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NO, NO_2 and HNO_3 below 35 km in the atmosphere

by

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FOREWORD

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NO, NO$_2$ AND HNO$_3$ BELOW 35 KM IN THE ATMOSPHERE

by

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Abstract

Experimental data on NO, NO$_2$ and HNO$_3$ in the atmosphere are reviewed. The low abundance of nitric acid in the tropospheric gas phase is emphasized as well as the high variability of NO$_x$ in the low stratosphere and in the troposphere. Some model predicted distributions of these odd nitrogen molecules are presented. Areas of agreement and of disagreement between theory and experiments are indicated.

Résumé

Une mise au point des données sur NO, NO$_2$ et HNO$_3$ dans l'atmosphère est présentée. L'accent est placé sur la faible teneur en acide nitrique de la phase gazeuse troposphérique ainsi que sur la variabilité de NO$_x$ dans la basse stratosphère et dans la troposphère. Des valeurs prédites théoriquement pour les concentrations de ces constituants contenant de l'azote non apparié sont présentées. Des points d'accord et de désaccord entre la théorie et l'expérience sont mis en évidence.

Samenvatting

Een overzicht van proefondervindelijke gegevens in verband met NO, NO_2 en HNO_3 in de atmosfeer wordt gegeven. De nadruk wordt gelegd op het lage gehalte aan salpeterzuur in de troposferische gasfaze alsook op de schommelingen van NO_x in de lage stratosfeer en in de troposfeer. Enkele theoretische verdelingsmodellen van deze niet gepaarde stikstof-moleculen worden voorgesteld. Punten van overeenstemming en afwijking tussen theorie en proefneming worden naar voor gebracht.

Zusammenfassung

Experimentale Ergebnisse über NO, NO_2 und HNO_3 in der Atmosphäre werden beschrieben. Das kleine Mischungsverhältnis der troposphärischen Salpetersäure Gas sowie die starke Verändlichkeiten von NO_x in der niedrige Stratosphäre und in der Troposphäre werden hervorgehoben. Einige theoretische Ausbreitungen diesen "odd" Stickstoff-molekülen werden vorgestellt.

Ubereinstimmungen und Uneinigkeiten zwischen Theorie und experimentale Ergebnisse werden angegeben.

Research about the stratosphere has remained rather academic untill recently. In 1971, it was assumed (Johnston, 1971), that the projected increase in oxides of nitrogen from aircrafts flying in the stratosphere could reduce the ozone shield by about a factor of 2, thus permitting the harsh radiation below 300 nanometers to permeate the lower atmosphere, and consequently endanger life at the earth surface. The interest of aeronautic industries and of governmental agencies in the problem has changed the level of activity in stratospheric research. The emphasis has been put on measuring and modeling the natural stratosphere in order to be able to predict possible modifications.

The ozone is formed from atomic oxygen resulting from the dissociation of molecular oxygen by the solar ultraviolet radiation

$$O_2 + h\nu \rightarrow O + O \qquad (1)$$
$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$
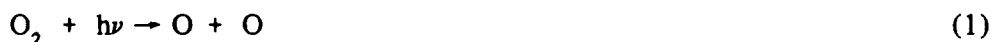
An ozone reduction would be the result of more scavenging of odd oxygen atoms in a catalytic set of reactions involving increased nitric oxide and nitrogen dioxide, as follows

$$NO_2 + O \rightarrow NO + O_2 \qquad (3)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4)$$

It is currently accepted that nitric oxide is formed in the stratosphere by reaction of nitrous oxide originating from biological activity at ground level. Since odd nitrogen molecules have not appeared to build up continuously, a removal mechanism has been suggested, based on nitric acid rain out.

Three years of experimental work have only transformed our ignorance of the real natural abundance of NO, NO_2 and HNO_3 in the stratosphere into a preliminary knowledge. It is time however to have a weighing up of the available results and to compare them with theoretical predictions.

