30 December 2014
Re: MS No. acp-2014-715

Dr. Huffman
Editor
Atmospheric Chemistry and Physics

Dear Dr. Huffman,

We have prepared a response to each of the reviewer's comments for MS no. acp-2014-715. We thank the reviewers for their time, insightful reviews, and assistance improving our manuscript. An updated manuscript that addresses all reviewers' comments has also been submitted for consideration for publication in Atmospheric Chemistry and Physics.

Sincerely,
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Response to Reviewer's Comments
Oxidant production from source-oriented particulate matter – Part 1: Oxidative potential using the dithiothreitol (DTT) assay
Jessica G. Charrier et al.
Submitted September 2nd 2014 to *Atmospheric Chemistry and Physics*
Revised Version Submitted December 30th 2014

Referee comments in bold text followed by authors' response in plain text.

Anonymous Referee #1

Section 2.1., P: 24153: method description is not sufficiently detailed. It is not clarified in the text why summer daytime samples were collected over one time period but winter daytime samples are segregated into three different periods (i.e. Table 1).

Detailed sampling information is available in (Bein et al., 2009). As described in Bein et al., sampling was adjusted in Winter 2009 based on knowledge gained during the Summer 2008 collection. The additional time-segregated sampling periods for morning and evening commute were added to attempt to separate source-specific information from the daytime sample. We have added *"These sampling adjustments were made in Winter 2009 based on sampling experience gained during Summer 2008"* to the discussion in section 2.1.

Also, although the authors mention in page 24154 (first paragraph) that the seasonal periods defined as "winter" and "summer" do not correspond to the typical definitions these of seasons, it is nowhere mentioned what months are clustered as "summer" and what months as "winter" ? This should be clarified in the text and a brief description of meteorological conditions should also be added to the Supplements, as this information can be useful in interpreting some of the seasonal trends and results (see the next comment).

We define the specific sampling period for summer and winter on page 24154 lines 1-2. We realize the dates were misinterpreted during ACPD's preparation of the manuscript: "Summer" sampling is from September 11th to October 21st 2008 so was actually conducted in fall based on a summer pre-study. "Winter" sampling was from March 1rd to April 3rd 2009 so corresponds to spring measurements. We have corrected the sampling dates in the manuscript in section 2.2.

In Figure 1, a distinct seasonal trend is evident with higher summer-time metal concentrations compared to winter. There is, however, no explanation regarding this trend and possible reasons in the text. In typical winter vs. summer conditions an elevated metal concentration in winter is often more expectable (due to the lower atmospheric mixing height). Is there any explanation why summer-time metal content of PM is found to be considerably higher than winter? Again, meteorological information about these two seasonal periods would simplify the interpretation of these results.

We expect spring and fall to have similar mixing height which is why we did not discuss this difference as a primary driver of the results. We do not have mixing height data to confirm this hypothesis. We were able to obtained precipitation data from NOAA (http://www.ncdc.noaa.gov/cdo-web/) to support our hypothesis that precipitation may account for some seasonal difference. We have added the following discussion to section 3.2.

"Because the sampling periods were actually Spring and Fall, we do not expected the mixing height to affect concentrations differently between these two seasons. It is possible that periodic rain during the Winter sampling explains some of the reduction in ambient concentrations of both PM mass and metals. NOAA precipitation data indicates no rain during summer sampling and 5 days of rain during winter sampling (NOAA, 2014)."

It is important (and intriguing) that water soluble metals are found to have a major contribution to the DTT assay. The extent of this effect is, however, somewhat overestimated in the manuscript. In Figure 3, the authors calculated DTT activity based on DTT rate associated with individual water soluble metals (method described in Charrier and Anastasio, 2012), and the results imply that Cupper and Manganese are the sole chemical species responsible for DTT activity in 36 out of 38 samples (Page 24161, last paragraph). It is difficult to make this direct conclusion without quantifying the DTT activity of the organic fraction as well. The authors explain higher summer-time DTT levels by higher corresponding summer-time metal concentrations. While metals abundance can indeed be one of the main factors, presence of other species (specifically secondary organics, not measured in this study), may also have significant contributions.

