Derivation of tropospheric NO₃ profiles using off-axis differential optical absorption spectroscopy measurements during sunrise and comparison with simulations

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[1] Early morning vertical profiles of tropospheric NO₃ were derived by spectroscopy of scattered sunlight in off-axis geometry during sunrise. The measurements were carried out in the urban area of Heidelberg, Germany (April, July, and August 1999). The retrieval algorithm is based on the nitrate radical's rapid photolysis during sunrise, radiative transfer, as well photochemical modeling. We derived NO₃ near-ground concentrations of typically (0.2–18) × 10⁷ cm⁻³, concentrations above 3 km of (5–50) × 10⁷ cm⁻³, and a NO₃ maximum at a height of ~350 m with concentrations of (100–900) × 10⁷ cm⁻³. Assuming the case of very high terpene levels even at higher altitudes, which is very unlikely for the atmospheric conditions during the measurements, we obtain a different mathematical solution of our inversion problem yielding the NO₃ maximum at altitudes of ~2.5 km. The enriched layer was found to hold the bulk of the tropospheric nighttime NO₃. The retrieved profile confirms earlier suggestions that ground-level measurements may be significantly underestimating the oxidative capacity of the boundary layer under stable nocturnal conditions. The NO₃ layer is probably formed as a result of the vertical profiles of the NO₃ educts (NO₂ and O₃), with NO₂ concentrations falling off more slowly with height than the NO₃ scavengers, e.g., anthropogenic NO as well as volatile organic compounds emitted at ground level. Independently from these measurements model simulations with a comprehensive three-dimensional model system were performed for an area, which includes the measurement site. A pronounced maximum (3.3 × 10⁹ cm⁻³) of the nocturnal NO₃ concentration was found at ~250 m above the surface, i.e., at the top of the nocturnal stable boundary layer. The average NO₃ concentration close to the surface was 5 × 10⁷ cm⁻³. The only significant difference between the observations and the model results was a steeper decrease of the NO₃ concentration above the maximum of the observed profiles.

INDEX TERMS: 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: DOAS, off axis, nitrate radical, vertical profile, vertical distribution, matrix algorithm

1. Introduction

[2] Free radicals play an important role in the catalytic self-cleaning of the atmosphere. During daytime, photolytically formed OH radicals govern the oxidation capability of the atmosphere [e.g., Perner et al., 1976]. During nighttime, nitrate radicals (NO₃) are the main atmospheric oxidants [Geyer et al., 2001a]. Since its detection by Platt et al. [1980] and Noxon et al. [1980] in the troposphere, NO₃ was found to oxidize many volatile organic compounds (VOC) like monoterpenes and phenols [e.g., Atkinson, 1991; Geyer et al., 2001a]. These reactions initiate the nighttime formation of peroxy- and hydroxyl radicals [Platt et al., 1990; Mihelec et al., 1993; Carslaw et al., 1997; A. A. Geyer et al., Nighttime production of peroxy and hydroxyl radicals during the BERLIOZ campaign: Observations and modeling studies, submitted to Journal of Geophysical Research,
2001, hereinafter referred to as Geyer et al., submitted manuscript, 2001) and finally generate organic nitrates and nitric acid.

[1] To date conclusions regarding the key role of NO$_3$ in the oxidation processes of the atmosphere are largely based on ground level measurements using the technique of long-path differential optical absorption spectroscopy (DOAS) [e.g., Platt et al., 1980; Noxon et al., 1980; Platt et al., 1981, 1984] or electron spin resonance (MIESR) [Mihelcic et al., 1990, 1993; Geyer et al., 1999]. Long-term measurements of the NO$_3$ concentration in the marine and continental boundary layer yielded average nighttime levels of 15–25 × 10$^7$ cm$^{-3}$ [Heintz et al., 1996] and 13 × 10$^7$ cm$^{-3}$ [Geyer et al., 2001b]; other studies focusing on the marine boundary layer were performed by Allan et al. [1999, 2000].

Total tropospheric columns of NO$_3$ [Weaver et al., 1996; Aliwell and Jones, 1998] have also been measured using ground-based instruments. Up to now no measured tropospheric NO$_3$ concentration profiles with sufficiently high vertical resolution have been presented in order to enable examination of the variation across the lower troposphere and boundary layer. Smith and Solomon [1990] derived a profile covering the stratosphere and reaching down to 3 km but not probing the boundary layer. Smith et al. [1993] repeated the experiment in the Antarctic region using a Gaussian retrieval to cover the entire troposphere, but there

found negligible abundances in this environment. Interpretation of the column measurements by Aliwell and Jones [1998] at Cambridge using local measurements of sink species and an idealized modeling study led to the conclusion that nighttime measurements of NO$_3$ at ground level were not representative of the average boundary layer concentration in urban regions and would thus significantly underestimate the oxidative capacity of this region. The conclusions were supported by the more detailed modeling study of Fish et al. [1999], whose model included more constituents. Both sets of results indicated that the bulk of the tropospheric NO$_3$ may not be situated at ground level. Fish et al. [1999], in particular, modeled near-ground concentrations of less than 1.3 × 10$^9$ cm$^{-3}$, and an increase to higher concentrations of between 1.75 and 2.5 × 10$^9$ cm$^{-3}$ located within an enriched layer between 300- and 1700-m altitude, followed by a sharp decrease above. Both groups explained the low values near the ground mainly with destruction by NO emissions. Povey et al. [1998] found nocturnal nitrate radical abundances averaged over one night each of up to 133 and 211 ppt, respectively, in a box centered at 1.5 and 1.2 km, respectively. An experimental verification of these suggested NO$_3$ profile structures with sufficient vertical resolution was not reported to date.

[4] This paper presents the first experimental verification of these suggested NO$_3$ profiles, obtained using ground-based measurements at the significantly polluted urban location of Heidelberg, southern Germany. Detailed profile information is obtained by applying a modified version of the matrix technique initially introduced by Smith and Solomon [Smith and Solomon, 1990; Smith et al., 1993] to measurements with an instrument operated in off-axis geometry [Smith and Solomon 1990; Smith et al., 1993; Weaver et al., 1996; Aliwell and Jones, 1998]. The method utilizes the rapid photolysis of NO$_3$ (which has accumulated during night) combined with the special illumination situation during sunrise. Before local sunrise, only elevated layers of the atmosphere are directly illuminated by sunlight; when the sun rises, the solar terminator decreases in height, which exposes lower layers to direct solar light as well (Figure 1). Within the directly illuminated part of the atmosphere (line A–B and above) the nitrate radical concentration is rapidly depleted. Information on the vertical distribution is obtained from a series of measurements of the slant column density (SCD), which is the integrated concentration along the line B–C as derived from recorded spectra using the differential optical absorption spectroscopy (DOAS). In addition, we report on numerical simulations carried out with a comprehensive three-dimensional model system [Vogel et al., 1995] for the conditions of the observations. The comparison with measured data provides a check of the quality of the numerical model with respect to NO$_3$.

Figure 1. Viewing geometry of off-axis spectroscopy for NO$_3$ measurements; the technique uses the light scattered into the detector when the sun is still below the horizon. Shown as dotted line is the instrument’s line of sight, which crosses the solar terminator (straight line). (top) At SZA 1 the scattered light traverses the distance between B and C in the dark airspace. (bottom) At the smaller SZA 2 the direct sunlight zone is located deeper, and the light path B’–C through the dark layers is shorter, leading to a smaller SCD NO$_3$. The method utilizes the rapid photolysis of NO$_3$ (which has accumulated during night) combined with the special illumination situation during sunrise. Before local sunrise, only elevated layers of the atmosphere are directly illuminated by sunlight; when the sun rises, the solar terminator decreases in height, which exposes lower layers to direct solar light as well (Figure 1). Within the directly illuminated part of the atmosphere (line A–B and above) the nitrate radical concentration is rapidly depleted. Information on the vertical distribution is obtained from a series of measurements of the slant column density (SCD), which is the integrated concentration along the line B–C as derived from recorded spectra using the differential optical absorption spectroscopy (DOAS). In addition, we report on numerical simulations carried out with a comprehensive three-dimensional model system [Vogel et al., 1995] for the conditions of the observations. The comparison with measured data provides a check of the quality of the numerical model with respect to NO$_3$.

