Letter

Extreme Concentrations of Nitric Oxide Control Daytime Oxidation and Quench Nocturnal Oxidation Chemistry in Delhi during Highly Polluted Episodes

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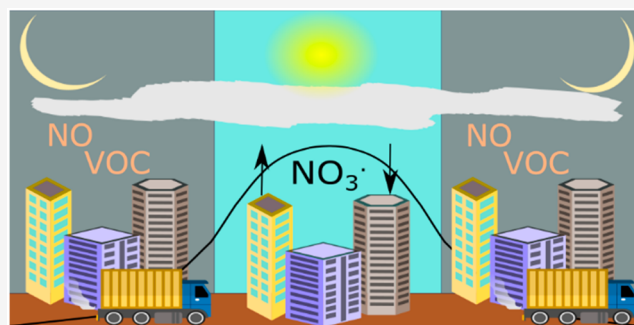
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ABSTRACT: Delhi, India, suffers from periods of very poor air quality, but little is known about the chemical production of secondary pollutants in this highly polluted environment. During the postmonsoon period in 2018, extremely high nighttime concentrations of NO_x (NO and NO_2) and volatile organic compounds (VOCs) were observed, with median NO_x mixing ratios of ∼200 ppbV (maximum of ∼700 ppbV). A detailed chemical box model constrained to a comprehensive suite of speciated VOC and NO_x measurements revealed very low nighttime concentrations of oxidants, NO_3, O_3, and OH, driven by high nighttime NO concentrations. This results in an atypical NO_3 diel profile, not previously reported in other highly polluted urban environments, significantly perturbing nighttime radical oxidation chemistry. Low concentrations of oxidants and high nocturnal primary emissions coupled with a shallow boundary layer led to enhanced early morning photo-oxidation chemistry. This results in a temporal shift in peak O_3 concentrations when compared to the premonsoon period (12:00 and 15:00 local time, respectively). This shift will likely have important implications on local air quality, and effective urban air quality management should consider the impacts of nighttime emission sources during the postmonsoon period.

KEYWORDS: *air quality, atmospheric oxidation chemistry, nocturnal atmospheric chemistry, ozone, VOC*

■ INTRODUCTION

Delhi, India, is one of the most polluted megacities in the world and has previously been shown to have levels of numerous air pollutants such as particulate matter (PM), NO_x (NO and NO_2), O_3, SO_2, and CO significantly above World Health Organization (WHO) guidelines.[1−4] High concentrations have led to an increase in morbidity and premature mortality, leading to economic losses.[5−7] Exposure to air pollution has been shown to reduce life expectancy on average by six years in Delhi.[8] Previous studies have highlighted significant amounts of premature mortality within Delhi, with estimates of up to 12 000 deaths per year associated with poor air quality.[3]

Measured concentrations of volatile organic compounds (VOCs) and NO_x in Delhi are among the highest recorded in a polluted urban environment, on a scale similar to those observed in Los Angeles in the 1970s.[9] The concentrations of pollutants are especially high during the winter periods, largely due to emissions from the burning of crop residues, domestic

