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Intercomparison of stratospheric NO_2 and NO_3
measurements during Map/Globus 1983

by

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FOREWORD

This text has been published with the other results of the MAP/Globus 1983 campaign, in a special issue of "Planetary and Space Science", 35, 615-629, 1987.

AVANT-PROPOS

Ce texte a été publié avec les autres résultats de la campagne MAP/Globus 1983, dans une édition spéciale de "Planetary and Space Science", 35, 615-629, 1987.

VOORWOORD

Deze tekst werd gepubliceerd samen met de overige resultaten van de MAP/Globus 1983 campagne, in een speciaal nummer van "Planetary and Space Science", 35, 615-629, 1987.

VORWORT

Dieser Text wurde veröffentlicht zusammen mit den übrigen Ergebnisse der MAP/Globus 1983 Kampagne, in einer speziellen Ausgabe von "Planetary and Space Science", 35, 615-629, 1987.

INTERCOMPARISON OF STRATOSPHERIC NO₂ AND NO₃ MEASUREMENTS DURING

MAP/GLOBUS 1983

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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 one hand and in situ methods on the other. The two sets of data which agree in the lower stratosphere at 20 km are diverging at higher altitude by a factor 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 nighttime remote measurement and preliminary in situ results show a disagreement by a factor 2.

Résumé

Le dioxyde et trioxyde d'azote ont été mesurés à partir du sol, en avion et en ballon stratosphérique pendant la campagne MAP/Globus 1983. La comparaison entre les rapports de mélange mesurés en ballon montre un accord entre les mesures faites in situ et par télédétection qui dépend de l'altitude. Les deux types de données sont en accord à 20 km mais divergent d'un facteur 2 et 4 respectivement aux environs de 27 km et 33 km. Les contenus intégrés mesurés depuis le sol au coucher du soleil sont en accord avec les observations en avion et en ballon, pour autant que le rapport de mélange en-dessous de 16 km est inférieure à 1.5×10^{-10} . La variation diurne du contenu intégré en NO₂ déterminée depuis le sol pendant la seconde moitié du mois de septembre diffère de celle observée dans la stratosphère. Une première comparaison entre les valeurs de NO₃ obtenues pendant la nuit avec les techniques in situ et de télédétection montre un désaccord d'un facteur 2.

Samenvatting

Stikstofdioxyde en -trioxyde werden waargenomen vanop de grond, alsook vanuit vliegtuigen en stratosferische ballons tijdens de MAP/GLOBUS campagne 1983. De vergelijking tussen de per ballon gemeten NO_2 mengverhoudingen toont een overeenkomst met de in situ uitgevoerde metingen en die d.m.v. teledetectie, afhankelijk van de hoogte. De twee soorten gegevens stemmen overeen op 20 km maar vertonen een afwijking van factor 2 en 4 respectievelijk op 27 km en 33 km hoogte. De geïntegreerde hoeveelheden gemeten vanop de grond bij zonsondergang stemmen overeen met de waarnemingen per vliegtuig en per ballon, voor zover de mengverhouding beneden de 16 km kleiner is dan 1.5×10^{-10} . De dagelijkse schommeling in de geïntegreerde hoeveelheid NO_2 bepaald vanop de grond tijdens de tweede helft van september verschilt van die waargenomen in de stratosfeer. Een eerste vergelijking tussen de NO_3 waarden die 's nachts bekomen werden met teledetectie - en in situ technieken, tonen een afwijking van factor 2.

Zusammenfassung

NO_2 und NO_3 wurden beobachtet vom Boden, Flugzeugen und stratosphärischen Ballons während der MAP/GLOBUS Kampagne 1983. Die Vergleichung zwischen den mit Ballons gemessenen NO_2 Mischungsverhältnissen zeigt eine Übereinstimmung mit den in situ getane Messungen und den durch Teledetektion, abhängig von der Höhe. Die zwei Typen Daten stimmen überein auf 20 Km aber zeigen eine Abweichung von Faktor 2 und 4 resp. auf 27 Km un 33 Km Höhe. Die integrierte Quantitäten gemessen vom Boden am Sonnenuntergang stimmen überein mit den Beobachtungen mit Flugzeugen und Ballons, unter der Bedingung dass das Mischungsverhältnis unter 16 Km geringer als 1.5×10^{-10} ist. Die tägliche Schwankung in der integrierten NO_2 Quantität bestimmt vom Boden während der zweiten Hälfte September differiert von die Schwankung beobachtet in der Stratosphäre. Eine erste Vergleichung zwischen den NO_3 Werten nachts bekommen mit Teledetektion - und in situ Techniken, zeigen eine Abweichung von Faktor 2.

I. EXPERIMENT OVERVIEW

During MAP/GLOBUS 1983 six instruments for NO_2 measurements have been flown on board balloons from the Centre National d'Etudes Spatiales (CNES) balloon range at Aire sur l'Adour (44°N , 0°W). Among them two used in situ techniques and four were remote sensors. In order to observe the diurnal variation one of the in situ experiments has been flown two times : first at noon time and later by night. Two of the instruments -one in situ and one remote- were also able to measure NO_3 by night [Helten et al. 1984 b ; Naudet et al. 1984 b]. The flight sequence began on september 9 and ended on september 28. During this period, column densities were also measured from a plane at sunset and from the ground at the Jungfrauoch station (47°N , 8°E , 3850 m) and at Aire sur l'Adour (43°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 NO_2 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} (Zander) and in the visible at 440 nm for NO_2 and 662 nm for NO_3 (Rigaud, Simon, Matthews, Pommereau) for remote sensing. Table 1 lists the observations dates, together with the prime-investigators, techniques used, species measured and solar observation time. 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.

TABLE 1.- NO₂ and NO₃ measurement performed during MAP/GLOBUS 1983.

Date	Time	Platform	Species	Technic	Author
Sept. 9	800-1400	Balloon	NO ₂	Matrix isolation	Helten, KFA, Julich
Sept. 9	Sunset	Plane	NO ₂	IR Absorption	Karcher, CNRM, Toulouse
Sept. 14	Night	Balloon	NO ₂ , NO ₃	Visible Spectrometry	Rigaud, LPCE, Orléans
Sept. 20	1000-1300	Balloon	NO ₂	Chemiluminescence	Fabian, MPAE, Lindau
Sept. 20	330-1000	Balloon	NO ₂ , NO ₃	Matrix Isolation	Helten KFA, Julich
Sept. 23	Night	Balloon	NO ₂	Thermal emission	Offermann, Wuppertal
Sept. 28	Sunset	Balloon	NO ₂	Visible Spectrometry	Simon, IAS, Bruxelles
Sept. 28	Sunset	Balloon	NO ₂	Visible Spectrometry	Pommereau, CNRS, Verrieres
Sept. 8 to Oct. 10	1500 and sunset	Jungfraujoch	NO ₂	IR Absorption	Zander, Liège
Sept. 13 to Sept. 24	1130 and 1500	Aire sur l'Adour	NO ₂	Visible Photometry	Matthews, DSIR, New Zealand

II. INSTRUMENTS DESCRIPTIONS AND PERFORMANCES

In situ instruments

In situ measurements by Helten consist (1) in extracting the radicals from ambient air with a balloon borne cryosampler at 70 K by matrix isolation, and (2) in an identification and a 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 molecular sieve. Overlapping samples are collected, each for about one hour, during the balloon descent, which is controlled at 1 m/s. The method allows measurement of NO_2 and NO_3 . 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 NO_2 the concentration in the primary standard from which the standard sample is prepared, is measured by chemiluminescence and differential optical absorption. The accuracy on the resulting NO_2 mixing ratios is estimated by error propagation : relative incertitude of $\pm 3\%$ on collected air volume for the standard, ≈ 3 to 8% dependent on altitude for the atmospheric volume sampled in flight, $\pm 2\%$ on the spectrometer gain, $\pm 3\%$ on the scaling factor between standard and actual measurements, and $\pm 10\%$ on the standard mixing ratio. The resulting total uncertainty on NO_2 concentration is estimated to $\pm 12\%$ [Helten et al., 1984 and 1985]. For NO_3 , the total uncertainty accuracy is evaluated to $\pm 40\%$.

NO_2 in situ observations by Fabian are based on NO_2 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, are already described [Fabian et al., this issue]. A series of laboratory simulation had shown the converter possesses a conversion efficiency of better than 95% over a 12 hour 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 NO_2 was measured during the flight portions when the main air flow was diverted and passed through the converter, no independent NO measurements were made. NO_2 mixing ratios were derived from the total $\text{NO} + \text{NO}_2$ by using interpolated NO data. Precision on NO measurements is evaluated to $\pm 12\%$ and calibration systematic error to $\pm 5\%$. For NO_2 , the uncertainty of the converter efficiency, i.e. $\pm 5\%$, must be added. Another $\pm 5\%$ may be introduced by the NO interpolation procedure. Thus a total error bar of about $\pm 25\%$ may be a realistic upper limit for NO_2 . The error of the first 2 data points measured during the ascent, however, is likely to be larger (see Fabian et al., this issue).

