

INTERCOMPARISON OF STRATOSPHERIC NO₂ AND NO₃ MEASUREMENTS DURING MAP/GLOBUS 1983*

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(Received in final form 22 October 1986)

Abstract—Nitrogen dioxide and trioxide have been observed from balloons, plane and from the ground during MAP/GLOBUS 1983. Comparison between NO₂ mixing ratios measured from balloons shows some agreement between remote sensing techniques on the one hand and *in situ* methods on the other. The two sets of data which agree in the lower stratosphere at 20 km diverge at higher altitudes by a factor of 2 around 27 km and 4 around 33 km. The NO₂ column densities observed at sunset from the ground are in agreement with plane and balloon determinations, provided that the average mixing ratio below 16 km was indeed lower than 1.5×10^{-10} . The diurnal variation of the NO₂ column as determined from ground observations during the second half of September differs from the one seen in the stratosphere. A first comparison between NO₃ night-time remote measurement and preliminary *in situ* results show a disagreement by a factor of 2.

* Joint publication of results from the MAP/GLOBUS campaign of 1983.

1. EXPERIMENT OVERVIEW

During MAP/GLOBUS 1983, six instruments for NO₂ measurements were flown on board balloons from the Centre National d'Etudes Spatiales (CNES) balloon range at Aire sur l'Adour (44°N, 0°W). Among these, two used *in situ* techniques and four were remote sensors. In order to observe the diurnal variation one of the *in situ* experiments was flown two times: first at noon and later at night. Two of the instruments—one *in situ* and one remote—were also able to measure NO₃ by night (Helten *et al.*, 1985; Naudet *et al.*, 1985). The flight sequence began on 9 September and ended on 28 September. During this period, column densities were also measured from a plane at sunset and from the ground at the Jungfraujoch station (47°N, 8°E, 3580 m) and at Aire sur l'Adour (44°N, 0°W, 50 m).

The observations during the campaign are based on a wide variety of techniques: electron spin resonance analysis of samples collected in a cooled matrix (Helten) and NO₂ reduction into NO followed by NO measurements by chemiluminescence (Fabian) for *in situ* instruments; atmospheric thermal emission spectrometry (Offermann) and observation of the atmospheric absorption in the infra-red at 1600 cm⁻¹ (Karcher) or 2900 cm⁻¹ (Roland) and in the visible at 440 nm for NO₂ and 662 nm for NO₃ (Rigaud, Simon, Matthews, Pommereau) for remote sensing. Table 1 lists the observation dates, together with the prime investigators, techniques used, species measured and solar observation times. Before comparing the data, each instrument, its performance, calibration procedures and error evaluation will be briefly presented. Literature references will be given for more detailed descriptions.

2. INSTRUMENT DESCRIPTIONS AND PERFORMANCES

In situ instruments

In situ measurements by Helten consist of (1) extracting the radicals from ambient air with a balloon-borne cryosampler at 70 K by matrix isolation, and (2) an identification and concentration measurement in the laboratory by Electron Spin Resonance Spectroscopy. The cryosampler is designed to collect 10 samples during one flight on 10 gold-plated copper fingers. The fingers are in a vacuum chamber, which is pumped by a cryopump, filled with a molecular sieve. Overlapping samples are collected, each for about 1 h, during the balloon descent, which is controlled at 1 m s⁻¹. The method allows measurement of NO₂ and NO₃. Absolute calibration is obtained by comparison with a standard prepared from a gas

flow sampled by a system simulating that of the balloon-borne cryosampler. For NO₂ the concentration in the primary standard from which the standard sample is prepared is measured by chemiluminescence and differential optical absorption. The accuracy of the resulting NO₂ mixing ratios is estimated by error propagation: relative uncertainty of ±3% on collected air volume for the standard, ±(3–8)% dependent on altitude for the atmospheric volume sampled in flight, ±2% on the spectrometer gain, ±3% on the scaling factor between standard and actual measurements, and ±10% on the standard mixing ratio. The resulting total uncertainty of NO₂ concentration is estimated to be ±12% (Helten *et al.*, 1984, 1985). For NO₃, the total accuracy is evaluated to ±40%.

NO₂ *in situ* observations by Fabian are based on NO₂ reduction into NO by a converter followed by NO measurements by chemiluminescent reaction with ozone produced on board the gondola. The NO instrument, its calibration procedure and the converter system have already been described (Fabian *et al.*, 1987). A series of laboratory simulations had shown that the converter possesses a conversion efficiency of better than 95% over a 12-h period. Additional tests showed no measurable change in the conversion efficiency when ozone was added to the air flow, in concentrations up to more than 100 ppmv. However, as NO plus NO₂ was measured during the flight portions when the main air flow was diverted and passed through the converter, no independent NO measurements were made. NO₂ mixing ratios were derived from the total NO+NO₂ by using interpolated NO data. Precision on NO measurements is evaluated to be ±12% and calibration systematic error to be ±5%. For NO₂, the uncertainty of the converter efficiency, i.e. ±5%, must be added. Another ±5% may be introduced by the NO interpolation procedure. Thus a total error bar of about ±25% may be a realistic upper limit for NO₂. The error of the first two data points measured during the ascent, however, is likely to be larger (see Fabian *et al.*, 1987).

Thermal emission instrument

Thermal infra-red emission of atmospheric trace constituents was measured by the Wuppertal group (Offermann and Rippel) in the wavelength range 5–19 μm. The instrument consists of an Ebert–Fastie grating spectrometer (spectral resolution about 600) and an off-axis telescope with Lyot optics. The vertical field of view of the instrument is ±0.015°, the horizontal fov is ±0.5°. Limb scan measurements are performed by a scanning mirror, which covers ±2.4° in the ver-

TABLE 1. NO₂ AND NO₃ MEASUREMENTS PERFORMED DURING MAP/GLOBUS 1983

Date	Time	Platform	Species	Method	Author
9 Sept.	8:00–14:00	Balloon	NO ₂	Matrix isolation	Helten, KFA, Jülich
9 Sept.	Sunset	Plane	NO ₂	i.r. Absorption	Karcher, CNRM, Toulouse
14 Sept.	Night	Balloon	NO ₂ , NO ₃	Visible spectrometry	Rigaud, LPCE, Orléans
20 Sept.	10:00–13:00	Balloon	NO ₂	Chemiluminescence	Fabian, MPAE, Lindau
20 Sept.	3:30–10:00	Balloon	NO ₂ , NO ₃	Matrix isolation	Helten, KFA, Jülich
23 Sept.	Night	Balloon	NO ₂	Thermal emission	Offermann, Wuppertal
28 Sept.	Sunset	Balloon	NO ₂	Visible spectrometry	Simon, IAS, Bruxelles
28 Sept.	Sunset	Balloon	NO ₂	Visible spectrometry	Pommereau, CNRS, Verrieres
8 Sept.– 10 Oct.	15:00 and sunset	Jungfraujoch	NO ₂	i.r. Absorption	Roland, Liège
13 Sept.– 24 Sept.	11:30 and 15:00	Aire sur l'Adour	NO ₂	Visible photometry	Matthews, DSIR, New Zealand

tical direction with respect to the local horizontal direction. The whole instrument is cooled by liquid helium. Due to a technical problem in the cryogenic system the hold time of the two cryostats and hence the measuring time was rather short (10 min). Therefore only a limited number of points of the altitude profile of NO₂ could be measured. NO₂ was observed in the 1600 cm⁻¹ region. Technical details of the instrument, its calibration, performance during flight and data evaluation are given by Rippel (1984) and Rippel *et al.* (1987).

