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Nighttime Organic Nitrates Drive New Particle Formation and Aerosol Growth in Urban Beijing

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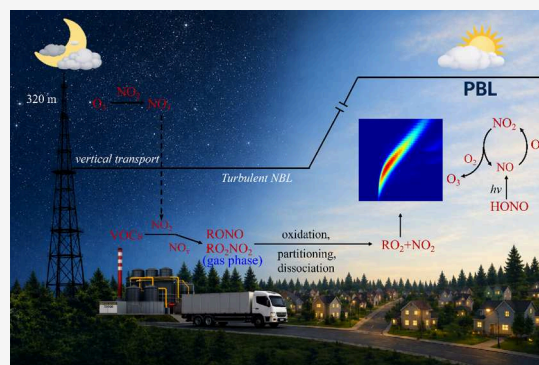
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ABSTRACT: Secondary organic aerosol (SOA) represents a major component of urban air pollution. This study presents observational evidence from summer 2017 in urban Beijing, supported by model simulations and a case study from summer 2023, demonstrating the crucial role of nighttime organic nitrates (ONs) production in subsequent daytime SOA formation. Our measurements revealed that total reactive nitrogen compound (NO_x) concentrations exceeded 40 ppb at night, resulting from nitrate radical (NO_3)-initiated oxidation of volatile organic compounds (VOCs) in the surface layer and through aloft production followed by downward transport. While these NO_x existed primarily in the gas phase during nighttime, they underwent atmospheric aging processes the following day, significantly contributing to SOA growth and potentially new particle formation. Model simulations identified reactive terpenoids as the dominant VOC precursors for nighttime ON formation. These findings underscore the need for an improved understanding of nocturnal ONs production mechanisms given their substantial impact on daytime SOA production.

KEYWORDS: secondary organic aerosol, organic nitrates, nighttime chemistry, new particle formation, vertical transport



INTRODUCTION

Organic nitrates (ONs) are key atmospheric constituents that significantly influence air quality, climate, and human health.^{1–7} These compounds mainly include alkyl nitrates (ANs, RONO_2) and peroxy nitrates (PNs, RO_2NO_2), which are primarily produced by reactions of organic radicals with nitrogen oxides ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) during daytime.⁸ At night, ONs production can also occur via reactions of volatile organic compounds (VOCs) with nitrate radicals (NO_3),³ substantially contributing to nocturnal atmospheric oxidation processes.

ONs are ubiquitous in the atmosphere. Field studies across forty-seven Chinese cities show that the most abundant short-chain ONs (C1–C4) in ambient air include 2-butyl nitrate and 2-propyl nitrate, highlighting the prevalence of alkyl nitrates in densely populated areas.⁹ Peroxyacetyl nitrate (PAN), another important gaseous organic nitrate, can accumulate to concentrations of tens of ppb during summertime in urban Beijing, making it a critical reactive nitrogen reservoir species and a key contributor to regional photochemical smog.¹⁰ In regard to particulate organic nitrates (pONs), literature estimated that pONs can account for 10–100% of total

nitrogen-containing compounds across different regions globally.¹¹ In China, pONs represent a nontrivial component of ambient aerosol. Snow samples collected from four different Chinese megacities revealed that the nitrogen-containing organic compounds were mainly present in oxidized form as ONs.¹² Studies showed that pONs constituted 15–28% of organic aerosol in the Beijing–Tianjin–Hebei region.¹³ Even in the relatively cleaner Pearl River Delta region, where total organic aerosol concentrations are significantly lower than in other parts of China, the proportional contribution of pONs remains substantial. For example, Yu et al. reported that pONs can account for up to 25% of total organic aerosol in Shenzhen (China), significantly influencing the physicochemical properties of atmospheric particulate matter.¹⁴

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ONs are key drivers in urban atmospheric chemistry. The formation of ONs terminates the chain reactions of RO_x ($\equiv\text{OH} + \text{HO}_2 + \text{RO}_2$) and NO_x . They thereby modulate the concentrations of OH and O_3 in the daytime and NO_3 radical at night, further regulating atmospheric oxidative capacity.¹ In particle phase, ONs provide an important pathway for nitrogen participating in secondary organic aerosol (SOA),¹⁵ contributing to particle mass and influencing their physicochemical properties such as light absorption, hygroscopicity, and heterogeneous reactivity, which in turn affect air quality and aerosol–cloud interactions.

