balachandran et al., 2014) is underway and here we only present the study average results from CMB to compare and validate the PMF analysis.

Data from YRK, RS and Alabama sites (CTR and BHM), were not included in PMF and CMB as they represent more extreme and generally different conditions than JST and GT, the sites representative of urban Atlanta. These other sites also had insufficient data for their own source apportionment analyses.

3. Results and Discussion

3.1 PM emission characteristics

3.1.1 Elemental, water-soluble organic and brown carbon (EC, WSOC, BrnC)

Figure 2 (a, b and c) shows the ambient concentrations of EC, WSOC and BrnC at all sites for different months of sampling. EC and WSOC are discussed first since they represent the diverse PM emissions characteristics at these sites, followed by BrnC. EC is a marker for incomplete combustion, such as vehicular emissions (Schauer, 2003), while secondary oxidation processes (Weber et al., 2007) and biomass burning (Zhang et al., 2010) are the major sources of WSOC in the southeast. From these figures, contrasts can be made between paired sites, and seasonal trends can be discerned. ~~-~~Measurements in the Atlanta region can also be contrasted to the Alabama sites.

The monthly average concentrations of EC (Figure 2a) are consistent with primary vehicular emissions being the dominant EC source; the concentrations are highly heterogeneous. Large concentration differences were observed for each pair, with highest EC at the RS, followed by urban background sites (JST, GT, and BHM), and lowest concentrations at the rural sites (YRK and CTR). The JST-GT EC concentrations were similar, suggesting that GT is not highly influenced by the roadway emissions, and so more representative of EC levels in the metro area, similar to JST. The largest contrast in EC among paired measurements is between urban and rural sites. For both summer and winter seasons, EC is more than double at the urban sites (JST and BHM) compared to their respective paired rural components (YRK and CTR) [mean ± standard deviation (1 σ) of ratio = 2.9±1.6 in summer, and 2.7±0.9 in winter for JST/YRK, and 2.92 ± 1.42 for BHM/CTR]. The RS site has the highest concentration of EC in both fall and winter seasons (RS/JST = 1.81±0.67 in fall, and 1.9±0.8 in winter, and RS/GT = 1.95±0.5 in fall). There is little seasonal variation in the EC levels across most sites. For example, the average EC concentrations at JST in summer (0.75±0.25 μg/m^3), fall (0.82±0.30 μg/m^3), and winter (0.67±0.33 μg/m^3) were similar. The mean EC concentration at RS was slightly lower in winter (1.18±0.43 μg/m^3) than fall (1.37±0.30 μg/m^3 in September, 2012 and 1.45±0.34 μg/m^3 in September, 2013). The marginally lower levels of EC in winter seasons in Atlanta (JST, GT and RS sites) might be attributed to higher rainfall during these periods (December-March; Figure S1). Precipitation scavenging could have superseded the effect of generally reduced mixing height in winter on primary aerosol concentrations.

Unlike EC, WSOC was more spatially uniform, but varied substantially between different seasons (Figure 2b). WSOC concentrations at the paired sites were very similar indicating that major WSOC sources extend to regional scales. These sources are mainly secondary organic aerosol (SOA) formation and biomass burning, (Zhang et al., 2010; Zhang et al., 2012), with possibly minor influence from primary WSOC associated with vehicular emissions at the urban sites (Yan et al., 2009). An overall stronger influence of summertime SOA than wintertime biomass burning on WSOC in the region is apparent from a gradually decreasing averaged concentration profile at JST from summer to winter (3.8±2.2 μg/m^3, 3.2±1.7 μg/m^3 and 2.0 ±1.1 μg/m^3 in summer, fall and winter). Similar decreases are also noted at other sites (3.7±1.9 μg/m^3 in summer to 1.8±0.8 μg/m^3 in winter at YRK, and 3.3±1.1 μg/m^3 and 3.9±2.3 μg/m^3 in fall, 2012 and 2013, respectively to 1.6±1.3 μg/m^3 in winter, 2013 at RS). These results are consistent with a more detailed analysis of the WSOC spatial and seasonal distribution conducted two years before in the southeast US (Zhang et al., 2010).

