

Tunable Diode Laser Measurements of Trace Gases during the 1988 *Polarstern* Cruise and Intercomparisons with other Methods

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Abstract. Measurements of NO_2 , HCHO, and H_2O_2 were made by the highly specific method of mid infra-red absorption spectroscopy using tunable diode lasers (TDLAS) during the 1988 *Polarstern* expedition. The TDLAS data are compared to those obtained during the cruise using less direct methods. Southern Hemisphere NO_2 levels suggest net photochemical destruction of O_3 in the boundary layer. Northern Hemisphere HCHO averaged 0.47 ± 0.2 ppbv; the HCHO measurements are used in a simple calculation to estimate OH noontime maxima of $3\text{--}6 \times 10^6 \text{ cm}^{-3}$.

Key words: Tunable diode lasers, atmospheric trace gases, nitrogen dioxide, hydrogen peroxide, formaldehyde, maritime boundary layer, measurement intercomparisons.

1. Introduction

Measurements of NO_2 , HCHO, and H_2O_2 were carried out aboard RV *Polarstern* during September–October 1988 using tunable diode laser absorption spectroscopy (TDLAS). A description of the cruise route and the synoptic meteorology is given by Platt *et al.*, (1992). Details of the TDLAS equipment and procedures are reported elsewhere (Harris *et al.*, 1989a; Zenker, 1990) but a new inlet system was employed during the cruise and is described in the next section. The apparatus is capable of monitoring up to four species simultaneously, however because of technical problems, TDLAS measurements of the above molecules were not carried out throughout the entire cruise. NO_2 was measured continuously from 30° N to 30° S , but HCHO and H_2O_2 data were obtained only in the Northern Hemisphere.

The TDLAS measurements overlapped with other measurements of the same

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molecules by potentially less specific techniques, aiding in the assessment of these other data. This paper presents the TDLAS data on HCHO, NO₂, and H₂O₂ and compares them to measurements of HCHO made by one of us (B.M.) using a chromatographic method and to other measurements of NO₂ and H₂O₂ made during the cruise, (Rohrer and Brüning, 1992; Jacob and Klockow, 1992). We also use our data to make an estimate of the OH radical levels and to discuss the nett photochemical ozone production in the measurement region.

2. TDLAS Sampling and Calibration Systems

In TDLAS, ambient air is pumped at reduced pressure through a multi-reflection White cell. As in all trace gas analysis methods in which the air must be sampled, particular attention must be given to the design and characterization of the sampling system. A specially designed inlet system, shown in Figure 1, was employed aboard *Polarstern* because we were concerned that sea-salt aerosol could modify the characteristics of Teflon surfaces and could release adsorbed or dissolved gas phase species when drawn into the reduced pressure region of the White cell.

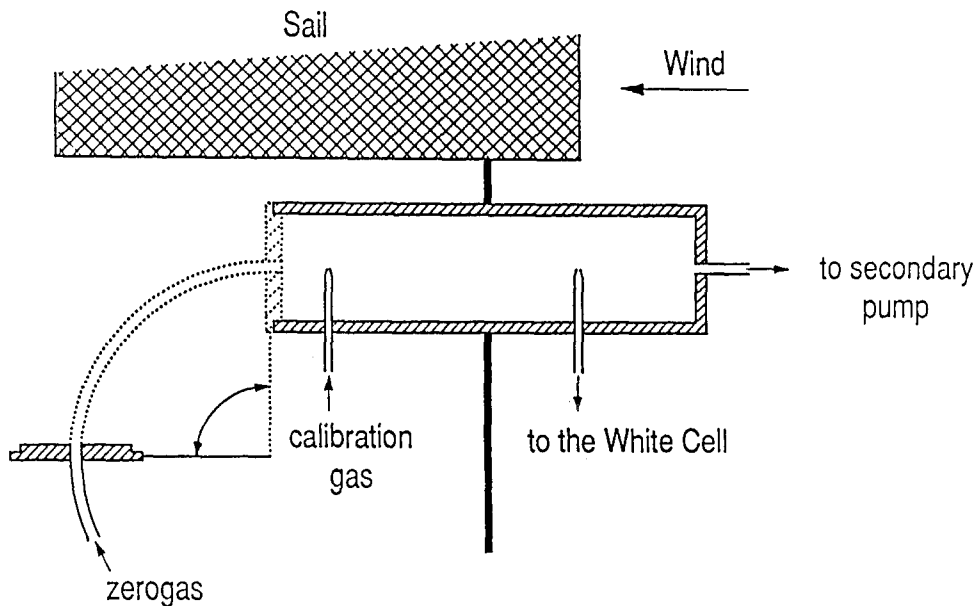


Fig. 1. Schematic of the inlet and calibration system used in the TDLAS measurement aboard *Polarstern*.

