Summertime C1-C5 alkyl nitrates over Beijing, northern China: Spatial distribution, regional transport, and formation mechanisms

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A B S T R A C T

Alkyl nitrates (RONO\textsubscript{2}) are an important class of nitrogen oxides reservoirs in the atmosphere and play a key role in tropospheric photochemistry. Despite the increasing concern for photochemical air pollution over China, the knowledge of characteristics and formation mechanisms of alkyl nitrates in this region is limited. We analyzed C\textsubscript{1}-C\textsubscript{5} alkyl nitrates measured in Beijing at a polluted urban site in summer 2008 and at a downwind rural site in summers of both 2005 and 2008. Although the abundances of NO\textsubscript{x} and hydrocarbons were much lower at the rural site, the mixing ratios of RONO\textsubscript{2} were comparable between both sites, emphasizing the regional nature of alkyl nitrate pollution. Regional transport of urban plumes governed the elevated RONO\textsubscript{2} levels at the rural site. The concentrations of C\textsubscript{4}-C\textsubscript{5} RONO\textsubscript{2} were significantly higher at the rural site in 2008 compared to 2005 despite a decline in NO\textsubscript{x} and anthropogenic VOCs, mainly owing to enhanced contributions from biogenic VOCs. The photochemical formation regimes of RONO\textsubscript{2} were evaluated by both a simplified sequential reaction model and a detailed master chemical mechanism box model. The observed C\textsubscript{4}-C\textsubscript{5} RONO\textsubscript{2} levels can be well explained by the photochemical degradation of n-butane and n-pentane, while the sources of C\textsubscript{1}-C\textsubscript{3} RONO\textsubscript{2} were rather complex. In addition to the C\textsubscript{1}-C\textsubscript{3} alkanes, biogenic VOCs and reactive aromatics were also important precursors of methyl nitrate, and alkenes and long-chain alkanes contributed to the formation of C\textsubscript{2}-C\textsubscript{3} RONO\textsubscript{2}. This study provides insights into the spatial distribution, inter-annual variation and photochemical formation mechanisms of alkyl nitrate pollution over the Beijing area.

1. Introduction

Alkyl nitrates (RONO\textsubscript{2}) are an important class of organic nitrates in the troposphere, and play key roles in the atmospheric carbon and nitrogen cycles (Bertman et al., 1995; Clemitshaw et al., 1997; Russo et al., 2010), and aerosol formation (Yan et al., 2016). They serve as temporary reservoirs of nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) due to their low reactivity and slow photolysis rate in the troposphere (Atkinson et al., 2006; Jenkin and Clemitshaw, 2000; Seinfeld et al., 1998). In the polluted urban and industrial atmospheres, formation of alkyl nitrates generally consumes NO\textsubscript{x} and may result in a negative contribution to ozone (O\textsubscript{3}) production (Ling et al., 2016), but in the rural and remote areas, alkyl nitrate can act as a potential supplier of NO\textsubscript{x} and thus can enhance O\textsubscript{3} formation (Aruzzo et al., 2014; Day et al., 2003). Therefore, alkyl nitrates have a potential to affect atmospheric chemistry and O\textsubscript{3} formation at a regional scale.

In the troposphere, alkyl nitrates are mainly produced by photochemical reactions of hydrocarbons (RH) and NO\textsubscript{x}, and their major sinks include photolysis reactions, oxidation by OH, and dry deposition (Russo et al., 2010; Wu et al., 2011). The detailed chemical processes of alkyl nitrates can be described by the following reactions:

\[ \text{RH} + \text{OH} \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \quad k_1, \alpha_1 \] (R\textsubscript{1})

\[ \text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^- \quad k_2 \] (R\textsubscript{2})

\[ \text{RO}_2^- + \text{NO} \rightarrow \text{RO}^- + \text{NO}_2 \quad k_3, 1-\alpha_2 \] (R\textsubscript{3})

\[ \text{RO}_2^- + \text{NO} \rightarrow \text{RONO}_2 \quad k_4, \alpha_2 \] (R\textsubscript{4})

\[ \text{RO}^- + \text{NO}_2 \rightarrow \text{RONO}_2^- \quad k_5 \] (R\textsubscript{5})
RONO$_2$ + hv $\rightarrow$ RO· + NO$_2$ \hspace{0.5cm} (R_6)