2. Instrumental Setup

[5] The measurements were performed in spring and summer 1999. The instrument was installed on the roof of the sixth floor of the institute building (30-m altitude) in the northern part of Heidelberg (see Figure 2). Heidelberg is located near three motorways and 20 km to the southeast of

ACH 5 - 2 VON FRIEDEBURG ET AL.: TROPOSPHERIC NO$_3$ PROFILES
the industrial cities of Mannheim and Ludwigshafen. It is surrounded by agricultural areas to the west and north and forests to the east.

[6] A mountain ridge located \(\sim 3\) km to the east of the measuring site provides shadow against the rising sun, reducing the photolysis frequencies near the ground during sunrise. To quantify this effect, data obtained with a filter radiometer for \(J_{\text{NO}_3}\) at clear days were compared to the data obtained with the same device at a location without mountains but also under clear-sky conditions. The result of this comparison yielded a delay in time, thus in the solar zenith angle (SZA) as well, of the time series of the photolysis frequency in the regions affected by the shadow. Using the solar azimuth for every sunrise evaluated, the shadow and its effect for the lower altitude layers were individually calculated using geometry and the appropriate SZA shift derived.

[7] Clouds in the instrument's line of sight can temporarily "hide" parts of the tropospheric \(\text{NO}_3\) column. In addition, they can strongly modify the photolysis frequency. Although the measurement data for most of the cloudy days show a behavior similar to clear days, for the above reasons, cloudy days are excluded from the profile retrieval presented in this paper. The cloud-free days were identified by visual identification in the morning, by examining the cloud cover on AVHRR satellite infrared photographs (Dundee Satellite Receiving Station, http://www.sat.dundee.ac.uk/ auth.html, 1999) taken around the time of local sunrise and by checking the smoothness of the increase in intensity of the measured spectra over time. Only days that passed all three tests were considered as clear days and selected for retrieval (9 days out of some 40 days in late spring and summer).

Figure 2. Map of the measurement site (red square) located in the city of Heidelberg (taken from the official Heidelberg homepage, http://www.heidelberg.de). The square indicates the institute’s location, the arrow the line of sight. The Odenwald mountains are covered by forest (shown in green), the agricultural areas are indicated by light gray. The motorways are the orange lines to the west of the institute. The surrounding environment consists of both urban and rural areas, with the edge of the Odenwald mountains providing shadow against the sun. See color version of this figure at back of this issue.
The light is collected by a lens telescope, pointing in westerly direction with an elevation of 15°; the telescope focuses the incoming light onto the end of a bundle of 10 quartz fibers, each of 400 micrometers in diameter, which conduct it to the entrance slit (width 400 μm, height 5 mm) of a 500-mm F/6.9 Czerny–Turner spectrograph. The grating is set to cover the wavelength range between 646 and 676 nm at a spectral resolution of 0.25 nm (full width at half maximum). The spectrometer is temperature-stabilized (35°C) to minimize spectral shift. The remaining shifts during a single sunrise series are ≤ 0.2 pixels.

The detector is a 1530-P-1024S CCD chip by EG&G with 1024 pixels per line in the horizontal (dispersion) axis and 256 pixels in the vertical. It is cooled to −40°C in order to reduce the dark current. The wavelength information is recorded in the chip’s horizontal axis with a dispersion of 0.029 nm per pixel, while the vertical dimension matches the entrance slit height. After readout and conversion to a digital signal each column of 256 pixels is co-added to form a spectral channel. The digital “count number” in each channel is thus proportional to the integrated light intensity received during each exposure time interval. Depending on the available intensities, integration times between 100 and 400 s were used.

The detector's electronic offset and dark current correction, which were found to be stable with time even over several days.

3. Data Analysis

3.1. Spectral Evaluation

The spectra were evaluated using the DOAS method [Platt, 1994]. The interfering structures in this case are the following: The Fraunhofer structures, Ring structures resulting from the filling in of the Fraunhofer lines due to rotational Raman scattering [Grainger and Ring, 1962; Bussemer, 1993; Fish and Jones, 1995], and water vapor absorption features. For the following, see Weaver et al. [1996], Solomon et al. [1989], and Platt et al. [1981].
Henceforth named J smaller than 80°C176, hence containing no NO3 absorption, as was confirmed afterward by comparing the results of a series of tests using daytime spectra with different SZA between 85° and 80°. To the logarithm of this ratio spectrum, reference spectra of water vapor and NO3 were fitted by a nonlinear least squares algorithm [Stutz and Platt, 1996]. Also included in the fitting algorithm was a so-called Ring spectrum calculated from the daytime spectrum with a routine by [Bussemer, 1993] simulating the effect of Raman scattering. A third-degree polynomial was applied to account for broadband scattering effects due to Rayleigh- and Mie-scattering. 

The water vapor reference spectrum was derived from two daytime spectra measured shortly one after the other at different but similar J, but with different water absorption optical densities. The ratio of the spectra contains the difference of their water vapor absorptions, while most of the Fraunhofer absorptions cancel out [see also Wagner et al., 2000].

For the structure of the NO3 cross section the spectrum published by Yokelson et al. [1994] was used. For our instrument’s resolution we determined a value for the differential absorption cross section s0 [Platt, 1994] of 2.09 × 10−17 cm2 at 662 nm and 298 K. To ensure a direct comparison with previous studies for the determination of s0, we chose the widely used recommendation by Wayne et al. [1991] for the broad database leading to this averaged value [see also Geyer et al., 1999]. Compared to the value derived from the Yokelson cross section, this results in ~6% larger SCD.

Figure 3 shows a typical result of a NO3 evaluation; displayed are a typical logarithmed and smoothed spectrum measured during sunrise compared to a daytime spectrum. The reference spectra are smoothed in the same way and then fitted to the measured spectrum after subtracting the daytime spectrum. Also displayed are the absorptions found by the fit in this spectrum of the water vapor, the ring effect, and the nitrate radical in solid thick lines. In gray lines the same absorptions with the residual of this evaluation added are overlaid to provide comparison between residuals and absorptions. The residuals (peak to peak) were typically (1–6) × 10−3 (maximum 1%) and anticorrelated with intensity, hence the SZA (θ), e.g., because of photon noise. The differential optical densities τ(θ) recorded at different θ resulting from the NO3 fitting routine are converted into the NO3 slant column density (S) by dividing by σ'.

\[ S(\theta) = \frac{\tau(\theta)}{\sigma'} \]  

The intensity during sunrise is varying rapidly within the integration time of a single spectrum; thus, for each spectrum an effective θ is calculated: The average spectral intensity of the spectrum, along with those of the preceding and succeeding spectra, is used to derive a time-dependent intensity function. From this the time is derived at which 50% of the recorded light has entered the measurement device; this time is adopted as the effective recording time of the spectrum. From the effective time θ is calculated with high numerical precision (0.3 arc seconds) using a software application based on the NOVAS astronomical software by the United States Naval Observatory (G. Burkardt, personal communication, 2000).