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 $\pm 0.015^\circ$, the horizontal fov is $\pm 0.5^\circ$. Limb scan measurements are performed by a scanning mirror, which covers $\pm 2.4^\circ$ in the vertical 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 minutes). Therefore only a limited number of points of the altitude profile of NO_2 could be measured.

NO_2 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. (1986).

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 NO_2 densities were computed for every altitude. They range from $\pm 19\%$ at the highest altitude (38.2 km) to $+ 24\% - 29\%$ at the lowest altitude (26.7 km). Details are given in the annex. 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. (this issue). At the two lowest altitudes (26.7 km and 30.0 km) the viewing directions were approximately towards north-west and south-east, respectively, with distances to the tangent points of 380 km and 320 km.

Visible absorption instrument

The three other balloon remote sensing instruments are visible spectrometers designed to observe the atmospheric absorption during a stellar or a solar occultation. NO_2 is measured by differential absorption around 440 nm and NO_3 , 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 span 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 with sunlight the two apparatus 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., same issue). A silicon photodiode EG & G, type UV-444B is used as detector. Its output current is measured by means of a 3 channel linear electrometer covering a dynamic range from 10^{-12} to 10^{-8} Amp. A high-pass filter with a cut-off at 300 nm has been set in front of the detector. Therefore wavelength scannings below this wavelength provide 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 nm and 450 nm at sampling intervals of 0.05 nm in 3 minutes. The final resolution is 0.25 nm.

The measuring method, common to the three experiments, consists in observing the absorption differences corresponding to the small spectral features which appear in NO_2 and NO_3 absorption cross-sections. Rigaud and Pommereau calculate the NO_2 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 at laboratory (H.S. Johnston, reported by Harrison (1979). Details of the method are given by Pommereau (1982) and Naudet et al. (1984). The NO_3 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 annex 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 on 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 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 on the laboratory absorption cross section data with which they are compared ($\pm 5\%$ for NO_2 and $\pm 30\%$ for NO_3) 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 NO_2 which consists in calibrations with a cell. The amount of NO_2 inside the cell is deduced by total absorption measurement. At best for NO_2 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, NO_2 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 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 NO_2 absorption in the infra-red at 1604.58 cm^{-1} . The experiment is described by Girard et al. 1977a, 1977b. 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]. The species vertical distribution is adjusted in order to reproduce the observed dependence between line equivalent widths and solar zenith angles. The random error of $\pm 8\%$ is estimated from the standard deviation of the 14 data points obtained during the sunset sequence. Systematic error contributions are incertitude of the species vertical distribution used to simulate the absorption spectra and the error of spectroscopic data ($\pm 5\%$). The total uncertainty is estimated at $\pm 13\%$.

Zander's NO_2 column density determinations are retrieved from the analysis of infrared solar spectra recorded near 2914.5 cm^{-1} from the Jungfraujoch station. The equipment is made of a heliostat feeding a 7.5 meter 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} per second 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 (EQW's) of NO_2 lines at 2914.65 cm^{-1} recorded under various slant path conditions. The EQW's are measured with a high precision CORADI planimeter and subsequently compared to EQW's deduced

from synthetic spectra calculated through a layered atmosphere with adjustable constituents concentrations ; these concentrations are indeed adjusted until good agreement is reached between the measured and the computer EQW's. 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 $\pm 10 \%$.

Matthew's 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 NO_2 absorption features in the 435 to 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 NO_2 absorption cross sections of H.S. Johnston as reported by Harrison (1979) are used to determine the NO_2 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 of $1 \times 10^{15} \text{ mol cm}^{-2}$, Matthews (1984).

III. FIELD OBSERVATIONS

In situ measurements by Helten were made during two balloon flights on september 9 and 20. 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 September 9 flight was made at late morning and September 20 started at night and was finished 4 hours later. The nighttime samples have provided NO_3 measurements around 30 km. HO_2 altitude profiles were also determined during daytime for both flights [Helten et al., 1985].

Nighttime visible absorption measurements were performed by Rigaud on September 14, at 0217 for NO_2 during the rising of Sirius and at 0329 for NO_3 during the rising of Venus. Unfortunately, telemetry interferences during the NO_2 sequence do not allow measurements for elevation below -1° . Therefore only data between 34 km and 38 km are available for this species. NO_3 observations were obtained without problems.

Chemiluminescent NO and NO_2 in situ observations were made by Fabian on September 20 together with another NO chemiluminescent instrument onto the same gondola [Fabian et al., this issue, Kondo et al., 1985]. Measurements started at 25 km during the ascent and were pursued at float and during a slow descent at 1 ms^{-1} . The ozone generator failed at 14:42 UT and no data are available afterwards.

Thermal emission IR observations were performed on September 23, 1983 at 04:30 UT by the Wuppertal instrument. Pommereau and Simon flew their visible spectrometers together on a common gondola on September 28. Their NO_2 vertical distributions at sunset are therefore simultaneous.

The grille spectrometer has been flown on board the Caravelle on September 9 during sunset. Ground observations at the Jungfraujoch were obtained on September 19, 20, 23, 24, 26, 28 and October 1 from mid-afternoon ($Z = 50^\circ$ to 70°) till sunset ($Z = 85^\circ$ to 90°). Matthews performed measurements every clear day around 1500 during the campaign: September 13, 14, 15, 17, 18, 19, 21, 23 and 24.

IV. DATA COMPARISON AND DISCUSSION

For intercomparison, measurements of short lived trace gas species should be executed in the same airmass 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.

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 figure 1. Most of the measurements were performed between 43°N and 45°N . Observations by Zander and by Karcher were obtained further north at 47°N and 48°N respectively. The average NO₂ column density variation expected from 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., this issue). The air masses remained four days before the launch of each flight between 40° and 48°N latitude. No fast transport from high or low latitudes was inferred from the metrological data.

Ozone measured by Brewer Mast sondes at Biscarosse and from Haute Provence Observatory the days of balloon flights [de La Noe et al., this issue] shows only small variations between 17 km and 35 km. At lower altitude, between 12 km and 17 km, observations of September 9 and September 14 show an indication of latitudinal transport in the higher troposphere (figure 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 NO₂ balloon flights. Although a long wave may have been present as discussed by Offermann et al., [this issue], long time series of measurements [McKenzie and Johnston, 1982] have shown that the stratospheric NO₂ column density at constant local time is