The error analysis took into account the following aspects: calibration errors, uncertainty of spectrometer slit function, uncertainty of atmospheric temperature and accuracy of the fit of calculated to measured spectra. The resulting total uncertainties of the NO₂ densities were computed for every altitude. They range from $\pm 19\%$ at the highest altitude (38.2 km) to $+24\text{--}29\%$ at the lowest altitude (26.7 km). Details are given in the Appendix. The figures quoted do not include possible uncertainties of the line parameters used for the retrieval calculations. These are difficult to estimate, but may be of the order of 5–15%. The altitude determination is accurate to ± 100 m at the highest altitude, the error increasing to ± 400 m at the lowest.

Because of the short measurement duration it was not possible to activate the azimuth control in due time. In consequence the measurements were taken at different viewing directions for the different trace constituents and altitudes, as the gondola slowly rotated. This is unimportant for data taken at or above 36 km, as the distance from the balloon to the tangent point is smaller than 160 km here. A possible influence at lower altitudes is discussed by Offermann *et al.* (1987). At the two lowest altitudes (26.7 and 30.0 km), the viewing directions were approximately

towards North-West and South-East, respectively, with distances to the tangent points of 380 and 320 km.

Visible absorption instruments

The three other balloon remote sensing instruments are visible spectrometers designed to observe the atmospheric absorption during a stellar or a solar occultation. NO₂ is measured by differential absorption around 440 nm and NO₃, present only by night in the stratosphere, around 662 nm.

The apparatus used by Rigaud is made of a 20 cm Cassegrain monochromator telescope, a commercial double grating monochromator Jobin-Yvon DH 10 and a photomultiplier used in photon counting mode (Rigaud *et al.*, 1983). A spectral scan of 25 nm is swept by 0.2 nm increments in 6.4 s with a final resolution of 1 nm. The instruments are set up onto a stellar pointing gondola.

The two other visible instruments are set up onto the same sun-oriented gondola. A sun seeker provides the two apparatuses with sunlight through optical fibers. Simon's spectrometer developed at the IASB is a double grating monochromator with holographic gratings of 10 cm focal length made by Jobin-Yvon (DH10-UV). The grating rotation is driven by a stepping motor. The bandpass of the instrument (FWHM) is 1 nm, with a triangular shape. The recorded wavelength range extends from 250 to 700 nm in order to also provide information on the absorption by ozone in the Huggins and Chappuis bands (Simon *et al.*, 1987). A silicon photodiode EG & G, type UV-444B is used as detector. Its output current is measured by means of a three channel linear electrometer covering a dynamic range from 10⁻¹² to 10⁻⁸ A. A high-pass filter with a cut-off at 300 nm was

set in front of the detector. Therefore, wavelength scannings below this wavelength provide an accurate measurement of the instrument "optical zero", including the electronic and telemetry zero and possible residual stray-light. A more detailed description of the instrument is given elsewhere (Simon *et al.*, 1987).

The spectrometer used by Pommereau is a commercial Jobin-Yvon grating monochromator H20 associated with a photomultiplier working in photon counting mode. It allows spectral scanning between 432 and 450 nm at sampling intervals of 0.05 nm in 3 min. The final resolution is 0.25 nm.

The measuring method, common to the three experiments, consists of observing the absorption differences corresponding to the small spectral features which appear in NO₂ and NO₃ absorption cross-sections. Rigaud and Pommereau calculate the NO₂ slant column densities by correlation between complete actual atmospheric absorption spectra and calibration cells spectra. The gas content in the cells is deduced from comparisons with absorption cross-sections measured in the laboratory (H. S. Johnston, reported by Harrison, 1979). Details of the method are given by Pommereau (1982) and Naudet *et al.* (1984). The NO₃ slant column is calculated by correlation with cross-sections measured by Graham and Johnston (1978) multiplied by a factor 0.7 to take into account the later measurements by Mitchell *et al.* (1980). Simon uses a three-wavelengths differential absorption technique, with the same cross-sections. Data are corrected for ozone absorption taking into account the vertical distribution given by a representative atmosphere defined for September 1983 given in the Appendix and the absorption cross-sections in the 430–450 nm spectral range given by Pommereau (1981). Balloon altitudes have been determined from pressure measurements on board the gondolas using the representative atmosphere. The species vertical distribution are retrieved by linear inversion as described by Naudet *et al.* (1984).

Error contributions are noise, calibration systematic errors and uncertainty of the temperature dependence of the absorption cross-sections. The major source of noise is atmospheric: flickering and aerosol inhomogeneities. The instrument contribution appears only at low tangent height when the solar flux becomes small, creating pointing instabilities and a low signal-to-noise ratio. Thus the random error increases when the observed altitude decreases. This effect is amplified by downward propagation into the retrieval process of atmospheric vertical distribution of the constituent. The resulting error varies from $\pm 5\%$ at high altitude up to $\pm 40\%$ just above the

tropopause. The calibration systematic errors come from the uncertainty of the laboratory absorption cross-section data with which they are compared ($\pm 5\%$ for NO₂ and $\pm 30\%$ for NO₃) and from the spectral resolution adjustments necessary to correlate two sets of data which are not measured with the same instrument. To avoid this difficulty, an alternative method is used by Pommereau and Rigaud for NO₂ which consists of calibrations with a cell. The amount of NO₂ inside the cell is deduced by total absorption measurement. At best for NO₂ the calibration error is estimated at $\pm 10\%$.

Another systematic error source is the temperature dependence of the absorption cross-section which is poorly known. From the data available (Hicks *et al.*, 1979) and for the lowest stratospheric temperature, NO₂ concentrations obtained by visible differential absorption might be reduced by up to 25%. More laboratory work is needed before correcting the data for this effect.

Plane and ground instruments

Observations from an airplane or from the ground can only provide integrated column densities above the observational altitude. All measurements are made in absorption using the sun as the source of radiation; therefore the ground measurements include a tropospheric contribution.

