Improvements in the profiles and distributions of nitric acid and nitrogen dioxide with the LIMS version 6 dataset

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Abstract

The quality of the Nimbus 7 Limb Infrared Monitor of the Stratosphere (LIMS) nitric acid (HNO$_3$) and nitrogen dioxide (NO$_2$) profiles and distributions of 1978/1979 is described after their processing with an updated, Version 6 (V6) algorithm and subsequent archival in 2002. Estimates of the precision and accuracy of both of those species are developed and provided herein. The character of the V6 HNO$_3$ profiles is relatively unchanged from that of the earlier LIMS Version 5 (V5) profiles, except in the upper stratosphere where the interfering effects of CO$_2$ are accounted for better with V6. The accuracy of the retrieved V6 NO$_2$ is also significantly better in the middle and upper stratosphere, due to improvements in its spectral line parameters and in the reduced biases for the accompanying V6 temperature and water vapor profiles. As a result of these important updates, there is better agreement with theoretical calculations for profiles of the HNO$_3$/NO$_2$ ratio, day-to-night NO$_2$ ratio, and with estimates of the production of NO$_2$ in the mesosphere and its descent to the upper stratosphere during polar night. The improved precisions and more frequent retrievals of the profiles along the LIMS orbit tracks provide for better continuity and detail in map analyses of these two species on pressure surfaces. It is judged that the chemical effects of the oxides of nitrogen on ozone can be examined quantitatively throughout the stratosphere with the LIMS V6 data, and that the findings will be more compatible with those obtained from measurements of the same species from subsequent satellite sensors.

1 Background

The Limb Infrared Monitor of the Stratosphere (LIMS) experiment was launched on 24 October 1978, on the near polar-orbiting Nimbus 7 satellite. LIMS operated from 25 October until 28 May 1979, measuring vertical radiance profiles across the atmospheric limb of the Earth (Gille and Russell, 1984). Its daily orbital data extend from...
64° S to 84° N and are available at two local times per latitude (at about 1300 h and 2300 h at the Equator). The radiances were processed to infer middle atmospheric temperature profiles and the concentrations of several chemical compounds important for the chemistry of stratospheric ozone. LIMS provided profiles of ozone (O₃), water vapor (H₂O), nitric acid (HNO₃), and nitrogen dioxide (NO₂). Thus, LIMS was the first satellite experiment to provide a simultaneous, near-global view of the key chemical compounds in the ozone/nitrogen oxide photochemical chain. The temperature, geopotential height, and constituent profiles have been used for many scientific investigations, including effects of radiation on the net transport, responses of the middle atmosphere to perturbations, and correlations between the temperature and species data.

The LIMS Version 5 (or V5) profiles were archived in 1982; its measurements, algorithms, and data products are described in Gille and Russell (1984) and references therein. Since that time, significant improvements have been realized in the original spectroscopic parameters (Drayson et al., 1984) that were used for the V5 retrieval of temperature/pressure or T(p) and for the gaseous constituent profiles that contribute to the radiances measured within the six channels of LIMS. For this reason a reprocessing of the LIMS Level 2 (or profile) data to Version 6 (V6) was undertaken using the high-resolution, transmission molecular absorption line parameters of HITRAN 91/92 and/or 96. As a result, these V6 data are appropriate for comparisons with the temperature and species distributions obtained from the several middle atmosphere instruments onboard the NASA Upper Atmosphere Research Satellite (UARS), the Earth Observing System (EOS) Aura satellite and on the Canadian, European, and/or Japanese satellites SCISAT, ODIN, ENVISAT, and ADEOS.

A single LIMS scan profile began with the center of its FOV array viewing the horizon at 153 km altitude, moving downward to a point 38 km below the solid Earth limb and then returning upward. The angular resolutions (in milliradians) for the detectors of the FOV array are 1 mrad for the NO₂ and H₂O channels and 0.5 mrad for the other four channels, including HNO₃. The optical characteristics of all the channels are given in
Russell and Gille (1978, their Table 1). The V6 dataset was also improved by a better knowledge of the orbital attitude for the LIMS measurements, by using all the radiance profile samples, spaced 0.375 km in altitude, and by applying a multiple interleave retrieval process. Descriptions of the V6 algorithms for the conditioned radiances of all the channels and for the retrieval of the temperature and geopotential height profiles are in Remsberg et al. (2004). Characterizations of the improvements for V6 ozone and water vapor are provided in two additional papers (Remsberg et al., 2007 and 2009).

This paper is focused on the improvements and scientific implications for the V6 HNO₃ and NO₂ profiles and distributions. The V6 Level 2 data files contain both the de-convolved radiances and the retrieved parameters, and they are tabulated at 18 levels per decade of pressure or at a spacing of about 0.88 km. Note that the UARS Level 3A profiles have 6 levels of data per decade of pressure and represent a matching subset to the LIMS V6 data for easy comparison. In addition, the time, location, and solar zenith angle for the tangent point of a LIMS measurement are included in the header lines of each profile. This information makes it easier to relate the LIMS profiles of O₃, HNO₃, and NO₂ to photochemical model output. The effective vertical resolution for both V6 HNO₃ and NO₂ is of order 3.7 km, and retrievals were performed for each of the down/up scan pairs spaced about 1.6 degrees of latitude along the LIMS orbital tangent tracks. Distributions of HNO₃ extend from near the tropopause to just above the 2-hPa level. The nighttime distributions of NO₂ extend from about 50 hPa to the lower mesosphere, especially for the polar night. Results for daytime NO₂ are useful from about 50 hPa to 1 hPa.

Section 2 shows several daily, zonally-averaged distributions of the V6 HNO₃ and NO₂ for comparisons with model output and with distributions from more recent satellite experiments that also were observing during periods when the stratospheric aerosol loading was near background levels. An extensive validation of the V6 products was not conducted, although their daily zonal mean cross sections have been assessed against those of the V5 data that had been compared with the few correlative measurements available during the LIMS timeframe (e.g., Gille et al., 1984; Gille, 1987; Russell et al.,
Qualitative improvements have been found for all the V6 data products.

