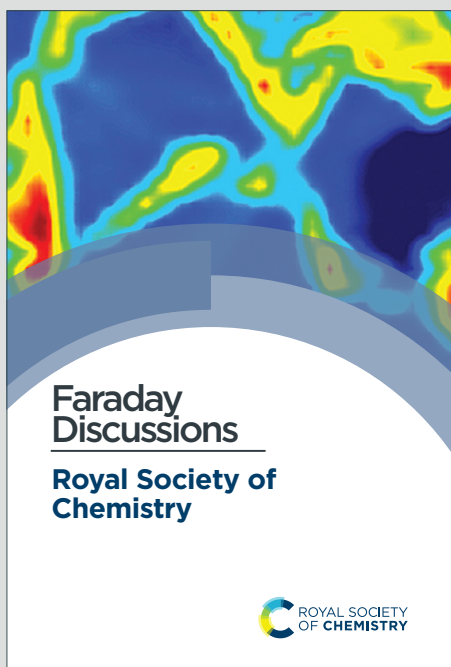


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## ARTICLE

## Avoiding high ozone pollution in Delhi, India

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Surface ozone is a major pollutant threatening public health, agricultural production and natural ecosystems. While measures to improve air quality in megacities such as Delhi are typically aimed at reducing levels of particulate matter (PM), ozone could become a greater threat if these measures focus on PM alone, as some air pollution mitigation steps can actually lead to an increase in surface ozone. A better understanding of the factors controlling ozone production in Delhi and the impact that PM mitigation measures have on ozone is therefore critical for improving air quality. Here, we combine in-situ observations and model analysis to investigate the impact of PM reduction on the non-linear relationship between volatile organic compounds (VOC), nitrogen oxides (NO<sub>x</sub>) and ozone. In-situ measurements of NO<sub>x</sub>, VOC, and ozone were conducted in Delhi during the APHH-India programme in summer (June) and winter (November) 2018. We observed hourly averaged ozone concentrations in the city of up to 100 ppbv in both seasons. We performed sensitivity simulations with a chemical box model to explore the impacts of PM on the non-linear VOC-NO<sub>x</sub>-ozone relationship in each season through its effect on aerosol optical depth (AOD). We find that ozone production is limited by VOC in both seasons, and is particularly sensitive to solar radiation in winter. Reducing NO<sub>x</sub> alone increases ozone, such that a 50% reduction in NO<sub>x</sub> emissions leads to 10-50% increase in surface ozone. In contrast, reducing VOC emissions can reduce ozone efficiently, such that a 50% reduction in VOC emissions leads to ~60% reduction in ozone. Reducing PM alone also increases ozone, especially in winter, by reducing its dimming effects on photolysis, such that a 50% reduction in AOD can increase ozone by 25% and it also enhances VOC-limitation. Our results highlight the importance of reducing VOC emissions alongside PM to limit ozone pollution, as well as benefitting control of PM pollution through reducing secondary organic aerosol. This will greatly benefit the health of citizens and the local ecosystem in Delhi, and could have broader application for other megacities characterized by severe PM pollution and VOC-limited ozone production.

## Introduction

Surface ozone exposure harms human health,<sup>1, 2</sup> reduces agricultural production<sup>3</sup> and threatens ecosystems.<sup>4, 5</sup> Rapid urbanization and expansion of traffic and industry have made ozone pollution an important air quality concern in India. In summer, the maximum hourly ozone concentration can reach as high as 140 ppbv

in the capital city Delhi.<sup>6</sup> This is comparable to the level in some polluted regions in China,<sup>7</sup> and higher than that in polluted areas in the U.S. and Europe.<sup>8-10</sup> About 12,000 premature deaths in India are estimated to have resulted from ozone exposure in 2011,<sup>11</sup> and this is likely to have increased during the past decade due to increasing anthropogenic emissions and commensurate increases in ozone.<sup>3, 12</sup> This estimate could be conservative, since a more recent study shows a much stronger risk of ozone-induced respiratory deaths than previous studies, especially over India where there may be an extra 40-60 deaths per 100,000 people.<sup>13</sup> However, most recent studies that have investigated mitigation of air pollution in Delhi focus on reducing particulate matter (PM).<sup>14-19</sup> Ozone could become a greater threat in India if mitigation measures focus on PM pollution alone,<sup>20</sup> as has recently been observed in China.<sup>21-23</sup> Thorough, science-based mitigation strategies to avoid high ozone pollution while also achieving goals for PM reduction are therefore urgently needed for India, especially for Delhi where a large population is regularly exposed to extremely unhealthy levels of air pollution.<sup>19, 24-28</sup>

