Nocturnal NO₃ radical chemistry in Houston, TX

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A B S T R A C T

Radical chemistry in the nocturnal urban boundary layer is dominated by the nitrate radical, NO₃, which oxidizes hydrocarbons and, through the aerosol uptake of N₂O₅, indirectly influences the nitrogen budget. The impact of NO₃ chemistry on polluted atmospheres and urban air quality is, however, not well understood, due to a lack of observations and the strong impact of vertical stability of the boundary layer, which makes nocturnal chemistry highly altitude dependent.

Here we present long-path DOAS observations of the vertical distribution of the key nocturnal species O₃, NO₂, and NO₃ during the TRAMP experiment in Summer 2006 in Houston, TX. Our observations confirm the altitude dependence of nocturnal chemistry, which is reflected in the concentration profiles of all trace gases at night. In contrast to other study locations, NO₃ chemistry in Houston is dominated by industrial emissions of alkenes, in particular of isoprene, isobutene, and sporadically 1,3-butadiene, which are responsible for more than 70% of the nocturnal NO₃ loss. The nocturnally averaged loss of NOₓ in the lowest 300 m of the Houston atmosphere is \( \frac{0.9}{C_0} \) ppb h⁻¹, with little day-to-day variability. A comparison with the daytime NOₓ loss shows that NO₃ chemistry is responsible for 16–50% of the NOₓ loss in a 24-h period in the lowest 300 m of the atmosphere. The importance of the NO₃ + isoprene/1,3-butadiene reactions implies the efficient formation of organic nitrates and secondary organic aerosol at night in Houston.

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1. Introduction

Chemical processing of urban air pollution differs substantially between night and day. In the nocturnal boundary layer (NBL) the OH radical becomes less important (Platt et al., 2002), and the nitrate radical, NO₃, and, to a lesser extent, O₃ become the dominant oxidants. The chemistry of NOₓ determines the nocturnal budget of NOₓ and VOCs and changes the composition of the aerosol (Dentener and Crutzen, 1993; Geyer, 2000; Geyer and Stutz, 2004; Platt et al., 2002; Wayne et al., 1991), thus influencing the levels of air pollutants at night and during the following day.

The lack of solar radiation also changes the micrometeorology from a well-mixed daytime boundary layer to the more stable, less mixed NBL, which is capped by a neutrally mixed residual layer. The suppressed vertical mixing causes surface-emitted trace gases to accumulate in the lower NBL throughout the night (Doran et al., 2003; Pisano et al., 1997; Wang et al., 2006). However, even in a very stable NBL, these gases are slowly transported vertically, while simultaneously undergoing chemical transformations (Geyer and Stutz, 2004).

Nocturnal chemistry in urban areas is dominated by the reactions of various nitrogen oxides. The titration of ozone with freshly emitted NO

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2,
\]

in combination with surface NO emissions and their slow vertical mixing, is responsible for much of the vertical dependence of nocturnal chemistry (Geyer and Stutz, 2004; Wang et al., 2006). Reaction (1) also influences the vertical profiles of ozone and NO₂, which are the precursor species for the NO₃ radical:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
\]

The NO₃ formation rate,

\[
P(\text{NO}_3) = k_{\text{NO}_3} \times [\text{O}_3] \times [\text{NO}_2]
\]
is thus also altitude dependent. The overall loss rate of NO3 due to various chemical reactions is
\[ \text{L(NO3)} = f_{\text{NO3}} \times [\text{NO3}], \]  
where \( f_{\text{NO3}} \), the total NO3 loss frequency, is also altitude dependent. In particular the reaction of NO3 with NO
\[ \text{NO3} + \text{NO} \rightarrow 2\text{NO2} \]  
with a loss frequency of
\[ f_{\text{NO3}}(\text{NO}) = k_{\text{NO} \cdot \text{NO3}} \times [\text{NO}] \]  
impacts the NO3 profiles in urban areas. The importance of this reaction depends on the NO emission rate, vertical mixing of NO, and the competing reaction of NO3 with ozone (Geyer and Stutz, 2004; Wang et al., 2006).