BrnC denotes the water-soluble organic compounds that absorb light in the UV-region of the UV-Vis spectrum (Hecobian et al., 2010). Biomass burning is by far the largest source of these compounds with additional contributions from vehicular sources and possibly aged SOA (Hecobian et al., 2010; Zhang et al., 2011). The spatial profile of BrnC (Figure 2c) is intermediate between EC (heterogeneous) and WSOC (homogeneous), indicating the diversity of its sources. The moderate impact of vehicular emissions on BrnC is probably reflected in generally higher concentrations of BrnC at RS and other urban sites (JST, GT, BHM) than rural (CTR, YRK). However, the strong seasonality is evident from its extreme values in winter periods resulting from biomass burning [average levels at JST in winter = 0.97±0.78 Mm^{-1}, compared to 0.42± 0.25 Mm^{-1}in summer and 0.53± 0.33 Mm^{-1} in fall).

3.1.2 Water-soluble metals

The selected elements (Figure 3), have a wide range of concentrations at various sites and differing seasonal trends, pointing to heterogeneous sources. A more in-depth discussion on the distribution of the measured water-soluble elements will follow in a subsequent publication, here we only briefly discuss the major trends in selected metals. BHM, a site heavily impacted by industrial emissions, has very high concentrations of all metals, with Ca, Mn, and Zn the highest among all sites. After BHM, RS has the highest levels of most metals among all sites in the Atlanta region (i.e. JST, GT, YRK, RS), indicating either road ~~-~~dust and/or direct vehicular emissions as their major source. Rural sites, YRK and CTR, have generally lower metals concentrations, while GT and JST levels are moderate.

Higher rainfall in winter compared to summer months could also affect the metals concentrations since the re-entrainment of ~~mineral~~ road dust, which is a major source of metals, is most effective in dry periods. The metals of predominantly crustal and vehicular origin (e.g. Ca, Fe, Mn and Cu) are generally higher in summer and fall compared to the winter (Figure 3). For example, the average Ca concentration at JST was 155±116, 160±87, and 67±37 ng/m^3 in summer, fall, and winter, respectively. Exceptions are K and Zn, which despite being associated with crustal dust [K; (Coz et al., 2010)] or vehicular sources [Zn; (Liu et al., 2008)] are also emitted in biomass burning (Echalar et al., 1995), which could account for a weaker seasonal variability due to multiple sources; average K concentration is 62±25, 59±22 and 65±32 ng/m^3 in summer, fall and winter, while the respective Zn concentration is 9.6±4.7, 9.3±4.8 and 9.9±5.8 ng/m^3 at JST.

3.2 PM ROS generation potential

Temporal and spatial differences in the water-soluble DTT activity are discussed to provide an overview of the PM ROS generation potential in Southeastern US.

Time series of daily average DTT activity from the sites in different months is shown in our previous publication (Fang et al., 2014) and also reproduced in the supplemental information (Figure S2). ~~Figures 4a and 4b.~~ The rate of DTT consumption ~~of DTT~~ is normalized by both the volume of sampled air (DTTv; expressed in units of nmol/min/m^3, ~~figure~~ Figure ~~4a~~S2a) and the particulate mass (DTTm; expressed in units of nmol/min/μg, ~~figure~~ Figure ~~4b~~S2b). A summary of the spatial and seasonal trends in mean DTT activity (both DTTv and DTTm) for the individual sampling periods and at various sites is shown in Figure ~~5~~4. ~~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.~~

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Our measurements of both volume and mass normalized DTT activity are generally in the typical range [(0.1-1.5 nmol/min/m^3 for DTTv and 0.005 -0.1nmol/min/μg for DTTm, as summarized in Fang et al., (2014)] observed for ambient particles at other locations. Figure ~~4~~ 4 shows that in general, both the extrinsic (DTTv) and intrinsic (DTTm) activity of ambient PM is spatially uniform. There is no ~~consistent and~~ substantial difference in DTT activity of ambient PM at the two sites for any paired measurement, except the JST-YRK pair in winter [DTTv(YRK) < DTTv(JST)] and GT-RS pair in fall [DTTm(RS) > DTTm(GT)]. ~~Intrinsic DTT activity is fairly uniform even on day-to-day scales for most sites, suggesting that the sources of ROS-associated~~