ONs are also important components of atmospheric brown carbon. Chamber experiments found that organonitrates as possible chromophores in BrC from pyrrole, furan, and thiophene precursors in nighttime.¹⁶ Laboratory simulations revealed that anthropogenic VOCs such as toluene can form substantial amounts of pONs through photochemical oxidation in the presence of NO_x . These pONs are major contributors to the light-absorbing properties of aromatic oxidation products.^{6,17,18} Furthermore, pONs can enhance the light absorption of secondary products from biogenic sources. Studies on the nighttime NO_3 oxidation of monoterpenes and other biogenic VOCs have identified organic nitrate monomers and dimers as significant light-absorbing species.¹⁹

In addition to their environmental and climatic roles, the toxicological properties of ONs are a major focus in environmental health research. Reactive nitrogen species in pONs can trigger inflammatory cellular responses.²⁰ Inhalation of nitrated organic compounds may induce immune reactions and promote allergic diseases.⁷ Organic nitrate esters may undergo hydrolysis in human body to form nitric acid, which can impair lung function.²¹

Collectively, these findings emphasize that ONs, in both gaseous and particulate phases, constitute a substantial fraction of reactive nitrogen and organic aerosol with significant environmental, climatic, and health impacts, and represent an important but under-constrained component of atmospheric pollution. Here, we present detailed observations of ONs in summer Beijing to elucidate their formation pathways and implications in linking atmospheric NO_x cycling, oxidant budget, and particle production in complex urban environments. The results show that nighttime chemistry is a large source of gas-phase ONs. These ONs are then oxidized the following day, leading to SOA production. We propose that this nighttime chemistry is driven both by NO_3 at the surface or transported from aloft. Such processes highlight the dynamic interplay between nighttime NO_3 oxidation and daytime photochemistry, yet they are currently absent from most atmospheric chemistry models, leading to underestimation of ONs contributions to oxidant and aerosol budgets in polluted regions.

MATERIALS AND METHODS

Field Campaigns

The data presented here are from the Atmospheric Pollution and Human Health in a Chinese Megacity (APHH-Beijing).⁴⁶ The summer campaign was carried out at the Tower Division of the Institute of Atmospheric Physics, Chinese Academy of Science (39° 58' N, 116° 22' E) in Beijing, China, from June 4 to 20, 2017, and June 2023. All data presented in this paper were hourly averaged (Beijing time, UTC + 8).

NO_y , NO , NO_2 , and O_3 concentrations were measured by the Thermo Fisher Scientific instruments (42C, 42i, and 49i),

respectively. Based on previous studies in summer Beijing,²² HNO_3 contribution to NO_y can be considered negligible so that we expect NO_y to represent the sum of nitrogen oxides less HNO_3 . NO_2 was also sampled by a Teledyne CAPS system. OH, HO_2 , and RO_2 radical concentrations were measured by a fluorescence assay by gas expansion (FAGE). A broadband cavity-enhanced absorption spectroscopy (BBCEAS) system was employed to measure HONO, NO_3 , and N_2O_5 concentrations. Individual VOCs and OVOCs were collected by a PTR-MS. PAN was observed by the GC-ECD instrument. NO_z ($\text{NO}_y - \text{NO}_x$) was derived from independent measurements of NO_y , NO , and NO_2 by Thermo Scientific model 42i-Y NO_y , model 42i-TL trace level NO_x analyzer, and Teledyne T500U CAPS analyzer, respectively.

An Aerodyne high-resolution aerosol mass spectrometer (HR-AMS) was deployed to measure the chemical composition of nonrefractory submicron particulate matter ($\text{NR-PM}_{1.0}$). pONs were estimated by the different ratios of $\text{NO}^+/\text{NO}_2^+$ between particulate organic nitrates and ammonium nitrate.^{13,15} In parallel, aerosol size distribution was obtained by a standard TSI scanning mobility particle sizer (SMPS) and a long-differential mobility analyzer (DMA) SMPS. Meteorological parameters were also collected simultaneously at the site.

