

Point-by-point responses:

Response to Anonymous Referee #1

In this work, the authors designed a novel instrument to measure oxidative potential in ambient PM_{2.5} on an hourly timescale. They use a mist chamber to collect particles and direct subject these particles to reaction with dithiothreitol, a model antioxidant to infer the ability of inhaled particles to cause oxidative stress. It represents an important improvement to previous filter-based methods, and while the new measurements show good agreement with measurements made using these methods, they were substantially higher. The instrument is well characterized and carefully designed. I have only one major concern about this manuscript, but I recommend publication in AMT after addressing this and other minor concerns.

We thank the reviewer for his/her recommendation on the acceptance. Our responses and corresponding changes made in the manuscript (highlighted in red) are given below. All line numbers refer to discussion manuscript

Major comment:

1. My only major concern is the section on comparison to composition measurements. The comparison was performed on two different time periods. While the authors claim that the composition should be similar between these two time periods, there is also no reason to believe they would be similar. For example, the diurnal variation in DTT activity may be heavily driven by a few anomalous days during July 4/5. This section is considerably weaker than the characterization tests described in the other sections. I also do not see why this comparison needs to be made in this manuscript. I believe it is sufficient to demonstrate the time-resolved capability of this instrument for this manuscript. I suggest removing this section, or re-writing this section, and performing the comparison experiments much more carefully in the future.

There seems to be a misunderstanding on the comparison study conducted in this paper which we hope to clear through our response below.

The PM chemical composition data was collected for a period of 10 “weekdays” between August 3 – August 16, 2017. The diurnal profile of the ambient PM_{2.5} extrinsic DTT activity (OP_{ex}) obtained during this period is also provided in Figure S4 (supplementary information). Since, the diurnal profile of DTT activity shown in Figure S4 was similar to the diurnal profile obtained during June 2017 (i.e. Figure 4a in the manuscript) (Page 23, line 1), we did not feel it necessary to include both the figures in the main manuscript. Now, given we performed only a *qualitative comparison* (e.g. high during the afternoon, low at night) between the DTT activity and chemical components, comparing the chemical composition data with either profile (i.e. either during August 3 - August 16, 2017 or June 2017) will essentially yield the same conclusion as reported in the manuscript.

Please note that we agree with the reviewer that during the Independence Day celebration week (July 4 - 5), the composition of the PM was probably very different, and the diurnal OP trend would have been significantly influenced by these “anomalous days”. *Therefore, we did not include the DTT activity data collected during that period for plotting the diurnal profile in Figure*

4. Rather, we have used the data only from May 31 to July 2, 2017. This has been explained in the caption of Figure 4 and the associated text:

Page 23, line 5

“Figure 4. Diurnal profile of the ambient PM_{2.5} DTT activity measured at the sampling site over (a) weekdays (n = 18 days), (b) weekends (n = 10 days). The data from May 31 to July 2, 2017 were used for plotting this profile. Error bars are the standard deviation (1σ) of the average DTT activity in that hour.”

Page 10, lines 19 - 23

“One of the primary motivations for developing the online instrument was to discern the diurnal variations in ambient PM_{2.5} OP_{ex}, so that it could be better linked with the chemical components and their emission sources. Therefore, hourly data obtained by running the instrument for 28 days (between May 31 and July 2, 2017) was composited to obtain a diurnal profile of the DTT activity as shown in Fig.4. The diurnal profiles were separately plotted for the weekdays and weekends in Fig.4a and 4b, respectively...”

Although, the comparison was only qualitative, we believe it adds valuable contribution to the manuscript by providing some insights into the possible emission sources, which could impact the DTT activity. Therefore, we would like to keep this section in the manuscript, hoping the reviewer is now clear on it.

Other comments:

2. Abstract: It is confusing to read that the measurements made by MC are higher than filter-based methods, and then see slopes of less than 1. I suggest reporting the slope of MC vs filter-based method.

We have made the changes suggested by the reviewer

Page 1, lines 12 – 15

“The online DTT activity measurements correlated well with the offline measurements but were higher than both methanol (slope = 1.08, $R^2 = 0.93$) and Milli-Q water (slope = 1.86, $R^2 = 0.86$) extracts of the PM filters, indicating a better efficiency of MC for collecting the water-insoluble fraction of PM.”

Page 9, lines 10 – 17

“The slope for the water extraction versus online measurement was 1.86 ($R^2 = 0.86$; $p < 0.001$; $N = 20$), while methanol extracts of the PM filters showed a much better agreement with the online system (slope = 1.08; $R^2 = 0.93$; $p < 0.001$; $N = 16$). This is probably due to significant contribution from some water-insoluble PM components in MC, which otherwise remain embedded in the filter fibers and are poorly extracted in water by sonication. Recently, Gao et al. (2017) also reported a ratio of the DTT activity measured on the water-soluble extracts of the ambient PM filters collected from Atlanta to the total OP_{ex} (i.e. DTT oxidation performed directly on the filter) as 1.54 – 1.72.

Additionally, the ratio of the DTT activity measured on methanol-soluble extracts of the filters to the total OP_{ex} was 1.06 - 1.1.”

Page 13, lines 19 – 20

“However, the online instrument yielded higher DTT activity than both water (slope = 1.86, N = 20) and methanol (slope = 1.08, N = 16) extracted filters.”

Figure 2 has been modified as:

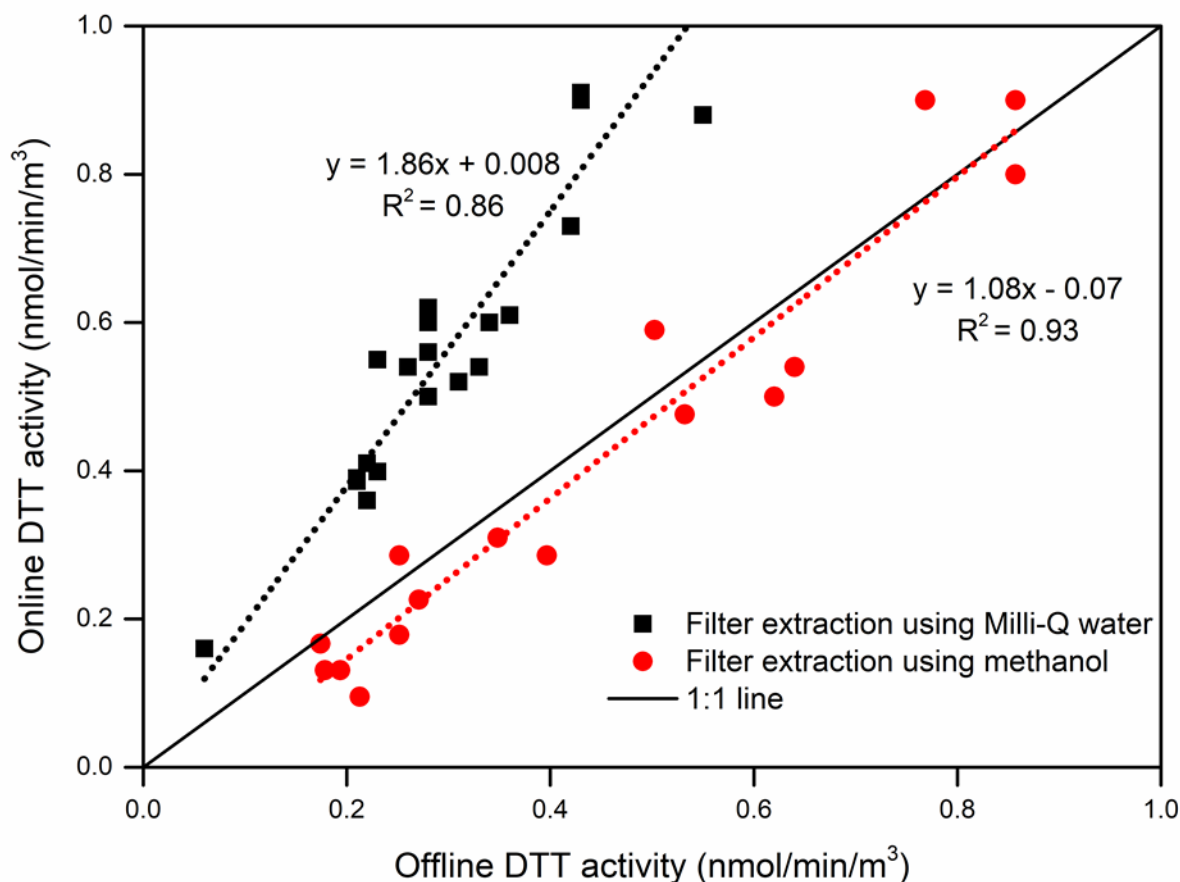


Figure 2. Comparison of the DTT activity obtained from the online instrument with the traditional filter collection and extraction methodology (i.e. offline DTT activity analysis of the PM extracts)

3. Introduction: The authors claim that the MC is substantially cheaper (of ~150 USD) is a vast overstatement. The cost of machining the MC alone would be greater than 150 USD. Also, the authors should consider that university facilities are highly subsidized and the cost that researchers see may be substantially lower than the true cost.

We agree with the reviewer. Our intention here was to compare the MC system with other existing sample collection systems. 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.”

4. Section 3.2: The tests described in this section are very appropriate. I believe that researchers in this field have largely neglected the importance of reactant concentration in determining reaction rates. Assuming a simple bimolecular reaction between DTT and PM, there should be a linear relationship between reactant concentration and measured DTT consumption, even at the same PM mass. What is puzzling me is that the authors only observe a 6% change for a 20% change in volume (or concentration). Do the authors have any explanation for this small change? Does this suggest that the DTT reaction with PM is not bimolecular?

Please see our detailed response to a similar comment raised by another reviewer (anonymous referee 3 comment 9). For the specific comment of the reviewer on bimolecular reaction between DTT and PM, we would like to clarify that the reaction is not between DTT and PM but rather between DTT and oxygen (which is in excess), and PM acts as a catalyst (Cho et al., 2005; Sauvain and Rossi, 2016). The various chemical components in PM, e.g. Cu, Mn, oxygenated organic compounds and quinones have a distinct (and not necessarily linear) response function with the DTT oxidation rate and can be considered as the particle's characteristics (see Charrier and Anastasio, 2012; Sauvain and Rossi, 2016). Recently, Yu et al. (2018) also reported potential synergistic and antagonistic effects of different chemical components in the PM on its DTT response. Thus, the total DTT activity of a PM sample is due to the combined response function from its various components. Furthermore, note that PM extract accounts for only 70% of the total volume in the reaction vial. That means, a 20% volume increase in the PM extract would result only into a 14% increase in the reaction volume, and a 12 % decrease in the concentration of DTT. The initial concentration of DTT also affects its self-oxidation rate as shown by Sauvain and Rossi (2016). Given these complexities, we tried to empirically derive the effect of change in the sample volume on the DTT activity measurements by conducting the experiments using four different PM samples. The difference in the DTT activity measurement bias (shown as error bars in Figure S3) is probably due to differences in the chemical composition of these samples. However, our main objective for performing this experiment was to determine the maximum acceptable variation in the sample volume from MC that leads to a negligible bias in the DTT activity measurement. We found that for a 20% variation in the sample volume, the % bias in DTT activity measurement was less than 6 %; which was neglected for the purpose of this study. We cannot comment on the DTT assay mechanism based on this experiment. A more systematic study with different standard chemicals and a larger sample set of ambient PM samples is probably needed to investigate and

provide an exact reaction mechanism of PM in DTT assay, which is beyond the scope of the current study.

