

Real-Time Measurements of PM_{2.5} Oxidative Potential Using a Dithiothreitol Assay in Delhi, India

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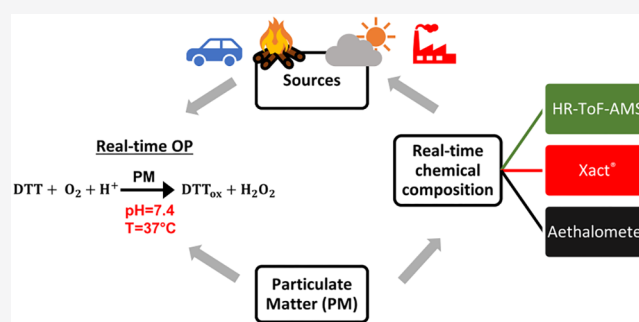
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ABSTRACT: The oxidative potential (OP) of ambient particulate matter (PM) is a metric commonly used to link the aerosol exposure to its adverse health effects. In this study, we report the first-ever real-time measurements of ambient PM_{2.5} OP based 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 to 3.60 nmol min⁻¹ m⁻³, with an average value of 1.57 ± 0.7 nmol min⁻¹ m⁻³. The secondary organic aerosols appear to be the major driver for the variation in the intrinsic OP of PM_{2.5}. Although the average PM₁ 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 (the average volume-normalized DTT activity of PM_{2.5} was only 5 times 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.



INTRODUCTION

Exposure to fine particulate matter (PM_{2.5}, particles with diameters of <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, more than 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 >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 a 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/m³,⁷ which is >8 times the National Ambient Air Quality Standards (60 μg/m³) 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 postharvest crop burning, vehicles, industry, 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 about the toxicological properties of PM_{2.5} in the Indian subcontinent are currently lacking.^{16,17}

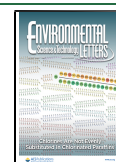
The oxidative potential (OP) of PM, i.e., the ability of particles to generate reactive oxygen species (ROS) or consume antioxidants, is an intrinsic property and has recently gained popularity as a potential health metric to estimate the PM toxicity.^{18–22} The OP of PM can be measured by different 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 rate of oxidation of DTT during this reaction (hereafter termed 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

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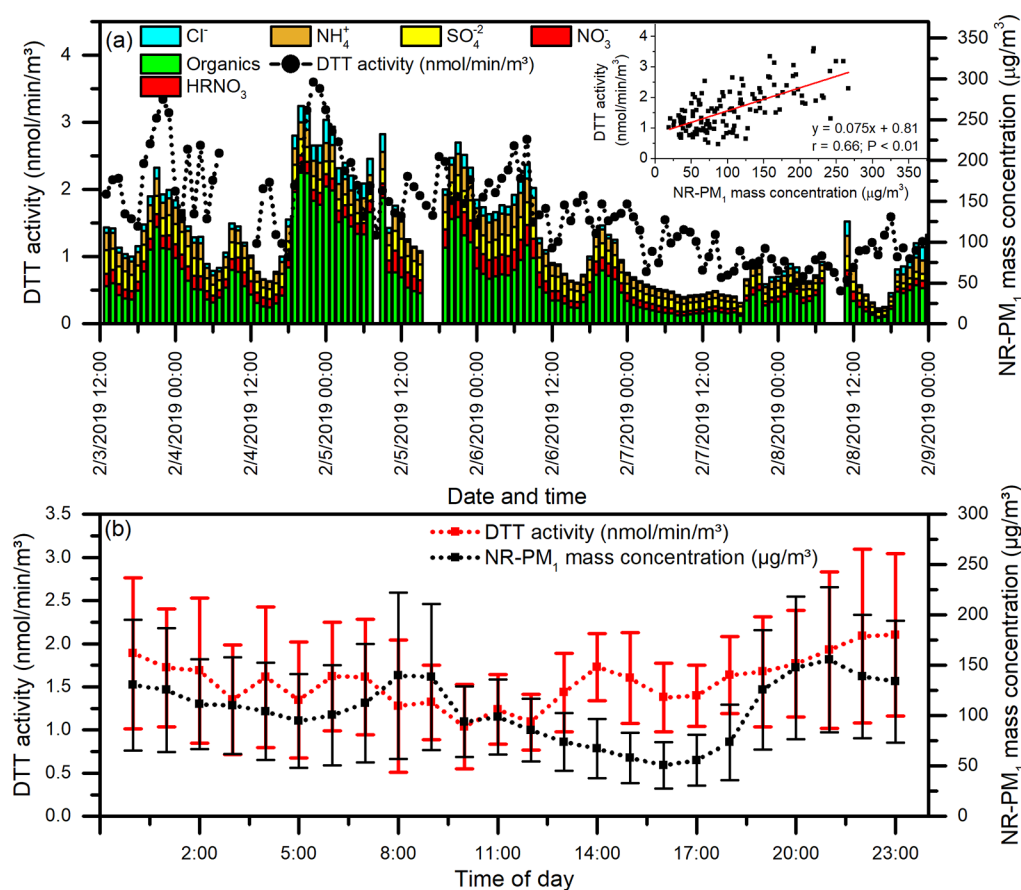