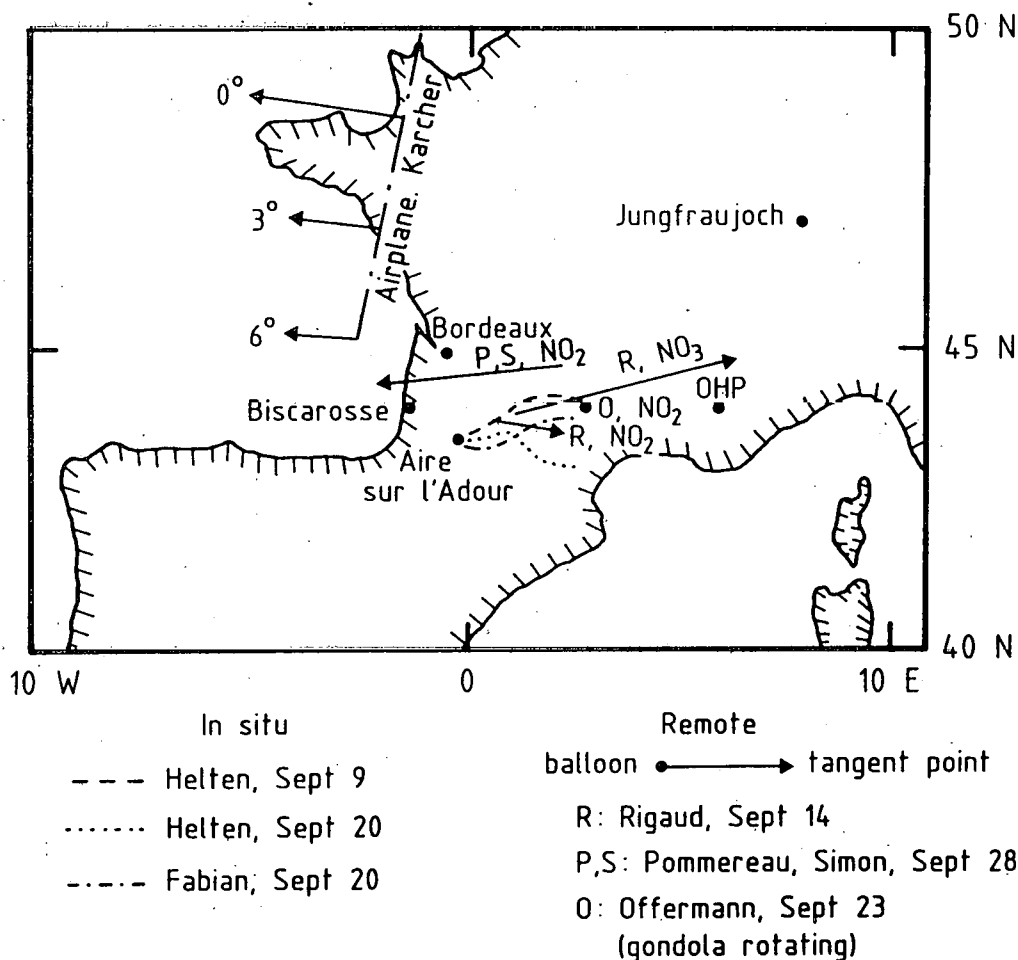


Fig. 1.- Location of NO_2 and NO_3 observations. In situ measurements are made along the indicated balloon trajectories. Remote sensing ones are reported by balloon location, and tangent point at 20 km or by lower observation altitude. Airplane measurements are presented by aircraft trajectory and intersection 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 observatories are also indicated.

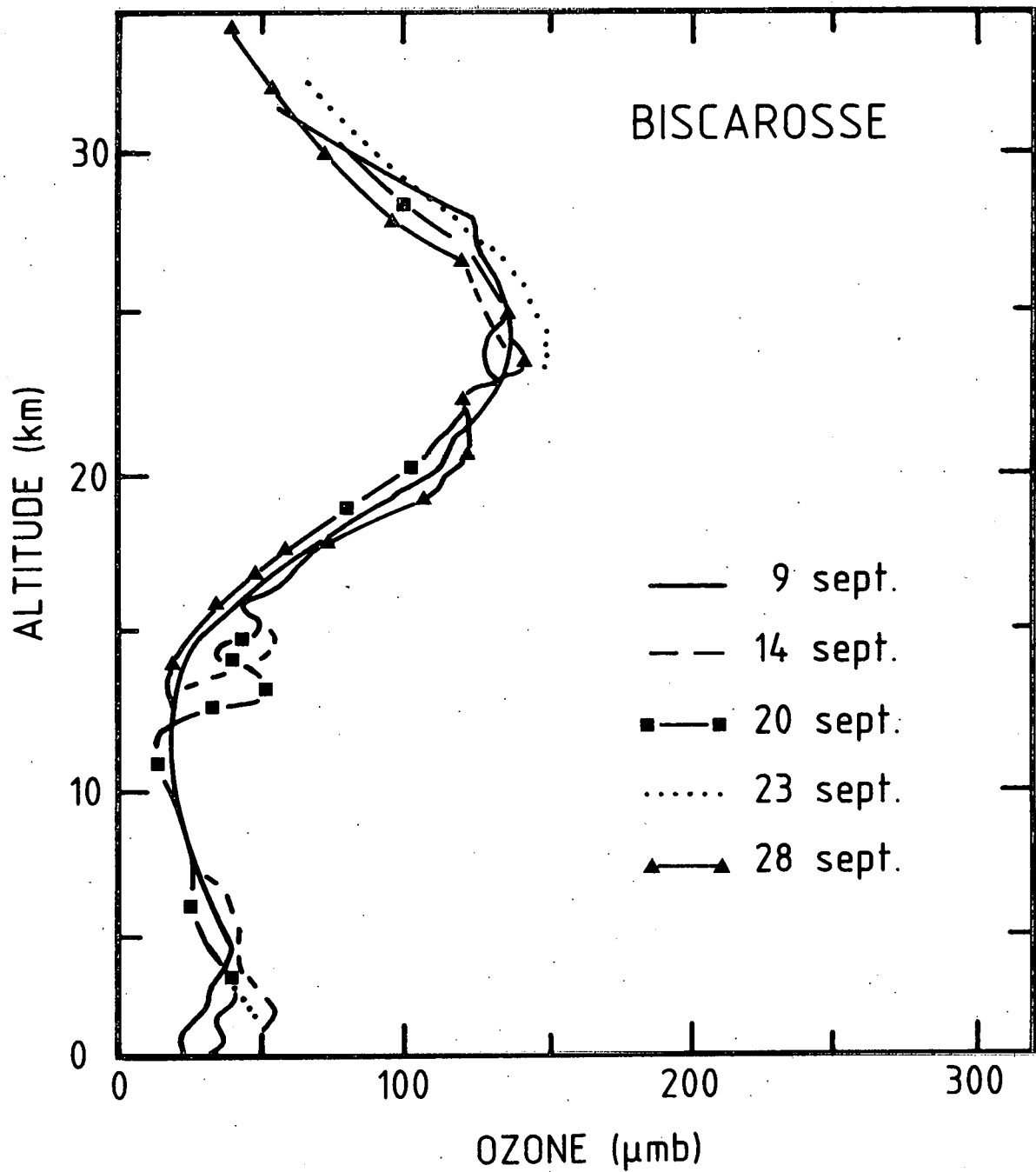


Fig. 2.- Ozone Brewer/Mast soundings from Biscarosse for the five days of NO_2 measurements from balloons. Above 17 km, only small variations appear between one day to another. Below there is some indication of advection from southern latitudes on September 9 and 14 in the upper troposphere.

not expected to vary by more than 20% from one day to an other. This conclusion is in agreement with Zander and Matthews observations from the ground showing day to day variations smaller than 20% from one day to an other. Therefore above 17 km, differences between different data sets larger than 20% must be attributed to diurnal variations or measurements systematic errors.

A. 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), mid-morning and noon time (panel b), sunset (panel c) and nighttime measurements (panel d). Actual data and total accuracy are reported in annex.

NO₂ in situ/in situ comparison

Both flights on 9-20-83 gave in situ measurements (figures 3a and 3b). 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 hours 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 9-9-83 (figure 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. Excepted 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 km down to 25 km are in agreement within their error bars. During the earlier ascent Fabian has measured mixing ratios more than three times larger. Because these data were obtained just after turning on the instrument before it has reached its proper working conditions and a contamination from the balloon during ascent can not be excluded, these