Surface ozone is produced by solar radiation-driven photochemistry that involves nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and volatile organic compounds (VOC). Human economic activities, such as transport, power generation and industrial production, are major anthropogenic sources of NO<sub>x</sub> and VOC in the urban region of

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Delhi,<sup>20, 29</sup> and biogenic emission is an important additional source for VOCs.<sup>30</sup> VOCs of anthropogenic (such as toluene and benzene) and biogenic (such as monoterpene and isoprene) origin usually differ in species and possess different ozone production potentials.<sup>31, 32</sup> These gaseous VOCs are typically oxidized by hydroxy radicals (OH), which are photochemically produced from ozone, formaldehyde, HONO and other precursors in the presence of sunlight. The oxidation products facilitate ozone production in the daytime, in the presence of NO<sub>x</sub> (see ref. <sup>33</sup> and references therein). PM also has a large impact on ozone photochemistry by attenuating incoming solar radiation (aerosol dimming effect)<sup>34</sup> and by scavenging radicals.<sup>21, 22</sup>

Most studies to investigating ozone photochemistry in India have focused on the contribution of gaseous precursors to ozone production, attributing increases in ozone to the rapid increase in anthropogenic emissions.<sup>3, 6, 35-37</sup> Recent studies argue that a reduction in PM could also lead to an increase in ozone,<sup>20-22</sup> making the non-linear NO<sub>x</sub>-VOC-ozone relationship even more complex. A better understanding of this relationship is critical for formulating effective mitigation strategies to achieve the reduction in PM in Delhi whilst avoiding increased ozone pollution.

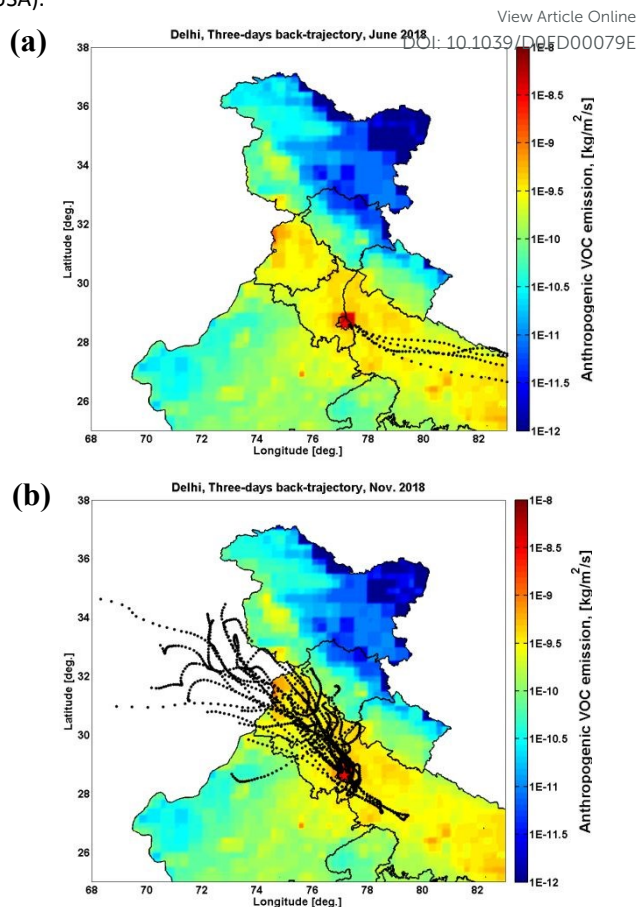
In this study, we combine in-situ observations and model analysis to improve understanding of the factors controlling ozone production in Delhi and investigate the impact of the aerosol dimming effect on the non-linear relationship between VOC, NO<sub>x</sub>, and ozone in summer and winter. We explore the relationship using a series of nearly nine thousand sensitivity simulations performed with a photochemical box model. To the best of our knowledge, this study presents the most exhaustive investigation of how the dimming effect of light scattering by PM impacts ozone photochemistry in Delhi. Our results provide guidance on the optimal choice of mitigation strategies to improve air quality in Delhi for both PM and ozone.