NITRIC OXIDE

Detection of nitric oxide in the stratosphere has been reported by various authors (Toth *et al.* 1973; Ridley *et al.* 1973; Girard *et al.* 1973). Vertical distributions of this constituent have been derived by absorption spectrometry using the sun as a source (Ackerman *et al.*, 1973, 1974) and by chemiluminescence with O_3 (Ridley *et al.*, 1974). After sunset, reaction (4) should transform, into NO_2 nitric oxide that has been observed (Patel *et al*, 1974) to appear again after sunrise by the photodissociation process

$$NO_2 + h\nu \rightarrow NO + O \qquad\qquad (5)$$

regenerating atomic oxygen available for ozone formation by reaction (2). Chemiluminescence has also been used on board of high flying aircrafts (Lowenstein *et al.*, 1974) to measure stratospheric NO. This method indicates large variations at 18 and 20 km over a period of several months (Savage *et al.*, 1974).

Nitric oxide has also been determined in the mesosphere and in the lower thermosphere.

Most of the experimental data are illustrated in Fig. 1. They indicate higher number densities in the stratosphere than in the mesosphere suggesting different production regimes as postulated on theoretical grounds (Nicolet, 1971). A steep decrease is observed below 30 km and possibly an increase in the vicinity of the tropopause below which no observation is available. Most of the measurements have been obtained at mid-latitudes so that the possible meridional variation of NO can only be conjectured. Its abundance is however known (Ackerman *et al.*, 1974; Ridley *et al.*, 1974; Savage *et al.*, 1974) to vary with time and location.

The nitric oxide observations at 19 km made by Savage *et al.* (1974) from November 1973 to June 1974 from 75° to 120° West and from 33° to 49° North indicate a sudden NO increase of a factor of 7, leading to a high value of 1.4×10^9 cm^{-3} persisting
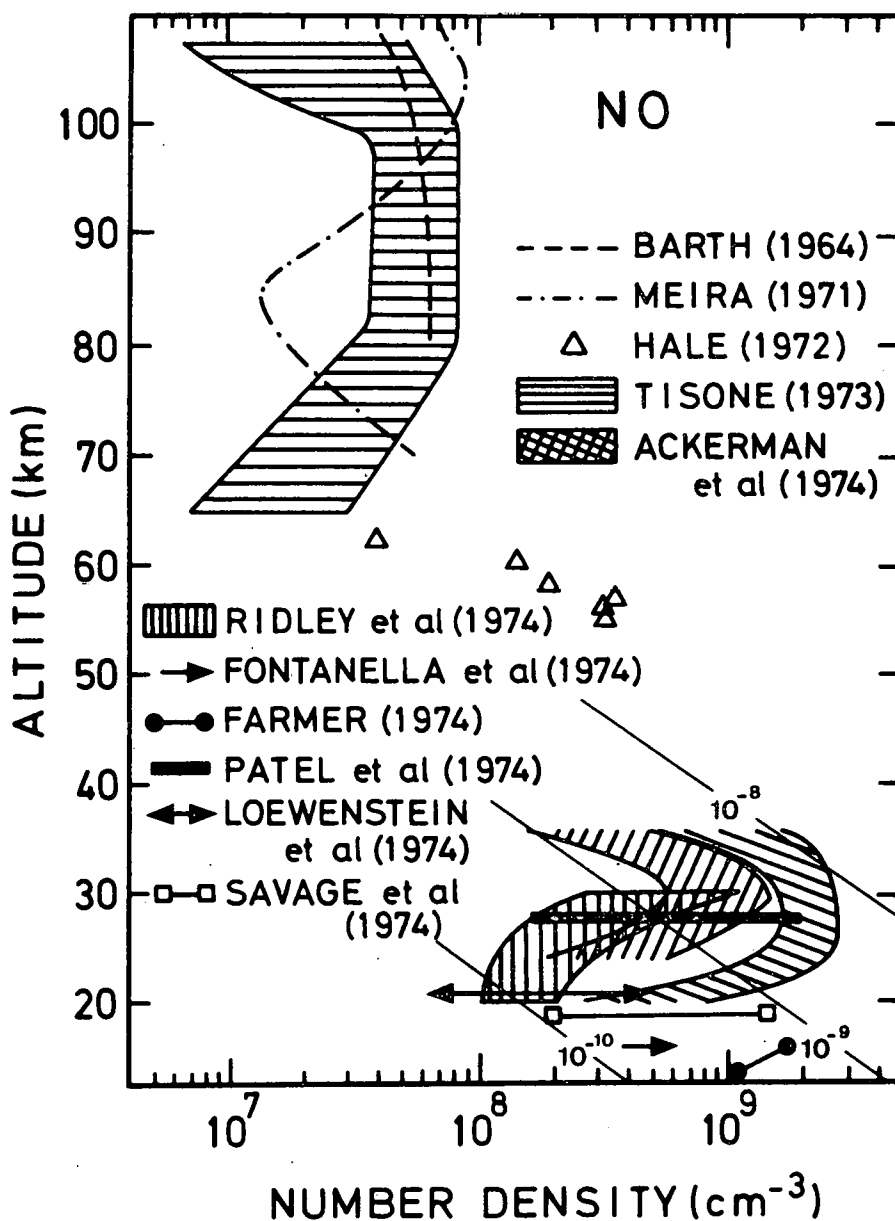
Fig. 1.- Measured nitric oxide number densities versus altitude in the chemosphere. In the stratosphere, Ackerman *et al.* (1974) have reported two very different vertical profiles respectively measured on May 14, 1973 (low) and on May 13, 1974 (high). Patel *et al.* (1974) have observed the NO variation at sunrise over more them one order of magnitude. The variation of NO in the vicinity of 20 km altitude over a few days reported by Savage *et al.* (1974) is also illustrated. Constant volume mixing ratios are roughly indicated by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