The inlet system consisted of a 2.5 cm internal diameter Teflon tube through which air was pumped at ~ 12 slm, resulting in a linear pumping velocity along the tube of ~ 0.4 m s⁻¹. The tube was mounted so that it rotated around an axis attached to a (Teflon) wind vane and thus always pointed 180° away from the relative wind vector. The relative wind speed during the cruise was typically more than 5 m s⁻¹, thus larger particles tended not to be drawn into this first part of the sampling system. Further discrimination against particles was gained by sampling the air (at 6–8 slm) into the White cell through a 1 mm diameter Teflon orifice mounted at right angles to the gas flow in the first tube. The orifice also served to reduce the pressure in the White cell to 35 mbar. As a further precaution, all TDLAS data for relative wind velocities lower than 2 m s⁻¹ ($\sim 5\%$ of all data) were rejected because of possible contamination from the ship or from sea-salt.

Four calibration gases could be added singly or simultaneously through Teflon injectors placed radially around the 2.5 cm inlet tube near its open end, thus allowing the spectrometer and its complete inlet system to be calibrated by addition of known flows of the target gases.

During calibrations and acquisition of background spectra, the ambient air flow could be replaced with a flow of zero gas by activating a pneumatically driven arm, (shown in Figure 1), which sealed the end of the inlet tube against ambient air and placed a tube carrying dry nitrogen at the mouth of the inlet system. Thus ambient air and calibration gases passed over exactly the same surfaces throughout the instrument. The Teflon 3-way solenoid valves used to switch the flows into the inlet system were mounted in a box directly under the plate carrying the wind vane and inlet system assembly to minimize response time to the calibration gases.

The inlet/calibration assembly was mounted 22 m above sea level on a mast on the roof of our container, located on the starboard side of the compass deck near the forward rail, (position B, Platt *et al.*, 1992).

During the cruise it became apparent that a ventilation exhaust located on the port side of the ship below the compass deck was sometimes causing contamination at our sampling position. The contamination was easily detectable using the NO₂ measurements which increased to over 100 pptv whenever the relative wind direction was $285 \pm 10^\circ$. This situation was common in the North-East Trades region of the northern hemisphere (see Platt *et al.*, (1992) for the synoptic meteorology) but fortunately occurred very rarely in the Southern Hemisphere. All data were rejected when the relative wind came from $285 \pm 15^\circ$. A further small amount of data was discarded because of probable contamination by emissions from nearby ships.

3. Measurement Intercomparisons and Discussion of the Data

3.1. Formaldehyde

TDLAS applied to HCHO measurement has been described in some detail (Harris *et al.*, 1989a). DNPH HCHO data were obtained by one of us (B.M.) using the

methods described earlier (Schubert *et al.*, 1988), employing both cooled (2–4 °C), and uncooled (~25 °C) samplers containing aqueous DNPH solutions at pH 2.4. Most samples were collected with the cooled samplers to allow the simultaneous determination of acetaldehyde, which is collected with only low efficiency in uncooled samplers. However, comparison of the HCHO data from the cooled samplers with that from both the uncooled DNPH samplers and the TDLAS, indicated significant positive interferences or artifacts for cooled samplers. Similar effects have previously been reported (Schubert *et al.*, 1988) for summertime conditions, but are apparently not observed during winter or other periods of low photochemical activity. The data on HCHO and acetaldehyde obtained with the cooled DNPH samplers during this cruise are considered unreliable, and are not reported.

