Particulate-bound alkyl nitrate pollution and formation mechanisms in Beijing, China

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Abstract
Fine particulate matter (PM2.5) samples were collected between November 2020 and October 2021 at the Minzu University of China in Beijing and the n-alkyl nitrate concentrations in the PM2.5 samples were determined to investigate n-alkyl nitrate pollution and formation mechanisms. C6–C16 n-alkyl nitrate standards were synthesized and the n-alkyl nitrate concentrations in PM2.5 were determined by gas chromatography triple quadrupole mass spectrometry. Temporal trends in and correlations between particulate-bound n-alkyl nitrate, ozone, PM2.5, and nitrogen dioxide concentrations were investigated to assess the relationships between particulate-bound n-alkyl nitrate concentrations and photochemical reactions and identify the n-alkyl nitrate formation mechanisms. The n-alkyl nitrate concentrations in the PM2.5 samples were 9.67–2730 pg/m3, and the mean was 578 pg/m3. The n-alkyl nitrate homologue group concentrations increased as the carbon chain length increased, i.e., long-chain n-alkyl nitrates contributed more than short-chain n-alkyl nitrates to the total n-alkyl nitrate concentrations in PM2.5. The n-alkyl nitrate concentrations clearly varied seasonally and diurnally, the concentrations decreasing in the order winter > spring > autumn > summer and the mean concentrations being higher at night than in the day. The particulate-bound n-alkyl nitrate and ozone concentrations significantly negatively correlated despite gas-phase alkyl nitrate and ozone concentrations previously being found to positively correlate. This indicated that long-chain alkyl nitrates may not be produced during photochemical reactions. The particulate-bound n-alkyl nitrate concentrations followed the same trends as and significantly positively correlated with the PM2.5 and nitrogen dioxide concentrations. Nitrogen dioxide is an important contributor of nitrates in particulate matter. This indicated that particulate-bound n-alkyl nitrates may form through reactions between alkanes and nitrates on particulate matter surfaces. Particulate-bound n-alkyl nitrates are important components of PM2.5 during haze events and strongly affect atmospheric visibility. Particulate-bound n-alkyl nitrates are secondary pollutants that strongly influence haze pollution.

1 Introduction
Air pollution problems in China are complex but have been alleviated by adjusting the energy structure
and controlling pollutant emissions. However, air pollution (caused by frequent sandstorms in spring, photochemical pollution with ozone and secondary particles forming in summer and autumn, and serious haze pollution caused by emissions caused by heating buildings in winter) remains a problem in urban areas in North China. Air quality in China will therefore continue to pose serious challenges for some time.

Photochemical smog and haze are important types of air pollution that affect ambient air quality. Interactions between photochemical pollution and particulate pollution have become the main foci of air pollution research (Ma et al., 2012). Nitrogen oxide (NOx) emissions have increased by >50% in the last 30 years (Liu et al., 2013) and NOx concentrations in the atmosphere continue to increase as the number of vehicles increases (Richter et al., 2005; Mijling et al., 2013). More oxidation occurs in the atmosphere as NOx concentrations increase, and the contributions of anthropogenic emissions to volatile organic compound (VOC) concentrations in the atmosphere are also increasing (Liu et al., 2020). Challenges caused by synergistic photochemical smog and haze pollution are affecting urban areas in which background NOx concentrations are high and large amounts of anthropogenic VOCs are emitted. Future improvements in ambient air quality require both photochemical and particulate pollution to be controlled. Organic nitrates (ONs) formed in the atmosphere from the precursors NOx and VOCs are important atmospheric pollutants.

The general term ONs is used for various atmospheric pollutants with the formula RONO2 and includes esters containing nitrate groups and polyfunctional derivatives. ONs are important reactive nitrogen oxides in the environment and are important participants in the atmospheric nitrogen cycle, which involves various atmospheric sources and sinks of nitrogen oxides that affect regional NOx cycles and balances (Barnes et al., 1993; Chen et al., 1998; Perring et al., 2010). ONs are important secondary air pollutants and are very important species affecting oxidation in the atmosphere and the formation of haze (Browne et al., 2012). ONs formation consumes atmospheric oxidants and affects the atmospheric lifetimes of free radicals, the ozone concentration, and photochemical reactions (Calvert et al., 1987). Semi-volatile ONs are important sources and components of secondary organic aerosols (SOAs) and make important contributions to fine particulate matter (PM2.5) (Rollins et al., 2012). Controlling particulate-bound ONs may therefore be key to controlling both PM2.5 and ozone in the atmosphere.