In figure 3 we plot DTT rate from soluble metals versus the measured DTT rate for the full PM extract. Using these data we can indirectly identify the contribution of DTT activity from species other than soluble metals, which include organic species (e.g., secondary PM, quinones, and HULIS) and may include insoluble metals as discussed on pg 24163. We discuss the potential for organics to contribute to the DTT assay throughout the manuscript (e.g., abstract pg 24150 lines 25-27; conclusion pg 24169 lines 10-13), and attempt to confirm the result that metals dominate the DTT response in a number of ways.

Figure 3 shows that metals can account for the measured DTT response in 36 out of 38 samples, indicating metals dominate the DTT response in most cases. We discuss that "*compounds other than the soluble metals we measured, likely quinones or other organics, sometimes make a significant contribution to PM oxidative potential*" (Pg 24163 lns 6-10) consistently pointing out the organics are important in most daytime samples. We further discuss organic carbon and its components that may contribute to the DTT response (pg 24163 ln 15-24). We then use another method to investigate the potential role of phenanthrenequinone (known to be highly DTT-active) based on median particle concentrations observed in the literature (pg 24163 ln 25 to pg 24164 ln 5). The results indicate phenanthrenequinone could represent between 2-36% of DTT response with an average value around 13%. This is similar to the results that we obtain from our samples: that Cu and Mn will likely account for the majority of DTT response from ambient PM while highly-redox active quinones will contribute a smaller percent of DTT activity, but can contribute significantly in some samples.

To further acknowledge the reviewer's point we have added the following to the discussion of Figure 3:

"Although generally not statistically different, there are a number of cases where the measured DTT rate is larger than the DTT rate calculated from soluble metals. In these cases there is likely some contribution from other species, probably organic compounds, but the difference is encompassed by large error bars. Even in these samples metals generally account for half or more of the DTT although

there is a small but significant contribution from other species, as would be expected from typical ambient concentrations of quinones (as discussed below). "

Anonymous Referee #2

The author's approach of conducting the source apportionment based on the single particle spectrophotometry seems interesting in terms of that it does not require a large sample size like conventional models, but from the actual results shown in the paper, it does not seem to work out practically. This is evident from the large fraction of PM (40-60 %) attributed to the unknown sources. This is one of the major concerns in this study and it is somewhat awkward to call it a source-apportionment analysis, if more than 50 % of sources are unidentified.

We thank the reviewer for the comment and agree. In recognition of this we used the term "source-oriented" instead of "source apportionment" throughout the text. This method is meant to identify and separate relatively pure but atmospherically processed source signals. The method did not identify the source of the majority of PM mass because the Fresno study site frequently experiences a regional mix of air pollution rather than pure sources associated with different wind directions. Still, the ability to separate and measure the oxidative potential from these sources, even if they are present in pure form for only short periods of time, does provide interesting and novel information. In a more favorable location this technique offers a powerful method to separate atmospherically processed source signals. Our paper represents the first application of this method to DTT data and provides useful insight into the oxidative potential of some specific PM sources. Our results also provide information about the weaknesses of this method, which should inform future research. While we have not identified the source of all PM mass, we do measure the oxidative potential of the whole PM mass so that we can investigate the relative importance of the identified sources (Figure 4). This also provides information on the oxidative potential of missing or mixed sources. While it has some weaknesses in this first iteration, this novel method has significant promise.

Another fundamental concern in the study is related with the mechanistic approach used by the authors to estimate the contribution of transition metals based on the empirical equations derived in their previous publication – Charrier and Anastasio, 2012. If this mechanistic method actually explains the dependence of the DTT activity measured in aerosol sample extracts (as the authors are claiming) it has major implications on the use of this assay. Note that the equations that describe the DTT response are in the form of liquid concentrations (i.e. µM), and since these are based on the nonlinear relationship between DTT and metals, it implies that the translation of DTT loss results from the extracts to ambient atmosphere (i.e. in terms of nmol/min/µg of PM or nmol/min/m3 of air) will be dependent on the concentration of metals in the extracts used for DTT assay. If Cu and Mn are the biggest contributors to the DTT activity as concluded by the authors, then the relationship between DTT activity and PM mass will also be non-linear. It follows then by this method the calculated DTT activity of the ambient PM nmol/min/ µg of PM) is dependent on the liquid concentration of the PM mass in the extract used for DTT assay.