heating, cooking, along with local meteorology.[10−17] High NO_x concentrations have been observed throughout the year,[2] with the highest observed during winter, and nighttime concentrations on average of >100 ppbV.[18,19] Within Delhi, the transport sector is the dominant source of NO_x emissions, accounting for 66−74%.[20] Of these transport emissions, heavy goods vehicles (HGVs) make the largest contribution (>50%).[21] To combat transport pollution, the Government of National Capital Territory of Delhi introduced prohibitive regulations impacting the transport of goods into and out of the city. Prohibitions on the movement of goods vehicles vary
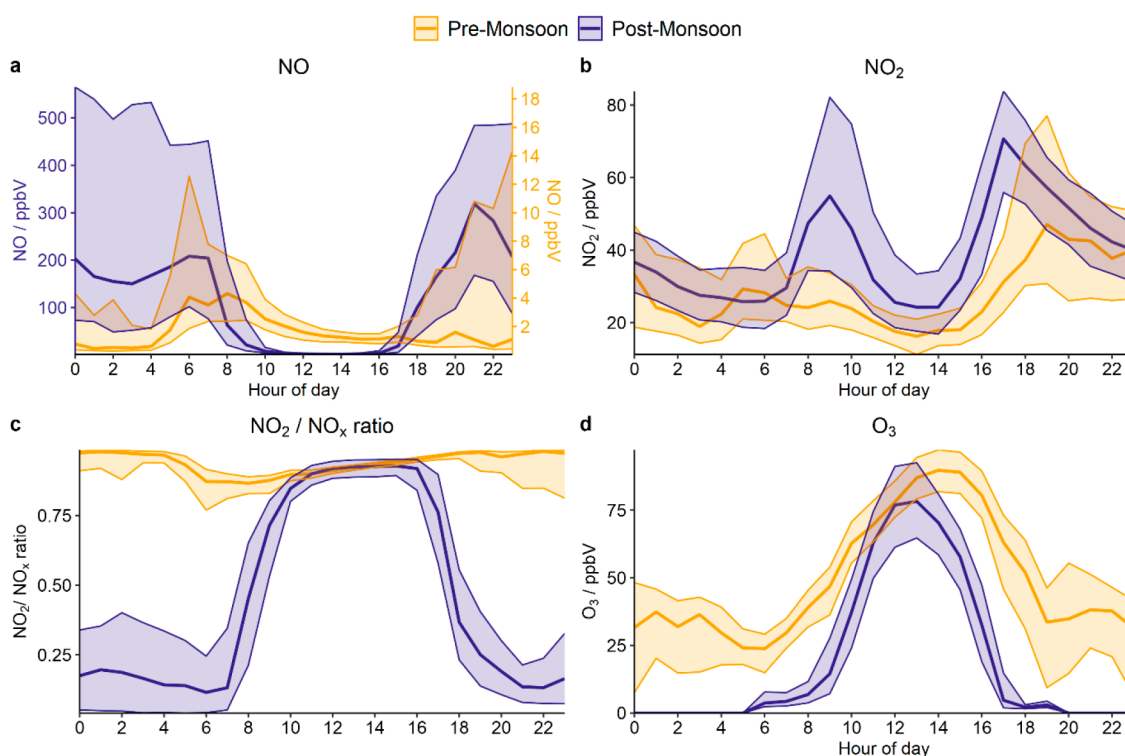
Figure 1. Median diel profiles of (a) NO, (b) NO_2, (c) NO_2:NO_x ratio, and (d) O_3 measured during the premonsoon (yellow) and postmonsoon (purple) campaigns. Note that pre/postmonsoon NO values are plotted on separate *y*-axes owing to the large differences in observed mixing ratios. The shaded region represents the interquartile range.

across Delhi but generally restrict HGVs during peak times for passenger vehicles [07:00−11:00 and 17:00−23:00 Indian Standard Time (IST)].[22] These daytime restrictions lead to increased HGV movement at night, and thus increased nighttime emissions. Delhi also suffers from unfavorable meteorological conditions, with shallow boundary layer heights and low wind speeds leading to stagnant conditions, especially during the winter. This, in turn, allows for the accumulation of pollutants at night, exacerbated by the high emission rates.[23]

The nature of radical chemistry at night, when pollution is high, may have significant consequences on the subsequent daytime oxidation chemistry and secondary pollution formation. A recent study by Bryant et al. presented evidence of the removal of nighttime NO_3 radicals by NO in Delhi via a decrease in the concentration of isoprene-derived nitrooxyorganosulfate (NOSi) species produced via NO_3 oxidation chemistry.[24] In addition, a study by Nelson et al., corroborated by Chen et al., found central Delhi to be VOC-limited with respect to O_3 production and significant titration of O_3, owing to very high NO concentrations at night during the winter periods.[18,19] The ratio of NO_x to non-methane VOCs has also been shown to impact rates of secondary organic aerosol formation.[25] These studies have highlighted the importance of reducing levels of VOCs alongside those of NO_x, to mitigate both O_3 and PM formation. Our findings build on the work by Nelson et al. and Bryant et al. by focusing on the role NO plays in regulating OH and NO_3 radical concentrations within Delhi.[19,24] The unique chemistry investigated in this study deviates from our typical understanding of nocturnal radical oxidation chemistry and has important policy implications, highlighting the need to reduce nighttime NO_x emissions alongside VOC emissions, to not further exacerbate PM and O_3 concentrations through secondary formation.

■ METHODOLOGY

Description of the Site. The APHH-India Delhi Flux campaigns took place during the premonsoon (May 28−June 5, 2018) and postmonsoon (October 4−November 5, 2018) periods. The primary site was located on the campus of the Indira Gandhi Delhi Technical University for Women in Delhi. The campus is situated close to major roads and highways, including National Highway 44 (0.3 km east). The campus has some green areas and is mostly pedestrianized with low-level traffic activity from delivery cars, taxis, and auto rickshaws. Observations were made from the roof of a one-story building (∼5 m) and included levels of VOCs, o-VOCs, NO_x, CO, SO_2, O_3, and HONO, photolysis rates, PM, and meteorological measurements. Further details on the site can be found in ref 19.