Section 3 describes the significant changes in the V6 algorithm that affect the V6 HNO$_3$ and NO$_2$ profiles. Independent estimates of precision and accuracy for those V6 data are included, based on calculations of the effects of their known error sources. The estimates of precision are shown to compare well with the variations in the retrieved parameters from among adjacent scans along an orbit, specifically for latitudes and times when zonal variations due to wave activity were minimal. Section 4 presents some scientific findings demonstrating the improved quality of the V6 HNO$_3$ and NO$_2$. Section 5 is a summary of our findings about the changes with V6.

2 Zonally-averaged distributions of HNO$_3$ and NO$_2$

Figure 1a and b are the zonally-averaged distributions of V6 HNO$_3$ from the combination of its Level 2 profiles along descending and ascending orbital segments for 15 November 1978, and 16 May 1979, respectively. Maximum mixing ratio values occur at the high latitudes near 30 hPa, and the variation of HNO$_3$ with latitude is similar to that from the earlier V5 dataset at that pressure level (Gille et al., 1984, 1993). However, the V6 HNO$_3$ profiles no longer exhibit nearly constant values in the upper stratosphere like those found from V5 by Jackman et al. (1985), due primarily to a better accounting for the effects of the interfering radiance from a “hot band” of carbon dioxide (CO$_2$) within the V6 algorithm. The V6 HNO$_3$ agrees reasonably well with photochemical model estimates; however, its day values are notably less than its night values near the 4-hPa level, most likely due to not having accounted for radiance contributions at higher altitudes from vibrationally-excited states of CO$_2$ and perhaps of O$_3$ in the 10 to 12-µm region during daylight (Edwards et al., 1996). V6 HNO$_3$ values are somewhat smaller than those of V5 in the lower tropical stratosphere, due to first-order corrections for the effects of interfering emissions from aerosols and from the chlorofluorocarbon (CFC) molecules CFCl$_3$ and CF$_2$Cl$_2$. The 1 ppbv contour extends to just above the 2773

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50-hPa level at equatorial latitudes; that value is at the upper limit of reactive nitrogen (NO$_y$) minus odd nitrogen (NO$_x$) from in situ measurements (Jensen and Drdla, 2002, and references therein).

One can see from Fig. 1a and b that there is very good seasonal symmetry between the HNO$_3$ distributions for November versus May of the Northern and Southern Hemispheres, which has already been explained by invoking heterogeneous chemical mechanisms (Austin et al., 1986). Note that there is an upward extension of moderately high values of HNO$_3$ to the upper stratosphere in November at high northern latitudes (Fig. 1a). This feature becomes prominent in winter due to a slow accumulation of HNO$_3$ after chemical conversion from NO$_2$ and dinitrogen pentoxide (N$_2$O$_5$) under polar night conditions. The distribution of 16 May (Fig. 1b) indicates that there was also an accumulation of HNO$_3$ in the 100 to 200-hPa layer in the Northern Hemisphere by late spring, due to diabatic descent in the region of the polar vortex.

Figure 2a and b show the zonally-averaged distributions of NO$_2$ from the descending (local nighttime at low and middle latitudes) and from the ascending (daytime at low and middle latitudes) orbital segments, respectively, for 15 November 1978. Maximum mixing ratio values for the nighttime LIMS NO$_2$ of Fig. 2a are of the order of 14 ppbv centered at about the 4-hPa level. The retrieved nighttime NO$_2$ profiles extend into the lower mesosphere, where they encounter their signal-to-noise (S/N) limit and are less accurate. The repartitioning of the NO$_x$ (nitric oxide (NO)+NO$_2$) at twilight occurs at about 55 to 60° S latitude. Those terminator NO$_2$ profiles are also less accurate because the rapidly changing NO$_2$ values along the tangent path were not accounted for (see Solomon et al., 1986).

Maximum mixing ratios for the daytime NO$_2$ of Fig. 2b are of the order of 6 to 7 ppbv and occur between 8 and 10 hPa. One can clearly see the crossover to polar night conditions, poleward of about 72° N. Daytime NO$_2$ is small in the upper stratosphere because most of the NO$_x$ is in the form of NO. H$_2$O emission becomes a significant part of the NO$_2$ channel radiance in the upper stratosphere, especially during daytime. The forward radiance model for the V6 NO$_2$ channel assumes that H$_2$O has a constant
value of 6.5 ppmv above the upper limit of 1.3 hPa for its V6 profile. Furthermore, there is a significant amount of extra emission in the mesosphere during daylight from excited states of the H$_2$O molecule that are difficult to characterize for LIMS, primarily because its ground-state H$_2$O populations are not known exactly in that region (Lopez-Puertas and Taylor, 2001; Kerridge and Remsberg, 1989). For this reason no corrections for non-LTE effects from H$_2$O were developed for the retrieval of the V6 NO$_2$. That source of positive radiance bias is the primary reason for the spurious, upward extension of the daytime NO$_2$ distributions to the lower mesosphere (see also Sects. 3 and 4).

Figure 3 is the distribution of NO$_2$ from the descending (nighttime) orbital segments of 15 January 1979, and it is similar to that of Fig. 2a in most respects. One exception is the occurrence of relatively large values of NO$_2$ near 50° S compared with those at equatorial latitudes. This difference is partly a diurnal effect. The LIMS NO$_2$ measurements were obtained at about 2130 h (local time) at 50° S versus 2300 h at the equator for the descending orbital segments, and there is a steady conversion of NO$_2$ to N$_2$O$_5$ from just after sunset and until sunrise. Furthermore, sunset occurs later in the day during summer at the high southern latitudes.