Particulate-bound nitrates are some of the main components of particulate matter in China, particularly during pollution events, and strongly affects human health, air quality, and the climate at the regional scale (Zhai et al., 2023). Particulate-bound ONs are important components of particulate nitrates. SOAs can contribute 30%–77% of the mass of PM2.5 during a strong atmospheric pollution event.

Between 5% and 40% of the mass of organic matter in particulate matter can be ONs (Rollins et al., 2012; Xu et al., 2015; Sun et al., 2012). ONs have been found to be bound to atmospheric particles in various size ranges (Garnes et al., 2002), indicating that ONs are widely present in atmospheric particulate matter. Recent studies of particulate-bound ONs have mainly been focused on biogenic ONs formed from precursors such as the olefins pinene (Shen et al., 2021; Rindelaub et al., 2015), limonene (Spittler et al., 2006), monoterpenes (Barnes et al., 1990), and isoprene (Rollins et al., 2009; Perring et al., 2009; Vasquez et al., 2020; Wu et al., 2020) emitted from plants. Less attention has been paid to particulate-bound ONs that are related to emissions of anthropogenic pollutants.
Alkylnitrates are common ONs. The alkanes that act as precursors for alkylnitrates have been found to be some of the main components of anthropogenic VOCs that are widely present in the atmosphere (Wei et al., 2018; Kang et al., 2018). It has been found that short-chain (C1–C3) alkylnitrates are secondary products of photochemical reactions between alkanes and OH· radicals in the gas phase (Jordan et al., 2008; Lim et al., 2009; Perring et al., 2013; Sun et al., 2018), so are associated with photochemical pollution (Simpson et al., 2006; Wang et al., 2013; Ling et al., 2016). The vapour pressure decreases as the carbon chain length increases, so long-chain alkylnitrates tend to enter the particle phase through gas–particle partitioning and can participate in particulate matter formation and contribute to haze pollution (Lim et al., 2005; Yee et al., 2012). Few studies of particulate-bound alkylnitrates have been performed, Yang et al. developed a gas chromatography triple quadrupole mass spectrometry (GC-MS/MS) method for determining n-alkylnitrate concentrations and detected n-alkyl nitrates in real PM2.5 samples (Yang et al., 2019). This indicated that n-alkylnitrates can be present in airborne particulate matter in urban areas. Particulate-bound alkylnitrates are important contributors to haze pollution, so it is important to improve our understanding of particulate-bound alkylnitrate pollution, temporal variations, and formation mechanisms.

In this study, we determined the concentrations of C7–C16 n-alkylnitrates in PM2.5 samples collected in Beijing in 2020 and 2021. The aim was to investigate n-alkylnitrate pollution and assess temporal variations in n-alkylnitrate compositions and concentrations. We also assessed the similarities in temporal trends and correlations between the particulate-bound n-alkylnitrate, ozone, PM2.5, and nitrogen dioxide (NO2) concentrations to investigate the mechanisms involved in the formation of particulate-bound alkylnitrates. The study was performed to improve our understanding of alkylnitrates in PM2.5 and improve our ability to control haze pollution.

2 Materials and methods

2.1 Sampling period and location

Beijing is a typical densely populated large city in China. The heavy traffic in Beijing means that large amounts of exhaust gases are emitted by motor vehicles, and this causes serious haze pollution. Large amounts of anthropogenic n-alkanes are emitted to the atmosphere and act as precursors for particulate-bound alkylnitrates. Haidian District is a relatively prosperous area in Beijing. Haidian District is a busy area with high traffic flows and heavy traffic, making it suitable for studying anthropogenic alkylnitrates in particulate matter. This study was performed at the Minzu University of China (116.19° E, 39.57° N) in Haidian District. PM2.5 samples were collected on the roof (about 20 m above the ground) of the College of Pharmacy at the Minzu University of China. Samples were collected in November and December 2021 and March, April, July, September, and October 2022. Separate day and night samples were collected for one week (23rd to 29th) in each of these months. Each day-time sample was collected from 07:00 to 20:00 and each night-time sample was collected from 20:30 to 06:30.

