Direct observations of daytime NO3: Implications for urban boundary layer chemistry

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[1] The nitrate radical (NO3) is the dominant atmospheric oxidant during the night in most environments. During the day, however, NO3 has thus far been considered insignificant. Here we present daytime measurements of NO3 by Differential Optical Absorption Spectroscopy near Houston, Texas, during the Texas Air Quality Study 2000. On 3 consecutive days in August/September 2000, NO3 reached levels from ~5 ppt 3 hours before sunset to 31 ppt around sunset. Daytime NO3 had a negligible effect on the photostationary state (PSS) between O3 and NOx, with the exception of the last hour before sunset, when it significantly accelerated NO-to-NO2 conversion. On August 31, chemical reactions involving NO3 destroyed 8 (±4) ppb O3 (= O3 + NO2) during the day and 27 (±6) ppb at night. NO3 chemistry contributed 10 (±7)% to the total O3 loss during the daytime, and 28% (±18%) integrated over a 24-hour period. It therefore played an important role in the O3 budget. NO3 also contributed significantly to the daytime oxidation of hydrocarbons such as monoterpenes and phenol in Houston. The observed daytime NO3 mixing ratios can be described as a function of O3 and NOx. Above [NO3]/[O3] ratios of 3%, daytime NO3 becomes independent of NOx and proportional to the square of O3. Our calculations indicate that elevated (>1 ppt) NO3 levels can be present whenever ozone mixing ratios exceed typical urban smog levels of 100 ppb.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0394 Atmospheric Composition and Structure: Instruments and techniques; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; KEYWORDS: photochemistry, nitrate radical, oxidation capacity, NO3 loss, ozone production, photosmog


1. Introduction

[2] The removal of hydrocarbons and nitrogen oxides emitted into the atmosphere by biological and anthropogenic activities is controlled by their oxidation by free radicals. Today at least four radical species have been found to be important in the boundary layer: OH, NO3, O3, and, in certain environments, reactive halogen species [e.g., Atkinson, 2000; Crosley, 1997; Finlayson-Pitts and Pitts, 2000; Lelieveld and Dentener, 2000; Platt et al., 2002; Wayne et al., 1995]. For many years, a clear distinction was made between daytime “photochemistry”, with OH being the key radical, and nighttime radical chemistry, which is controlled by NO3. Consequently, OH was neglected during the night and NO3 during the day [e.g., Armerding et al., 1997; Atkinson, 2000; Crosley, 1997; Eisele et al., 1997; Finlayson-Pitts and Pitts, 2000; Fuentes et al., 2000; Kleinman, 2000; Logan et al., 1981; Monks et al., 1998; Platt, 1991; Wayne et al., 1991; Weaver et al., 1996]. In fact, OH and NO3 measurements were often paused during nighttime and daytime, respectively [e.g., Allan et al., 1999; Brune et al., 1995; Geyer et al., 2001a; Hard et al., 1995; Heintz et al., 1996; Holland et al., 1998; Mount et al., 1997; Platt et al., 1981]. Today it is becoming clear that this separation is not generally valid. Recent observations and model studies give evidence of significant levels of OH (and peroxy radicals) during the night [Aliwell and Jones, 1998; Bey et al., 1997; Bey et al., 2001a, 2001b; Cantrell et al., 1997; Carslaw et al., 1997; Falloona et al., 2001; George et al., 1999; Geyer et al., 2003; Kanaya et al., 1999; Mather et al., 1997; Monks et al., 1996; Paulson et al., 1999; Paulson and Orlando, 1996; Platt et al., 1990; Salisbury et al., 2001; Tanner and Eisele, 1995; Tanner et al., 1997].

[3] The possible role of NO3 for the oxidation of phenols and cresols even during day was suggested by [Atkinson,
1991; Carter et al., 1981]. More recently model results by Bey et al. [2001a] also indicated enhanced late afternoon NO3 values of a few ppt for a polluted urban scenario. Direct measurements of daytime NO3 have not been discussed in literature. In a publication by [Pitts et al., 1984], however, elevated NO3 observations are shown, but not further commented. Indirect evidence for a possible role of NO3 during the day was recently found in urban air [Kurtenbach et al., 2002], where observed daytime ratios of p-cresol to toluene could only be explained by assuming oxidation of p-cresol by NO3 at mixing ratios of ~0.5 ppt NO3.

In this paper, we present the direct detection of daytime NO3 during three consecutive days in August/September 2000. The measurements were performed at La Porte near Houston, Texas, in the framework of the Texas Air Quality Study 2000 [http://www.utexas.edu/research/ceer/texaqs/visitors/index.html]. The concentrations of NO3 were determined by Differential Optical Absorption Spectroscopy (DOAS) [Geyer et al., 1999; Platt, 1994]. The cause of the unexpected high daytime NO3 levels is discussed. An expression for daytime NO3 concentrations as a function of [O3] and [NO2] is derived and validated by observations. We discuss the significance of the observed and calculated NO3 concentrations for the following aspects of tropospheric chemistry: (1) the O3-NO-NO2 photo stationary state (PSS), (2) the budget of O3 (= O3 + NO2), and (3) the loss of VOCs, such as α-pinene, isoprene, trans-2-pentene, and para-cresol.

