Real-Time Measurements of $PM_{2.5}$ Oxidative Potential using Dithiothreitol (DTT) Assay in Delhi, India

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Abstract

The oxidative potential (OP) of ambient particulate matter (PM) is a commonly used metric to link the aerosol exposure to its adverse health effects. In this study, we report the first-ever real-time measurements of ambient $PM_{2.5}$ OP based on a dithiothreitol (DTT) assay in Delhi, during a late winter season (February 2019). The chemical composition of PM was also measured using various collocated online instruments to identify the chemical components driving the $PM_{2.5}$ OP. The hourly averaged OP during the entire campaign ranged from 0.49 – 3.60 nmol/min/m^3, with an average value of 1.57±0.7 nmol/min/m^3. The secondary organic aerosols appear to be the major driver for the variability in the intrinsic OP of $PM_{2.5}$. Although, the average PM_1 mass concentration at Delhi was 13-times the average $PM_{2.5}$ mass concentration reported in Illinois, USA in a similar study, it was not accompanied by a proportionate increase in the OP (average volume normalized DTT activity of $PM_{2.5}$ was only 5 times of that reported in Illinois). These findings reveal substantial spatial heterogeneity in the redox properties of PM and highlight the importance of determining the PM chemical composition along with its mass concentrations for predicting the overall health impacts associated with aerosol exposure.

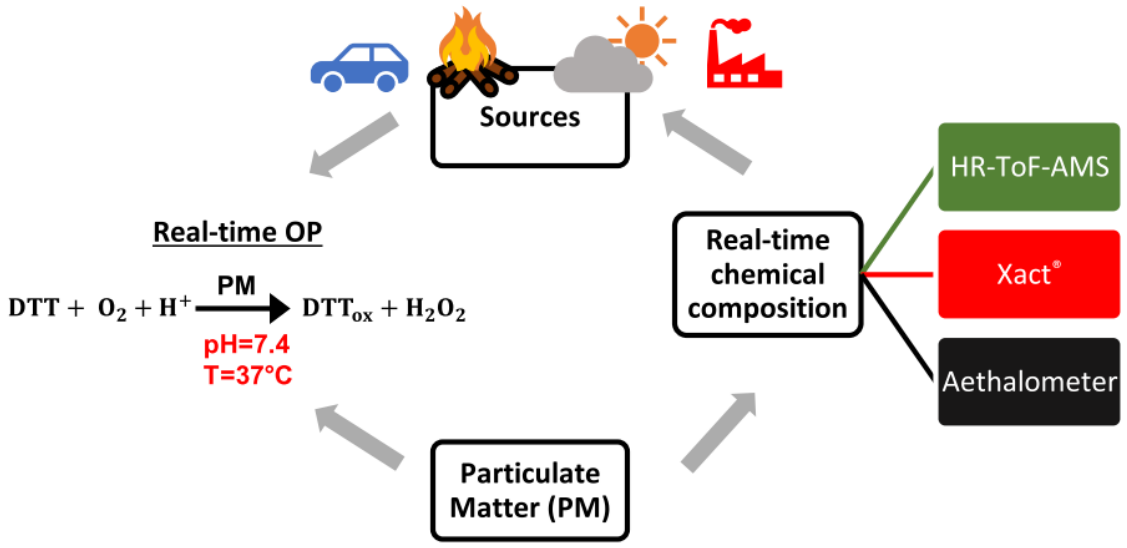

Figure: "For Table of Contents Use Only"

Introduction

Exposure to fine particulate matter ($PM_{2.5}$, particles with diameter less than 2.5 μm) has been linked to various adverse health effects such as asthma, cardiovascular diseases, pulmonary dysfunction and respiratory illnesses.[1–3] In 2015, over 4.2 million deaths worldwide were attributed to ambient $PM_{2.5}$ exposure, of which 59% were in east and south Asia.[4] Air pollution accounts for over 12.5% of the total deaths in India.[5] Delhi, the capital of India, has the worst air quality among all major megacities in the world.[6] Due to calm wind conditions and lower boundary layer depth, particularly prevalent during Delhi's winter, the hourly averaged $PM_{2.5}$ mass concentrations have been reported to exceed even 500 μg/m^3,[7] which is over 8 times the National Ambient Air Quality Standards (60 μg/m^3) stipulated by the Central Pollution Control Board (CPCB) of India.[8] The overall toxicity of $PM_{2.5}$ is dependent on both its mass concentration and the composition.[9,10] Previous studies conducted in the Indo-Gangetic Plains have indicated that $PM_{2.5}$ in Delhi is a mixture of particles (or their precursors) emitted from various emission sources including post-harvest crop burning, vehicles, industries, waste burning, and construction activities.[11–13] These mixtures of