5. Section 3.4: Is there any evidence of water insoluble components in MC samples? For example, can the MC samples be filtered and the DTT measurements be repeated? Which is more biologically relevant? I can imagine the insoluble components remain in the lung lining fluid and continue to consume antioxidants.

There is no direct evidence for the collection of water-insoluble components in MC samples. MCs have traditionally been designed to collect the ambient water-soluble PM components and gases. Our study is probably the first to indicate the collection of insoluble PM components in MC. Although, we have not performed any experiments after filtering the MC samples, we observed the DTT activity of these samples to be almost similar to the DTT activity measured after extracting the filters in methanol (Figure 2). Based on this, we have concluded that MC was probably collecting part of the water-insoluble PM fraction, which is contributing to the DTT consumption. We acknowledge the reviewer's suggestion of filtering the MC sample, and we will attempt to include it in our future investigations for a systematic determination of the contribution of insoluble fraction by comparing the OP of filtered and unfiltered MC PM suspensions (i.e. running 2 MCs in parallel), but it is practically infeasible to include this analysis in the current manuscript.

We are not in position to answer the second part of the reviewer's comment on the relative importance of soluble versus insoluble components. Although, it is biologically plausible that water-insoluble components remain in the lung lining fluid for a longer period and continue to consume antioxidants, this hypothesis has not been tested in the toxicological studies, which were traditionally more focused on assessing the water-soluble PM components. There are definitely growing evidences on the biological relevance of water-insoluble PM components with recent studies showing a substantial fraction of the PM OP stemming from the water-insoluble fraction (Akhtar et al., 2010; McWhinney et al., 2011; Verma et al., 2012; Li et al., 2013; Gao et al., 2017). Therefore, it is important to account for this fraction when determining the overall OP of inhalable PM and incorporating it in the toxicological and epidemiological studies assessing the health effects of PM.

6. Section 3.6.1: The authors argue that EC, Cu and Fe are all coming from traffic sources. However, the diurnal patterns are not consistent with each other. EC is higher in the morning and at night, but Cu and Fe decreases substantially at night. The authors appear to be contradicting themselves here.

We disagree with the reviewer about the contradiction in our interpretation. EC is directly emitted from the vehicular exhausts (mainly from diesel vehicles) (Shah et al., 2004), while water soluble Cu and Fe are emitted from both exhausts and non-exhaust components of the vehicular emissions, i.e. brake and tire wear, and abrasion of the road surface (Thorpe and Harrison, 2008). In addition

to that, resuspension of road dust, which is enhanced at drier environmental conditions, is another major source of the airborne metals (Wang et al., 2005; Thorpe and Harrison, 2008; Chen et al., 2012). Therefore, EC is mostly influenced by the traffic intensity and atmospheric mixing height (Lin et al., 2009; Mues et al., 2017), which is probably the reason for its peak at morning (traffic) and at night (low mixing height). In contrast, the ambient RH influences the road dust resuspension, yielding a different pattern in the metal concentration (highest during afternoon and lowest at night). This has been mentioned in the manuscript:

Page 13, lines 4 - 8

“The difference in the diurnal trends of metals and EC concentrations (i.e. EC peaks in the morning while metals peak in the afternoon) indicates a lesser influence of direct vehicular exhausts on the metals concentrations than the resuspended dust, which is generally driven by higher vehicular speeds (due to relatively lower traffic) and drier conditions in the afternoon (Pant and Harrison, 2013). Figure S6 in SI shows the diurnal pattern of ambient RH at the sampling site. The very high RH (> 75 %) substantially suppresses the dust resuspension and the resultant metals concentrations during nighttime.”

7. Throughout the manuscript, the authors have used OP to describe DTT consumption rate per volume of air, whereas it is also often used to describe DTT consumption rate per mass of PM. I suggest defining it outright in the introduction. The per volume DTT consumption is often referred to as the “extrinsic” oxidative potential, or the oxidative capacity.

We agree with the reviewer here. We have replaced oxidative potential reported in our study as extrinsic DTT activity and denoted it as OP_{ex} throughout the manuscript. We have further defined it outright on section 2.2 (where we have discussed about normalizing it with the volume of air) and made changes in the abstract

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.”

We have added the following sentence in section 2.2:

“This DTT consumption rate was normalized by the volume of sampled air and reported in the units of $nmol\ min^{-1}\ m^{-3}$; referred hereafter as extrinsic DTT activity or OP_{ex} .”

Minor technical comments:

Page 2 line 9: times

We have modified the sentence as:

Page 2, line 9

“These assays are laborious, complex and require long analysis times (Dungchai et al., 2013).”

Page 2 line 10: what does it mean by “less controlled environment”. Cell-free assays would be conducted under a more well-controlled environment than cellular assays.

What we meant here is that cell-free assays are easier to perform, but we agree with the reviewer that this sentence is confusing. Therefore, we have deleted the term “less controlled environment”.

The revised sentence reads as:

Page 2, lines 10

“Cell free assays, on the other hand, are easier to perform and provide faster estimation of OP (Fang et al., 2015).”

Page 2 line 34: the word “data” is plural; remove “a”

Thank you for pointing out this error. We have made the suggested changes in the manuscript.

Page 2, lines 34

“Moreover, it requires relatively long sampling duration, i.e. at least six hours to collect enough volume of the concentrated slurry, making this approach unsuitable for obtaining highly time-resolved OP data for the ambient particles.”

Page 5 line 14: “the” analytical part

Thank you for pointing out this error. We have made the suggested changes in the manuscript

Page 5, line 14

“While the analytical part of the instrument measured the DTT activity of a given PM suspension, the MC simultaneously collected a new PM suspension.”

Page 5 line 30: “the” analytical part

Thank you for pointing out this error. We have made the suggested changes in the manuscript

Page 5, line 30

“The instrument performance was assessed by calibrating the analytical part (DTT activity determination) of the instrument using positive controls...”

Page 7 line 19: replace “reduces” with “is reduced” or “decreases”

We have modified the sentence as:

Page 7, line 19

“During air sampling, the volume of water inside the MC decreases due to evaporative loss.”

Page 7 line 31: “The second concern”

Thank you for pointing out this error. We have made the suggested changes in the manuscript.

Page 7, line 31

“The second concern associated with the evaporation of water is the variable volume of the PM suspensions collected after different sampling runs depending on the ambient...”

Section 3.3: It may be more useful to report LOD in terms of oxidative capacity in nmol DTT/(min-m³ air)

We have reported the LOD in units of nmol/min, because it is consistent with earlier studies using automated (Fang et al., 2015) and online DTT activity measurement systems (Eiguren-Fernandez et al., 2017) and would help the readers to make an easy comparison with those systems.

LOD in the units of nmol/min/m³ is operation-specific because it can be adjusted by changing the sampling duration in MC. For example, in an environment, where the PM is less redox active, more mass needs to be collected for the DTT activity analysis by increasing the sampling duration in MC. Therefore, we prefer to report the LOD in the same units (nmol/min) as used by other researchers.

Page 9 line 24: “the time series”

We have made the changes suggested by the reviewer

Page 9, line 24

“Figure 3 shows the time-series of the hourly ambient PM_{2.5} DTT activity (blank-corrected) measured by the online instrument between May 31, 2017 and August 16, 2017.”

Section 3.6.1: EC might be more a marker of diesel traffic

We agree with the reviewer’s comment and have included this point in the manuscript.

Page 11, line 22

“EC can be assumed as a marker of exhaust emissions from diesel vehicles (Shah et al., 2004; Shirmohammadi et al., 2016).”

Page 11 line 24: awkward language: “getting elevated”

We have modified the sentence as:

Page 11, line 24

“It then subsides in the afternoon and remains constant till evening, before increasing again at night.”

Page 12 line 33: there may be too many significant digits for Fe concentrations

We have modified the sentence as:

Page 12, line 33

“However, the concentration of Fe (3.7 - 6.9 ng/m³) was significantly lower than reported in other studies”

Page 24 line 6: again, the word “data” is plural; replace “was” with “were”

Thank you for pointing out this error. We have made the suggested changes in the manuscript.

Page 24, line 6

“Figure 4. Diurnal profile of the ambient PM_{2.5} DTT activity measured at the sampling site over (a) weekdays (n = 18 days), (b) weekends (n = 10 days). The data from May 31 to July 2, 2017 were used for plotting this profile. Error bars are the standard deviation (1σ) of the average DTT activity in that hour.”

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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. All line numbers refer to the discussion manuscript

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 discussion 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:

Page 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).”

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Development and field-testing of an online instrument for measuring the real-time oxidative potential of ambient particulate matter based on dithiothreitol assay

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Abstract. We developed an online instrument for measuring the oxidative potential (OP) of ambient particulate matter (PM) using the dithiothreitol (DTT) assay. The instrument uses a mist chamber (MC) to continuously collect the ambient PM_{2.5} in water, followed by its DTT activity determination using an automated syringe pump system. The instrument was deployed at an urban site in the University of Illinois campus, and its field performance was evaluated by comparing the results with the offline DTT activity measurements of simultaneously collected PM-laden filters. The online DTT activity measurements correlated well with the offline measurements but were higher than both methanol (slope = 0.861.08, $R^2 = 0.93$) and Milli-Q water (slope = 0.521.86, $R^2 = 0.86$) extracts of the PM filters, indicating a better efficiency of MC for collecting the water-insoluble fraction of PM. The hourly measurements of ambient PM_{2.5} OP were obtained by running the online instrument intermittently for 50 days with minimal manual assistance. The daytime DTT activity levels were generally higher than at night. However, a four-fold increase in the hourly averaged activity was observed on the night of 4 July-04 (Independence Day fireworks display). Diurnal profile of the hourly averaged OP during weekdays showed a bimodal trend, with a sharp peak in the morning (around 7:00 AM), followed by a broader afternoon peak, which plateaus around 2:00 PM, and starts subsiding at night (around 7:00 PM).

To investigate the association of the diurnal profile of DTT activity with the emission sources at the site, we collected time-segregated composite PM filter samples in four different time periods of the day [morning (7:00 AM - 10:00 AM), afternoon (10:00 AM - 3:00 PM), evening (3:00 PM - 7:00 PM) and night (7:00 PM - 7:00 AM)] and determined the diurnal variations in the redox active components [i.e. water soluble Cu, Fe, Mn, organic carbon, elemental carbon and water soluble organic carbon]. 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.~~Based on this comparison, we attributed the daytime OP of ambient PM_{2.5} to the water soluble Cu from both exhaust and non-exhaust emissions, whereas secondary particles formed by the photochemical transformation of primary emissions appear to enhance the OP of PM during the afternoon and evening period.~~

1 Introduction

Several recent studies have used the oxidative potential (OP) of ambient particulate matter (PM) as an indicator of the aerosol toxicity (Li et al., 2003; Knaapen et al., 2004; Steenhof et al., 2011; Bates et al., 2015; Tuet et al., 2016; Yang et al., 2016). The underlying hypothesis in these studies is that ambient particles upon inhalation can catalyze the generation of reactive oxygen species (ROS), creating a biochemical imbalance between oxidants and antioxidants, which lead to a state of the cellular oxidative stress (Knaapen et al., 2004). This inherent property of the ambient PM to induce oxidative stress is supposed to be more closely associated with the PM related adverse health effects (such as congestive heart failure, myocardial infarction, asthma etc.) than conventionally used PM mass concentrations (Bates et al., 2015; Maikawa et al., 2016; Weichenthal et al., 2016; Yang et al., 2016; Abrams et al., 2017).