2. Experimental

2.1. Location

The measurements were performed at the La Porte Municipal Airport (95°03′51.1″W, 29°40′09.3″N, altitude: 8 m asl), Texas. The airport is located 30 km southeast of the city center of Houston, and is surrounded by a residential area. Large chemical manufacturing plants and refineries are located north and south of this area.

The DOAS telescope was set up on the southern end of the airport together with other remote sensing instruments. The light path of the DOAS system pointed in the northwesterly direction, from a height of 2 m above the ground, toward three reflector arrays mounted on a tower at a distance of 6.1 km at 77 m, 99 m, and 115 m height above the ground. A freeway (La Porte freeway) passed under the NW end of the light paths. A second DOAS system measured on a shorter light path (1.9 km distance, reflector height 44 m) in a northern direction. In situ measurements were performed on a 10 m high tower located ca. 500 m NW of the DOAS telescopes.

2.2. DOAS Measurements

DOAS is a technique that quantifies the concentrations of trace gases that have narrow band absorption structures in the UV and visible wavelength region in the open atmosphere. For a detailed description of DOAS, see Platt [1994]. The DOAS long-path systems used in Houston are very similar to those described by Geyer et al. [1999] and Alicke et al. [2002]. We sequentially measured the average concentration of NO3, NO2, O3, SO2, HCHO, and HONO along the light paths described above. The measurements of NO2, O3, SO2, HCHO, and HONO (spectral range 300–380 nm, resolution 0.5 nm) employed the MultiChannel-Scanning Technique (MCST) [Alicke et al., 2002; Bruekers et al., 1995] to correct the variation in diode sensitivity of the detector. For the NO3 measurements, the atmospheric absorption spectrum from 600–680 nm was recorded. The spectral resolution was 0.5 nm. A measurement algorithm described by Geyer et al. [1999] was applied, and included regular measurements of background scattered sunlight, lamp references and neon wavelength standards. A filter (OG590, Schott, Germany) was used to cut off light below 590 nm.

The DOAS evaluation used for NO3 and O3, (SO2, HCHO, and HONO are not reported here) is described in detail by Alicke et al. [2002]. Statistical uncertainties of the DOAS data averaged at 70 ppt and 1.3 ppb for NO2 and O3, respectively. It should be noted that uncertainties of DOAS data are calculated for each individual measurement and therefore vary from data point to data point. The uncertainty of both cross sections is ~5% [Sander et al., 2003].

In order to prevent daytime references from having high NO3 absorptions, only daytime references measured under conditions of low ozone, high NO, and high JNO3 were used. Using equation (14) derived below we estimated that our daytime reference spectra contained NO3 absorption equivalent to a NO3 mixing ratio of less than 0.2 ppt in all cases. Since this value is much lower than the statistical error in our measurements, we did not correct it in the final data. Figure 1 shows an example of the DOAS evaluation of a daytime spectrum recorded on August 30, 2000, 17:10 CST at a solar zenith angle of 70°. The differential optical density of the absorption bands of NO3 is 0.3 nm, corresponding to a mixing ratio of 9 (±1) ppt during this measurement. The statistical uncertainty of NO3 was generally on the order of 1 ppt, corresponding to a detection limit of 2 ppt. The uncertainty of the NO3 absorption cross section is ~10% [Geyer et al., 1999].

Since the concentrations of daytime NO3 measured along the different paths agreed within the error limits, no measurable vertical profiles or horizontal differences of daytime NO3 were observed. For the rest of the text we will therefore only use DOAS data obtained on the light path aiming at the highest retroreflector.

2.3. In Situ Measurements

A number of other measurements were made during our study. Here we will only list those needed for the interpretation of the NO3 data. A comparison of compounds measured simultaneously by DOAS and in situ instruments, such as O3, NO2, and SO2 show that during most of the time the concentrations agreed within 5–10%. In these cases, a reasonably well-mixed boundary layer can be assumed. During the day on August 30, in situ and DOAS measure-
ments differed by up to 20% from 10:00–16:00, and care must be taken to interpret this data. Since for most cases it is difficult to determine how representative the comparison is, we will assume in the remainder of the paper (except in the case of NO) that in situ data and long-path data are comparable.

2.3.1. Photolysis Frequencies

[13] Spectrally resolved downwelling actinic flux measurements from 280 to 420 nm were made every 10 s with a spectroradiometer. The instrument consists of a 2π hemispherical quartz light collector, double monochromator, and low dark current photomultiplier [Shetter et al., 2003; Shetter and Miller, 1999]. The photolysis frequencies of various compounds, in particular ozone and NO2, were calculated from the actinic flux measurements. Since the photolysis frequency of NO3 (maximum around wavelength of 600 nm) was not directly measured, it was calculated from the photolysis of NO2 and a function of the ratio between JNO3 and JNO2 (for clear sky). The uncertainty of JNO3 mainly arises from the errors of the NO2 and NO3 cross sections. The total error of JNO3 is therefore ±15%.

2.3.2. O3 and NOx In Situ Measurements

[14] In situ (IS) concentrations of NO, NO2, and O3 were measured by chemiluminescence, a photolytic NO2 converter, and UV absorbance, respectively. Total uncertainties of the data are ±5% (detection limit 5 ppt) for NO, ±7% (detection limit 20 ppt) for NO2, and ±2% (detection limit 1 ppb) for O3.

