

Response to Anonymous Referee #3

Review of “Development and field-testing of an online instrument for measuring the real-time oxidative potential of ambient particulate matter based on dithiothreitol assay” by J. V. Puthussery et al.

This study describes the development of an automated, on-line system to measure the oxidative potential (OP) of particulate matter using the DTT assay. Measurements of OP and DDT activity have been increasing substantially in recent years with the acknowledgement that this may represent an indicator of the toxicity of PM. The system described in this manuscript represents the first automated measurement of DTT activity, and is therefore an important contribution to the atmospheric measurement community. Overall, the authors present a detailed, careful, and deliberate characterization of the system performance. The extensive ambient deployment of the system goes beyond most method papers. The writing is clear, the paper is well organized, and the figures are of high quality. I have several issues with the manuscript: I see some problems with the authors’ attribution of the DTT activity to specific sources – it seems they are trying to explain their results based on what they expect, which does not necessarily agree with their actual observations. I also think that the different contributions of insoluble particles to the mist chamber samples is a bigger deal than the authors describe, and certainly contributes to the differences in OP between the offline and online measurements, but also to their troubles attributing the DTT activity to specific sources. I recommend the manuscript for publication after my comments have been addressed.

Response

We thank the reviewer for the insightful questions and comments. Our responses and corresponding changes made in the manuscript (highlighted in red) are given below.

Specific Comments:

1. I assume that this has been addressed in the references cited, but some discussion of the particle collection efficiency by the mist chamber is needed.

We agree with the reviewer’s comment and have added some discussion in section 2.1. Note, previous studies have characterized the collection efficiency of MC only for the water-soluble components. For example, Hennigan et al. (2009) reported a collection efficiency of 95% with nitric acid aerosols at a flow rate of 21 LPM. King and Weber (2013) also calculated the collection efficiency of MC by simultaneously operating a particle into liquid sampler and measuring the sulfate collected by both systems. The sulfate collection efficiency in the MC was close to 100 % at flow rates greater than 25 LPM but was below 80% at flow rates less than 15 LPM. The air flow-rate of MC is directly related with the formation of jet spray of water, i.e. a high flow rate is required for a stronger jet spray, which could rinse the hydrophobic filter and

bring the particles into the MC suspension. Note, we operated the MC in our current study at a much higher flow rate (42 LPM) than used in previous works. Therefore, it is reasonable to assume that the collection efficiency of our MC is almost 100 % for at least the water-soluble components. However, we cannot comment on the collection efficiency for the water-insoluble components as no prior study has investigated it. Our study is probably the first to suggest the collection of water-insoluble components in MC.

Page 4, line 2:

“however few studies (Anderson et al., 2008; King and Weber, 2013) have also used these devices for collecting the water soluble fraction of the ambient particles. Hennigan et al. (2009) estimated the collection efficiency of MC as ~95% using nitric acid aerosols at a flow rate of 21 LPM. King and Weber (2013) also calculated the collection efficiency of MC by operating it simultaneously with a PILS and measuring the sulfate collected by both systems. The collection efficiency in the MC was close to 100 % at flow rates greater than 25 LPM.”

2. The difference between the MC ROS and filter ROS is quite surprising (50% higher in the online system), and definitely indicates the contribution of insoluble components. Some discussion of Phillips and Smith (2017) should be included here. I think the major implication of this is that a direct comparison of the MC and filter samples is not so straightforward. The MC samples include a lot of insoluble particles which clearly contribute to the DTT activity (similar to the MeOH extracted samples), which is not the case for the water-soluble extracts. This muddles the comparison of the DTT activity to the other chemical components.

We agree with the reviewer that a higher activity obtained from the MC indicates the contribution from water-insoluble components in DTT activity. In fact, our results are consistent with previous studies which show that the insoluble particles have a significant influence on the DTT activity and should be accounted while measuring the OP of ambient PM (Daher et al., 2011; Gao et al., 2017). However, we don't believe that including the discussion of Phillips and Smith (2017) is relevant to our study. Phillips and Smith (2017) reports that the suspended insoluble fraction of PM, which is not removed even after filtering the methanol PM extracts can cause interference in the absorbance measurements and thus would overestimate the measurement of brown carbon. We agree this is a very important aspect to consider while developing the protocol for the measurement of atmospheric brown carbon; however, there are important differences to be considered while comparing their method with ours. First, they used a cuvette method on a Cary 60 UV-vis spectrophotometer instead of the liquid waveguide capillary cell (LWCC) used in our setup. Note, they themselves stated that such particle extinction might not be present to the same degree with the use of a narrow-bore LWCC as others have used (Phillips and Smith, 2017; page 1116, section 3.1.2). Second, they observed the interference in the spectra obtained only from the methanol extracts and not in the water extracts, even after various degrees of filtration, i.e. 0.22 μm and 0.45 μm syringe filtration of the water-extracts. Finally, it is important to note that in the DTT assay protocol, we are not measuring the absorbance caused by the aerosols, but rather from 2-nitro-5-thiobenzoic acid (TNB, the reaction product of DTT with DTNB), that too at a specific wavelength of 412 nm, in