until the end of May. This has most probably to be attributed to transport by motion of air masses since the difference is to large to be accounted for by ozone fluctuations that would change the NO_2 over NO ratio by reactions (4) and (5). It is thus not astonishing that two vertical distributions observed (Ackerman *et al.*, 1974) by means of the same instrumentation in the same experimental conditions but separated by almost exactly one year and shown by Fig. 1 exhibit a difference of a factor of 2 to 10 at 24 km. The meteorological situations shown in Fig. 2a and b were very different at the two dates at the observation sites (44^0 North; -1^0 to 3^0 West). These situations where rather typical for the period preceeding the experiments, namely low pressures reaching lower latitudes in May 1974 than in May 1973. It might also be interresting to notice that soundings made over Arosa showed a very different behavior of the ozone layer below the peak at the periods of the first experiment (May 14, 1973) and the second experiment (May 13, 1973) as shown in Fig. 3a and b. A well marked tropospheric air injection process into the stratosphere was taking place in the second case from 10 to 18 km and a well marked variability existed also from 22 to 28 km as illustrated in Fig. 3b.

There are however to few measurements of nitric oxide at present to attempt quantitative evaluations of the observed variations. They exist and their interpretations require obviously the simultaneous observation of several parameters including minor constituents and dynamic processes on a synoptic basis of reasonable extent.