This is an important point as it raises the following fundamental concerns on the use of this assay in measuring the oxidative potential of PM:

1. The different methodologies used for extraction of PM (i.e. different volumes of extraction liquid) would yield different results of the calculated DTT activity of PM and different estimates of contribution from Cu and Mn.

2. It means that the mass normalized DTT activity of the ambient PM has no meaning, as this would be a function of the mass of the PM extracted in the solution for DTT assay (a function of the method).

3. It also means that any comparison of the DTT activity among different ambient samples (as they have different PM masses) or even among different ambient studies is meaningless.

We agree with the referee's main point: the non-linear dependence of the DTT result on PM mass for samples with significant contributions from Cu and/or Mn is a fundamental, and previously unappreciated, concern for this assay. We are currently working on a manuscript exploring this issue based on experimental observations of this effect from a set of PM samples from southern California, which were studied after the current Fresno set. In the southern CA samples we find that the DTT result is non-linearly related to the PM mass added to a fixed volume of extract solution. It is quite possible that some past DTT measurements from ambient PM in the literature are fundamentally confounded by this issue. In our manuscript-in-preparation we are developing a method to deal with this issue using a larger ambient PM sample set where we were able to measure DTT response from multiple mass concentrations of PM in the DTT extracts and where we have both transition metal and quinone data.

As we describe in the new supplemental section S1, in our current version of the normalization method we calculate the expected DTT rate at a standard PM mass concentration in the extract of 10 µg mL^{-1}. Normalizing results to a single mass concentration allows comparisons across samples and studies. To do this normalization we: (1) determine the contributions of Cu and Mn to the measured DTT rate based on measured transition metal concentrations, (2) adjust the Cu and Mn DTT responses to what would be expected in a 10 µg mL^{-1} extract based on our previously published, non-linear concentration-response curves, (3) adjust the residual DTT response (from unknown redox-active species) to what would be expected in a 10 µg mL^{-1} extract (by assuming a linear response), and (4) sum the Cu, Mn, and unknown contributions to DTT to get the "normalized" result for a 10 µg mL^{-1} sample extract. As we describe in supplemental section S1, we applied this method to the Fresno samples in the current work, but it makes little difference in the mass-normalized result because most of our extracts used a PM concentration near 10 µg mL^{-1}. In contrast, the normalization procedure has a large effect on many of other samples from southern CA (data not yet published), which used a much wider range of PM mass concentrations in the DTT extracts.

We are not implying the PM measured here does not have a mass-dependent DTT response, but rather, the PM masses used were generally very close to 10 µg / mL so the result is not much different when normalized. In addition, the substantial increase in error of the normalized method would mask any changes made by normalization. This will not be true for all other PM samples, as we have seen from our Southern CA data. Since the normalization makes only a small change in the results for the current samples, but significantly increases the errors on the results, we have not normalized the results in the manuscript. However, we have included a complete description of the normalization procedure, the normalized results, and a comparison of the results with and without normalization, in supplemental section S1.

Another concern of the study is that the authors highly generalize the results obtained from a single site and from a very limited number of samples (n<40). Even if it turns out that metals make a substantially large contribution to the DTT activity of these samples, extrapolation of the results to the linkages between epidemiological results and metals concentration in California in general (e.g. most of the discussion on Page 24167; "Vehicular emissions", and Page 24169, Line 15-17) seems exaggerated.

On pg 24167 ln 15-19 and 24169 ln 15-7 we cite research that has consistently found traffic emissions and/or Cu to be associated with oxidant production and adverse health effects in humans. We state that our results agree with current literature data and do not try to extrapolate the results to California. Instead we cite an article (Ostro et al., 2007) that found Cu to be statistically related to mortality in California. Placing our results in context of previous literature seems warranted.