comparison to the broad range of wavelengths (300-800 nm) used for brown carbon measurements. Our DTT assay protocol requires the reaction volume to be diluted by 50 times (from the original concentration of PM extract used in the reaction) before passing it through the LWCC for absorbance measurement. This is due to a relatively high concentration of DTT (100 μ M) used in the reaction vial which could saturate the absorbance spectra. Therefore, any interference from the insoluble aerosol particles, if present, in the absorbance measurement will be negligible.

As for the second part of the comment (comparison of MC with the filter measurement), we agree that a direct comparison of the MC results with chemical components is not straightforward. However, our objective was not to point out the specific water-soluble components that might be participating in the DTT consumption. Rather, we wanted to provide the insights into the emission sources contributing to the DTT activity. For example, WSOC and metals were considered as the tracers for SOA (Cheung et al., 2012; Verma et al., 2014) and vehicular emissions (including vehicle-induced road dust resuspension) (Wang et al., 2005; Hulskotte et al., 2007; Thorpe and Harrison, 2008; Chen et al., 2012), respectively. Considering this, we have modified our discussion in section 3.6.2, replacing the specific components with the possible emission sources, as follows:

Page 13, lines 9 - 11:

“A close similarity of the diurnal profile of the water-soluble metals with DTT activity suggests a significant contribution of both vehicular emissions (the morning peak) and resuspended dust (in the afternoon) to $PM_{2.5} OP_{ex}$ at the sampling site...”

3. Pg. 9, line 18 – 20: I disagree with this statement. The collection of insoluble particles does not indicate that the MC performs better than conventional filter collection and extraction, but rather that the MC is subject to an artifact that may need to be accounted for.

Please note that this particular statement was made in the context of DTT activity measurement using MC. Numerous studies have shown that in addition to the soluble components (i.e. either water- or methanol-soluble) in the PM, the insoluble fraction that remains after extraction, also influences the DTT activity (Daher et al., 2011; Eiguren-Fernandez et al., 2017; Gao et al., 2017). There have been recent efforts to incorporate this insoluble fraction by using methods such as, performing the DTT reaction directly on the filter instead of extracting the particles with a solvent (Gao et al., 2017), or directly collecting the particles into liquid (e.g. liquid spot sampler) followed by its DTT activity determination (Eiguren-Fernandez et al., 2017). MCs have been traditionally used for collecting the water-soluble PM fraction (Anderson et al., 2008; King and Weber, 2013) and therefore our first step was to compare the online system results with conventional filter measurements. What we found during this analysis is that the online system (MC samples) results were consistently higher than the conventional filter extraction using DI water, and were closer to the values obtained by extracting the filters in methanol. Now assuming that MC has almost 100 % efficiency for collecting the water-soluble components

(Anderson et al., 2008; King and Weber, 2013), it implies that the additional contribution in MC DTT activity results is from the water-insoluble components, which are not captured in the conventional filter extraction techniques using DI. We don't understand how we can say this is an artifact, when we know that these water-insoluble components are actually present in the ambient PM and do contribute to the DTT activity, as reported in previous studies (Daher et al., 2011; McWhinney et al., 2011; Eiguren-Fernandez et al., 2017; Gao et al., 2017). Rather, it should be considered as an advantageous feature of MC, which provides a more holistic assessment of the PM oxidative potential, as indicated from our results discussed on page 9, lines 12 – 20 of the revised manuscript. Therefore, we disagree with the reviewer's perspective on considering this as an artifact of MC.

4. Discussion on Pg. 2, lines 25 – 27: I agree there is great utility in an on-line measurement of oxidative potential, but this argument is rather weak. If Cu is really the most important species driving DTT activity, is there any evidence that Cu undergoes chemical changes during filter sampling?