The elevated values of NO$_2$ in the mesosphere at the high latitudes of the Northern Hemisphere are another feature of Fig. 3. Such enhanced values of NO$_2$ were first reported by Russell et al. (1984b) based on a special, radiance-averaged version of the LIMS data, and they were attributed to the formation of NO$_x$ in the mesosphere followed by a gradual descent of the air to the uppermost stratosphere during polar night. Findings from more recent satellite sensors support that conclusion (e.g., Randall et al., 2009). A time series of the V6 polar night NO$_2$ will be shown in Sect. 4, indicating improved estimates for its values and better continuity for its descent during the winter months of 1978/1979.
3 LIMS V6 retrieval algorithms and error estimates

3.1 The V6 algorithm for HNO$_3$ and NO$_2$

New emissivity data tables were prepared for the forward models of the primary gases in both the HNO$_3$ and NO$_2$ channels. The HNO$_3$ channel contains secondary radiance contributions from the “hot band” of CO$_2$ at 10.4 micrometers and from the primary CFCs (CFCl$_3$ and CF$_2$Cl$_2$). To achieve better accuracy for the emissivity of CO$_2$ along a tangent ray path, emissivity look-up tables were calculated at 55 pressure levels and 33 temperature levels and encompassing their expected atmospheric ranges. In addition, polynomial fits are no longer applied to account for the temperature dependence within the emissivity tables; linear interpolation is used instead. These upgrades have led to a more accurate representation of the effects of the “hot band” of CO$_2$.

The V6 forward model for the primary gas, HNO$_3$, makes use of emissivity tables generated using its band model data on HITRAN 91 (Rothman et al., 1992a). That model is based on the laboratory measurements of Giver et al. (1984), and a parameterization of them is appropriate for the broadband channel of LIMS. The interfering effects of CO$_2$ and of its “hot band” at 10.4 µm were obtained using the line parameters on HITRAN 92 (Rothman et al., 1992a and b; Dana et al., 1992), which are improved over the parameters used with the original LIMS V5 algorithm. To summarize, the updated emissivity tables for CO$_2$ account for much of the excess of retrieved HNO$_3$ that characterized the V5 HNO$_3$ profiles from about 5 to 2 hPa, as originally reported in Gille et al. (1984, 1993) and Jackman et al. (1985) (see also Sect. 4).

Line parameters for the original V5 retrievals of NO$_2$ were obtained from the AFGL trace gas compilation (Rothman et al., 1981). Spin-rotation effects of NO$_2$ became known by the late 1980s, and the fine structure of the lines for the primary $\nu_3$ cold band were included in the HITRAN 92 compilation via a perturbation calculation (Perrin et al., 1992). That change accounts for most of the improvements in the V6 NO$_2$ (Remsberg et al., 1994). Further, minor changes in the retrieved NO$_2$ may be found for those spin-rotation effects from the more explicit calculations of the strengths of the
resolved lines that were obtained later and are available in HITRAN 96 (Toth, 1992). The LIMS NO\(_2\) channel also contains contributions from H\(_2\)O, CH\(_4\), and the oxygen (O\(_2\)) continuum. Spectral parameters for the underlying O\(_2\) were not available, so the empirical model of Thibault et al. (1997) was used for consistent calculations of the effects of the continuum-induced absorption from O\(_2\) in both the H\(_2\)O and the NO\(_2\) channels.

The LIMS V6 profiles were used to correct for the forward radiance contributions of H\(_2\)O up to about the 1.5-hPa level, and then they were extended upward using a constant value of 6.5 ppmv. In addition, the entire H\(_2\)O profile for the forward model was smoothed by a Gaussian function having a 1.5 km half-width at half maximum. As indicated earlier, no corrections were developed to account for probable non-LTE radiances from mesospheric H\(_2\)O during daytime. Even so, there is no indication of a bias in the retrieved NO\(_2\) due to that neglect, except at and above about 48 km (or the 1-hPa level). Emissions from excited states of daytime NO\(_2\) were postulated for the upper stratosphere by Kerridge and Remsberg (1989), but no correction for those effects was developed for V6 because the populations of those states are not known well. The effects of horizontal mixing ratio gradients in the tangent layer have also been shown to be important for the retrieval of LIMS NO\(_2\) in the region of the day/night terminator (Solomon et al., 1986). However, because such a gradient correction is needed only for solar zenith angles near 90 degrees, a second-pass processing was not considered for the V6 NO\(_2\) profiles prior to their archival in 2002.

The original V5 profiles of NO\(_2\) and HNO\(_3\) are used as a priori estimates for the V6 forward models, although there is no dependence upon them for the onion-peeling retrievals of LIMS once a reasonable S/N for the radiances is achieved. Estimated concentrations of the interfering gases were obtained as follows. Updated, seasonal zonal-mean distributions of CH\(_4\) were generated from the UARS HALOE dataset for use with the V6 retrievals of NO\(_2\) but with an extrapolation of their magnitudes back to 1979, based on the approximate linear emission rate for CH\(_4\) at the ground. A similar extrapolation was performed for CFCl\(_3\) and CF\(_2\)Cl\(_2\) for the HNO\(_3\) channel, based on
their measured distributions from the UARS CLAES Version 8 dataset plus knowledge of the growth rates for their emissions since 1975.

Interfering emission due to aerosols has its largest effect on the LIMS-retrieved HNO$_3$ at low latitudes of the lower stratosphere; the LIMS V5 dataset had no such correction. A first-order broadband emission was generated for V6, based on estimates for the background stratospheric aerosol layer of 1978/1979. Specifically, a single zonal-mean distribution of aerosol extinction was adopted for the V6 algorithm based on March/May 1996 results for the HALOE 5.26 µm (NO) channel (Hervig et al., 1995). The magnitude of that distribution was then scaled back to 1978/1979 using a factor obtained by comparing the SAGE II 1-µm channel aerosol extinction values of 1996 versus the SAGE I aerosol extinction for the same months of 1979. That single modified, zonal mean aerosol distribution was used for each of the seven months of the LIMS dataset and must be considered as somewhat qualitative with latitude and likely not representative of its seasonal cycle variations. However, tropical aerosol distributions vary most noticeably according to the phase of the QBO cycle, and both the 1996 and 1979 March/May periods occurred at nearly the same QBO phase. Finally, aerosol extinction at the wavelengths of the LIMS channels versus that at 5.26 µm of HALOE was obtained by employing the sulfuric acid/H$_2$O composition and wavelength-dependent, refractive index model for its aerosol absorption in the manner of Hervig et al. (1995).