NO3 also reacts rapidly with unsaturated hydrocarbons. These reactions proceed primarily via the addition of the NO3 radical to hydrocarbons, transforming NO3 into secondary products such as nitrate esters and other products upon further reaction of the initial radical (Wayne et al., 1991).

\[ \text{NO3} + \text{R1} - \text{C} = \text{C} - \text{R2} \rightarrow \text{R1} - \text{C} - \text{C(NO3)} - \text{R2} \]  
The overall loss frequency of NO3 through the reactions with hydrocarbons can be quantified by:
\[ f_{\text{NO3}}(\text{HC}) = \sum f_{\text{NO3} + \text{HC}} \times [\text{HC}] \]  
The reactions of NO3 with hydrocarbons, in particular isoprene and terpenes, can also lead to the formation of secondary organic aerosol (SOA). For example, the SOA yield of the NO3 + isoprene reaction is 4.3–23.8% (Ng et al., 2008). NO3 can also react with aerosol particles (Docherty and Ziemann, 2006; Mak et al., 2007), although the uptake coefficients are not well known.

The often dominant pathway of NO3 and NO3 removal at night is the aerosol uptake of NO3:
\[ \text{N2O5} + \text{H2O(s)} \rightarrow 2\text{HNO3(s)} \]  
N2O5 is in a temperature dependent equilibrium with NO2 and NO3 (Wängberg et al., 1997), and its vertical profile depends on those of NO2 and NO3:
\[ \text{NO2} + \text{NO3} + \text{M} \rightarrow \text{N2O5} + \text{M} \]  
The reactive uptake coefficient of N2O5 on real atmospheric particles is highly variable (Brown et al., 2006), due to the varying composition of the aerosol. Uptake coefficients have been measured for a number of surfaces: \( \sim 0.07 \) for ammonium bisulfate particles at high RH, 0.005 for soot (Mak et al., 2007), and 0.001 and below for organic particles and particles coated with organic material (Thornton et al., 2003; Thornton and Abbatt, 2005). The loss of N2O5, with a frequency of \( f_{\text{N2O5}} \), indirectly leads to a loss of NO3:
\[ f_{\text{NO3}}(\text{N2O5}) = K_{\text{T}}(T)[\text{NO2}]f_{\text{N2O5}} \]  
A common approach to study nocturnal NO3 chemistry is to compare the overall NO3 loss frequency, \( f_{\text{NO3}}(\text{tot}) \), calculated from the individual loss pathways, i.e., based on observations of NO, NO2, hydrocarbons, aerosol surface area, and temperature,
\[ f_{\text{NO3}}(\text{tot}) = f_{\text{NO3}}(\text{NO}) + f_{\text{NO3}}(\text{HC}) + f_{\text{NO3}}(\text{aer}) + f_{\text{NO3}}(\text{N2O5}) \]  
with the pseudo steady-state loss frequency determined from observations of O3, NO2 and NO3 (Geyer and Stutz, 2004):
\[ f_{\text{NO3}}(\text{PSS}) = \frac{1}{f_{\text{NO3}}} = \frac{k_{\text{NO} + \text{O3}}[\text{NO2}]/[\text{O3}]}{[\text{NO3}]} \]  
We will define the steady-state NO3 lifetime, \( \tau_{\text{NO3}} \), as the inverse of \( f_{\text{NO3}}(\text{PSS}) \). An agreement between \( f_{\text{NO3}}(\text{tot}) \) (Equation (12)) and \( f_{\text{NO3}}(\text{PSS}) \) (Equation (13)) indicates that NO3 chemistry is well described by the different loss pathways in Equation (12), while a disagreement indicates inaccuracies in the description.

While this approach is quite powerful, care must be taken to ensure that it provides an accurate understanding of NO3 chemistry. First and foremost, it must be ensured that the steady-state assumption is appropriate, which requires a NO3 lifetime on the order of a few minutes or shorter. While this is not the case in rural and remote areas (Brown et al., 2003), the high levels of O3, NO2, NO, hydrocarbons, and aerosol in urban areas typically reduce the lifetime to these levels. Another challenge is the altitude dependence of the chemistry (Geyer and Stutz, 2004), which can be addressed by measuring vertical profiles of O3, NO2 and NO3, and by using vertical transport models.