We want to clarify here that although our results indicate that Cu is one of the important species influencing the DTT activity, our results cannot be generalized for other locations and environment. The range of Cu concentrations measured at our study location (4-23 ng/m³) was highest among three commonly reported redox active transition metals (i.e. Cu, Fe and Mn). Therefore, it probably contributes more substantially to the DTT activity at our location. However, there are other species like organic compounds (e.g. SOA), which are also known to significantly influence the DTT activity. For example, Verma et al. (2012) reported that HULIS fraction (free from Cu) of the PM in Atlanta accounted for 60% of the water-soluble DTT activity. Similarly, although Fe doesn't play a major role in the DTT oxidation, it can enhance the [•]OH generation in DTT assay in the presence of organic compounds (Xiong et al., 2017; Yu et al., 2018). Therefore, OP of the ambient PM is due to a combined effect of various transition metals, organic compounds and probably other redox active chemical species. Even in our current study, the SOA appears to have a significant contribution to the DTT activity (Page 12, lines 24 - 25); however, we have not performed a detailed analysis to quantify the relative contributions of each of these species (which is beyond the scope of our current study, but we plan to do it in future investigations). Although we agree that there are currently no studies suggesting the chemical changes of Cu during filter sampling, there are several studies indicating the loss or alteration in the speciation of other redox-active components during sampling or storage. For example, Eatough et al. (2003) and Daher et al. (2011) have reported a significant loss of semi volatile organic species [known to contribute to the DTT activity (Verma et al., 2009)] in the conventional filter sampling techniques. Sampling artifacts in the measurement of ammonium, nitrate, chloride, and sulfate are commonly reported in conventional long duration (> 24 h) filter sampling, thus influencing composition of the collected PM (Yao et al., 2001; Pathak et al., 2004). The loss of these inorganic ions can change the acidity and subsequently the solubility of the transition metals, thereby indirectly alter the OP of the collected PM (Fang et al., 2017). Moreover, ambient Fe (II) collected over filters has been found to reduce the oxidized manganese (a DTT-active metal as shown in Charrier and Anastasio, 2012) present on the filter

(Majestic et al., 2007). Therefore, based on this literature, it is safe to assume that any artifact, either associated with sampling or storage of the filters, which affects the stability or chemical characteristic of any of the redox active species has the potential to influence the OP. And, our MC sampling technique would potentially reduce the impact of these artifacts on the OP measurement.

We have included these references to further strengthen our sentence on page 2, line 25 - 27:

“Generally, PM collected over filters might undergo chemical alteration during sampling, storage and extraction procedures, such as loss of semi-volatile organic (Daher et al., 2011) and inorganic (Yao et al., 2001; Pathak et al., 2004) compounds, and change in the oxidation state of metals, e.g. Mn (Majestic et al., 2007). Some of these components are known to directly contribute to OP [e.g. semi-volatile organic compounds (Verma et al., 2009) and Mn (Charrier and Anastasio, 2012)], while others (e.g. inorganic ions) can affect it indirectly by altering the solubility of redox-active metals (Fang et al., 2017b).”

5. Pg. 3, line 5: I do not understand this sentence?

A widely accepted hypothesis on the mechanism for how PM_{2.5} affects human health is associated with the reactive oxygen species (ROS). The ROS can be either formed endogenously after particle deposition in the human respiratory tract or it can be present directly on the particle itself (Knaapen et al., 2004; Venkatachari and Hopke, 2008). Majority of the existing studies on online OP measurement system measures the latter, i.e. the particle bound ROS (Venkatachari and Hopke, 2008; Wang et al., 2011; King and Weber, 2013; Wragg et al., 2016; Zhou et al., 2017) while adopting the dichlorofluorescein (DCFH) fluorescence probe to determine the ROS concentration. However, the in situ formation of free radicals after particle inhalation due to the presence of highly redox active species (such as transition metals, polycyclic aromatic hydrocarbons) is another major pathway for causing the PM induced oxidative stress in human body, which is probably more important than the particle bound ROS as suggested by Ayres et al., 2008. To the best of our knowledge, only two online systems have been developed till now, which measure the OP based on DTT assay, i.e. Sameenoi et al., 2012 and Eiguren-Fernandez et al., 2017. Therefore, we stated “However, most of these instruments measure the particle-bound ROS, which represents only a small part of the particles’ OP”, on page 3, line 5. We hope it is now clear to the reviewer.

6. Pg. 3, lines 17 – 20: this is somewhat misleading, since the ancillary components (syringe pumps, distribution valves, LWCC, spectrometer) will in total cost many thousands of dollars. My guess at the total system cost is \$12k - \$16k, and while this represents a lower cost than a method using the PILS or LSS, I don’t think this qualifies as “low-cost”.

Our intention here was to compare only the MC system to other existing sample collection systems (LSS or PILS) which are significantly costlier. But we agree with the reviewer that in combination with ancillary components, it doesn’t qualify for the “low-cost” system. Therefore, we have omitted the “low cost” term from the manuscript and removed the cost comparison discussion with other online systems.

Page 3, lines 16 - 21

“Here, we discuss the development of an automated online instrument to measure the hourly averaged OP of ambient PM_{2.5} using DTT assay and its evaluation in the field conditions for over 50 days. A custom-built glass MC was used for collecting the ambient PM suspension, which is then transferred to an automated analytical system for DTT activity determination.”