The archived V6 profiles were screened for anomalies using several criteria. First, retrieval variances were calculated and written to an intermediate Level 2 file that was not archived. Those variances were defined in terms of $(N\text{EN}/K)^2$, where NEN is the noise equivalent radiance for each channel in watts/m$^2$-sr (Gille and Russell, 1984) and K is the derivative of the measured signal profile as a function of the given species mixing ratio. During the retrieval process the variances were set to the negative of their actual values whenever convergence was not achieved or the retrieval needed to be restarted (at tops of profiles). Note that a restart causes the algorithm to default to a constant, top-layer, mixing ratio based on the value from the layer of its first,
successfully-retrieved level; the thickness of that constant, top-layer extends upward several scale heights. Valid profile segments have positive variances, and only retrieved values from those segments were retained in the final Level 2 output file. The variance parameters effectively set the extreme upper altitude limits for good data for all the parameters. Negative variances often indicate the low altitude extent of good data, too. Variance checking occurred only outside of the pressure ranges of 1.9 hPa to 46 hPa for HNO$_3$ and of 0.88 hPa to 46 hPa for NO$_2$. Independent estimates of random error indicate that there is adequate tangent layer signal within those ranges. An additional algorithm was applied to identify and screen for contaminating radiances from cloud tops, at least to first order (see Remsberg et al., 2007, for the details).

3.2 Single profile error estimates

The V6 HNO$_3$ profile values are not much different from those of V5, except in the upper stratosphere where the interference from CO$_2$ has been accounted for better in the V6 algorithm. In the lower tropical stratosphere there are differences due to the corrections for emissions from the CFCs and due to the first-order correction for the aerosol emission. Random radiometric errors for V6 HNO$_3$ are reduced from those of V5 by a factor of 2.2 because of the larger number of samples used with the interleave procedure for the retrieval of a V6 profile (Remsberg et al., 2004). Offset errors due to pointing jitter are included in the random uncertainties. The calculated precisions shown in Fig. 4 vary from 0.15 ppbv at 80 hPa to 0.05 ppbv at 3 hPa, based on the average profile at 30° S. Those calculated values are provided in percent in the top row of Table 1, and they compare well with empirical estimates of the precision from the Level 2 data themselves – the standard deviation (SD) profile in Fig. 4. The SD values were obtained as minima of the variances for each pressure level from among the sets of scans along each of the orbits that crossed 25° S to 35° S latitude on 1 February 1979. Of course, a part of the empirical SD values in Fig. 4 may be a result of real variations in the atmospheric HNO$_3$. 2779
Sources of systematic uncertainty were reported in Gille et al. (1984), based on simulations of their effects for V5 from a model HNO₃ profile for 32°N. Many of those error estimates are retained for V6, as shown in the middle rows of Table 1. However, the effects of temperature bias are based on the revised estimates of $T(p)$ error in Remsberg et al. (2004). Uncertainties in the aerosol and CFC corrections are greatest for the lower tropical stratosphere but do not dominate the total error during 1978/1979. Biases at the tops of the V6 HNO₃ profiles are small because the a priori profile values are also small near the stratopause and extend above the pressure level of the first retrieved point. Uncertainties for the effects of the horizontal temperature gradients are not included, since sensitivity to temperature biases are relatively small for an optically thin species like HNO₃.

The largest elements of potential bias error are the ±20% uncertainties in the integrated areas of the field-of-view (FOV) side lobes and from a possible 0.05% bias in the total measured signal due to regions of the channel filter that are outside the main spectral band, as discussed in Gille et al. (1984) and shown in the bottom rows of Table 1. The FOV side lobes from the HNO₃ channel are not all of the same sign. To judge their effects, the measured HNO₃ radiance profiles were analyzed for the vertical distances of the side lobes from the main HNO₃ lobe or at effective separations of 17 and 34 km at the horizon. For instance, are there any positive or negative radiance correlations at those separations when the main lobe is viewing the low radiances of the mid to upper stratosphere and when the side lobes are viewing the much larger radiances at altitudes 17 or 34 km below? Our investigations indicate no significant correlations for altitudes below about 40 km. Thus, it is concluded that the magnitude of that error in Table 1 must be an upper limit at all levels, except perhaps at 3 hPa. Uncertainties for the out-of-band spectral response can impart a positive bias in HNO₃ of order 20% at 30 hPa, as pointed out in Gille et al. (1984). Yet, qualitative comparisons with other HNO₃ datasets indicate agreement that is better than 20%, at least for those datasets that were obtained at times of relatively low stratospheric aerosol loading. Therefore, neither of those sources of error is included in the combined root-sum-squares (RSS)
estimates of accuracy in Table 1. In summary, the overall accuracy for V6 HNO$_3$ is believed to be very good from 30 hPa to 10 hPa – of order 10% at middle latitudes.

Table 2 contains the estimates of precision and accuracy for the profiles of NO$_2$. First, the reader is reminded that the nighttime values of V6 NO$_2$ have peak mixing ratios near 4 hPa that are about 15% to 20% lower than those of V5. Most of that change is due to the effects of the spectral spin splitting of the strong lines that was not included in earlier versions of the AFGL or HITRAN line lists. On the other hand, the peak daytime V6 NO$_2$ values at 8 to 10 hPa are reduced from V5 by only about 5% because the effect of saturation for the strongest lines is not nearly so pronounced for the lower mixing ratios of daytime. In the upper stratosphere near 3 hPa, the daytime V6 NO$_2$ is larger than that of V5 due to the improved values from the interfering V6 H$_2$O. Below the 30-hPa level of the lower stratosphere both the day and night V6 NO$_2$ values are somewhat larger than V5. At this point it is noted that the V5 algorithm contained a merger of its retrieved NO$_2$ with a balloon-based average NO$_2$ profile from 30° N, constraining its results below the 30-hPa level at least when the S/N for the tangent-layer radiance was low. The V6 NO$_2$ algorithm is not constrained by any such climatological profile.