## Materials and Methods

### Observations

Measurements of ozone, NO<sub>x</sub>, CO and non-methane VOC concentrations near the surface were made during 1-8<sup>th</sup> June and 5-23<sup>rd</sup> November 2018 in Delhi, during the APHH-India programme (<https://www.urbanair-india.org/>). The observational site is located at the Indira Gandhi Delhi Technical University for Women (IGDTUW, 28.665°N, 77.232°E), at 7 m above ground level in June and at 35 m in November. The IGDTUW campus is located in the densely populated district of Old Delhi. Ozone concentrations were measured with a TEI 49C UV absorption analyser, which was calibrated to the UK's National Physical Laboratory standard using a TEI 49PS. NO<sub>x</sub> concentrations were measured with a dual-channel high-resolution chemiluminescence instrument (Air Quality Designs Inc., Colorado). CO concentrations were measured with an Aerolaser AL 5002 UVU instrument. VOC concentrations were measured using a Proton Transfer Reaction-Quadrupole ion guide Time of Flight-Mass Spectrometer (PTR-QiTOF 2000, Ionicon Analytik, Innsbruck, Austria). The instruments for NO<sub>x</sub> and CO measurements were well calibrated during the observations using procedures similar to those described by ref. <sup>38</sup>. The PTR-QiTOF was calibrated daily using a 19

component VOC standard (Apel-Riemer Environmental, Miami, USA).



**Figure 1. Three-day air mass back-trajectory for Delhi, for the selected days in June (a) and November (b).** The back-trajectories for 00:00 and 12:00 UTC on each day are calculated based on the high-resolution meteorology field from WRF model. The background colors indicate the anthropogenic VOC emissions from EDGAR-HTAP 2010 dataset (<https://edgar.jrc.ec.europa.eu/>). The data of the boundaries of administrative areas are sourced from <https://gadm.org/>.

This standard was dynamically diluted into zero air to provide a three point calibration. Background measurements were made hourly using zero air. In order to focus on ozone photochemical production, we selected data obtained on clear-sky days when photochemistry was the major factor governing the diurnal variation of ozone, as indicated by sinusoidal behaviour.<sup>31</sup> Data from the 2<sup>nd</sup> and 4<sup>th</sup> June 2018, and 9<sup>th</sup>, 10<sup>th</sup>, 12-15<sup>th</sup>, 17-19<sup>th</sup>, and 21-23<sup>rd</sup> November 2018 were analysed in this study. Surface temperature and relative humidity were recorded at Indira Gandhi International Airport in Delhi, which is about 17 km southwest of the observational site. These meteorological data were obtained from the National Oceanic and Atmospheric Administration, National Climatic Data Center (<https://www.ncdc.noaa.gov/>), as described in ref. <sup>39</sup>. The planetary boundary layer height was adopted from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-interim model reanalysis at a spatial resolution of 0.125° × 0.125° and 3-hour temporal resolution (<https://www.ecmwf.int/>). These ECMWF



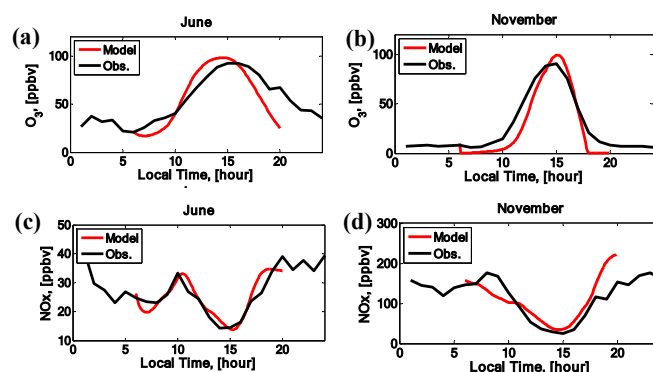
reanalysis data were also used to drive the Weather Research and Forecasting Model (WRF, <https://www.mmm.ucar.edu/weather-research-and-forecasting-model>). WRF simulations were performed over two nested domains, an outer domain covering the whole of India and surrounding regions to minimize the boundary impacts on meteorology simulation over India, and an inner domain over north India at a horizontal resolution of 15 km, as detailed in ref. <sup>20</sup>. We apply the Hysplit back-trajectory model (<https://www.ready.noaa.gov/HYSPLIT.php>) using high resolution hourly meteorology from WRF to provide detailed transport footprints for air masses arriving in Delhi. For the selected days, the air masses exclusively came from the southeast in June but from the northwest in November (Fig. 1), indicating a consistent background for the observations throughout each period. The Terra-MODIS aerosol optical depth (AOD at 550 nm wavelength) over Delhi was about 1.2 and 0.8 in June and November, respectively (MOD08\_M3 level-3 product<sup>40</sup>). These monthly average AOD values were adopted for calculating the present-day aerosol dimming effect in the model simulations.