In the summer of 2023, a new field campaign was carried out employing a thermal dissociation laser-induced fluorescence (TD-LIF) instrument to measure the NO_2 and alkyl nitrates (RONO_2) and the peroxy nitrates (RO_2NO_2) in both gas and particle phases, by a charcoal denuder. The campaign took place at the same site as the APHH campaign in Beijing, China from June 1 to 30, 2023. Details about the TD-LIF instrument can be found elsewhere.⁴⁷ A Vocus PTR-MS (TOFWERK, Switzerland) was conducted parallelly to collect individual VOC species, details of the configuration of the Vocus PTR-MS can be found a previous work.⁴⁸

FOAM–WAM Simulations

Local air chemistry was simulated using the framework for 0D atmospheric modeling (FOAM), a 0D box model based on MATLAB⁴⁹ to simulate gas phase. The simulations were constrained using NO , NO_2 , O_3 , individual VOC species (Table S2), CO , NO_3 , N_2O_5 , and HONO measurement data sets during the APHH-Beijing summer field campaign. The meteorological parameters of pressure, temperature, and relative humidity were also included as inputs of the model. Photochemistry was simulated by using the solar zenith angle (SZA) trigonometric function in the FOAM model. We included a residual 10 ppb HNO_3 in the FOAM simulations to account for nighttime nitric acid levels influencing organic nitrate chemistry. To simulate the ONs in both stage I and II, as shown in Figure 3 and Figures S7 and S10, we used simply the basic FOAM model.

The FOAM–WAM simulations have been constrained by using some of the species given as output of the aforesaid simulations by the FOAM, which simulated only the gas phase. In detail, we used the same input employed in simple FOAM simulations adding to them the modeled 2-oxopropyl nitrate, PAN, and methylglyoxal. We set 100 seeds per cm^3 with a radius of 25×10^{-7} cm as initial values to initiate the particle simulation. The WAM is a custom dynamic gas-particle partitioning module that explicitly resolves condensation and evaporation kinetics. Gas-to-particle transfer is governed by diffusion-limited mass transport and a mass accommodation coefficient of 0.1, while compound-specific saturation concentrations determine reversible uptake. We used the WAM module only to independently confirm the daytime production and subsequent growth of particles, as shown in Figure S9.

RESULTS AND DISCUSSION

Field Observations

Measurements were made at a rooftop lab 8 m above street level of the Institute of Atmospheric Physics, Chinese Academy of Sciences, in Beijing, in June 2017. The temporal variations of the concentrations of key species are presented in Figure 1. Concentrations of NO , NO_2 , and total nitrogen oxides (NO_y)

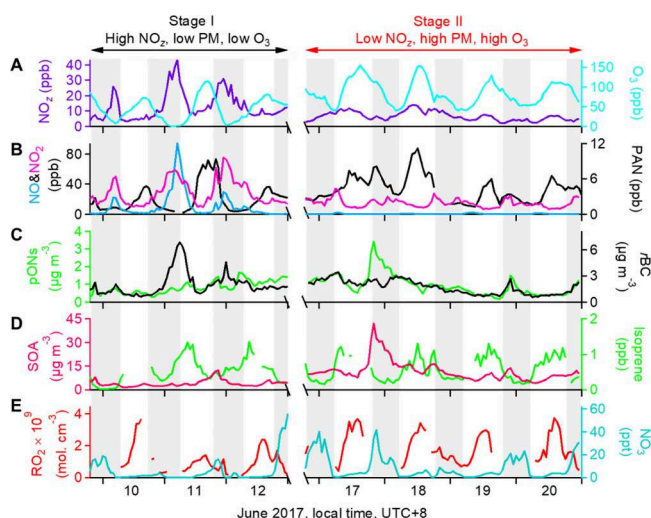


Figure 1. Time series of selected variables during the atmospheric pollution and human health (APHH) summer campaign in Beijing: (A) NO_z (sum of NO_x oxidation products) and O_3 ; (B) NO , NO_2 , and peroxyacetyl nitrate (PAN); (C) particulate organic nitrates (pONs) and refractory black carbon (rBC) in PM_1 measured by an Aerodyne soot-particle aerosol mass spectrometer; (D) SOA in PM_1 and isoprene; and (E) total RO_2 radicals and NO_3 . Nighttime (19:00–6:00) is colored in gray.

were measured. A useful quantity for our analysis is NO_z ($\equiv \text{NO}_y - \text{NO}_x$), representing the sum of gas- and particle-phase NO_x oxidation products. Previous campaigns in summer Beijing²² have shown that when NO_2 averaged around 32 ppb, HNO_3 remained below 1 ppb. Since the conditions during the Beijing summer 2017 campaign were similar to those of previous campaigns, we considered the contribution of HNO_3 to NO_y negligible. Indeed, during our June 2023 campaign at the same site in similar conditions, HNO_3 was observed with a negligible concentration close to zero ppb (Figure S1).