various chemical species (e.g. organic compounds, inorganic ions, transition metals, etc.) coming from different sources are expected to be highly toxic, [14,15] but data on the toxicological properties of $PM_{2.5}$ in the Indian subcontinent are currently lacking.[16,17]

The oxidative potential (OP) of PM, i.e. the ability of particles to generate reactive oxygen species (ROS) or consume antioxidants, is an intrinsic property and has recently gained popularity as a potential health metric to estimate the PM toxicity.[18–22] The OP of PM can be measured by different chemical and biological assays.[19,20,23,24] One commonly used chemical assay to measure the OP of ambient PM is the dithiothreitol (DTT) assay.[18–20,25,26] DTT, in the presence of ambient PM, acts as an electron donor and converts oxygen to its superoxide radical.[27] The oxidation rate of DTT during this reaction (hereafter referred as the DTT activity) is assumed to be proportional to the amount of redox active species present in ambient PM.[19] Recent studies have also found better associations of OP based on DTT assay with the adverse health effects, such as asthma, wheezing, and cardiovascular disorders, as compared to $PM_{2.5}$ mass concentrations.[28–32]

In this study, we report the first-ever measurements of the real-time $PM_{2.5}$ OP in Delhi using a recently developed online instrument based on the DTT assay in our lab.[33] The real time OP instrument has the advantage of capturing highly time-resolved data (1 hour resolution), and is less prone to sampling artifacts, such as loss of short-lived radicals and unstable redox-active species.[33–35] We also investigated the chemical components driving the DTT activity using the measurements obtained by other collocated real-time chemical speciation instruments. This short (~ one week) measurement campaign provided us a unique opportunity to link the chemical composition of ambient $PM_{2.5}$ to its OP in one of the most air-polluted cities on the Earth, during an important season (late winter) for air pollution.

Materials and Methods

The real-time OP of ambient $PM_{2.5}$ was measured using an automated analytical system coupled to a mist chamber (MC), which collects ambient particles directly into water. A schematic and the daily operational protocol of the instrument are explained in Figure S1 (and related discussion) in the supporting information (SI), and a more detailed information of the instrument and its field characterization are provided in Puthussery et al.[33] Briefly, ambient $PM_{2.5}$ was collected by connecting a $PM_{2.5}$ cyclone inlet [42 LPM flow rate; University Research Glassware (URG)] at the inlet port of an MC using a 0.5" (outer diameter) copper tube. A TefSep polytetrafluoroethylene (PTFE) membrane hydrophobic filter (1 µm pore size; Whatman) was kept in a filter pack (URG), attached at the top of the MC to collect $PM_{2.5}$. The MC is initially filled with a predefined volume of water. As air flows through the MC, mist forming inside the chamber continuously washes out the particles collected onto the PTFE filter, yielding a $PM_{2.5}$ suspension in water. After every hour, this $PM_{2.5}$ suspension is withdrawn and fed to an analytical system to measure the OP based on the DTT assay. In the analytical component of the automated system, the $PM_{2.5}$ suspension is mixed with potassium phosphate buffer (pH 7.4, 0.5 µM) and DTT (final concentration in the reaction vial: 100 µM), and incubated at 37ºC using a thermomixer (400 rpm; Eppendorf North America, Inc.). The analytical system measures the decay of DTT with time, based on a spectrophotometric technique [liquid waveguide capillary cell (LWCC-M-3100; World Precision Instruments) coupled to a miniature online spectrophotometer assembly (Ocean Optics)] using 5,5'-dithiobis-(2-nitrobenzoic acid), and determines the volume normalized DTT activity in the units of nmol of DTT consumed per minute per m^3 of air (nmol $min^{-1}m^{-3}$; hereafter referred as the extrinsic DTT activity or OP_{ex}).