NITROGEN DIOXIDE

Observations of nitrogen dioxide number densities available for the troposphere and for the stratosphere are plotted in Fig. 4. Chemical analysis (Moore, 1974, Nash, 1974; Georgii and Jost, 1964) of air samples performed from ground level up to 6 km altitude and remote spectrometry (Brewer *et al.*, 1973) have been used in the troposphere to determine NO_2. The experimental values are spread over almost two orders of magnitude. Measurements of supposed unpolluted ground level air indicate values that could differ by more than 100. Georgii and Jost (1964) conclude from their measurements made on board of aircrafts that tropospheric NO_2 originates partly from biological activity in soils, the latter
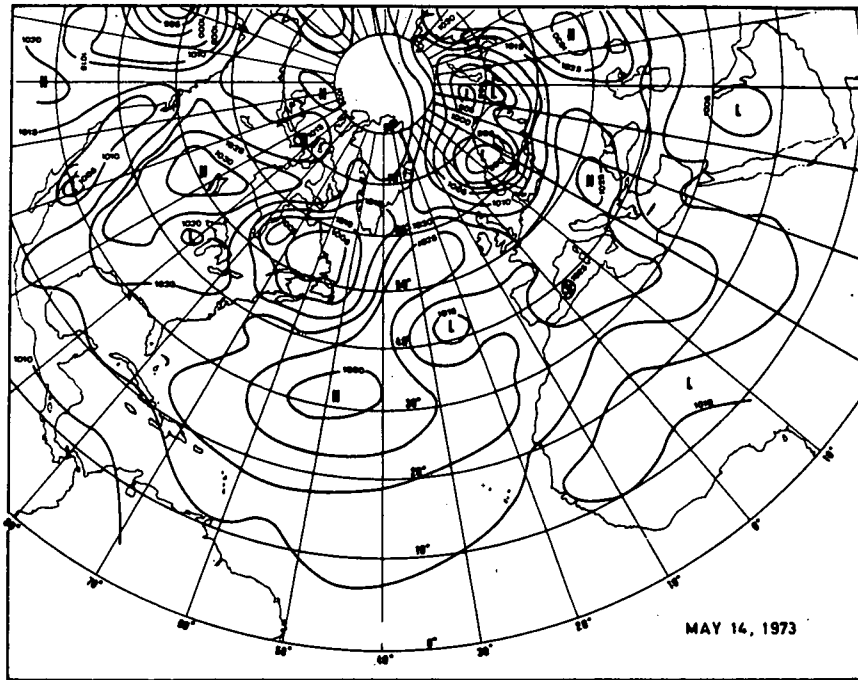
2a
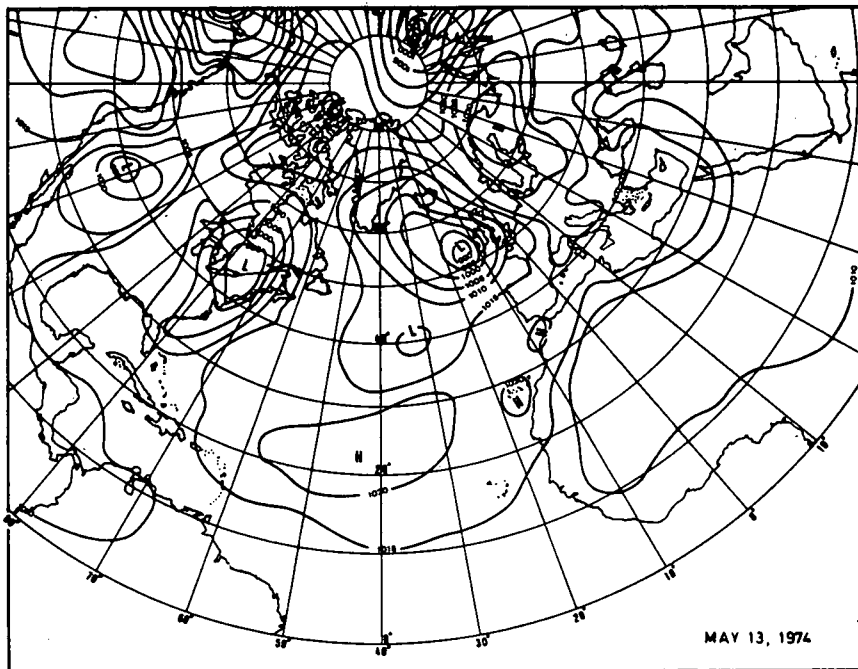
2b