~~aerosol components don't change rapidly. There is, however, a substantial daily variability in the extrinsic activity, which reflects variations in emissions, dispersion and sinks, factors that also control overall PM mass concentrations.~~

~~A summary of the spatial and seasonal trends in mean DTT activity (both DTTv and DTTm) for the individual sampling periods and at various sites is shown in Figure 5.~~ A significant seasonal variability in both the volume and mass normalized DTT activity is evident; the levels are generally higher in the colder months than summer (Figure 4). A one-sample t-test showed that the DTTv at JST in December was significantly ($p \leq 0.05$) higher from that in June-July (51±34 %), August (48±22 %), and September (27±14%). These results are in agreement with a recent study conducted in the Los Angeles Basin, which showed a generally higher DTT activity (both mass and volume normalized) of quasi-ultrafine particles in cooler months compared to warmer periods (Saffari et al., 2014). The authors in that study attributed the higher DTT activity to an elevated concentration of redox-active semi-volatile organic compounds (SVOC) caused by their enhanced partitioning to the particulate phase and the lowered atmospheric mixing height in winter. Although, SVOC have been suggested to make a substantial contribution to the DTT activity of ultrafine particles (Verma et al., 2011), the $PM_{2.5}$ samples collected via HiVol filters in our study are not expected to contain a significant fraction of these species due to losses associated with large flow-rate and long sampling duration (Ashbaugh and Eldred, 2004; Warner et al., 2001).

The seasonal variability is even more pronounced in the intrinsic DTT activity (Figure 4). For example, differences in DTTm levels in December vs. June-July (119±48 %), August (86±31 %) and September (44±14 %) are higher compared to the respective differences in DTTv levels. Similar increases in the intrinsic DTT activity in winter were observed at other sites too (38±13 % at GT from average of August, 2012 and September, 2013, and 53±24 % at YRK), but not at RS, where average fall level (0.032±0.009 nmol/min/µg) was nearly the same as in winter (0.036±0.008 nmol/min/µg).

To further assess the spatiotemporal variability in DTTv activity in the region, correlation coefficients (R^2) were calculated for all of the site pairs and are shown in Figure ~~6~~5. To put the DTT activity comparison in a larger context, we have also included the corresponding coefficients for EC and WSOC. A high spatial correlation for a species indicates it has more spatially uniform emission sources in the region, on the scale of distances between the paired sites.

The site pair JST-GT shows high correlation coefficients ($R^2 > 0.5$) for many PM species (DTT, EC and WSOC), which was expected given their spatial proximity and absence of nearby strong sources, e.g., roadways. The other site pairs show disparate patterns for the different PM species depending upon their sources. For example, EC has relatively low correlation coefficients for the urban-rural site pairs, i.e. JST-YRK in both summer ($R^2 = 0.42$) and winter (0.45), and BHM-CTR ($R^2 = 0.39$), as expected. Despite relatively close proximity, the low correlation in fall for JST-RS pair (R^2=0.10) and GT-RS pair (R^2=0.48) for EC is due to the strong influence of freeway emissions (I-85) at the RS site. However, the JST-RS correlation is high in February

(R^2=0.74), possibly suggesting some contributions from a common source of EC, such as biomass burning.

WSOC on the other hand exhibits high correlations for most site pairs (JST-YRK, JST-GT, CTR-BHM; R^2>0.5) in all seasons (Figure 5). The correlations are generally higher in summer (R^2 >0.70), indicating a more regional influence of SOA formation as a source of WSOC in summertime, compared to biomass burning in winter (R^2<0.65). The correlations are generally weaker for the pairs involving RS (R^2=0.08-0.46), probably due to the added contribution of freeway emissions to WSOC.

Compared to WSOC and EC, the spatial correlations for DTT activity are moderate in all seasons. For example, R^2 for DTT are not as high as for EC for the sites in closer proximity (R^2= 0.68 and 0.67 for JST-GT in fall and winter, respectively). Similarly, in summer when the correlations for WSOC are very high even for the far-apart sites (JST-YRK and CTR-BHM), correlations for DTT are only moderate (R^2=0.47 and 0.59). It appears that DTT activity is impacted by both regional sources and local emissions associated with individual site characteristics. The role of various emission sources in the DTT activity of ambient PM in different seasons and sites is the major point of discussion in the next section and also the subsequent papers from this study.