The OP instrument was deployed on the fourth floor (height from the ground level ~ 15 m) of a building inside the Indian Institute of Technology (IIT) Delhi campus from Feb 03, 2019 to Feb 09, 2019, along with other collocated instruments for measuring the real-time chemical composition of ambient PM (either PM_1

- the sub-micron fraction of the particles, or $PM_{2.5}$), such as, high resolution time of flight mass spectrometer (HR-ToF-AMS), aethalometer, gas analyzers (NO_x and CO) and Xact®. IIT Delhi is spread over an area of 1.3 square km and there are no commercial or industrial activities inside the institute. The campus is located in South Delhi, and is surrounded by major industrial towns, Gurugram (22 km south west), Faridabad (24 km south), Noida (24 km south east), Ghaziabad (37 km north east) and the Delhi National Capital Territory (NCT, 25 km north west). The building housing the sampling site is adjacent to the outer periphery wall of the campus, which is 100 m away from a busy 4-lanes street (Outer Ring Road). The HR-ToF-AMS (Aerodyne Inc, USA) was used to measure the mass concentrations of different non-refractory species like organics, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^- in PM_1 with a time resolution of 2 minutes.[36,37] Additionally, the real time concentrations of mass equivalent black carbon (eBC; measured at 880 nm wavelength) in $PM_{2.5}$ were determined using an aethalometer (AE-33, Magee Scientific; resolution =1 minute).[38] The Xact® 625i Ambient Metals Monitor (Cooper Environmental Services) was used for measuring the real time concentrations of different metal species in the ambient $PM_{2.5}$ with a time resolution of 30 minutes.[39] Additional details of the instruments, time-resolution for their data acquisition, sample size and the PM inlet used for sampling is summarized in Table S1 in SI. Note, due to some technical issues, the Xact® did not collect continuous data from Feb 4 – Feb 6, thus yielding a substantially smaller sample size (N=70 for hourly averaged data points) than obtained by other real time instruments (N>120). The real-time concentrations (resolution =2 minutes) of carbon monoxide (CO) and nitrogen oxides (NO_x = NO + NO_2) were measured using collocated gas analyzers (Serinus 30 CO and Serinus 40 NO_x, Ecotech).[40] Data from the different instruments were hourly averaged prior to any comparison or statistical analysis. We used Origin Pro 2016 and IBM SPSS Statistics 26 software to create the linear regression plots and the Pearson's correlation matrices, respectively.

Results and Discussion:

Figure 1a shows the hourly averaged DTT activity of ambient $PM_{2.5}$ and mass concentration of non-refractory (NR) PM_1 (estimated from the HR-ToF-AMS measurements by summing organics + SO_4^{2-} + NO_3^- + NH_4^+ + Cl^-). Note, HR-ToF-AMS measured PM_1, while our DTT instrument measured $PM_{2.5}$. But as shown in Figure S2 (and the related discussion), these different cut-off diameters of the PM-inlets are not expected to significantly influence the results of our comparison and the regression analysis (presented later) between OP and HR-ToF-AMS-measured chemical composition data.

Organic aerosols (OA) were the major contributors (average contribution ~46%) to the total NR-PM_1 mass (Figure 1a). The DTT activity measured during the entire campaign ranged from 0.49 – 3.60 nmol/min/m^3, with an hourly averaged (± 1σ) value of 1.57 ± 0.7 nmol/min/m^3. This average value is about 5 times the average DTT activity of ambient $PM_{2.5}$ measured using the same instrument in our earlier study at an urban site in Illinois, USA (0.33 ± 0.19 nmol/min/m^3)[33] during summer 2017. The average OP_{ex} measured at Delhi in our study is approximately twice the ambient $PM_{2.5}$ OP_{ex} reported by Vreeland et al.[41] for a southern Indian city of Bangalore (0.79 ± 0.13 nmol/min/m^3) during October 2013, but within the range of the OP_{ex} [(0.09 – 3.04 nmol/min/m^3 for PM_{10}[42] and 1.3 – 7.2 nmol/min/m^3 for $PM_{2.5}$[16] extracted in a water + methanol (1:1) mixture] reported for a few northwest regions (Rajasthan and Punjab) in India. Despite a short duration of our sampling campaign, the range of OP_{ex} at Delhi was much wider than $PM_{2.5}$ OP_{ex} reported in other cities of the world such as Chicago, USA (0.04 – 1.28 nmol/min/m^3),[43] Atlanta, USA (0.1–1.5 nmol/min/m^3),[44] Paris, France (0.1 – 0.36 nmol/min/m^3),[45] Rome, Italy (0.11 – 0.34 nmol/min/m^3),[45] Athens, Greece (0.1 – 0.36 nmol/min/m^3),[45] and Beijing, China (0.11 to 0.49 nmol/min/m^3).[46] The differences in the OP_{ex} at these sites are possibly due to differences in the intrinsic redox activities and ambient $PM_{2.5}$ mass concentrations. Please note that the DTT activities at all these locations were measured using the traditional offline filter collection and analysis approach, in comparison to the near real-time