### 3.2. Profile Derivation

In this section we describe the derivation of vertical concentration data from the SZA-dependent measurement values of the SCD, that is, the S(θ) function of NO3. The altitudes stated are relative to the location of the instrument.

Typically, the measurements show a monotonic decrease of S with decreasing SZA θ (Figure 4). This is expected from the geometry (the distance A–C decreases, see Figure 1) and the decrease in the atmospheric NO3 concentration during sunrise. One uncertainty exists in horizontal gradients in the NO3 distribution in connection with transport effects (see also Aliwell and Jones [1998]), which cannot be excluded at our site (see above). Therefore,
even monotonically decreasing $S(J)$ can be influenced by transport effects that cannot be detected in the data itself and thus constitute a possible error.

In the following we first present a simple (henceforth named geometric approximation) method to derive vertical NO$_3$ profiles from the measured NO$_3$ SCDs during sunrise. This method is subject to several important shortcomings (e.g., scattering effects and chemistry, see below). Thus, for the actual determination of the NO$_3$ profiles we have to apply a more sophisticated approach. However, the simple geometric inversion scheme already shows the basic findings of our measurements. We discuss and apply it first here because it is well suited to demonstrate the key principles of our method.

In this geometric approximation the NO$_3$ present within the atmospheric volume already illuminated by direct sunlight is assumed to be instantaneously depleted by photolysis, while the NO$_3$ in the region below is considered unaffected (Figure 1). At a given SZA $\vartheta_1$ (Figure 1, top), the line of sight through the dark volume of air, and hence, through the area containing significant nitrate radical concentrations, extends from the observation point C to B (which is the intersection point of the line with the direct light zone), and a value $S_1$ is obtained. At the next, lower SZA $\vartheta_2$ (Figure 1, bottom), the zone of direct light has lowered, and the path through the not directly illuminated layers is shorter (C–B'), yielding a smaller $S_2$. Subtracting $S_2$ from $S_1$ and dividing by the respective difference in the light path lengths, yields the NO$_3$ concentration in the layer between the altitudes of B and B'. The vertical resolution of this method is governed by the $\vartheta$ dependence of the intersection point's height as well as the sampling rate of the measurement. The geometric calculations were done including spherical geometry as well as atmospheric refraction [Meeus, 1992]. Weaver et al. [1996] showed, comparing direct moon and scattered solar light in off-axis geometry with a similar line of sight, that multiple scattering effects are not significant for their location.

Results obtained by this method indicate NO$_3$ near-ground concentrations of typically $(5–50) \times 10^7$ cm$^{-3}$, an enhanced layer between 300 and 400 m, with concentrations above 3 km of $(5–50) \times 10^7$ cm$^{-3}$. For an example, see Figure 5. The geometric approximation bears inherent errors, since it assumes instantaneous destruction of NO$_3$ in the illuminated part and neglects NO$_3$ photolysis by scattered light as well as chemical sources or sinks of NO$_3$. To overcome these shortcomings, a modified variation of the matrix algorithm [Smith and Solomon, 1990] was developed. The problem is formulated as linear equation system; we have to convert a SZA-dependent SCD vector $S(\vartheta)$ containing $n$ measured
SCD into a profile vector \( c(z) \) representing \( m \) \( z \)-dependent concentration values at \( m \) altitude levels at the end of the night, that is at \( \vartheta = 97^\circ \), before photolysis sets in, when the \( \text{NO}_3 \) abundances are assumed to be unaffected. The forward problem is formulated:

\[
M \cdot c(z) \cdot \Delta z(z) \cdot \alpha(z) = S(\vartheta) \tag{2}
\]

Here \( c(z) \) represents the concentration values, \( \Delta z(z) \) the altitude layer’s vertical extension and \( \alpha(z) \) the air mass factor, which accounts for the telescope’s slant viewing direction and is defined by the elevation angle (at 15\(^\circ\) the air mass factor is \( \alpha = 3.86 \)). The right-hand side vector consists of the SCD values \( S(\vartheta) \) measured at SZA \( \vartheta \).

[22] The elements of the matrix \( M \) consist of two factors, \( f(\vartheta_i, z_j) \) and \( v(\vartheta_i, z_j) \). The degradation factors \( f(\vartheta_i, z_j) \) describe the remaining fraction of the initial \( \text{NO}_3 \) concentration at an altitude \( z_j \) and a SZA \( \vartheta_i < 97^\circ \), during sunrise. The \( f(\vartheta_i, z_j) \) are governed by the degree of photochemical degradation valid for the considered altitude \( z_j \) and the SZA \( \vartheta_i \). Their derivation is described in the next section.

[23] Since the line of sight is directed in a westerly direction, a given point of altitude \( z_j \) along this line also has a horizontal distance to the observation point. Thus a different local \( \vartheta_i \) has to be calculated for each altitude.

[24] The “visibility factor” \( v(\vartheta_i, z_j) \) of each layer \( j \) accounts for a radiative transfer effect. In off-axis geometrical observations the detected light is scattered from several altitudes of the atmosphere along the line of sight; the relative contributions from different altitudes influence the height sensitivity of the method. Light scattered at, e.g., 5-km altitude out of the direct solar light beam has not traversed the layers above under the viewing direction and thus carries no signature of the \( \text{NO}_3 \) above 5 km (we assume no significant nitrate radical concentrations along the way from the sun to the scattering point). The radiative transfer model AMFHD [Frank, 1991] was used to calculate the relative light contributions of vertical layers at a given \( \vartheta \). From these data the fraction of the total detected light, which has traversed a specific layer, is calculated. A visibility factor \( v \) of, e.g., 0.75 of a given layer at a specified \( \vartheta \) means that 75% of the light forming the spectrum recorded at this \( \vartheta \) has traversed this layer. The visibility factor of a given layer characterizes the relative fraction of the measurement light at a given \( \vartheta \) which has “seen” the nitrate radical contained within that layer as compared to the “ideal” case when all recorded photons had traversed this layer. In principle, the visibility factors are greatest for the lowermost layers (for example, the visibility for the lowermost 1000 m is \( \geq 90\% \) for \( \vartheta \geq 80^\circ \)). Figure 6 illustrates the concept of the visibility factors.

[25] Studies of the influence of air pollution on the AMFHD results yielded variations of 10% in \( v(\vartheta, z) \). This
was adopted as the visibility factor’s error. The linear equation system is thus written as

\[
\begin{align*}
(f(\theta_1, z_1) \cdot v(\theta_1, z_1) \cdots f(\theta_i, z_m) \cdot v(\theta_i, z_m)) \\
(f(\theta_n, z_1) \cdot v(\theta_n, z_1) \cdots f(\theta_n, z_m) \cdot v(\theta_n, z_m))
\end{align*}
\]

\[
\begin{align*}
\frac{c(z_1) \cdot \Delta z_1 \cdot \alpha}{c(z_m) \cdot \Delta z_m \cdot \alpha} = \left( \frac{S(\theta_i)}{S(\theta_j)} \right)
\end{align*}
\]

Thus each measured SCD \( S(\theta_i) \) is given by

\[
S(\theta_i) = \sum_{j=1}^{m} f(\theta_i, z_j) \cdot v(\theta_i, z_j) \cdot c(z_j) \cdot \Delta z_1 \cdot \alpha
\]  

### 3.2.1. Photochemical modeling

[26] In the real atmosphere, NO\(_3\) is not destroyed instantaneously but gradually reduced during sunrise. The photochemical depletion frequency of NO\(_3\) is also a function of altitude. To identify the parameters of importance for the NO\(_3\) decay, a box model for nighttime radical chemistry developed by Geyer et al. (submitted manuscript, 2001) was applied to a typical continental atmosphere.