Karcher uses a grille spectrometer on board a Caravelle flying at 11.9 km to observe the NO₂ absorption in the infra-red at 1604.58 cm^{-1} . The experiment is described by Girard *et al.* (1977a, b). Measurements are performed at several large zenith angles (between 84° and 91°) before sunset. Column densities are determined by comparison with calculated synthetic spectra. Spectroscopic data are taken from the AFGL Compilation (Rothman *et al.*, 1982). A mean value is derived from the 42 different observed spectra and gives a column density of $4.43 \times 10^{16} \text{ molecules cm}^{-2}$. The random error ($\pm 6\%$) is estimated from the standard deviation (15%) of the data points and corresponds to an interval of probability 0.99 for the mean value. In the general case, the species vertical distribution is adjusted in order to get the synthetic spectra reproducing the observed variation of the line equivalent widths as a function of solar zenith angle. For the flight at sunset on 9 September, two different reference vertical distributions (60° North summer, 45° North equinox) have been tried, both leading to a good representation of the equivalent widths variation. The maximal standard deviation was 21%, which corresponds to a random error of $\pm 8\%$. This

value is adopted for the total random error. It takes into account the noise of the data points as well as the uncertainty of the species vertical distribution used to simulate the absorption spectra. Systematic error contribution is mainly due to the error of spectroscopic data ($\pm 5\%$). The total uncertainty is estimated at $\pm 13\%$.

Zander's NO₂ column density determinations are retrieved from the analysis of infra-red solar spectra recorded near 2914.5 cm⁻¹ from the Jungfraujoch station. The equipment is made of a heliostat feeding a 7.5 m focal length grating spectrometer used in double pass with an intermediary slit. The detector is a liquid nitrogen-cooled InSb element. Order sorting and specific spectral regions are selected by a circular variable interference filter. Individual spectra swept at about 0.1 cm⁻¹ s⁻¹ are added to increase the S/N ratio of the resulting tracings to be analysed; the achieved spectral resolution is 0.02 cm⁻¹. Column densities are deduced from equivalent width measurements (EQWs) of NO₂ lines at 2914.65 cm⁻¹ recorded under various slant path conditions. The EQWs are measured with a high precision CORADI planimeter and subsequently compared to EQWs deduced from synthetic spectra calculated through a layered atmosphere with adjustable constituent concentrations; these concentrations are indeed adjusted until good agreement is reached between the measured and the computed EQWs. Line parameters necessary in the calculations are taken from the "1982-AFGL line parameters compilation" (Rothman *et al.*, 1982). The dispersion of the results gathered during the campaign is $\pm 20\%$ and the absolute error, mainly due to uncertainties in the line parameters, is estimated at $\pm 10\%$.

Matthews' equipment consists of a visible interference filter photometer set up at Aire sur l'Adour. Three narrow band (0.5 nm bandwidth at half peak) interference filters are used to scan the NO₂ absorption features in the 435–450 nm region in the solar spectrum at the ground. The incident angle of the filters relative to the solar beam is changed sequentially to enable this scan in wavelength to be performed. The solar intensity, measured with a photomultiplier and recorded with 12 bit precision, as a function of filter angle, is integrated for a selected number of filter wheel revolutions to increase the signal-to-noise ratio. Laboratory NO₂ absorption cross-sections of H. S. Johnston as reported by Harrison (1979) are used to determine the NO₂ amount in the column using a differential absorption technique. The absolute error of the system is estimated to be $\pm 30\%$ with a lower detection limit of equivalent vertical column 1×10^{15} mol cm⁻², see Matthews (1984).

3. FIELD OBSERVATIONS

In situ measurements by Helten were made during two balloon flights on 9 and 20 September. Ten samples were collected during each flight. For the first flight only nine samples could be extracted from the sampler because of a mechanical problem. The 9 September flight was made at late morning and 20 September started at night and was finished 4 h later. The night-time samples have provided NO₃ measurements around 30 km. HO₂ altitude profiles were also determined during the daytime for both flights (Helten *et al.*, 1984).

Night-time visible absorption measurements were performed by Rigaud on 14 September at 02:17 for NO₂ during the rising of Sirius and at 03:29 for NO₃ during the rising of Venus. Unfortunately, telemetry interferences during the NO₂ sequence do not allow measurements for elevation below -1° . Therefore, only data between 34 and 38 km are available for this species. NO₃ observations were obtained without problems.

Chemiluminescent NO and NO₂ *in situ* observations were made by Fabian on 20 September together with another NO chemiluminescent instrument on the same gondola (Fabian *et al.*, 1987; Kondo *et al.*, 1985). Measurements started at 25 km during the ascent and were pursued at float and during a slow descent at 1 m s⁻¹. The ozone generator failed at 14:42 U.T. and no data are available afterwards.

Thermal emission i.r. observations were performed on 23 September 1983 at 04:30 U.T. by the Wuppertal instrument. Pommereau and Simon flew their visible spectrometers together on a common gondola on 28 September. Their NO₂ vertical distributions at sunset are therefore simultaneous.

The grille spectrometer was flown on board the Caravelle on 9 September during sunset. Ground observations at the Jungfraujoch were obtained on 19, 20, 23, 24, 26 and 28 September and on 1 October from mid-afternoon ($Z = 50^\circ$ – 70°) till sunset ($Z = 85^\circ$ – 90°). Matthews performed measurements every clear day around 15:00 during the campaign: on 13, 14, 15, 17, 18, 19, 21, 23 and 24 September.

4. DATA COMPARISON AND DISCUSSION

For intercomparison, measurements of short-lived trace gas species should be executed in the same air-mass at the same time and location. Differences in these conditions for different data sets have to be considered. Only the residual discrepancy can be attributed to systematic errors of the data sets.

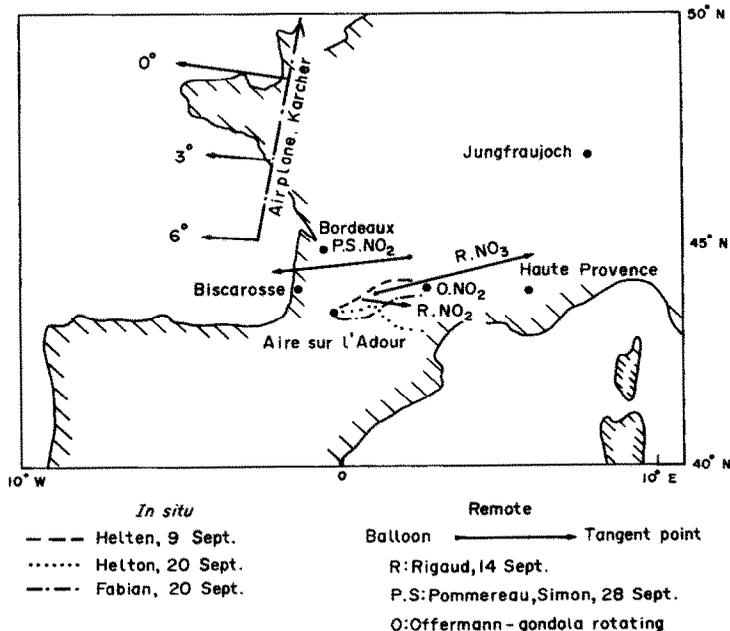


FIG. 1. LOCATION OF NO_2 AND NO_3 OBSERVATIONS.