Two stages during the campaign were selected based on back-trajectory analyses.²³ June 9 to 12, denoted as stage I, sampled air from eastern NCP (North China Plain) (Figure S2). Mean concentrations of O_3 and PM_1 (PM less than $1 \mu\text{m}$ diameter) during that stage were relatively low at 44 ± 30 ppb and $15 \pm 7 \mu\text{g m}^{-3}$, respectively. Stage II, covering the period from June 16 to 20, sampled air from western NCP (Figure S2). This time period was characterized by mean concentrations of O_3 and PM_1 of 89 ± 31 ppb and $30 \pm 13 \mu\text{g m}^{-3}$, respectively, roughly double the values of stage I, indicating a shift in regional air quality conditions. Similar results have been observed in another campaign at the same site in June 2023 (Figure S1).

Different Nighttime Nitrate Formation Pathways in the Two Stages

NO_z had different behavior in stages I and II (Figure 1A). In stage I, NO_z and O_3 exhibited a strong anticorrelation at night ($r = -0.73$) (Figure S3A). A maximum NO_z concentration of 43 ppb and a minimum O_3 concentration of less than 1 ppb were observed. It is important to note that, although high concentrations of NO were observed in nighttime stage I, the presence of NO_3 was still detected (Figure 1). By comparison, NO_z in stage II correlated weakly with O_3 ($r = 0.33$ at night) (Figure S3B). The maximum nighttime concentration of NO_z in stage II was <10 ppb, while O_3 maintained greater than 40 ppb. Interestingly, peroxyacetyl nitrate (PAN), pONs, the

nitrogen-to-carbon ratio (N/C) of total organic aerosol, and SOA in PM_1 , all had higher nighttime values in stage II than in stage I (Figures 1C and D and 2; Materials and Methods and

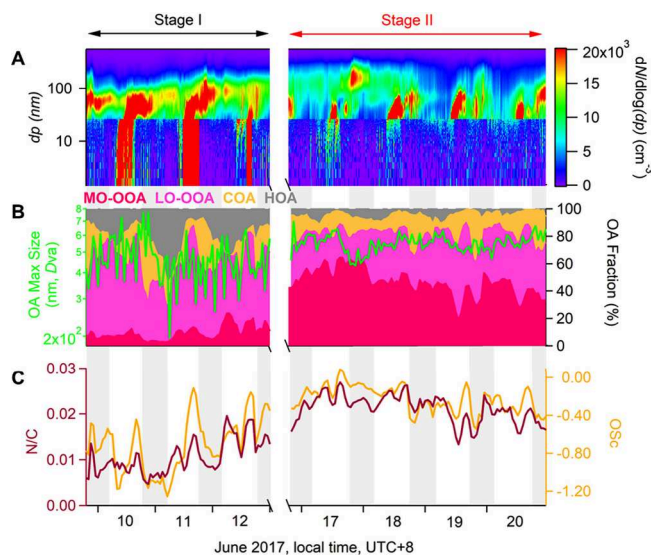


Figure 2. New particle formation (NPF) events during stages I and II of the APHH-Beijing summer campaign: (A) scanning mobility particle sizer (SMPS) measured size distributions with NPF events identified as surges in the concentrations of <10 nm particles; (B) Aerodyne AMS measured peak diameters of OA size distributions and fractions of four OA factors (more oxidized oxygenated MO-OOA, less oxidized oxygenated OA (LO-OOA), cooking OA (COA), and hydrocarbon-like OA (HOA)) identified by positive matrix factorization (PMF); and (C) Aerodyne HR-AMS measured nitrogen to carbon ratios (N/C) in PM_1 and OA oxidation state ($\text{OSc} = 2 \times \text{O/C} - \text{H/C}$). Gray boxes represent the nighttime.