### Model description

To investigate how the control of PM, VOC and NO<sub>x</sub> emissions can impact ozone pollution, we performed sensitivity simulations using the National Center for Atmospheric Research Master Mechanism photochemical box model (NCAR-MM version 2.5, <https://www2.aom.ucar.edu/modeling/ncar-master-mechanism>). This model includes a detailed gas phase chemical mechanism coupled with the Tropospheric Ultraviolet and Visible (TUV, version 5.0) radiation scheme. In the TUV scheme, the four-stream radiative transfer equations are solved within the wavelength range of 120–735 nm to account for the scattering and absorption of shortwave radiation by gases, particles and clouds in the atmosphere, thereby calculating photolysis rates to drive the chemical mechanism.<sup>41</sup> In this study, 1267 gaseous species and 3699 reactions were considered in the chemical mechanism and integrated with a Gear solver, a benchmark solver for comprehensive chemical mechanisms.<sup>42</sup>

The NCAR-MM model was used to simulate the photochemical evolution of an air parcel over Delhi using the temperature, relative humidity and planetary boundary layer height datasets. To simulate ozone evolution in the daytime, we initialize model simulations in the early morning (6:00 am, local time) before the onset of rapid photochemistry and end simulations in the evening (8:00 pm). The initial concentrations of ozone, NO, NO<sub>2</sub>, CO, VOC and AOD were constrained to the observed averages at 6:00 am in June and November. We applied an iterative approach to adjust the NO<sub>x</sub> and VOC emissions for the base case simulation, to capture the ozone diurnal pattern and reproduce hourly peak ozone within 10% uncertainty, as shown in Fig 2a and 2b. In the base case, the diurnal variation of NO<sub>x</sub> is also reproduced when ozone is developing, and the uncertainty of NO<sub>x</sub> concentration is within 10% at ozone peak timing, as shown in Fig. 2c and 2d. NO<sub>x</sub> concentrations are overestimated at 6:00–8:00 pm in November, but this does not influence simulation of the daytime development of ozone in our analysis. This overestimation may be due to neglect of heterogeneous chemistry in the model, therefore missing the chemical sinks of NO<sub>x</sub> that lead to production of particulate nitrate, the concentration of which is about four times higher in winter than

in summer.<sup>43</sup> We use toluene emissions as a proxy to represent the ozone produce potential of anthropogenic VOCs emissions. Note that these constrained VOC and NO<sub>x</sub> emission fluxes (see Fig. S1) represent effective emissions that include the influences of fresh emissions, transport processes, and effects from dilution and deposition, and they are therefore not directly comparable with observed fluxes or emission inventories. We then performed 8820 sensitivity simulations for each season varying the NO<sub>x</sub> emission (0% to 200% at 10% intervals), VOC emission (0% to 200% at 10% intervals), and AOD (twenty different values in the range of 0–3.0). Based on this large set of sensitivity simulations, we investigated the factors governing ozone production in each season in Delhi, the non-linear NO<sub>x</sub>–VOC–ozone relationship and how AOD impacts this relationship. We then demonstrate mitigation strategies that reduce both ozone and PM in Delhi, based on our results.



**Figure 2. Observed and simulated ozone and NO<sub>x</sub> diurnal variations.** (a) Ozone in June; (b) ozone in November, (c) NO<sub>x</sub> in June, and (d) NO<sub>x</sub> in November. The black line indicates observations and the red line indicates NCAR-MM model results.