Few studies have thus far discussed the vertical variation of NBL chemistry in urban areas (Aliwell and Jones, 1998; Friedeburg et al., 2002). During a previous field study by our group in a suburban area near Houston, TX, in 2000 we observed frequent negative vertical gradients of NO2 (larger concentrations near the surface than aloft) and positive vertical gradients of NO3 and O3 (smaller concentrations near the surface than aloft) when temperature inversions and calm wind conditions were encountered (Stutz et al., 2004). Wang et al. (2006) showed more pronounced gradients of these species in downtown Phoenix and identified the NO + O3 reaction as one of the main causes for the vertical variation in nocturnal chemistry. NO3 mixing ratios in Phoenix reached above 100 ppt aloft with \( \tau_{\text{NO3}} \) in the range of 0–1000 s. More recently (Brown et al., 2007a,b) confirmed the strong altitude dependence from combined aircraft/ground observations in the polluted marine boundary layer and on a tower in a polluted suburban area. Modeling studies attribute positive vertical gradients of both O3 and NO3 mainly to the reactions with surface-emitted NO and VOCs (Fish et al., 1999; Galmarini et al., 1997; Geyer and Stutz, 2004; Stutz et al., 2004). The impact of NO3 chemistry on nocturnal NO3 levels was discussed in detail by Geyer and Stutz (2004) and Stutz et al. (2004), who showed that the rates of various ozone and NO3 loss processes at 3 and 10 m were considerably different from those averaged over the lowest 100 m of the atmosphere.

The combined chemical and meteorological processes at night, and the poorly known NO3 and N2O5 aerosol uptake coefficients, pose a challenge for the description of the composition of the NBL and processes such as NOx removal, in particular in urban areas with enhanced ground emissions. Here we present results from the 2006 TexAQS Radical Measurement Program (TRAMP) (Lefer and Rappenglück, 2010), a component of the TexAQS-2006 field effort, in Houston, TX, where measurements of the vertical distribution of the most important nocturnal trace gases, meteorology, and other parameters were performed. The observations are interpreted using steady-state calculations as well as a highly resolved 1D chemical transport model calculations to quantify the impact of nocturnal chemistry on the nocturnal NO3 mixing ratio and the NOx budget.

2. Experimental

Measurements were performed from August 15 to September 22, 2006 on the North Moody tower on the University of Houston...
2.1. LP-DOAS

UCLA’s LP-DOAS instrument (Stutz et al., 2004; Wang et al., 2006) uses a 1.5 m double Newtonian telescope to send and receive a parallel beam of light from a Xe-arc lamp, which is reflected once by an array of quartz corner-cube retroreflectors. The received light is fed through a 200 μm diameter quartz-fiber mode-mixer into a 500 mm Czerny-Turner Spectrometer (ACTON Spectra-Pro 500) with a photodiode array detector (Hoffmann Messtechnik). Three retroreflector arrays were set up in downtown Houston at a distance of ~5 km from the telescope at three altitudes: 20 m, 130 m, 300 m. The telescope sequentially aimed at these reflector arrays, measuring the atmospheric absorptions of O3, NO2, and NO3 between the telescope and the retroreflectors (Fig. 1). The path-integrated absorptions were analyzed using least squares fitting techniques (Stutz and Platt, 1996) to derive path-integrated concentrations and their statistical error on all three light paths. To derive vertical profiles, the concentrations on the middle and upper light paths were first linearly interpolated to the time of the measurement of the lower light path. The middle and upper concentrations were then used to retrieve the trace gas concentrations in the 130–300 m height interval (Wang et al., 2006). The final results of this procedure are trace gas concentrations averaged in three height intervals: lower (20–70 m); middle (70–130 m); and upper (130–300 m). It should be noted that the horizontal location of upper concentrations is more heavily weighted towards the downtown area. The statistical error of the final data was derived through error propagation of the original uncertainties. All statistical errors reported here are 1σ. The error propagation of the statistical errors was calculated based on the mixing ratios and errors of NO2 and NO3, as well as the original uncertainties. All statistical errors reported here are 1σ (Stutz and Platt, 1996). The uncertainty of the NO2, O3, and NO3 absorption cross-sections is ±5%, ±3%, and ±10%, respectively (Bass and Paur, 1984; Voigt et al., 2002; Yokelson et al., 1994). The systematic error of the DOAS spectrometer was determined to be <3% (Stutz and Platt, 1996).