RONO$_2$ + OH $\rightarrow$ RC(O)R' + NO$_2$ \hspace{0.5cm} (R_7)

where, $k_i$ is the reaction rate constant, and $\alpha_i$ is the branching ratio of the reactions. It should be noted that alkyl nitrates are mainly formed via the reactions of alkyl peroxy radicals (RO$_2$) with NO (R$_{10}$), whereas R$_5$ is not likely the major source of alkyl nitrates under normal atmospheric conditions (Simpson et al., 2002). In addition to secondary formation, marine emission is also proposed as an important source of methyl nitrate (MeONO$_2$) and ethyl nitrate (EtONO$_2$), especially in the coastal areas (Blake et al., 2003; Chuck et al., 2002; Simpson et al., 2006), and biomass burning is another source of alkyl nitrates (Simpson et al., 2002). Understanding the sources of alkyl nitrates presents a crucial aspect of atmospheric chemistry research.

The relationship between RONO$_2$ and their direct parent hydrocarbons (c.a., methyl nitrate vs. CH$_4$, ethyl nitrate vs. C$_2$H$_6$, etc.) can provide valuable information about the photochemical processing of air masses. Bertman et al. (1995) developed a simplified sequential reaction model to examine the photochemical evolution of alkyl nitrates. The measured ratios of RONO$_2$/RH can be compared with the theoretical values calculated using laboratory kinetic data to assess the photochemical age of air masses and to diagnose the potential existence of additional sources of alkyl nitrates. If the measured ratios agree well with the theoretical values, it suggests that alkyl nitrates are mainly formed from the oxidation of their direct parent hydrocarbons (i.e., C$_1$–C$_5$ alkanes); otherwise it indicates the presence of other sources such as photochemical reactions of hydrocarbons other than C$_1$–C$_5$ alkanes if the measured ratios exceed the theoretical ones. This approach has been widely used in many previous studies (Ling et al., 2016; Reeves et al., 2007; Russo et al., 2016; Simpson et al., 2006; Wang et al., 2013; Worton et al., 2010). Nonetheless, this method cannot directly identify the additional precursor species to which the formation of RONO$_2$ is the most sensitive. It is of much interest and necessity to directly identify the individual precursor species of alkyl nitrates and quantify their relationships from both atmospheric chemistry and air quality management points of view.

In recent years, photochemical air pollution has become a major environmental concern in China (Wang et al., 2017; Xue et al., 2014). Despite the increasing concern about photochemical pollutants such as O$_3$ and peroxyacetyl nitrate (PAN), only limited studies have focused on the characteristics and sources of alkyl nitrates in China. Wang et al. (2013) measured C$_1$–C$_5$ alkyl nitrates and investigated their relationships with parent hydrocarbons, carbonyls and O$_3$ in 47 Chinese cities. Ling et al. (2016) and Lyu et al. (2015) examined the spatiotemporal variability and photochemical formation processes of C$_1$–C$_5$ alkyl nitrates in Hong Kong. In this study, we analyzed the measurement data of C$_1$–C$_5$ alkyl nitrates, hydrocarbons, O$_3$, NO$_x$ and NO$_y$ collected at a polluted urban site and a downwind rural site in Beijing in the summers of 2005 and 2008. The spatial distribution and temporal variations of alkyl nitrates and their parent hydrocarbons were evaluated. In addition to the sequential reaction model, we also utilized the Master Chemical Mechanism (MCM) model to directly identify the precursor species and quantify the RONO$_2$-precursor relationships. Overall, this study provides some insights into the characteristics and formation mechanisms of alkyl nitrates and photochemical pollution in the polluted atmospheres of Beijing.

2. Methods

2.1. Sampling sites

To achieve a better understanding of the photochemical processes on a regional scale, two study sites, representing typical polluted urban and rural areas of Beijing, were carefully selected. The urban site was located at the Chinese Research Academy of Environmental Science (CRAES; 40°2’N, 116°25’E), which is approximately 15 km to the north of Tiananmen square and close to the 5th ring road (Fig. 1). The site was set up on the rooftop of a three-story building with an altitude of ~15 m above the ground level. The details of this site have been described elsewhere (Wang et al., 2010). The measurements were conducted from 10 July to 27 September 2008, during which the 29th Olympic Games was hosted in Beijing and strict anti-pollution measures were implemented (Wang et al., 2010).