In situ measurements are made along the indicated balloon trajectories. Remote sensing ones are reported by balloon location and tangent point at 20 km or by lower observation altitude. Airplane measurements are presented by aircraft trajectory and intersection of the observed direction with the 20 km altitude surface. Because of the lack of azimuth control, only the balloon location is reported for Offermann's flight. Location of ozone and temperature observations are also indicated.

The location of each measurement, balloon trajectories for *in situ* instruments, observing directions and tangent points at 20 km for remote sensing and locations of ground observations are shown in Fig. 1. Most of the measurements were performed between 43° and 45°N. Observations by Roland and by Karcher were obtained further North at 47° and 48°N, respectively. The average NO_2 column density variation expected from a previous latitudinal survey for such a difference in summer should not exceed 10% (Coffey and Mankin, 1981).

Isentropic trajectories were calculated for the air masses investigated by the measurements (Langematz *et al.*, 1987). Four days before the launch of each flight the air masses remained between 40° and 48°N latitude. No fast transport from high or low latitudes was inferred from the meteorological data.

Ozone measurements during days of balloon flights by Brewer-Mast sondes at Biscarosse and from the Haute Provence Observatory (de La Noe *et al.*, 1987) show only small variations between 17 and 35 km. At lower altitude, between 12 and 17 km, observations of 9 September and 14 September show an indication

of latitudinal transport in the higher troposphere (Fig. 2).

South Western France was in an anticyclonic regime during the whole campaign. The cloud cover reported by weather satellites was light or absent during the daytime NO_2 balloon flights. Long-time series of measurements (McKenzie and Johnston, 1982) have shown that the stratospheric NO_2 column density at constant local time is not expected to vary by more than 20% from one day to another at mid-latitude. This conclusion is in agreement with the Zander and Matthews results from the ground, showing day-to-day variations smaller than 20%. A vertical long wave as discussed by Offermann *et al.* (1987) could cause some variations of local concentrations but would not influence the column density as wave maxima and minima tend to cancel. As large perturbations do not appear in the temperature vertical distribution it seems unlikely that this process could contribute by more than 20%. Therefore, above 17 km differences between data sets larger than 40% must be attributed to diurnal variations or measurement errors.

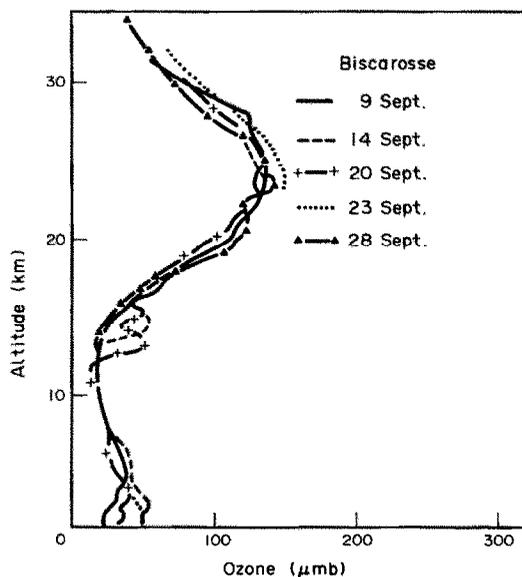


FIG. 2. OZONE BREWER-MAST SOUNDINGS FROM BISCAROSSE FOR THE FIVE DAYS OF NO₂ MEASUREMENTS FROM BALLOONS. Above 17 km, only small variations appear between one day and another. Below there is some indication of advection from southern latitudes on 9 and 14 September in the upper troposphere.

4.1. NO₂ balloon observations

The results are presented following the solar time of observation. Figure 3 shows the early morning vertical distribution, beginning just after sunrise (panel a), at mid-morning and noon (panel b), at sunset (panel c) and at night-time (panel d). Actual data and total accuracy are reported in the Appendix.

NO₂ in situ/in situ comparison. Both flights on 20 September 1983 gave *in situ* measurements (Figs 3a, b). Daytime and location were a little different, but—as the trajectory analysis showed—these measurements were executed in the same airmass. Fabian's data were measured roughly 3–4 h later than Helten's and are higher by a factor of nearly 2 in the same altitude. For easier intercomparison, Fabian's data are also plotted together with the NO₂ profile measured by Helten on 9 September 1983 (Fig. 3b). Both measurements were made at nearly the same daytime in each altitude. The air masses in the altitude range in which both flights gave data were similar, as the analysis of the trajectories showed. Except around 15 km, the O₃ profiles measured by Brewer-Mast sondes on both days are similar within 5%. The weather was clear for both flights. The data recorded by the experiments during their slow balloon descent from 30 down to 25 km are in agreement within their error

bars. During the earlier ascent, Fabian measured mixing ratios more than three times larger. Because the data were obtained just after turning on the instrument, before it had reached its proper working conditions, and a contamination from the balloon during ascent cannot be excluded, these data points will not be considered later (Fabian *et al.*, 1987). Therefore, the *in situ* measurements obtained by two completely different techniques between 25 and 30 km appear to be in good agreement.

NO₂ remote/remote comparison. Two comparisons of remote techniques were executed during the campaign. The two visible absorption instruments of Simon and Pommereau flown on board the same gondola gave NO₂ altitude profiles at sunset (Fig. 3, panel c). These measurements are in very good agreement within their error bars. A second intercomparison for remote techniques is possible between the thermal emission observations (Offermann) at 4:30 U.T. and Rigaud's visible spectrometric data at 2:20 U.T. (Fig. 3, panel d). These measurements were made 9 days apart. In the altitude range where they do overlap, 34–38 km, the two data sets are in agreement within their error bars. Around 27 km the ratio between night-time thermal emission and sunset visible data is about 2 ($\pm 40\%$), greater than the one of 1.4 measured from orbit by LIMS between midnight and noon (Russell *et al.*, 1984). All remote data except for the peak value measured by thermal emission at 33.3 km are within the zonal monthly mean at 45°–50°N as observed by LIMS. Within the altitude range 27–34 km, only the lower estimate of thermal emission data would be compatible with both balloon sunset visible observations and LIMS data. To interpret this peak, the possibility of a long wave perturbation is proposed by Offermann *et al.* (1987).