To quantify the OP associated with ambient PM, researchers have used both cell-based and cell-free assays. Cell based assays generally involve the use of fluorescent probes (such as 2',7'-dichlorodihydrofluorescein diacetate, DCFH-DA) for measuring the PM induced intracellular ROS in alveolar macrophages or other cell lines (Landreman et al., 2008; Saffari et al., 2014; Tuet et al., 2016). These assays are laborious, complex and require long analysis times (Dungchai et al., 2013). Cell free assays, on the other hand, use less controlled environment are easier to perform and provide faster estimation of OP (Fang et al., 2015). The dithiothreitol (DTT) assay is one of the most widely used cell free assay to measure the ambient particles' OP, which has shown good correlation with several biological markers of PM-induced adverse health effects (Steenhof et al., 2011; Delfino et al., 2013; Bates et al., 2015; Tuet et al., 2016; Yang et al., 2016; Abrams et al., 2017). In the DTT assay, PM catalyzes the transfer of electrons from DTT to oxygen, generating superoxide radicals. The consumption of DTT over time, which is reported as the DTT activity or OP of the ambient PM, is assumed to be proportional to the concentration of redox active compounds in the PM sample (Kumagai et al., 2002; Cho et al., 2005).

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). Moreover, few studies have also indicated that the ambient particles' OP changes during the course of the day, due to influence of atmospheric processing and aging (Verma et al., 2009; Saffari et al., 2014). The conventional approach for measuring the DTT activity of ambient PM involves long-duration sampling (typically 24-72 hours) using filters and extracting them in a suitable medium (e.g. water or methanol) (Verma et al., 2012; Fang et al., 2015). The laborious and time-consuming protocol of these methods limit their applications to only few samples, and thus make it almost impossible to fully capture the diurnal variations in the ambient particles' OP. Another issue in measuring OP of the ambient particles collected over filters is related with the chemical stability of the PM samples. 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). Generally, PM collected over filters might undergo chemical alteration during storage and extraction procedures (Majestic et al., 2007; Daher et al., 2011).~~ Therefore, OP measured on the archived filters might not be truly representative of the real potential of ambient particles to generate ROS in a biological system after inhalation. For reducing some of these artefacts, certain researchers (e.g. Cho et al., 2005; Daher et al., 2011) used a liquid impinger (Biosampler, SKC West Inc.) to collect the concentrated slurry of ambient aerosols and measured its OP using the DTT assay. The direct collection of particles into liquid helps to minimize the PM loss during sampling and extraction processes. However, this method is not fully automated, i.e. frequent manual observation is needed to maintain the optimum conditions for an upstream aerosol concentrator (Kim et al., 2001). Moreover, it requires relatively long sampling duration, i.e. at least six hours to collect enough volume of the concentrated slurry, making this approach unsuitable for obtaining a highly time-resolved OP data for the ambient particles.

Over the past decade, various online instruments have also been developed for measuring the ROS associated with ambient PM (Venkatachari and Hopke, 2008; Wang et al., 2011; Sameenoi et al., 2012; King and Weber, 2013; Wragg et al., 2016; Eiguren-Fernandez et al., 2017; Zhou et al., 2017). These instruments couple a direct aerosol into water collection device, e.g. particle-into-liquid sampler (PILS), liquid spot sampler (LSS) or mist chamber (MC) to an analytical system. However, most of these instruments measure the particle-bound ROS, which represents only a small part of the particles' OP. 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. Sameenoi et al. (2012) used a PILS coupled directly to a microfluidic electrochemical sensor for measuring the DTT activity of ambient particles. The online system performance was tested in the lab using standard reference dust and fly ash aerosolized samples. The measured DTT activity was reported to have a linear correlation with the aerosol concentration. Eiguren-Fernandez et al. (2017) used an LSS for particle collection, followed by its DTT activity determination in a traditional protocol (i.e. light absorbance spectroscopy). However, a major shortcoming in these two studies was the lack or limited days of field measurements. The online system based on microfluidic electrochemical sensor (Sameenoi et al., 2012) was characterized only in the lab using simulated aerosol samples and has never been tested in the ambient environment (at least not reported in any publication). While, the system developed by Eiguren-Fernandez et al. (2017) was tested in the field for only three days (with 3-hour time resolution), and the long-term stability of the system is yet to be evaluated. ~~Moreover, the aerosol sampling devices, i.e. PILS (Sameenoi et al., 2012) and LSS (Eiguren Fernandez et al., 2017) used for collecting the PM in these online systems are expensive (> USD 20,000).~~

Here, we discuss the development of a low-cost, 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, ~~which is substantially cheaper (~USD150) than PILS or LSS~~ was used for collecting the ambient PM suspension, which is then transferred to an automated analytical system for DTT activity determination. Our study reports, for the first time, the complete diurnal profile of the DTT activity of ambient PM_{2.5} at an hourly resolution, obtained from 50 days of field deployment of the instrument. The diurnal variations in DTT activity were further compared with the diurnal variations in

PM_{2.5} chemical composition. The results presented in our study demonstrate the usefulness of obtaining a highly time-resolved data on PM_{2.5} OP, to comprehend various emission sources and their relative importance in assessing the risk from PM_{2.5} exposure over the course of the day.

2 Materials and Methods

5 2.1 Instrument set up

The basic layout of the instrument setup for measuring the PM_{2.5} OP is shown in Fig.1. The entire system is housed in a 6'x 4'x 2' insulated aluminium chamber, built by the Civil and Environmental Engineering Machine Shop of the University of Illinois at Urbana-Champaign (UIUC). The temperature inside the chamber is maintained at 18°C using a portable air conditioner (Black and Decker BPACT14HWT). An MC was used for collecting the ambient PM_{2.5} suspension in water.

10 MCs were originally designed for collecting the water-soluble gases with Henry's constant (K_H) > 10³ M/atm (Cofer III et al., 1985; Spaulding et al., 2002; Hennigan et al., 2009), 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

15 collected by both systems. The collection efficiency in the MC was close to 100 % at flow rates greater than 25 LPM. however few studies (Anderson et al., 2008; King & Weber, 2013) have also used these devices for collecting ambient particles. The MC used in this study was custom built in the glassblowing shop at UIUC and operated at a flow rate of 42 LPM. Exact dimensions of the MC are given in Fig.S1 (supplementary information, SI). A 0.5" (OD) copper tube was used to connect inlet port of the MC to a PM_{2.5} cyclone (University Research Glassware; URG, Carrboro, NC, USA). The working

20 principle for particle collection in MC is explained in previous studies (Anderson et al., 2008; King and Weber, 2013). In brief, a predetermined volume of Milli-Q water is added, such that the water level remains above the bottom tip of the capillary tube inside the MC. As air flows through the tapered inlet, air pressure drops at the capillary nozzle tip, which causes the water in the bottom reservoir to rise through the capillary tube and create a fine mist inside the chamber. This mist impinges on a 47 mm TefSep polytetrafluoroethylene (PTFE) membrane hydrophobic filter (1µm pore size) (GVS, Life

25 sciences, ME, USA) loaded in a filter pack (URG, Carrboro, NC, USA), attached at top of the MC. The mist continuously washes the particles as they are collected onto the filter, in addition to some direct scrubbing from the air stream. The air flow exiting the hydrophobic filter was continuously measured by an inline flow meter (10 – 100 SLPM, Dwyer Instruments, MI, USA). The airflow rate eventually starts decreasing with an increasing PM loading on the filter, i.e. gradual accumulation of some water-insoluble PM, which is not recovered in the MC suspension. Typically, the flow rate was found to decrease by

30 approximately 10 % after 16 hours of continuous operation of the MC in our case. Therefore, the filter was changed twice in a day (at 7 AM and 7 PM) to ensure a near-constant flow rate of 42 LPM (± 2.5%). The online system couples the MC to an

automated DTT activity determination system, consisting of two automated syringe pumps and a continuously shaken thermomixer (Fang et al., 2015; discussed in section 2.2) as shown in Fig.1.

2.2 Instrument operation and procedures

At the start of each sampling run, a fixed amount of Milli-Q water (which was varied depending on time of the day, discussed in section 3.2) was added to the MC using a programmable 10 mL syringe pump [Versa Pump 6 (V6); Kloehn Inc., Las Vegas, NV, USA]. The PM suspension (~1.75 mL) at the end of the sampling run (one hour) was withdrawn from MC and fed to the reaction vial (RV) of the automated analytical system for DTT activity measurement, using the same syringe pump. The DTT activity measurement system is based on the same protocol as described in Xiong et al. (2017) using two syringe pumps [V6 and Versa Pump 3 (V3); Kloehn Inc., Las Vegas, NV, USA), but slightly modified to handle small volume of the PM suspensions. The RV was placed in a thermomixer (550 rpm, Eppendorf North America, Inc., Hauppauge, NY, USA) maintained at a constant temperature of 37 °C, and continuously shaken. DTT [0.25 mL, 1 mM, final concentration in the reaction vial = 100 µM (Sigma Aldrich, St. Louis, MO, USA; > 99% purity)] and potassium phosphate buffer [0.5 mL, pH 7.4, 0.5 µM (Sigma Aldrich, St. Louis, MO, USA; > 99% purity)] were then added to the RV, using a V3 and V6 syringe pump, respectively.~~0.25 mL DTT (1 mM solution, final concentration in the reaction vial = 100 µM) and 0.5 mL potassium phosphate buffer (pH 7.4; 0.5 µM) were then added to the RV, using a V3 and V6 syringe pump, respectively.~~ To determine the DTT consumption rate, 50 µL aliquot from the RV was withdrawn by a V3 pump at fixed time points (3, 13, 23, 33 and 43 min), and mixed immediately with 0.5 mL of 5,5'-dithiobis(2-nitrobenzoic acid) [DTNB, 0.2 mM (Sigma Aldrich, St. Louis, MO, USA; > 98 % purity)].~~DTNB (0.2 mM)~~, added by the V6 pump in the measurement vial (MV). The residual DTT in the aliquot reacts with DTNB to form 2-nitro-5-thiobenzoic acid (TNB). TNB absorbs light sharply at a wavelength of 412 nm, and therefore, the absorbance was measured by pushing the mixture (using the V6 pump) through a liquid waveguide capillary cell (LWCC-M-3100; World Precision Instruments, Inc., FL, USA) with an optical path length of 100 cm. The LWCC was coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, FL, USA), which includes both ultraviolet-visible (UV-vis) light source (DH-Mini) and a multiwavelength light detector (Flame – S). The absorbance intensity at 600 nm was chosen as a reference (where there was no absorption from the reaction mixture) to correct for the temporal drift in the absorbance spectrum. The absorbance at both wavelengths (412 and 600 nm), were continuously recorded and saved as a .CSV file using a data acquisition software (Spectra Suite, Ocean Optics, USA). Since, the absorbance is proportional to the quantity of DTT left in RV, the slope of the absorbance versus time (5-time points) gives the DTT consumption rate of the sample. This DTT consumption rate was normalized by the volume of sampled air and reported in the units of nmol min⁻¹ m⁻³; referred hereafter as extrinsic DTT activity or OP_{ex}. The analytical part of the instrument along with MC were cleaned twice in a month by replacing all the chemicals first with methanol, followed by Milli-Q water, and running the automated system script for a routine DTT assay protocol (five times with each solvent).