measurements in our study. Therefore, caution needs to be exercised while making a direct comparison among these studies. Lower magnitudes of DTT activity observed during second half of the sampling campaign (Feb 07, 2019 – Feb 09, 2019) was probably due to intermittent rain incidences (see Figure S3 in SI) in the area. A similar decrease in NR-PM_1 mass concentrations was also observed during this period (Figure 1a). We hypothesize that the rain during this period lowered the $PM_{2.5}$ concentration (possibly by wash out mechanism)[47] in our study area, which could have led to an overall decrease in the $OP_{ex.}$ In general, the hourly averaged OP_{ex} measurements at Delhi roughly follow the hourly NR-PM_1 mass concentrations (r=0.66, P<0.01; see inset in Figure 1a).

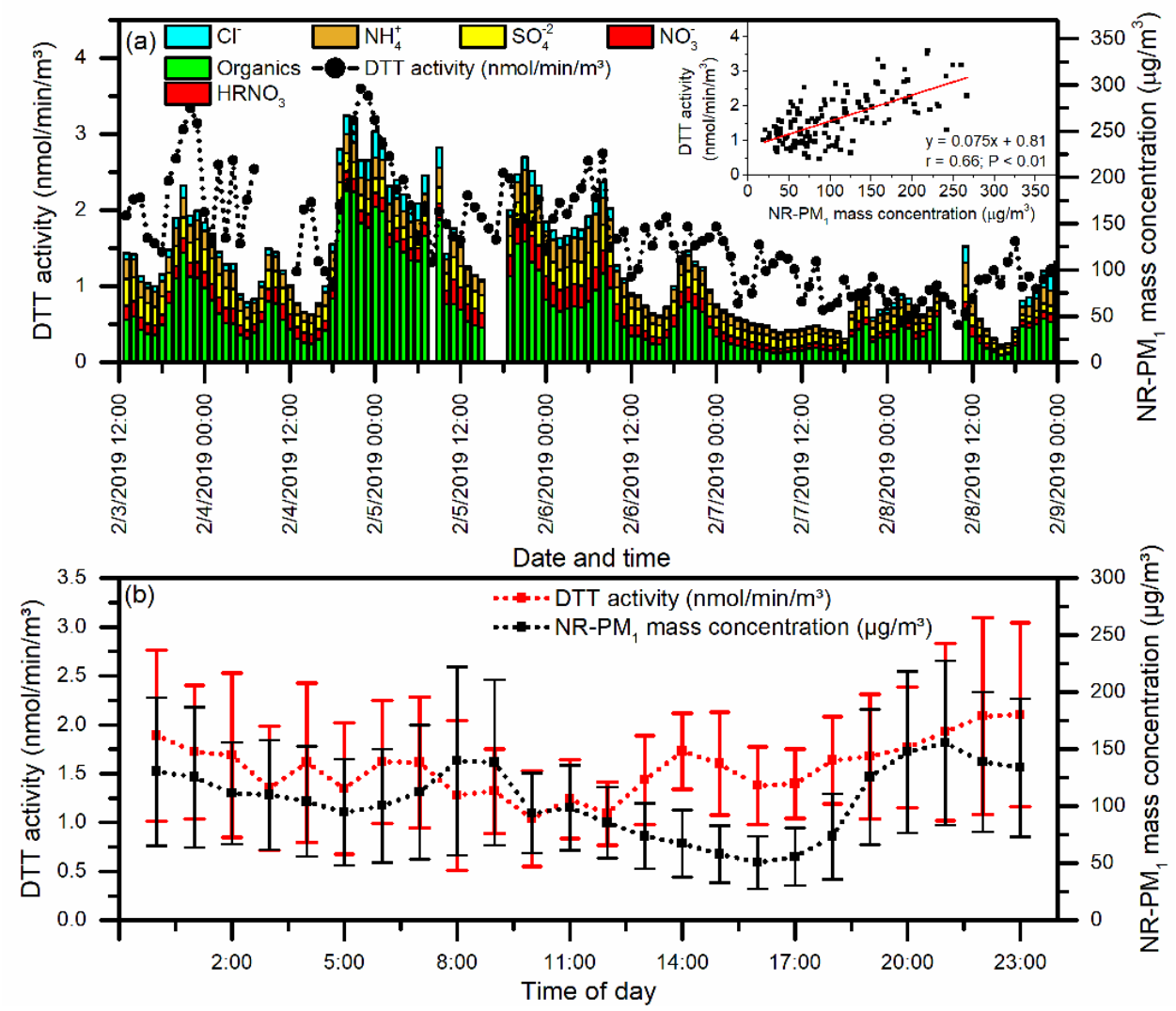

Figure 1. Time series (a) and diurnal profile (b) of the blank corrected hourly averaged DTT activity of ambient $PM_{2.5}$ (OP_{ex}) and hourly averaged NR-PM_1 mass concentration (as summed from HR-ToF-AMS measurements of organic and inorganic ions) from Feb 03, 2019 – Feb 09, 2019 at Delhi. The inset in 1(a) shows the linear regression between OP_{ex} and NR-PM_1 mass concentration

Figure 1b shows diurnal profiles of the hourly averaged OP_{ex} of ambient $PM_{2.5}$ and NR-PM_1 mass concentration for the entire sampling campaign. The two prominent peaks observed in NR-PM_1 mass concentrations during early morning (7:00 – 9:00) and late evening (19:00 – 21:00) coincide with the rush hour vehicular traffic near the site. The mass concentrations were lowest during the afternoon period (15:00

– 17:00) but higher at nighttime. We attribute this diurnal trend in NR-PM_1 mass concentration partially to the diurnal variation in the mixing layer height [high during daytime and low at night], use of domestic solid fuel for heating at night, and partitioning of semi-volatile compounds (e.g. NH_4Cl and NH_4NO_3) to the particle phase at lower temperatures.