The rural site was located in a mountainous area in Changping district (40°22’N, 116°18’E; 280 m above sea level), about 50 km northwest of the city center (Fig. 1). The instruments were installed in an orchard growing many kinds of fruit trees such as peach and apricot. There is sparse population and few anthropogenic emissions near the study site. Under the influence of the summer Asian monsoon, the Changping site was usually located downwind of downtown Beijing with the prevailing southerly winds. A detailed description of this study site has been provided previously (Wang et al., 2006). Two phases of intensive measurements were carried out during 28 June – 31 July 2005 and 10 July – 25 August 2008, respectively. The 2008 rural campaign was in parallel with the observations made at CRAES, facilitating an analysis of regional distribution of alkyl nitrates and hydrocarbons over Beijing, and the two phases of measurements at Changping in 2005 and 2008 promoted an evaluation of the inter-

Fig. 1. Maps showing (a) the study area and anthropogenic NO$_x$ emissions (Zhang et al., 2009) and (b) the locations of the two study sites in Beijing. CRAES is the urban site and Changping is the rural site.
In the present study, ambient whole air samples were collected in evacuated 2-Liter stainless-steel canisters for the measurements of C1-C5 hydrocarbons, temperature, pressure and RH, to simulate the daytime formation of RONO2. All the measurement data were chemiluminescence sensors at each station (Wang et al., 2010).

2.3. Master chemical mechanism (MCM) model

An observation-based chemical box model (OBM) was used to assess the sensitivity of alkyl nitrate formation to their hydrocarbon precursors. The model is built on the newest version of the Master Chemical Mechanism (MCM v3.3.1) that explicitly describes the degradation of 143 primary VOCs together with the latest IUPAC inorganic nomenclature (Jenkin and Clemmish, 2000; Jenkin et al., 2015; Saunders et al., 2003), and has been applied in many previous studies to unravel several essential aspects of atmospheric photochemistry, such as O3 and PAN formation, reactive chlorine chemistry, and radical chemistry (e.g., Xue et al., 2016; and references therein).

The model was prescribed to a mean condition for the photochemical pollution episodes during which multiple VOC samples were collected. The base model was initialized by the measured average concentrations of C1-C6 alkyl nitrates in the early morning and was constrained in real-time by the average diurnal profiles of O3, CO, SO2, NO, C1-C6 hydrocarbons, temperature, pressure and RH, to simulate the daytime formation of RONO2. All the measurement data were averaged or interpolated to 1-h concentrations and used as the model inputs. For the nighttime period when VOC data were not available, we molybdenum oxide catalytic converter (Wang et al., 2010). Nitrogen dioxide (NO2) was monitored by another chemiluminescence analyzer (TEI, Model 42i) equipped with a blue light converter (Xu et al., 2013). Ambient temperature, pressure, relative humidity (RH), wind speed and direction, and solar radiation were measured by a set of commercial meteorological sensors at each station (Wang et al., 2010).
assumed constant VOC levels and used the average values of the VOC measurements at 19:00 LT. Such treatment of nighttime VOC input data should not affect the daytime photochemistry simulation results. The model was run for 24 h from 7:00 AM LT. Before each simulation, the model pre-ran for four days with constraints of the campaign-average data so that the model approached a steady state for the unmeasured species (mainly for radicals). The model output of the fifth run was then used for the final analyses.

In addition to the base run, sensitivity modeling studies with 50% reductions of target hydrocarbon species were conducted to estimate the sensitivity of RONO₂ production to their precursors. In the present study, the 50+ measured C₁-C₁₀ hydrocarbons were classified into 6 categories, namely, parent alkanes (PA; methane for MeONO₂, ethane for EtONO₂), propane for 1-PrONO₂ and 2-PrONO₂, n-butane for 2-BuONO₂, i-pentane for 3-Me-2-BuONO₂, and n-pentane for 2-PeONO₂ and 3-PeONO₂), alkanes with ≥ 4 carbons (C4HC), alkenes, reactive aromatics (R-AROM; comprising all measured aromatics except benzene), low-reactivity hydrocarbons (LRHC, including acetylene and benzene) and biogenic hydrocarbons (BHC; including isoprene and α/β-pinenes). Relative incremental reactivity (RIR), a metric commonly used to diagnose O₃ formation regimes (Cardelino and Chameides, 1995), was adopted analogously to estimate the RONO₂-precursor relationships. It is defined here as the ratio of decrease (in percentage) in model-simulated peak mixing ratios of RONO₂ to the decrease in the precursors concentrations (in percentage). The hydrocarbon species with higher positive RIR values are the precursors to which the alkyl nitrate formation is most sensitive.