2.3 Field deployment of the instrument

The online instrument was deployed on the roof (height from the ground level ~ 25m) of a parking deck (north campus parking) located adjacent to a 4-lane street (University Avenue) in the university campus and operated intermittently for approximately 50 days (between May 31 and August 16, 2017). While the analytical part of the instrument measured the DTT activity of a given PM suspension, the MC simultaneously collected a new PM suspension. Thus, hourly measurements of ambient PM_{2.5} OP_{ex} were obtained with minimal manual assistance, i.e. only for replacing the filters (twice in a day), resetting the computer program script (once in a day), and refilling the DTT solution (once in a day) and other reagents as needed (typically after 4-5 days).

2.4 Instrument blanks

- Two different types of instrument blanks were analyzed in this study: system blanks and method blanks. System blank was determined by filling Milli-Q water in MC, but without collecting any air sample, i.e. vacuum pump remained switched off. The water remained in MC for few (2-3) minutes after which its DTT activity was measured by the analytical system. Method blank (particle-free) was determined by connecting a HEPA filter upstream of MC and running it for one hour. Thus, measured DTT activity in the method blank would be due to possible contribution from water-soluble gases. System blanks were collected everyday (i.e. 1 blank per day) while method blanks were collected 4 times in a week, during field deployment of the instrument (discussed in section 3.2). Thus, a total of 50 system blanks and 28 method blanks were collected throughout the sampling period.

2.5 Instrument performance

- The instrument performance was assessed by calibrating the analytical part (DTT activity determination) of the instrument using positive controls (both before field deployment and during operation), determining the limit of detection (LOD; from the blanks data), and comparing the online versus offline results (see section 2.6). All the results pertaining to the instrument performance are discussed in the results sections (sections 3.1, 3.3 and 3.4).

2.6 Online versus offline system comparison

- The DTT activity measurements from the online system were compared with a conventional filter sampling and extraction method followed by offline DTT activity analysis of the extracts. Ambient filters (N=36), each for a duration corresponding to the MC sampling (i.e. 60 minutes), were collected for offline analysis from the same site (roof of north campus parking) on different days (see Table S1 in SI), while the online instrument was also running continuously. 47 mm TefSep hydrophobic filters (same as used in the filter pack of the MC) were used for collecting PM_{2.5}, at a flow rate of 42 LPM. After each sampling run, the filters were brought back to the lab and immediately stored in a freezer (-20°C). All the filters were extracted and analyzed within 12 hours of sampling. Limited mass loadings on these filters didn't allow us to extract

each filter in both water and methanol. Therefore, 20 filters were extracted in Milli-Q water (1.75 mL volume per filter), while the remaining 16 filters were extracted in methanol, by sonication (Cole-Parmer Ultrasonic Cleaner 8891, IL, USA) for 30 minutes. The methanol extracts were evaporated (to <100 μ L) by blowing high-purity nitrogen into the vial. The concentrated extracts were then reconstituted by adding Milli-Q water (final volume = 1.75 mL). The samples were immediately analyzed for DTT activity by a semi-automated system developed in our lab (Xiong et al., 2017). Field blank filters (N = 6) were similarly collected, processed (i.e. 3 filters extracted in Milli-Q water and 3 in methanol) and analyzed for the DTT activity.

2.7 Time-segregated composite sampling and chemical analysis

To infer the associations between diurnal trend in the ambient PM_{2.5} DTT activity and PM_{2.5} chemical composition, time-segregated composite PM_{2.5} samples were collected for 10 weekdays in August 2017 (the exact dates are provided in the SI; Table S1). The composite samples were collected onto both pre-baked 8"x10" quartz filters (Tissuquartz 2500QAT-UP, Pall life Sciences, Port Washington, NY; referred as QS thereafter) and 8"x10" teflon filters (Zefluor PTFE Membrane Filters, Pall Laboratory, NY; referred as TS thereafter) using two high volume samplers (HiVol, Tisch Environmental, nominal flow rate 1.13m³ min⁻¹, PM_{2.5} impactor), at the same site. These composite samples were collected in four different time periods of the day: morning (7:00 AM - 10:00 AM), afternoon (10:00 AM - 3.00 PM), evening (3:00 PM – 7:00 PM) and night (7:00 PM – 7:00 AM), i.e. the filters were changed four times in a day, but the same set of filters were used for all ten days. Thus, a total of eight samples were collected: QS1 and TS1 (morning; total hours of sampling = 30 hours), QS2 and TS2 (afternoon; total hours of sampling = 50 hours), QS3 and TS3 (evening; total hours of sampling = 40 hours), and QS4 and TS4 (night; total hours of sampling = 120 hours). All samples were stored in a freezer at -20°C between sampling intervals.

The total PM_{2.5} mass loading on the filters was determined by weighing (both pre- and post-sampling) the filters using a lab scale digital balance ($\pm$ 0.2 mg readability, A-120S, Sartorius, Gottingen, Germany). Prior to weighing, the filters were equilibrated for 24 hours at 20°C and 50% relative humidity (RH).

The concentrations of elemental carbon (EC) and organic carbon (OC) were measured on a small section (1 cm²) of the quartz filters as per National Institute for Occupational Safety and Health (NIOSH) protocol, using a thermal/optical transmittance (TOT) analyzer (Sunset Laboratory) (Birch and Cary, 1996). For the rest of the chemical analysis, teflon filter punches (25 mm diameter) were extracted into Milli-Q water by sonication (30 minutes). The water-soluble organic carbon (WSOC) concentration in these extracts was measured using a total organic carbon analyzer (TOC-VCPH, Shimadzu Co. Japan) (Wang et al., 2018). The concentrations of water-soluble Cu, Fe and Mn in the extracts were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer, Waltham, MA) (Yu et al., 2018).

3 Results and Discussion

3.1 Calibration of the analytical system for DTT activity measurement

Before field deployment, the analytical measurement part of the online DTT instrument was calibrated by measuring DTT activity of 9,10-phenanthraquinone (PQN, [Sigma Aldrich, St. Louis, MO, USA; > 99% purity](#)). Here, sampling part of the instrument, i.e. MC, was replaced with a 14-port multi-position valve (VICI® Valco Instrument Co. Inc., USA) to consecutively select different PQN standard solutions of known concentrations for analysis. The linear plot of DTT consumption rate (nmol/min) versus PQN concentration had a slope of 7.55 ± 0.54 , with a coefficient of determination (R^2) of 0.98 (Fig.S2 in SI). The slope of calibration is very close to the slope obtained earlier by Fang et al. (2015) using a similar automated DTT system. During the field operation, the analytical part of the instrument was calibrated at least once in 15 days by following the same procedure, i.e. replacing the MC with the multi-position valve.

3.2 Effect of evaporation in MC on DTT activity of ambient PM

During air sampling, the volume of water inside ~~the~~ MC ~~decreases~~~~reduces~~ 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). ~~The~~~~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. ~~Therefore, to~~To address this concern, the KloeHN control program script was modified to adjust the amount of water added to the MC at the beginning of each sampling run, based on the forecasted hourly RH at the site (AccuWeather, 2018). Typically, the RH was highest (78 ± 6 %) during night and early morning, and lowest (50 ± 8 %) in the afternoon period. Table S2 in SI shows the volume of water added to the MC for various ranges of RH observed at the sampling location. Adjusting this amount of water ensured at least 55 minutes of wet sampling (i.e. sampling PM with simultaneous mist formation) for each collected PM suspension, with rest as the dry sampling. Note, a fraction of the particles collected during dry sampling is extracted in the next run of wet sampling, which could lead to a small bias in the PM mass carried over to RV from the actual PM mass corresponding to a sampling run. However, this bias is not expected to be significant given a very low duration of dry sampling (< 5 minutes) out of total 60 minutes of sampling.

~~The~~~~S~~second concern associated with the evaporation of water is the variable volume of the PM suspensions collected after different sampling runs depending on the ambient RH, i.e. larger volume at high RH, while smaller volume at low RH. Note, evaporation can still continue (although substantially slower than during mist formation) after the water level drops below the capillary level. Based on the design of the MC used in this study, final volume of the PM suspension remaining inside the reservoir after the water level drops just below the capillary should be 1.75 mL. However, the volume of PM suspensions obtained from MC during the field sampling was found to vary from 1.5 to 2 mL (i.e. within ± 15 % of the theoretically designed volume of 1.75 mL; as observed from numerous trials in extreme RH conditions). We suspected that a variation in

the sample volume could potentially affect the DTT activity measurements in RV. To quantify this effect, we conducted a laboratory study, where we measured the DTT activity of a PM extract in different reaction volumes, but all containing the same amount of PM mass. Six circular punches (4.9 cm² each) from a PM_{2.5}-laden HiVol quartz filter (24-hour sample collected from the same site) were extracted in 35 mL of Milli-Q water by sonication for 30 minutes. The extract was filtered by passing through a 0.45 µm PTFE syringe filter (Fisherbrand™, Fisher Scientific, PA, USA). 0.875 mL aliquot of this filtered extract was added in 12 different sample vials, which ensured the same PM_{2.5} mass in each vial. To the reference sample vial, 0.875 mL Milli-Q water was added to make the total sample volume as 1.75 mL (equivalent to the theoretically designed volume of the PM suspension obtained from MC after one hour of sampling). To the remaining sample vials, different amount of Milli-Q water (0, 0.175, 0.35, 0.525, 0.7, 1.05, 1.225, 1.4, 1.575 and 1.75 mL) were added to obtain variable sample volumes (0.875, 1.05, 1.225, 1.4, 1.575, 1.925, 2.1, 2.275, 2.45 and 2.625 mL). This experiment simulated the changes in the volume of PM suspensions obtained from MC due to evaporation. The DTT activities of all these samples were then measured (in triplicates) using the semi-automated system in our lab. The same experiment was repeated for three more PM_{2.5} filters and all the results are compiled in Fig.S3 (SI). As expected, there is an overall inverse trend in the DTT activity versus sample volume; samples containing larger volumes showed lower DTT activity than those containing smaller volumes. However, maximum bias in the 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. Note, a larger variation in the sample volume could significantly affect the measurement of DTT activity (e.g. bias > 12 % for a 50 % variation in the sample volume, as shown in Fig.S3). Therefore, an appropriate control, e.g. a nafion or a diffusion dryer should be used upstream of MC at locations where the ambient RH can vary substantially and more abruptly, to minimize its impact on the variations in sample volume and subsequent bias in the DTT activity measurement.