Table S1). In addition, higher concentrations of radical oxidants (daytime RO_2 and nighttime NO_3) were observed in stage II (Figure 1E and Figure S4). These findings suggest that NO_z contributed more significantly to particle-phase formation in stage II at night. The lower RO_2 levels observed in stage I under high- NO_x conditions suggest that RO_2 is predominantly consumed through reactions with NO_x , promoting the formation of organic nitrates and consequently yielding less SOA (Figure 1). In contrast, the higher RO_2 concentrations and low NO_x levels measured in stage II indicate that RO_2 is more likely to react with HO_2 or undergo accretion reactions, pathways that are substantially more efficient at producing SOA (Figure 1).

The evolution of NO_z exhibited distinct characteristics between the two stages, reflecting different chemical regimes and formation pathways (Figure S5). In stage I, NO_z concentration showed strong nocturnal production closely linked to local NO_x emissions ($r = 0.94$, Figure S3C), indicating rapid nighttime oxidation of freshly emitted NO_x under conditions that favored gas-phase products; this was evidenced by minimal contributions of PAN and pONs to total NO_z ($<2\%$), suggesting the formation of less functionalized compounds that remained predominantly in the gas phase. Further aerosol composition analysis in stage I supported this interpretation, with PM_1 showing relatively low oxidation state (OSc), minimal contribution from more-oxidized oxygenated organic aerosol (MO-OOA), and elevated levels of refractory black carbon (rBC), while total secondary organic aerosol

(SOA as LO-OOA + MO-OOA) reached only $12 \mu\text{g m}^{-3}$ (lower than the average value during the campaign, Figure 1). In marked contrast, stage II exhibited fundamentally different NO_z chemistry, where the loss of correlation with NO_x implied regional production and transport, while PAN became the dominant component (slope ≈ 1 against NO_z at night) and PONs contributed a significantly greater fraction (10%) of total NO_z , signatures of more aged and processed air masses. This shift toward more functionalized compounds was further reflected in the aerosol phase through enhanced partitioning to particles during daytime, consistent with the observed increases in both MO-OOA contribution and overall SOA loading (peaking at $42 \mu\text{g m}^{-3}$), along with higher overall oxidation state, demonstrating the progression from locally dominated, night-focused chemistry in stage I to regionally influenced, daytime-driven oxidation processes in stage II.

Nighttime ONs are expected to be produced at the surface level via O_3 reacting with alkenes in the presence of NO_x . Additionally, ONs can be produced at night via reactions between NO_3 and VOCs, directly generating nitrated alkylperoxy radicals.^{24–26} NO_3 is produced by the reaction between O_3 and NO_2 , which itself is formed by oxidation of NO by O_3 . In stage I at night, O_3 in surface air was titrated by fresh NO emissions (Figure 1 and Figure S5D). The formation of NO_3 was limited, consistent with the observed low NO_3 concentration (Figure 1E). However, significant NO_3 production may still occur in the residual layer, where elevated O_3 and relatively high NO_2 concentrations were present,^{27,28} facilitating ON formation. The surface layer (occurring intermittently during nighttime and more prominently during the transitional periods immediately preceding and following sunrise) was sustained by mechanical turbulence extending from 50 to 500 m above ground level, as evidenced by vertical wind speed profiles (Figure S6A). Under these conditions, model simulations demonstrate that NO_3 generated in the residual layer could be transported downward to the surface layer through either mechanical turbulence or concentration gradient-driven diffusion (Text S1 and Figure S6B). Similarly, residual layer-produced ONs may also undergo downward mixing into the surface layer. The confinement of high NO and suppressed O_3 within the shallow, stably stratified nocturnal surface layer—where fresh emissions rapidly titrate O_3 , contrasts sharply with the chemically active residual layer aloft. This decoupled layer preserves late-afternoon O_3 and NO_2 , sustaining a reservoir of precursors for nocturnal NO_3 production via $\text{O}_3 + \text{NO}_2$. Such vertical segregation is well documented in urban airsheds, including the North China Plain.^{29,30} Nocturnal low-level jets and intermittent mechanical mixing can erode the stable boundary layer,³¹ episodically transporting O_3 , NO_2 , and potentially NO_3 radicals downward. These dynamics support the assumption of elevated oxidant levels aloft, with the residual layer functioning as a persistent nocturnal chemical reservoir capable of intermittently coupling with the surface.