7. Section 2.2: give the manufacturer and purity of all chemicals and reagents.

We have added the manufacturer and purity information for all the chemicals.

8. Section 3.2: the strong RH-dependence on the remaining water volume is not consistent with other M.C. studies (e.g., Hennigan et al., 2018) – this may be due to inconsistencies between different mist chambers, but this difference is worth mentioning.

We agree with the reviewer that the strong dependence of the evaporative loss in MC on RH as seen in our study was not observed in previous studies. But, it is not due to inconsistencies between different mist chambers. There are two reasons for that: flow rate and the sampling duration, both of which were much higher in our system than those used in the previous studies. The flow rate in our system was 42 LPM compared to 21-28 LPM in previous works (Hennigan et al., 2009, 2018; King and Weber, 2013). Similarly, the duration of sampling in our system was 60 minutes compared to 5 minutes used in earlier studies. Therefore, the evaporative losses were minimal in those other studies but cannot be ignored in our case. Following the reviewer's suggestion, we have added a discussion on this in the manuscript:

Page 7, lines 19 - 22

“During air sampling, the volume of water inside the MC decreases due to evaporative loss. There are two concerns associated with this loss of water. First, if the water level drops below the capillary, the mist formation is stopped, and the filter will collect particles by dry sampling (i.e. without mist formation). We found that the rate of evaporation is largely governed by the ambient relative humidity (RH), which changes diurnally. Note, strong dependence of the evaporative loss in MC on RH as seen in our study was not observed in previous studies (Hennigan et al., 2009, 2018; King and Weber, 2013). This is probably due to significantly higher flow rate (42 LPM) and longer sampling duration (60 minutes) adopted in our study as compared to previous studies (flow rate = 21 - 28 LPM; sampling duration ~ 5 minutes). Therefore, the evaporative losses were minimal in those studies (Hennigan et al., 2009, 2018; King and Weber, 2013) but cannot be ignored in our case.”

9. I really do not understand the results in Fig. S3 (and associated discussion in Pg. 8 lines 10 – 25). Why does a 50% change in the sample volume (either + or -) not result in a 50% change in the DTT activity measurement?

First, we would like to clarify here that a 50 % change in the sample volume does not result in a 50 % change in the reaction volume. Reaction volume consist of 1.75 mL sample + 0.5 mL buffer + 0.25 mL DTT (total reaction volume = 2.5 mL). Therefore, a 50 % change in the sample volume will result into a 35 % change in the reaction volume. Second, a change in the reaction volume is also accompanied by a corresponding change in initial DTT concentration in the reaction vial, which influences the self-oxidation rate of DTT (Sauvain and Rossi, 2016). Finally, different components in ambient PM can have different response functions with the DTT oxidation as shown by Charrier and Anastasio, 2012, and thus can result into a varying degree of bias in the DTT activity measurements caused by a change in the reaction volume.

To further understand this, consider the following example. Let's assume we have 1.75 mL of PM extract of concentration 10 µg/mL (thus total PM mass = $10 \times 1.75 = 17.5$ µg). If we dilute this extract to 2.625 mL (i.e. dilute it by 50 %), and then add it to the reaction vial for DTT assay, the total reaction volume will increase to 3.375 mL (a 35 % increase in the reaction volume). But, the initial DTT concentration in the reaction volume will reduce from 100 µM to 74 µM (a 25 % change), which will also affect the auto-oxidation rate of DTT. Note, the total amount of PM available to catalyze the oxidation of DTT is still same, i.e. 17.5 µg as in the original reaction volume (i.e. 2.5 mL). Given, different components in PM (e.g. Cu, Mn, quinones etc.) have different response curve with the DTT oxidation rate, it is difficult to predict the net impact on the measured DTT activity. Therefore, we conducted this experiment using four different PM samples (i.e. to account for the variations in chemical composition) and empirically derived the effect of change in the sample volume on the measurement bias for DTT activity. As mentioned in the manuscript, maximum bias in the DTT activity for a 20 % variation in the sample volume was less than 6 % (average 3 ± 3 %); therefore, this small bias was neglected for the purpose of this study.

10. Pg. 12, line 10 – 11: I don't agree with this logic – the authors state that traffic at their site after 10pm is almost nonexistent, which would suggest some of the EC is aged.

Here we would like to again clarify that the “night” time filter sample was collected from 7 PM in the evening to 7 AM the following morning. Therefore, we expect that most of the EC collected on the filter will be from the evening traffic (7 - 10 PM), which is still fresh. Moreover, yes, the traffic at the site after 10 pm is almost nonexistent, but there will be no photochemical reactions at night. Even the ozone concentrations are at their minimum from 10 PM - 7 AM (Figure S5). Therefore, we don't believe that EC will be significantly aged at this site. Finally, given the site is adjacent to a busy roadway, it is reasonable to assume that most of the EC (if not all) is fresh and unoxidized.