Figure 1. (a) Time series and (b) diurnal profile of the blank-corrected hourly averaged DTT activity of ambient $PM_{2.5}$ (OP_{ex}) and hourly averaged NR- PM_{10} mass concentration (as summed from HR-ToF-AMS measurements of organic and inorganic ions) from February 3 to 9, 2019, in Delhi. The inset in panel a shows the linear regression between OP_{ex} and NR- PM_{10} mass concentration.

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 h resolution) and is less prone to sampling artifacts, such as a 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 (~1 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 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 in water. A schematic and the daily operational protocol of the instrument are explained in Figure S1 (and related discussion) in the Supporting Information, and more detailed information about the instrument and its field characterization are provided by 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 in. (outer diameter) copper tube. A TefSep polytetrafluoroethylene (PTFE) membrane hydrophobic filter (1 μ m 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 into 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 μ M) and DTT (final concentration in the reaction vial = 100 μ M) and incubated at 37 °C 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 units of nanomoles of DTT consumed per minute per cubic meter of air (nanomoles per minute per cubic meter; hereafter termed the extrinsic DTT activity or OP_{ex}).

The OP instrument was deployed on the fourth floor (height from the ground of ~15 m) of a building inside the Indian Institute of Technology (IIT) Delhi campus from February 3 to 9, 2019, along with other collocated instruments

for measuring the real-time chemical composition of ambient PM (either PM₁, the submicrometer fraction of the particles, or PM_{2.5}), such as a 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 km², 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 southwest), Faridabad (24 km south), Noida (24 km southeast), Ghaziabad (37 km northeast), and the Delhi National Capital Territory (NCT, 25 km northwest). The building housing the sampling site is adjacent to the outer periphery wall of the campus, which is 100 m from a busy four-lane street (Outer Ring Road). The HR-ToF-AMS (Aerodyne Inc.) was used to measure the mass concentrations of different nonrefractory species like organics, SO₄²⁻, NO₃⁻, NH₄⁺, and Cl⁻ in PM₁ with a time resolution of 2 min.^{36,37} Additionally, the real-time concentrations of mass equivalent black carbon (eBC; measured at a wavelength of 880 nm) in PM_{2.5} were determined using an aethalometer (AE-33, Magee Scientific; resolution of 1 min).³⁸ The Xact 62Si Ambient Metals Monitor (Cooper Environmental Services) was used to measure the real-time concentrations of different metal species in ambient PM_{2.5} with a time resolution of 30 min.³⁹ Additional details of the instruments, time resolution for their data acquisition, sample size, and PM inlet used for sampling are summarized in Table S1. Note that, due to some technical issues, the Xact did not collect continuous data from February 4 to 6, thus yielding a substantially smaller sample size ($N = 70$ for hourly averaged data points) than that obtained by other real-time instruments ($N > 120$). The real-time concentrations (resolution of 2 min) of carbon monoxide (CO) and nitrogen oxides (NO_x = NO + NO₂) were measured using collocated gas analyzers (Serinus 30 CO and Serinus 40 NO_x, Ecotech).⁴⁰ Data from the different instruments were averaged hourly 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 the mass concentration of nonrefractory (NR) PM₁ (estimated from the HR-ToF-AMS measurements by summing organics, SO₄²⁻ + NO₃⁻ + NH₄⁺ + Cl⁻). Note that the HR-ToF-AMS measured PM₁, while our DTT instrument measured PM_{2.5}. However, as shown in Figure S2 (and the related discussion), these different cutoff 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 (OAs) were the major contributors (average contribution of ~46%) to the total NR-PM₁ mass (Figure 1a). The DTT activity measured during the entire campaign ranged from 0.49 to 3.60 nmol min⁻¹ m⁻³, with an hourly averaged ($\pm 1\sigma$) value of 1.57 ± 0.7 nmol min⁻¹ m⁻³. This average value is ~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⁻¹ 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 the