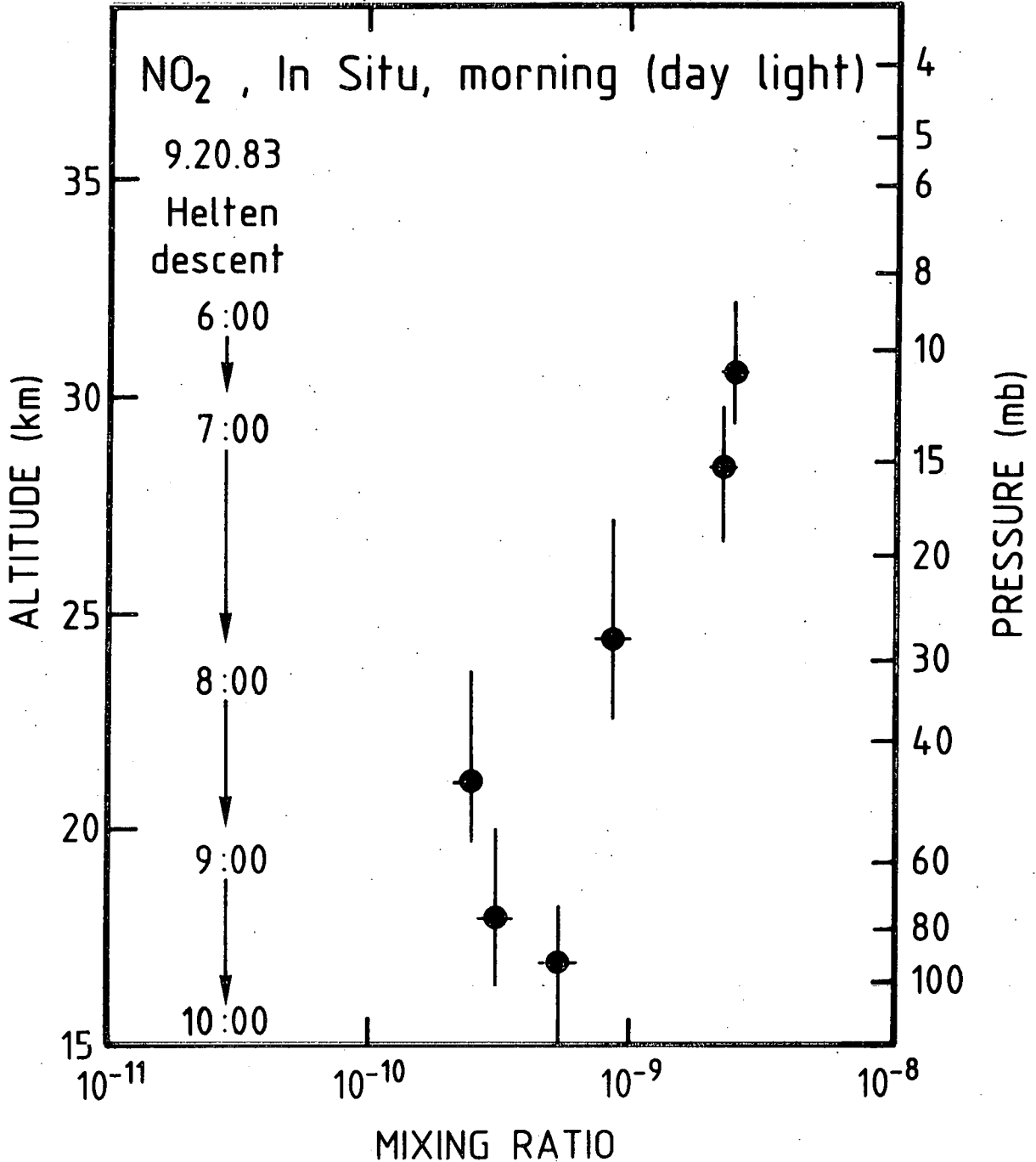


Fig. 3a.- NO₂ mixing ratio observed from balloons during early morning, beginning after sunrise. In situ measurements are reported by points, error bars and UT time of performances. UT time differs from solar time by only 15 minutes. Remote sensing observations are indicated by total error areas.

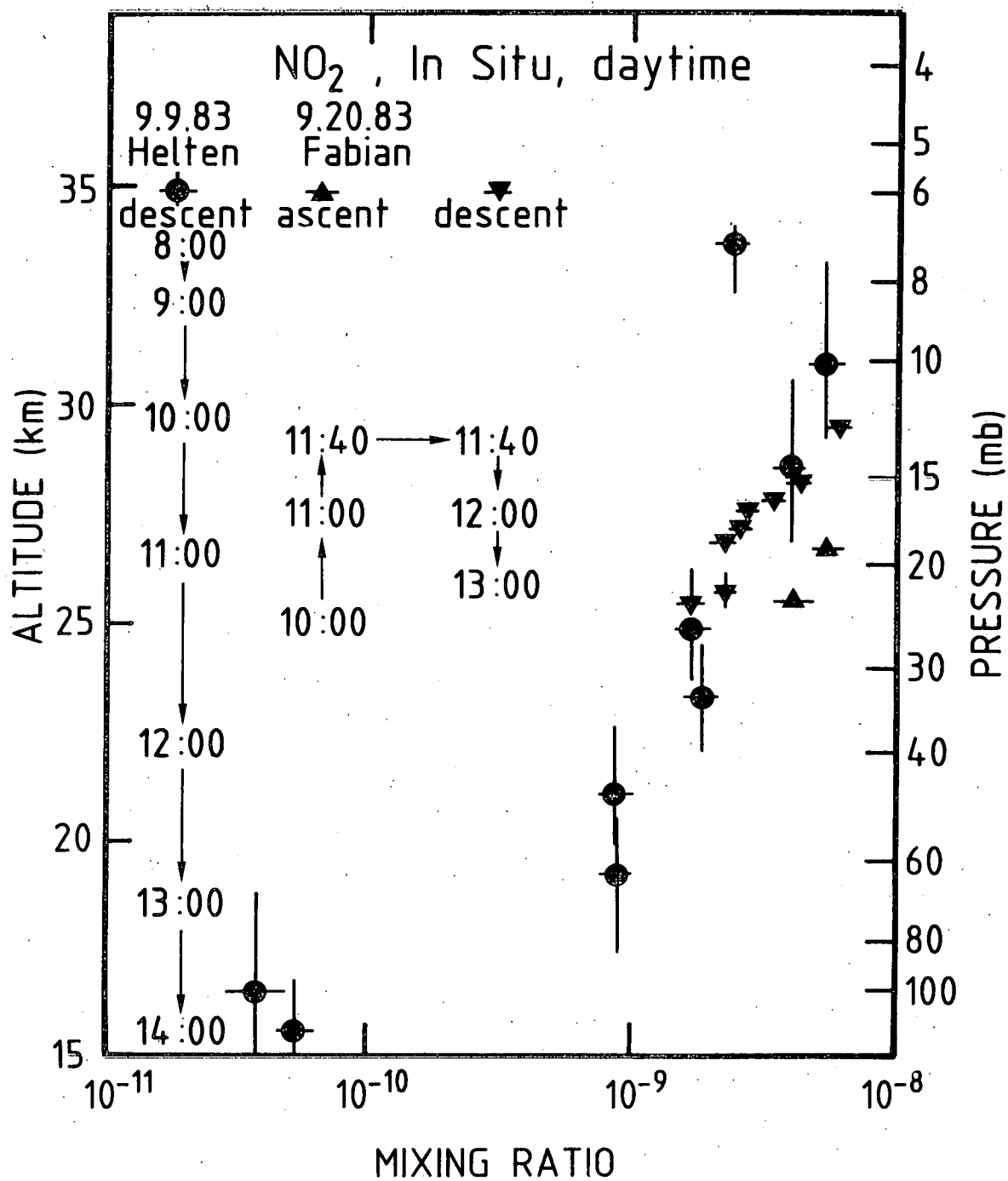


Fig. 3b.- NO₂ mixing ratio observed from balloons, during mid morning and noon. In situ measurements are reported by points, error bars and UT time of performances. UT time differs from solar time by only 15 minutes. Remote sensing observations are indicated by total error areas.

data points will not be considered later. (Fabian et al, same issue). 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 at sunset NO₂ altitude profiles (figure 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 UT and Rigaud's visible spectrometric data at 2.20 UT (figure 3, panel d). These measurements were made one week 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 nighttime thermal emission and sunset visible data is of about 2(± 40%), greater than the one of 1.4 measured from orbit by LIMS between midnight and noon. [Russel et al., 1984]. All remote data but the peak value measured by thermal emission at 33.3 km, are within the zonal monthly mean at 45°N to 50°N as observed by LIMS. Within the altitude range 27 km-34 km, only the lower estimate of thermal emission data would be compatible with both balloon sunset visible observations and LIMS data.

NO₂ in situ/remote comparison

The previous nighttime remote observations can be compared with Helten's in situ measurements (figure 3d). Offermann's and Helten's observations at 33 km altitude, at the same local time are only 2 days apart. The in situ data are lower by a factor 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 reduce partially this factor. It remains also to be seen whether