We feel we can accurately explain the DTT response based on PM composition, and, based on the median composition of soluble metals and quinones in the U.S. a significant fraction of DTT response will be from Cu and Mn. It is clear that the DTT response will depend on the specific chemical composition of the sample. We acknowledge that DTT activity from organic species is not completely understood so organic species besides quinones may be important. Because we only include quinones in our "typical ambient PM2.5 sample" DTT calculations, we may underestimate the contribution of organics to DTT response at other sites, though this site matches our expectations very well. To acknowledge this we have removed the comparison to our "typical ambient PM2.5 sample" in Section 3.4 and updated the following discussion (includes additions and deletions from existing text):
"On average (± σ), soluble Cu and Mn account for 83 ± 40 % and 26 ± 14 % of the measured DTT response in our Fresno samples, respectively. Fe, V, and Pb each contribute less than 1% to DTT response; these contributions are too small to be seen for most samples in Figure 3. These results represent the DTT response for the specific chemical composition of PM collected at this site. The DTT response from PM measured at other sites will depend on the composition of the particles and may not be dominated by transition metals. On the other hand, our interpretation of recent results from Atlanta and other sites in the southeast U.S. also indicate that Cu and Mn play important roles in the DTT response (Verma et al., 2014); see reviewer's discussion at http://www.atmos-chem-phys-discuss.net/14/19625/2014/acpd-14-19625-2014-discussion.html)."

When discussing the potential contribution of PQN in section 3.4 we have also added:
"The specific organic species that contribute to DTT response are still incompletely understood, and may include species other than the PQN. These hypothetical results are a lower estimate for organic contribution to DTT response if other DTT-active organic species are present."

Page 24150: Line 7: This sentence is somewhat arbitrary. What is meant by the source's ability to generate ROS? Are the authors talking about ROS on the particles itself? If yes, then how is it related with transition metals? If not, then this sentence doesn't mean anything.

We have clarified "produce reactive oxygen species" to "produce reactive oxygen species in the body". This sentence is meant to reflect that ROS are related to PM health effects thus the amount of ROS produced by a source may drive its toxicity.

Page 24151: "true toxicity of PM": What does it mean? What is false toxicity?

We have removed the word “true”.

Page 24152, Line 25-26: The authors in this study measured only metals, which constitutes less than 5 % of the PM mass. Can the authors really refer to it as chemical composition when they didn’t measure the major chemical components such as carbonaceous species, which generally constitutes more than 50 % of the PM mass?

We have clarified the sentence from “*we examine the differences in chemical composition and oxidative potential*” to “*we examine the differences in soluble metal composition and oxidative potential…*”

Page 24153, Line 26: word is repeated: : :. “time”, “times”

Corrected

Page 24154, Line 1: Dates of sample collection: 9 November 2008 to 21 October 2008?

Thank you for catching this error; the dates were incorrect and we have updated them.

Page 24154, Lines 7-10: The SMF and UF fraction of the particles were collected on different substrates? Have the authors investigated the effects of substrate type on the oxidative potential of PM in any of their or others previous study?

We measured triplicate blank samples from each filter media and do blank correct each filter type by its corresponding filter blank as mentioned briefly in the methods. We did not see a difference in blank values based on filter type. We have added a more detailed description, including the filter blank values to the methods section.

Page 24156, line 18: “After 1.5 or 24 h of incubation”- Why there is a time-range? Was the extraction time different for different filters?

The soluble metals were extracted in concert with other measurements, which were made after either 1.5 or 24 hours of extraction. Some PM samples were extracted for both times to ensure extraction time did not affect the results.

Page 24159, 8-12: There is some problem in the structure of this sentence.

We have updated the sentence to read: “However, the percent of particulate Fe that is soluble is generally low in ambient PM, with values ranging from <1% to 6%.…”.

Page 24159, Line 27-28: The fact that authors themselves accept that the differences in the mass normalized activity of UF and SMF fractions compared to the previously reported studies might be due to different chemical composition at different sites demonstrates that the author’s results based on a single site cannot be generalized, as has been done in this study.

See previous response: we but have clarified this in the manuscript. The DTT response will depend on the specific chemical composition of the PM sample.