Table 1 gives an overview of the typical concentrations and errors for the trace gases measured by the LP-DOAS.

2.2. Supplemental measurements

A number of supplemental measurements were performed at Moody tower; see Lefer and Rappenglück (2010) for an overview. The measurements relevant for our study will briefly be described here. Details of the measurements can be found in the respective manuscripts of this special issue. A trace level TEI 42C chemiluminescence instrument was used to provide measurements of NO and NO2. Hydrocarbons were measured by gas chromatography using a Perkin–Elmer VOC-system consisting of a Clarus 500 GC (Perkin–Elmer, Shelton, CT, USA) with heart cut device and equipped with two FIDs and two columns (Alumina PLOT column and BP-1). Hydrocarbons were sampled for 40 min each hour at a rate of 15 mL min⁻¹ (Leuchner and Rappenglück, 2010). Aerosol surface area was measured by an Aerodyne quadrupole aerosol mass spectrometer as described by Ziemba et al. (2010). A laser induced fluorescence instrument was used to detect OH radicals (Mao et al., 2010).

3. Results

Surface ozone and NO2 (Fig. 2) showed the typical diurnal variation found in polluted urban areas, with small ozone and large NO2 mixing ratios at night, and the opposite during the day. Ozone and NO2 above 130 m showed a much less pronounced diurnal variation. Daytime ozone reached 88 ppb on 9/6 and 107 ppb on 9/7/06, making these some of the more polluted days during the 2006 TRAMP experiment. During the week displayed in Fig. 2, and throughout the entire experiment, ozone and NO2 shows recurring positive and negative nocturnal vertical gradients, respectively. The gradients disappear after sunrise at the onset of photolysis and enhanced vertical mixing. In particular, the nights following the most polluted days, 9/7 and 9/8, showed ozone mixing ratios over 75 ppb above 130 m, while ozone in the lower and middle intervals decrease to near zero levels. NO2 shows the opposite behavior, with mixing ratios up to 50 ppb near the surface and smaller than 2 ppb aloft.

Nocturnal NO3 mixing ratios were often elevated during the TRAMP experiment, indicating an active radical chemistry in the NBL of Houston. For example, during the nights between 9/6 and 9/9 over 50 ppt NO3 were present, with a maximum near 150 ppt around midnight on 9/7. The vertical profiles of NO3 do not show a clear pattern that one would expect from previous modeling studies (Geyer and Stutz, 2004). Often, the middle height interval showed larger mixing ratios than the upper interval, while the lower interval tended to have the smallest and most highly variable mixing ratios.

Steady-state N2O5 mixing ratios and their uncertainties were calculated based on the mixing ratios and errors of NO2 and NO3, as well as temperature following the chemical equilibrium in Reaction (10) (Wångberg et al., 1997). N2O5 was present at large levels of 200–500 ppt and showed clear vertical profiles during many nights of the TRAMP experiment. Most often the steady-state N2O5 mixing ratios were smallest aloft.

To analyze the behavior of NO3 and N2O5, we calculated τNO3 using our observations (Fig. 2) and Equation (13). Generally τNO3 was shortest in the lower NBL and longest aloft. During many nights τNO3 was shorter than 500 s in all three intervals, except for the nights of 9/6–9/7 and 9/7–9/8, when the lifetime exceeded 1000 s.