southern Indian city of Bangalore (0.79 ± 0.13 nmol min⁻¹ m⁻³) during October 2013, but within the range of the OP_{ex} [0.09 – 3.04 nmol min⁻¹ m⁻³ for PM₁₀⁴² and 1.3 – 7.2 nmol min⁻¹ 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 the short duration of our sampling campaign, the range of OP_{ex} at Delhi was much wider than that of PM_{2.5} OP_{ex} reported in other cities of the world such as Chicago (0.04 – 1.28 nmol min⁻¹ m⁻³),⁴³ Atlanta (0.1 – 1.5 nmol min⁻¹ m⁻³),⁴⁴ Paris (0.1 – 0.36 nmol min⁻¹ m⁻³),⁴⁵ Rome (0.11 – 0.34 nmol min⁻¹ m⁻³),⁴⁵ Athens (0.1 – 0.36 nmol min⁻¹ m⁻³),⁴⁵ and Beijing (0.11 – 0.49 nmol min⁻¹ 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 of 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 the second half of the sampling campaign (February 7–9, 2019) were probably due to intermittent rain incidences (see Figure S3) in the area. A similar decrease in NR-PM₁ mass concentrations was also observed during this period (Figure 1a). We hypothesize that the rain during this period decreased the PM_{2.5} concentration (possibly by a wash-out mechanism)⁴⁷ in our study area, which could have led to an overall decrease in OP_{ex}. In general, the hourly averaged OP_{ex} measurements at Delhi roughly follow the hourly NR-PM₁ mass concentrations [$r = 0.66$; $P < 0.01$ (see the inset of Figure 1a)].

Figure 1b shows diurnal profiles of the hourly averaged OP_{ex} of ambient PM_{2.5} and NR-PM₁ mass concentration for the entire sampling campaign. The two prominent peaks observed in NR-PM₁ mass concentrations during the 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 night. We attribute this diurnal trend in NR-PM₁ mass concentration partially to the diurnal variation in the mixing layer height (high during the day and low during the night), use of domestic solid fuel for heating at night, and partitioning of semivolatile compounds (e.g., NH₄Cl and NH₄NO₃) to the particle phase at lower temperatures.^{7,11,12,48} In contrast, the diurnal OP_{ex} profile showed a dip during the morning to forenoon period (7:00–12:00) but an increase from noon and a peak at midnight. The ratio of the volume-normalized DTT activity (OP_{ex}) to NR-PM₁ 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, in which an increase in OP_{in} during the afternoon period was attributed to an increase in the concentration of photochemically formed secondary organic aerosols (SOAs).^{33,49,50} On the basis of 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