Fig. 2.- Surface pressure maps at the two dates of the NO measurements
reported by Ackerman *et al.* 1974. Low pressures were extending
towards lower latitudes on May 14, 1974 (Fig. 2a) than in the case of
May 13, 1973 (Fig. 2b). These situations were rather characteristic of
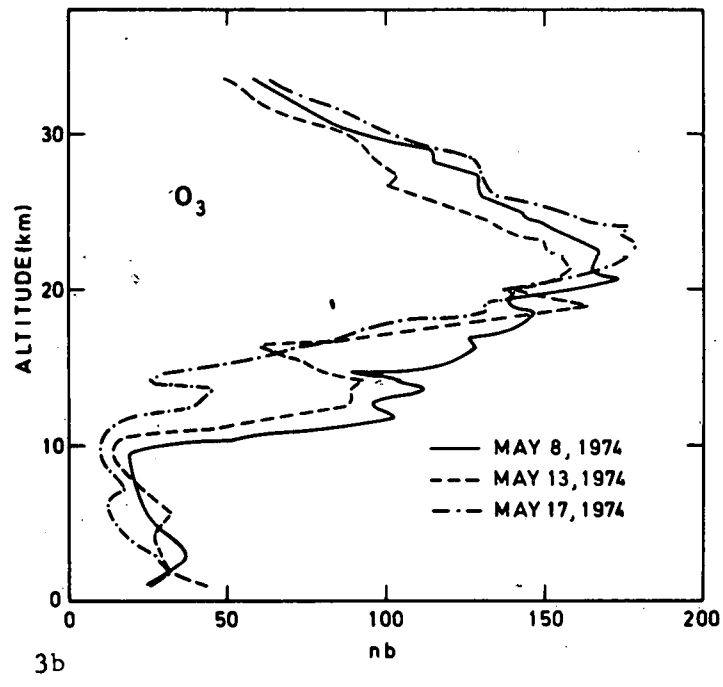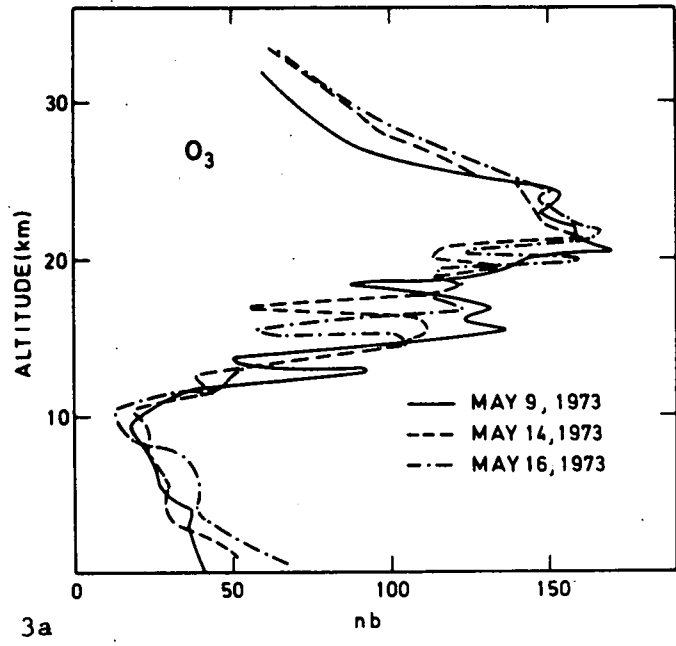the two periods.

Fig. 3.- Ozone partial pressure versus altitude over Switzerland
at the two periods of NO observations by Ackerman *et
al.* (1974) : (a) in 1973 ozone appears to vary from
day to day at random while in 1974 (b) a trend is
observed in the ozone below 18 km : an organized
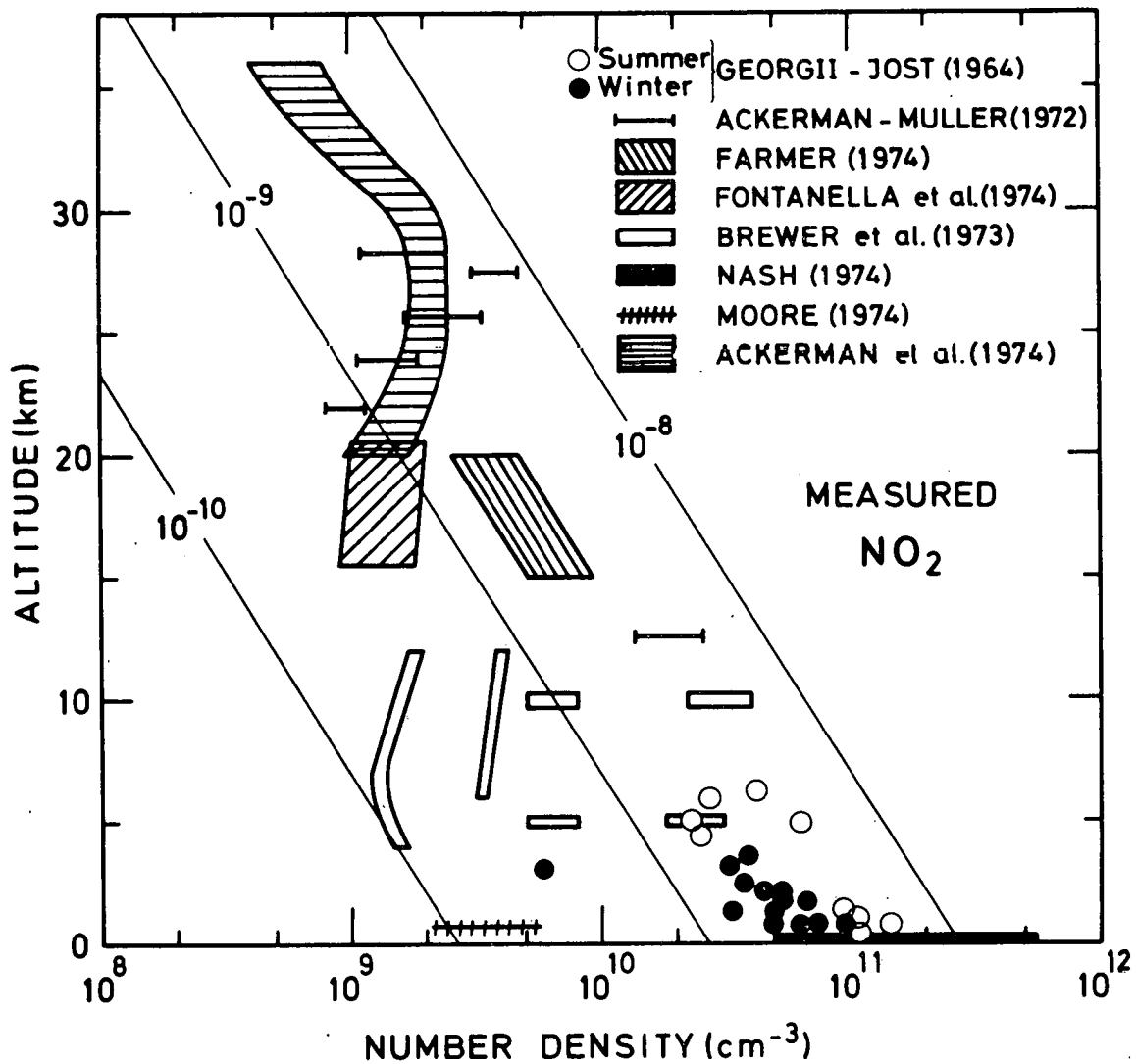decrease occurs from May 8 to May 17.