2.3.3. Hydrocarbon Measurements

[15] Mixing ratios of more than 50 VOCs including alkanes, alkenes, and oxygenated VOCs were measured by GC-MS. Degradation rates calculated from this data set must be considered as lower limits, since not all reactive VOCs were measured at La Porte.

2.3.4. HOx Measurements

[16] The OH and HO2 radicals were measured using laser-induced fluorescence (LIF) of the OH molecule, based on the fluorescent assay by gas expansion (FAGE) technique originally developed by Hard et al. [1984]. To avoid any possible influence of surface contact on the OH and HO2 concentrations of the sampled air, the detection module was mounted on top of a 10 m scaffolding tower. An air sample is expanded through a pinhole inlet into a reduced pressure detection chamber. As the air passes through a laser beam that is passed through a multipass White cell, the OH molecules are excited by spectrally narrow laser pulses at one of several vibronic transition lines near 308 nm. The OH fluorescence at the same wavelength extends beyond the prompt scattering and is detected with time-gated microchannel plate detectors. HO2 is measured simultaneously through quantitative conversion into OH by reaction with NO followed by LIF detection of OH in a second detection axis that is 10 cm downstream from the first axis. A description of the prototype instrument is given by Stevens et al. [1994]. Precisions for 30 min integration times are 0.006 ppt and 0.03 ppt for OH and HO2, respectively. Calibration uncertainties are 40% with 2σ confidence.

2.3.5. Aerosol Surface Area

[17] The aerosol surface area (from 0.014–2.5 μm diameter) was measured by a Scanning Mobility Particle Sizer (SMPS, Model 3071A, TSI).

2.4. Calculation of NO Along the DOAS Path

[18] The mixing ratio of NO along the DOAS light path was calculated assuming matching steady state rations of O3/NO-NO2 at the airport and along the light path (LP) according to equation

\[
[\text{NO}]_{LP} = [\text{NO}]_{IS} \frac{[\text{O}_3]_{IS}}{[\text{NO}_2]_{IS}} \frac{[\text{NO}_3]_{LP}}{[\text{O}_3]_{LP}}
\]

The uncertainty of \([\text{NO}]_{LP}\) was calculated by error propagation to ~11%. This approach gives better estimates of NO levels along the light path than the direct measurements. Since the reaction of NO3 with NO is fast, a precise determination of the NO concentrations is important.

3. NO3 Daytime Measurements

[19] During the afternoons on 3 consecutive days (August 30 to September 1, 2000), the mixing ratio of NO3 rose above the detection limit (DL) of 2 ppt (Figure 2). The level
Photolysis of NO3 was already weaker (JNO3 = 0.05 s−1). During the following day, the behavior of NO3 was similar. While NO3, NO2, and O3 were measured by DOAS, the mixing ratio of NO was calculated from equation (1). Daylight NO3 above the detection limit (indicated by red box) is observed during the afternoon of all 3 days about 2 hours before sunset. Nighttime (SZA > 90°) is indicated by hashed bars.

Figure 2. Time series of NO3, O3, O2 (= O3 + NO2), NO, NOx, and JNO3 from August 30 to September 1, 2000, at La Porte, Texas (all error bars show the 1σ statistical uncertainty). While NO3, NO2, and O3 were measured by DOAS, the mixing ratio of NO was calculated from equation (1). Daylight NO3 above the detection limit (indicated by red box) is observed during the afternoon of all 3 days about 2 hours before sunset. Nighttime (SZA > 90°) is indicated by hashed bars.

The concentration of NO was highest during the morning hours, which is a consequence of the low ozone, rush hour, and weak vertical mixing during this time of the day. It continuously decreased after this morning peak until sunset. While the NO mixing ratios were around 500 ppt when the daytime NO3 rose above the DL in the afternoon, they were below 200 ppt at sunset. A significant impact of the afternoon rush hour on NO3 was not found at La Porte. During the night NO was below the detection limit (10 ppt) most of the time.

4. Discussion

4.1. Analytical Expression for Daytime NO3

High daytime NO3 levels similar to those shown in Figure 2 have thus far not been discussed in literature. This raises the question of why NO3 reached high daytime concentrations in Houston and in Los Angeles [Pitts et al., 1984], while it has not been observed at other locations. To answer this question we derived an analytical expression for daytime NO3 as a function of ozone and NO3, and compared it to the data measured in Houston. The expression can also be used to estimate daytime NO3 levels at other locations.

The sole source of NO3 in the boundary layer is the reaction of NO2 with O3:

\[
\text{NO2} + \text{O}_3 \rightarrow \text{NO3} + \text{O}_2 \tag{2}
\]

(All kinetic constants are taken from Sander et al. [2003]). The production rate of NO3 can therefore be calculated on the basis of the measured ozone and NO2 concentrations according to Wayne et al. [1991]:

\[
P_{\text{NO3}} = k_2 \cdot [\text{NO2}] \cdot [\text{O3}] \tag{3}
\]

In Houston the production rate (see Figure 3b) was generally low during night because of moderate ozone levels. The O3 mixing ratios around 10–20 ppb and NO2 levels of 5–15 ppb lead to NO3 production rates in the range of 0.1–0.2 ppt/s. During the day however, when ozone levels were elevated at Houston, PNO3 reached levels of 2.5 ppt/s during the late afternoon (at ozone mixing ratios of up to 200 ppb). Often the influence of lower ozone levels caused by NO titration, on PNO3 is counterbalanced by higher NO2 levels at night. In the case of Houston however, NO2 levels in the afternoon did not differ much from nighttime values. This will be further explained below.