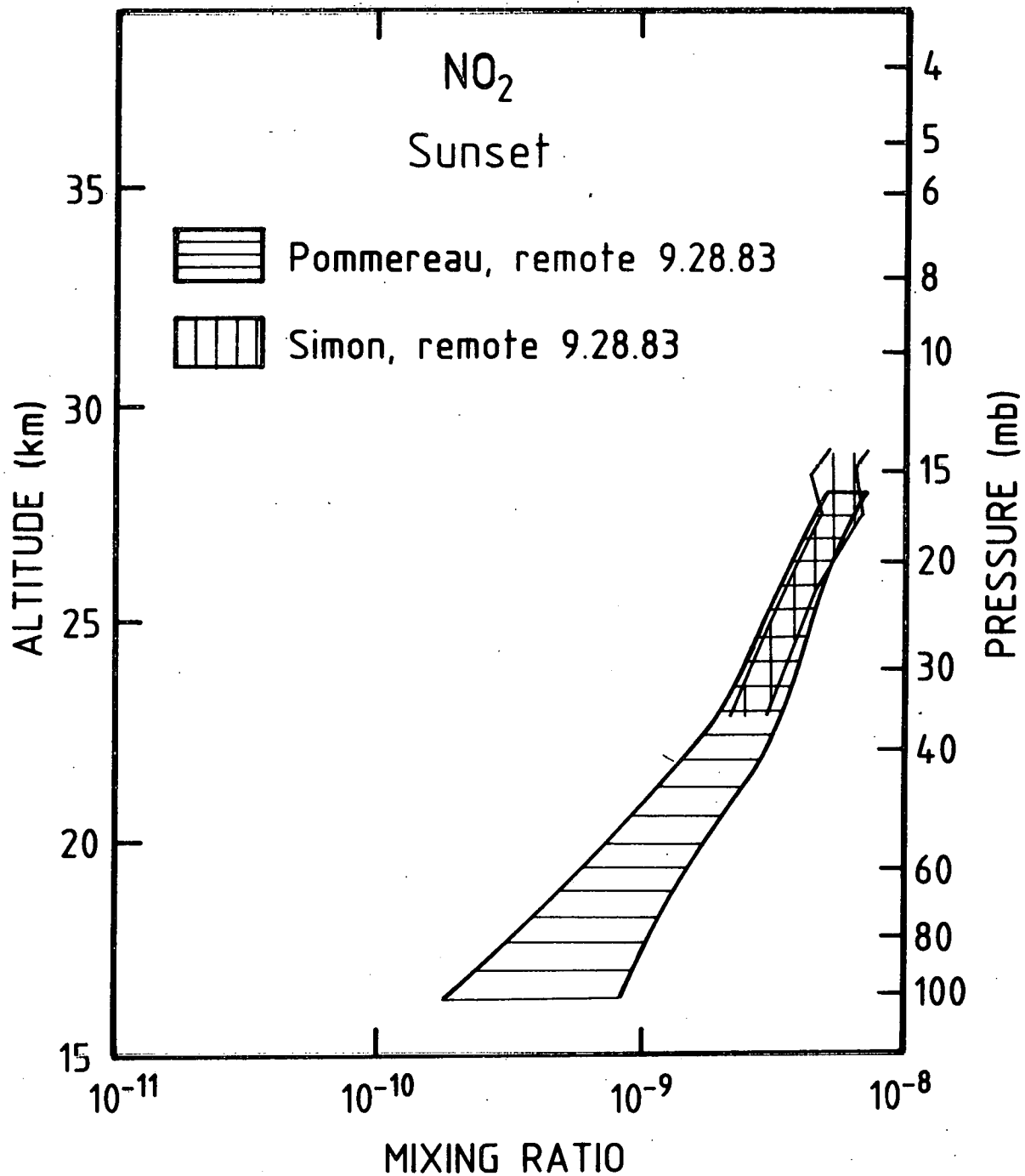


Fig. 3c. - NO₂ mixing ratio observed from balloons, during sunset. In situ measurements are reported by points, error bars and UT time of performances. UT time differs from solar time by only 15 minutes. Remote sensing observations are indicated by total error areas.

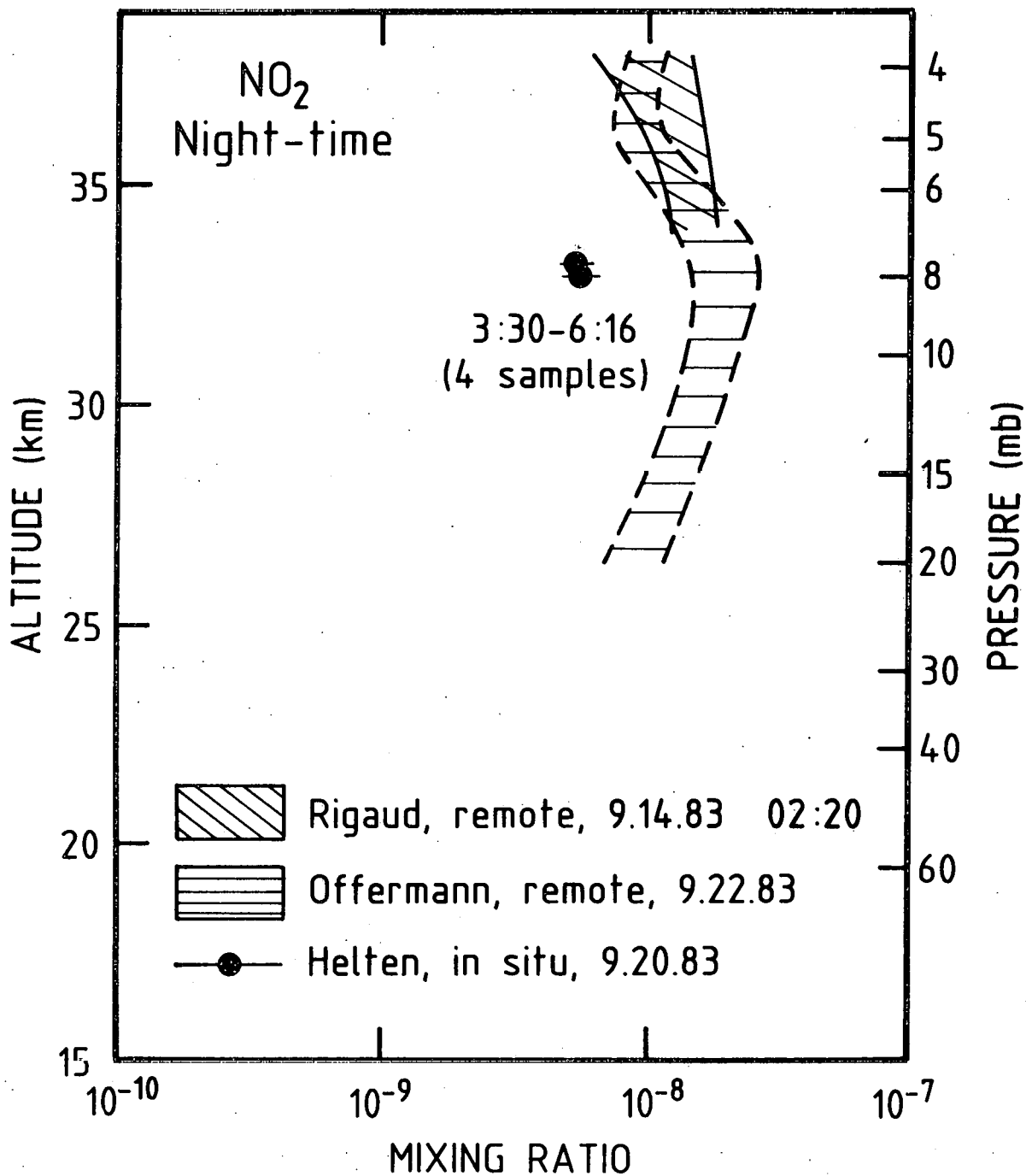


Fig. 3d. - NO₂ mixing ratio observed from balloons during night. In situ measurements are reported by points, error bars and UT time of performances. UT time differs from solar time by only 15 minutes. Remote sensing observations are indicated by total error areas.

the above mentioned wave influence [Offerman et al., same issue] could diminish the discrepancy and to what extend.

In order to compare the other in situ and remote data, the results have been plotted versus local time for 6 altitude levels (figure 4). Roughly and excepted at 17 km, the direction of the diurnal variation corresponds to the one expected from model simulations [Brasseur et al., this issue]. At 33 km a reduction by a factor 2 between Helten's measurements before sunrise and at 0900 is acceptable. A reduction by a factor 8 between nighttime thermal emission at 0430 and sampling at 0900 is not. The same conclusion applies at 30 km and 27 km. As nighttime and daytime in situ observations are coherent on 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 2 times larger than daytime in situ (figure 4). At lower altitude at 24 km 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 4 times higher than the one after noon. A closer inspection shows, that for this flight on 9-20-83 the airmasses came from lower Southern latitudes. In the altitude range between the tropopause and 18 km there is a significant increase of O_3 as sometimes observed when subtropical air from the lower stratosphere is transported to higher latitudes. Since at this altitude $[NO_2] \sim [O_3]^{2/3}$ [Mc Elroy, 1982], a higher NO_2 mixing ratio would be expected. A look into the altitude profile of this flight (figure 3a) demonstrates clearly the increase of the NO_2 mixing ratio below 20 km due to this higher O_3 level. The data of both flights are therefore not comparable in this latitude range.