[7,11,12,48] In contrast, the diurnal OP_{ex} profile showed a dip during morning-to-forenoon period (7:00 – 12:00), but increased from noon and peaked at mid-night. The ratio of the volume normalized DTT activity (OP_{ex}) to NR-PM_1 mass concentration, can be used to indicate the intrinsic OP (OP_{in}; mass normalized DTT activity) of the particles. The diurnal profile of OP_{in} as plotted in Figure S4 shows much higher values during the afternoon period (13:00 – 18:00) than the rest of the day (see Figure S4 and the associated discussion). This is consistent with the previous studies, where an increase in OP_{in} during the afternoon period was attributed to an increase in the concentration of photochemically formed secondary organic aerosols (SOA).[33,49,50] Based on these results, we hypothesize that the OP_{ex} at Delhi is influenced by both intrinsically redox active SOA formed during the afternoon period, and the elevated aerosol mass concentrations at night due to a stable nocturnal boundary layer with its restricted vertical exchange. However, it should be noted that the diurnal profile shown here was from a very limited number of days (~ 1 week) with varying weather conditions (i.e. rainy and sunny days), and therefore should not be considered as the representative OP diurnal profile for the entire winter season in Delhi.

Figure 2 shows the simple linear regression between mass normalized DTT activity (nmol/min/µg; OP_{in}) and a few selected species (mass-normalized, i.e. µg/µg of NR-PM_1) measured using the collocated HR-ToF-AMS and Xact® instruments. A more detailed correlation matrix among various measured species is provided in SI (Table S2). Note, the correlation can be performed both on volume normalized and mass normalized levels. However, the volume normalized correlations are more susceptible to the confounding collinearity of the individual chemical species with $PM_{2.5}$ mass concentrations. Therefore, we believe that the regression analysis after mass normalization could be better in reducing (but not necessarily eliminating) the bias from this collinearity, and thus more suitable for identifying the components which influence the intrinsic redox activity of ambient $PM_{2.5}$. We have also included the volume-normalized correlations in SI (Table S3) in case the readers are interested.