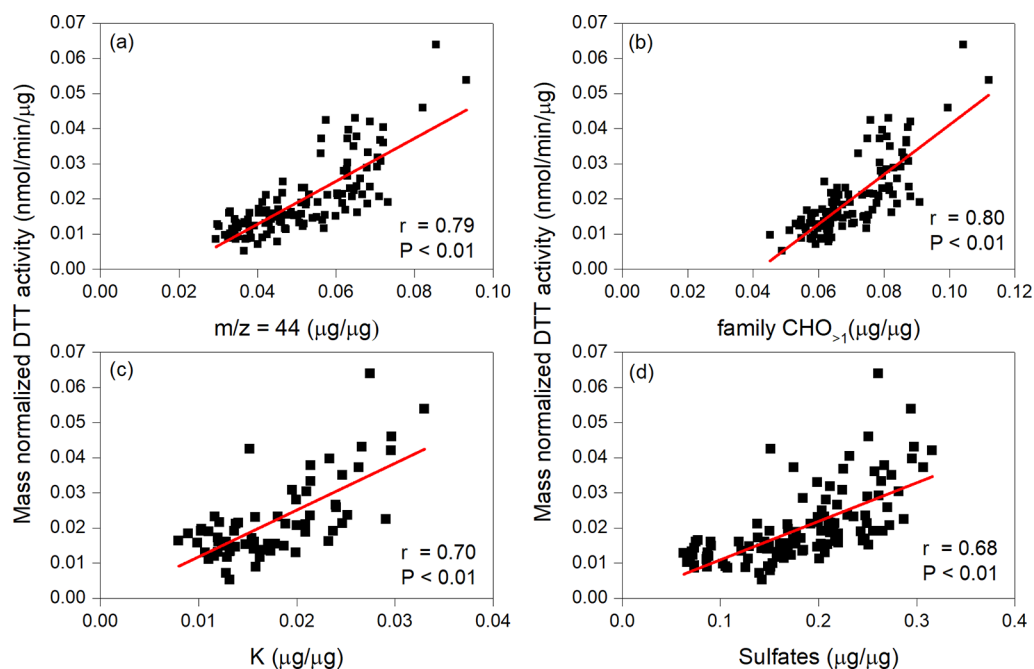


Figure 2. Simple linear regression between DTT activity and a few selected species (i.e., those for which $r > 0.60$) measured by the HR-ToF-AMS (PM_{10} fraction) and Xact ($\text{PM}_{2.5}$ fraction). Regression was done on the mass-normalized levels of both DTT activity and chemical constituents.

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 (nanomoles per minute per microgram, OP_{in}) and a few selected species (mass-normalized, i.e., micrograms per microgram of NR- PM_{10}) measured using the collocated HR-ToF-AMS and Xact instruments. A more detailed correlation matrix among various measured species is provided in Table S2. Note that the correlation can be performed on both volume-normalized and mass-normalized levels. However, the volume-normalized correlations are more susceptible to the confounding collinearity of the individual chemical species with $\text{PM}_{2.5}$ mass concentration. 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 that influence the intrinsic redox activity of ambient $\text{PM}_{2.5}$. We have also included the volume-normalized correlations in 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 $\text{CHO}_{>1}$ (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 the Supporting Information) 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 the HR-ToF-AMS showed a good correlation with OOA (m/z 44 and family $\text{CHO}_{>1}$; $r > 0.70$) (Table S2), indicating a substantial contribution to secondary photochemical particle formation by both SO_4^{2-} and OA. Note that 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 formation⁵³) and at

night (possibly due to lowering of the boundary layer as reported earlier). The tight correlation among SO_4^{2-} , OOA, and OP_{in} corroborates our hypothesis that photochemical formation and aging are some 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 study presented here, it showed a poor correlation with mass-normalized HR-ToF-AMS-measured BB emission 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 a good correlation with m/z 44 and $\text{CHO}_{>1}$ species [$r = 0.78$ (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 the related discussion).

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 $\text{PM}_{2.5}$. Despite limited measurements in the study presented here, 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} versus aerosol mass measured at Delhi ($\text{OP}_{\text{ex}} = 1.57 \pm 0.7 \text{ nmol min}^{-1} \text{ m}^{-3}$; average NR- $\text{PM}_{10} = 105 \pm 60 \mu\text{g}/\text{m}^3$) with the typical levels observed in our earlier study in Illinois ($\text{OP}_{\text{ex}} = 0.33 \pm 0.19 \text{ nmol min}^{-1} \text{ m}^{-3}$; average $\text{PM}_{2.5}$ concentration of $8 \pm 0.25 \mu\text{g}/\text{m}^3$)³³ clearly shows a nonproportional relationship between aerosol mass concentration and extrinsic DTT activity. Despite a >13-fold increase in the concentration of $\text{PM}_{2.5}$ mass, the increase in the extrinsic DTT activity is only 5-fold, which provides good arguments for studying the aerosol chemical composition in estimating its intrinsic toxicity. This

finding is consistent with mounting evidence of 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.

On the basis of 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 a weaker influence on DTT activity. Note that these results could be slightly biased due to the different particle collection efficiency of water-soluble (such as aged OAs, which tend to be more efficiently collected) versus 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 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.0c00342>.

Summary of the instruments used in the campaign, Pearson's *r* correlation matrices, schematic and description of the real-time OP instrument, comparison between PM₁ and PM_{2.5}, precipitation data, diurnal intrinsic OP profile, Van Krevelen diagram, diurnal SO₄²⁻ profile, and wind rose plot (PDF)

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Notes

The authors declare no competing financial interest.

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