## Results and Discussion

### Factors controlling ozone production in Delhi

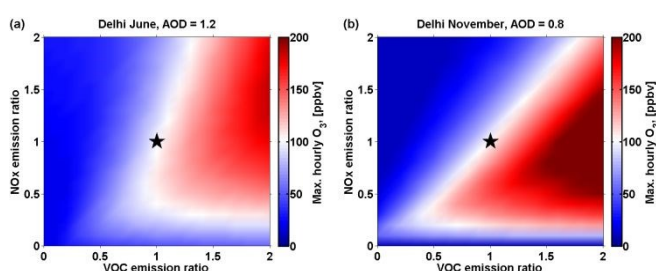
As shown in Fig. 2, hourly ozone concentration can approach ~100 ppbv in both summer and winter in Delhi. In June, the daily average NO<sub>x</sub> concentration was ~30 ppbv for the days considered and hourly averaged NO<sub>x</sub> was ~16 ppbv when ozone approached its daily peak at around 3:00 pm. Toluene, a good indicator of anthropogenic VOC, had a daily average of 3.5 ppbv and hourly average of 2.4 ppbv at around 3:00 pm. Total monoterpenes, a good indicator of biogenic VOC, had a daily average of 0.8 ppbv and hourly average of 0.6 ppbv at 3:00 pm. In November, the daily average NO<sub>x</sub> concentration was ~120 ppbv for the days considered and hourly NO<sub>x</sub> was ~25 ppbv when ozone approached its daily peak. Toluene reached a daily average of 19.1 ppbv (hourly average of 5.1 ppbv at peak ozone) and total monoterpenes reached a daily average of 8.5 ppbv (hourly average of 2.6 ppbv at peak ozone). This situation of much higher NO<sub>x</sub> than toluene and monoterpenes in Delhi is similar to that in Shanghai, where ozone production is VOC-limited.<sup>31</sup>

Under these high-NO<sub>x</sub> conditions, ozone production in Delhi is limited by the abundance of VOC in both summer and winter in Delhi. Model results for June (Fig. 3a) show that daily maximum hourly ozone concentration increases as VOC emissions increase. A 50%





increase in VOC emissions could increase the maximum hourly ozone concentration by 50%, from  $\sim 100$  ppbv to  $\sim 150$  ppbv, while a 50% reduction could decrease ozone by 60%, to  $\sim 40$  ppbv. In contrast, a 50% increase in NO<sub>x</sub> emission would decrease ozone by 20%, to  $\sim 80$  ppbv in June, while a 50% reduction would increase ozone by 5%, to  $\sim 105$  ppbv. Decreasing ozone with NO<sub>x</sub> controls alone would require a reduction in NO<sub>x</sub> emissions of more than 65%. VOC limitation on ozone production in Delhi is even more pronounced in November (Fig. 3b), and a 50% increase in VOC emissions could increase maximum hourly ozone concentration by 80%, from  $\sim 100$  ppbv to  $\sim 180$  ppbv, while a 50% reduction would decrease ozone by 65%, to  $\sim 35$  ppbv. The titration of ozone by NO is also much stronger in November, and a 50% increase in NO<sub>x</sub> emissions could reduce ozone by 50%, to  $\sim 50$  ppbv. A reduction in NO<sub>x</sub> emissions of more than 80% would be needed to reduce daily maximum ozone in November under current VOC concentrations.



**Figure 3.** Daily maximum hourly ozone in Delhi as a function of NO<sub>x</sub> and VOC emissions in (a) summer (June) and (b) winter (November). Current conditions are marked by a black star.