The precision estimates for the V6 NO$_2$ in Table 2 were adopted from those of V5 in Russell et al. (1984a), after accounting for the improvements due to the use of all the samples from the measured radiance profiles. Random uncertainties from single profiles of the retrieved H$_2$O were adopted from Remsberg et al. (2009) and included because H$_2$O is a major source of interfering emission, especially for daytime NO$_2$ in the upper and the lowermost stratosphere. The effects of those random H$_2$O errors are scaled further, according to the fraction of the signal in the NO$_2$ channel that is due to H$_2$O. Estimates of percentage NO$_2$ precision profiles from the data are shown in Fig. 5 and are based on average day and average nighttime SD profiles at 30° S for 1 February 1979. Those values range from about 5% in the middle stratosphere, to 8% for nighttime or 30% for daytime at 1 hPa, and then to 15–20% at 40 hPa. The estimated SD values in Fig. 5 agree with the RSS precisions in Table 2 for the middle and upper stratosphere but are larger at 30 and 50 hPa, presumably because of the
effects of the natural variability of the atmospheric NO$_2$. For the V6 NO$_2$ bias errors a linear scaling was applied to the entries in the V5 error table of Russell et al. (1984a), which were appropriate for a model-generated, daytime profile at 32° N. Its primary sources of systematic uncertainty are from temperature bias and from the interfering effects of H$_2$O, based on the V6 uncertainties in Remsberg et al. (2004, 2009), respectively. There are uncertainties in the lower stratosphere due to the O$_2$ interference, but they should be considered as an upper limit because corrections for its emission were applied to the retrievals of both the LIMS H$_2$O and NO$_2$ and therefore carry the same sign. There is also a possible bias due to a 20% uncertainty for the area of the measured FOV side lobes, but its effect on the retrieved NO$_2$ is small and remains unverified.

Table 2 indicates RSS V6 NO$_2$ uncertainties of 17% at 3 hPa and about 18% from 5 to 10 hPa. RSS values increase sharply in the lower stratosphere and are dominated by the estimates of error for the interfering O$_2$ continuum and the H$_2$O. At stratopause levels (1 hPa) the ascending (daytime) NO$_2$ may have a bias of order 33% across most latitudes. However, the larger, descending (nighttime) NO$_2$ values at that level are not affected much by the interfering H$_2$O, so they are more accurate (17%). Also, the increasing values of NO$_2$ in the lower mesosphere at the high northern latitudes of Fig. 3 are judged to be reasonably accurate (see also Sect. 4.4). One source of bias error that has been neglected for that situation is the likelihood that the retrieved V6 polar night NO$_2$ values are too low due to not accounting for the effects of non-LTE emissions of the ground-state of NO$_2$ itself (e.g., see Funke et al., 2005).

4 Scientific implications of the V6 data

The previously, archived LIMS V5 HNO$_3$ and NO$_2$, along with the temperature, O$_3$, and H$_2$O data have been used in scientific studies and reported in the literature. In the subsections that follow several of the issues that they raised with respect to the
V5 HNO$_3$ and NO$_2$ profiles and distributions are re-visited and re-evaluated using the V6 data.

### 4.1 HNO$_3$/NO$_2$ ratio profiles

Simultaneous measurements of HNO$_3$ and NO$_2$ by LIMS provide an opportunity to check the partitioning of NO$_y$ species in comparison with that predicted with theoretical models. In particular, Jackman et al. (1985) reported that between 5 and 1 hPa the ratio of LIMS daytime HNO$_3$ to NO$_2$ was inconsistent with model values and that the HNO$_3$ derived from photochemical relations should be used instead of those from the LIMS. They based their conclusion on a comparison of daytime hydroxyl (OH) values derived from the V5 data using two different procedures. In the first approach they invoked an instantaneous photochemical equilibrium assumption for HNO$_3$ and, thereby, expressed OH concentrations as a function of the ratios of HNO$_3$/NO$_2$. Their second approach used an equilibrium assumption for odd hydrogen (HO$_x$) along with the LIMS O$_3$ and H$_2$O data to derive the daytime OH values. In the upper stratosphere those two approaches yielded different results. The V5 HNO$_3$/NO$_2$ ratios overestimated OH in the upper stratosphere by a large margin, at least when compared to other available observations and model results. The second approach yielded much better agreement. Jackman et al. (1985) concluded that this discrepancy was due to errors in the LIMS HNO$_3$ in the 5 to 1 hPa region. Natarajan et al. (1986) reached a similar conclusion regarding the HNO$_3$/NO$_2$ ratio, but on the basis of diurnal photochemical model calculations that were constrained by LIMS V5 nighttime data. The V5 HNO$_3$/NO$_2$ ratios also showed a positive bias in the upper stratosphere in comparison with their modeled estimates.

Figure 6 is a comparison of the daytime ratio of V6 HNO$_3$/NO$_2$ for 15 February 1979, versus that from the updated, diurnal photochemical model of Natarajan et al. (2002), which incorporates the recommended chemical kinetics data of Sander et al. (2006). Distributions of long-lived species, such as nitrous oxide (N$_2$O), that are used to initialize the diurnal calculations are taken from a simulation with the NASA Langley...
two-dimensional model of Callis et al. (2001) using surface source gas mixing ratios corresponding to the 1978/1979 time period. The bottom panel of Fig. 6 shows LIMS HNO$_3$/NO$_2$ ratios that are less than 0.2 in the upper stratosphere, except at the winter high latitudes. At the top boundary of the data domain (near 2 hPa) the V6 ratios are lower than the ones from the V5 data. The better determination of the V6 temperature profile and its effects for the “hot band” of CO$_2$ has led to a large decrease in the retrieved, upper stratospheric HNO$_3$ and a corresponding decrease in the HNO$_3$/NO$_2$ ratio. The model results are shown in the top panel, and they agree well with the ratios from the V6 data.