3.3 Blanks and limit of detection (LOD)

The average ($\pm 1\sigma$) system and method blanks obtained by the instrument were 0.32 ± 0.06 and 0.33 ± 0.08 nmol/min, respectively, and the difference between these two blanks was not statistically significant ($p > 0.05$; unpaired t -test). Therefore, LOD of the instrument for measuring the PM-induced DTT activity was determined as 0.24 nmol/min, i.e. 3 times the standard deviation of the method blanks. The insignificant difference between the system and method blanks indicates that the ambient gases (e.g. ozone) have minimal interference in the DTT activity measured by the online instrument. Ozone has very low solubility in water (Henry's law constant $\sim 1.03 \times 10^{-2}$ M/atm) (Sander, 2015), which makes it unlikely to get collected in MC. To further confirm the insignificant contribution from ambient gases in the DTT activity, we connected a custom-built activated charcoal denuder [22" long and 3" diameter tube (with a concentric meshed tube for airflow), filled with 4 mm pellet activated charcoal, Enviro Supply & Service, Irvine, CA], upstream of MC. The field blanks collected for a day ($N = 24$) with an upstream denuder (i.e. HEPA filter + denuder) were not significantly different (0.33 ± 0.09 nmol/min) than without the denuder (i.e. only HEPA filter). A possible explanation for the nil contribution from

ambient gases in our DTT activity measurement could be their low ambient concentrations and a very low residence time (72 ms) in our MC, leading to their insignificant concentration in the MC suspension.

3.4 Online instrument results versus filters measurements

Figure 2 shows a comparison of the results obtained by the online instrument with the DTT activity measured on the water and methanol extracts of the filters (47 mm), which were simultaneously collected while running the instrument. The online measurements from the instrument have a high coefficient of determination ($R^2 > 0.80$) with the results obtained by offline filter extraction method, both using Milli-Q water and methanol. The slope for the water extraction versus online measurement was only ~~0.52~~1.86 ($R^2 = 0.86~~7~~; $p < 0.001$; $N = 20$), while methanol extracts of the PM filters showed a much better agreement with the online system (slope = ~~0.86~~1.08; $R^2 = 0.93$; $p < 0.001$; $N = 16$). This is probably due to significant contribution from some water-insoluble PM components in MC, which otherwise remain embedded in the filter fibers and are poorly extracted in water by sonication. Recently, Gao et al. (2017) also reported a ratio of the DTT activity measured on the water-soluble extracts of the ambient PM filters collected from Atlanta to the total OP_{ex} (i.e. DTT oxidation performed directly on the filter) as ~~0.58~~1.54 – ~~1.72~~0.65. Additionally, the ratio of the DTT activity measured on methanol-soluble extracts of the filters to the total OP_{ex} was ~~0.9~~0.94~~1.06~~ - ~~1.1~~. The higher OP_{ex} measured directly on the filters was attributed to the contribution from water-insoluble PM fraction remained on the filters, which is not fully extracted even by methanol. Collectively, our results, which are very similar to Gao et al., (2017), demonstrate a much better PM collection efficiency of the MC for ~~PM collection~~OP measurements than a conventional filter sampling and extraction protocol.$

3.5 Time-series of the ambient $PM_{2.5}$ DTT activity

Figure 3 shows the time-series of the hourly ambient $PM_{2.5}$ DTT activity (blank-corrected) measured by the online instrument between May 31, 2017 and August 16, 2017. The instrument was almost continuously operated for collecting the ambient data (except few days for method or denuder blanks and calibration of the analytical part) between May 31 and July 11, 2017, followed by a break of 22 days (July 12, 2017 - August 3, 2017), before running it again for 13 days in the month of August, 2017. The average ($\pm 1 \sigma$) DTT activity obtained during the entire sampling period was 0.33 ± 0.19 nmol/min/ m^3 , which is in typical range of the total OP_{ex} as observed in Atlanta ($0.2 - 0.4$ nmol of DTT/min/ m^3 ; Gao et al., 2017) and is higher than the water-soluble OP_{ex} measured at the same site ($0.04 - 0.18$ nmol of DTT/min/ m^3) in our previous studies (Xiong et al., 2017; Wang et al., 2018; Yu et al., 2018). Around 65% of the hourly measurements of DTT activity were above the instrument LOD. However, measurements during the weekends were mostly below the LOD. The low activity over the weekends is possibly due to less vehicular traffic resulting in lower $PM_{2.5}$ emissions. Additionally, very low DTT activity (or below LOD) was measured on days with exceptionally high RH ($> 90\%$) and during rain events, probably due to reduced $PM_{2.5}$ concentrations (Lou et al., 2017). A significant diurnal variation in the DTT activity can also be inferred from

the time-series plot, with nighttime measurements generally lower than the daytime levels (except few peaks, e.g. on 7/4/2017 and 7/5/2017). A more detailed analysis of the diurnal trend of DTT activity is provided in section 3.6.

The fireworks display during the Independence Day (July 04, 2017) celebration in Champaign County had a pronounced effect on the ambient $PM_{2.5}$ [OP_{ex}](#). The DTT activity measured on the night of July 04 and following 2 days, showed a significantly elevated value (peak value = 1.4 nmol/min/m^3), which was approximately four times the average DTT activity obtained during the entire sampling period. This is probably due to an overall increase in the ambient $PM_{2.5}$ concentration emitted from fire-crackers. The $PM_{2.5}$ concentration measured at a nearby Environmental Protection Agency (EPA) monitoring site (Bondville, located ~ 8 miles from the study area) reported an increase of 124 %, 42 % and 49 % in the average $PM_{2.5}$ concentration between July 04 and July 06 (average of three days = $14.0 \pm 1.2 \text{ }\mu\text{g/m}^3$), compared to July 2 ($6.27 \text{ }\mu\text{g/m}^3$), July 3 ($9.9 \text{ }\mu\text{g/m}^3$) and July 7 ($9.4 \text{ }\mu\text{g/m}^3$; assumed control days), respectively. Pervez et al. (2016) reported a 13- and 7-fold increase in ambient Cu and Mn concentration, in the local background $PM_{2.5}$ after a firework pollution episode in Bhilai, India. Note, Cu and Mn are among the most important metals in PM, which have been reported to be associated with the DTT activity (Charrier and Anastasio, 2012).

3.6 Diurnal profile of the ambient $PM_{2.5}$ [OP_{ex}](#) and chemical components

One of the primary motivations for developing the online instrument was to discern the diurnal variations in ambient $PM_{2.5}$ [OP_{ex}](#), so that it could be better linked with the chemical components and their emission sources. Therefore, hourly data obtained by running the instrument for 28 days (between May 31 and July 2, 2017) was composited to obtain a diurnal profile of the DTT activity as shown in Fig.4. The diurnal profiles were separately plotted for the weekdays and weekends in Fig.4a and 4b, respectively. The diurnal profile of [OP_{ex}](#) in weekdays appears to have a trimodal trend with peaks at 7:00 – 8:00 AM, 12:00 – 1:00 PM, and 6:00 – 7:00 PM. The highest peak was observed around 1:00 PM, and night time nadir was around 3:00 AM. In contrast, the weekend diurnal profile appears to be flat with no clear trend. To test if the identified peaks in the diurnal profile of DTT activity are statistically significant (given the large variation in day-to-day activity), we first performed a single factor ANOVA test [SPSS (V24.0.0.0)] on all points of the diurnal plot ($N = 24$). The diurnal profile for the weekends did not yield any statistically significant peak ($F=1.51$, $F_{\text{critical}} = 1.59$, $p = 0.07$) for the entire data. However, F value obtained for the weekday diurnal profile data was higher than the critical F value ($F = 6.38$, $F_{\text{critical}} = 1.56$, $p < 0.01$) indicating significant differences in certain hourly measurements during weekdays. To further test the statistical significance of the three identified peaks in the diurnal profile for weekdays, we conducted a Student's t -test between different pairs of the hourly data. For example, all 7:00_AM measurements were compared with 5:00 AM and 9:00 AM measurements; 1:00 PM measurements were compared with 9:00 AM and 4:00 PM measurements, and 7:00 PM peak was compared with 1:00 PM, 4:00 PM and 9:00 PM data, individually. The measurements at 7:00 AM were found to be statistically different from 5:00 AM and 9:00 AM ($p < 0.05$). Similarly, the measurements at 9:00 AM and 1:00 PM were also statistically different ($p < 0.01$). Although, the difference among the 1:00 PM, 4:00 PM and 7:00 PM data was not statistically different ($p = 0.16$ for t -test between 1:00 PM and 4:00 PM, 0.45 between 4:00 PM and 7:00 PM and 0.58 between 1:00 PM and 7:00 PM), the 7:00

PM and 9:00 PM measurements were statistically different ($p < 0.05$). Thus, it was inferred based on these tests that the diurnal OP_{ex} trend is actually bimodal with the first peak during the morning period, followed by an afternoon peak, which flattens out (i.e. extends from 1:00 PM to 7:00 PM, but with a slight dip at 4:00 PM), before subsiding at night (around 9:00 PM).

- 5 To further investigate the diurnal profile of the DTT activity and its association with various emission sources at the site, we analyzed chemical composition of PM_{2.5} collected on eight time-segregated composite filters, i.e. QS1-QS4, and TS1-TS4 in August. The schedule of this time-segregated sampling was determined based on the diurnal profile of the DTT activity in weekdays (Fig.4). Note, the diurnal profile in DTT activity obtained by the instrument during the time-segregated sampling (Fig.S4 in SI), had a similar trend as obtained in the month of June (Fig.4). We measured the concentration of key chemical
- 10 species, i.e. WSOC, OC, EC and transition metals (Cu, Mn and Fe), which ~~all~~ have all been shown to be associated with the DTT activity (Charrier and Anastasio, 2012; Saffari et al., 2014; Verma et al., 2014; Yang et al., 2014) in our time-segregated samples, along with the PM mass, to infer their diurnal variations and compare it with that in the DTT activity. The average PM_{2.5} concentration during the time-segregated sampling was $7.8 \pm 0.16 \mu\text{g}/\text{m}^3$, $8.5 \pm 0.36 \mu\text{g}/\text{m}^3$, $8.1 \pm 0.16 \mu\text{g}/\text{m}^3$ and $7.6 \pm 0.29 \mu\text{g}/\text{m}^3$ (not shown) for the morning, afternoon, evening, and night samples, respectively. Given, there
- 15 are no substantial variations in PM_{2.5} mass concentrations, the diurnal variations in the DTT activity are hypothesized to be mainly attributed to the varying chemical composition of PM_{2.5} resulting from different emission sources at the site.