DTT activity (OP_{in}) was best correlated with the oxygenated organic aerosols [OOA; species with m/z=44) and family of $CHO_{>1}$ (ions with one or more oxygen atoms)].[36,51,52] The Van Krevelen (VK) diagram of HR-ToF-AMS data (see Figure S5 and the related discussion in SI) revealed a possible fragmentation along with the formation of acid groups in the OA fraction (Figure S5), which is typically observed during the transition from less oxidized to more oxidized OA.[51] Additionally, SO_4^{2-}measured using HR-ToF-AMS showed good correlation with OOA (m/z=44 and family $CHO_{>1}$; r>0.70) (Table S2), indicating a substantial contribution from secondary photochemical particle formation to both $SO_4^{2-}$and OA. Note, the diurnal profile of SO_4^{2-} (Figure S6) showed a bimodal trend with elevated values during the noon period [possibly from photochemical secondary particle formation[53]] and at night-time [possibly due to lowering of the boundary layer as reported earlier]. The tight correlation among SO_4^{2-}, OOA and OP_{in} corroborate our hypothesis that photochemical formation and aging is one of the important factors driving the variability in OP_{in} at this site.

In addition to the oxygenated organic species, OP_{in} was decently correlated with K (r=0.70) (see Figure 2 and Table S2). K is a stable and redox-inactive species, and commonly used as a tracer for biomass burning (BB) emissions.[53–55] However, in the present study, it showed a poor correlation with mass normalized HR-ToF-AMS measured BB emissions markers (m/z 60 and 73 species; see Table S2), both of which also showed poor correlations with OP_{in} (Table S2). Instead, K showed good correlation with m/z=44 and $CHO_{>1}$ (r=0.78; see Table S2), suggesting possible contributions of BB aerosols to the OOA, as reported in several

previous studies.[56–59] This could partly explain the strong association of K with OP_{in}. No other chemical species was significantly correlated with OP_{in} (see Table S2 and related discussion).