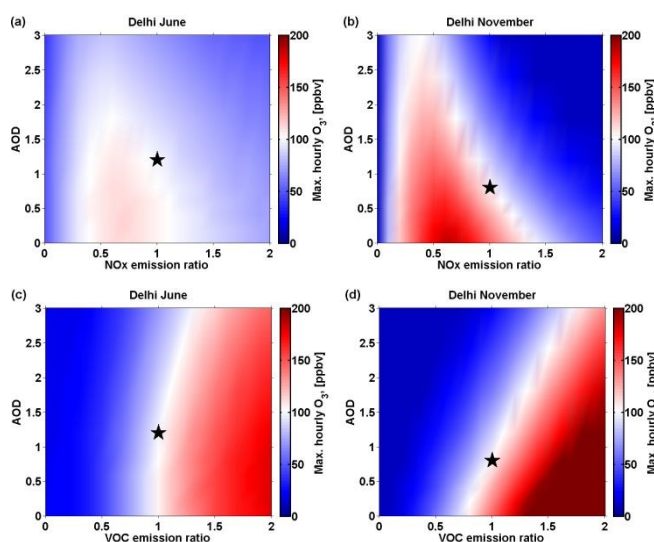
The sensitivity of ozone to VOC emissions, defined here as the change in ozone associated with a change in VOC emissions in a range of  $\pm 50\%$ ,  $\Delta O_3 / \Delta \text{VOC}_{\text{emission}}$ , is about 30% greater in November than in June. This stronger VOC limitation in November than in June is likely to be the result of weaker solar radiation and a shallower planetary boundary layer in this season. Based on ECMWF reanalysis, we find an early afternoon planetary boundary layer height of about 1800 m in November but about 2500 m in June. The weaker mixing in November constrains the greater amount of freshly emitted NO<sub>x</sub> in the surface layer, and enhanced VOC limitation. Weaker solar radiation could also enhanced the VOC limitation, as discussed in the next section. Our results are consistent with previous studies that have shown ozone production is typically VOC-limited in urban environments,<sup>31, 44, 45</sup> but highlights the extent of this in Delhi in both the summer and winter seasons.

#### Impact of aerosol changes on ozone production

Atmospheric aerosol, represented here by AOD, can strongly influence ozone photochemistry and thus alters the NO<sub>x</sub>-VOC-ozone relationships shown above. In June, the midday photolysis rate of NO<sub>2</sub>,  $J[\text{NO}_2]$ , increased by 3% (from  $9.7 \times 10^{-3} \text{ s}^{-1}$  to  $10.0 \times 10^{-3} \text{ s}^{-1}$ ) when AOD is reduced by 50%. In November the midday photolysis rate increased by 14% (from  $7.0 \times 10^{-3} \text{ s}^{-1}$  to  $8.0 \times 10^{-3} \text{ s}^{-1}$ ) for 50% reduction in AOD. These  $J[\text{NO}_2]$  values are lower than reported values in Beijing for June and November<sup>34</sup> even though Delhi is closer to the Tropics. This is due to the heavier aerosol loading in Delhi,

where the AOD is about 0.4 larger than in Beijing in both summer and winter and exerts a greater dimming effect.

Figure 4 shows that a 50% reduction in AOD increases maximum hourly ozone concentrations by 5%, from  $\sim 100$  ppbv to  $\sim 105$  ppbv in June, but increases it by 25%, to  $\sim 125$  ppbv, in November. This highlights that wintertime ozone production is not only VOC-limited but also strongly radiation-limited in Delhi. The sensitivity of ozone to VOC emission also increases as AOD decreases in November (Fig. 4d). This is likely to be because stronger solar radiation significantly enhances photochemical processing and local ozone production from VOC oxidation in Delhi. In contrast, changes in AOD of  $\pm 50\%$  do not significantly influence the sensitivity of ozone to NO<sub>x</sub> and VOC emissions in June (Fig. 4a and Fig. 4c), see also Fig. S2. A detailed tomography figure of the non-linear AOD-NO<sub>x</sub>-VOC-ozone relationship is given in Fig. S3. These results highlight that aerosols play a critical role in the photochemistry of ozone production, and this is overlooked in most previous mitigation strategy studies and needs to be fully considered when developing a comprehensive regulatory framework for the control of surface ozone pollution.



**Figure 4.** The impact of AOD on the non-linear VOC-NO<sub>x</sub>-ozone relationship in Delhi. (a) Impact on relationship between NO<sub>x</sub> and ozone in summer (June), (b) between NO<sub>x</sub> and ozone in winter (November), (c) between VOC and ozone in summer, and (d) between VOC and ozone in winter. Current conditions are marked by a black star.