![Fig. 1. Setup of the LP-DOAS light path during TRAMP.](image-url)
aloft and the concept of a steady-state lifetime is not applicable. Nevertheless, \( \tau_{\text{NO}_3} \), during these nights is an indicator that the upper height interval was fully, or at least to a large extent, in the residual layer, which would also explain large ozone and small NO\(_2\) aloft. This interpretation is also supported by simultaneous radiosonde and tethersonde measurements during this night, which show a strong ground inversion up to \( \sim 70\) m. For comparison, the night of 9/5–9/6 shows highest NO\(_3\) mixing ratio in the upper interval, with a NO\(_3\) lifetime shorter than 500 s. The NBL during this night appears to have reached up to 300 m altitude.

4. Discussion

To understand the factors driving the nocturnal radical chemistry in Houston, we performed a NO\(_3\) budget analysis comparing Equations (12) and (13) using our lower and middle LP-DOAS observations and the measurements of hydrocarbons, NO, and aerosol surface area made on the Moody tower. Because the LP-DOAS observations represent different altitudes than the in situ observations, we employed two different approaches to consider the altitude dependence of this problem.

The first approach relies on the direct comparison of \( f_{\text{NO}_3,\text{tot}} \) based on in situ data from Moody tower with the linear interpolation between \( f_{\text{NO}_3,\text{PSS}} \) of the lower and middle height intervals, using the mean altitudes in each height interval for the calculation (Fig. 3). Table 2 lists the measured hydrocarbons together with the rate constants of their reactions with NO\(_3\) that we considered in the calculation of \( f_{\text{NO}_3,\text{HC}} \). It should be noted that terpenes, which are often the most important organic reactants with NO\(_3\), were not measured, and thus our calculation gives a lower limit for \( f_{\text{NO}_3,\text{HC}} \). However, we will show later that the contributions of missing hydrocarbons are probably minor. \( f_{\text{NO}_3,\text{HC}} \) is in the range of 0–0.05 s\(^{-1}\) (Fig. 3) and highly variable from day-to-day, and throughout one night. For example, the loss rate increases from 0.005 s\(^{-1}\) at midnight to 0.032 s\(^{-1}\) at 3:18 on 9/8.

Because of the insufficient detection limit of the NO monitor at Moody Tower, we relied on calculations by our vertical transport model and a comparison to the observed O\(_3\), NO\(_2\) and NO\(_3\) profiles, to determine NO levels. These NO levels were most often too small to influence nocturnal NO\(_3\) at and above 70 m. However, the lower height interval, and thus the interpolated \( f_{\text{NO}_3,\text{PSS}} \) values, are sometimes impacted by NO, as can be seen when much higher values and temporal variability of the lower interval compared to the middle interval are observed. For example, at midnight on 9/9, \( f_{\text{NO}_3,\text{PSS}} \) in the lower interval is higher by \( \sim 0.04\) s\(^{-1}\) than \( f_{\text{NO}_3,\text{PSS}} \) in the middle interval, and the lower interval values 1 h before and after midnight, indicating an event that mixed air with high NO from the surface into the lower height interval. This is also reflected in the ozone mixing ratios in the two height intervals (Fig. 2).

We used measured aerosol surface areas to determine \( f_{\text{NO}_3,\text{aer}} \) and \( f_{\text{NO}_3,\text{(N}_2\text{O}_3)} \). Because the uptake coefficients for NO\(_3\) and N\(_2\)O\(_3\) are highly variable in the atmosphere (Brown et al., 2006), we considered an upper limit of 0.05 for both uptake coefficients. Fig. 3 shows that, compared to \( f_{\text{NO}_3,\text{HC}} \), the direct NO\(_3\) uptake, with loss rates in the range of 0.005 s\(^{-1}\), has little impact at 70 m altitude. \( f_{\text{NO}_3,\text{(N}_2\text{O}_3)} \) was typically around 0.005 s\(^{-1}\), and thus most often also lower than \( f_{\text{NO}_3,\text{HC}} \). During the early morning, just before sunrise, \( f_{\text{NO}_3,\text{(N}_2\text{O}_3)} \) was larger, due to elevated aerosol levels during the onset of the urban rush hour.