NO₂ in situ/remote comparison. The previous night-time remote observations can be compared with Helten's *in situ* measurements (Fig. 3d). Offermann's and Helten's observations at 33 km altitude, at the same local time, are only 3 days apart. The *in situ* data are lower by a factor of 4. If the lower limit of thermal emission data is retained the disagreement is still of a factor of 3. As the discrepancy occurs exactly at the peak of Offermann's profile, small changes in the height position of the peak between the two flights and inaccuracies of pressure or altitude determinations could partially reduce this factor. It also remains to be seen whether the above-mentioned wave influence (Offermann *et al.*, 1987) could diminish the discrepancy and to what extent.

In order to compare the other *in situ* and remote

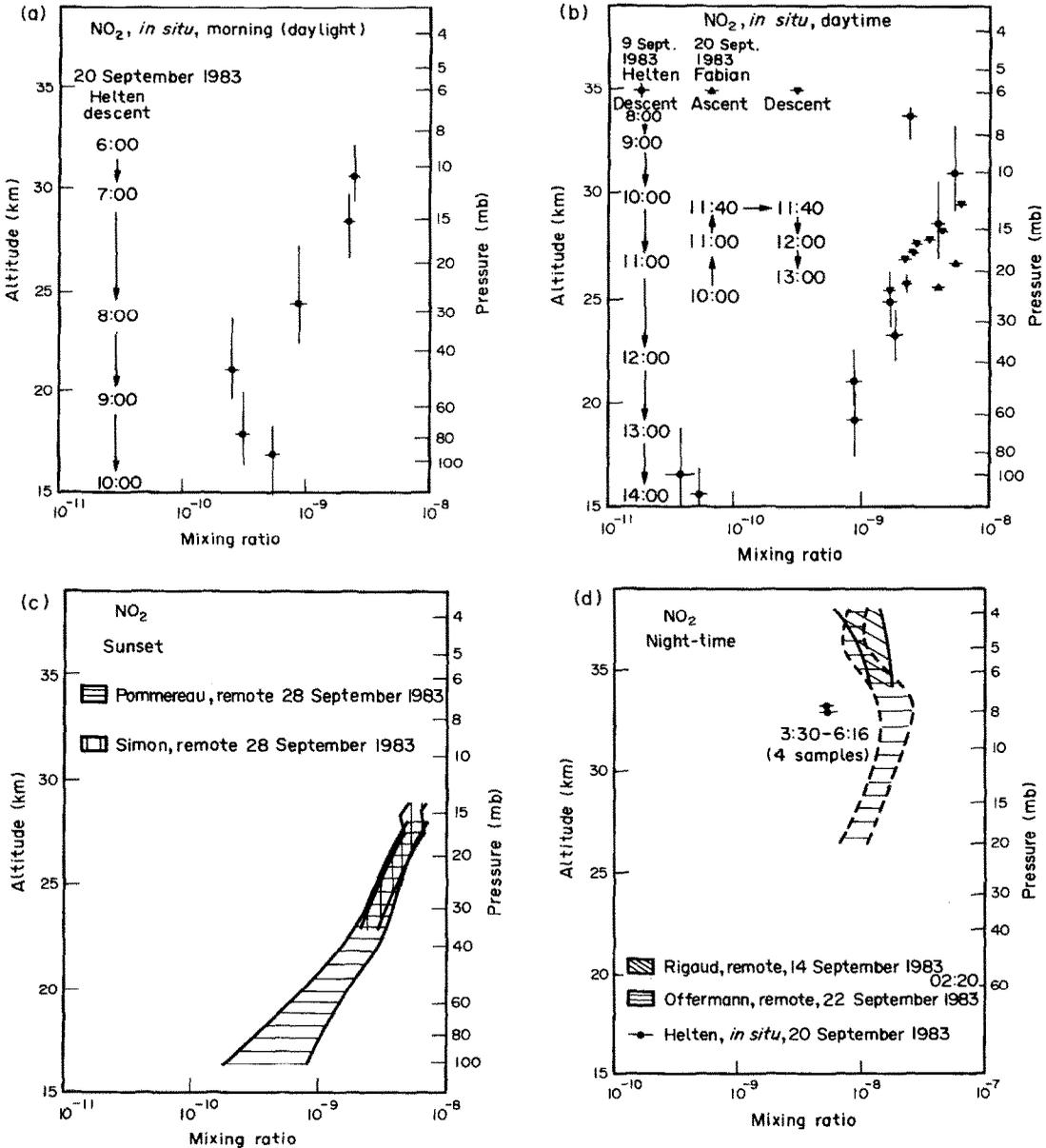


FIG. 3. NO_2 MIXING RATIO OBSERVED FROM BALLOONS DURING EARLY MORNING, BEGINNING AFTER SUNRISE (a), MID MORNING AND NOON (b), SUNSET (c) AND NIGHT (d).

In situ measurements are reported by points, error bars and U.T. time of performances. U.T. time differs from solar time by only 15 min. Remote sensing observations are indicated by total error areas.

data, the results have been plotted vs local time for six altitude levels (Fig. 4). Roughly and as expected at 17 km, the direction of the diurnal variation corresponds to the one expected from model simulations (Brasseur *et al.*, 1987). At 33 km a reduction by a factor of 2 between Helten's measurements before

sunrise and at 09:00 is acceptable. A reduction by a factor of 8 between night-time thermal emission at 04:30 and sampling at 09:00 is not. The same conclusion applies at 30 and 27 km. As night-time and daytime *in situ* observations are coherent on the one hand and remote data consistent on the other, there

is a systematic difference between the two sets at high altitudes. At 27 km, sunset remote sensing mixing ratios are two times larger than daytime *in situ* ratios (Fig. 4). At lower altitude, at 24 and 21 km, all the data are consistent "with model predictions" and therefore there is no apparent disagreement. At 17 km, the morning *in situ* measurement is found to be as high as the remote sunset data and four times higher than the one after noon. A closer inspection shows that for this flight on 20 September 1983 the airmasses came from lower southern latitudes. In the altitude range between the tropopause and 18 km there is a significant increase of O₃, as sometimes observed when subtropical air from the lower stratosphere is transported to higher latitudes. Since at this altitude $[\text{NO}_2] \sim [\text{O}_3]^{2/3}$ (McElroy, 1982), a higher NO₂ mixing ratio would be expected. A look into the altitude profile of this flight (Fig. 3a) clearly shows an increase of the NO₂ mixing ratio below 20 km which could be related to this higher O₃ level. The data of both flights are therefore not comparable in this altitude range.