The TDLAS is calibrated relative to a permeation device whose output is determined both gravimetrically and colourimetrically using the chromotropic acid method as described by Harris *et al.* (1989a). On *Polarstern*, the TDLAS permeation device output was also determined using the DNPH analytical system and the agreement between the standards was within the uncertainty of the TDLAS standard ($\pm 5\%$).

A total of eight fully overlapping measurements of atmospheric HCHO by TDLAS and the uncooled DNPH method were made and are presented in Table I. The TDLAS data was averaged over the DNPH sampling periods (usually approximately one hour). The mean ratio of the DNPH data to the spectroscopic measurement is 0.91 ± 0.28 ($N = 8$), with only one measurement pair differing by more than the combined estimated uncertainty. If this latter measurement pair is rejected, the mean ratio (DNPH/TDLAS) is 0.98 ± 0.23 ($N = 7$). The correlation between individual data points is only moderate ($r = 0.71$) because the errors are large compared to the range of observed values, but the results do suggest that the DNPH method with an uncooled sampler does not suffer from undue interference or artifacts, and that both methods are sufficiently sensitive to make formaldehyde

Table I. Directly overlapping HCHO measurements made by tunable diode laser spectroscopy and the DNPH-HPLC method

TDLAS		DNPH		Ratio DNPH/TDLAS
ppbv	\pm	ppbv	\pm	
0.48	0.09	0.44	0.17	0.92
0.39	0.09	0.41	0.07	1.05
0.62	0.17	0.57	0.05	0.92
0.57	0.25	0.48	0.04	0.84
0.29	0.24	0.40	0.05	1.38
0.48	0.19	0.28	0.05	0.58
0.29	0.06	0.33	0.03	1.14
0.50	0.14	0.21	0.10	0.42

measurements in the remote marine boundary layer, as previously reported (Lowe and Schmitt, 1983; Schubert *et al.*, 1988; Harris *et al.*, 1989a, b; Zenker, 1990).

The mean mixing ratio of formaldehyde measured by TDLAS was 0.47 ± 0.2 ppbv between 40° N and 17° N, exhibiting no systematic diurnal variation, but with a gradient towards lower values in the south of the measurement region. Weak diurnal HCHO variation in the remote boundary layer has been observed previously (Lowe and Schmitt, 1983; Schubert *et al.*, 1988; Harris *et al.*, 1989b), although the first of these reports indicates diurnal variations with an amplitude of up to 0.1 ppbv for a four day period near the equator. Such a weak variation would lie within the error bars of our data. Arlander *et al.* (1990) also report small HCHO diurnal variations from ship board measurements in the Pacific and Indian Oceans, (April–July 1987), except for cases where elevated measured alkene mixing ratios indicated local photochemical production of the HCHO.

In the atmosphere over the ocean, the predominant source of HCHO is thought to be methane oxidation, especially in areas of low biological activity such as in the present case (Plass *et al.*, 1990) where emissions of reactive hydrocarbons from the ocean surface are less important. Since the gas phase source (OH attack on methane), and the gas phase sinks (OH attack on HCHO and photolysis of HCHO) vary similarly throughout the day, the mean diurnal variation is determined largely by deposition of HCHO.

Zafariou *et al.* (1980) deduced a deposition velocity for HCHO to the ocean surface of 0.4 cm s^{-1} . Previous TDLAS studies of the diurnal variation of HCHO in the marine boundary layer (Harris *et al.*, 1989b; Zenker, 1990) have been used to estimate the deposition velocity for HCHO to the ocean surface as $< \sim 0.3 \text{ cm s}^{-1}$ and this seems to be consistent with the majority of the data reported by Lowe and Schmitt (1983). Thus under clean air conditions over the oceans, with a mixed boundary layer depth of $\sim 1 \text{ km}$, deposition probably accounts for less than about 10% of the total HCHO loss and the HCHO mixing ratio is largely determined by the gas-phase chemistry, at least under cloud free, non precipitating conditions.