2.2 Sample collection and pretreatment

Each PM2.5 sample was collected at a flow rate of 16.7 L/min using a TH-16A low flow sampler (Wuhan Tianhong, Wuhan, China) containing a Whatman QMA quartz fibre filter (Ø 47 mm; GE
Healthcare Bio-Sciences, Pittsburgh, PA, USA). Before use, the quartz fibre filters were baked at
550 °C for 5 h to remove organic matter. Each sample was wrapped in aluminium foil and stored at
−20 °C.

The n-alkyl nitrate in a PM2.5 sample were extracted using an ultrasonic extraction method that was
described in detail in previous publications (Yang et al., 2019; Yang et al., 2023). The filter was cut into
pieces and extracted with 15.0 mL of dichloromethane for 15 min with ultrasonication. The extraction
step was repeated five times and the extracts were combined and evaporated to 2.0 mL using a rotary
evaporator. The extract was then transferred to a 15 mL centrifuge tube and centrifuged at 3000 rpm for
5 min. The supernatant was then evaporated almost to dryness under a stream of high-purity nitrogen
and transferred into 100 μL toluene for instrumental analysis. The sample pretreatment processes were
performed with light excluded to prevent photolysis of nitrates.

2.3 Synthesis of standards

Standards of n-alkyl nitrates could not be purchased, so we synthesized C$_7$–C$_{10}$ n-alkyl nitrate standards
by performing substitution reactions involving treating brominated n-alkanes with silver nitrate using a
previously published method (Luxenhofer et al., 1994; Luxenhofer et al., 1996; Yang et al., 2019). The
standards were then analysed by GC-MS/MS.

2.4 Instrumental analysis

The n-alkyl nitrates (C$_7$–C$_{10}$) were qualitatively and quantitatively analysed using a Trace 3130 gas
chromatograph and TSQ 8000 Evo triple quadrupole mass spectrometer (Thermo Fisher Scientific,
Waltham, MA, USA). Separation was achieved using a J&W Scientific DB-5M column (30 m long,
0.25 mm inner diameter, 0.1 μm film thickness; Agilent Technologies, Santa Clara, CA, USA). The
injection volume was 1.0 μL and splitless injection mode was used. The carrier gas was high-purity
helium and the flow rate was 1.0 mL/min. The oven temperature program started at 60 °C, which was
held for 3 min, then increased at 10 °C/min to 280 °C, which was held for 3 min. The triple quadrupole
mass spectrometer was used in electron impact ionization mode. The ion source temperature was
280 °C and the transmission line temperature was 290 °C. The mass spectrometer was used in selected
ion detection mode and n-alkyl nitrates were detected by monitoring the characteristic [NO$_3$]$^-$ ion (m/z
46.07) and [CH$_2$ONO$_2$]$^-$ ion (m/z 76.07), which were used as the confirmation and quantitation ions.
The GC-MS/MS data were processed and the n-alkyl nitrates were quantified using TraceFinder 2.0
software (Thermo Fisher Scientific).

2.5 Quantitative analysis

The n-alkyl nitrates were quantified using an external standards method. We used the synthesized
C$_7$–C$_{10}$ n-alkyl nitrate standards to prepare standard solutions at concentrations of 1000, 100, 50, 20, and 10
ng/mL. A calibration curve was plotted for each analyte with the concentrations of the standards on the
x-axis and the GC-MS/MS instrument responses on the y-axis. The linear ranges of the standard curves
for the C$_7$–C$_{10}$ n-alkyl nitrate homologues were 10–1000 ng/mL, and the correlation coefficients were
all >0.998. The n-alkyl nitrate concentrations in the PM2.5 sample extracts were quantified using the
 calibration curves.
2.6 Quality assurance and control

Method and spiked blanks were extracted with each batch of samples. The \( n \)-alkyl nitrate concentrations found in the blank samples were subtracted from the \( n \)-alkyl nitrate concentrations found in the samples. The detection and quantification limits of the GC-MS/MS instrument were defined as the concentrations giving signal-to-noise ratios of 3 and 10, respectively. The instrument detection limits for the \( n \)-alkyl nitrates were 1.0–10.0 pg and the method quantification limits were 0.1–1.0 pg/m³.