The HNO$_3$/NO$_2$ ratios in Fig. 6 from both the model and LIMS show a steady decline with decreasing pressure, although the LIMS ratios are larger at the top-most boundary. The reason for that remaining disagreement is most likely a high bias in the daytime HNO$_3$ due to the influence of non-LTE emission in this spectrally-broad channel that has not been corrected. Edwards et al. (1996) also observed differences between the day and night radiances of the 10.83-µm blocker channel of the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument, and they ascribed them to non-LTE effects from ozone and CO$_2$ near the stratopause during daytime. Estimations of the effects of those emissions on the retrieved HNO$_3$ were not obtained for this paper. However, it is noted that the lifetime of HNO$_3$ against photolysis in the upper stratosphere is several hours and, therefore, an assumption of instantaneous equilibrium between HNO$_3$ and NO$_2$ is not strictly valid at the local measurement times of LIMS across all latitudes. Such an assumption introduces uncertainties in both the evaluation of the OH concentration from the ratio HNO$_3$/NO$_2$ and in the derivation of HNO$_3$ based on OH values from other sources. Nevertheless, because of the improved results from LIMS V6 there is no need to substitute model daytime HNO$_3$ for the retrieved LIMS values in the upper stratosphere.
4.2 Lower stratospheric HNO$_3$ and NO$_y$

The LIMS dataset provides global scale information on the latitudinal distribution of stratospheric HNO$_3$ and NO$_2$. Earlier analyses of the V5 data in conjunction with model studies highlighted a deficiency with respect to the HNO$_3$ mixing ratios of the winter high latitudes as calculated by models using only gas-phase chemistry. For instance, Austin et al. (1986) compared LIMS V5 HNO$_3$ with other measurements and model results. They reported that an additional source of HNO$_3$ was needed at high latitudes in winter and suggested that the hydrolysis of N$_2$O$_5$ on aerosol surfaces could be important. Considine et al. (1992) also described results from their two-dimensional model compared with the V5 data and noted the importance of heterogeneous chemistry for their calculations of HNO$_3$. They also pointed out that while the inclusion of heterogeneous chemistry improved the model/data agreement for HNO$_3$, its addition led to larger discrepancies between the calculated and observed NO$_2$.

At this point it is emphasized that the latitudinal variations of the lower stratospheric HNO$_3$ and NO$_2$ from the V6 algorithm are very similar to those from V5 and also similar to the observations from several more recent satellite instruments (not shown). This lack of change is not surprising because the updated spectroscopic line parameters for V6 have very little effect on their retrieved lower stratospheric mixing ratios. However, minor changes from V5 to V6 were noticed at tropical latitudes due to the improved treatments for the interfering species.

The dashed curve in the top panel of Fig. 7 shows zonally-averaged V6 HNO$_3$ at 30 hPa as a function of latitude for December 1978. The solid line corresponds to the HNO$_3$ from the two-dimensional model of Callis et al. (2001), which includes a formulation for heterogeneous chemistry similar to contemporary models. The model HNO$_3$ agrees with the data reasonably well with respect to their latitudinal distributions, showing higher mixing ratios at winter high latitudes. The vertical line represents the estimated LIMS uncertainty of 8% (Table 1) based on a mid-latitude summer profile. It is clear that the LIMS HNO$_3$ is higher than that of the model and has a different slope.
across the middle latitudes, particularly for the winter hemisphere. Figure 8 shows the V6 HNO$_3$ distribution on the 31.6 hPa surface for early January 1979, and it exhibits a lot of zonal variability at middle and high latitudes of the Northern Hemisphere. Remsberg and Bhatt (1996) showed that the effects of wave activity led to the pattern of the middle latitude surf zone plus a subtropical barrier region by early January. It is difficult to simulate such a pattern with the parameterized transport of a two-dimensional model. Conversely, there is little to no zonal variability in Fig. 8 for the tropics, where the LIMS and model results agree well in Fig. 7.

The lower panel of Fig. 7 shows the latitudinal variations of the sum of LIMS V6 descending or nighttime HNO$_3$ and NO$_2$ mixing ratios (dashed line) versus the model calculated total NO$_y$ (solid line). The nighttime LIMS (HNO$_3$+NO$_2$) data should be considered as a lower bound for the total NO$_y$ because the contribution from other nitrogen containing species, such as N$_2$O$_5$ and ClONO$_2$, is likely non-negligible. Again, the vertical line is the uncertainty for the data obtained as the RSS of the estimated errors of NO$_2$ and HNO$_3$. The model estimate of the total NO$_y$ is clearly lower than that inferred from LIMS. It is recognized though that the level of agreement between the data and model comparisons of Fig. 7 depends on the sources of NO$_y$, such as N$_2$O, and to the transport formulations used in the model. For a given NO$_y$ distribution the effect of heterogeneous chemistry increases the ratio of HNO$_3$/NO$_2$ in the model.

Figure 9 is a polar plot of the Northern Hemisphere distribution of LIMS V6 nighttime NO$_2$ at 31.6 hPa for 5 January 1979. Note that the distribution shows a decrease from about 3 ppbv in the tropics to less than 1.8 ppbv poleward of about 40° N, a clear indication of the so-called “Noxon cliff phenomenon” (Noxon, 1979). This wintertime decrease of NO$_2$ with latitude was not so apparent and coherent within the V5 dataset. One can now readily follow the evolution of this feature with the V6 data. It is an example of another improvement that has been gained for NO$_2$ with the V6 algorithm.
4.3 Day-to-night NO$_2$ ratios

The availability of day and nighttime measurements of a diurnally varying species like NO$_2$ allows one to examine the photochemistry of this species using theoretical models in conjunction with data. For example, Solomon et al. (1986) used LIMS nighttime NO$_2$ data at high northern latitudes in May to show that the decay of NO$_2$ to form N$_2$O$_5$ was consistent with theory. On the other hand, Kerridge and Remsberg (1989) examined profiles of the day-to-night ratios of NO$_2$ and found a region of discrepancy with theory in the upper stratosphere. In particular, the LIMS V5 data showed much larger ratios than expected from photochemical models above about 42 km (or 2 hPa).