Page 24160: Equation 3: Mass Weighted Oxidative Potential: I am unable to understand the physical significance of this parameter. If I understand correctly, the mass normalized activity of PM in itself is a complete parameter no matter how low or high the PM mass. Now if you multiply the mass normalized oxidative potential by its mass fraction, I do not understand what additional information you get. It does not represent the total exposure from this fraction, which is obtained by multiplying the mass normalized oxidative potential with mass concentration. The authors need to state its significance.

There are two ways to consider the oxidative potential of the entire PM mass: DTT response relative to PM mass and DTT response relative to air volume. Eqn 2 calculates the DTT response for the entire PM mass relative to air volume and Eqn 3 calculates the total DTT response relative to PM mass. The oxidative potential of the total PM mass (Eqn 3) is dependent on both the mass-normalized oxidative potential of the source (Eqn 1) and the abundance of the source ($F_{i,k}$ in Eqn 3). We have added a clarifying sentence to discuss the meanings of equation 3 in the context of eqn 2:
"This metric is similar to Eqn.2, which calculated the DTT response of the total PM relative to air volume, but instead calculates the DTT response of the total PM relative to PM mass."

Page 24161, Line 28: "are contribute"- wrong sentence structure.

Corrected

Page 24162, Line 2-6: As the authors themselves admit that the agreement between measured and estimated DTT is due to large error bars, I see it in almost all samples, particularly in the estimated DTT activity from metals. The authors seem to ignore this issue and discussed it only to explain the higher estimated activity than measured for a few samples. This explanation is clearly biased towards showing the dominant contribution of metals and I wonder if the authors should explicitly address it.

Thank you, we have added the following discussion to that section:
"*Although generally not statistically different, there are a number of cases where the measured DTT rate is larger than the DTT rate calculated from soluble metals. In these cases there is likely some contribution from other species, probably organic compounds, but the difference is encompassed by large error bars. Even in these samples metals generally account for half or more of the DTT although there is a small but significant contribution from other species, as would be expected from typical ambient concentrations of quinones (as discussed below).*"

We have also updated the discussion of PQN contribution to DTT response in the same section as follows (red text is added; strike through text is removed):
"*We can estimate the likely contribution of quinones to our Fresno PM samples by using previously measured particulate concentrations of phenanthrenequinone (PQN), the most DTT-active quinone tested (Kumagai et al., 2002;Charrier and Anastasio, 2012;Chung et al., 2006). PQN has a median particulate-phase concentration of 0.32 ng/m^3 based on (limited) measurements in Southern California (Cho et al., 2004). If we assume this ambient concentration for all of our Fresno source-oriented mixtures (SMF + UF), the resulting PQN concentration in solution is between 1 – 12 nM. This would correspond to DTT responses in the range of 0.01 – 0.16 µM DTT / min, which represents 2 – 36 % of the measured DTT rates (with an average ± 1σ contribution of 13 ± 9 %). This result agrees well with the observations in Figure 3, which show a consistent but relatively small contribution of species besides Cu and Mn to*

measured DTT response. ~~*This calculation suggests that PQN will have, at most, a small contribution to overall DTT response, and that Cu and Mn dominate DTT loss in the Fresno source-oriented PM$_{1.0}$ (Fig. 3).*~~ ~~"~~

Page 24162, Line 24: Ca or Cu?

Clarified Ca to California

Page 24162, Line 27-28: Do the authors believe that dust would contribute to the SMF and UF sampled in their study? Can they provide any reference to it?

Dust will not likely contribute to UF PM. Mineral dust, paved road dust, and break and tire wear likely contribute to SMF mass (Pakkanen et al., 2003;Kleeman and Cass, 1998). Vicars et al. (2011) observed mineral dust (7-33%) in SMF PM in California. Mineral dust does not have many DTT active species so its contribution to the DTT assay will be limited. Bukowiecki et al. (2009) found Cu emissions from brake wear in the submicron range, especially from heavy duty vehicles. We have added a discussion of Cu emissions in the submicron PM size range from brake wear to the manuscript.