Another way to understand *in situ* and remote sensing data is to add NO and NO₂ daytime concentrations for comparison with NO₂ night-time results (Fig. 5). NO was measured by two *in situ* instruments during the campaign and the results have been found to be in agreement (Fabian *et al.*, 1987). Between 27 and 31 km where the comparison is made possible, (NO+NO₂) noontime *in situ* data are smaller or on the lower edge of the NO₂ night-time observations at 04:30, but they agree within their error limits. As N₂O₅ should be dissociated in large part at noon and recombined at the end of the night, the difference is not in the expected direction. Below 20 km, the remote sensing measurements correspond to solar zenith angles greater than 92°. NO is therefore recombined into NO₂ (Kondo *et al.*, 1985). (NO+NO₂) *in situ* data at noontime agree with NO₂ observations at sunset. The conclusion about the NO₂ remote/*in situ* instruments comparison is that the systematic difference increases with altitude: lower than uncertainty at 20 km, it reaches a factor of about 2 at 27 km and of 4 at 33 km.

4.2. Comparison with other campaign results

In September 1982 and June 1983 another NO_x balloon instruments intercomparison was held in the United States; the BIC or Balloon Intercomparison Campaign (Roscoe *et al.*, 1985). The analysis has shown a large dispersion of the data; the visible and infra-red occultation techniques were found grouped within 30% on the upper side, the thermal emission radiometric results (pressure-modulated radiometer) on the lower side and the emission spectrometry in

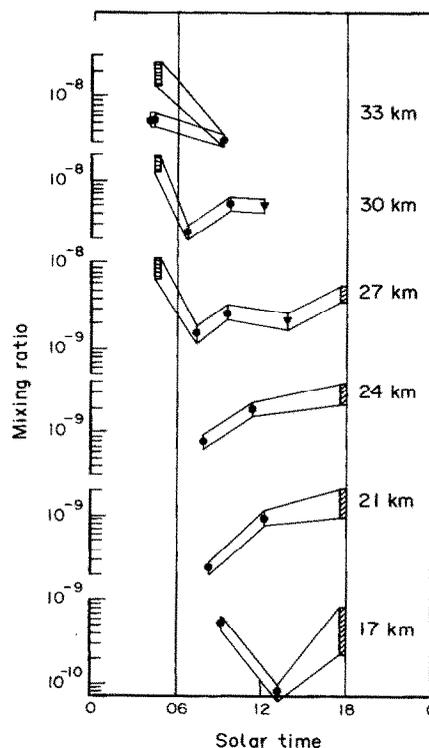


FIG. 4. NO₂ MEASUREMENTS AT SIX STRATOSPHERIC LEVELS PLOTTED VS SOLAR TIME.

In situ and remote data are reported by the same symbols as in Fig. 3. The general trend of the diurnal cycle—maximum by night and increase between sunrise and sunset—is reproduced. However, above 27 km the ratio between remote and *in situ* data cannot be interpreted and indicates systematic differences between the two sets of measurements.

between. All data were found to agree within their estimated errors at high altitude (38 km) but diverged rapidly below. The difference reached a factor of 3 around 26 km. One visible instrument participated in the two campaigns, GLOBUS and BIC (Pommereau), and therefore can be used as a secondary standard. If this is done, all remote sensing measurements except for the PMR appear to be roughly in agreement. The PMR and the two *in situ* samplers are found to disagree significantly with other remote sensing results, but they do not disagree with each other. The discrepancy increases when the altitude decreases for the PMR and in the opposite direction for the *in situ* instruments.

4.3. Comparison of NO₂ balloon, plane and ground observations

In order to compare the data, NO₂ concentrations observed from balloons were integrated from the

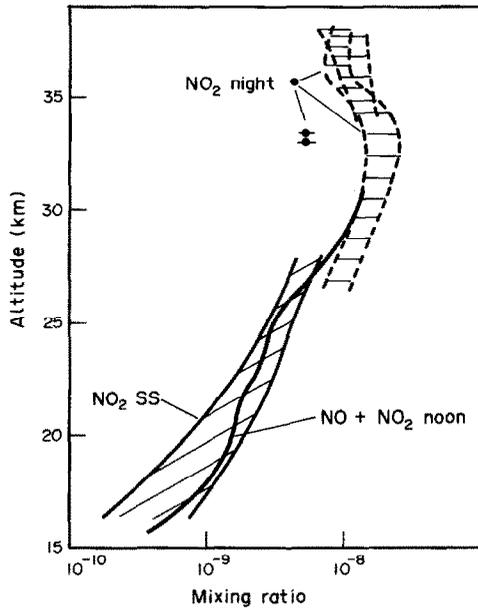


FIG. 5. COMPARISON BETWEEN $(\text{NO} + \text{NO}_2)$ IN SITU MEASUREMENTS AROUND NOONTIME AND NO_2 BY NIGHT AND AT SUNSET. As NO_2 recombines by night into N_2O_5 , NO_2 should be lower than $\text{NO} + \text{NO}_2$ at noon. Around 27 km where the comparison is made possible, the difference between experimental data is in the opposite direction. At low altitude, around 20 km, remote measurements at sunset when NO is recombined into NO_2 agree with $(\text{NO} + \text{NO}_2)$ *in situ* at noon.

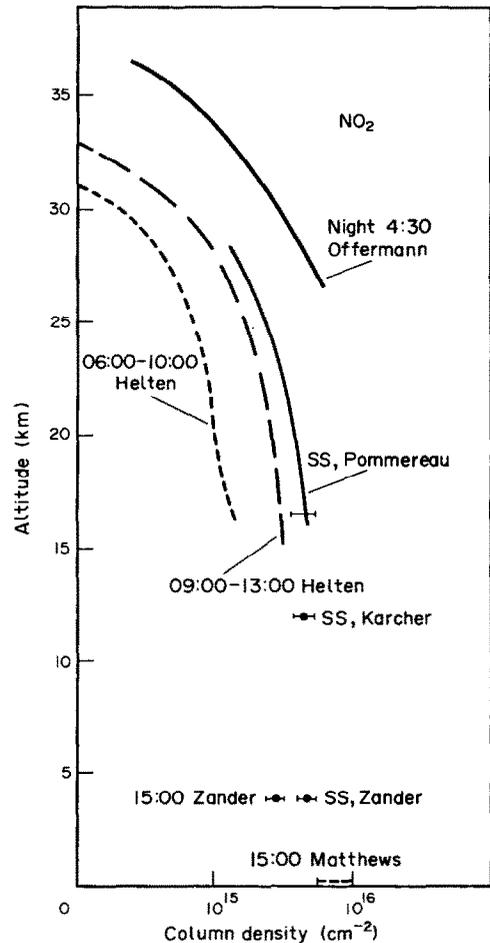


FIG. 6. NO_2 COLUMN DENSITY ABOVE ALTITUDE. Balloon *in situ* and remote sensing observations have been integrated down to the lowest measurement. Balloon, plane and ground determinations at sunset would be in agreement only if the average mixing ratio below 16 km was lower than 1.5×10^{-10} . Comparison between ground measurements at 15:00 at 3000 m altitude and at sea level would imply a high pollution level at Aire sur l'Adour. Diurnal variation observed from the ground at Jungfraujoch is not compatible with the one observed from balloons.