#### Mitigation strategies to avoid high ozone

The Central Pollution Control Board of India (CPCB) reports that measures currently adopted to improve the air quality in Delhi focus mainly on controlling traffic, biomass burning, industrial and construction emissions.<sup>46</sup> These mitigation strategies address PM pollution,<sup>14-19, 46, 47</sup> but do not reduce VOC sufficiently to avoid ozone increase. Traffic is the major target of the current mitigation measures and is the largest VOC emission source within Delhi contributing  $\sim 80$  kiloton/year (60%),<sup>48</sup> but control of traffic emissions alone can lead to large ozone increases due to the associated reduction in NO<sub>x</sub> and PM (Fig. S4).<sup>20</sup> Transport from domestic emissions in surrounding regions could contribute substantially to



VOC in Delhi (Fig. 1). For example, VOC emitted from domestic sources in Uttar Pradesh (southeast of Delhi) and Haryana (northwest of Delhi) are about 1100 kiloton/year and 110 kiloton/year, respectively, which are much larger than local traffic emissions in Delhi.<sup>48</sup>

Our results suggest that strategies reducing PM under current conditions will lead to enhanced, and possibly severe, ozone pollution. Reduction in PM enhances surface solar radiation and ozone production, and also weakens the removal of hydroperoxyl radicals on particle surfaces, therefore further enhancing ozone production.<sup>21,22</sup> The importance of later mechanism remains unclear,<sup>49</sup> and as more comprehensive observations are needed to quantify the impacts, it is not included here. The increase in ozone from measures to control PM could therefore be even greater than we show here. Our results suggest that control of VOC emissions is critical to avoid high ozone pollution in Delhi while also achieving the intended air quality goal of reduced PM levels. In addition, VOC is an important precursor of PM in Delhi where large fractions of secondary organic aerosol are present in all seasons.<sup>43</sup> Reducing VOC emissions is therefore a key measure to benefit Delhi air quality with respect to both PM and ozone pollution, while avoiding the trade-offs associated with other PM mitigation measures. Regional joint intervention with more attention on domestic sources would be required for controlling VOC and avoiding high ozone pollution in Delhi. Future studies to characterize the VOC species, apportion their sources, and investigate their potentials for ozone production and secondary organic aerosol formation in Delhi would be particularly useful. These studies would provide further insight and help inform more effective and targeted mitigation strategies.

## Conclusions

Measurements of ozone and its precursors were performed in June and November 2018 in Delhi, India. High ozone pollution with hourly concentration up to ~100 ppbv was observed in both seasons. We performed nearly nine thousands simulations using a photochemical box model to investigate the contributions of VOC and NO<sub>x</sub> emissions to ozone production, and to explore the influence of aerosol dimming on ozone photochemistry. We find that ozone production in Delhi is limited by VOC concentrations in both seasons, but particularly strongly in winter. In addition, ozone production in winter is strongly limited by solar radiation. Therefore, some measures to reduce PM could increase ozone through increased photolysis, especially in winter, and this effect would be exacerbated as it also enhances the extent of VOC-limitation. High ozone, and consequently high OH radical, could facilitate the oxidation of gaseous precursors and enhance secondary formation of PM,<sup>50</sup> and this could partly offset the reduction in PM. This effect is not investigated in this study and should be quantified in future studies.

These results highlight the importance of controlling VOC emissions alongside particulate matter and NO<sub>x</sub>, which is overlooked in current mitigation strategies for Delhi. This would help to avoid major problems with ozone pollution in Delhi whilst reducing particulate matter. Measures that focus on particulate matter alone could see ozone increases alongside reduction in particulate matter, as has happened recently in China.<sup>21-23</sup> Furthermore, reductions in VOC emissions could

contribute to mitigation of particulate matter, a high fraction of which is sourced from semi-volatile organic compounds, the oxidation products of VOCs.<sup>43</sup> Therefore, reducing VOC emissions is a win-win measure with respect to both ozone and particulate matter pollution in Delhi. High ozone pollution not only has negative impacts on human health but also on agriculture and ecosystems.<sup>4, 5</sup> These measures would benefit the health of citizens and ecosystems in Delhi, with potential broader application in other megacities worldwide characterized by VOC-limited ozone production.

## Conflicts of interest

The authors declare no competing financial interest.

## Statement of contributions

YC and OW conceived the study. YC performed the simulations, processed and interpreted the results with help from all co-authors. GB, WD, WJFA, BN, JL, SKS, RSS, VS, RG, CNH and EN organized the APHH-India campaign and performed the observations. SAN, AA, DL and GM contributed to the WRF simulation and chemistry interpreting. RL, YW and ZW helped with the NCAR-MM model simulation. YC wrote the manuscript with inputs from all co-authors.

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