ONs Formation in Stage I. The co-occurrence of high gas-phase NO_z concentrations and low particle number concentrations during the night in stage I (Figure 1) suggests these conditions may have triggered new particle formation (NPF) events the following day, where less oxidized oxygenated organic aerosol (OA) was the dominant OA species (Figure 2A and B).³² The RONO_2 produced at night could undergo photochemical functionalization in the daytime, decreasing their vapor pressure and leading to NPF and further

to particle growth.³³ The daytime increase in the OA N/C ratio (Figure 2C and Figure S4) provides evidence for the contribution of ONs to the growth of particles. This rapid oxidation of NO_x to NO_z was also reported for nighttime Houston urban plumes,³⁴ and NO_3 chemistry was identified as a driver for the production of ONs and SOA.³⁵ Although urban NPF is typically dominated by sulfuric acid–base chemistry, the low sulfate concentrations observed during stage I in 2017 (not shown) suggest that the canonical acid–ammonia nucleation pathway was likely suppressed. Under these conditions, the abundant ONs present in our measurements could efficiently condense onto and grow freshly nucleated clusters, thereby acting as the dominant driver of early particle growth into the detectable size range. Recent studies have shown that ONs may also participate directly in the initial nucleation step. Field observations in the Amazon³³ and CLOUD chamber experiments³⁶ demonstrate that isoprene-derived ONs can nucleate under cold upper tropospheric conditions, particularly in synergy with trace inorganic acids. Whether such ONs-mediated nucleation pathways operate in the warmer, more chemically complex, and polluted urban boundary layer remains uncertain. Nonetheless, the uniquely low-sulfate regime of stage I highlights the need to reassess the potential contribution of ONs to the earliest stages of NPF in nontraditional urban environments.

A zero-dimension box model (F0AM), based on the master chemistry mechanism (MCM) (Materials and Methods), was used to assess the dominant processes governing the formation of nighttime gas-phase ONs in stage I. The simulations were constrained by the summer data set of O_3 , NO, NO_2 , NO_3 , OH, HONO, and independent VOC species (Table S2). The F0AM model does not reproduce the ONs peak at 6:00 AM based on the measured NO_3 (Figure 3A and B). We therefore hypothesized that additional NO_3 or ONs were transported from aloft, based on flux observations (Figure S6). Adding these sources in the simulation reproduced the nighttime peak of the RONO_2 (Figure 3C). Furthermore, the simulations showed that biogenic alkenes could play a crucial role in explaining the nighttime production of ONs compared to other VOCs. With the observed VOC input, the model well captured NO_z formation and evolution at night (Figure S7B and C), with dominant ONs species such as $\text{C}_3\text{H}_5\text{O}-\text{ONO}_2$ and $\text{C}_5\text{H}_7\text{O}-\text{ONO}_2$ produced from isoprene oxidation and $\text{C}_9\text{H}_{15}\text{O}-\text{ONO}_2$ from monoterpene oxidation (Table S2 and Figure S7A). The main mechanism for isoprene and α -pinene derived ONs production at night is illustrated in Figure S8.

The model results support that RONO_2 at night was produced mainly by the oxidation of reactive terpenoids by NO_3 (Figure 3C), consistent with previous observations.³⁷ Hu et al.³⁸ reported that isoprene was the dominant species for NO_3 reactivity during the summer in urban Beijing (up to 80%). Yang et al.³⁹ indicated that isoprene played a key role in the nighttime NO_3 chemistry in a suburban site in Beijing. The nighttime production of gas phase RONO_2 in the presence of high NO concentration with little pre-existing PM (i.e., similar conditions found in stage I in Beijing) has been previously suggested based on smog chamber experiments.³²

To further verify the daytime production and growth of particles, we used the F0AM model integrated with the Washington Aerosol Module (WAM).⁴⁰ Figure S9 shows that the observed SOA formation and growth in stage I can be effectively modeled and reproduced during the daytime (peaked at midday). The NO_z undergoes functionalization