VOC Measurements. VOCs were measured via a dual-channel gas chromatography flame ionization detector (DC-GC FID, C_2−C_8), a two-dimensional GC flame ionization detector (GC × GC-FID, C_6−C_{13}), and a proton transfer reaction time-of-flight mass spectrometer with a quadrupole ion guide (PTR-QiTOF, Ionicon Analytik, Innsbruck, Austria). The two GC instruments shared an inlet, located 5 m above ground level. The sample line from the inlet to the laboratory was made from $1/2$ in. (outside diameter) perfluoroalkoxy (PFA) and was heated. VOCs were calibrated using standard cylinders containing a variety of VOCs. Further details can be found in refs 19 and 26.

Measurements of NO_x, O_3, and HONO. Measurements of nitrogen oxides (NO and NO_2) were made using a dual-channel chemiluminescence instrument (Air Quality Designs Inc.) that was calibrated every 2−3 days throughout the campaign using standard gas cylinders from the National
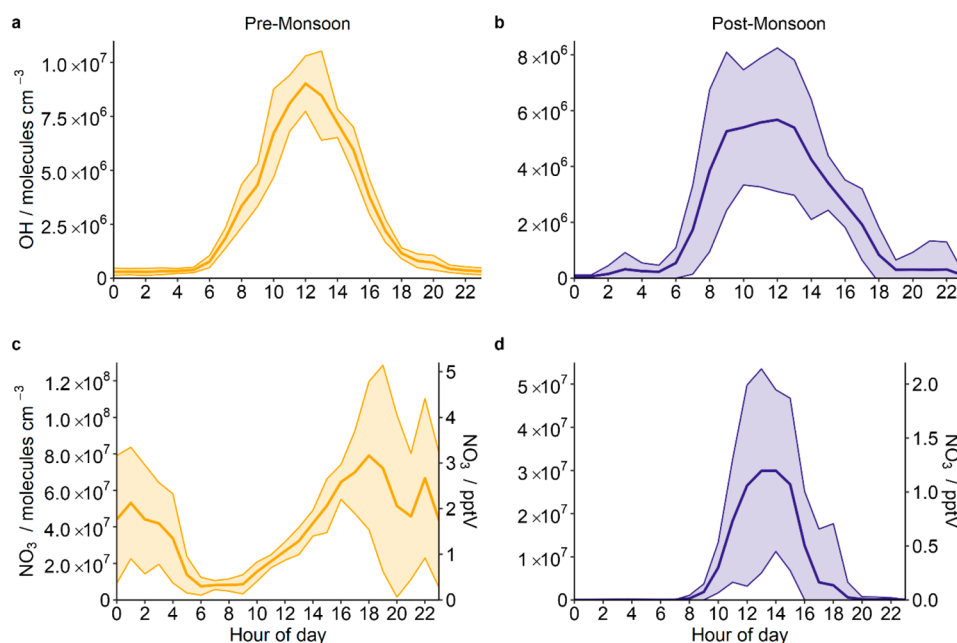
Figure 2. Mean diel variations of modeled OH and NO_3 concentrations across the (a and c) premonsoon and (b and d) postmonsoon periods. The shaded band represents one standard deviation from the mean. Note that the y-axis scales on all plots are distinct.

Physical Laboratories in the U.K. O_3 was measured using an O_3 analyzer (49i, Thermo Scientific). The instrument setup and calibration methodology are as described by Squires et al.[27] HONO was measured using a long-path absorption photometer (LOPAP) with baseline measurements taken at regular intervals (8 h). Further details along with measurement descriptions for the aerosol surface area, photolysis rates, and meteorological data can be found in refs 19 and 22.