highest measurement down to the lowest. The results together with airplane and the ground data are presented in terms of integrated column densities above the various *ad hoc* altitudes (Fig. 6). Column densities reported during the campaign are also displayed vs date in Fig. 7. If the NO_2 tropospheric column was lower than 2×10^{15} mol cm^{-2} (average concentration of 1.5×10^9 cm^{-3} or average mixing ratio of 1.5×10^{-10}), balloon, plane and ground observations at sunset, by Pommereau, Simon, Karcher and Zander would be in agreement. The mean diurnal variation measured by Zander showing a column increase from 2.75×10^{15} to 4.65×10^{15} molecules cm^{-2} cannot be reconciled with balloon findings. Matthews' observations from sea level at Aire sur l'Adour would imply a high pollution level above the area independent of the wind direction during the campaign (Fig. 7). Since the vertical distribution was not observed below the tropopause and as the observations were not performed from the same altitude, it is not possible to draw a definitive conclusion but only to report the above inconsistencies.

4.4. NO_3 balloon measurements comparison

Two instruments have provided us with night-time NO_3 stratospheric observations and for the first time a comparison was made possible (Fig. 8). The estimated accuracy of the *in situ* determination is $\pm 40\%$, while the hatched area indicated for the remote observations by Rigaud corresponds to noise contribution only. An uncertainty still exists with regard to the visible absorption cross-sections required for the interpret-

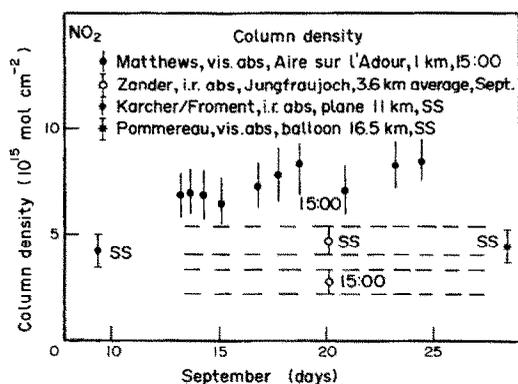


FIG. 7. NO₂ COLUMN DENSITY VARIATION DURING GLOBUS. Mattheus' measurements sequence do not show any significant variations which should be the case if the difference with Zander's average retrievals at 3580 m was the result of high pollution above Aire sur l'Adour.

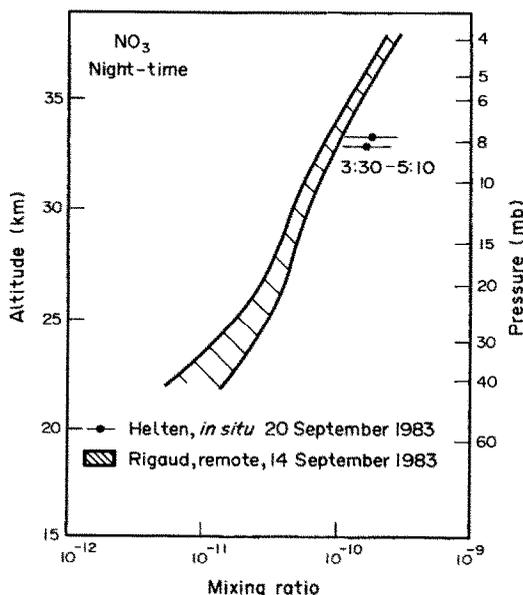


FIG. 8. NO₃ OBSERVATIONS DURING GLOBUS.

In situ results are two times higher than remote. This could be explained by systematic calibration errors on both instruments. More laboratory work is in progress to resolve the discrepancy.

ation of the NO₃ data (Naudet *et al.*, 1985). Due to the final evaluation of the sampling parameters, the *in situ* results are given here with small corrections compared to their first publication (Helten *et al.*, 1984). The calibration was not changed and is still preliminary. If these large uncertainties are taken into account, the two data sets overlap. More work is needed to improve the accuracy of the NO₃ observations.

Acknowledgements—This work was partly supported by the Bundesministerium für Forschung und Technologie, F.R.G., and by the Centre National de la Recherche Scientifique and Centre National d'Etudes Spatiales, France. The Jungfrauoch Laboratory is operated by the University of Liège through a grant from the Fonds de la Recherche Fondamentale Collective (Belgium). The support given by the CNES balloon center at Aire sur l'Adour and the MAP/GLOBUS 1983 coordinator Prof. Offermann is gratefully acknowledged.

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APPENDIX

TABLE A1. MAP/GLOBUS REPRESENTATIVE ATMOSPHERE AVERAGE 9 28 SEPTEMBER 1983

Altitude (km)	Pressure (mb)	Temperature (°C)	Ozone partial pressure (nb)
14	150	-65	32
16	107	-62	50
18	77	-58	80
20	56	-55	116
22	41.5	-53	140
24	30.2	-51	143
26	22.5	-49	137
28	16.3	-45	110
30	12.0	-40	68
32	8.7	-35	
34	6.5		

TABLE A2. NO₂ IN SITU, CHEMILUMINESCENCE AND CONVERTER, BALLOON FLIGHT OF 20 SEPTEMBER 1983. FABIAN, MPAE, LINDAU

Time (U.T.)	Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)	Accuracy (%)
09:59	27.6	-50	24.6	4.23	4.32	≥ 30
10:03	23.4	-50	25.7	4.87	5.94	≥ 30
10:42	12.9	-41	29.6	2.75	6.24	25
00:47	13.4	-41	29.3	2.53	5.39	
12:05	16.0	-45	28.1	2.51	4.49	
00:09	16.5	-45	27.9	2.08	3.64	
00:14	17.0	-46	27.7	1.73	2.88	
00:23	18.1	-46	27.3	1.70	2.69	
12:32	19.0	-47	27.0	1.54	2.33	
00:59	23.5	-48	25.7	1.89	2.31	
13:03	24.0	-48	25.5	1.47	1.71	