Fig. 3 reveals that the observed \( f_{\text{NO}_3,\text{PSS}} \) and calculated \( f_{\text{NO}_3,\text{tot}} \) agree well, in particular during times when the difference between the lower and the middle light paths, as indicated by the gray bars, are small and NO loss is unlikely. This allows us to draw the conclusion that the NO\(_3\) loss through the observed hydrocarbon reactions dominates the nocturnal budget of NO\(_3\) in Houston. In some cases \( f_{\text{NO}_3,\text{PSS}} \) is smaller than \( f_{\text{NO}_3,\text{tot}} \), leading to the conclusion that either the Moody Tower VOC and aerosol observations were not
representative for the entire DOAS light-path length or that aerosol uptake was lower than our estimate. The latter is likely since our calculations were based on upper estimates of the NO$_3$ and N$_2$O$_5$ uptake coefficients. Unfortunately the dominance of the VOC reactions does not allow us to learn more about the aerosol uptakes coefficients. Only in a few cases was $f_{\text{NO}_3}(\text{PSS})$ larger than $f_{\text{NO}_3}(\text{tot})$. Some of these cases were associated with the influence of NO reactions in the lower height interval. In these cases $f_{\text{NO}_3}(\text{PSS})$ in the middle interval was closest to the calculations.

The NO$_3$ loss by hydrocarbons is dominated by three compounds, which are responsible for more than 70% of the loss (Fig. 4). Isoprene is the most important HC during most nights, followed by isobutene and, during certain periods, 1,3-butadiene. The presence of isoprene is surprising because this compound is commonly associated with biogenic emissions, which are negligible at night. Because the isoprene lifetime in the presence of 50 ppt of NO$_3$ is on the order of 20 min, one would not expect any unreacted daytime isoprene to be left at midnight. Other nocturnal sources must therefore be active. In Houston those are most likely emissions from industrial facilities, for example from rubber production. Elevated nighttime isoprene mixing ratios are often linked to wind directions pointing to the Ship Channel (Leuchner and Rappenglück, 2010). Industrial sources are also responsible for the emissions of isobutene and 1,3-butadiene. It should be noted that the dominance of these compounds is due to their fast reaction with NO$_3$ as well as their presence at concentrations of several hundred ppt up to several ppb (Leuchner and Rappenglück, 2010).

The second approach to understanding nocturnal NO$_3$ chemistry in Houston uses our 1D chemical transport model to analyze one night of the experiment, 9/7–9/8, in more detail. The model,

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>$k_{\text{NO}_3, \text{HC}} \times 10^{-17}$ molec $\cdot$ cm$^{-3}$ $\cdot$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane/propane/n-butane/n-pentane/2,3-dimethylbutane/2-methylpentane/3-methylpentane/n-hexane/2,4-dimethylpentane/cyclohexane</td>
<td>0.14/1.7/4.59/8.7/4.8/18/22/11/14/19/23</td>
</tr>
<tr>
<td>Ethylene/propylene/1-butene/trans-2-butene/cis-2-butene/2-methyl-1-butene/3-methylpentene/2(2-methyl-2-butene + cyclopentene)/cis-3-hexene</td>
<td>20.5/949/1350/37 800/35 000/37 000/33 000/10 000/38 000/(37 800$^a$)/37 000/37 000</td>
</tr>
<tr>
<td>Benzene/toluene/ethylbenzene/m,p-xylene/o-xylene</td>
<td>3/6.8/70/40/37/</td>
</tr>
<tr>
<td>Acetylene</td>
<td>5.1</td>
</tr>
<tr>
<td>Isobutene</td>
<td>33 000</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>10 000</td>
</tr>
<tr>
<td>Isoprene</td>
<td>67 800</td>
</tr>
</tbody>
</table>