3.6.1 Carbonaceous aerosol

- Figure 5 shows PM_{2.5} carbonaceous content, in terms of the ambient concentrations of EC, OC and WSOC during time-segregated sampling. EC can be assumed as a marker of the exhaust emissions from diesel vehicles ~~vehicular emissions~~ (Shah et al., 2004; Shirmohammadi et al., 2016). EC showed a peak in the morning and also at night. The morning peak coincided with the rush hour traffic and can be attributed to the vehicular emissions. It then subsides in the afternoon and remains constant till evening, before ~~getting elevated~~increasing again at night. Based on our personal observation, vehicular traffic is almost negligible after 10:00 PM at this location. Therefore, EC peak observed at night is probably a result of the
- 25 decrease in atmospheric mixing height at the site (Liu and Liang, 2010). The lower temperature and higher relative humidity [average values = 19°C and 78 % at night (7:00 PM-7:00 AM) compared to 27°C and 48 % in daytime during the time-segregated sampling] might have resulted into limited atmospheric mixing at night. Furthermore, EC has been reported to be distributed uniformly in the vertical direction and is thus greatly influenced by the atmospheric mixing height (Lin et al., 2009; Mues et al., 2017). A similar pattern in EC (i.e. peaks in morning and late evening) has been reported in few other
- 30 studies (Mues et al., 2017; Sharma et al., 2017; Singh et al., 2018), where the lower concentrations in daytime were attributed to a higher mixing height and stronger turbulence than at nighttime. Note, our nighttime composite filter was sampled from 7:00 PM – 7:00 AM, thus probably including part of the EC from evening rush hour traffic, which is trapped in the lowered mixing height at night. Overall, the diurnal trend in EC does not follow the trend in DTT activity, which indicates a negligible role of EC in determining the DTT activity at this location. These results contrast with earlier studies

showing a high correlation between EC and DTT activity (Verma et al., 2012; Gao et al., 2017). However, it should be noted that EC concentrations measured in this study ($0.15 - 0.24 \mu\text{g}/\text{m}^3$) were much lower than the values reported by other studies conducted at similar urban locations. For instance, Verma et al. (2014) reported monthly averaged summer EC concentration of $0.75 \pm 0.25 \mu\text{g}/\text{m}^3$ in Atlanta, while the concentrations in the range of $0.4 - 0.52 \mu\text{g}/\text{m}^3$ were reported for the samples collected in Los Angeles during summer 2012 (Shirmohammadi et al., 2016). Therefore, EC concentration at our sampling location is probably too low to make a significant contribution in the DTT activity. Additionally, fresh EC is less active and needs to be oxidized to participate in the DTT assay, as indicated by Antiñolo et al. (2015), which reported an almost exponential increase in the DTT activity of soot particles after exposure to high levels ($>10^{12} \text{ molecule cm}^{-3} \text{ h}$) of ozone. Given the $\text{PM}_{2.5}$ collected at the site, which is adjacent to a roadway, contain mostly fresh and unoxidized EC, it probably leads to a poor association between the diurnal trends in EC and DTT activity in our study.

The secondary organic aerosols (SOA) formed by photochemical reactions has been reported as one of the major contributor to the ambient $\text{PM}_{2.5}$ OP (Snyder et al., 2009; Verma et al., 2009, 2014; Saffari et al., 2015). WSOC is a substantial component of SOA formed during photochemical reactions (Cheung et al., 2012; Verma et al., 2014). On the other hand, OC is emitted from both primary (i.e. combustion) and secondary (e.g. photochemical formation) sources (Cabada et al., 2004). 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.

3.6.2 Trace metals

Vehicular sources, which include both direct exhausts and non-tailpipe emissions (e.g. brake and tire wear, abrasion of the road surface and resuspension of road dust) contribute majorly to the concentration of trace metals in the atmosphere (Thorpe and Harrison, 2008). Hulskotte et al. (2007) identified brake wear as one of the main sources of airborne Cu emission. In addition, resuspended road-dust is a mixture of various elements including the redox-active transition metals (e.g. Cu, Mn and Fe) (Wang et al., 2005; Thorpe and Harrison, 2008; Chen et al., 2012). Figure 6 shows the ambient concentrations of three metals, i.e. Cu, Mn and Fe measured at the sampling site. The concentrations of Cu varied between 4 and $22 \text{ ng}/\text{m}^3$, and was comparable to the concentrations reported in other studies conducted in urban areas (Verma et al., 2009, 2014). However, the concentration of Fe ($3.68 - 6.859 \text{ ng}/\text{m}^3$) was significantly lower than reported in other studies.

Fe concentrations typically found in urban atmosphere are in the range of 90 – 280 ng/m³ (Verma et al., 2009, 2014; Xia and Gao, 2011). The concentration of Mn at this site was very low (≤ 1.1 ng/m³) during the entire sampling period.

Both Cu and Fe followed a very similar diurnal trend as the DTT activity (Fig.4), with highest concentration in the afternoon and lowest at night. The difference in the diurnal trends of metals and EC concentrations (i.e. EC peaks in the morning while metals peak in the afternoon) indicates a lesser influence of direct vehicular exhausts on the metals concentrations than the resuspended dust, which is generally driven by higher vehicular speeds (due to relatively lower traffic) and drier conditions in the afternoon (Pant and Harrison, 2013). Figure S6 in SI shows the diurnal pattern of ambient RH at the sampling site. The very high RH (> 75 %) substantially suppresses the dust resuspension and the resultant metals concentrations during nighttime.

~~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. Among all the metals, Cu is known to be the strongest oxidizer of DTT (Charrier and Anastasio, 2012). Therefore, a close similarity of the diurnal profile of Cu with DTT activity indicates a significant contribution of both directly emitted Cu from vehicular exhausts (the morning peak) and resuspended Cu (in the afternoon) to PM_{2.5} OP at the sampling site.~~

4 Conclusions

We developed and field-tested ~~a low-cost~~ an online instrument for the near real-time measurement of ambient PM_{2.5} OP_{ex} with an hourly resolution. The instrument is based on coupling an automated analytical system for DTT activity determination to an MC designed to collect PM_{2.5} suspension in water. The MC, equipped with a hydrophobic filter collects PM_{2.5} suspension by generating a fine mist of water, which scrubs the particles, both directly from air and those collected onto the filter. The PM suspension collected in MC is then fed to an automated analytical system for the measurement of DTT activity.

The OP_{ex} data collected using the online instrument showed strong correlation ($R^2 > 0.8$; $p < 0.001$) with the measurements obtained by the conventional filter sampling and extraction (in water and methanol) methodology. However, the online instrument yielded higher DTT activity than both water (slope = ~~0.521.86~~, N = 20) and methanol (slope = ~~0.861.08~~, N = 16) extracted filters. We attribute this higher DTT activity to the contribution from water-insoluble components, which are more effectively collected in MC than the conventional filter sampling and extraction protocol. The instrument was tested in the field for 50 days in summer 2017 with minimal manual assistance. The instrument's LOD as tested under field condition is 0.24 nmol/min and around 65% of the hourly DTT activity measurements during field sampling were above the LOD. Substantially lower DTT activity levels (i.e. either below or very close to LOD) were observed on the days with very high RH (> 90%) or rain events. Interestingly, the DTT activity showed a four-fold increase on the night of July ~~04-4~~ (Independence Day), caused by the fireworks display, as compared to the average OP_{ex} measured during the entire sampling period.

The hourly data collected during field sampling allowed us to plot the first-ever recorded diurnal profile of the DTT activity of ambient PM_{2.5}. The diurnal profile for weekdays showed a bimodal trend with first peak in the morning (around 7 AM), followed by a broad peak (extending from 1 PM to 7 PM, but with a slight dip at 4 PM) during afternoon and early evening periods. We further investigated this bimodal profile of ambient PM_{2.5} DTT activity in relation to the diurnal variation in PM_{2.5} chemical composition, by collecting time-segregated composite filters for 10 consecutive weekdays. 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.~~metals emissions from vehicular sources (exhausts and non-exhausts), whereas both secondary formation (i.e. SOA) and metals from resuspended dust seem to contribute to the afternoon peak.~~ Overall, the extensive field-testing of the instrument in our study demonstrates its stability and consistency to yield the long-term measurements of ambient PM_{2.5} OP_{ex}. Further studies in this direction should be aimed to integrate the highly time-resolved data obtained by online ~~OP and other real time~~ instruments for measuring the PM_{2.5} OP and chemical composition, and thus infer the diurnal contribution of various emission sources in the risk associated with PM_{2.5} exposure.

15 *Competing interests:* The authors declare that they have no conflict of interest.