[27] The degradation of a given NO\(_3\) concentration was calculated as a function of altitude level and SZA using the following main reactions:

\[
\begin{align*}
\text{NO}_2 + O_3 & \rightarrow NO_3 \quad \text{(production reaction)}, & (5a) \\
\text{NO}_2 + NO_3 & \Leftrightarrow \text{N}_2\text{O}_5 \quad \text{(chemical equilibrium)}, & (5b) \\
\text{NO}_3 + NO & \rightarrow \text{NO}_2 + \text{NO}_2, & (5c) \\
\text{NO} + O_3 & \rightarrow \text{NO}_2 + O_2, & (5d) \\
O + O_2 + M & \rightarrow O_3 + M, & (5e) \\
\text{NO}_3 + \text{VOC} & \rightarrow \text{organic products} & (5f) \\
\text{N}_2\text{O}_5 + \text{Aerosol} & \rightarrow \text{products}, & (5g) \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow \text{products}, & (5h) \\
\text{NO}_3 + h\nu & \rightarrow \text{NO} + O_2 \text{(photolysis, first channel)}, & (5i) \\
\text{NO}_3 + h\nu & \rightarrow \text{NO}_2 + O_2 \text{(photolysis, second channel)}, & (5j) \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + O \text{(photolysis)}. & (5k)
\end{align*}
\]

The behavior of the species involved in reactions (5a)–(5j) is modeled for the duration of a simulated night with both photolysis frequencies set to zero. During sunrise \( J_{\text{NO}_3} \) and \( J_{\text{NO}_2} \geq 0 \) are introduced. Model calculations were made for altitudes \( z_j = 0, 0.5, 1, 2, \ldots, 10 \text{ km} \) at a time resolution of 10 s.

[28] The modeled \( \theta \)-dependent NO\(_3\) concentrations \( [\text{NO}_3](\theta, z_j) \) for each altitude \( z_j \) are normalized to the value at the “end of night” \( \theta_n = 97^\circ \), which yields the \( \theta \)- and \( z_j \)-dependent relative remaining fractions \( f(\theta, z_j) \) of the end of night nitrate radical concentration \( [\text{NO}_3] \) \( \theta_n, z_j \).

\[
f(0, z_j) = \frac{[\text{NO}_3](\theta, z_j)}{[\text{NO}_3](\theta_n, z_j)}.
\]  

The \( f(\theta, z) \) (henceforth named degradation curves) yield the degradation factors \( f(\theta, z) \) in equations (3) and (4). The input parameters and their respective uncertainties are discussed below. No measured vertical profiles for the relevant species (e.g., NO\(_3\), O\(_3\), aerosols, VOCs, etc.) were available for the measurement location. Thus we derived upper and lower estimates of the different parameters based on data available for other locations. The margin between the upper and lower estimate values was governed by the uncertainty of the respective parameter and set generously in order to encompass the situation of Heidelberg.

[29] The photolysis frequencies \( J_{\text{NO}_3} \) were calculated (H. Coe, personal communication, 2000) using the radiative transfer code PHODIS (A. Kylling. PHODIS, a program package for calculation of photodissociation rates in the Earth’s atmosphere, available by anonymous ftp ftp://kaja.gi.alaska.edu/pub/phodis/phodis.ftp, 1995), based on the discrete ordinate method [Dahlbeck and Stamnes, 1991]. The model takes into account the atmosphere’s curvature. The photolysis frequencies were calculated by multiplying the cross-section quantum yield product measured by Magnotta and Johnson [1980] with the modeled actinic fluxes and integrating over the whole wavelength range.

[30] In order to estimate the uncertainty in \( J_{\text{NO}_3} \), the photolysis frequencies were calculated for clean and polluted continental air with accordingly different visibilities (50 and 15 km, respectively), thus upper and lower estimates of \( J_{\text{NO}_3} \) were derived. The calculations were performed for \( \theta \) between \( 97^\circ \) and \( 80^\circ \) in \( 0.5^\circ \) steps and for altitudes between 0 and \( 10 \text{ km} \) in steps of \( 1 \text{ km} \) (Figure 7). For the photolysis frequencies of NO\(_2\), \( (3.3 \pm 0.3)\% \) of \( J_{\text{NO}_2} \) was used determined from spectroradiometer measurements performed at the same time of the year on the roof of a building near Berlin by (E. Eckstein, personal communication, 2000). The spectroradiometer measured the spectral irradiance with absolute calibration, and both \( J_{\text{NO}_3} \) and \( J_{\text{NO}_2} \) were calculated from these data, which made it possible to derive a proportionality factor. The profiles of NO\(_3\) and N\(_2\)O\(_5\) are assumed to be zero at the beginning of the night.

[31] The temperature at ground level was taken from the temperature sensor installed at the weather station on top of the institute building. The vertical decrease above the mixing layer was assumed as 0.6 K per kilometer (see, e.g., U.S. Standard Atmosphere for middle-latitude summer (AFGL-TR-86-0110)). Since no data were available for higher altitudes, and the time resolution of the ground data is limited, we assumed an uncertainty of 1 K at ground level, and 2 K above. Ground level data for O\(_3\), NO\(_2\), and NO was provided by UMEG (Gesellschaft für Umweltmesungen und Umwelterhebungen mbH, Karlsruhe). Since no data were available on the typical vertical profiles of O\(_3\), NO\(_2\), NO, and VOC and aerosols at Heidelberg, vertical profiles measured at other, comparable sites in the continental troposphere were used as model input. For the free troposphere, NO\(_2\) profiles measured with balloon-borne
devices (F. Goutail, personal communication, 2000) and the NO2 profile of the U.S. Standard Atmosphere served as upper and lower estimates. The tropospheric ozone profile was taken from ozone sonde measurements at Lindenberg near Berlin in August 1998. For NO, additional measurements with a NO monitor (Eco Physics CLD 770 AL ppt) located at the same place on the roof as the spectrograph were used to estimate the profile structure of NO and its decrease in concentration with altitude. The data yielded an upper estimate of 1.7 ppb NO at night at the ground close to a street (i.e., close to the sources), and below 100 ppt (the system’s detection limit) at 30-m altitude. This yielded a scaling height of \(\frac{\text{C}_2}{\text{C}_0} 11\text{ m}\), indicating that the NO present at night only affects the very lowest part of the boundary layer and has no significant influence on the layers probed with the off-axis instrument. Concerning VOC, no on-site ground level or profile data is available for Heidelberg. Therefore, instead of specific concentrations, degradation frequencies of NO3 from reactions with VOC measured at a rural site near Pabstthum in the vicinity of Berlin during the BERLIOZ-campaign 1998 were used [Geyer et al., 2001a] ranging from \(2 \times 10^{-4}\) s\(^{-1}\) to 0.4 s\(^{-1}\). The average nighttime degradation frequency was \(1.57 \times 10^{-2}\) s\(^{-1}\). The VOC reactivity toward NO3 in the work of Geyer et al. [2001a] was dominated by monoterpenes emitted from a near forest. These frequencies were scaled with height using tethered balloon soundings at the same site (Glaser et al., Vertical profiles of O3, NO2, NOx, VOC and meteorological parameters during the BERLIOZ-Campaign, submitted to Journal of Geophysical Research, 2001).

[32] The aerosol surface density available at ground level for uptake of N2O5 are typically in the range of (100–900) \(\mu\text{m}^2/\text{cm}^3\). Observed aerosol data (B. Wehner, personal communication, 2000) for the urban areas of Eichstätt and Leipzig (summer 1998 and 1999, respectively) were used to determine the upper and lower estimates on the ground level value. To account for the vertical aerosol profile structure relative vertical profile estimations (A. Ansmann, personal communication, 2000) from Lidar experiments were used to scale the ground level surface data. Thus we obtained upper and lower estimates of vertical profiles of the aerosol surface density. These studies in general indicate a maximum in aerosol backscattering signal at \(\text{C}_2 500\text{ m}\) altitude, a sharp drop by a factor of 2 to 5 above and no significant signal beyond \(3\text{ km}\).