11. Pg. 12, line 23 – 24: this does not seem consistent with the data in Figure 5. The WSOC diurnal profile is flat throughout the day. Most (if not all) of the WSOC during summer at this location should be secondary – how then do the authors attribute the afternoon increase in DTT to SOA?

To explain why we attribute this increase in the afternoon DTT activity to SOA, we would like to first explain the EC diurnal trend. The EC profile shown in Figure 5 was similar to those reported by several other studies (Mues et al., 2017; Sharma et al., 2017; Singh et al., 2018) where they have attributed the low EC concentration during daytime to an increase in the mixing layer height. Now, if all of the OC at our site is only from the background SOA as suggested by the reviewer, then the OC and WSOC profile should follow the same diurnal profile as EC, i.e. low concentration during afternoon but higher in early morning and at nighttime. However, that's not the case, rather both OC and WSOC remain flat. Therefore, there must be some additional OC contribution during the afternoon period. To further test this, we plotted the ratio of OC/EC and WSOC/EC in Figure 5 (assuming EC as a conservative species emitted only from primary sources such as diesel vehicles), which follows a diurnal trend, i.e. high in the afternoon and low at night. Please note that OC/EC ratio has been used by several other researchers to predict the contribution of SOA to the total OC (Turpin and Huntzicker, 1995; Castro et al., 1999; Cabada et al., 2004; Pio et al., 2011) and we have followed the same approach here. Thus, the increase in the OC/EC or WSOC/EC ratio during the afternoon is a clear indicator for an additional source of OC, which we hypothesized to be from the fresh SOA formation at the site in afternoon.

This has been explained in the manuscript as well:

Pages 12, lines 15 - 24

“As depicted in Fig.5, neither OC nor WSOC show any diurnal pattern. Figure 5 also shows OC/EC ratio, which peaked in the afternoon. Considering a higher mixing height and relatively lower traffic in the afternoon than morning, an elevated OC/EC ratio indicates an additional OC contribution, which compensates its decrease from reduced vehicular emissions and enhanced atmospheric mixing. We attribute this additional OC to the secondary particle formation via photochemical reactions, which keeps the OC concentration almost constant throughout the day. Figure S5 in SI shows a diurnal profile of ozone measured at Bondville (EPA site). The ozone concentration peaked from 11:00 AM to 6:00 PM indicating secondary formation of particles in the afternoon period. To further confirm the contribution from SOA to OC, WSOC/EC ratio was also plotted (Fig.5), which ranged from 6.6 (morning) to 11.3 (evening) and followed a similar diurnal profile as ozone or OC/EC ratio. Thus, the broad peak in DTT activity during afternoon and evening periods could partly be caused by the redox-active SOA components.”

12. Pg. 13, lines 4 – 11: I disagree with this interpretation of the data. I do not think that Figures 4 and 6 show a strong contribution of Cu to the measured OP. See prior comments, but it's important to acknowledge that Figures 4 and 6 cannot be directly compared due to the contribution of insoluble particles to the Fig. 4 measurements.

By comparing the data in Figures 4 and 6, we want to show that the diurnal trend of Cu measured on the water-soluble PM fraction of the time segregated filter samples and the DTT activity measured by the online system is qualitatively similar (i.e. high levels during daytime while low at night). Our purpose of investigating this association is not to imply the direct contribution of water-soluble Cu to the measured DTT activity but indicate towards the possible emission

sources, i.e. vehicular exhausts and road-dust resuspension contributing to the DTT activity. Therefore, water-soluble Cu shown Figure 6 and its comparison with Figure 4 should be interpreted as the markers for the emission sources which could have a substantial impact on the DTT activity of ambient PM. Please note that we do acknowledge the reviewer's comment that the Figures 4 and 6 cannot be directly compared due to the contribution of insoluble particles to the measurements shown in Figure 4. Therefore, considering his/her comment, we have modified the associated text in the abstract, conclusion and in the results and discussion section:

Page 1, lines 24 - 26

“Based on this comparison, we attributed the daytime OP of ambient PM_{2.5} to the vehicular (both exhaust and non-exhaust) emissions and resuspended dust, whereas secondary photochemical transformation of primary emissions appear to enhance the OP of PM during the afternoon and evening period.”

Page 13, lines 9 – 11

“A close similarity of the diurnal profile of the water-soluble metals with DTT activity suggests a significant contribution of both vehicular emissions (the morning peak) and resuspended dust (in the afternoon) to PM_{2.5} OP_{ex} at the sampling site.”

Page 13, lines 32 – 33 and page 14, lines 1 – 2

“By comparison of the DTT activity with various chemical components, i.e. OC, EC, WSOC, Cu, Fe and Mn, the morning peak in DTT activity profile was attributed to the vehicular sources (exhausts and non-exhausts), whereas both secondary formation (i.e. SOA) and resuspended dust seem to contribute to the afternoon peak.”