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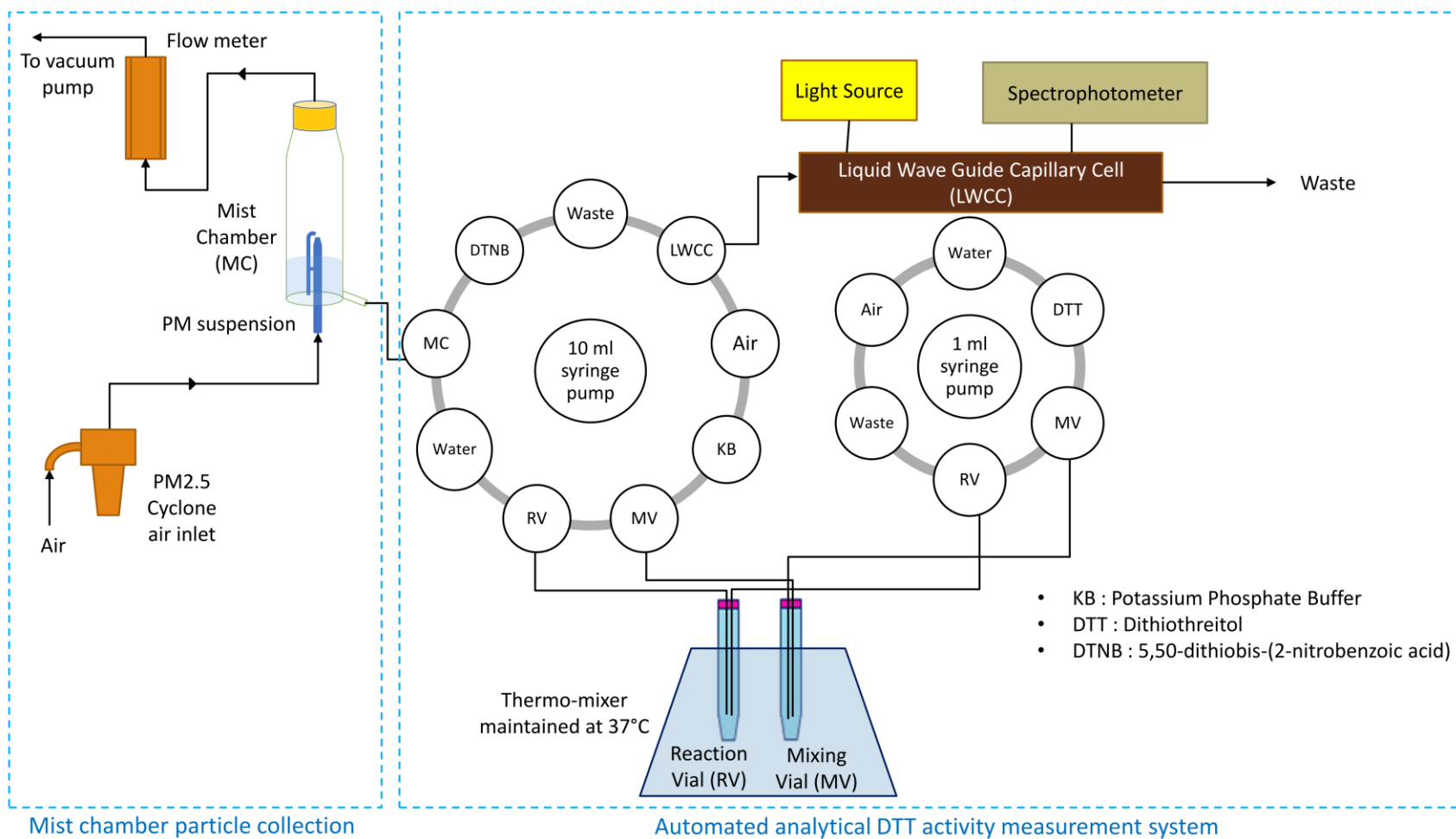
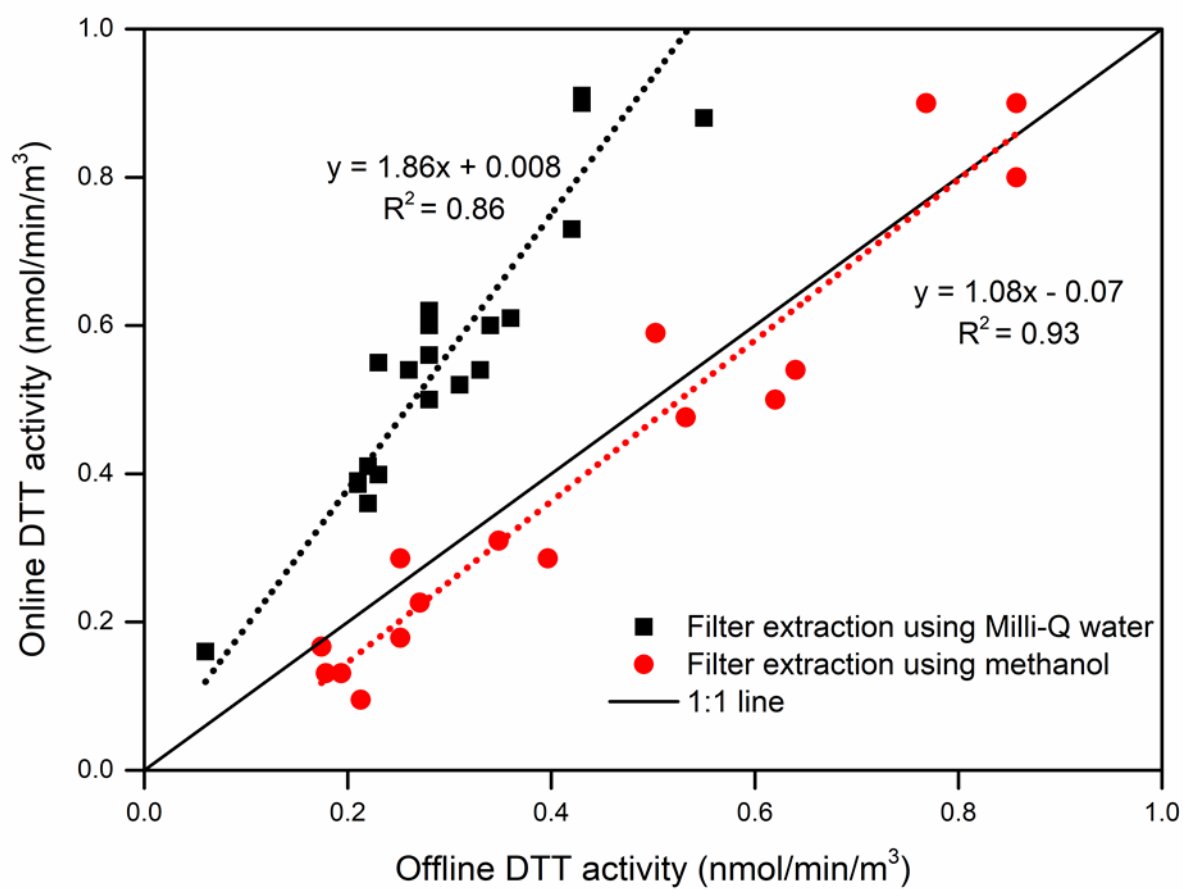


Figure 1. Layout of the online instrument for measuring the DTT activity of ambient PM_{2.5}



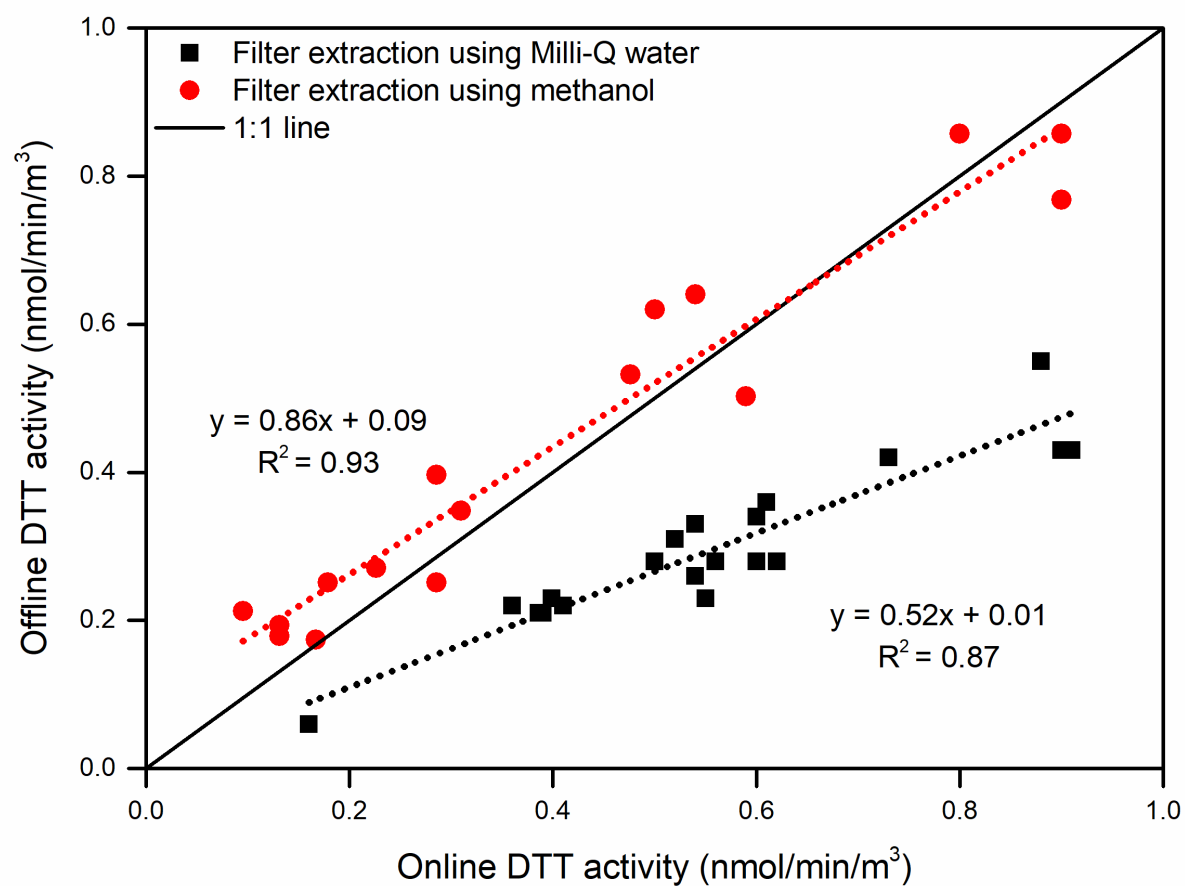


Figure 2. Comparison of the DTT activity obtained from the online instrument with the traditional filter collection and extraction methodology (i.e. offline DTT activity analysis of the PM extracts)

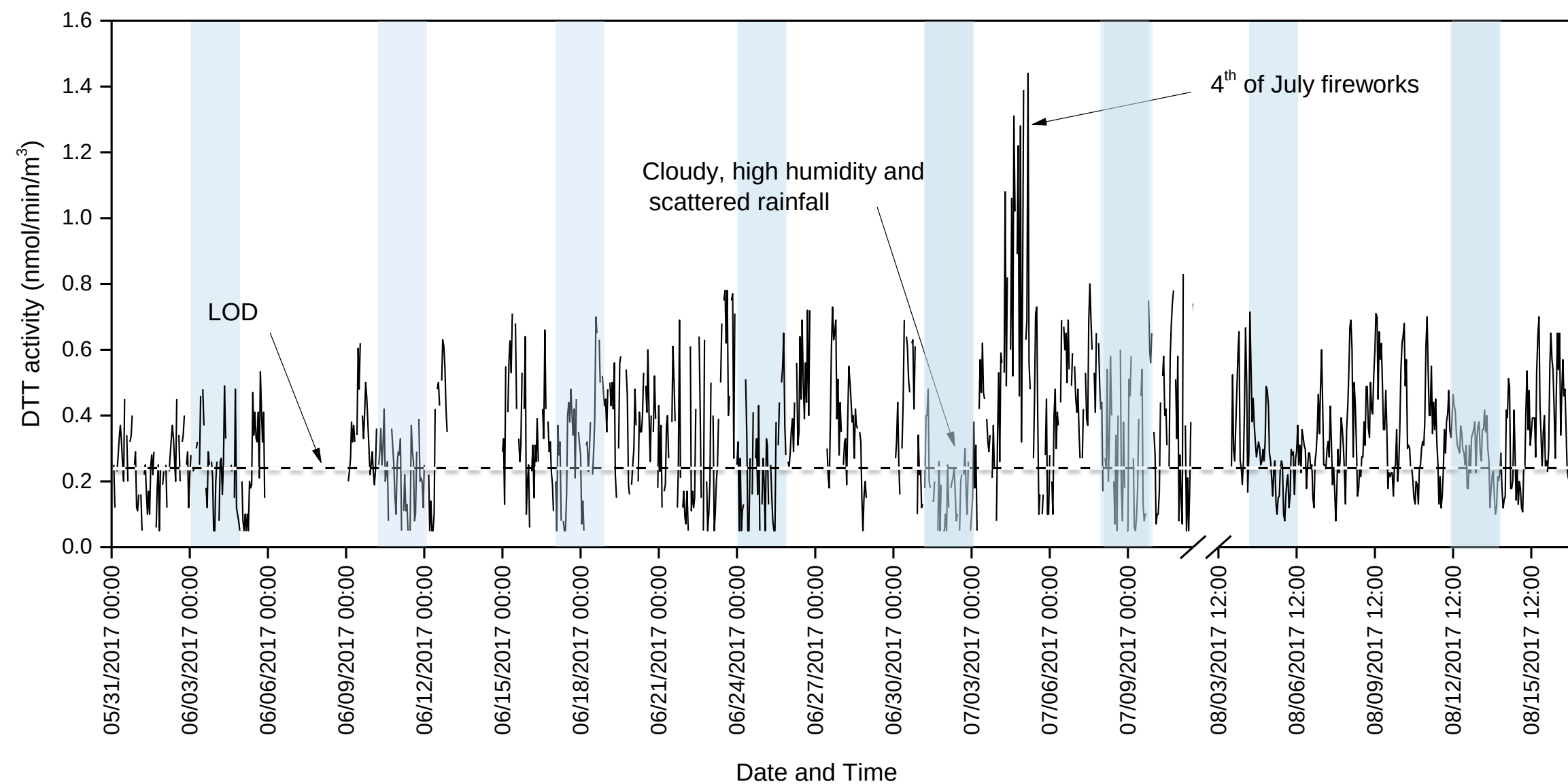
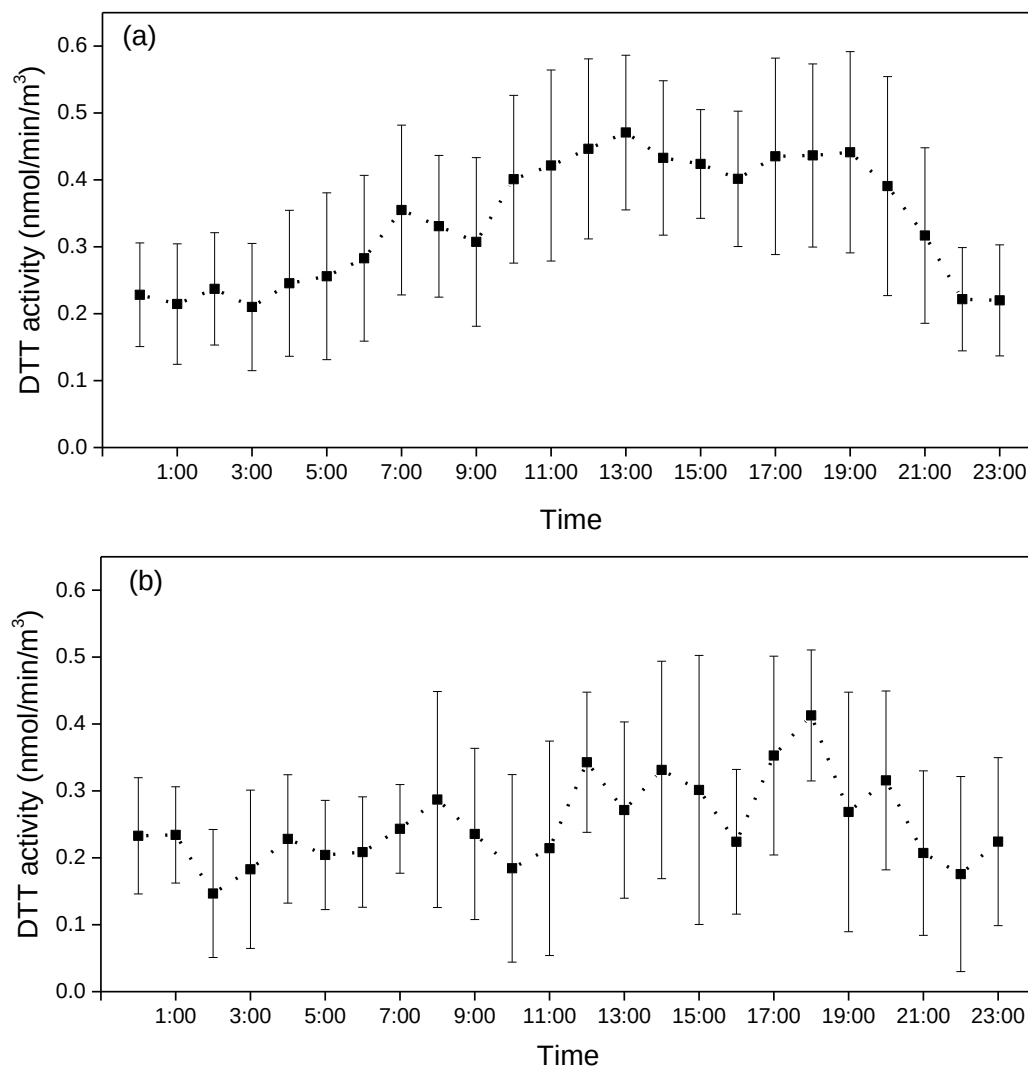