The recoveries of the \( n \)-alkyl nitrates in the PM\(_{2.5} \) samples were determined by performing spike recovery experiments, and the recovery was defined as the ratio between the measured and spiked concentrations. Three parallel spiked blank samples were analysed, and 20 µL of a standard solution containing each \( C_9-C_{16} \) \( n \)-alkyl nitrate at a concentration of 100 ng/mL was added to each. The spiked blanks were then treated and analysed using the method described above. The \( n \)-alkyl nitrate concentrations in the spiked blank samples were determined by GC-MS/MS and the recoveries were calculated. The \( n \)-alkyl nitrate recoveries were 62.6%–95.3% and the relative standard deviation was 2.65%.

2.7 Data analysis

The PM\(_{2.5} \), ozone, and NO\(_2 \) concentrations were obtained from the China Meteorological Administration (www.cma.gov.cn/, last access: 31 October 2021). The particulate-bound \( n \)-alkyl nitrate concentration data were statistically analysed using SPSS 26.0 software (IBM, Armonk, NY, USA). Correlations between concentrations of different species were identified by performing Pearson correlation and Spearman correlation tests (two-tailed), and differences between the concentrations in different samples were assessed by performing independent sample t-tests, paired sample t-tests, and one-way ANOVAs.

3 Results and discussion

3.1 Particulate-bound \( n \)-alkyl nitrate pollution

3.1.1 Concentrations and compositions

The \( C_9-C_{16} \) \( n \)-alkyl nitrates were detected in the PM\(_{2.5} \) samples collected during day and night in all of the seasons, and the concentrations are shown in Figure 1. The concentration ranges, mean concentrations, and detection rates for the different homologues are shown in Table 1.

The \( C_9 \) and \( C_{10} \) \( n \)-alkyl nitrate detection rates were <50%, the \( C_{11} \) \( n \)-alkyl nitrate detection rate was ~70%, and the \( C_{12}-C_{16} \) \( n \)-alkyl nitrate detection rates were ~90%. The particulate-bound \( n \)-alkyl nitrate detection rates generally increased as the carbon chain length increased. These results indicated that particulate-bound \( n \)-alkyl nitrates are widely present in airborne particulate matter in Beijing and that long chain \( n \)-alkyl nitrates are more abundant than short chain \( n \)-alkyl nitrates.

The total \( C_9-C_{16} \) \( n \)-alkyl nitrate concentrations were 9.67–2730 pg/m³, and the mean was 578 pg/m³. As shown in Table 1, the particulate-bound \( n \)-alkyl nitrate homologue concentration range and mean increased as the carbon chain length increased. The \( C_{16} \) \( n \)-alkyl nitrate homologue had the highest concentration range, and the mean concentration was significantly higher than the mean concentrations.
of the other homologues (p<0.01). The C_{12–C_{16}} n-alkyl nitrate concentrations were significantly higher than the C_{9–C_{11}} n-alkyl nitrate concentrations (p<0.01), i.e., the long-chain n-alkyl nitrate concentrations were higher than the short-chain n-alkyl nitrate concentrations in the PM2.5 samples. The particulate-bound n-alkyl nitrate homologue group compositions in the day and night in the different seasons during the sampling period are shown in Figures 2 and 3. It can be seen that the C_{12}, C_{14}, C_{16}, and C_{18} n-alkyl nitrate homologues made relatively high contributions to the total n-alkyl nitrate concentrations and that n-alkyl nitrates with longer carbon chains (C_{12–C_{16}}) generally contributed more than n-alkyl nitrates with shorter carbon chains (C_{9–C_{11}}) to the total n-alkyl nitrate concentrations during the sampling period.

The long-chain n-alkyl nitrate concentrations and contributions to the total n-alkyl nitrate concentrations in PM2.5 may have been high because of high concentrations of precursor n-alkanes in the atmosphere and the abilities of n-alkyl nitrates to form on airborne particles. n-Alkane volatility decreases as the carbon chain length increases, and long-chain n-alkanes are more abundant than short-chain n-alkanes in airborne particulate matter. The alkyl nitrate yield increases as the carbon chain lengths of the precursor alkanes increase (Lim et al., 2009; Matsunaga et al., 2009; Yeh et al., 2014). The n-alkyl nitrate (monofunctional organic nitrate) stability increases and the saturated vapour pressure decreases as the carbon chain length increases. Long-chain alkyl nitrates therefore tend more than short-chain alkyl nitrates to be associated with airborne particles and to be involved in particulate matter formation (Lim et al., 2005; Yee et al., 2012). The increasing n-alkyl nitrate concentrations in the particulate phase as the n-alkyl nitrate carbon chain length increased needed to be investigated further by investigating the mechanisms involved in n-alkyl nitrate formation.