Technical Corrections:

Pg. 1, line 9: “using the dithiothreitol...”

The sentence has been modified as:

Page 1, lines 8 - 9

“We developed an online instrument for measuring the extrinsic oxidative potential (OP) of ambient particulate matter (PM) using the dithiothreitol (DTT) assay.”

Pg. 1, line 17: date format should be 4 July

The sentence has been modified as:

Page 1, lines 17 - 18

“However, a four-fold increase in the hourly averaged activity was observed on the night of 4 July (Independence Day fireworks display) ...”

Pg. 2, line 17: delete comma before 'PM'

Comma has been deleted

Page 2, line 17

“Previous studies have suggested that OP of the ambient particles is affected by various factors such as PM composition, size, and source (Li et al., 2003; Steenhof et al., 2011; Janssen et al., 2014; Tuet et al., 2016; Fang et al., 2017a).”

Pg. 4, line 28: try to avoid beginning a sentence with a number

The sentence has been modified as:

Page 4, line 28

“DTT [0.25 mL, 1 mM, final concentration in the reaction vial = 100 μ M (Sigma Aldrich, St. Louis, MO, USA; > 99% purity)] and potassium phosphate buffer [0.5 mL, pH 7.4, 0.5 μ M (Sigma Aldrich, St. Louis, MO, USA; > 99% purity)] were then added to the RV...”

Figure 3: I believe the incorrect dates are given in the caption for the time the instrument was not operated.

We thank the reviewer for pointing out this error. We have corrected the dates in the revised manuscript.

“Figure 3. Time-series plot of the DTT activity from May 31, 2017 to Aug 16, 2017. The shaded portions in the graph are weekend DTT activity measurements. The instrument was not operated between July 12 and Aug 3, 2017 (shown as a break in the X-axis).”

References:

- Anderson, C. H., Dibb, J. E., Griffin, R. J., Hagler, G. S. W. and Bergin, M. H.: Atmospheric water-soluble organic carbon measurements at Summit, Greenland, *Atmos. Environ.*, 42(22), 5612–5621, doi:10.1016/j.atmosenv.2008.03.006, 2008.
- Ayres, J. G., Borm, P., Cassee, F. R., Castranova, V., Donaldson, K., Ghio, A., Harrison, R. M., Hider, R., Kelly, F., Kooter, I. M., Marano, F., Maynard, R. L., Mudway, I., Nel, A., Sioutas, C., Smith, S., Baeza-Squiban, A., Cho, A., Duggan, S. and Froines, J.: Evaluating the toxicity of airborne particulate matter and nanoparticles by measuring oxidative stress potential - A workshop report and consensus statement, in *Inhalation Toxicology*, vol. 20, pp. 75–99., 2008.
- Cabada, J. C., Pandis, S. N., Subramanian, R., Robinson, A. L., Polidori, A. and Turpin, B.: Estimating the Secondary Organic Aerosol Contribution to PM_{2.5} Using the EC Tracer Method Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program, *Aerosol Sci. Technol.*, 38, 140–155, doi:10.1080/02786820390229084,

2004.

Castro, L. M., Pio, C. A., Harrison, R. M. and Smith, D. J. T.: Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations, *Atmos. Environ.*, 33(17), 2771–2781, doi:10.1016/S1352-2310(98)00331-8, 1999.

Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: Evidence for the importance of soluble \newline transition metals, *Atmos. Chem. Phys.*, 12(19), 9321–9333, doi:10.5194/acp-12-9321-2012, 2012.

Chen, J., Wang, W., Liu, H. and Ren, L.: Determination of road dust loadings and chemical characteristics using resuspension, *Environ. Monit. Assess.*, 184(3), 1693–1709, doi:10.1007/s10661-011-2071-1, 2012.

Cheung, K., Shafer, M. M., Schauer, J. J. and Sioutas, C.: Diurnal trends in oxidative potential of coarse particulate matter in the Los Angeles basin and their relation to sources and chemical composition, *Environ. Sci. Technol.*, 46(7), 3779–3787, doi:10.1021/es204211v, 2012.

Cho, A. K., Sioutas, C., Miguel, A. H., Kumagai, Y., Schmitz, D. A., Singh, M., Eiguren-Fernandez, A. and Froines, J. R.: Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, *Environ. Res.*, 99(1), 40–47, doi:10.1016/j.envres.2005.01.003, 2005.

Daher, N., Ning, Z., Cho, A. K., Shafer, M., Schauer, J. J. and Sioutas, C.: Comparison of the chemical and oxidative characteristics of particulate matter (PM) collected by different methods: Filters, impactors, and BioSamplers, *Aerosol Sci. Technol.*, 45(11), 1294–1304, doi:10.1080/02786826.2011.590554, 2011.