Description of the Model. Two campaign-tailored zero-dimensional chemical box models (premonsoon and postmonsoon) incorporating a subset of the Master Chemical Mechanism (MCM version 3.3.1)[28,29] were used to investigate radical production chemistry, utilizing the AtChem2 modeling toolkit.[30] The pre- and postmonsoon models were constrained to the measured concentrations of ambient VOCs (57 and 86, respectively), NO_x, CO, O_3, SO_2, aerosol surface area (postmonsoon only), 34 photolysis rates derived from the measured photolysis frequencies of $j(O^1D)$, $j(NO_2)$, and $j(HONO)$, temperature, pressure, and relative humidity. The premonsoon model was constrained to a reduced range of VOCs due to the concentration of some species being below the instrumental limits of detection. Measurement data were averaged or linearly interpolated to 15 min time resolution prior to inclusion in the models. The first 24 h of measurements were repeated for 3 days prior to the full campaign time series. These modeled data were then discarded before analysis to ensure radical spin-up was achieved. Measured species not described in the MCM were incorporated using a surrogate mechanism (Table S1), chosen on the basis of the structural similarity to the species of interest (more details in ref 19). For these species, reaction rates with OH, HO_2, and NO_3 were set to values found in the IUPAC evaluated chemical kinetics database.[31,32] For both campaigns, a fixed deposition rate of 1.2×10^{-5} s^{-1} was applied to all model-generated species, resulting in a lifetime with respect to dry deposition of ~24 h. Where vertical velocity data were available (postmonsoon only), the concentration of HONO

was adjusted to account for variations within the vertical profile due to its very short lifetime relative to that of VOCs, and the atmospheric mixing time.[33] This adjustment is particularly important for the postmonsoon period, given the very high levels of HONO measured at ground level. The model also accounted for aerosol uptake of HO_2. A more detailed description of the adjustments to HONO observations, calculation of photolysis rates, and HO_2 uptake is presented in ref 19.

■ RESULTS

The median diel profiles of NO mixing ratios observed during both campaigns are shown in Figure 1. The observed NO levels are at a minimum during the day, likely driven by differences in emissions but also corresponding to the period during which the planetary boundary layer height (PBLH) is greatest (Figure S1). The reaction of NO with O_3 converts NO to NO_2, resulting in NO mixing ratios in the afternoon of ~1−2 ppbV. The NO_2:NO_x ratio in the afternoon is ~0.92−0.96, indicating a high NO_2 conversion rate under strong photochemically active conditions. In the evening, a shallow nocturnal boundary layer is formed (Figure S1), leading to a rapid increase in the mixing ratio of NO. The nighttime PBLH minimum is much lower during the postmonsoon period (median PBLH is 33 m, vs 210 m during the premonsoon), leading to a median nocturnal mixing ratio of 200 ppbV for NO, ~400 times higher than during the premonsoon period (~0.50 ppbV). On some nights, extremely high NO mixing ratios were observed, up to a maximum of ~700 ppbV.[19] Simultaneously, O_3 mixing ratios decreased due to reaction with NO, with median nocturnal O_3 mixing ratios in the postmonsoon period of <2 ppbV, compared to ~30 ppbV during the premonsoon period (Figure 1). However, measured nighttime O_3 concentrations should be treated with caution as chemical interference from, for example, aromatic compounds can cause small positive artifacts.[34] The extremely high levels of NO at night during the postmonsoon period are likely to
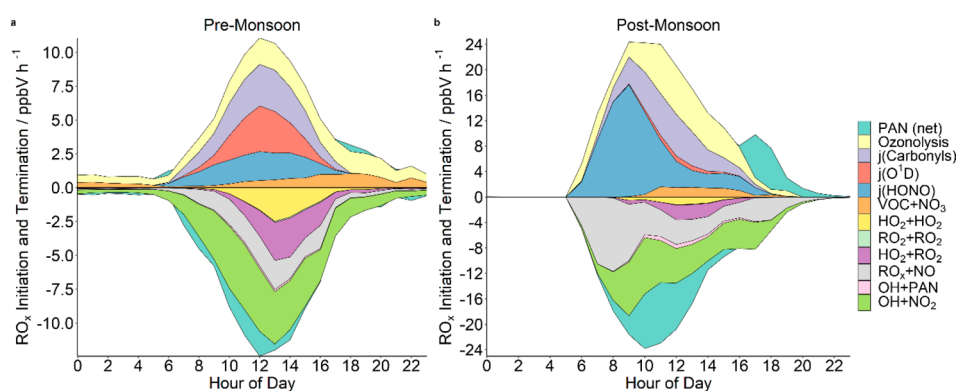
Figure 3. Stacked area plots showing the average modeled diel production (initiation, positive) and loss (termination, negative) rates for OH + HO$_2$ + RO$_2$ (RO$_x$) radicals during the (a) premonsoon and (b) postmonsoon campaigns, under zero oxidant nighttime conditions during the postmonsoon period. PAN (net) refers to the PAN $\rightleftharpoons$ CH$_3$CO$_3$ + NO$_2$ equilibrium, where CH$_3$CO$_3$ is being formed in the positive direction (PAN loss) and being lost in the negative direction (PAN formation). Note the magnitudinal difference between the y-axes scales on the two plots.