[33] In summary, the upper and lower limit profiles of the parameters are shown in Figure 8. With the same model a possible influence of stratospheric nitrate radical on our measurements was investigated. Owing to the high photolysis frequency of NO3 in the stratosphere even for large \(\text{C}_2 94\) the remaining stratospheric NO3 concentration is less than 1% of the nocturnal value in spite of the uncertainties; e.g., for the assumed stratospheric NO3 slant column density \(\text{C}_2 94\) is typically <\(10^{13}\) cm\(^{-2}\) [see, e.g., Norton and Noxon, 1986]. In contrast, the NO3 slant column density measured with our instrument at \(\text{C}_2 94\) is typically \(\approx 10^{15}\) cm\(^{-2}\), ~2 orders of magnitude larger than the stratospheric NO3 slant column density.

[34] Hence our measurements and the following considerations (chemical modeling and profile retrieval) address the troposphere only.

### 3.2.2. Monte Carlo retrieval approach

[35] The problem (equation (2)) now presents itself as a matrix-based retrieval problem. Extensive work aimed at solving equation systems for atmospheric sounding has been performed by Rodgers [1976].
First, the chemical environment that shapes the decrease of the nitrate radical concentration during a sunrise, has to be converted into a function of concentration with SZA (θ) for each of the vertical levels selected. This is done by solving the equations (5a)–(5j) for NO₃ for every time step (time is equivalent to θ). These values, normalized as stated, form the components in θ and altitude axes of an equation system, which serves to map the measurement space into profile space.

Here we have to deal with the large uncertainties in reactant concentrations, which means we do not know the actual degradation curve (and thus the mapping). So we have to construct a range of possible chemical environments which encompasses the actual one at a given measurement day.

First, we investigated the influence of the uncertainties in the input parameters, e.g., NOx, O₃, aerosols, VOCs, etc., on the degradation curves f(θ, zj). In all cases the effect was a change in the curve’s steepness. With low NO and VOC and aerosol concentrations the degradation curve falls off very steeply, because in these cases, the NO₃ concentration decrease is mainly governed by direct photolysis. When introducing higher concentrations of NO₂, the gradient is less steep due to thermal decomposition of N₂O₅ (5b, backreaction), which has formed in higher concentrations during the night. The influence of enhanced VOC, NO, or aerosol concentrations, too, was found to lead to a more gradual NO₃ decrease. During the night a quasi-equilibrium between the NO₃ formation and destruction is formed: In the presence of high concentrations of VOC, aerosols, and NO the resulting NO₃ concentration is small and vice versa. At sunrise this quasi-equilibrium is disturbed by the photolysis of NO₃. The relative influence of this NO₃ photolysis, however, depends on the magnitude of the other NO₃ destruction mechanisms and thus on the concentration of VOC, aerosols, and NO: If high concentrations of VOC, aerosols, and NO are present the relative contribution of the NO₃ photolysis to the total destruction is small; thus the relative change of the NO₃ concentration during sunrise is also small (while the absolute magnitude of the NO₃ concentration is, of course, significantly smaller compared to the case with low concentrations of VOC, aerosols, and NO). In the case of low VOC, aerosols, and NO the NO₃ photolysis constitutes a more dominant NO₃ destruction process compared to the total NO₃ destruction; thus the relative change of the NO₃ concentration in that case during sunrise is much stronger.

We composed two “extreme” sets of degradation curves, henceforth called the steepest and least steep set of curves, respectively. The steepest curve for a given altitude is the curve using the specific combination of upper and lower estimates (see Figure 8) that leads to the steepest reduction in the nitrate radical concentration with θ during sunrise (high clean air photolysis frequencies, higher estimates on temperature and ozone and lower estimates on NO₂, VOC, and aerosol load). The least steep realistic curve

![Figure 8](image-url)
values are based on the reactant combination leading to the least steep decrease in relative nitrate radical concentration (polluted air photolysis frequencies, lower temperature and ozone estimates, and upper estimates on NO₂, NO, VOC and aerosol load). Figure 9 shows the obtained degradation curves.

[40] Note that a deviation of one of the components, e.g., NO₂, from its original value in a given scenario that leads to a certain degree of steepness can be compensated for by a deviation of one or more of the other components, e.g., a less steep decrease in nitrate radical can be “made steeper” again by a higher photolysis rate. This means that we do not constrain the single reactants one by one, but rather the chemical situation that they form altogether.

[41] In order to visualize the effect of the uncertainties in the different input parameters on the curve’s steepness, we calculated normalized steepest and least steep degradation curves with one of the input parameters set to the other extreme value. For example, to investigate the effect of the VOC, we combined the other parameter’s values for the least steep with the VOC-related value for the steepest curve, and vice versa. In Figure 10 the absolute differences between these new curves to the original steepest (least steep, respectively) curves are shown. Clearly visible is the prominent influence of the VOC-related uncertainty on the curve’s steepness for 500 m altitude, while for the free troposphere errors in NO₂ and temperature uncertainties become more important.

[42] With the use of these two sets of curves we apply constraints to the problem by constraining not the profile space directly but, in fact, the range of mappings which generate the profiles. For the sake of not excluding physical meaningful solutions, we set the estimates very generously.

[43] From these two sets of curves, two analogously extreme matrices (see equation (2)) as actual mappings are derived, which convert a vector in measurement space (SCD as function of SZA, or S(J)) into one in profile space (concentration as function of altitude), while the J are governed by the measured data points and the vertical levels by theoretically arbitrary choice. We did select a discretization with less vertical levels than data points, and with high resolution in the lower troposphere than in the higher, thus reflecting both the actual gradients in e.g. air density and concentrations of, e.g., VOC as well as the higher resolution of the geometric approximation at lower altitudes.

[44] This discretization constitutes a second constraint [Rodgers, 1976] we apply to the problem, which must not exclude solutions. When varying our choice in the frame of sensitivity studies, we did either obtain the same principal profile structures as final solutions or no solution at all, indicating a gross mismatch between the resolution chosen and the chemical gradients of the real atmosphere. We also conducted a sensitivity study on the effect of variations in profile structure on the modeled S(δ). Among several other cases investigated, we (1) shifted the enriched layer of
model profiles, e.g., from the second lowest to the two adjacent boxes, and we (2) used a uniform concentration throughout the troposphere, and compared the resulting \( S(J) \) with each other. We found, e.g., at \( J = 90^{\circ} \), differences of up to 80% between the \( S(J) \) obtained with a given matrix.

[45] The matrix components each belong to a \( \bar{\vartheta} \) value (row, index \( i \)) and vertical level (column, index \( j \)) and are taken from the appropriate curve at the respective \( \bar{\vartheta} \).

[46] To probe the range of chemical environments with these mappings, we compose a set of \( N \) matrices representing the whole range of the modeled degradation curves; the components of those matrices are linear, equidistant interpolations between their counterparts in the two extreme matrices. For example, the \( i \)th and \( j \)th component \( c_{ij}^M \) of the \( M \)th matrix is \( N-(M-1) \) times \( c_{ij}^{ST} \) plus \( (M-1) \) times \( c_{ij}^{LS} \), divided by \( N \), and with \( c_{ij}^{ST}, c_{ij}^{LS} \) as respective components of the steepest (ST) and least steep (LS) matrix. We did select \( N = 30 \) but did not obtain other solutions with \( N = 50 \) or higher. We henceforth call \( M \) the degree of steepness.