It is therefore possible to make estimates of the prevailing hydroxyl radical concentrations from the HCHO mixing ratios by using measured or expected hydrocarbon concentrations and HCHO photolysis rates. With the aid of hydrocarbon measurements carried out on board (Koppmann *et al.*, 1992), HCHO photolysis rates adapted from the 2D model of Kanakidou *et al.* (1991a) and a simple stationary state model, we used the mean HCHO data from the TDLAS and DNPH data sets for 5° latitude intervals to estimate the mean noontime OH concentrations shown in Table II. We assumed unit HCHO yield from hydrocarbon and a HCHO lifetime against deposition of ~ 90 hrs. We ignored the $\text{NO}_3 + \text{HCHO}$ reaction, which, based on the NO_2 data (this work, Brüning and Rohrer, 1990), and on the DOAS measurements aboard *Polarstern*, (Platt *et al.*, 1990) could not have been important under the conditions. The errors associated with these OH calculations are very large, arising from the uncertainty in the HCHO measurements themselves and from the use of model-derived rather than directly measured J values. How-

Table II. Mean calculated OH concentrations based on the HCHO data

5° Int. of latitude	[Alkene] ^a (pptv)	10^{-5} $J_{\text{HCHO}}^{\text{b}}$ (s^{-1})	HCHO ^c (ppbv)	Mean noon OH _{calc} ^d 10^6 cm^{-3}
45–40° N ^c	200	3.6	0.65	5.4
40–35° N ^f	150	3.9	0.55	4.5
35–30° N ^g	60	4.8	0.53	6.1
30–25° N	40	5.0	0.46	4.9
25–20° N	50	5.3	0.34	3.1
20–15° N	50	5.5	0.32	2.9
15–10° N	50	5.8	0.41	4.5

^a Estimated from Koppmann *et al.* (1990): Composition taken as two-thirds ethene, one-third propene.

^b Adapted from the Mainz 2D model for September, no clouds; (Kanakidou *et al.*, 1991a).

^c Mean of TDLAS and DNPH measurements.

^d See discussion in text.

^{e,f,g} Mean longitude 17°, 24°, 28° W: Other data at 30° W.

ever, despite the crudeness of the estimates, the OH concentrations are consistent with expectations based on the results of more sophisticated modelling exercises (e.g. Kanakidou *et al.*, 1991b), or, conversely put, our HCHO measurements are, within the measurement accuracy, consistent with the chemistry included in such models.

3.2. Hydrogen Peroxide

The TDL H_2O_2 calibration source is a permeation device of the type described previously (Slemr *et al.*, 1986) calibrated colorimetrically using TiCl_4 and by titration with KMnO_4 . A chemiluminescence technique used by Jacob *et al.* to determine H_2O_2 is described elsewhere (Jacob *et al.*, 1986) and the ambient measurements obtained during this cruise are reported separately (Jacob and Klockow, 1992). Three samples collected from our permeation device were also analysed using the chemiluminescence method. In two cases, the analyses were within 10% of the expected values, but for unknown reasons the third chemiluminescence analysis indicated only about half of the expected H_2O_2 . Unexpected variability in the H_2O_2 permeation source output was not observed during the frequent calibrations of the TDLAS and we believe that the low result of the third analysis may have been due to contamination of the vessel used to collect the sample.

Overlapping TDLAS and chemiluminescence measurements were made from the evening of 20 September until shortly after dawn on 22 September in the Azores region of the Atlantic. Light rain occurred from 01:00 until 04:00 on 21 September during the 6 h overnight sample collection for the chemiluminescence method (Jacob and Klockow, 1992). After the rain event, both methods indicated a

parallel increase in the H_2O_2 mixing ratio during the morning of the 21 September to values of 1.2–1.4 ppbv during the afternoon (see Figure 2). Both methods then showed rather steady values of H_2O_2 until midnight, which then decreased to 0.6–0.8 ppbv throughout the rest of the night. The agreement between the two techniques was reasonable during this period. However, at the beginning of the overlapping measurements shown in Figure 2, during and preceding the light rain event of the night of the 21st, the TDLAS showed values of H_2O_2 which were much lower than those from the chemiluminescence method (TDLAS 0.6–0.1 ppbv, CL 1.2–0.5 ppbv), although the trends were similar, (Figure 2). The reason for the discrepancy is not clear, but possibly either the chemiluminescence samples became contaminated by aqueous phase H_2O_2 , or the throughput of the TDLAS inlet system was lower for ambient levels of H_2O_2 under conditions of near 100% relative humidity, than for the calibration H_2O_2 carried by dry nitrogen.