Eatough, D. J., Long, R. W., Modey, W. K. and Eatough, N. L.: Semi-volatile secondary organic aerosol in urban atmospheres: Meeting a measurement challenge, *Atmos. Environ.*, 37(9–10), 1277–1292, doi:10.1016/S1352-2310(02)01020-8, 2003.

Eiguren-Fernandez, A., Kreisberg, N. and Hering, S.: An online monitor of the oxidative capacity of aerosols (o-MOCA), *Atmos. Meas. Tech.*, 10(2), 633–644, doi:10.5194/amt-10-633-2017, 2017.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A. and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, *Environ. Sci. Technol.*, doi:10.1021/acs.est.6b06151, 2017.

Gao, D., Fang, T., Verma, V., Zeng, L. and Weber, R. J.: A method for measuring total aerosol oxidative potential (OP) with the dithiothreitol (DTT) assay and comparisons between an urban and roadside site of water-soluble and total OP, *Atmos. Meas. Tech.*, 10(8), 2821–2835, doi:10.5194/amt-10-2821-2017, 2017.

Hennigan, C. J., Bergin, M. H., Russell, A. G., Nenes, A. and Weber, R. J.: Gas/particle partitioning of water-soluble organic aerosol in Atlanta, *Atmos. Chem. Phys.*, 9(11), 3613–3628, doi:10.5194/acp-9-3613-2009, 2009.

Hennigan, C. J., El-Sayed, M. M. H. and Hodzic, A.: Detailed characterization of a mist chamber for the collection of water-soluble organic gases, *Atmos. Environ.*, 188, 12–17, doi:10.1016/J.ATMOSENV.2018.06.019, 2018.

Hulskotte, J. H. J., van der Gon, H. A. C. D., Visschedijk, A. J. H. and Schaap, M.: Brake wear from vehicles as an important source of diffuse copper pollution, in *Water Science and Technology*, vol. 56, pp. 223–231., 2007.

King, L. E. and Weber, R. J.: Development and testing of an online method to measure ambient fine particulate reactive oxygen species (ROS) based on the 2',7'-dichlorofluorescein (DCFH) assay, *Atmos. Meas. Tech.*, 6(7), 1647–1658, doi:10.5194/amt-6-1647-2013, 2013.

Knaapen, A. M., Borm, P. J. A., Albrecht, C. and Schins, R. P. F.: Inhaled particles and lung cancer. Part A: Mechanisms, *Int. J. Cancer*, 109(6), 799–809, doi:10.1002/ijc.11708, 2004.

Majestic, B. J., Schauer, J. J. and Shafer, M. M.: Development of a manganese speciation method for atmospheric aerosols in biologically and environmentally relevant fluids, *Aerosol Sci. Technol.*, 41(10), 925–933, doi:10.1080/02786820701564657, 2007.

McWhinney, R. D., Gao, S. S., Zhou, S. and Abbatt, J. P. D.: Evaluation of the Effects of Ozone Oxidation on Redox-Cycling Activity of Two-Stroke Engine Exhaust Particles, *Environ. Sci. Technol.*, 45(6), 2131–2136, doi:10.1021/es102874d, 2011.

Mues, A., Rupakheti, M., Münkel, C., Lauer, A., Bozem, H., Hoor, P., Butler, T. and Lawrence, M. G.: Investigation of the mixing layer height derived from ceilometer measurements in the Kathmandu Valley and implications for local air quality, *Atmos. Chem. Phys.*, 17(13), 8157–8176, doi:10.5194/acp-17-8157-2017, 2017.

Pathak, R. K., Yao, X. and Chan, C. K.: Sampling Artifacts of Acidity and Ionic Species in PM_{2.5}, *Environ. Sci. Technol.*, doi:10.1021/es0342244, 2004.

Phillips, S. M. and Smith, G. D.: Spectroscopic comparison of water- and methanol-soluble brown carbon particulate matter, *Aerosol Sci. Technol.*, 51(9), 1113–1121, doi:10.1080/02786826.2017.1334109, 2017.

Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B. and Matos, M.: OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon, *Atmos. Environ.*, 45(34), 6121–6132, doi:10.1016/J.ATMOENV.2011.08.045, 2011.

Sameenoi, Y., Koehler, K., Shapiro, J., Boonsong, K., Sun, Y., Collett, J., Volckens, J. and Henry, C. S.: Microfluidic electrochemical sensor for on-line monitoring of aerosol oxidative activity, *J. Am. Chem. Soc.*, 134(25), 10562–10568, doi:10.1021/ja3031104, 2012.