[47] Additionally, to account for the fact that at different heights the chemical conditions might fit different matrices, we introduce a further pattern of variation. The columns of each matrix are systematically varied depending on the altitude range represented by them.

1. The leftmost column (representing the uppermost altitude level) is increased by 50% of the difference to its counterpart in the next neighboring (smoother) matrix; the rightmost column (ground level) is analogously decreased.

2. The operations are performed in the opposite way.

3. The columns are increased (decreased, respectively) by 25% of the difference to their counterparts in the nearest neighbor matrix.

[48] This leaves us with 150 matrices altogether (30 original matrices + 4 variations of each). With these matrix variations the system is offered a range of photochemical environments, thus mappings from measurement space into profile space, to "choose" from. The straightforward way to facilitate this choice is to probe the range systematically using the parameter \( M \).

[49] The final step is to find the solution(s) of a given equation system (equation (2)). In principle, an analytical algorithm using direct matrix inversion is preferable to solve equation (2).

[50] Unfortunately, the following facts constitute a potential obstacle to do this. First, the mapping used can be
values have to be considered. For the model uncertainties and the measurement noise, we could not a priori rule out multiple solutions for a given matrix. Since we have found more than one solution per run, large oscillations can occur in the inverted matrix.

Nonstandard ad hoc approaches have also been addressed by [Rodgers, 1976]. He points out that they bear the danger of being nonoptimum but may deliver solutions which agree with the optimum solution within its covariance. For each \( \theta \) series, the calculated SCD value is located within the 2\( \sigma \)-error ranges of the respective measured data points. Only if for each \( \theta \), the calculated SCD series. Only if for each \( \theta \), the calculated SCD value is located within the 2\( \sigma \)-error ranges of the respective measured data points, is the solution considered valid, otherwise rejected. This procedure is performed for all 150 matrices.

For each matrix, random profiles are generated as outlined above. Each random-generated profile is multiplied with the matrix yielding a modeled \( S(\theta) \) series. Only if for each \( \theta \), the calculated SCD value is located within the 2\( \sigma \)-error ranges of the respective measured data points, is the solution considered valid, otherwise rejected. This procedure is performed for all 150 matrices.

For each of the valid profiles, the profile error; this process must not minimize the error of one part of the profile vector at the expense of the others, since the location of interesting features within this vector is not a priori known. Third, profiles yielding modeled \( S(\theta) \) vectors that are in better agreement with the measured one shall contribute more to the finally resulting profile vector.

We therefore decided to use a Monte Carlo approach as follows. The NO3 concentration in each vertical layer was selected randomly and the NO3 profile vector was multiplied by the degradation matrix \( M \). By performing a large number of runs the absolute minimum in solution space is, within the measurement errors, found with greater certainty.

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First, only profiles which yielded, multiplied with one of the matrices, a modeled \( S(\theta) \) with all data points located within the 2\( \sigma \)-error ranges of the respective measured data points are used for further processing. Second, the number and magnitude of the measurement errors must be reflected in the profile error; this process must not minimize the error of one part of the profile vector at the expense of the others, since the location of interesting features within this vector is not a priori known. Third, profiles yielding modeled \( S(\theta) \) vectors that are in better agreement with the measured one shall contribute more to the finally resulting profile vector.

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Using $1/\chi$ to weight the respective profiles a mean profile is calculated from all valid profiles. Analogously, for the error of this final profile a modified standard deviation using the same $1/\chi$ as weighting factor is used. These errors thus are largely governed by the measurement errors. It is obvious that the more measured data points are available, and the smaller their errors are, the fewer possibilities exist to obtain a valid profile, the smaller its variations are, and the smaller the resulting profile errors are.

The method turned out to be ambiguous. Valid profiles (as defined above) were obtained from groups of different matrices representing contradicting chemical conditions. In most cases the matrices yielding valid profiles were found to be grouped around one or two points on the steepness axis (see Figure 11). (The 26 July, though, represents an exception as valid profiles were obtained from virtually all matrices.) The profiles belonging to one group were similar to each other but systematically different from the other group’s profiles.

### 3.3. Results

Figures 12, 13, and 14 show the resulting NO$_3$ vertical profiles for all clear days for which measurements were performed in Heidelberg in summer 1999. The color coding of the profiles indicates the matrix group from which they were derived. The horizontal bars describe the statistical error in concentration. According to the meteorological conditions at the measurement site, we conclude that the red profiles (steepest matrices) are the true profiles. See color version of this figure at back of this issue.
For this group the NO$_3$ maximum is located at altitudes around 350 m; the blue profiles refer to the smooth matrix group; the NO$_3$ maximum of this group is situated at altitudes around 2.5 km. The green profiles belong to the matrices in between of the extremes. In most cases, no valid profiles were found in this area of the steepness axis, and if so, the resulting profiles resembled closely the blue ones.

Although the profiles belonging to the “steepest matrices” can be very probably regarded as the true profiles (see below), some important conclusions can be drawn without any selection between the two solutions; first, for all cases an enriched layer is found, that is, a pronounced nitrate radical concentration maximum within the lower troposphere; the respective maximum concentrations range from (100 to 900) \(10^7\) cm$^-3$. Above this layer, the concentrations sharply drop to less than 50 \(10^7\) cm$^-3$. Below the layer, especially near the ground, all derived profiles show very low concentrations of typically far less than 10% of the enriched layer’s concentration. This is a clear confirmation of the suggestions of Aliwell and Jones [1998] and Fish et al. [1998]. The mathematical algorithm gives no direct indication which profile is the true one. However, one can find some indirect indications considering which environment the different matrices represent. Owing to the strong influence of the VOC at low altitudes (refer to Figure 10) the steepness is largely governed by VOC. The matrices that correspond to the blue profiles represent the cases with very high VOC concentrations and hence \(f_{\text{NO}_3-\text{VOC}}\) of up to 0.4 s$^{-1}$ (see Figure 8) throughout the mixing layer, while the matrices corresponding to the red profiles are associated to \(f_{\text{NO}_3-\text{VOC}} \leq 0.13\) s$^{-1}$, which is still larger than the great majority of the derived data by Geyer et al. [2001a]. The VOC that are relevant for NO$_3$ depletion are mainly emitted by trees, i.e., at an altitude of \(~20\) m [Geyer et al., 2001a]. Even with low ground-level nitrate radical concentrations the lifetime of these VOC against NO$_3$ and ozone does not allow them to reach altitudes higher than 200 m within the mixing layer. Under standard meteorological conditions at night (no convection) the transfer of VOC to higher levels is restricted. For these reasons we believe the blue (and, if applicable, the green) matrices to represent chemical conditions that are very unlikely (e.g., strong upwinds above the forest during night). In addition, the results from an independent model (see below) confirm the profiles with NO$_3$ maxima at lower altitudes. Thus we conclude that the red profiles must be the “true” atmospheric profiles.

It cannot completely be ruled out, though, that unusual upwind situations can carry VOC to higher altitudes within the mixing layer. For this reason and due to the

Figure 13. Weighted mean nitrate radical vertical profiles derived from DOAS-SCD-measurements in summer 1999: 29, 30, and 31 July. See color version of this figure at back of this issue.
lack of on-site data, we had to include this possibility in our choice of the upper estimate of $f_{\text{NO}_3\text{-VOC}}$.