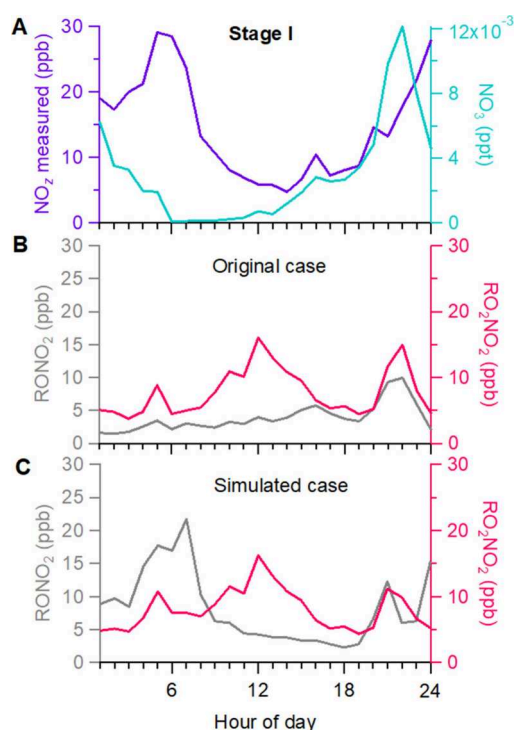


Figure 3. F0AM-MCM model simulations for stage I: (A) measured NO_2 and the measured and transported NO_3 ; (B) RONO_2 and RO_2NO_2 simulated by using the measured concentration of NO_3 ; and (C) similar to panel (B) but with the hypothesized transported trend of NO_3 .

when photochemistry is activated, thereby enhancing the partitioning of oxidation products into the particle phase, and promoting the formation and growth of daytime SOA (Figure 2A). The findings and analyses discussed above are further substantiated by the field campaign conducted in June 2023 at the same site in Beijing (Figure 4A). The meteorological situation on June 11, 2023 is similar to stage I in June 2017 (Figure S1). In stage I, the temperature is 23.8 ± 4.1 °C, closely matching the conditions on June 11, 2023 (23.6 ± 3.1 °C). The RH differs with values of $26.9 \pm 8.8\%$ in stage I compared with $50.5 \pm 12.2\%$ on June 11, 2023. In both cases, the wind direction is consistent, with air masses arriving from the southeast. In the summer 2023, ONs were directly sampled by using a thermal dissociation laser-induced fluorescence (TD-LIF) instrument. This instrument provided ONs speciation by distinguishing between RONO_2 and RO_2NO_2 . It also measured gas-to-particle partitioning by separately measuring gas and particle-phase products.³² Figure 4B shows that the directly measured gas phase RONO_2 (gRONO_2) had a peak between 3:00 and 6:00 AM. The particle phase (pRONO_2) had a peak at around 10:00 AM, which was synchronous with an NPF event as shown in Figure 4A. Literature also presented comprehensive in situ aircraft measurements demonstrating that highly oxidized isoprene derivatives, especially specific organonitrate compounds with extremely low volatility, can initiate NPF in the upper troposphere above the Amazon rainforest.³³

ONs Formation in Stage II. Unlike stage I, stage II exhibited only particle growth without any occurrence of NPF events (Figure 2A). The SOA mass loading was approximately 300% greater than that in stage I. The chemistry in stage II was different from that in stage I. First, the daytime trend of NO_2

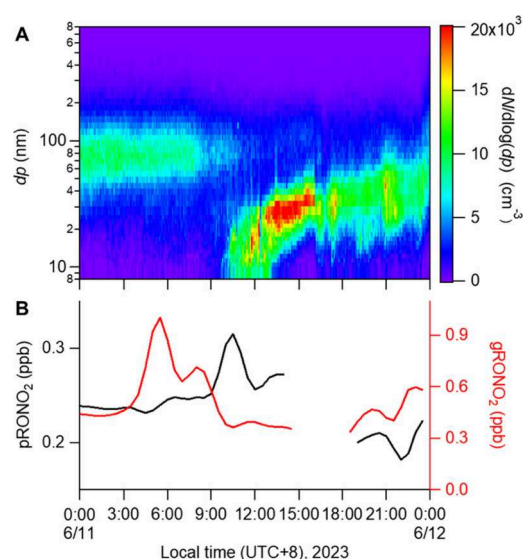


Figure 4. New particle formation (NPF) during Beijing summer 2023 campaign: (A) scanning mobility particle size (SMPS) measured size distributions with NPF events identified as surges in the concentrations of <10 nm particles and (B) alkyl nitrates (RONO_2) in gas and particle phase measured by a thermal dissociation laser-induced fluorescence (TD-LIF).

concentration in stage II peaked at noon (Figure 1 and Figure S4), suggesting that photochemistry played a dominant role in NO_2 formation unlike in stage I. Model simulations revealed that the most abundant RO_2NO_2 in stage II was PAN (up to 60% of RO_2NO_2), produced through the photooxidation of VOCs such as butane, methylglyoxal, and methyl vinyl ketone in the presence of NO_x . PAN served as an important reservoir for reactive nitrogen species. Decomposition of PAN can significantly contribute to daytime O_3 formation by releasing NO_2 back into the atmosphere, particularly during warmer daytime conditions. We attributed the overestimation of RO_2NO_2 , during the day, in both stage I (Figure 3) and II from the model (Figure S10) to missing lost mechanism for RO_2NO_2 , due to the aerosol uptake and the gas-particle partitioning that are not included in F0AM-MCM.