Another way to understand in situ and remote sensing data is to add NO and NO_2 daytime concentrations for comparison with NO_2 nighttime results (figure 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., this issue]. Between 27 km and 31 km where the comparison is made possible, $(NO + NO_2)$ noontime in situ is smaller or on the

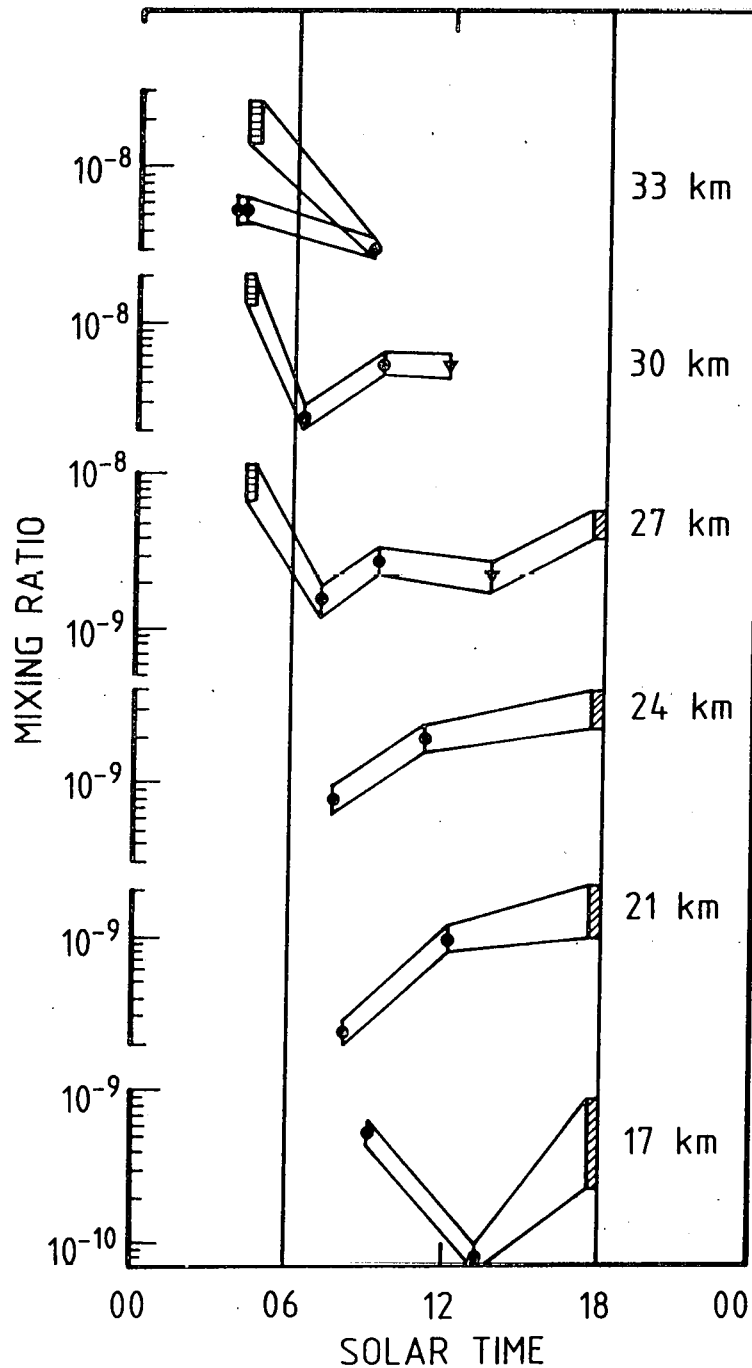


Fig. 4.- NO₂ measurements at six stratospheric levels plotted versus solar time. In situ and remote data are reported by the same symbols as on figure 3. The general trend of the diurnal cycle - maximum by night and increase between sunrise and sunset - is reproduced. However above 27 km, the ratio between remote and in situ data cannot be interpreted and indicates systematic differences between the two sets of measurements.

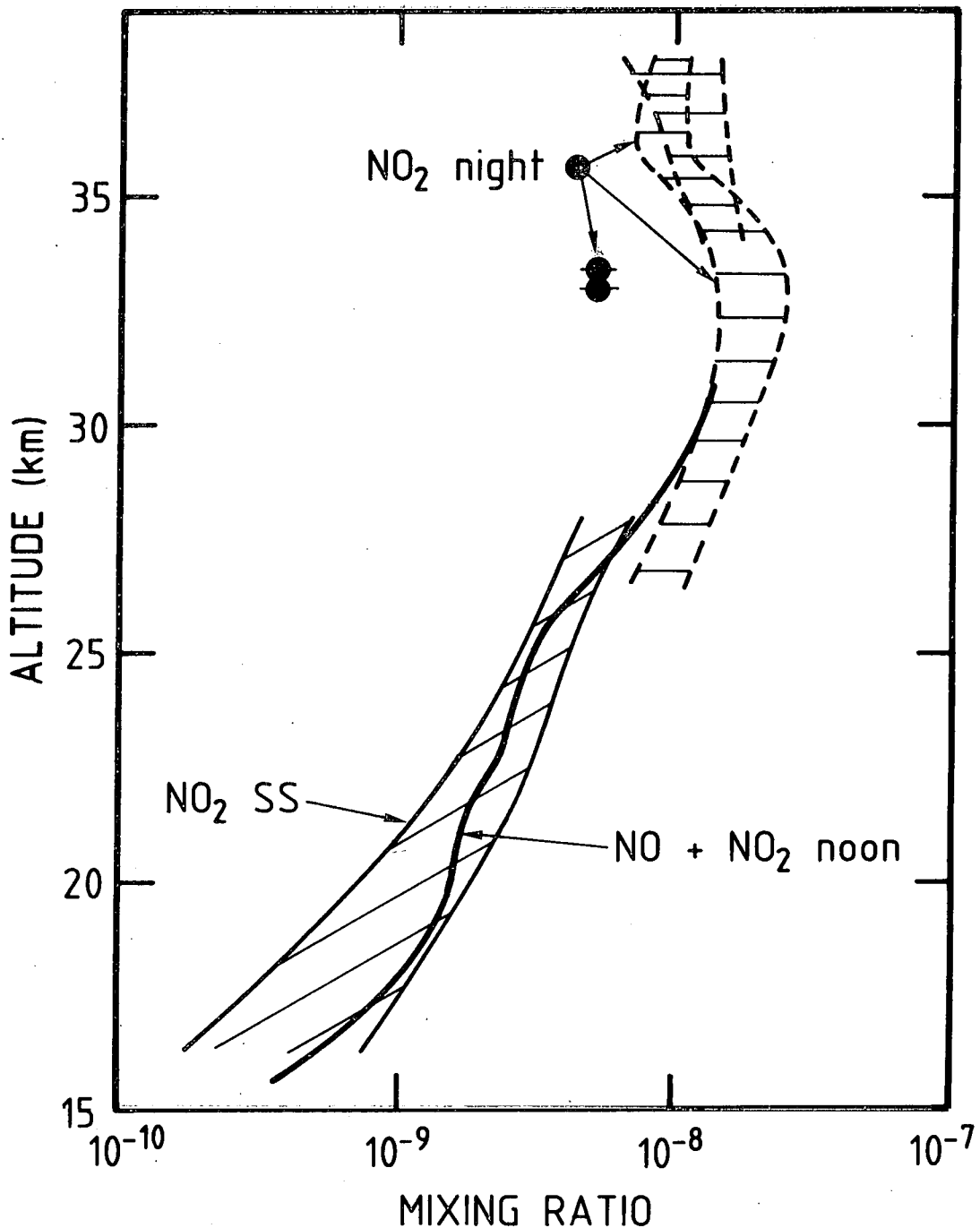


Fig. 5.- Comparison between $(\text{NO} + \text{NO}_2)$ in situ measurements around noontime and NO_2 by night and at sunset. As NO_2 recombines by night into N_2O_5 , NO_2 should be lower than $\text{NO} + \text{NO}_2$ at noon. Around 27 km where the comparison is made possible, the difference between 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.

lower edge of the NO_2 nighttime observations at 0430, but they agree within their error limits. As N_2O_5 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 NO_2 [Kondo et al., 1985]. ($\text{NO} + \text{NO}_2$) in situ at noontime agree with NO_2 observations at sunset. The conclusion about NO_2 remote/in situ instruments comparison is that the systematic difference increases with altitude : lower than uncertainty at 20 km, it reaches a factor about 2 at 27 km and 4 at 33 km.

Comparison with other campaign results

In September 1982 and June 1983 another NO_x balloon instruments intercomparison was held in United States, 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 between. All data were found to agree within their estimated errors at high altitude (38 km) but diverging rapidly below. The difference reaches a factor of 3 around 26 km. One visible instrument participated into the two campaigns Globus and BIC (Pommereau) and therefore can be used as a secondary standard. If this is done, all remote sensing measurements but 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 agree with each other. The discrepancy increases, when the altitude decreases for the PMR and in the opposite direction for the in situ instruments.

B. COMPARISON OF NO₂ BALLOON, PLANE AND GROUND OBSERVATIONS

In order to compare the data, NO₂ concentrations observed from balloons have been integrated from the 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 (figure 6). Column densities reported during the campaign are also displayed versus date on figure 7. If the NO₂ tropospheric column was lower than $2 \times 10^{15} \text{ mol.cm}^{-2}$ (average concentration of $1.5 \times 10^9 \text{ cm}^{-3}$ 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 $4.65 \times 10^{15} \text{ molecules cm}^{-2}$ 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 (figure 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.