3.4. Comparison Between the Geometric Approximation and the Modified Matrix Method

The comparison between the profiles derived with the geometric approximation and with the matrix method (Figure 5) yields some information on the usability of the two techniques. The fact that the geometric approximation seems to confirm the “red” profiles is not too surprising when considering the matrices that yielded the profiles. Since the geometric approximation is equivalent to a very steep curve (in fact, a theta function dropping from one to zero when the terminator passes through the altitude considered), the steep matrices yield similar curves. Apparently the effect of nitrate radical photolysis within the not directly illuminated part of the atmosphere (Figure 1), which accelerates the degradation, is, for the cases reported here, compensated for by the thermal decomposition of $\text{N}_2\text{O}_5$ that has been accumulating during the night along with the buildup of $\text{NO}_3$ and that slows down the degradation.

The concentration in the upper free troposphere is slightly overestimated by the geometric approximation, and the enriched layer appears to be thicker. This could be a result of the fact that the layer, holding most of the tropospheric nitrate radical, governs the whole SCD time series during sunrise; since the approximation treats a difference in SCD between two successive measurements as resulting only from the photolytical destruction of the nitrate radical located between the two intersection points of the line of sight with the zone of direct sunlight, it apparently “smears out” concentration of the layer with the high $\text{NO}_3$ concentrations into the adjacent layers; when the solar terminator, for example, passes through layers above the enriched layer, the nitrate radical concentrations contained within already are in the process of destruction, causing a SCD decrease that is falsely attributed to the layers the terminator passes through. In general, the matrix method obviously can be considered the more accurate method of retrieval; it additionally has the advantage that the spatial resolution can be chosen finer or coarser at any altitude, given a constant number of layers. This can reflect knowledge concerning reactant profiles, given that principal solutions are not excluded. The geometric approximation’s vertical resolution is determined by the respective positions of the sun and the viewing geometry. At locations like Heidelberg the geometric approximation, which is more simple to use and does not require profile data as input, seems to be a viable alternative, once it has been validated to the matrix method.

The need for vertical profile data is not too limiting, since, as mentioned in section 3.2.2, the only important parameter for the retrieval is the steepness parameter of the degradation curve. This steepness is the magnitude determined to give the best fit to the data, and it is the result from

Figure 14. Weighted mean nitrate radical vertical profiles derived from DOAS-SCD-measurements in summer 1999: 1, 2, and 4 August. See color version of this figure at back of this issue.
the combination of a number of vertical profiles of the relevant species, which as a whole form a specific chemical situation “toward” NO$_3$. This means that the reactant profiles do not have to be known in full detail. An error in, e.g., NO$_2$ may be compensated for by an error in VOC, for example, to yield the same degree of steepness, as stated. Thus it is only necessary to choose the upper and lower reactant concentration estimates large and small enough, respectively, to encompass the real situation with the steepness range obtained. This fact makes the modified matrix algorithm a method for profile retrieval, which is applicable to a wide range of atmospheric conditions. However, if the uncertainties in the parameters are too great, more than one solution can occur, which stresses the need for at least a limited set of chemical data.

4. Simulations with KAMM/DRAIS

In addition to the experiments we carried out numerical simulations with the comprehensive non-hydrostatic mesoscale model KAMM/DRAIS [Vogel et al., 1995, 1999]. The comparison of the simulated profiles of NO$_3$ with the observed ones is useful for the following reasons. First, it is important to check to what extent the model is able to simulate the observed concentration levels of NO$_3$ and the shape of the profile. This could be done in a limited way up until now since the majority of the observations gave NO$_3$ concentrations close to the surface only. Second, as was shown in this paper, the retrieval algorithm presented two possible solutions and the model simulations could help to identify the most reasonable one. The model domain covers not only the southwestern part of Germany including the site where the observations were carried out, but also the Vosges mountains and the northern parts of Switzerland (see Figure 15). We performed model runs for a typical summer day.

4.1. The Model System KAMM/DRAIS

The meteorological driver of the model system is the nonhydrostatic mesoscale model KAMM [Adrian and Fiedler, 1991]. It is coupled with a surface vegetation model to describe the lower boundary conditions for temperature and humidity [Schädler, 1990]. The submodule DRAIS is used to treat the transport and the diffusion for the reactive trace species. The dry deposition is parameterized using a big leave multiple resistance model [Baer and Nester, 1992]. To calculate the chemical transformations, the gas phase mechanism RADM2 [Stockwell et al., 1990] was included. The biogenic VOC emissions are calculated depending on the land use, the modeled temperatures, and the modeled radiative fluxes [Vogel et al., 1995]. The biogenic NO emissions are parameterized using a modified scheme [Ludwig et al., 2000] based on the work of Yienger and Levy [1995]. The anthropogenic emissions of SO$_2$, CO, NO$_x$, and 32 individual classes of VOC’s according to the RADM2 mechanism were precalculated with a spatial resolution of $1 \times 1$ km$^2$ and a temporal resolution of 1 hour. These emission data take into account traffic emissions, emissions by big point sources, and area sources like households and industrial areas. The method used to determine these emissions is described by Obermeier et al. [1995], Wickert et al. [1999], and Seier et al. [2000].

In the vertical direction, 25 layers are used. The vertical grid size varies from 20 m close to the surface up to...
400 m at the top of the model domain that is at 8 km above sea level. In this study the horizontal grid size is 4 x 4 km². The time steps, which are used, are in the order of seconds. The whole model system runs in a fully coupled mode.

A geostrophic wind of 4 m s⁻¹ from the southwest is prescribed. The maximum temperatures are above 30 °C in the Rhine Valley and the maximum ozone concentration is in the order of 2.5 x 10¹² cm⁻³ (~100 ppb). Owing to the high temperatures the contribution of the biogenic VOC emissions (isoprene and terpenes) to the total VOC emissions is of biogenic origin.

In this study we did not treat the aerosol processes explicitly but used a parameterization, based on that originally proposed by Chang et al. [1987], for the rate constant of the heterogeneous hydrolysis of N₂O₅. On the basis of measurements of the reaction probability by Wahner et al. [1998] and Mentel et al. [1999] and additional model runs including aerosol processes we updated this parameterization [Riemer et al., 2001]. The rate constant for the heterogeneous hydrolysis kₙ₂o₅ is then a function of the relative humidity as it is calculated at each grid point and at each timestep.

4.2. Model Results

Figure 15 gives the simulated distribution of NO₃ at ~250 m above surface at 0400 Central European Time (CET). The highest NO₃ concentrations are simulated at that height. It is obvious that NO₃ shows a high spatial variability, with a maximum concentration of 1.360 x 10¹⁰ molecules cm⁻³. Elevated concentrations of NO₃ are simulated in the plumes of the main industrial areas several kilometers behind the sources. For several reasons we did not simulate each single observed profile in detail. First, the high spatial variation of the NO₃ reduces the significance of such a comparison. Second, we did not have all the input

![Figure 16. Modeled mean vertical profiles of the NO₃ concentration and standard deviation at 0400 CET. See color version of this figure at back of this issue.](image-url)
data as emissions to simulate the individual days. Moreover, we wanted to see to what extent the model is able to simulate the main features of the observed vertical profiles of NO$_3$ and whether these features apply to the nitrate radical profiles of the modeled area in general; i.e., we wanted to see if the simulated maximum values of the NO$_3$ concentration are of the same order of magnitude as the observed ones, and if the model was able to simulate the maximum of the NO$_3$ concentration at the same height interval as the observed one. Therefore we simulated a typical summer day and calculated the mean vertical profile of NO$_3$ using the individual profiles of each of the 3996 horizontal grid points. Figure 16 gives the mean vertical profile of the NO$_3$ concentration together with the standard deviations at 0400 CET. It shows a maximum NO$_3$ concentration of $330 \times 10^7$ molecules cm$^{-3}$ at 250 m above surface.