Assuming steady state conditions for NO3, the total loss frequency (defined as the inverse NO3 lifetime) of NO3 can be expressed as:

\[
f(\text{NO3}) = \frac{P_{\text{NO3}}}{[\text{NO3}]} = \frac{k_2 \cdot [\text{NO2}] \cdot [\text{O3}]}{[\text{NO3}]} \tag{4}
\]
At typical urban daytime NO levels of one to several ppb the main NO loss proceeds through reaction (7). The photolysis, in comparison, is almost negligible as an NO sink. Loss frequencies of reaction (7) are 0.68–6.8 s\(^{-1}\) at NO levels of 1–10 ppb, and much larger than \(J_{\text{NO}3}\) which reaches a maximum of 0.18 s\(^{-1}\) at noon. This is also the case in Houston for most of the day, with the exception of the later afternoon (\(J_{\text{NO}3} = J_5 + J_6\), dark yellow line and \(f_{\text{VOC}(\text{NO}3)}\), red stars in Figure 3c).

[27] Other NO sinks include the reaction of NO\(_3\) with hydrocarbons [e.g., Geyer et al., 2001b; Götz et al., 2001; Mihelcic et al., 1993] and the loss of N\(_2\)O\(_5\) [Longfellow et al., 2000; Wahner et al., 1998a, 1998b]. N\(_2\)O\(_5\) is generally in thermal steady state with NO\(_2\) and NO\(_3\) [Wängberg et al., 1997b]. In an urban or suburban environment, the degradation of NO\(_3\) by reactions with VOCs can be neglected during the day. In Houston, the loss through hydrocarbon reactions \(f_{\text{VOC}(\text{NO}3)}\) was on the order of 0.01–0.1 s\(^{-1}\) (\(f_{\text{VOC}(\text{NO}3)}\), green line in Figure 3c). During the night, however, \(f_{\text{VOC}(\text{NO}3)}\) often controlled the total NO\(_3\) degradation frequency, as is evident in Figure 3c. The photolysis of N\(_2\)O\(_5\), as well as its hydrolysis on surfaces, can also be neglected for the NO\(_3\) budget during the day. In Houston, the sum of both values was below 0.01 s\(^{-1}\) (not shown here).

[28] The dominating calculated NO\(_3\) loss mechanism during the morning hours in Houston was the NO\(_3\) + NO reaction (7), with loss frequencies of more than 10 s\(^{-1}\). Following the NO diurnal variation this frequency continuously decreased during the day, and reached values of ~0.2 s\(^{-1}\) at the time NO\(_3\) exceeded the DL. At sunset, \(f_{\text{VOC}(\text{NO}3)}\) was around 0.03 s\(^{-1}\) during these 3 days. The photolysis frequency of NO\(_3\) was highest during noon (0.18 s\(^{-1}\) and ~0.11 s\(^{-1}\) when NO\(_3\) exceeded the DL. The sum of \(J_{\text{NO}3}\) and \(f_{\text{NO}(\text{NO}3)}\) (plotted as blue squares in Figure 3c) is in good agreement with the total NO\(_3\) degradation frequency \(f(\text{NO3})\) calculated from equation (4). This shows that during the day it is sufficient to consider only these two NO\(_3\) loss paths in order to derive a steady state NO\(_3\) concentration.

[29] To a good approximation, the steady state NO\(_3\) concentration during the day can therefore be expressed as a function of [O\(_3\)], [NO], and [NO\(_2\)] (and the actinic flux):

\[
[\text{NO}_3] = \frac{k_2 \cdot [\text{NO}] \cdot [\text{O}_3]}{J_{\text{NO}3} + k_7 \cdot [\text{NO}]} \tag{8}
\]

The uncertainty of the NO\(_3\) values calculated from equation (8) is around 30%, considering the errors of NO, NO\(_2\), O\(_3\), and \(J_{\text{NO}3}\). In Figure 3a, daytime NO\(_3\) calculated by equation (8) is plotted as blue line. Calculated morning levels of NO\(_3\) are very low (0.1 ppt and less). They continuously increase during the afternoon, exceeding 2 ppt at 16:00–17:00. The good agreement with the observed NO\(_3\) during the afternoon justifies the use of equation (8) to estimate daytime NO\(_3\) concentrations.