3.3. Sources of PM ROS generation potential

Sources of ROS generation potential were identified and apportioned using combination of linear regression, factor analysis and chemical mass balance techniques as described below.

3.3.1 Linear regression of DTT activity with PM chemical composition

Pearson's correlation coefficients for the linear regression between DTT activity and the measured chemical components were calculated for each site and season and are shown in Table 2. Considering the limited daily variability in mass normalized DTT activity at most sites in a given season (Figure S2b), the regression was conducted on the volume normalized levels of DTT activity (nmol/min/m^3) and chemical components (μg/m^3). To consolidate the data for convenience, individual time-series at JST and GT sites from June-to-August were merged (named "JST-GT Summer"), given their similar concentration profiles. Similarly, JST and GT time series from December to March were merged as "JST-GT winter". The complete regression matrix showing the correlation between all pairs of selected species, for each site and season, is provided in the supplemental information (Table S1).

DTT activity is almost always correlated with OC in the present study. OC results from all major sources in the region (e.g. vehicular emissions, SOA, and biomass burning) and comprises the greatest fraction of PM mass [OM /$PM_{2.5}$>60 %, not shown]. Thus, the strong correlation of OC underlines the general contribution of PM organic compounds in the ROS generation potential, and also likely accounts for the DTT correlation with PM mass, as reported in Fang et al., (2014). However, it doesn't yield any novel information on the specific PM species or the emission sources associated with the DTT activity. Associations between water-soluble DTT activity and organic compounds are consistent with a number of previous studies (Biswas et al., 2009a; Verma et al., 2012; Cho et al., 2005; Yang et al., 2014), but in contrast to other reports showing metals as the major drivers in this reaction (Charrier and Anastasio, 2012).

In summer, DTT activity is well correlated with WSOC at all sites; JST-GT (R=0.81), YRK (R=0.79), CTR (R =0.78) and BHM (R=0.67). Inorganic ions such as SO_4^{-2} and NH_4^+ are also correlated with WSOC and DTT activity (R>0.60 at most sites) indicating secondary photochemical formation as their common source in summer. This is consistent with the results of ambient (Verma et al., 2009a) and chamber studies (McWhinney et al., 2013; Li et al., 2009b) suggesting higher DTT activity of secondary organic compounds than their parent gases and primary particles.

In addition to WSOC, summertime DTT activity at urban sites, i.e. JST-GT and BHM, is also correlated with certain transition metals [Mn (R=0.72), Fe (0.78), and Cu (0.71) at JST-GT, and Mn (0.75), Fe (0.66) and Zn (0.66) at BHM]. At BHM, the iron foundry and coke oven plants are the likely sources of these DTT-correlated metals. None of these metals are strongly correlated with any specific emission markers at JST-GT. However, a moderate correlation of EC with DTT activity (R=0.69) and also somewhat with metals (R= 0.59, 0.75 and 0.58 for Mn, Fe, and Cu; Table S1), suggests that vehicular emissions could be one of their common source.

BrnC is also correlated with DTT activity in summer at JST-GT, CTR, and BHM sites (R>0.65). However, its correlation with both WSOC and EC (R>0.65 at all sites; Table S1) doesn't allow isolating its predominant source. Both vehicular emissions and possibly aged SOA appear to contribute to these chromophores in summer.

In fall, DTT activity appears to be derived from a mixed contribution from primary vehicular emissions and secondary formation, as supported by its correlation with WSOC (R=0.72), and EC (R=0.90) at JST. Metals such as Fe and Zn are also correlated with DTT activity (R=0.70 and

0.82) and EC (R=0.90 and 0.75) at JST. The stronger correlation of primary emissions (EC) than secondary species (WSOC, SO_4^{-2}, NH_4^+) indicates a diminishing effect of photochemistry on the DTT activity. This is even more apparent in fall 2013, when the highest correlation of DTT at GT is with EC (R=0.78), while the correlation with WSOC is low (R=0.47).