3.1.2 Diurnal and seasonal variations in n-alkyl nitrate concentrations and homologue patterns

As shown in Table 1, the mean C_{9–C_{16}} n-alkyl nitrate concentrations in PM2.5 were higher at night than in the day and the mean C_{12–C_{16}} n-alkyl nitrate concentrations were significantly higher at night than in the day (p<0.01). However, the contributions of the different n-alkyl nitrates to the total n-alkyl nitrate concentrations in the day and night samples were not significantly different, as shown in Figures 2 and 3. We concluded that the diurnal changes in the particulate-bound n-alkyl nitrate concentrations may have been caused by diurnal changes in meteorological conditions affecting partitioning of the semi-volatile compounds between the gas and particle phases or by diurnal changes in particulate-bound alkyl nitrate formation.

Temporal trends in the total C_{9–C_{16}} n-alkyl nitrate concentrations during the sampling period are shown in Figure 4. The n-alkyl nitrate concentrations varied seasonally, with the maximum total concentration occurring in winter and the mean concentration decreasing in the order winter > spring > autumn > summer. The contributions of the different n-alkyl nitrate homologues varied seasonally, with the contributions in summer being significantly different from the contributions in the other seasons (p<0.01) but the compositions in winter, spring, and autumn not being significantly different. The mean particulate-bound n-alkyl nitrate concentrations in winter and spring were significantly higher than the mean particulate-bound n-alkyl nitrate concentrations in summer and autumn (p<0.01). The mean particulate-bound n-alkyl nitrate concentration was lowest in summer even though the maximum short-chain (C_{1–C_{3}}) alkyl nitrate concentration in the gas phase was previously found to occur in the summer (Simpson et al., 2006; Wang et al., 2013; Ling et al., 2016; Sun et al., 2018). We concluded that long-chain particulate-bound n-alkyl nitrates and short-chain alkyl nitrates have different formation mechanisms.
3.2 Particulate-bound n-alkyl nitrate formation mechanisms

3.2.1 Involvement of particulate-bound n-alkyl nitrates in photochemical reactions

It is generally agreed that organic nitrates are secondary products of gas-phase photochemical reactions in the atmosphere (Perring et al., 2013; Ng et al., 2017) and that organic nitrates enter the particulate phase through gas–particle partitioning (Capouet et al., 2005; Gu et al., 2017). At high background NOx concentrations, short-chain (C_1–C_3) alkyl nitrates are mainly produced through gas-phase reactions between alkanes and OH· radicals during the day (i.e., in the presence of sunlight) (Robert, 1990; Wisthaler et al., 2008). Alkanes react with OH· radicals to form alkyl radicals through hydrogen subtraction, and the alkyl radicals are further oxidized to give RO_2· radicals. Finally, the RO_2· radicals react with nitric oxide to give alkyl nitrates. Short-chain (C_1–C_3) alkyl nitrates have been found to be secondary products of photochemical reactions, and short-chain alkyl nitrate concentrations have been found to correlate with the concentrations of photochemical pollutants and in particular to significantly positively correlate with the ozone concentration (Wang et al., 2013; Ling et al., 2016; Sun et al., 2018).

Short-chain alkyl nitrate concentrations vary temporally in a similar way to the peroxycetyl nitrate concentration, with the maximum concentration occurring in summer (Simpson et al., 2006). However, the temporal trends in particulate-bound long-chain n-alkyl nitrate concentrations we found were different from the temporal trends in gas-phase short-chain alkyl nitrate concentrations found in previous studies.