[30] On the basis of equation (8) it is possible now to discuss the reasons for the high NO\(_3\). In a first approximation, the ratios of [O\(_3\)], [NO], and [NO\(_2\)] in equation (8) are linked to each other by the Leighton photo stationary state (PSS):

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

\[
k_0(298K) = 1.8 \times 10^{-14}\text{molec.}^{-1}\text{cm}^3\text{s}^{-1}
\]

\[
j_{\text{NO}3} = J_5 + J_6
\]

\[
(\text{km}(298K) = 2.6 \times 10^{-11}\text{molec.}^{-1}\text{cm}^3\text{s}^{-1})
\]

\[
(\text{km}(298K) = 2.6 \times 10^{-11}\text{molec.}^{-1}\text{cm}^3\text{s}^{-1})
\]

\[
(\text{km}(298K) = 2.6 \times 10^{-11}\text{molec.}^{-1}\text{cm}^3\text{s}^{-1})
\]
\[ \text{NO}_2 + \text{hv} (+ \text{O}_2) \rightarrow \text{NO} + \text{O}_3 \quad (J_{\text{NO}_2} \approx 0.01 \text{s}^{-1} \text{at noon}) \]  

\[ \frac{[\text{NO}]}{[\text{NO}_2]} = \frac{J_{\text{NO}_2}}{k_9 \cdot [\text{O}_3]} \]  

Equations (11) and (13) show that at high ozone concentrations, such as those observed in Houston (mixing ratio up to 190 ppb), the Leighton PSS favors low NO-to-NO\(_2\) ratios hence leading to low NO levels. This has two effects on daytime NO\(_3\) chemistry at La Porte.

1. The NO\(_3\) production rate (equation (3)) linearly depends on the ozone and NO\(_2\) concentrations. At high ozone levels the NO\(_2\) levels are enhanced because of the shift in the NO/NO\(_2\) PSS. This leads to a higher NO\(_3\) production rate.

2. At high ozone levels, the [NO]/[NO\(_2\)] ratio is smaller compared to low ozone levels, leading to lower NO levels and therefore smaller NO\(_3\) loss frequency by reaction (7). It is therefore clear that high ozone levels are the reason for the high NO\(_3\) levels, since the production rate is increased and the loss is decreased. Periods of enhanced daytime NO\(_3\) levels will often occur during the late afternoon, when ozone is highest.

3. Considering only the Leighton PSS (11), which is justified by the PSS analysis below, equation (8) can be further expressed as a function of [O\(_3\)] and [NO\(_3\)]:

\[ [\text{NO}_3] = \frac{k_2 \cdot k_9}{J_{\text{NO}_3} + k_{12} \cdot [\text{O}_3]} \cdot \frac{[\text{NO}_3] \cdot [\text{O}_3]^2}{J_{\text{NO}_3} + k_{12} \cdot [\text{O}_3] + k_7 \cdot [\text{NO}_3]} \]  

The first factor in the denominator of equation (14), \(J_{\text{NO}_3}\), is negligible compared to the two other factors in the denominator at O\(_3\) levels above 30 ppb or NO\(_2\) level above 0.5 ppb. These mixing ratios are typically exceeded in urban and suburban environments. The second factor in the denominator is smaller than the third factor at [NO\(_3\)]/[O\(_3\)] ratios above 3\% (for example NO\(_3\) levels of more than 3 ppb at O\(_3\) = 100 ppb), while it will dominate below this value. We can therefore distinguish two different regimes for the ozone dependence of NO\(_3\). At [NO\(_3\)]/[O\(_3\)] ratios clearly above 3\%, daytime NO\(_3\) levels will be proportional to the square of the O\(_3\) concentration and independent of NO\(_2\) levels. At [NO\(_3\)]/[O\(_3\)] ratios clearly below 3\%, daytime NO\(_3\) is a linear function of [O\(_3\)]:

\[ [\text{NO}_3] \propto [\text{O}_3]^2 \quad \text{if} [\text{NO}_3]/[\text{O}_3] > 3\% \]  

\[ [\text{NO}_3] \propto [\text{O}_3] \quad \text{if} [\text{NO}_3]/[\text{O}_3] < 3\% \]  

4.2. Effect of Daytime NO3 on the O3/NO/NO2 Photo Stationary State

Daytime NO\(_3\) can affect the photo stationary state (PSS) of O\(_3\), NO, and NO\(_2\) (equation (11) or (13)) in two ways: (1) reaction (7) converts NO and NO\(_3\) into two NO\(_2\) molecules, and (2) the NO\(_3\) formation reaction (2) destroys NO\(_2\) and O\(_3\) (recycling of a minor part of NO\(_2\) by reaction (6) is not considered here). Considering reactions (2) and (7), the PSS equation (13) changes to

\[ \frac{[\text{NO}]}{[\text{NO}_2]} = \frac{J_{\text{NO}_2} + k_3 \cdot [\text{O}_3]}{k_9 \cdot [\text{O}_3] + k_{12} \cdot ([\text{HO}_2] + [\text{RO}_2]) + 2 \cdot k_7 \cdot [\text{NO}_3]} \]  

Figure 5 compares the measured NO-to-NO\(_2\) ratio at La Porte during the daytime NO\(_3\) periods to the ratios calculated assuming (1) only Leighton PSS (equation (11)), (2) Leighton PSS including HO\(_2\) (equation (13),
Comparison of measured NO-to-NO$_2$ ratios

The relative change of the PSS by daytime NO$_3$ is of the order of a few percent during day but increases rapidly before sunset.

Figure 5. Comparison of measured NO-to-NO$_2$ ratios with ratios calculated from Leighton PSS (equation (11), crosses), Leighton PSS including peroxy radicals (equation (13), circles), and Leighton PSS including the peroxy radicals and daytime NO$_3$ (equation (16), diamonds) at La Porte, Texas. The relative change of the PSS by daytime NO$_3$ is of the order of a few percent during day but increases rapidly before sunset.