C. NO₃ Balloon measurements comparison

Two instruments have provided during nighttime NO₃ stratospheric observations and for the first time a comparison has been made possible (figure 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 interpretation of 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., 1984b]. The calibration was not changed and is still preliminary. If these large uncertainties are taken into

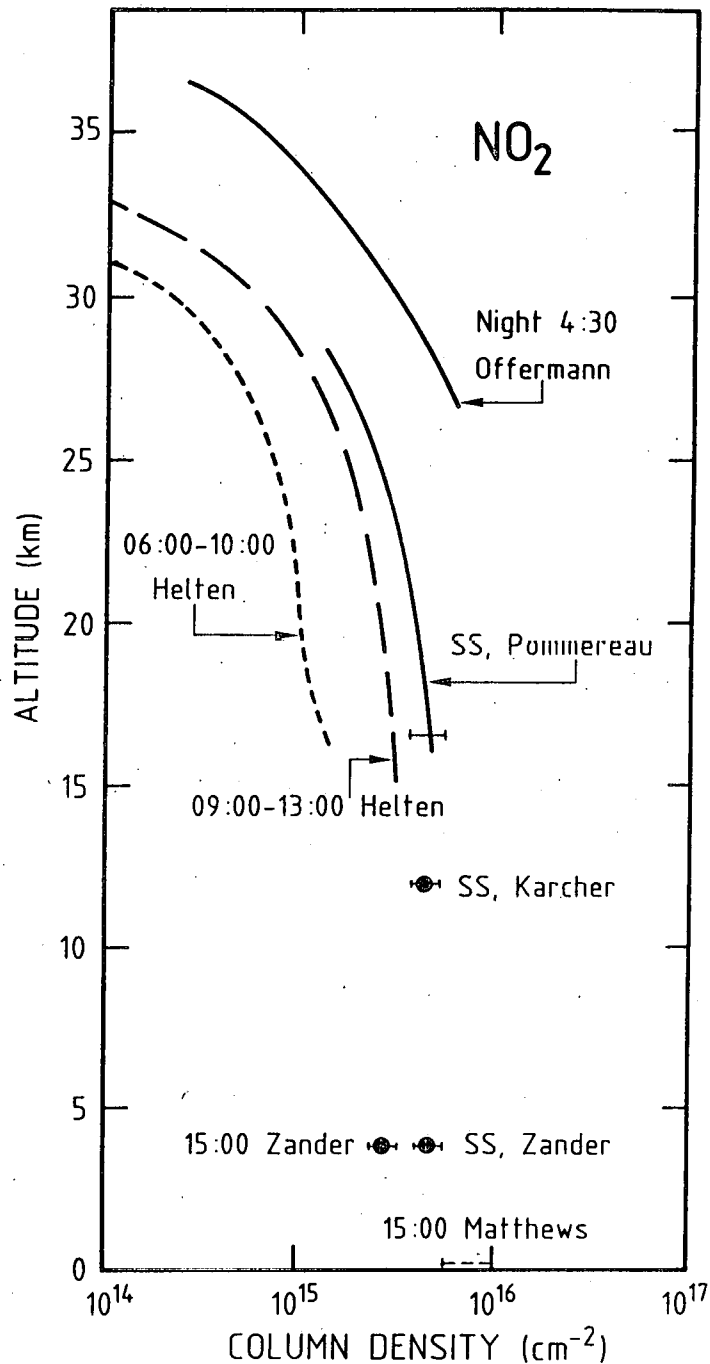


Fig. 6.- NO₂ column density above altitude. Balloon in situ and remote sensing observations have been integrated down to the lowest measurement. Balloon, plane and ground determinations at sunset would be in agreement only if the average mixing ratio below 16 km was lower than 1.5×10^{-10} . Comparison between ground measurements at 1500 and 3000 m altitude and at sea level would imply 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.

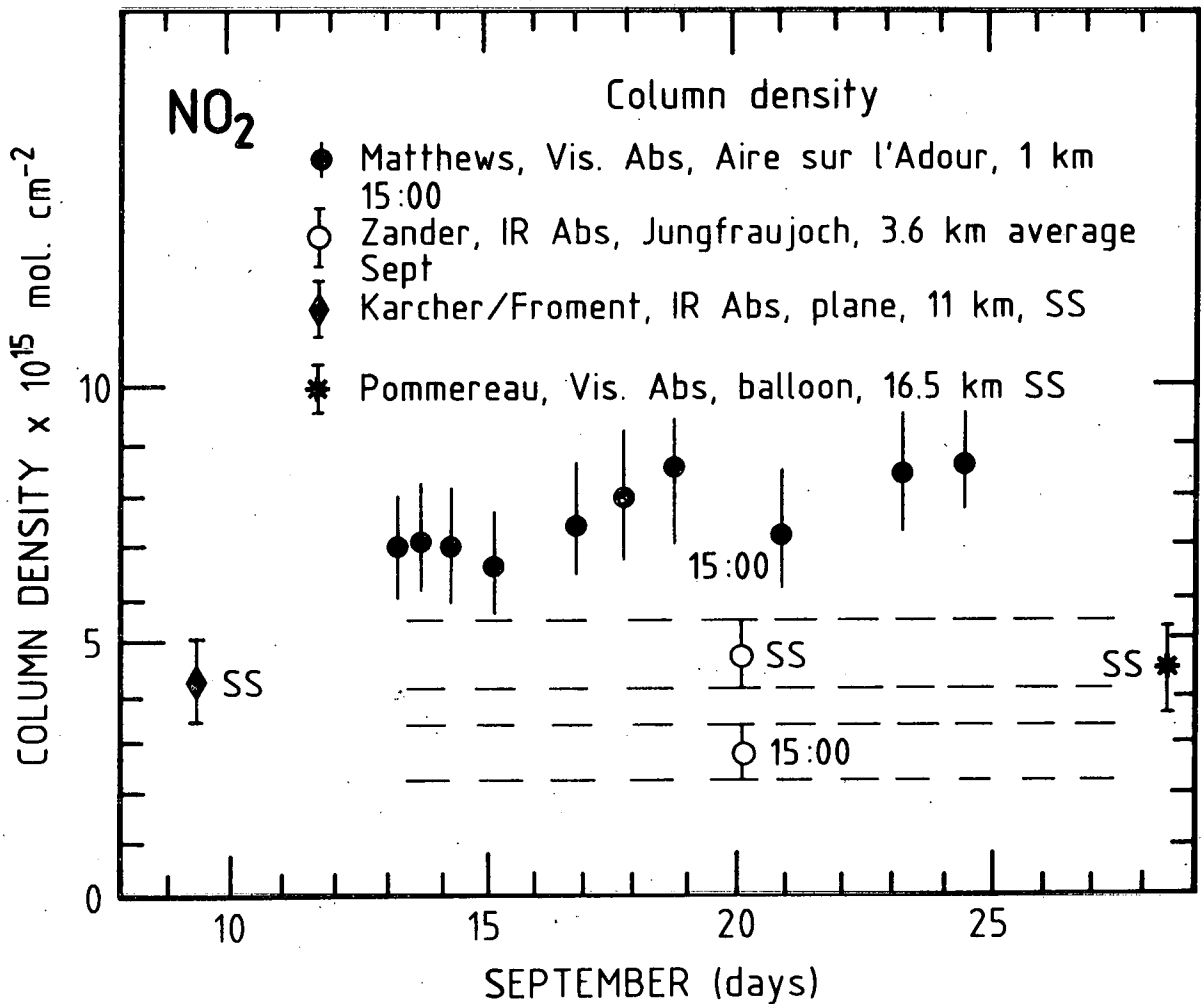


Fig. 7.- NO₂ column density variation during Globus. Matthews measurements sequence do not show any significant variation which should be the case if the difference with average Zander observation at 3000 m was the result of high pollution above Aire sur l'Adour.