Page 24162, Line 24: Expand VMT

Corrected

Page 24164, Line 2: How did the authors calculate the concentration of quinones in liquid extract based on their atmospheric concentration? Did they assume quinones are all soluble in water?

Yes. Our calculations attempt to encompass the entire possible range of quinone contribution to DTT response. We do believe PQN will likely be soluble in the DTT solution at 1-12 nM based on both reported solubility in water (~10 µM) and because concentration response curves of pure solutions were linear between 0-200 nM (Charrier and Anastasio, 2012). However, solubility from PM will be more complicated than from a pure stock solution so we cannot be certain PQN would dissolve. Assuming 100% solubility gives the upper limit of DTT response from PQN which is useful to understand the maximal possible contribution of PQN to the DTT response. We have clarified this in the discussion by adding a statement that we assume all PQN is soluble.

Page 24164, Line 22: From the figure S5, the correlation between measured DTT and metals seem to somewhat fit the mechanistic curve (green and purple line) derived for Cu, but it is far-off for Mn. Do authors have any explanation for this?

In figure S5 a-c we show the total DTT response (from all chemical components) versus each individual component. The purple line corresponds to pure Cu, the green line corresponds to pure Mn and the orange line corresponds to pure Fe. Because Cu accounts for most DTT response, the total DTT response mirrors the pure Cu curve (purple) best. Mn also makes a measurable contribution to DTT response so there is some relationship while Fe does not contribute to DTT response so there is no relationship. There is still some correlation between DTT response and Fe content in Figure S5c because Fe is covariate with Mn and Cu, especially in cases of very high Mn and Cu. This analysis illustrates the difficulty in using correlations to identify which chemical species are responsible for DTT loss. We have clarified the legend text to more explicitly state the meaning of the purple, green and orange lines.

Page 24166, Line 1-4: As mentioned before, these appear quite strong statements attributing all DTT activity to Mn and Cu, based on a single site and limited sample size? Also, wrong spelling – "Speces".

Please see our responses above. In response to these comments we have added additional qualifiers to our text, limiting this statement to Fresno.

Page 24168, Line 16-17: The authors need to give rain data in the supplemental information to substantiate their argument.

We have added a discussion of rain prevalence based on NOAA data to section 3.2.

Page 24168, Line 24-26: This statement is inconsistent with the authors' conclusion as it implies that Fe is one of the major components of DTT activity, which doesn't seem to fit with their results.

We have clarified the line to read:

"*PM collected in summer 2008 has a higher metals content on average and a three times higher ambient SMF mass concentration.*"

Anonymous Referee #3

Specific comments

1. **Iron is known to catalyze ROS formation through Fenton reaction; however, the DTT activity of Fe was measured to be very low (significantly lower than the DTT activity of Cu) (Lin and Yu, 2011; Charrier and Anastasio, 2012). As such, the DTT assay is not suitable to evaluate the redox activity of Fe and the oxidative potentials of PM sources that contain significant Fe content, such as vehicular emissions and unknown metals (seen from Figure 1) would be under-estimated. The bias caused by inability of DTT assay reflecting ROS production capability by Fe needs to be explained in text and briefly mentioned in the abstract.**

Thank you, we have added the following to the introduction:

"It should be noted that the DTT assay is insensitive to ROS production from iron (Fe) (Charrier and Anastasio, 2012;Lin and Yu, 2011), though Fe effectively produces hydroxyl radical ($^{\cdot}$OH) in particle extracts via the Fenton reaction (Vidrio et al., 2009). Thus, use of the DTT assay may underestimate oxidative potential from sources that are high in Fe."

2. It appears that the research group also measured the rate of production of OH radical and will report the results in the companion manuscript (page 24152, lines 21-24). Was there any correlation observed between Fe content and OH production rate? It will be good to include in this manuscript a brief description of the relevant OH radical production results.

The companion manuscript will report $^{\cdot}$OH and HOOH production from the particles and compare the results with both soluble metals and the DTT assay. We prefer to reserve those results for the companion manuscript since it is not yet published and this manuscript is already long.