However, at the RS site, road-dust ~~suspension~~ also appears to be a significantly contributing factor to DTT activity in fall as indicated from the moderate to strong correlation (R=0.61-0.84) of certain metals including those from crustal sources (Cu and Zn in fall 2012, and K, Ca, Mn, and Zn in fall 2013). The added contribution from dust probably dilutes the association of DTT activity with other emission sources. For example, DTT at RS is not as strongly correlated with EC ($R \leq 0.55$) or WSOC (R =0.71 and 0.21 in Fall, 2012 and 2013, respectively) as at JST and GT.

In winter months, DTT activity is again correlated with WSOC at all sites; JST-GT (R=0.69), YRK (R=0.84), and RS (R=0.78), however, this correlation is not accompanied by a similar correlation with inorganic ions (R <0.55 for SO_4^{-2} and NH_4^+) as in summer months. It implies that another emission source of WSOC – biomass burning, starts contributing more to the DTT activity in winter. This is further reflected in the strong correlation of BrnC and K with DTT activity and WSOC (R>0.65; Table 2 and Table S1) at all sites. In a study conducted in Los Angeles, the ambient concentrations of K and WSOC were elevated (~2x) during the 2007 Southern California wildfires compared to the post-fire period (Verma et al., 2009b). More importantly, these wood-smoke particles were found to be at least two times more oxidative than the post-fire ambient $PM_{2.5}$ typically dominated by vehicular emissions. The redox-active WSOC emitted in the biomass burning particles probably explain the higher intrinsic DTT activity of ambient PM in winter compared to other seasons in the present study (Figure ~~4 and 5~~4).

Interestingly, EC is also highly correlated with DTT activity (R≥0.75) in winter at all sites. However, the concurrent correlation of EC with BrnC and K (R>0.60 at all sites; Table S1) somewhat confounds the contribution of vehicular sources with biomass burning to the DTT activity in winter. Although, EC/OC ratio for wood smoke can be very low [0.2-0.3 (Harrison et al., 2012)], it is possible that some fraction of EC at the sampling sites is also contributed by biomass burning in addition to the vehicular emissions. Transition metals are also correlated with DTT activity in winter months at JST-GT [Fe (R=0.65), Cu (R=0.63) and Zn (R=0.63)], and YRK [Mn (R=0.68), and Zn (R=0.72)]. However, the co-variability of major emission markers in winter (i.e. EC, WSOC, K and BrnC) makes it difficult to identify their dominant source(s) at these sites.

3.3.2 Source contributions to DTT activity

To provide a more quantitative assessment of the contribution of various sources to the fine particle oxidative properties in urban Atlanta, a PMF analysis was conducted using the DTT activity and measured chemical composition data. The five factors resolved by PMF are shown in Figure ~~7~~6. Factors 1 and 2 are characterized with high WSOC and high inorganic ions (NH_4^+ and SO_4^{-2}) loadings, respectively. Both of these factors have higher relative contributions in summer and therefore are thought to be mostly associated with secondary oxidation processes, however a significant EC fraction in factor 1 suggests some contribution of vehicular emissions to SOA. The lack of WSOC loading in secondary factor 2 is curious. Previous $PM_{2.5}$ source apportionment studies conducted in Southeast US (Zhang et al., 2012; Zhang et al., 2010) also showed a very low but non-zero WSOC fraction in this PMF factor. The results suggest that multiple mechanisms are involved in the formation of secondary WSOC and SO_4^{-2}. More detailed analysis of the specific components of SOA to DTT activity will be reported in the future. Here we assume that factor 2 is more representative of regional secondary aerosols, including some redox-active SOA, as there are no studies showing the DTT activity associated with inorganic ions NH_4^+ and SO_4^{-2}.

Factor 3 has a very high loading of all metals and is attributed to ~~mineral~~ road-dust. This factor is also most significant in summer and fall, which is consistent with Figure 3 showing a generally lowered concentration of metals in winter. Factor 4 has a clear signature of biomass burning with very high concentrations of BrnC and K, and is prominent in winter. Lastly, the EC peak in factor 5 is a distinct feature suggesting it is linked to primary vehicular emissions. Also consistent with the vehicular sources, this factor does not have an obvious seasonal pattern.