$^a$ Assuming that all of this (2-methyl-2-butene + cyclopentene) is cyclopentene.
which has been described in detail in Geyer and Stutz (2004), is based on a highly resolved log-linear grid, which is ideal for the study of the NBL. Its chemistry is based on the RACM mechanism, and it includes uptake on aerosol and the ground of various species, including NO$_3$ and N$_2$O$_5$. NO and hydrocarbons are emitted near the surface at variable rates. To use the model in our interpretation we optimized the surface NO and hydrocarbon (which are linked to those of NO) emission rates and the vertical exchange coefficients in the model to provide a good agreement of the O$_3$ and NO$_2$ concentrations and their nocturnal variations (Fig. 5). We found in earlier studies (Geyer and Stutz, 2004) that these profiles are very sensitive to variations of either parameter and that our approach provides a good constraint on the conditions in the NBL. Because the model did not consider industrial emissions of VOCs, we added emissions of isoprene and dienes (as a substitute for 1,3-butadiene) between 30 and 60 m to simulate the observed concentrations during this night (not shown). Please note that we did not optimize the model to reproduce NO$_3$ and that the NO$_3$ mixing ratios shown in Fig. 5 are solely the result of the constraints on O$_3$, NO$_2$, and VOCs in the model.

The O$_3$ and NO$_2$ model results integrated over the three height intervals agreed fairly well with the observations (Fig. 5), with the exception of NO$_2$ in the upper interval, which is too high in the model. This can be explained by the observations that the upper height interval was in the residual layer during this night and the fact that the model is not able to reproduce the weak mixing into the residual layer and/or the possible air mass exchange above 130 m. The NO$_3$ levels in the middle interval were captured well in the model until 03:00, while NO$_3$ in the lower interval is somewhat smaller than the observations. The cause for the one high NO$_3$ mixing ratio observed shortly after midnight in the lower interval is currently unclear. The observed increase on the middle light path after 3:00 is most likely due to horizontal transport phenomena not considered in our model.

Fig. 6 shows the modeled vertical profiles of various gases and $f_{NO_3}$(tot) for 22:30, 00:30 and 2:30. The model confirms the absence of NO above 20 m altitude and clearly shows the opposite profiles of ozone and NO$_2$. The model also correctly finds high ozone above 100 m altitude, in agreement with observations. NO$_3$ mixing ratios show a complex profile. This is caused by the industrial hydrocarbon emissions, which, in the model, are emitted between 30 m and 60 m altitude. This vertical variation is, to a certain extent, artificial since we cannot be sure at which altitude the hydrocarbons are emitted in Houston and how well they are mixed within the NBL when the air mass arrives at Moody tower. Nevertheless, the NO$_3$ profile shows the increase in mixing ratios from the ground, where the NO + NO$_3$...
reaction dominates, to levels of 60–80 ppt at ~100 m. \text{N}_2\text{O}_5 profiles follow the trend in \text{NO}_3 and also show a maximum at ~100 m. The altitude dependence of \text{NO}_3 chemistry is also illustrated in \text{f}_{\text{NO}_3}(\text{PSS}), which was calculated based on the model output and Equation (13). It should be noted that the model has a more active \text{NO}_3 chemistry aloft due to the elevated \text{NO}_2 levels compared to the observations.

Despite the differences in \text{O}_3, \text{NO}_2 and \text{NO}_3 between the model and the observations, the model results provide a framework to study the processes controlling \text{NO}_3 and \text{N}_2\text{O}_5 chemistry in Houston with a better vertical resolution, and allow us to validate our analysis based on the observations alone. Fig. 7 shows the \text{NO}_3 and \text{N}_2\text{O}_5 reaction rates and net \text{d}[\text{NO}_3]\text{/d}t. The production of \text{NO}_3 shows a maximum at ~10–50 m and decreases to a constant value aloft. The low production near the surface is due to the reduction of ozone by NO titration. The loss of \text{NO}_3 is dominated by its NO reaction near the surface and hydrocarbon reactions, i.e., here by isoprene and later 1,3-butadiene, below 100 m. Above the nocturnal inversion however the model predicts that the main loss is \text{N}_2\text{O}_5 aerosol uptake. While we have no independent confirmation, we believe that the restriction of hydrocarbon reactions to within the NBL is realistic given the observed long \text{NO}_3 lifetime aloft during this night. Other \text{NO}_3 reactions and \text{NO}_3 aerosol uptake do not play an important role in the model.