TABLE A3. NO₂ IN SITU, MATRIX ISOLATION, BALLOON FLIGHT OF 9 SEPTEMBER 1983 AND 20 SEPTEMBER 1983. HELTEN, KFA, JÜLICH

Time (U.T.)	Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)	Accuracy (%)
9 September 1983						
08:10-09:05	7.0-8.3	-37.7	33.9	0.561	2.57	± 13.6
08:54-09:54	7.5-13.6	-41.0	31.2	1.82	5.55	± 12.6
09:25-10:37	10.0-19.3	-44.5	28.7	2.18	4.53	± 12.1
10:38-11:44	19.3-34.1	-49.4	25.0	1.56	1.81	± 11.8
11:03-12:03	23.9-41.2	-51.0	23.5	2.16	1.97	± 11.7
11:45-12:42	35.3-64.5	-54.2	21.3	1.53	0.975	± 11.7
12:04-13:03	41.5-86.0	-55.9	19.5	2.03	0.969	± 11.7
12:43-13:37	64.9-115	-58.8	16.6	≤ 0.16	≤ 0.048	
13:04-13:53	87-130	-59.9	15.7	0.22	0.056	± 11.7
20 September 1983						
03:30-04:30	7.3-7.5	-43.6	33.2	1.24	5.23	± 13.5
04:08-05:10	7.3-7.5	-43.6	33.3	1.24	5.29	± 13.4
04:31-05:26	7.4-7.5	-43.6	33.0	1.36	5.59	± 13.4
05:11-06:16	7.5-9.7	-44.3	32.8	1.36	5.44	± 13.3
06:00-06:52	8.3-13.2	-45.4	30.6	0.886	2.51	± 12.5
06:33-07:30	11.4-20.6	-48.0	28.4	1.17	2.35	± 12.1
07:19-08:16	18.2-37.3	-51.4	24.3	0.845	0.898	± 11.8
08:00-08:55	30.6-57.7	-54.5	21.3	0.370	0.244	± 11.7
08:49-09:38	53.5-100	-58.0	17.8	0.852	0.314	± 11.7
09:03-09:51	69.7-129	-58.9	17.1	1.68	0.554	± 11.7

TABLE A4. NO₂ REMOTE SENSING, THERMAL EMISSION, BALLOON FLIGHT OF 23 SEPTEMBER 1983. OFFERMANN, WUPPERTAL

Time (U.T.)	Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)	Accuracy (%)	Column density (10 ¹⁵ cm ⁻²)
04:30	3.77	-32	38.2	1.13	10.0	±19	0.24
	4.85	-34.5	36.5	1.32	9.0	+19	
						-29	
	5.02	-35	36.2	1.45	9.5	+19	1.12
						-29	
	7.62	-41	33.3	5.4	22.6	+19	
						-34	2.90
12.6	-46.5	30.0	6.5	16.1	+20		
					-23		
						+24	5.54
						-29	

TABLE A5. NO₂ REMOTE SENSING, VISIBLE SPECTROMETRY AT NIGHT, BALLOON FLIGHT OF 14 SEPTEMBER 1983. RIGAUD, LPCE, ORLÉANS

Time (U.T.)	Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)	Accuracy (%)
02:17	3.8	-32	38	1.17	10.5	±42
	5.1	-35	36	1.96	13.0	±26
	6.9	-39	34	3.03	14.7	±24

TABLE A6. NO₂ REMOTE SENSING, VISIBLE SPECTROMETRY AT SUNSET, BALLOON FLIGHT OF 28 SEPTEMBER 1983. P. C. SIMON, IAS, BRUXELLES

Altitude (km)	Concentration (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)
29.1	2.18-2.77	5.12-6.51
28.6	1.97-2.97	4.31-6.50
27.5	2.59-3.58	4.71-6.50
25.6	2.52-3.11	3.32-4.10
22.9	1.58-1.91	1.31-2.79

TABLE A7. NO₂ REMOTE SENSING, VISIBLE SPECTROMETRY AT SUNSET, BALLOON FLIGHT OF 28 SEPTEMBER 1983. POMMEREAU, CNRS, VERRIÈRES

Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁹ cm ⁻³)	Mixing ratio (ppbv)	Accuracy (%)	Column density (10 ¹⁵ cm ⁻²)
15.5	-51	28.3	3.2	6.3	±21	1.35
20.5	-53	26.5	2.9	4.3	±22	1.94
28.0	-57	24.5	3.0	3.3	±22	2.60
38.0	-58	22.5	3.1	2.5	±26	3.15
52.0	-59	20.5	2.4	1.4	±35	3.65
72	-62	18.5	2.0	0.82	±50	4.10
100	-67	16.5	1.7	0.50	±70	4.40

TABLE A8. NO₂ REMOTE SENSING. COLUMN DENSITIES AND MEASUREMENTS FROM PLANE AND GROUND; KARCHER, CNRM, TOULOUSE; ZANDER, LIÈGE, BELGIUM; MATTHEWS, DSIR, NEW ZEALAND

Date	Altitude (km)	Time	Column density (10 ¹⁵ mol cm ⁻²)	Accuracy (%)	Author
19 Sept.	11.9	Sunset	4.43	±13	Karcher
8 Sept.	3.6	15:00	2.75	±16	Zander
10 Oct.	3.6	Sunset	4.65	±13	Zander
13 Sept.	0.0	11:30	6.9	±30	Matthews
		15:00	7.5		
14 Sept.		15:00	7.0		
15 Sept.		15:00	6.5		
17 Sept.		15:00	7.3		
18 Sept.			8.0		
19 Sept.			8.5		
21 Sept.			7.0		
23 Sept.			8.2		
24 Sept.			8.5		

TABLE A9. NO₃ REMOTE SENSING OBSERVATIONS DURING BALLOON FLIGHT OF 14 SEPTEMBER 1983 AROUND 03:30. RIGAUD, LPCE, ORLÉANS

Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁷ cm ⁻³)	Mixing ratio (pptv)	Accuracy (%)
3.8	-32	38	2.94	264	±12
5.1	-35	36	2.69	178	±8
6.9	-39	34	2.41	117	±13
9.2	-43	32	2.13	75.6	±18
12.5	-46	30	2.18	57.0	±15
16.5	-51	28	2.18	41.8	±15
22.0	-53	26	2.15	30.2	±21
30.0	-57	24	1.78	18.2	±38
41	-58	22	1.78	18.2	±61

TABLE A10. NO₃ IN SITU MEASUREMENTS DURING BALLOON FLIGHT OF 20 SEPTEMBER 1983 AT THE END OF NIGHT AND SUNRISE PERIOD. HELTEN, KFA, JÜLICH

Time (U.T)	Pressure (mb)	Temp. (°C)	Altitude (km)	Conc. (10 ⁷ cm ⁻³)	Mixing ratio (ppt)	Accuracy (%)
3:30-4:30	7.3-7.5	-43.6	33.2	5.3	196	40
4:08-5:10	7.3-7.5	-43.6	33.3	5.3	176	40
4:31-5:26	7.4-7.5	-43.6	33.0	≤0.7	≤34	
5:11-6:16	7.5-9.7	-44.3	32.8	≤0.5	≤12	
6:00-6:52	8.3-13.2	-45.4	30.6	≤0.7	≤16	
6:33-7:30	11.4-20.6	-48.0	28.4	≤1.3	≤22	