The time-series of reconstituted DTT activity resolved by the five PMF factors, along with the residuals (not predicted), and a distribution of these factors in each season, is shown in Figure ~~8~~7. In summer, secondary oxidation processes [WSOC (29 %) +SO_4^{-2} (17%), factors 1 and 2] are the dominant contributors (46 %) to DTT activity, with additional contributions from biomass burning (24 %, factor 4) and vehicle emissions (19 %, factor 5). In fall, the contribution from secondary formation drops to 32% (22 % associated with WSOC and only 10 % with SO_4^{-2} factors) with an increase in the contribution from vehicle emissions (25 %). Biomass burning dominates the ROS generation potential in winter, contributing 47 % to the DTT activity, while relatively low contribution from secondary formation (20 %) and vehicle emissions (12%) is observed. ~~Mineral~~ Road dust (factor 3)~~, possibly including road dust resuspension~~ also makes a non-zero contribution to DTT activity, but is significant only in summer (13 %) and fall (11 %).

~~Relative loadings of individual species in various PMF factors, and the contributions of each of these factors to the DTT activity, could provide some insights on the specific chemical components in an emission source driving the aerosol oxidative potential. For example, WSOC has been associated with the DTT activity in previous studies (Verma et al., 2012; Biswas et al., 2009a) and our results showing the substantial DTT activity associated with factor 1 (Figure 7 and 8) support these findings. A few laboratory studies have also noted the capability of transition metals, particularly Fe, Cu and Mn to transfer the electrons from DTT, (Charrier and Anastasio, 2012). In this study, metals were mostly concentrated in factor 3, i.e. mineral dust, which has the smallest contribution suggesting a lesser role for metals. However, the substantial contribution of biomass burning aerosols (factor 4) to DTT activity could be attributed in part to metals, along with WSOC components. The occurrence of trace amount of redox active metals (Fe, Cu, Mn and Zn) in other factors (1, 2 and 5) might also be contributing to the DTT activity associated with those factors. It is noteworthy that at BHM and RS sites, where metals concentrations tend to be higher (Figure 3), DTT activity is not significantly different from that of the corresponding paired site (CTR, JST and GT). Overall, these data do not suggest that metals are the only dominant players in driving the DTT activity of water-soluble~~ ~~$PM_{2.5}$~~ ~~in the southeast, but they likely play an important role. This is addressed in a subsequent paper where~~

~~multiple linear regression is used to asses the contributions of specific organic components and metals to the observed DTT activity.~~

The seasonal contributions of various emission sources to DTT activity were averaged over the complete sampling year to estimate their aggregate contributions. Figure ~~9a~~ 8a shows that the major drivers of DTT activity of fine PM in Atlanta are biomass burning and secondary aerosols, with their respective annual contributions of 35 % and 31 %. This is followed by vehicle emissions contributing 16 % annually, while ~~mineral~~ road dust contributes minimally (9 %) to the DTT activity of $PM_{2.5}$. Together, all of these emission sources explained 91 % of the water-soluble DTT activity and 70 % of its variability (R^2 between reconstituted and measured DTT activity = 0.70; not shown) in Atlanta, demonstrating the robustness of our PMF model.

For the CMB analysis, step-wise regression provided a method for selecting the source contributions that significantly affect DTT activity, the others were removed from the regression to avoid over-fitting. Thus, *SDUST*, *CFPP* and *AMBSULF* were removed from the regression through this process. The final regression was:

$$DTTv = 0.10\ LDGV + 0.072\ HDDV + 0.065\ BURN + 0.023\ AMSULF + 0.028\ SOC + 0.0069\ PMOther \quad \text{Eq. (1)}$$

PMOther, or the residual, was calculated by difference between the measured $PM_{2.5}$ mass and sum of the significant source contributions (i.e., *LDGV*, *HDDV*, *BURN*, *AMSULF*, *SOC*), for each day. All coefficients have p-values less than 0.01 except *PMOther*. The resulting Pearson's correlation coefficients (R) between DTTv and the various sources were; *LDGV* 0.60, *HDDV* 0.27, S*DUST* 0.15, *BURN* 0.49, *CFPP* 0.16, *AMSULF* 0.33, *AMBSLF* 0.03, and *SOC* 0.44.