Figure 3. Time-series plot of the DTT activity from May 31, 2017 to Aug 16, 2017. The shaded portions in the graph are weekend DTT activity measurements. The instrument was not operated between ~~May 31~~July 12 and ~~July 11~~August 3, 2017 (shown as a break in the X-axis).



5 Figure 4. Diurnal profile of the ambient PM_{2.5} DTT activity measured at the sampling site over (a) weekdays (n = 18 days), (b) weekends (n = 10 days). The data from May 31 to July 2, 2017 ~~was~~were used for plotting this profile. Error bars are the standard deviation (1σ) of the average DTT activity in that hour.

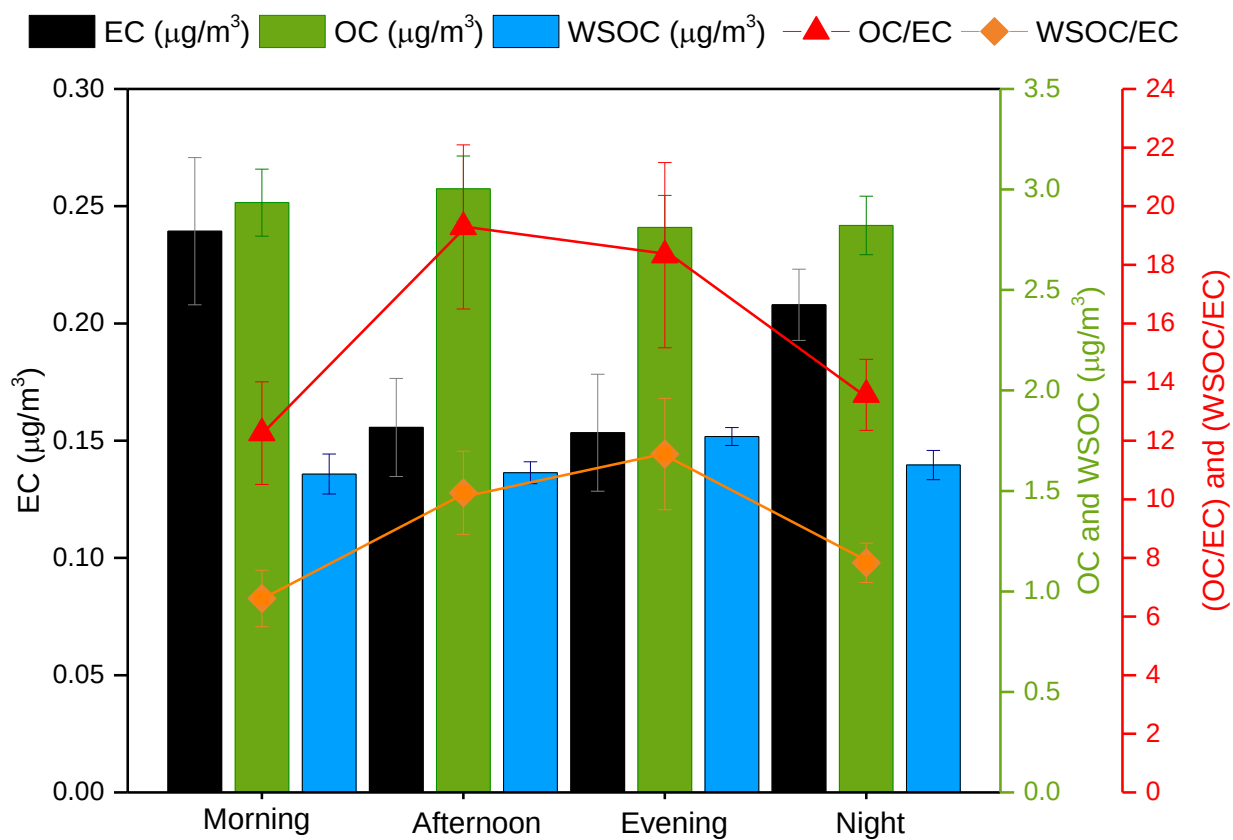


Figure 5. Diurnal trend in the ambient concentrations of carbonaceous aerosols, i.e. EC, OC, and WSOC, and the ratio of OC/EC and WSOC/EC, as measured from the time-segregated integrated filters. Error bars denote standard deviation (1σ) of the triplicate measurements.

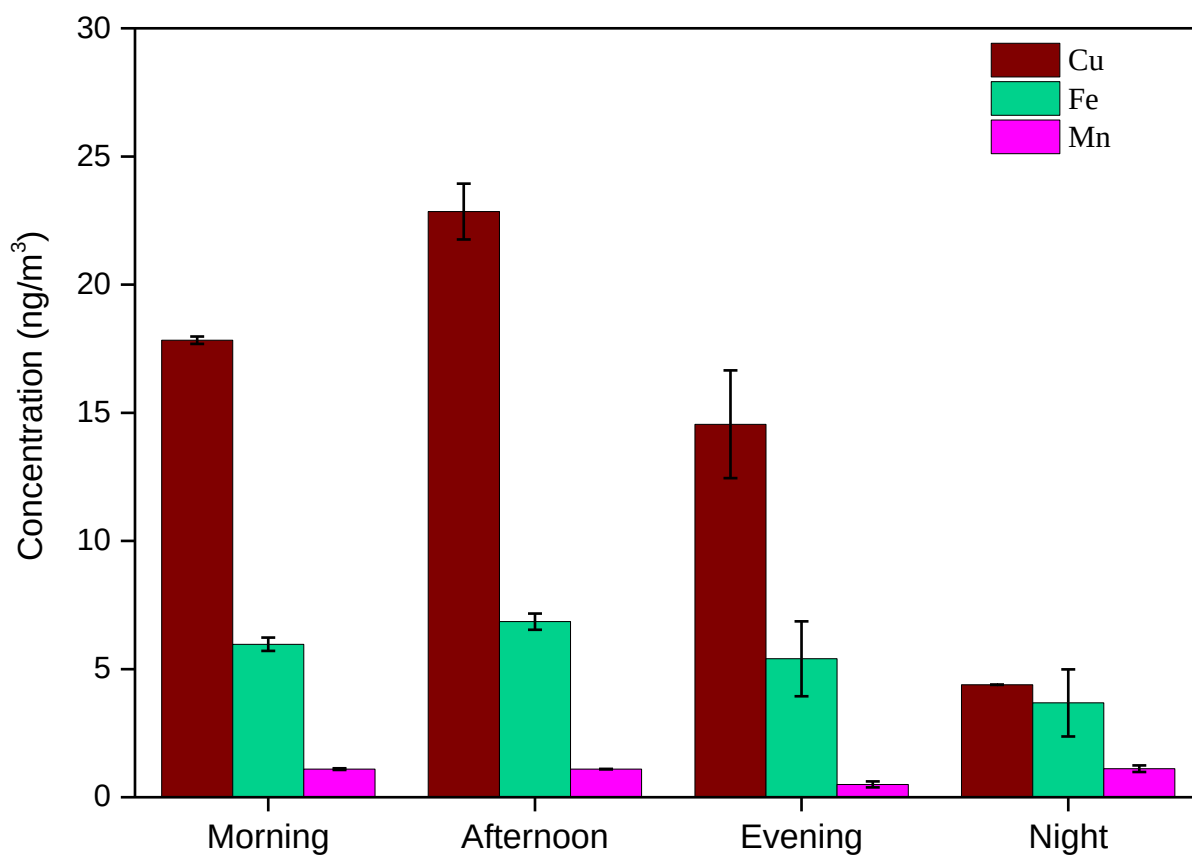


Figure 6. Diurnal trend in the ambient concentrations of metals, i.e. Cu, Fe and Mn, as measured from the time-segregated integrated filters. Error bars denote standard deviation (1σ) of the triplicate measurements.