entirely remove all nighttime O$_3$ through chemical titration, evidenced by model simulations of O$_3$ (Figure S2). The lifetime of NO in a typical urban atmosphere is relatively short, such that NO$_2$:NO$_x$ ratios can increase significantly within tens of seconds after emission.[35] Overnight, the postmonsoon NO$_2$:NO$_x$ ratio was ~0.15 on average, indicative of direct combustion emissions of NO.[36] The observed ratio is comparable to previous observations in road tunnels, indicating a lack of NO oxidation at night in Delhi once all of the O$_3$ produced during the day has been consumed.[37]

NO$_x$ plays a key role in the production of all three major oxidants (OH, NO$_3$, and O$_3$) in polluted atmospheres and therefore impacts radical production and loss.[32,38] VOC oxidation is predominantly driven by OH and O$_3$ during the day and NO$_3$ and O$_3$ at night. We used an observationally constrained zero-dimensional chemical box model to predict short-lived radical oxidant concentrations during the pre- and postmonsoon periods. During the premonsoon period, the OH radical followed the expected diel profile, peaking at solar noon with a concentration of ~9 × 10^6 molecules cm^{-3} (Figure 2a). During the postmonsoon period, the OH radical concentrations peak in the morning, reaching a maximum of 6 × 10^6 molecules cm^{-3} at 9:00 IST which begins to decrease only after 13:00 IST (Figure 2b). NO$_3$ showed more significant seasonal differences. During the premonsoon period, the modeled NO$_3$ concentrations peaked just after sunset (17:00–19:00 IST, 8 × 10^7 molecules cm^{-3}, 3.2 pptV) and remained high overnight before rapidly decreasing after sunrise due to photolysis (Figure 2c). NO$_3$ concentrations then increased throughout the day due to NO concentrations being suppressed through reactions with O$_3$, reducing this important NO$_3$ sink. During the postmonsoon period, modeled NO$_3$ concentrations peaked between 12:00 and 14:00 IST, at a concentration comparable to that observed at the same time during the premonsoon period (~3 × 10^7 molecules cm^{-3}, 1.2 pptV) (Figure 2d). A comparison between NO$_3$ photolysis rates and modeled NO$_3$ suggests that daytime peaks in NO$_3$ are not significantly influenced by haze events (see Figure S3). The differences seen in the NO$_3$ diel profiles are striking, with the extreme levels of NO at night rapidly scavenging any NO$_3$ that is formed during the postmonsoon period. It should be noted that the model does not account for N$_2$O$_5$ uptake, though we expect the impact of this to be minimal as our modeled N$_2$O$_5$ midday peak is small (<10 pptV), relative to the daytime concentration

of NO (>1.8 ppbV). The impact of N$_2$O$_5$ uptake on modeled NO$_3$ concentrations is investigated in more detail in ref 39.

To further investigate the drivers of Delhi's radical chemistry, the rates of radical production and loss were determined for each campaign. The average modeled diel rates of production (initiation, positive values) and loss (termination, negative values) of OH, HO$_2$, and RO$_2$ (RO$_x$) radicals are shown as a stacked plot in Figure 3 for both campaigns. The pre- and postmonsoon percentage contribution to radical initiation/termination (by time of day) for each source is shown in Figures S4 and S5. During the premonsoon period, the radical production rate is symmetrical around noon (maximum of ~10 ppbV h^{-1}), with roughly similar contributions from ozonolysis, photolysis of carbonyls, photolysis of O$_3$ (j(O^{1}D)), and HONO photolysis. VOC + NO$_3$ reactions start to make a significant contribution to radical initiation in the late afternoon (Figure 3). In contrast, there is a large burst of RO$_x$ radical formation after sunrise during the postmonsoon period (maximum of ~24 ppbV h^{-1}), more than double the radical production observed during the premonsoon period (Figures S6). This is largely driven by the photolysis of high levels of HONO (~12 ppbV) remaining from the previous night (Figure S7). The morning radical production peak is sustained into the afternoon by ozonolysis and carbonyl photolysis, whereas the photolysis of O$_3$ plays an only minor role (Figures S4 and S5). The postmonsoon morning burst in radical production results in a temporal shift in the peak O$_3$ concentration, from 15:00 IST during the premonsoon period to 13:00 IST during the postmonsoon period, although overall the maximum O$_3$ mixing ratios are similar between the two campaigns. The temporal O$_3$ peak shift observed in the measurements was also seen by the model in a simulation in which O$_3$ was unconstrained, with modeled O$_3$ also peaking around midday.