3. Results and discussion

3.1. Chemical speciation and spatiotemporal variations

Table 1 summarizes the statistics of measurement data of alkyl nitrates, major hydrocarbons, O₃, NOₓ, NOᵧ and meteorological parameters obtained in Beijing during summertime of 2005 and 2008. The average chemical speciation of the observed C₁-C₅ alkyl nitrates is presented in Fig. 2. During the three measurement campaigns, serious photochemical air pollution was observed at both CRAES and Changping sites. For example, the maximum hourly O₃ concentrations were recorded at 286 ppbv at Changping in 2005 and at 191 and 174 ppbv at CRAES and Changping in 2008, respectively. Detailed analyses of O₃ pollution and formation regimes have been documented in our previous publications (Wang et al., 2006; Wang et al., 2010), and we focus on the alkyl nitrates in the present study. The measured average mixing ratios (± SD) of summed C₁-C₅ alkyl nitrates were 93 ± 9, 147 ± 12 and 146 ± 13 pptv at Changping in 2005 and at CRAES and Changping in 2008, respectively (recall that the 2005 campaign does not include 3-Me-2-BuONO₂, which may account for a small part of the difference). Such levels of ambient alkyl nitrates are among the highest records obtained elsewhere from previous pollution studies, such as Alabama, USA (51 pptv for C₂-C₃ RONO₂ in summer 1988; Bertman et al., 1995), Hong Kong (78 pptv at Tai O in 2001–2002, Simpson et al., 2006; 83 pptv at Tai Mo Shan and 90 pptv at Tsuen Wan in summer 2010, Ling et al., 2016) and Beijing in summer 2011 (109 pptv for C₁-C₄ RONO₂; Wang et al., 2013). During our study, 2-BuONO₂ was the most abundant RONO₂ species at both sites, accounting for 26–28% of the total measured C₁-C₅ RONO₂, followed by 2-PrONO₂ (17–27%), EtONO₂ (12–22%), 2-PrONO₂ (8–14%), 3-Me-2-BuONO₂ (10–11%) and MeONO₂ (6–10%), 3-PeONO₂ (5–9%) and 1-PrONO₂ (3–4%) only presented a minor contribution to the measured alkyl nitrates.

We compared the measurement data at Changping and CRAES in 2008 to illustrate the regional distribution of photochemical air pollution in Beijing. As expected, the levels of photochemical precursors, i.e., NOₓ and various hydrocarbons, were substantially higher at CRAES than at Changping (p < 0.01; see Table 1). This is attributed to the extensive fresh emissions in the urban area and photochemical processing of air masses during transport to the rural areas. However, the average mixing ratios of C₁-C₅ alkyl nitrates were comparable at the two sites (p > 0.1) even though the abundances of their parent alkanes at Changping were much lower than at CRAES. This is consistent with the regional transport of urban plumes from Beijing to the rural site considering the relatively low reactivity and long lifetime of alkyl nitrates as well as the photochemical formation of alkyl nitrates during transport. Furthermore, the average mixing ratio of O₃ at Changping (47 ± 25 ppbv) was higher than at CRAES (43 ± 30 ppbv; p < 0.01). The above comparison clearly demonstrates the regional nature of photochemical air pollution and alkyl nitrate formation over the Beijing area.

We also compared the measurement results at Changping in both 2005 and 2008 to examine the inter-annual changes of alkyl nitrate pollution and/or assess the effects of anti-pollution measures commenced during the Olympic Games in 2008. Overall, the ambient concentrations of NOₓ and most anthropogenic hydrocarbons at Changping in 2008 were lower than those observed in 2005 (although the differences for some VOC species are not statistically significant). However, the most reactive compounds such as isoprene and C₂-C₄ alkenes had higher levels in 2008 compared to 2005 (Table 1). Such difference should be due to the irregular emissions around the study site given the short lifetimes of these species. For secondary pollutants, the O₃ pollution levels in 2008 (47 ± 25 ppbv) was lower than in 2005 (60 ± 34 ppbv). In comparison, C₂-C₅ alkyl nitrates did not significantly change between 2005 and 2008, except for 3-PeONO₂ that showed a slight decrease due to the significant decline of n-pentane (p < 0.05; Table 1). Moreover, MeONO₂ (11.6 ± 5.3 pptv vs. 5.0 ± 2.7 pptv), EtONO₂ (29.4 ± 17.3 pptv vs. 9.5 ± 4.8 pptv) and 2-BuONO₂ (40.2 ± 31.5 pptv vs. 27.9 ± 21.4 pptv) were higher in 2008 than in 2005 (p > 0.05). Examination of VOC data showed a slight or moderate decrease in the abundances of the direct RONO₂ precursors (i.e., C₂-C₅ alkenes) but an increase of biogenic hydrocarbons (i.e., isoprene and α/β-pinenes; p < 0.01) from 2005 to 2008, implying the important role of biogenic emissions in the photochemical formation of alkyl nitrates in 2008. We will analyze in detail the photochemical formation mechanisms of alkyl nitrates in Section 3.4.
3.2. Effect of regional transport