NO$_2$ was not measured at La Porte, and (3) Leighton PSS including HO$_2$ and daytime NO$_3$ (equation (16)). The measured NO-to-NO$_2$ ratio was highest in the morning hours (up to 90%), and continuously decreased to ~10% (2 hours before Sunset). This ratio is already well described by equation (11), indicating that reaction (9) was the major NO$_2$ production path at La Porte. Even in the hour before Sunset, when the PSS cannot any longer rapidly react on sudden changes because $J_{NO2}$ is already very low, the calculated NO-to-NO$_2$ ratios were in good agreement with the observed ratios. This good agreement indicates that there were no direct emissions of NO, which would likely not be in PSS with NO$_2$, near the measurement site.

The change of the PSS due to daytime NO$_3$ relative to equation (13) was negligible during most of the day and increased to ~10% in the last hour before sunset. It should be noted here that the concept of a PSS is somewhat arbitrary in the hours before sunset, since the lifetime of NO$_2$ is long because of the weak photolysis [Kleinman, 2000}. It is better to interpret these values as an indicator for the NO to NO$_2$ conversion during this time of the day.

One reason for the small changes of the PSS due to NO$_3$ chemistry during the day is that the additional factors in the numerator and denominator of equation (16) partially eliminate each other. The importance of the factor $k_2 \cdot [O_3]$ increased toward sunset ($J_{NO2}$ is decreasing) as well as the factor $k_7 \cdot [NO_3]$ (because NO$_3$ was increasing).

4.3. Influence of Daytime NO$_3$ on the O$_3$ Budget

The quantification of processes that form or destroy O$_3$ or NO$_2$ in the atmosphere, such as the chemistry of NO$_3$, is difficult because of the constant interconversion of O$_3$ and NO$_2$ through reactions (9) and (10) [e.g., Blanchard, 2000; Carsey et al., 1997; Hidy, 2000; Kleinman, 2000; Leighton, 1961]. This is particularly true for the chemistry of the nitrate radical that involves both, O$_3$ and NO$_2$. Therefore it is convenient to use the sum of ozone and NO$_2$, defined as $O_x = O_3 + NO_2$, instead of the individual molecules [e.g., Jaegle et al., 1999; Perrino et al., 2001]. One can interpret $O_x$ also as a way of describing a photochemical “oxidant” in its active form, ozone, and in a reservoir, NO$_2$. This interpretation becomes obvious regarding the conversion of ozone into NO$_2$ by NO titration in the evening, and the photolysis of NO$_2$ forming ozone in the following morning. In principle we would have to include NO$_3$ and N$_2$O$_5$ in $O_x$ since they can also store ozone and NO$_2$ and release them back through reaction (6). Nevertheless, the mixing ratios of NO$_3$ and N$_2$O$_5$ are so low in comparison to those of ozone and NO$_2$ that this introduces only a small error.

While the reactions of NO with peroxy radicals are practically the only source of $O_x$ in the troposphere (direct NO$_2$ emission is mostly negligible [Kurtenbach et al., 2001; Sawyer et al., 2000]), there are many different sinks. Here we investigate how much the observed daytime NO$_3$ contributed to the loss of $O_x$ at La Porte. Since two $O_x$ molecules (one O$_3$ and one NO$_2$ molecule) are used for the formation of NO$_3$ (reaction (2)), any sink of NO$_3$, which is not directly re-forming O$_3$, again, constitutes a sink for 2 $O_x$ molecules. The pathways destroying $O_x$ related to NO$_3$ are therefore as follows.

1. Photolysis of NO$_3$ into NO and O$_2$ (reaction (5)). Two $O_x$ molecules are destroyed by this reaction.

2. Reaction of NO$_3$ with VOCs. Two $O_x$ molecules are destroyed by this reaction if organic nitrates are the products. In the case of monoterpenes (which were the most important organic scavenger for NO$_3$ during afternoon), however, a large fraction of nitrogen is being released during the course of the oxidation in the form of NO$_2$ (for example $\approx$80% in the case of $\alpha$-pinene, [Wångberg et al., 1997a]). We assume in the following calculation that 1.5 $O_x$ molecules are destroyed by each reaction of NO$_3$ with VOCs.

3. Reaction of NO$_3$ with NO$_2$ to N$_2$O$_5$ and subsequent formation of HNO$_3$ (mostly on aerosol surfaces, cf. for example to Martinez et al. [2000]). Three $O_x$ molecules are destroyed by this pathway.

Figure 6a shows the $O_x$ loss rates caused by daytime NO$_3$ at La Porte calculated for the processes 1–3. Daytime NO$_3$ was derived from equation (8) whenever the direct measurements were below the detection limit. The photolysis of NO$_3$ was of minor importance for $O_x$ loss with rates generally below 0.5 ppb/h. The reaction of NO$_3$ with VOCs was quantified on the basis of direct VOC measurements. Reactions with biogenically emitted monoterpenes [Guenther et al., 2000; Martinez et al., 1999; Wångberg et al., 1997a] and anthropogenic higher alkenes [Atkinson et
night were comparable to the daytime loss rates, with a maximum of 10 ppb/h. During the later part of the night the O₃ loss rate decreased to ∼2 ppb/h. The higher loss rate in the evening was caused by a higher NO₃ production rate and elevated VOC concentrations remaining from daytime emissions.