The agreement between the two techniques, at least under the nonprecipitating conditions predominant during the cruise, lends support to the H_2O_2 data set reported by Jacob and Klockow, (1992). Our previous studies of H_2O_2 in the tropical and equatorial regions of the Atlantic Ocean (Harris *et al.*, 1989b; Zenker,

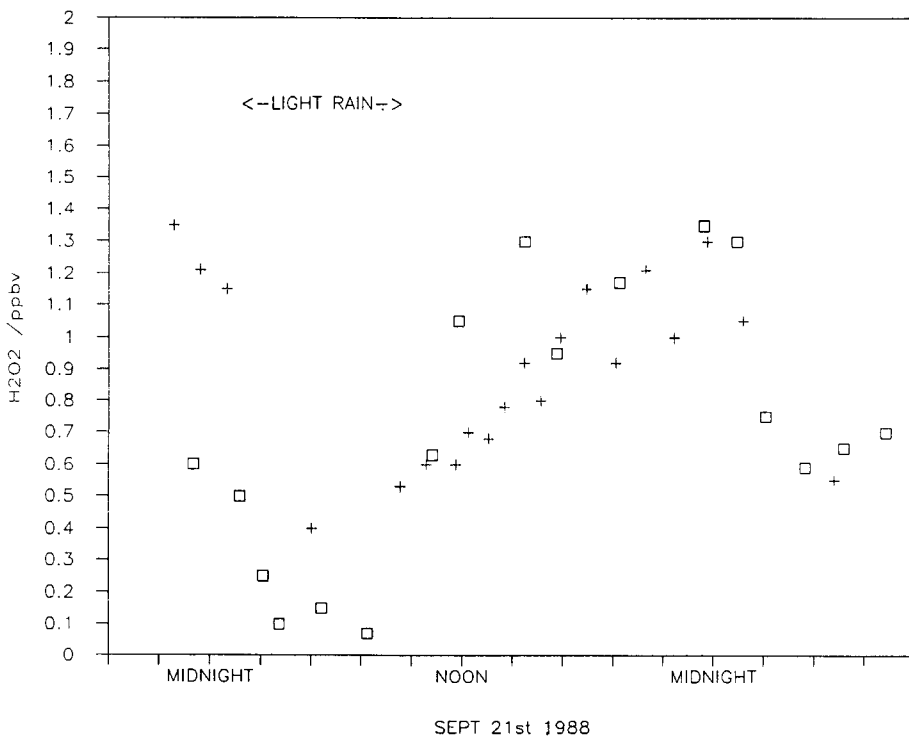


Fig. 2. Hydrogen peroxide data obtained using TDLAS (squares) and chemiluminescence (crosses). The CL data are adapted from Jacob and Klockow (1990).

1990) showed similar levels and latitude dependence for H_2O_2 , but did not suggest the diurnal variation with nighttime maxima reported by Jacob and Klockow (1992). Unfortunately, further TDLAS H_2O_2 measurements could not be carried out during the *Polarstern* cruise due to the failure of the diode laser and the restricted data set does not allow us to comment on the latitudinal distribution or diurnal variation of H_2O_2 during this cruise.

3.3. Nitrogen Dioxide

The calibration source for the NO_2 measurements is a permeation device whose output at 40 ± 0.2 °C has been determined by repeated weighings to be 332 ± 20 ng min^{-1} . NO_2 was also measured on *Polarstern* by Brüning and Rohrer using a photolytic converter – NO/O_3 chemiluminescence device (Brüning and Rohrer, 1990). After the ambient measurements during the cruise were completed, the chemiluminescence instrument was used to check the output from our calibration source. This was not done earlier because the chemiluminescence instrument was located elsewhere on the ship (position C, Platt *et al.*, 1992). The output of our permeation device appeared to oscillate on a time scale of minutes between values of 265 ng min^{-1} and 290 ng min^{-1} based on the standard and the dilution system of Brüning and Rohrer (1990), in a manner which suggested a possible defect in the temperature control circuitry. This behaviour was not observed later in Mainz, but nevertheless this observation introduces an additional uncertainty in our NO_2 data. We have used our measured permeation rate of 332 ng min^{-1} to analyse our data but recognize a possible ~20% calibration error. For the measurements reported here, where the ambient NO_2 was usually near (or below) our detection limits, the major uncertainty comes from the measurement precision (see below) rather than from the decreased calibration accuracy.