The aggregate contribution of each of these sources to the $PM_{2.5}$ DTT activity over the whole study period is also shown in Figure ~~9b~~8b. Overall, CMB yielded a similar picture as PMF; biomass burning (*BURN*) and secondary oxidation processes (*SOC+ AMSULF*) were the dominant sources of DTT activity in Atlanta with contributions of 33 % and 29 %, respectively, in addition to vehicular sources (*LDGV+HDDV*, 32 %). CMB-identified vehicle sources also include ~~resuspended~~ road dust, which may explain, to some extent, a higher vehicular contribution to DTT activity by CMB compared to PMF.

4. Conclusion

Based on a large data set (N=483), the ability of water-soluble $PM_{2.5}$ to generate oxidants determined by the DTT assay was linked with aerosol sources in the Southeastern US. Spatial and temporal profiles of DTT activity in the region were produced from more than a year of sampling conducted intermittently at multiple sites, ranging from urban to rural environments. PM chemical components indicated diverse emission characteristics at these sites in different seasons. While WSOC was spatially uniform from widespread summertime SOA formation and wintertime biomass burning emissions, primary pollutants such as EC and ~~crustal~~ metals were less uniformly distributed and were higher at the urban sites. The results show that DTT activity per volume of air sampled is also spatially uniform, but has seasonal variability, with significantly higher levels in winter compared to summer and fall.

Despite the spatial uniformity, the moderate correlations of DTT activity between paired sites indicate the influence of both regional and local emissions on the PM's ability to generate ROS. A simple linear regression conducted between DTT activity and chemical components at each site in various seasons indicated that DTT activity is associated with WSOC in summer at both urban and rural sites, and probably influenced by vehicle emissions at urban sites. The DTT activity associations with WSOC moderated in fall while those with vehicular emissions and road dust increased. In winter, DTT activity was best correlated with biomass burning (BrnC and K) at both urban and rural sites.

PMF analysis was conducted on the representative urban Atlanta dataset to quantify the contribution from each of these sources to the ROS generating potential of PM. Biomass burning and secondary aerosol formation were quantified as the strongest sources of DTT activity, with their respective study-average (summer 2012 to spring 2013) contribution of 35 %, and 31 %, followed by vehicular emissions (16 %). There was strong seasonality in the contribution from secondary and biomass burning aerosols, i.e. secondary processes dominated in summer accounting for 46 % of the DTT activity, while biomass burning in winter (47 %). The dust contribution was minimal (9%) and was significant only in summer and fall. Source apportionment conducted using an alternative approach, CMB, also yielded similar study-average contributions from secondary sources (29 %) and biomass burning (33 %), but higher contributions from vehicular emissions (32 %), which is partly due to ~~resuspended~~ road dust included in the CMB-identified vehicular source.

This is perhaps the first study integrating an extensive dataset on PM ROS generating potential with chemical components using source apportionment models and was made possible by a recently developed automated DTT analytical system. Previous studies, relying on a small sample size collected from single sites and typically in a specific season have associated similar chemical species to aerosol DTT activity, but often from a limited range of sources. Further analysis is underway to resolve the specific components of SOA and biomass burning that contributed to the DTT activity. Finally, we note that the large spatial distribution of two major sources of DTT activity, secondary aerosols and biomass burning emissions, suggests a wide-spread exposure of populations to aerosol species capable of generating oxidants in vivo, and possibly leading to oxidative stress induced adverse health effects.

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Table 1: Sampling plan and details of sampling dates at each site.