An updated comparison of the day-to-night NO$_2$ ratio profiles from the V6 data is shown in Fig. 10 along with those from a contemporary, diurnal photochemical model. Monthly average LIMS results for May 1979 are in the bottom panel, and they show steadily declining ratios at levels above 5 hPa, reaching a minimum of less than 0.05 at 1.0 hPa before increasing to about 0.15 at 0.5 hPa. The photochemical model simulations were conducted using results from the two-dimensional model of Callis et al. (2001) for initialization. The model day-to-night NO$_2$ ratios are shown in the top panel and correspond to the local times of the LIMS day and night measurements. The model ratios are in good agreement with the data in the 5 to 1 hPa region but continue to show decreasing values in the lower mesosphere. Interfering radiance from H$_2$O is the primary source of uncertainty for the LIMS forward model of NO$_2$ at upper altitudes, especially for daytime. H$_2$O was accounted for by considering the retrieved H$_2$O up to 1.5 hPa plus a fixed H$_2$O value above that level, even though non-LTE emissions from H$_2$O are known to be significant in the lower mesosphere (Remsberg et al., 2009). As with V5, the LIMS V6 algorithm does not correct for such non-LTE effects, leading to a positive bias in the retrieved daytime NO$_2$. In addition, Kerridge and Remsberg (1989) postulated a possible role for non-LTE emissions during daytime from NO$_2$ itself. But in a recent analysis of the spectrally-resolved NO$_2$ measurements from the MIPAS instrument of ENVISAT, Funke et al. (2005) found no evidence for non-LTE emissions.
from higher-vibrational states of NO₂, at least for altitudes below 50 km. Therefore, it is concluded that any non-LTE effects from NO₂ must be secondary to the much larger influence of the non-LTE emissions from H₂O. It is estimated that the upper boundary region of accurate V6 daytime NO₂ values is 1.5 to 1.0 hPa.

### 4.4 Mesospheric NO₂ during polar night

The production of NOₓ in the mesosphere and lower thermosphere by energetic particle precipitation has been described in connection with its downward transport into the high latitude winter stratosphere (e.g., Callis et al., 2001; Natarajan et al., 2004; Randall et al., 2006). Russell et al. (1984b) reported the first satellite-based observation of wintertime increases in upper stratospheric NO₂. Upon averaging 5 days of LIMS radiances within a 60-degree longitude sector, they were able to extend their retrievals of LIMS NO₂ to higher altitudes. By focusing on polar night conditions in January 1979, they obtained NO₂ mixing ratios exceeding 100 ppbv in the lower mesosphere. Although odd nitrogen can be produced directly by solar proton events in the high latitude upper stratosphere, there is no evidence of such high-energy events in January 1979. The enhanced NO₂ in the LIMS data must be due to transport processes following the production of NOₓ by energetic particle precipitation in the mesosphere and above, the so-called “indirect effect” (Randall et al., 2006).

The V6 algorithm does not employ a radiance-averaging procedure, so the single profiles of V6 NO₂ extend only up to about 0.15 hPa at the winter high latitudes. Elevated mixing ratios of NO₂ are still found in the mesosphere (Fig. 3), although those values are lower than reported in Russell et al. (1984). Nevertheless, these V6 values are considerably higher than what is expected if there are only stratospheric sources of NOₓ. The occurrence of smaller V6 NO₂ mixing ratios is primarily because the V6 radiance profiles are registered better and the V6 temperatures are warmer by as much as 6 K at 0.1 hPa (Remsberg et al., 2004). Although the single profile error estimates for NO₂ in Table 2 apply strictly to its climatological profile and do not extend to altitudes above 1 hPa, the effects of a 2 K temperature bias and of an H₂O bias at 1 hPa are 10%
and 28%, respectively. Total error in Table 2 for NO\textsubscript{2} is estimated to be 33% at 1 hPa. The EOS Aura MLS experiment is obtaining H\textsubscript{2}O that has relatively small values in the wintertime, polar vortex regions of the mesosphere (http://mls.jpl.nasa.gov/). Thus, the uncertainties due to the interfering effects of H\textsubscript{2}O on the V6 NO\textsubscript{2} are estimated to be reduced considerably in that situation.

Figure 11 is a time series of the zonally-averaged V6 nighttime NO\textsubscript{2} mixing ratio as a function of pressure for latitudes greater than 74° N. Data from 1 November 1978 to 31 March 1979 are represented. For the several days when the LIMS instrument did not take data, their NO\textsubscript{2} values are averages from the adjacent days at all pressure levels. NO\textsubscript{2} mixing ratios exceeding 10 ppbv occurred in the 0.2 to 0.5 hPa region from late November 1978 to early February 1979 along with a clear indication of atmospheric descent with time of that elevated NO\textsubscript{2}. Comparisons of the fields of geopotential height and nighttime NO\textsubscript{2} during January at 0.46 hPa indicate that the highest NO\textsubscript{2} values corresponded to observations within the polar vortex region (not shown). The reaction of NO\textsubscript{x} with O\textsubscript{3} in the upper stratosphere leads to a gradual conversion of NO\textsubscript{2} to nitrogen trioxide (NO\textsubscript{3}) and then to N\textsubscript{2}O\textsubscript{5} in the polar night region. The NO\textsubscript{2} variation in Fig. 11 between 2 and 10 hPa and during November and December is mostly a result of transport of air from lower latitudes followed by a photochemical conversion of its NO\textsubscript{2}. In particular, early December 1978 was the time of a wave-1 stratospheric (Canadian) warming event. The LIMS observations of Fig. 11 provide support for the hypothesis that under such dynamic conditions there can be increases of high latitude upper stratospheric NO\textsubscript{x} as a result of accelerated descent within the polar vortex. More dramatic perturbations, such as solar proton events, are not a necessary condition for such enhancements of upper stratospheric NO\textsubscript{x}.