The detection limit for NO_2 by TDLAS using 5 min signal averaging was usually ~20 pptv. Co-addition of the individual 5 min spectra, and numerical reprocessing to reduce the effects of noise and drift, improved mixing ratio retrieval from the spectra at the expense of time resolution. Individual spectra were corrected for changes in the optical power due to slow drifts in the alignment of the spectrometer before co-addition to form the averages.

The mean retrieved NO_2 mixing ratios for each 2° latitude interval are shown in Table III, and graphically in Figure 3. In the table, the third column shows the statistical 95% confidence intervals (not including calibration uncertainty) on the central values calculated by consideration of the residuals after a least-squares fit of the calibration spectra to the averaged, background corrected, ambient air spectra. It can be seen that in about one half of the measurements, and especially in the Southern Hemisphere, the confidence intervals include zero NO_2 mixing ratios. However, the method used to derive ambient mixing ratios from the spectra is equally likely to produce positive and negative results if NO_2 is truly absent (log-normal distribution about zero), while only one of the 22 calculated NO_2 mixing

Table III. Mean mixing ratios of NO₂ in 2° latitude intervals as measured by TDLAS

Centre of latitude interval (N+, S-)	Mean NO ₂ (pptv)	95% confidence interval (pptv)	No. of spectra in avg.
29	62.6	± 12.0	12
27	52.8	± 18.5	16
17	44.5	± 14.5	5
13	34.5	± 11.0	20
11	34.7	± 22.0	23
5	12.0	± 12.6	71
3	18.5	± 12.7	84
1	13.1	± 14.8	105
-1	19.5	± 14.8	41
-3	16.7	± 15.5	90
-5	21.8	± 9.5	54
-7	11.1	± 11.0	51
-9	6.4	± 7.4	116
-11	8.4	± 8.0	90
-13	5.8	± 7.3	66
-15	15.2	± 10.6	94
-17	15.3	± 8.3	74
-19	-1.7	± 8.9	60
-21	2.6	± 5.7	45
-23	5.1	± 10.1	84
-25	12.3	± 9.6	63
-27	3.1	± 12.7	86

ratios in Table II is negative. This gives us confidence that the TDLAS data may be used to draw semi-quantitative conclusions about the NO₂ mixing ratios encountered during the cruise. In Figure 3, the indicated error bars include the 95% statistical confidence limit and the calibration uncertainty of ± 20%.

The data may be compared with the measurements using chemiluminescence (CL) and a photolytic converter by Rohrer and Brüning (1992). For the Southern Hemisphere they report an upper limit for the mean NO₂ of ~22 pptv, the upper limit arising because of probable contamination from the ship at their sampling position (position C, Platt *et al.*, 1992). In the Southern Hemisphere our relative wind direction filter (285 ± 15°) passed virtually all of the TDLAS data and the mean Southern Hemisphere result was 10 ± 13 pptv NO₂ which may further suggest slight contamination at position C. In the Northern Hemisphere much of the TDLAS data was rejected by the wind direction filter (see Platt *et al.*, (1992) for the relative wind direction data), however from 30° N to about 15° N, the remaining TDLAS data were in reasonable agreement with those reported by Rohrer and Brüning. The higher mixing ratios (40–80 pptv) observed using CL between 12° N and the equator are not apparent in our data set. During the first part of this period the relative wind direction lay within the sector causing contamination at our measurement location and we rejected our data. The relative