ATMOSPHERIC IMPLICATIONS

This study reveals that rapid nighttime production of ONs, dominated by gas-phase RONO_2 from anthropogenic NO_x , occurred in summertime urban air in Beijing. This process is critical for understanding the intricate dynamics of urban air pollution, as ONs played a central role in the formation of new particles and their subsequent growth, significantly influencing air quality. In addition, in stagnant air masses originating from the southeast North China Plain, we observed elevated concentrations of NO_x oxidation products (NO_2) generated through NO_3 radical-initiated oxidation of reactive terpenoids at the surface, or the residual layer followed by downward transport.

These findings have several important implications. They highlight that nocturnal ONs chemistry is a key driver of urban pollution episodes, as nighttime processes directly influence particulate composition and size distribution of the following day. The formation of ONs at night and their subsequent daytime transformation reflect the complex interplay between local anthropogenic emissions and regional transport. ONs are also related to the formation of tropospheric O_3 . Summer O_3

pollution is one of the most challenging environmental issues in China, particularly since the implementation of the “Clean Air Act” in 2013.⁴¹ The chemistry behind the ONs formation (i.e., the reactions between RO_x and NO_x) also produces O_3 . The production of ONs, therefore, suppresses O_3 formation locally by providing a sink for HO_x , RO_x , and NO_x , but the subsequent thermal decomposition and photochemistry of ONs increases O_3 production.⁴² Current air quality models may underestimate SOA and O_3 formation due to the omission of these nighttime pathways, highlighting the need to integrate nocturnal ONs production into predictive frameworks. The persistent underrepresentation of nocturnal organic nitrate chemistry in atmospheric models—particularly the NO_3 initiated pathways that strongly modulate competition among oxidants—leads to systematic biases in simulated SOA yields and misrepresents the redistribution of NO_x that shapes next day ozone production.^{2,11,43–45} Moreover, with SO_2 emissions declining globally as a result of effective control strategies, the relative role of nitrogen chemistry in shaping air quality is becoming increasingly important. This shift enhances the relevance of ONs formation and transformation in driving future urban air pollution, with direct implications for mitigation strategies targeting SOA and O_3 . Elevated nighttime NO_x , especially from heavy-duty diesel traffic, enhances the formation of nitrate radicals and reactive nitrogen reservoirs that accelerate early morning SOA production and intensify ozone build-up after sunrise. These findings highlight nighttime NO_x control as a strategically powerful intervention point. Targeted mitigation of nocturnal emissions could substantially reduce daytime SOA and O_3 peaks in urban environments undergoing a transition toward nitrogen-dominated oxidation regimes.

Another critical aspect is the role of vertical transport during the night, which efficiently redistributes ONs and their precursors. ONs generated in the residual layer can be preserved overnight and then entrained into the morning boundary layer, delivering reactive nitrogen and organic compounds to the surface. This downward mixing not only promotes early morning O_3 and SOA production but also helps sustain pollution episodes under stagnant conditions. In parallel, the lofting of fresh anthropogenic emissions during the day enhances ONs production at higher altitudes, influencing regional aerosol burdens and long-range transport. ONs contribute to atmospheric brown carbon and may increase aerosol oxidative potential, raising concerns about adverse climate and health effects. These vertical exchange processes demonstrate how ONs integrate local surface processes with multiscale atmospheric chemistry, with implications extending from local air quality to regional climate and public health.

■ ASSOCIATED CONTENT

Data Availability Statement

Data sets, including time series of species concentrations and meteorological variables during the campaign, are available at [10.5281/zenodo.10802900](https://doi.org/10.5281/zenodo.10802900).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.6c01200>.

Information about the modeling setting and figures to support the mechanism on organic nitrate formation at night (PDF)

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Notes

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