Sauvain, J. J. and Rossi, M. J.: Quantitative Aspects of the Interfacial Catalytic Oxidation of Dithiothreitol by Dissolved Oxygen in the Presence of Carbon Nanoparticles, *Environ. Sci. Technol.*, 50(2), 996–1004, doi:10.1021/acs.est.5b04958, 2016.

Sharma, M. C., Pandey, V. K., Kumar, R., Latief, S. U., Chakrawarthy, E. and Acharya, P.: Seasonal characteristics of black carbon aerosol mass concentrations and influence of meteorology, New Delhi (India), *Urban Clim.*, doi:10.1016/j.uclim.2017.12.002, 2017.

Singh, V., Ravindra, K., Sahu, L. and Sokhi, R.: Trends of atmospheric black carbon concentration over United Kingdom, *Atmos. Environ.*, 178, 148–157, doi:10.1016/J.ATMOENV.2018.01.030, 2018.

Thorpe, A. and Harrison, R. M.: Sources and properties of non-exhaust particulate matter from road traffic: A review, *Sci. Total Environ.*, 400(1–3), 270–282, doi:10.1016/j.scitotenv.2008.06.007, 2008.

Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS, *Atmos. Environ.*, 29(23), 3527–3544, doi:10.1016/1352-2310(94)00276-Q, 1995.

Venkatachari, P. and Hopke, P. K.: Development and laboratory testing of an automated monitor for the measurement of atmospheric particle-bound reactive oxygen species (ROS), *Aerosol Sci. Technol.*, 42(8), 629–635, doi:10.1080/02786820802227345, 2008.

Verma, V., Ning, Z., Cho, A. K., Schauer, J. J., Shafer, M. M. and Sioutas, C.: Redox activity of urban quasi-ultrafine particles from primary and secondary sources, *Atmos. Environ.*, 43(40), 6360–6368, doi:10.1016/j.atmosenv.2009.09.019, 2009.

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 subfractions to the reactive oxygen species-generating potential of fine ambient aerosols, *Environ. Sci. Technol.*, 46(20), 11384–11392, doi:10.1021/es302484r, 2012.

Verma, V., Fang, T., Guo, H., King, L., Bates, J. T., Peltier, R. E., Edgerton, E., Russell, A. G. and Weber, R. J.: Reactive oxygen species associated with water-soluble PM_{2.5} in the southeastern United States: Spatiotemporal trends and source apportionment, *Atmos. Chem. Phys.*, 14(23), 12915–12930, doi:10.5194/acp-14-12915-2014, 2014.

Wang, C.-F., Chang, C.-Y., Tsai, S.-F. and Chiang, H.-L.: Characteristics of road dust from different sampling sites in northern Taiwan., *J. Air Waste Manag. Assoc.*, 55(8), 1236–44, doi:10.1080/10473289.2005.10464717, 2005.

Wang, Y., Hopke, P. K., Sun, L., Chalupa, D. C. and Utell, M. J.: Laboratory and field testing of an automated atmospheric particle-bound reactive oxygen species sampling-analysis system, *J. Toxicol.*, 2011, doi:10.1155/2011/419476, 2011.

Wragg, F. P. H., Fuller, S. J., Freshwater, R., Green, D. C., Kelly, F. J. and Kalberer, M.: An automated online instrument to quantify aerosol-bound reactive oxygen species (ROS) for ambient measurement and health-relevant aerosol studies, *Atmos. Meas. Tech.*, 9(10), 4891–4900, doi:10.5194/amt-9-4891-2016, 2016.

Xiong, Q., Yu, H., Wang, R., Wei, J. and Verma, V.: Rethinking Dithiothreitol-Based Particulate Matter Oxidative Potential: Measuring Dithiothreitol Consumption versus Reactive Oxygen Species Generation, *Environ. Sci. Technol.*, 51(11), 6507–6514, doi:10.1021/acs.est.7b01272, 2017.

Yao, X., Fang, M. and Chan, C. K.: Experimental study of the sampling artifact of chloride depletion from collected sea salt aerosols, *Environ. Sci. Technol.*, doi:10.1021/es000964q, 2001.

Yu, H., Wei, J., Cheng, Y., Subedi, K. and Verma, V.: Synergistic and Antagonistic Interactions among the Particulate Matter Components in Generating Reactive Oxygen Species Based on the Dithiothreitol Assay, *Environ. Sci. Technol.*, acs.est.7b04261, doi:10.1021/acs.est.7b04261, 2018.

Zhou, J., Bruns, E. A., Zotter, P., Stefenelli, G., Prévôt, A. S. H., Baltensperger, U., El-Haddad, I. and Dommen, J.: Development, characterization and first deployment of an improved online reactive oxygen species analyzer, *Atmos. Meas. Tech. Discuss.*, 1–27, doi:10.5194/amt-2017-161, 2017.