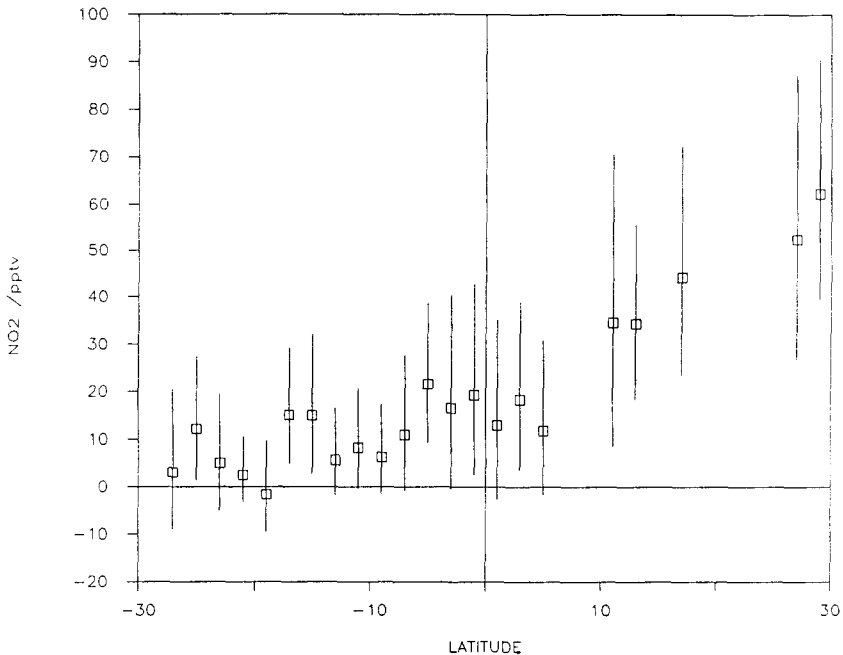


Fig. 3. Mean measured NO₂ mixing ratios in 2° latitude intervals. The errors include the calibration uncertainty (see text.)

wind speed was also often very low resulting in further data rejection. However between 6° N and 0°, the relative wind was favourable but the TDLAS values lay between 10 and 17 pptv, considerably lower than the CL values. The comparison of the two data sets suggests that the main difficulty in making accurate remote boundary-layer measurements of NO₂ from a ship is the inevitable presence of sources of NO_x aboard the vessel itself. At the sampling point used for the TDLAS (22 m above sea level) the influence of local sources seems to have been easier to identify and, after the application of the wind speed and relative wind direction filters, we believe that the remaining NO₂ measurements were free from influence by local emissions.

The Northern Hemisphere NO₂ mixing ratios measured by TDLAS were generally between 30 and 60 pptv, with lower values nearer the ITCZ. Although the NO₂ was very near or below the TDLAS system detection limits, the averaged data shown in Table III indicate that the Southern Hemisphere NO₂ levels were 10–20 pptv from the equator to about 8° S and suggest even lower levels between 10° and 28° S. The median value for NO₂ measured south of the ITCZ was 11.9 pptv, which is very similar to the median value of 10.4 pptv reported for the maritime boundary layer over the eastern Pacific Ocean in August 1986 (Carroll *et al.*, 1990).

Under background conditions the net effect on ozone production caused by the

OH initiated oxidation of CO (and hydrocarbon) depends on the level of NO (Crutzen, 1979) through the competition between the reactions of the HO₂ radical with NO and with O₃ itself. Below a critical NO/O₃ ratio of approximately 4×10^{-4} (Carroll *et al.*, 1990), ozone is destroyed. An upper limit on the noontime Southern Hemisphere NO mixing ratios can be obtained from the NO₂ measurements by considering the simple photostationary state relationship (Leighton, 1961), which yields a median NO value of ~ 5 pptv. This may be compared to the upper limit on NO of 7 pptv reported by Rohrer and Brüning (1992) for the Southern Hemisphere and to the median maritime boundary-layer value of 4 pptv reported by Carroll *et al.* (1990). Since the actual values of NO will be further reduced from those calculated using our NO₂ data and the simple photostationary state relationship (because of oxidation of NO by HO₂ and CH₃O₂ radicals), the ratio of NO/O₃ in the Southern Hemisphere can be stated to have been $< 1.5 \times 10^{-4}$ and nett destruction of O₃ is predicted.

Thus the interpretation that the elevated O₃ mixing ratios observed in the southern hemisphere during the cruise were the result of long-range transport of airmasses previously associated with biomass burning in the tropics (Platt *et al.*, 1992) is supported by the TDLAS NO₂ data.

Acknowledgements

This work was supported in part by a grant from the German Ministry for Research and Technology (BMFT Contract No. 0744111).

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