Our \text{NO}_3 budget analysis has some interesting consequences. Most \text{NO}_3 in Houston is permanently lost through reactions with \text{VOCs} and \text{N}_2\text{O}_5 aerosol uptake. Because \tau_{\text{NO}_3} is shorter than 5 min, except for the nights of 9/7 and 9/8 above 130 m, we can argue that any \text{NO}_3 formed in the Houston NBL is also rapidly lost, i.e., \text{P}_{\text{NO}_3}, and \text{L}_{\text{NO}_3} are in steady state. Consequently, we can use \text{P}_{\text{NO}_3} as a measure of ozone and \text{NO}_3 loss in the NBL in the altitude interval between 20 and 300 m, thus providing a loss rate averaged over a large height interval in the nocturnal urban atmosphere. Fig. 8 shows the \text{NO}_3 loss for all three height intervals and the 20–300 m average. We considered the upper interval loss for 9/7 and 9/8 despite the fact that a steady state is not applicable. However, its contribution to the averaged loss rate is small during these nights and the error is minor. The altitude averaged loss rates are in the range of 0.5–2 ppb h\(^{-1}\), with higher values in the evening and the morning. We further integrated our observations throughout each night (bars in Fig. 8). Surprisingly, the time averaged values for all 7 nights shown in Fig. 8 are close to 0.9 ppb h\(^{-1}\) and show little day-to-day variation. We believe that this is, in part, caused by the influence of vertical mixing on NBL chemistry, which impacts the loss rates at specific altitudes but does not strongly impact the height integral.

To assess the importance of the nocturnal \text{NO}_3 loss, we also calculated the daytime \text{NO}_3 loss rate based on the daytime average of the \text{OH} + \text{NO}_2 reaction and the observations of these two species. The averaged daytime loss (Fig. 8) shows a much higher variability than the nocturnal loss and varies from 0.8 to 4.7 ppb h\(^{-1}\). Over a 24 h period nocturnal chemistry thus contributes between 16%, as observed on 9/7, and 50%, as observed on 9/10, to the removal of \text{NO}_3 from the lower, i.e., below 300 m, boundary layer. To study the impact of the industrial hydrocarbon emissions in Houston on the \text{NO}_3 budget we also ran our 1D model for the 9/7–9/8 periods without these emissions. The model found generally larger \text{NO}_3 and \text{N}_2\text{O}_5 mixing ratios (not shown here), in particular below 100 m. However, the nocturnal \text{NO}_3 loss rate was not strongly influenced by the absence of isoprene and 1,3-butadiene, because the missing \text{NO}_3 + \text{VOC} loss was, in large part, compensated by much higher \text{N}_2\text{O}_5 uptake rates.
5. Conclusions

Nocturnal NO₃ radical chemistry, with strong altitude dependence, was observed in Houston in Summer 2006. NO₂ mixing ratios in the lowest 300 m of the atmosphere often exceeded 50 ppt, and steady-state N₂O₅ was in the range of 200–500 ppt. The chemistry of NO₃ was controlled by reaction with a few industrially emitted hydrocarbons, i.e., isoprene, isobutene, and 1,3-butadiene. The dominance of hydrocarbon reactions for NO₃ chemistry in Houston is different from other urban locations where N₂O₅ and/or NO₃ aerosol uptake are often more important (Geyer and Stutz, 2004; Stutz et al., 2004), and has a number of consequences. The reactions with these hydrocarbons are known to predominantly produce organic nitrates. One can estimate the formation rate of organic nitrates to be ~0.4 ppb h⁻¹ in Houston. In addition, the NO₃ + isoprene reaction is known to produce secondary organic aerosol (SOA) (Ng et al., 2008).

A closer look into the nocturnal formation of organic nitrates and SOA in Houston therefore seems warranted. Our study also showed that NO₃ chemistry removes 0.9 ppb h⁻¹ of NOx at night from the lowest 300 m of the atmosphere. The averaged loss shows surprisingly little day-to-day variation, most likely because the altitude and temporal averaging reduces the influence of changing vertical mixing. This should make the validation of air quality models easier. During TRAMP nocturnal chemistry is responsible for 16–50% of the 24 h NO₃ loss. Tests with our 1D model showed that this value will not be significantly impacted by a reduction of industrial hydrocarbon emissions due to an increase in the N₂O₅ aerosol.

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References