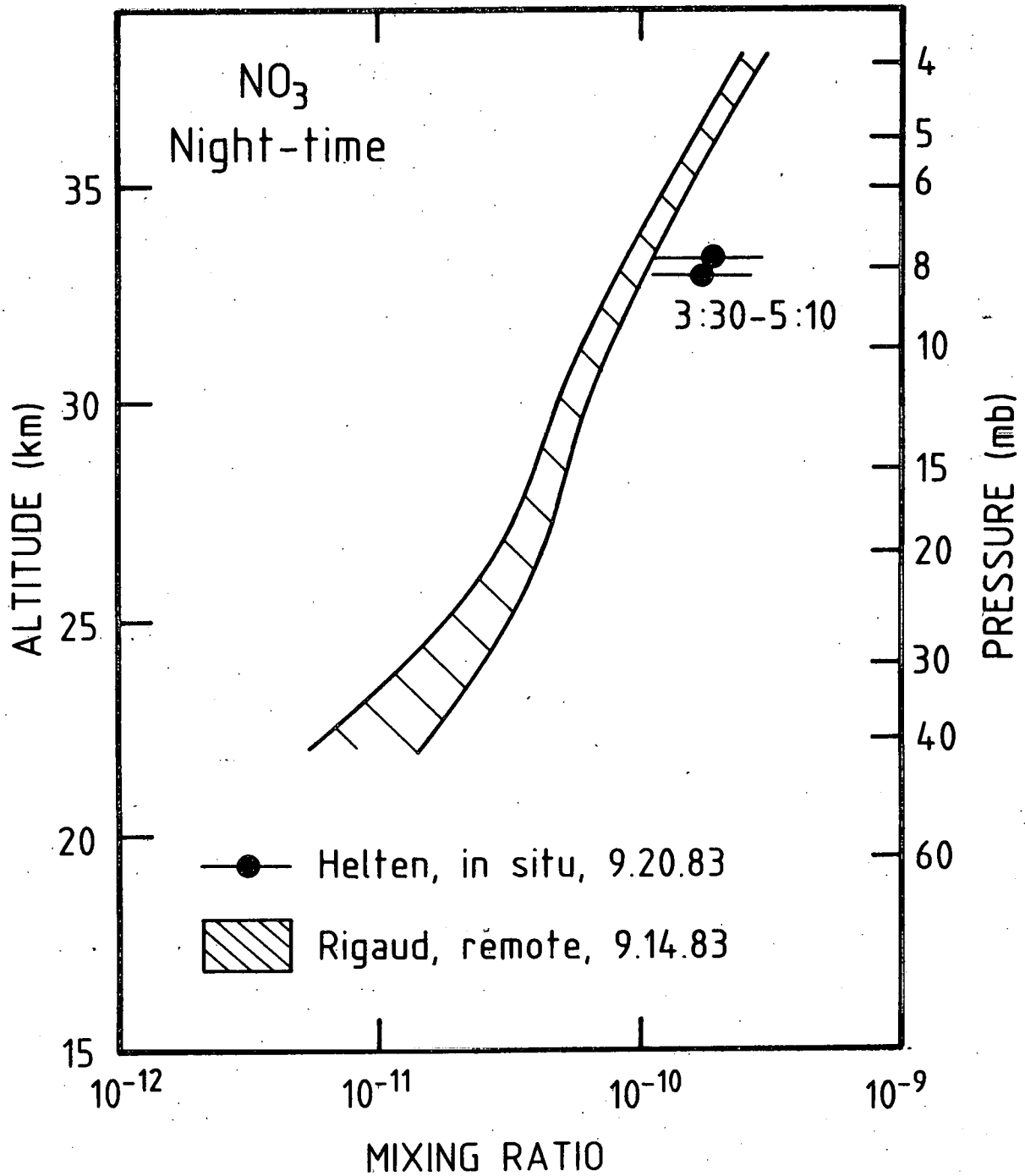


Fig. 8.- NO₃ observations during Globus. In situ results are 2 times higher than remote. This could be explained by systematic calibration errors on both instruments. More laboratory work is in progress to resolve the discrepancy.

account the two data sets overlap. More work is needed to improve the accuracy of NO_3 observations.

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ANNEX

TABLE 1.- MAP/GLOBUS representative atmosphere average 9-28 September 1983.

Altitude	Pressure	Temperature	Ozone partial
KM	MB	C°	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 2.- NO₂ in situ, chemiluminescence and converter, balloon flight
of 9-20-1983. Fabian, MPAE, Lindau.

Time UT	Pressure mb	Temps °C	Altitude Km	Conc 10 ⁹ cm ⁻³	Mixing ratio ppbv	Accuracy
9.59	27.6	- 50	24.6	4.23	4.32	> 30 %
10.03	23.4	- 50	25.7	4.87	5.94	> 30 %
1042	12.9	- 41	29.6	2.75	6.24	25%
47	13.4	- 41	29.3	2.53	5.39	
1205	16.0	- 45	28.1	2.51	4.49	
09	16.5	- 45	27.9	2.08	3.64	
14	17.0	- 46	27.7	1.73	2.88	
23	18.1	- 46	27.3	1.70	2.69	
1232	19.0	- 47	27.0	1.54	2.33	
59	23.5	- 48	25.7	1.89	2.31	
1303	24.0	- 48	25.5	1.47	1.71	

TABLE 3.- NO₂ in situ, matrix isolation, balloon flight of 9-9-1983 and 9-20-1983. Helten, KFA, Julich.

Time UT	Pressure mb	Temp °C	Altitude Km	Conc 10 ⁹ cm ⁻³	Mixing ratio ppbv	Accuracy %
9,9,1983						
8.10-9.05	7.0-8.3	-37.7	33.9	.561	2.57	± 13.6
8.54-9.54	7.5-13.6	-41.0	31.2	1.82	5.55	± 12.6
9.25-10.37	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	.975	± 11.7
12.04-13.03	41.5-86.0	-55.9	19.5	2.03	.969	± 11.7
12.43-13.37	64.9-115	-58.8	16.6	< .16	< 0.048	
13.04-13.53	87 -130	-59.9	15.7	.22	.056	± 11.7
9,20,1983						
3.30-4.30	7.3 - 7.5	-43.6	33.2	1.24	5.23	± 13.5
4.08-5.10	7.3 - 7.5	-43.6	33.3	1.24	5.29	± 13.4
4.31-5.26	7.4 - 7.5	-43.6	33.0	1.36	5.59	± 13.4
5.11-6.16	7.5 - 9.7	-44.3	32.8	1.36	5.44	± 13.3
6.00-6.52	8.3 -13.2	-45.4	30.6	.886	2.51	± 12.5
6.33-7.30	11.4-20.6	-48.0	28.4	1.17	2.35	± 12.1
7.19-8.16	18.2-37.3	-51.4	24.3	.845	.898	± 11.8
8.00-8.55	30.6-57.7	-54.5	21.3	.370	.244	± 11.7
8.49-9.38	53.5-100	-58.0	17.8	.852	.314	±11.7
9.03-9.51	69.7-129	-58.9	17.1	1.68	.554	± 11.7

TABLE 4. NO₂ remote sensing, thermal emission, balloon flight of
9-23-1983. Offermann, Wuppertal.

Time UT	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	
	4.85	-34.5	36.5	1.32	9.0	+ 19 - 29	.24
	5.02	-35	36.2	1.45	9.5	+ 19 - 29	
	7.62	-41	33.3	5.4	22.6	+ 19 - 34	1.12
	12.6	-46.5	30.0	6.5	16.1	+ 20 - 23	2.90
	20.9	-51.5	26.7	6.8	10.0	+ 24 - 29	5.54

TABLE 5.- NO₂ remote sensing, visible spectrometry at night,
balloon flight of 9-14-1983. Rigaud, LPCE, Orléans.

Time UT	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 6.- NO₂ remote sensing, visible spectrometry at sunset, balloon flight of 9-28-1983. 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 7.- NO₂ remote sensing, visible spectrometry at sunset, balloon flight of 9-28-1983. Pommereau, CNRS, Verrières-le-Buisson.

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	.82	± 50	4.10
100	-67	16.5	1.7	.50	± 70	4.40

TABLE 8.- NO₂ remote sensing. Column densities measurements from plane and ground Karcher, CNRM, Toulouse; Zander, Liège, Belgium and Matthews, DSIR, New Zealand.

Date	Altitude km	Time	Column density 10 ¹⁵ mol cm ⁻²	Accuracy	Author
Sept. 19	11.9	Sunset	4.43	± 0.58	KARCHER
Sept. 8 to Oct. 10	3.8	1500	2.75	± 0.45	ZANDER
	3.8	Sunset	4.65	± 0.60	ZANDER
Sept. 13	0.	1130	6.9	± 30%	MATTHEWS
		1500	7.5		
Sept. 14		1500	7.0		
Sept. 15		1500	6.5		
Sept. 17		1500	7.3		
Sept. 18			8.0		
Sept. 19			8.5		
Sept. 21			7.0		
Sept. 23			8.2		
Sept. 24			8.5		

Pressure	Temp	Altitude	Conc	Mixing	Accuracy
mb	°C	km	10^7 cm^{-3}	ratio ppbt	%
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 9.- NO_3 remote sensing observations during balloon flight of 9-14-1983 around 03:30. Rigaud, LPCE, Orléans.

TABLE 10.- NO₃ in situ measurements during balloon flight of 9-20-1983 at the end of night and sunrise period. Helten, KFA, Julich.

Time UT	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	< .7	< 34	
5.11-6.16	7.5-9.7	-44.3	32.8	< .5	< 12	
6.00-6.52	8.3-13.2	-45.4	30.6	< .7	< 16	
6.33-7.30	11.4-20.6	-48.0	28.4	< 1.3	< 22	

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