[44] On August 31, for example, 8 (±4) ppb O₃ were removed by daytime NO₃ chemistry. During the night, 27 (±6) ppb O₃ were destroyed by NO₃, resulting in approximately 35 (±10) ppb O₃ destroyed by NO₃ for a full diurnal cycle of 24 hours.

[45] Other O₃ sinks, which are not related to NO₃, include (one O₃ molecule is destroyed in each loss path):

[46] 4. O₃ photolysis to O¹D followed by the reaction of H₂O with O¹D (∼18% branching efficiency at La Porte).

[47] 5. Reaction of O₃ with VOCs.

[48] 6. Dry deposition of O₃ and NO₂.

[49] 7. Reaction of OH radicals with NO₂ to form HNO₃:

\[
\text{OH} + \text{NO}_2(\pm M) \rightarrow \text{HNO}_3(\pm M)
\]

\[
(k_{17}(298\text{K}, 1\text{bar}) = 8.7 \times 10^{-12} \text{ molec.}^{-1} \text{ cm}^3\text{s}^{-1})
\] (17)

Figure 6b shows the O₃ loss rates at La Porte calculated for processes 4–7 on the basis of direct measurements of the reactants and the photoysis rates. Photolysis of ozone was of minor importance, peaking at an O₃ loss rate of 2 ppb/h at noon. The reaction of O₃ with VOCs (5), especially with C₂–C₆ alkenes at La Porte, exceeded a loss rate of 1 ppb/h only during short periods, and was mostly in the region of 0.5 ppb/h (lower limit). To estimate the importance of O₃ loss by O₃ and NO₂ deposition (6), we assumed dry deposition velocities of \( v_d = 0.5 \text{ cm/s} \) for both gases [Lovett, 1994; Wesely and Hicks, 2000] and a mixing height of \( h = 1 \text{ km} \) during the day (night: \( v_d = 0.05 \text{ cm/s}, h = 0.1 \text{ km} \)). Estimated O₃ deposition rates were highest during the afternoon (up to 3 ppb/h) and below 1 ppb/h during night (lower ambient ozone concentration). The contribution of reaction (17) was the highest of all O₃ loss paths during most of the daytime, with values approaching \( 7 \pm 3 \text{ ppb/h} \) during some periods.

[50] On August 31, 75 (±41) ppb O₃ were destroyed during the day and 14 (±6) ppb during the following night by sinks, which are not related to NO₃. The 24-hour integrated O₃ loss by these paths of 89 (±6) ppb was roughly a factor of 2.5 higher than the NO₃-induced O₃ loss of 35 (±10) ppb (sum of 8 (±4) ppb during day and 27 (±6) ppb during night). NO₃ chemistry contributed 10 (±7)% to the total O₃ loss during the daytime, and 28% (±18%) integrated over a 24-hour period. A comparison of Figures 6a and 6b illustrates that in the late afternoon the O₃ loss by NO₃ chemistry became comparable to the loss through other processes. This calculation shows that daytime NO₃ played a significant role for the O₃ budget at La Porte and therefore also for the budget of both ozone and NO₂ during the day.

4.4. VOC Oxidation by Daytime NO₃

[51] It is well known that NO₃ significantly contributes to the oxidation of alkenes, in particular monoterpenes during the night [Calogirou et al., 1999; Geyer et al., 2001b; Götz et al., 2001]. Our measurements and calculations of daytime NO₃ allow us to calculate the oxidation rates of various
VOCs by NO3 during the daytime at La Porte, and compare these rates to those of OH and O3. Figure 7 shows the time series of the different oxidation rates calculated for α-pinene, isoprene, and trans-2-pentene under sunlit conditions on August 31, 2000. It is obvious that daytime NO3 was an important oxidant for α-pinene during the afternoon and clearly dominated the α-pinene oxidation during the hours before sunset. We expect similar results for other monoterpenes, which were not measured directly, such as limonene and myrcene. For isoprene, the oxidation rate by daytime NO3 was similar to that of O3, and about one order of magnitude below that of OH. Isoprene oxidation by daytime NO3 was only significant in the hour before sunset. For t-2-pentene, OH and O3 were the major oxidants, and NO3 was generally negligible. Table 1 shows the amount (in ppb) of α-pinene, isoprene, and trans-2-pentene oxidized by OH, O3, and daytime NO3, integrated over the daytime of August 31. NO3 contributed 32% to the α-pinene oxidation during daytime. OH was the dominant oxidant for isoprene. The contributions of ozone (3%) and daytime NO3 (2%) were negligible. Trans-2-pentene mostly reacted with OH and ozone. The daytime NO3 contribution to trans-2-pentene oxidation was only 3% during this day.

A number of unsaturated hydrocarbons are known to react rapidly with NO3, such as monoterpenes [Calogirou et al., 1999; Martinez et al., 1999], phenol [Bolzaci et al., 2002], or 2-methyl-2-butene [Atkinson, 1991]. For the budget of these organics it is likely that daytime NO3 cannot be neglected in polluted situations.