Fig. 3 shows the average diurnal profiles of alkyl nitrates, O₃, NOₓ and wind sectors observed at CRAES and Changping in 2008. It clearly displays the well-defined daytime formation of O₃ and alkyl nitrates with broad concentration peaks in the afternoon. The amplitudes of O₃ and alkyl nitrate daytime accumulation were comparable between both sites, confirming again the nearly uniform regional distribution of photochemical pollution over Beijing. The maximum values of O₃ and alkyl nitrates at Changping occurred approximately two hours later than at CRAES, which in combination with the prevailing southerly winds during the daytime indicate the transport of urban plumes from downtown to the rural areas. Therefore, regional transport of urban pollution played an important role in the observed O₃ and alkyl nitrates at the Changping site.

To further elucidate the effect of regional transport on the alkyl nitrates, O₃ and peroxyacetyl nitrate (PAN) are co-products of atmospheric photochemical reactions of NOₓ and VOCs. Fig. 5 shows the scatter plots of the measured alkyl nitrates versus O₃ concentrations.

Fig. 3. Average diurnal variations of alkyl nitrates, O₃, NOₓ and wind sectors at CRAES (in red) and Changping (in blue) in 2008. Error bars are the standard errors of the measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Relationships with O₃ and PAN

Alkyl nitrates, O₃ and peroxyacetyl nitrate (PAN) are co-products of atmospheric photochemical reactions of NOₓ and VOCs. Fig. 5 shows the scatter plots of the measured alkyl nitrates versus O₃ concentrations.
at both Changping and CRAES during summer 2005 and 2008. Moderate to strong positive correlation can be clearly seen, with correlation coefficients ($r^2$) of 0.41–0.79. The reduced major axis (RMA) slopes of $O_3$ versus $RONO_2$ were 0.25 ppbv/pptv at CRAES in 2008, and 0.45 and 0.42 ppbv/pptv at Changping in 2005 and 2008, respectively. This means that approximately 25–45 ppbv of $O_3$ could be formed along with each 100 pptv of alkyl nitrates being photochemically produced in Beijing. Thus, alkyl nitrates can also be used to infer the $O_3$ formation potential at a given location (e.g., Simpson et al., 2006).

Fig. 6 presents the positive correlation ($r^2 = 0.70$) between alkyl nitrates and PAN, both of which were concurrently observed at CRAES in 2008. The RMA slope of PAN versus $RONO_2$ was 0.015 ppbv/pptv, indicating that about 1.5 ppbv of PAN was produced along with each 100 pptv of alkyl nitrates being photochemically formed. Indeed, PAN has much higher photochemical production efficiency than alkyl nitrates, and usually composes a higher fraction of the oxidized nitrogen oxides (i.e., NOx) in urban environments (Liu et al., 2010).

### 3.4. Photochemical formation mechanisms of alkyl nitrates

Photochemical oxidation of parent hydrocarbons is a vital source of alkyl nitrates. As mentioned above, a simplified sequential reaction model has been developed by Bertman et al. (1995) to examine the relationship between alkyl nitrates and their direct parent hydrocarbons, which has been widely applied to diagnose the presence of additional precursors of $RONO_2$ other than parent alkanes (Ling et al., 2016; Russo et al., 2010; Wang et al., 2013). The ratio of a target $RONO_2$ to its parent hydrocarbon ($RONO_2/RH$) in an air parcel with a certain photochemical age is determined by the initial $RONO_2/RH$ ratio, photochemical formation of $RONO_2$, and degradation of both $RONO_2$ and RH. By assuming that RO$_2$ radicals mainly react with NO in high NOx environments (cross reactions of peroxy radicals are considered to be less important) and the reaction of hydrocarbon with OH is the rate-limiting step for the $RONO_2$ production, the $RONO_2/RH$ ratio can be calculated as a function of photochemical processing time ($t$) according to the following expression (Bertman et al., 1995):

$$\frac{[RONO_2]}{[RH]} = \frac{\beta}{k_A^2} \frac{k_A}{k_B} e^{(k_A - k_B)t} + \frac{[RONO_2]_0}{[RH]_0} e^{(k_A - k_B)t}$$