5 Summary findings

The radiances of the Nimbus 7 LIMS experiment have been reconditioned and new retrievals of them conducted with an updated (V6) algorithm to generate HNO\textsubscript{3} and...
NO$_2$ profiles that are more compatible with those of follow-on satellite experiments. The V6 HNO$_3$ profiles are nearly unchanged in the middle and lower stratosphere from those of the earlier V5 algorithm. However, in the upper stratosphere V6 HNO$_3$ is smaller due to improvements in the accounting for interfering emissions from CO$_2$. That change yields daytime HNO$_3$/NO$_2$ ratios that agree better with results from theoretical model calculations than before. The V6 NO$_2$ profiles have smaller values than those of V5, most noticeably for nighttime profiles of the upper stratosphere due to the accounting of spin-rotation effects within the updated, spectroscopic line parameters of NO$_2$. More accurate retrievals of the V6 temperature and H$_2$O from the lower mesosphere to near the stratopause are responsible for the realistic V6 NO$_2$ profiles of that region of the atmosphere, most notably in the polar night regions. Day-to-night ratios of V6 NO$_2$ also agree well with photochemical model calculations in the middle and upper stratosphere.

Individual V6 profiles of HNO$_3$ and NO$_2$ have points every 0.375 km and an effective vertical resolution of 3.7 km. The V6 retrievals were applied to adjacent pairs of profiles along orbits, yielding a spacing of 1.6 degrees of latitude between retrieved profiles, on average. Single HNO$_3$ profiles have precisions of 3–4% from 10 to 50 hPa but of order 10% at 3 hPa and 21% at 80 hPa. Single NO$_2$ profiles have precisions of 4–6% from 3 to 10 hPa, 6% at 30 to 50 hPa, and 14% at 1 hPa. The improved precisions and more frequent retrievals of profiles along the orbit tracks provide better continuity and detail for mapping analyses of these two species on pressure surfaces.

Estimated accuracies for single profiles of V6 HNO$_3$ are better than 10% from 10 to 50 hPa, and about 12% at 3 hPa and 16% at 80 hPa. Estimates of accuracy for the V6 NO$_2$ profiles are of order 18% from 3 to 10 hPa, but degrading to about 30% at 30 hPa and 1 hPa. Even so, good quality retrievals of V6 NO$_2$ extend downward to at least the 50-hPa level at polar latitudes in northern winter, which was not the case for NO$_2$ from the earlier V5 dataset. A time series plot of V6 NO$_2$ at northern high latitudes illustrates NO$_x$ enhancement through wintertime descent from the lower mesosphere to the upper stratosphere. This finding is significant, especially when one considers that
there were no notable increases in solar disturbance or geomagnetic storm activity late in 1978 or early in 1979.

The V6 HNO$_3$ distributions suggest that one must still include heterogeneous chemical mechanisms in stratospheric models for the partitioning of NO$_y$, even during the 1978/1979 period of low volcanic aerosol loading. However, it is more apparent from the V6 data that there are deficiencies for the seasonal transport of the N$_2$O source molecule and of its end product NO$_y$, as simulated with most two-dimensional models of the lower stratosphere.

The V6 Level 2 (profile) data can be obtained by ftp download from the Goddard Earth Sciences and Data Information Services Center or GES DISC (http://daac.gsfc.nasa.gov/) under the menu entitled “Remote Sensing Data.” A LIMS V6 Level 3 (zonal Fourier coefficient or mapped) product is also available at GES DISC.

**Acknowledgements.** We recognize the extensive efforts of John Gille and Jim Russell III (Co-PIs) and the members of the original Project and Science Teams for their development and conduct of the LIMS experiment. Yun-fei Wang conducted analyses of the LIMS HNO$_3$ radiances for evidence of any spurious effects from its FOV side lobes. The research leading to the improvement and generation of the LIMS V6 Level 2 dataset was conducted with the consistent support of Jack Kaye of NASA Headquarters. The analyses in this manuscript were conducted with funds from the NASA NRA NNH08ZDA001N for the MAP Program administered by David Considine.

**References**


Table 1. Estimates of precision and accuracy (%) for profiles of LIMS V6 HNO$_3$.

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Table 2. Estimates of precision and accuracy (%) for profiles of LIMS V6 NO₂.

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Fig. 1. (a) V6 HNO₃ distribution for 15 November 1978, based on the combination (COMB) of the profile data from its ascending and descending orbital segments; blackened regions indicate no data. (b) As in (a), but for V6 HNO₃ of 16 May 1979.
Fig. 2. (a) LIMS V6 distribution of descending (DES or nighttime) NO\textsubscript{2} for 15 November 1978; blackened regions indicate no data. (b) As in (a), but for ascending (ASC or daytime) NO\textsubscript{2}.
Fig. 3. As in Fig. 2a, but for descending (DES or nighttime) NO$_2$ of 15 January 1979; blackened region near 50° S, 5 hPa has NO$_2$ exceeding 15 ppbv.
Fig. 4. Estimates of precision based on the minimum standard deviations (SD) of the retrieved LIMS V6 HNO$_3$ profiles from the sets of ascending (solid) or descending (dashed) orbital crossings of the latitude band of 25° S and 35° S on 1 February 1979.
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Fig. 6. \( \text{HNO}_3/\text{NO}_2 \) ratios for February 1979 – (top) model and (bottom) LIMS V6 data.
Fig. 7. LIMS V6 (dashed) and model (solid) comparisons for December 1978 – (top) HNO₃ and (bottom) HNO₃+NO₂ for the LIMS descending (DES or nighttime) orbital segments. The vertical lines on the LIMS data at 32° S denote their associated uncertainties.
Fig. 8. Polar plot of ascending plus descending V6 HNO$_3$ for 5 January 1979. Bluish regions are low values and orange to pink regions are high values; contour interval is 0.8 ppbv.
Fig. 9. Polar plot of V6 descending NO\textsubscript{2} for 5 January 1979. Bluish regions are low values and greenish regions are high values; contour interval is 0.6 ppbv.
Fig. 10. Ascending/descending (or day/night) NO$_2$ ratio (top) diurnal model and (bottom) LIMS V6.
Fig. 11. Time series of LIMS V6 NO$_2$ for latitudes $>74^\circ$N. For those few days when no data were taken, the NO$_2$ values are averages from the adjacent days.