4.5. P-cresol Chemistry

Oxidation rates of para-cresol by OH, O3, and NO3 at La Porte are also included in Table 1. According to our calculations, the oxidation by OH and daytime NO3 were equally important at La Porte. Although not directly measured at La Porte, it is possible to calculate the p-cresol concentration from the measured concentration of toluene during the day, as suggested by Kurtenbach et al. [2002]. The calculation is based on the oxidation of toluene with OH, in which p-cresol is a product, which itself is destroyed by OH radicals and in our case also significantly by NO3.

We expanded the equation derived by Kurtenbach et al. [2002] by including daytime NO3 chemistry:

$$[p - \text{cresol}] = \frac{\alpha k_{p\text{-cresol}}}{k_{\text{OH}} + k_{p\text{-cresol}}}[\text{OH}] + \frac{k_{p\text{-cresol}}}{k_{\text{NO3}}}[\text{NO3}] \cdot [\text{toluene}].$$

where $\alpha$ is the yield of p-cresol from the toluene-OH reaction and $k_p$ refers to the respective rate constants. Para-cresol concentrations at La Porte derived from equation (18) were of the order of 1–10 ppt. The contribution of daytime NO3 chemistry lowered these concentrations by 20–50% during noon and up to a factor of 4 in the hour before sunset compared to the case with OH alone.

5. Conclusions

Daytime NO3 concentrations above typical detection limits of 2 ppt were observed during a smog period at La Porte, Texas. NO3 reached levels of 3–5 ppt in the afternoon (2 hours before sunset) and up to 31 ppt in the hour before sunset during 3 days in August/September 2000. During this period daytime NO3 significantly influenced boundary layer photochemistry in various ways:

1. The conversion efficiency of NO to NO2, and therefore the NO-NO2-O3 photo stationary state (PSS), changed when elevated NO3 levels are present during the day. Our observations show that this change is only significant in the late afternoon. In the last hour before sunset the PSS (or the NO to NO2 conversion) was changed significantly by daytime NO3 and the [NO]/[NO2] ratio increased by ~10%.

2. The O3 (= O3 + NO2) loss by daytime NO3 chemistry (NO3 photolysis, NO3 + VOC reactions, N2O5 hydrolysis) was found to contribute significantly to the overall O3 removal that includes loss paths such as O3 photolysis, O3 + VOC reactions, O3 and NO2 deposition, and the reaction of NO2 with OH forming HNO3. On August 31, for example, 8 (±4) ppb O3 were removed by daytime NO3. In comparison, 75 (±41) ppb O3 were destroyed by processes not related to NO3 chemistry. The O3 loss by NO3 during the day therefore contributed 10 (±7)% and was comparable to loss processes such as the reaction of O3 with VOCs. Additionally, 27 (±6) ppb O3 were destroyed by NO3 during night, and therefore 35 (±10) ppb O3 were destroyed by NO3 in a full diurnal cycle of 24 hours. The 24-hour integrated O3 loss by other pathways.

### Table 1. Comparison of VOC Oxidation by OH, O3, and Daytime NO3 Integrated Over the Day (SZA < 90°) on August 31, 2000, at La Porte, Texas

<table>
<thead>
<tr>
<th>VOC</th>
<th>ΔVOCC(OH) ppb</th>
<th>ΔVOCC(O3) ppb</th>
<th>ΔVOCC(NO3) ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Pinene</td>
<td>0.21</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>Isoprene</td>
<td>5.9</td>
<td>0.23</td>
<td>0.15</td>
</tr>
<tr>
<td>Trans-2-pentene</td>
<td>0.38</td>
<td>0.24</td>
<td>0.02</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>0.02</td>
<td>0</td>
<td>0.016</td>
</tr>
</tbody>
</table>
was 89 (±46) ppb. Integrated over a 24h period, the contribution of NO3 chemistry was 28 (±18)%, NO3 therefore played a significant role for the O3 budget both during the day and night.

[57] 3. The daytime NO3 initiated oxidation of certain VOCs, such as α-pinene, para-cresol and other monoterpenes, was sizable to those by ozone and OH radicals. In some cases, the oxidation rates of NO3 integrated over a day approached those of OH. The NO3 oxidation rates surpassed those of OH in the late afternoon in the case of α-pinene and para-cresol.

[58] While our measurements were restricted to the Houston area, our calculations demonstrate that we can generally expect elevated NO3 concentration in polluted environments. The equations (for example equation (14)) derived above show that daytime NO3 levels for most urban and suburban environments ([O3] > 30 ppb, [NO]/[O3] > 3%) depend on the square of the ozone concentration and are independent of NO3. This somewhat counterintuitive result is based on the fact that the production and the destruction of NO3 under these conditions proceed through the reaction with either NO2 or NO, which are connected through their chemistry with ozone.

[59] We expect that daytime NO3 will become significant at ozone concentrations above 100 ppb. Because of air pollution control efforts ozone mixing ratios above 100 ppb are not often observed in industrialized countries. Therefore, with exception of few smog periods during the summer months, daytime NO3 is most likely not important for photochemistry in Europe and North America. Polluted mega cities, such as Mexico City, Sao Paulo, or Beijing, however, regularly exceed these levels [Cheng, 2001; Gouviea and Fletcher, 2000, Shao et al., 2000]. In these regions, elevated NO3 levels can be expected and NO3 could play an important role, which is likely to increase in the future.

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