Temporal trends in the total C_5–C_{16} n-alkyl nitrate concentrations and ozone concentrations during the sampling period were compared to investigate the relationships between particulate-bound n-alkyl nitrates and photochemical reactions. The C_5–C_{16} n-alkyl nitrate and ozone concentrations are shown in Figure 5. The total particulate-bound n-alkyl nitrate and ozone concentrations followed opposite temporal trends, with the lowest ozone concentration and highest total particulate-bound n-alkyl nitrate concentration occurring in winter and the highest ozone concentration and lowest particulate-bound n-alkyl nitrate concentration occurring in summer. A significant negative correlation was found between the ozone and particulate-bound n-alkyl nitrate concentrations (p<0.01, r=-0.411). The C_6, C_{10}, and C_{11} n-alkyl nitrate concentrations did not significantly correlate with the ozone concentration but the C_{12}–C_{16} n-alkyl nitrate concentrations significantly negatively correlated with the ozone concentration (p<0.01). This and the particulate-bound n-alkyl nitrate concentration being higher at night than in the day suggested that particulate-bound n-alkyl nitrates are not indicators of photochemical pollution and form through different mechanisms from gas-phase short-chain (C_1–C_3) alkyl nitrates. This means that particulate-bound n-alkyl nitrates are not formed through photochemical reactions involving ozone and that long-chain (C_{12}–C_{16}) n-alkyl nitrates are not secondary products of photochemical reactions.

3.2.2 Possible particulate-bound n-alkyl nitrate formation mechanisms

We found that particulate-bound n-alkyl nitrates are not products of gas-phase photochemical reactions, so other mechanisms must be involved in particulate-bound n-alkyl nitrate formation. The particulate-bound n-alkyl nitrate and PM_{2.5} concentrations significantly correlated (p<0.01, r=0.618) in a previous study performed in Beijing (Yang et al., 2023). The temporal trends in the particulate-bound n-alkyl nitrate and PM_{2.5} concentrations are shown in Figure 6. The C_5–C_{16} n-alkyl nitrate and PM_{2.5} concentrations followed similar temporal trends, and the concentrations of both changed synchronously,
indicating that the C9–C16 n-alkyl nitrate and PM2.5 concentrations may have correlated. Statistical tests were performed, and, indeed, a significant positive correlation was found between the particulate-bound n-alkyl nitrate and PM2.5 concentrations (p<0.01, r=0.664).

The particulate-bound C9–C11 n-alkyl nitrate homologue concentrations did not significantly correlate with the PM2.5 concentration, and the C9–C11 n-alkyl nitrates and precursor n-alkanes were found at low detection rates and concentrations in the PM2.5 samples. We concluded that C9–C11 n-alkyl nitrates in particulate matter may form through both gas-phase and particle-phase reactions. The C13–C16 n-alkyl nitrate homologue concentrations significantly positively correlated with the PM2.5 concentration (p<0.01). We concluded that the C13–C16 particulate-bound n-alkyl nitrate and particulate matter concentrations probably correlated because of reactions involving precursors of n-alkyl nitrates on the particulate matter, meaning the particulate matter acted as a medium on which particulate-bound n-alkyl nitrates formed.

It has previously been found that organosulfate compounds, which have similar structures to organic nitrates, can form through non-homogeneous reactions involving sulfate and organosulfate compound precursors on surfaces of particles (Farmer et al., 2010). Organosulfates and organic nitrates are important organic pollutants in particulate matter and play important roles in the formation of haze (Li et al., 2018). Similar compounds may form through similar mechanisms, so we hypothesized that particulate-bound n-alkyl nitrates may form through reactions between alkanes and nitrate on particulate matter. Semi-volatile n-alkanes (precursors of n-alkyl nitrates) are widely present in particulate matter (Kang et al., 2018; Han et al., 2018; Lyu et al., 2019; Yang et al., 2023), and the n-alkane concentration in particulate matter increases as the carbon chain length increases (Aumont et al., 2012). Abundant n-alkanes in particulate matter make it possible for reactions to occur to form n-alkyl nitrates. Nitrogen oxides are precursors of organic nitrates and may be involved in the formation of particulate-bound n-alkyl nitrates, so we compared the temporal trends in the NO2 and particulate-bound n-alkyl nitrate concentrations. The NO2 and particulate-bound n-alkyl nitrate concentrations are shown in Figure 7. The C9–C16 particulate-bound n-alkyl nitrate and NO2 concentrations significantly positively correlated (p<0.01, r=0.626). The C12, C13, C14, C15, and C16 nitrate concentrations significantly positively correlated with the NO2 concentration (p<0.01), indicating that NO2 may be involved in the formation of particulate-bound n-alkyl nitrates.