When comparing the simulated (Figure 16) and the observed (Figures 12–14) profiles of NO$_3$ it can be seen that the absolute values of the NO$_3$ maximum are comparable to the measurements. Although the observed profiles at Heidelberg showed higher maximum values than the simulated ones, one has to take into account the high spatial variability of the simulated NO$_3$ distribution in that part of the model domain. In addition, the height of the maximum of the NO$_3$ concentration is reproduced very well by the model simulations. The major difference we found between observations and the results of the simulations is a steeper decrease of the observed NO$_3$ concentration above the enriched layer.

The vertical NO$_3$ column for the averaged profile shown in Figure 16 is $3.5 \times 10^{16}$ molecules cm$^2$, in good agreement with our observations where total NO$_3$ vertical columns between (2.4 and 3.3) $\times 10^{14}$ molecules cm$^2$ were found.

5. Discussion and Conclusions

We applied a modified matrix technique to derive nitrate radical vertical profiles from off-axis measurements of the NO$_3$ slant column density during sunrise in summer 1999 at Heidelberg. The degradation of the nitrate radical is modeled with high time resolution and the resulting functions, the so-called degradation curves, converted into a matrix that, together with the vector containing the measured data, forms a linear equation system. Since there are large uncertainties in the input parameters, we cannot exactly reproduce the chemical environment but have to rely on upper and lower estimates of the reactant concentrations. We exploit the fact that variations in all of the parameters can be summarized in variations in the steepness of the degradation curve. A given steepness represents an overall chemical environment toward the nitrate radical and does not depend on one single reactant concentration alone, which reduces the sensitivity of our approach to parameter uncertainties. We vary the steepness between two extremes to offer the algorithm a variety of chemical environments to solve the equation system using a Monte Carlo technique.

The results indicate that the majority of the tropospheric nitrate radical during the night is accumulating within an enriched layer in the lower troposphere. The absolute values of the maximum concentration range from 100 to $900 \times 10^7$ cm$^{-3}$, while the concentrations below this layer and above are much smaller. Although the algorithm in principle yields two different sets of profiles (with maxima at 350 m and 2.5 km, respectively), for the measurement conditions at Heidelberg the solution for 2.5 km can very probably be ruled out.

The profiles with the maximum at 2.5 km correspond to very high VOC abundances which are not likely to exist in the general case for the reasons stated above; hence these profiles are unlikely to represent the actual atmospheric profiles. An additional indication for the lower height of the nitrate radical maximum was derived from the comparison with model simulations with the comprehensive model KAMM/DRAIS.

The simulated nocturnal profiles yield the NO$_3$ maximum at a height of $\sim 250$ m above surface, which is at the top of the nocturnal boundary layer. The simulated concentration levels are comparable to the observed ones. With respect to the shape of the vertical profiles the model results would confirm that the profiles with the concentration maximum at 350 m (see Figures 12–14) are the most reasonable ones. The simulated profiles of NO$_3$, though, show a slower decrease with height when compared to the observations, the reason for this being not yet clear. A profile with maximum in the free troposphere could not be reproduced with any realistic parameter combination.

An interesting question could be raised which kind of profile would have been measured in highly polluted (thus NO-rich) areas, e.g., in Mannheim, or at sites with high VOC source strengths. In these places, only less steep degradation matrices apply. Assuming the same initial SCD, this would place the majority of the nitrate radical in the free troposphere as it, in these cases, cannot exist within the boundary layer. However, since KAMM/DRAIS could not reproduce the enriched layer in the FT, it is reasonable to assume that in highly polluted areas there are much smaller SCD, and no enriched layer at all. Our profiles may also be not representative for clean areas, such as the Arctic, or elevated sites, since the educt concentrations are far lower at these sites.

This study has provided experimental proof to substantiate previous suggestions that NO$_3$ concentrations vary considerably across the lower troposphere and the boundary layer. Measurements performed at ground level therefore could strongly underestimate the total tropospheric nitrate radical abundance and hence the oxidative capacity of the atmosphere.

References


Baer, M., and K. Nester, Parametrization of trace gas dry deposition
Figure 2. Map of the measurement site (red square) located in the city of Heidelberg (taken from the official Heidelberg homepage, http://www.heidelberg.de). The square indicates the institute’s location, the arrow the line of sight. The Odenwald mountains are covered by forest (shown in green), the agricultural areas are indicated by light gray. The motorways are the orange lines to the west of the institute. The surrounding environment consists of both urban and rural areas, with the edge of the Odenwald mountains providing shadow against the sun.
Figure 3. Typical NO$_3$ DOAS evaluation; upper left: measured twilight spectrum, SZA 90.9°, 31 July 1999, Heidelberg (thick line), daytime spectrum taken at SZA = 77.2° (thin line); upper right: H$_2$O vapor absorption as obtained in this specific evaluation (black line), and with added residual of the evaluation (gray line); lower left: absorption ring effect spectrum and lower right: NO$_3$ absorption from this example, as found (black lines), and with added residual of the evaluation (gray lines).
Figure 7. Nitrate radical photolysis frequencies as a function of SZA derived using the PHODIS radiative transfer modeling package. Shown are the data sets for (left) clean and (right) polluted continental air. Read $1 \times 10^{-3}$ as $1 \times 10^{-3}$.

Figure 9. Derived (left) steepest and (right) least steep possible degradation curves (showing the modeled decay of $[\text{NO}_3]$ at different altitudes normalized to $[\text{NO}_3]$ at an SZA of 97°) to serve as input for the respective matrix (refer to subsection 3.2.1); Between 97° and 94° SZA, when photolysis is still very low, the curves represent the different nighttime evolutions representing the specific chemical conditions in the respective altitude levels. For example, at 4- and 6-km altitude nitrate radical concentrations are slightly increasing because production is still ongoing. In contrast, at 0 and 500-m altitude, the production is reduced by the depletion of the precursors (mainly NO$_2$).
Figure 10. Sensitivity study on the different reactant’s influence on the shape of the degradation curves. For the (left) steepest curve model each of the parameters in turn were set to their respective (right) “least steep” values (e.g., the lower estimates on NO$_2$ were replaced by the upper estimates) and vice versa for the least steep curve. The effect is shown as absolute difference between the resulting curve and the original one. Near the ground, VOC are most important in terms of uncertainty, while in the free troposphere, NO$_2$ and temperature assume the prominent role.
Figure 12. Weighted mean nitrate radical vertical profiles derived from DOAS-SCD-measurements in summer 1999 using the modified matrix method (2 April, 26 and 27 July). The profiles are grouped according to the position on the steepness axis of the matrix, which yielded the profiles. Shown below each profile graph is the number of valid profiles found for the matrices represented by the axis number (see Figure 11). The red profiles refer to the red (steepest) section of this axis and show their concentration maximum at around 350-m altitude; the blue profiles belong to the smooth matrices (blue section) and possess their maximum within the 2.5-km altitude box. The green profiles refer to the matrices in between, which in most cases did not deliver valid profiles. Please note that the profile shape is controlled by the vertical extensions of the boxes holding the randomly generated concentrations; these box sizes were chosen according to the tropospherical chemistry’s spatial variability being higher near the ground than in the free troposphere. The vertical bars represent the vertical resolution of the model, while the horizontal bars describe the statistical error in concentration. According to the meteorological conditions at the measurement site, we conclude that the red profiles (steepest matrices) are the true profiles.
Figure 13. Weighted mean nitrate radical vertical profiles derived from DOAS-SCD-measurements in summer 1999: 29, 30, and 31 July.
Figure 14. Weighted mean nitrate radical vertical profiles derived from DOAS-SCD-measurements in summer 1999: 1, 2, and 4 August.
Figure 16. Modeled mean vertical profiles of the NO$_3$ concentration and standard deviation at 0400 CET.