A similar pattern is seen for radical loss processes, with the premonsoon period showing a symmetrical diel profile, with OH + NO$_2$, RO$_2$ + HO$_2$, RO$_x$ + NO, and HO$_2$ + HO$_2$ all acting as important termination reactions. The postmonsoon radical losses are driven by high NO levels present after sunrise with the RO$_x$ + NO reaction dominating the termination reactions initially. The RO$_x$ + NO term is a combination of OH + NO (=HONO) and RO$_2$ + NO (=RONO$_2$) terminating loss routes and is dominated by OH + NO loss during the pre- and postmonsoon periods (~60% and ~86%, respectively).

During the premonsoon period, RO_2 products derived from isoprene and monoterpenes make the next largest contributions (~20%). During the postmonsoon period, dodecane-derived RO_2 makes the next largest contribution (~2%). All other pathways in both campaigns make minor contributions to the overall $RO_x + NO$ termination term, with $OH + NO_2$ and net peroxyacetyl nitrate (PAN) formation becoming increasingly important by 9:00 IST. This balance between radical production and loss, driven by the high levels of NO_x, likely stops O_3 concentrations during the postmonsoon period reaching the increased levels observed in Los Angeles in the 1970s.

DISCUSSION

We conclude that the very high NO levels observed in Delhi at night during the postmonsoon period quench nocturnal oxidation chemistry, evidenced by very low levels of measured O_3 and modeled NO_3 present and extremely low model radical initiation rates. This also suggests a concurrent lack of N_2O_5 formation at night. Therefore, even though very high levels of chloride (Cl^-) in the particle phase have been reported in Delhi,[40] limited nighttime $ClNO_2$ formation, which is an important photochemical Cl radical reservoir, is likely to occur. The lack of nocturnal oxidation chemistry can also be confirmed using the VOC observations. Very high nighttime levels of monoterpenes were observed (mean of 2.5 ppbV), with eight nights having a peak over 5 ppbV (Figure S8).[19] Species such as α-phellandrene, α-terpinene, and terpinolene are extremely reactive toward OH, O_3, and NO_3 (see Table S2) but did not accumulate overnight, reaching maximum mixing ratios of 120−350 pptV. During the premonsoon period, nighttime concentrations of these reactive monoterpenes were usually below the instrument detection limits and so were not included in the premonsoon model. The absence of nighttime oxidation chemistry is further corroborated by a study by Cash et al., which reported a reduction in oxidized aerosol levels in Delhi during the postmonsoon period at night, alongside increased levels of hydrocarbon-like organic aerosol (HOA).[41] Together, these model and measurement observations provide strong evidence for a deviation from the typical nocturnal oxidation chemistry observed in other highly polluted urban atmospheres. More details about the observed VOC concentrations and diel profiles can be found in refs 19 and 42.

The observed postmonsoon overnight accumulation of a highly reactive mix of NO_x and oxidized nitrogen species (NO_y) and VOCs, in a very shallow boundary layer, has important consequences for the subsequent day's photochemistry. These trapped emissions act as a reservoir of photochemical fuel leading to high radical formation rates, initially driven by nitrous acid photolysis in the morning, and efficient photochemical O_3 formation, shifting the postmonsoon maximum O_3 peak earlier (by 3 h compared to the premonsoon peak). The observed temporal shift in maximum O_3 coinciding with solar noon supports the presence of highly active oxidation chemistry in the morning. As the sun rises and the nocturnal boundary layer collapses in the morning, some of the accumulated pollution will be ventilated away from the surface. However, we observed that the modeled radical initiation pathways during the morning were very efficient after these stagnation events.

Recent pollution abatement policies that restrict the movement of HGVs during the day may be exacerbating

nighttime pollution leading to the modeled early morning burst in secondary pollutant formation initiated by photolysis at sunrise. We propose that pollution reduction policies in central Delhi should focus on diel emission reductions, as policies that move emissions from daytime to nighttime may not be effective at reducing O_3 and may lead only to a temporal shift in its peak. Further work is needed to determine the impact of reducing nighttime emissions on changes to daytime exposure to secondary pollutants, and future policies should consider the emission profile and atmospheric chemistry across the entire 24 h period.

ASSOCIATED CONTENT

Ⓢ Supporting Information

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