3. The earlier work of the authors (Charrier and Anastaio, 2012) showed that the rate of DTT loss due to Cu and Mn is not linearly proportional to the metal concentration in the DTT assay. This concentration dependency is an artifact of the analytical procedure as the concentration of Cu or Mn in extracts could be arbitrarily varied by using different proportions of PM mass and the DTT solution volume in the DTT assay. This concentration dependency needs to be removed when calculating contributions of individual metal species to DTT activity for comparison with the measured overall DTT activities by the mixture. To remove this concentration dependency, the lower concentration range that generates linear response should be used. It is also perhaps more reasonable that the lower concentration levels (generating linear DTT response) simulate more closely the concentrations actually encountered in lung fluids inside humans.

Please see our response to reviewer #2 on this topic.

4. The part on apportionment of volume-normalized oxidative potential using modeling results of emission inventory sources is highly speculative and uncertain. Identification and separation of sources using the single particle mass spectrometry data as illustrated in this work did not work out very well. The authors did not present evidence for evaluating how well the matching of the source categories as identified by single particle mass spectrometry and those listed in emission inventories.

In addition, the source-based oxidative potential determination was based on a very limited set of data, i.e., one ChemVol source sample per season. The combined uncertainties could be huge. I suggest removing this part of the results from the paper.

The purpose of using modeling results from (Hu et al., 2014) was to identify the prevalence of each source type in Fresno. This information could not be obtained from our sample method because only pure sources could be identified, though the sources were undoubtedly present as mixtures for other periods of time. We feel it is common practice to use emission inventories to identify the sources at a site. The results from (Hu et al., 2014) had the additional benefit of being specific to Fresno, allowing matched temporal attribution of sources, including ultrafine PM speciation, and having some verification of the emission inventory with ambient samples.

We agree that the apportionment work is uncertain, and the supplement contains a more detailed discussion of the method and limitations. These results represent an important first step in using source-oriented particles to apportion oxidative potential. To further qualify and clarify our approach, we added some additional discussion of this to Section 3.5 of the manuscript:

"There is some additional uncertainty not explicitly accounted for due to the assumptions of matching our data to that in Hu et al. (2014), which are discussed in more detail in supplemental section S6. The inventory in Hu et al. (2014) is the best available information of Fresno PM sources because it has been validated using ambient measurements, contains temporal information that allows matching to our specific measurement season, and is the only source of ultrafine PM source contributions available."

We updated the sentence following the discussion above to read (red text added, strike through removed):

"While there is significant uncertainty in our results, and major sources are unidentified or unknown, ~~in~~ Figures 4c and 4d show that cooking and mobile sources make important ~~are the largest identified~~ individual contributions, accounting for 18 – 29 % and 16 – 28 %, respectively, of the volume-normalized oxidative potential."

We have also removed the discussion of these results from the abstract in recognition of the high potential uncertainty in the result. The following was removed from the abstract: *"When we apportion the volume-normalized oxidative potential, which also accounts for the source's prevalence, cooking sources account for 18 – 29 % of the total DTT loss while mobile (traffic) sources account for 16 – 28 %."*

Minor comments

Figure 3 shows two source categories with * identifying cases where the measured and calculated rates are statistically different. But visual inspection suggests the last two source categories in summer UF and winter UF plots (Figs. 3a and 3c) (which are not marked with *) are also cases where the measured and calculated rates are statistically different. At least the authors also indicate in the text (page 24162, lines 9-10) that winter UF "nighttime inversion (CV10)" (last source category in fig. 3c) is such a case. Please check and rectify the inconsistence

We have double checked the calculations and only the two samples in figure 3 already marked with asterisks are statistically significantly different at the 95% confidence level. The sample indicated does indeed look quite different but the large error bars and small sample size prevents the measured and calculated values from being statistically different. For verification, the values are 74.83 +/- 25.45 n=3 and 25.31 +/- 2.14 n=3.

P24160, line 15: change "where j refers to season" to "where i refers to season".

Thank you for catching this error, we have made the correction.

P24164, line 17: change "Fig. S4a-c" to "Fig. S5a-c".

Corrected

References

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