It has been found that the formation of nitrate (NO3–) in particulate matter is related to the presence of NO2 and that the NO2 and NO3– concentrations significantly positively correlate (Su et al., 2018). NO2 in the atmosphere can be oxidized to NO3– through non-homogeneous reactions on particulate matter surfaces, and most particulate-phase NO3– forms through these non-homogeneous reactions (Zhu et al., 2010). The high NO2 concentrations found in the atmosphere in urban areas mean particulate-phase nitrate can form. Particulate-bound n-alkyl nitrates may form through non-homogeneous reactions between n-alkanes and nitrate on particulate matter surfaces. It has previously been found that n-alkanes can react with nitrate at room temperature with catalysis by metallic copper to give alkyl nitrates (Luxenhofer et al., 1994; Luxenhofer et al., 1996). Copper is widely present in airborne particulate matter in urban areas (Duan et al., 2014; Gonzalez et al., 2016) and could catalyse the formation of particulate-bound n-alkyl nitrates. The similar temporal trends in the particulate-bound n-alkyl nitrate, PM2.5, and NO2 concentrations and the significant positive correlations between the n-alkyl nitrate, PM2.5, and NO2 concentrations led us to conclude that particulate-bound n-alkyl nitrates form through reactions between precursor alkanes and particulate-bound nitrate on particulate matter surfaces.
3.3 Contributions of particulate-bound \( n \)-alkyl nitrates to haze pollution

The temporal trends in the particulate-bound \( n \)-alkyl nitrate and PM\(_{2.5}\) concentrations were similar, as shown in Figure 6. The particulate-bound \( n \)-alkyl nitrate and PM\(_{2.5}\) concentrations significantly positively correlated (\( p<0.01, r=0.664 \)), indicating that particulate-bound \( n \)-alkyl nitrates contributed to the formation of particulate matter. The particulate-bound \( n \)-alkyl nitrate and PM\(_{2.5}\) concentrations increased sharply during haze pollution events in winter, spring, and autumn, indicating that particulate-bound \( n \)-alkyl nitrates are important components of SOAs and make marked contributions to atmospheric particulate matter and haze. Similar results were found in previous studies of organic nitrates (Rollins et al., 2012). Changes in the \( C_9-C_{16} \) particulate-bound \( n \)-alkyl nitrate homologue concentrations during the sampling period are shown in Figure 8. It can be seen that the temporal changes in the \( n \)-alkyl nitrate homologue concentrations became more similar to the temporal changes in the PM\(_{2.5}\) concentration as the carbon chain length increased. Each \( C_{13}-C_{16} \) \( n \)-alkyl nitrate homologue concentration significantly positively correlated with the PM\(_{2.5}\) concentration (\( p<0.01 \)), and the correlation coefficient increased as the \( n \)-alkyl nitrate carbon chain length increased. This indicated that the contribution of \( n \)-alkyl nitrates to the formation of particulate matter and haze increased as the carbon chain length increased. Because of the high background NOx concentration in ambient air in urban areas, particulate-bound \( n \)-alkyl nitrate SOAs can make important contributions to the particulate matter concentration and therefore to haze. Organic nitrates have been found to contribute 2\%–12\% of particulate matter in SOAs (Fry et al., 2008; Rollins et al., 2012; Fry et al., 2013; Xu et al., 2015), meaning that the contributions of organic nitrates to particulate matter in the atmosphere should not be ignored and that anthropogenic precursors for long-chain particulate-bound \( n \)-alkyl nitrates are abundant in the environment and should therefore be of more concern than is currently the case. The particulate-bound \( n \)-alkyl nitrate concentration and atmospheric visibility significantly negatively correlated (\( p<0.01, r=-0.698 \)), indicating that an increase in the particulate-bound \( n \)-alkyl nitrate concentration will strongly decrease atmospheric visibility during a haze event. We concluded that particulate-bound \( n \)-alkyl nitrates strongly affect haze pollution and that controlling anthropogenic emissions of NOx and VOCs (precursors of particulate-bound \( n \)-alkyl nitrates) would effectively control particulate matter pollution and improve air quality in urban areas.