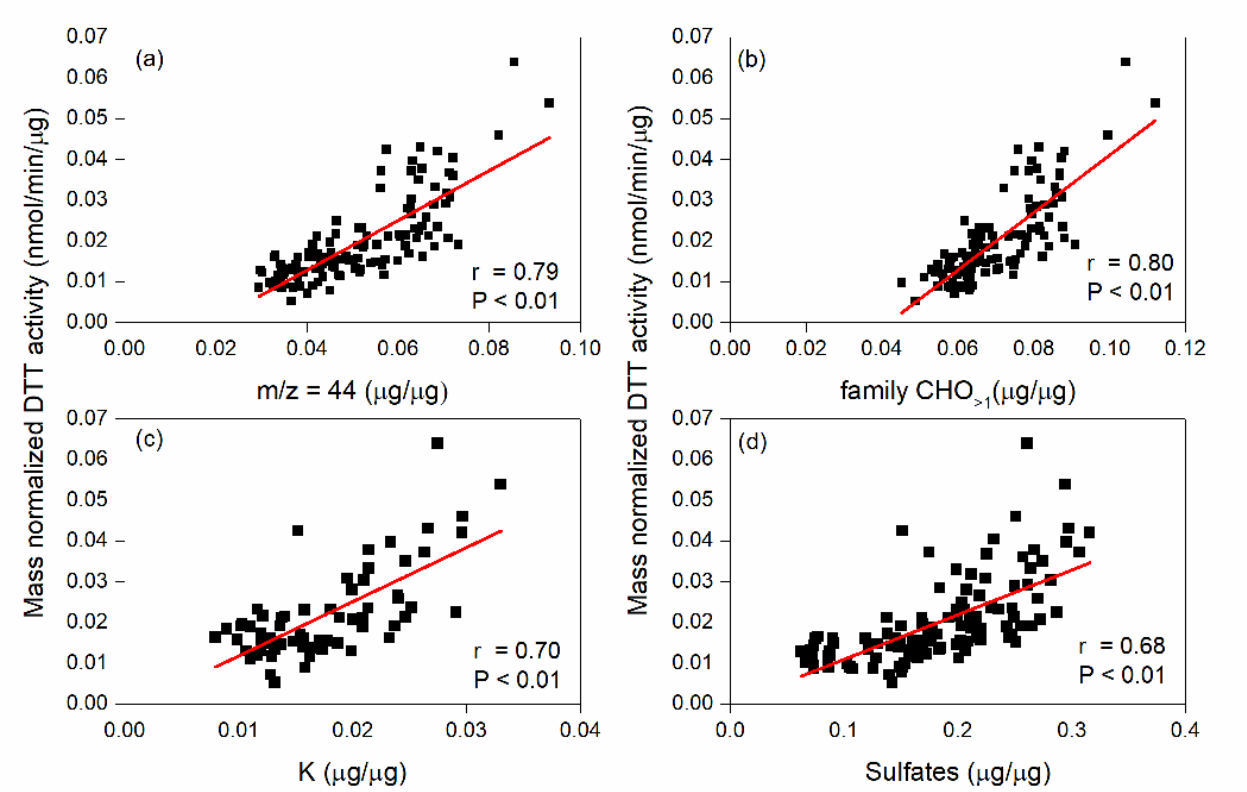

Figure 2. Simple linear regression between DTT activity and a few selected species (i.e. those with r>0.60) measured by HR-ToF-AMS (PM_1 fraction) and Xact® ($PM_{2.5}$ fraction). Regression was done on the mass normalized levels of both DTT activity and chemical constituents.

Our study highlights the usefulness of the real-time online instruments in identifying various aerosol components and their emission sources contributing to the OP of ambient $PM_{2.5}$. Despite limited measurements in the present study, we could see statistically significant correlations with important chemical species, due to highly time resolved data obtained by these instruments. Comparison of the OP_{ex} vs. aerosol mass measured at Delhi (OP_{ex}=1.57±0.7 nmol/min/m^3; average NR-PM_1 =105±60 µg/ m^3), with the typical levels observed in our earlier study in Illinois (OP_{ex}=0.33±0.19 nmol/min/m^3; average $PM_{2.5}$ concentration 8±0.25 µg/ m^3)[33] clearly shows a non-proportional relationship between aerosol mass concentrations and extrinsic DTT activity. Despite more than a 13-fold increase in the concentration of $PM_{2.5}$ mass, the increase in the extrinsic DTT activity is only 5 times, which provides good arguments to study the aerosol chemical composition in estimating its intrinsic toxicity. This finding is consistent with mounting evidence for the spatial heterogeneity in the health response functions of ambient $PM_{2.5}$.[60–62] As summarized by Li et al.[10], the $PM_{2.5}$ mixtures arising from pertinent sources in different regions could be vastly different and therefore priority should be given to finding the sources of these toxic combinations first rather than those contributing to the bulk aerosol mass.

Based on our simple regression analysis, photochemically aged OA appears to be the main driver for the variability in $PM_{2.5}$ OP in Delhi during the study period, and fresh vehicular emissions seem to have lower influence on the DTT activity. Note, these results could be slightly biased due to different particle collection efficiency of water-soluble (such as aged OA, which tend to be more efficiently collected) vs. water-

insoluble or less-soluble (e.g. hydrocarbon like OA) $PM_{2.5}$ components in the MC. Moreover, a backward air mass trajectory and the wind rose analysis showed that the aerosols reaching the study location during the sampling campaign were from different locations and directions (see Figure S7). Therefore, a more detailed source apportionment study is required to quantify the contributions from the local and regional emission sources driving the $PM_{2.5}$ OP. Future work should focus on conducting longer field campaigns to study the seasonal trends and the influence of episodic events like crop burning and firecracker emissions during festivals etc. on the redox activity of ambient particles. These findings would assist policy makers in developing new frameworks for controlling the particulate pollution in Delhi and other major cities in the world.

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The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org

Summary of the instruments used in the campaign, Pearson's r correlation matrices, schematic and description of the real time OP instrument, comparison between PM_1 and $PM_{2.5}$, precipitation data, diurnal intrinsic OP profile, Van Krevelen diagram, diurnal SO_4^{2-} profile, Windrose plot.

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