Season, Year	**Sapling dates**		**Sampling Site**			
	Start Date	End Date	Fixed Site	Samples collected (N)	Mobile Site	Samples collected (N)
Summer, 2012	6/8/2012	7/20/2012	JST	31	YRK	33
	7/24/2012	8/31/2012	JST	37	GT	38
Fall, 2012	9/6/2012	10/4/2012	JST	26	RS	29
Winter, 2012-13	11/15/2012	11/30/2012	JST	13	JST	14
	12/6/2012	1/4/2013	JST	22	YRK	22
	1/27/2013	2/27/2013	JST	30	RS	31
	3/5/2013	3/27/2013	JST	23	GT	22
Summer, 2013	*6/16/2013*	*7/16/2013*	*CTR*	*31*	*BHM*	*31*
Fall, 2013	9/9/2013	10/3/2013	GT	25	RS	25
Total Number of Samples				238		245

Note: In the summer of 2013 (shown in italics) measurements were made at sites outside of the State of Georgia as part of other studies to provide a greater context and were not part of the paired sampling approach with JST as the central site.

Table 2: Regression analysis (Pearson's R) between DTT activity and selected PM components

Season	**Site**			**Inorganic ions**				**Water-soluble metals**					
		WSOC	**BrnC**	**SO_4^{-2}**	**NH_4^+**	**OC**	**EC**	**K**	**Ca**	**Mn**	**Fe**	**Cu**	**Zn**
Summer, 2012	*JST-GT*	**0.81**	**0.67**	**0.68**	**0.73**	**0.81**	**0.69**	0.49	0.20	**0.72**	**0.78**	**0.71**	0.62
	YRK	**0.79**	0.53	0.58	0.59	**0.76**	0.56	0.51	**0.68**	0.63	0.48	0.09	0.48
Fall, 2012	*JST*	**0.72**	**0.81**	0.49	0.52	**0.83**	**0.90**	0.61	-0.08	0.37	**0.74**	0.20	**0.82**
	RS	**0.71**	0.59	0.62	**0.66**	**0.77**	0.55	0.52	0.12	0.28	0.44	0.61	**0.68**
Winter, 2012-13	*JST-GT*	**0.69**	**0.78**	0.15	0.13	**0.85**	**0.82**	**0.78**	-0.13	0.46	**0.65**	0.63	0.63
	YRK	**0.84**	**0.88**	0.34	0.45	**0.82**	**0.80**	**0.75**	0.31	**0.68**	0.04	0.43	**0.72**
	RS	**0.78**	**0.86**	0.47	0.52	**0.86**	**0.75**	**0.69**	0.31	0.49	0.57	0.35	0.60
Summer, 2013	*CTR*	**0.78**	**0.88**	**0.71**	**0.78**	**0.77**	**0.72**	**0.66**	0.23	0.36	0.41	-0.12	0.62
	BHM	**0.67**	**0.74**	**0.66**	**0.66**	**0.85**	**0.68**	0.41	0.55	**0.75**	**0.66**	0.23	**0.66**
Fall, 2013	*GT*	0.47	**0.75**	0.39	0.37	**0.79**	**0.78**	**0.65**	0.29	0.58	**0.66**	0.46	0.46
	RS	0.21	0.48	0.60	0.47	0.58	0.53	**0.74**	**0.79**	**0.84**	0.53	-0.09	**0.74**

Note: R>0.65 are bolded.

Figure 1: Map of Sampling Sites

Figure 2: Monthly average ambient concentrations of EC (a) WSOC (b) and BrnC (c) at the sampling sites

Figure 3: Monthly average ambient concentrations of water-soluble metals at the sampling sites

~~Figure 4: Time-series of the daily average DTT activity (DTTv; Figure 4a and DTTm; Figure 4b) of ambient $PM_{2.5}$ at the sampling site~~

Figure ~~5~~4: Monthly averages of volume- (DTTv) and mass-normalized (DTTm) DTT activity at the sampling sites

Figure ~~6~~5: Site-to-site correlations (R^2) for volume normalized DTT activity (DTTv), elemental carbon (EC) and water-soluble carbon (WSOC) of $PM_{2.5}$.

Figure ~~7~~6: Composition profiles (% of each species) for the five factors resolved by PMF (left panel), and the time series of their relative contribution (right panel).

Figure ~~8~~7: Time series of $PM_{2.5}$ DTT activity segregated into different factors as predicted by PMF and their season-wise contributions

Figure ~~9~~8: Annual aggregate contributions of different sources identified by PMF (Figure ~~9a~~8a) and CMB method (Figure ~~9b~~8b) to the water-soluble DTT activity of ambient $PM_{2.5}$ in urban Atlanta