(E1)

where, $k_A$ and $k_B$ represent the production and destruction rate constants of alkyl nitrates ($k_A = k_1[OH]$, $k_B = k_6[OH] + J_{RONO_2}$), and $k_1$ and $k_6$ are the rate constants for reactions of RH and $RONO_2$ with OH. $\alpha_1$ and $\alpha_2$ are the branching ratio of Reaction (R1) and product yield of $RONO_2$ from Reaction (R4), the values of which were taken from Kwok and Atkinson (1995), Atkinson and Arey (2003), and Bertman et al. (1995). The OH concentration is a key parameter and was not measured in the present study, and we adopted a daytime average value of $1 \times 10^7$ molecule cm$^{-3}$ according to the OH measurements available in suburban Beijing (Lu et al., 2013). $J_{RONO_2}$ is the photolysis frequency of alkyl nitrates, and was obtained from the literatures (Bertman et al., 1995; Wang et al., 2013; and references therein). $[RONO_2]_0/[RH]_0$ is the initial ratio of $RONO_2/RH$, and was approximated by the average...
alkanes showed the highest RIRs for all the C1-C3 RONO2, highlighting the importance of parent hydrocarbons at both Changping and CRAES. The photochemical degradation of isoprene and aromatic VOCs produce an amount of methyl peroxy radical (CH3O2) as an intermediate, which then reacts with NO to form methyl nitrate. At high NOx conditions, the reactions of CH3O with NO2 may be also an important formation pathway of methyl nitrate (Simpson et al., 2006; Archibald et al., 2007). In addition, degradation of isoprene and aromatics also yields an amount of other ROx radicals, which may indirectly prompt the formation of alkyl nitrates. For ethyl nitrate, alkanes with ≥ 4 carbons showed the highest RIR, followed by alkenes at Changping. Alkenes and alkanes with ≥ 4 carbons were also the major precursors for ethyl nitrate at CRAES. The chemical degradation of alkenes and alkanes with ≥ 4 carbons forms ethyl peroxy radical (C2H5O2), which can react with NO to form ethyl nitrate. Alkenes and alkanes with ≥ 4 carbons were also the most significant contributors to the photochemical formation of C3 RONO2 (1-PrONO2 and 2-PrONO2) at Changping and CRAES. Overall, in addition to the parent alkanes, biogenic VOCs and reactive aromatics potentially contributed to the formation of methyl nitrate, while longer chain alkanes and alkenes may result in the formation of C2-C3 alkyl nitrates.

We should note that the observational data analyzed in the present study were obtained in 2005 and 2008, almost ten years ago. Long-term measurements have indicated a 37% decline of the NMHC mixing ratios in Beijing from 2004 to 2012, although the anthropogenic emission inventory estimation suggested an increase of 28% during the same period (Wang et al., 2015). However, the observed NMHC decrease in Beijing was mainly contributed by the significant reduction of vehicle emissions, whilst the VOC emissions from solvent usage and industry did not show significant temporal changes (Wang et al., 2015). Reactive aromatics are important components of industrial solvents. Moreover, there are not effective control measures for biogenic emissions to date. Therefore, our findings based on such a relatively old data set can still provide useful information to support the formulation of control strategy towards photochemical pollution in Beijing.

4. Summary

We analyzed three sets of measurement data of C1-C9 alkyl nitrates and related parameters collected at both urban and rural sites in Beijing in summers of 2005 and 2008. Elevated concentrations of alkyl nitrates were observed along with high O3 mixing ratios, indicating the serious photochemical pollution status over Beijing. The alkyl nitrate levels were comparable at both sites even though the abundances of NOx and VOCs were much lower at the rural site. Regional transport of urban plumes played an important role in the observed pollution levels at the rural site. The C2-C3 alkyl nitrates measured at the rural site in 2008 were significantly higher than in 2005, despite a decrease in some anthropogenic VOCs. The increase in biogenic VOCs in 2008 may explain this difference. Photochemical oxidation of n-butane and n-pentane dominated the formation of C4-C5 alkyl nitrates, whilst the C1-C3 species showed more complex sources. In addition to the direct parent
alkanes, biogenic VOCs and reactive aromatics may significantly contribute to MeONO₂ formation, and alkenes and longer chain alkanes are potential precursors of C₂-C₅ alkyl nitrates. This study reveals the spatial distribution and inter-annual variation of photochemical air pollution, and helps clarify the photochemical formation regimes of alkyl nitrates in Beijing.

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