4 Conclusions

The concentrations of \( n \)-alkyl nitrates in PM\(_{2.5}\) were determined, and all eight \( C_9-C_{16} \) \( n \)-alkyl nitrate homologues were detected in PM\(_{2.5}\), indicating that long-chain alkyl nitrates are present in airborne particulate matter in Beijing. The total \( C_9-C_{16} \) \( n \)-alkyl nitrate concentrations during the sampling period were 9.67–2731.82 pg/m\(^3\), and the mean was 578.44 pg/m\(^3\). The detection rate, concentration range, and mean concentration of each \( n \)-alkyl nitrate homologue group in the particulate matter samples increased as the carbon chain length increased. The \( C_{12}-C_{16} \) \( n \)-alkyl nitrates contributed more than the \( C_9-C_{11} \) \( n \)-alkyl nitrates to the total \( n \)-alkyl nitrate concentrations, indicating that long-chain \( n \)-alkyl nitrates were more abundant than short-chain \( n \)-alkyl nitrates in the particulate matter. There were marked diurnal and seasonal differences in the particulate-bound \( n \)-alkyl nitrate concentrations. The mean \( C_{12}-C_{16} \) \( n \)-alkyl nitrate concentrations were significantly higher at night than in the day (\( p<0.01 \)). The maximum particulate-bound \( n \)-alkyl nitrate concentrations occurred in winter, and the mean concentrations decreased in the order winter > spring > autumn > summer. The lowest mean concentration was found in summer even though the maximum short-chain (\( C_1-C_3 \)) alkyl nitrate
concentrations in the gas phase has previously been found to occur in summer. The particulate-bound
n-alkyl nitrate concentration followed the opposite temporal trend to and significantly negatively
 correlated with the ozone concentration. We concluded that long-chain particulate-bound n-alkyl
nitrates form through different mechanisms to gas-phase short-chain alkylnitrates and are not
secondary products of gas-phase photochemical reactions. The particulate-bound n-alkyl nitrate
concentration followed the same temporal trend to and significantly positively correlated with the
PM$_{2.5}$ and NO$_2$ concentrations (p<0.01). Particulate-bound n-alkyl nitrates may form through
non-homogeneous reactions between alkanes and nitrate on particulate matter surfaces, meaning that
particulate matter acts as a reaction substrate and reactant carrier. Particulate-bound n-alkyl nitrates are
important contributors of airborne particulate matter and strongly affect atmospheric visibility, meaning
the roles of particulate-bound n-alkyl nitrates in the formation of haze cannot be ignored and
controlling anthropogenic emissions of precursors of particulate-bound n-alkyl nitrates in urban areas
with high background NOx concentrations will effectively control haze pollution and improve air
quality.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [grant no. 91744206]
and the Beijing Science and Technology Planning Project [Z181100005418016]. We also thank Dr.
Gareth Thomas for his help editing this paper to improve the grammar.

Data availability

The data presented in this article are available from the authors upon request (junjin3799@126.com).

Author contribution

JJ conceived and designed the study, provided direct funding, and helped with manuscript revision.
JYY and GYL mainly conducted the sampling and sample analysis and wrote and revised the
manuscript. The other authors helped with sampling and analysis. All authors read and approved the
final manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Figure 1. Concentrations of C₉–C₁₆ n-alkyl nitrates found during the sampling period.
Figure 2. Contributions of the C₉–C₁₆ n-alkyl nitrate homologues to the total C₉–C₁₆ n-alkyl nitrate concentrations in the day samples collected in different seasons.

Figure 3. Contributions of the C₉–C₁₆ n-alkyl nitrate homologues to the total C₉–C₁₆ n-alkyl nitrate concentrations in the night samples collected in different seasons.
Figure 4. Total C9–C16 n-alkyl nitrate concentrations during the sampling period

(“D” indicates samples collected in the day and “N” indicates samples collected at night)

Table 5. Total C9–C16 n-alkyl nitrate and ozone concentrations
Table 6. Total C9–C16 n-alkyl nitrate and PM2.5 concentrations

Figure 7. Total C9–C16 n-alkyl nitrate and NO2 concentrations
Figure 8. C₉–C₁₆ n-alkyl nitrate homologue and PM₂.₅ concentrations

Table 1. C₉–C₁₆ n-alkyl nitrate concentration ranges, mean concentrations, and detection rates
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<tr>
<th>n-Alkyl nitrates</th>
<th>Concentration range (pg/m³)</th>
<th>Mean concentration (pg/m³)</th>
<th>Detection rate</th>
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<td>Day (n=46)</td>
<td>Night (n=46)</td>
<td>Total (n=92)</td>
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<tr>
<td>C₉H₁₉ONO₂</td>
<td>ND-12.70</td>
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<td>683.48</td>
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</table>

Total (n=92)

9.67-2731.82

495.09

683.48

589.29

100%

100%

100%