Fig. 4.- Number densities of nitrogen dioxide versus altitude measured by means of ground based, aircraft and balloon-borne instruments. Constant volume mixing ratios are roughly indicated by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

source would explain that the values observed in summer are higher than those observed in winter. The enrichment in N^{14} observed (Moore, 1974) for tropospheric NO_2 could be due to the biological contribution. An important variability of tropospheric NO_2 seems to be firmly established as well as the influence of human activities. Robinson and Robins (1971) propose a latitudinal variation (4 ppb over tropic and temperate land areas, 0.5 ppb over polar land areas and oceans).

The abundance of NO_2 in the stratosphere is known from infrared remote spectrometry (Ackerman and Muller, 1972, 1973; Farmer, 1974; Ackerman et al., 1974; Fontanella et al., 1974) performed from balloon gondolas and from aircrafts. As it is the case for NO, the few determinations are also at mid-latitudes limiting the possible comparison with theoretical models at roughly 45^0 North which could be representative of average conditions.

Several models have yielded NO and NO_2 vertical distributions for average conditions and even for specific latitudes and seasons. Some of the results are illustrated in Fig. 5. Models where various sets of possible vertical distributions are proposed can hardly be compared with experimental results. In one case (Levy, 1973) represented in Fig. 5 a tropospheric abundance of NO_2 was assumed to deduce other parameters. The agreement between modeling data are consistent, one with each other and with experimental results at 30 km altitude. The situation is different at lower altitudes. It should be pointed out that the various models considered give NO_2 values at 30 km that agree within a factor of two for values à 15 km spreading over a factor of twenty. Does this mean a weak coupling between the two altitudes? Particularly in the tropopause region, values used or deduced in models spread over two orders of magnitude even if it does not seem to have been the authors intention to represent various aspects of a variability. Models can produce double and single peaks in the vertical distributions, only the latter situation has been observed.

Due to the short interconversion characteristic time ($\simeq$ 100 sec) of NO into NO_2 and of NO_2 into NO in day light through reactions (4), (5) and (3), the latter one being negligable in the low stratosphere, the balance of these two oxides of nitrogen can better be
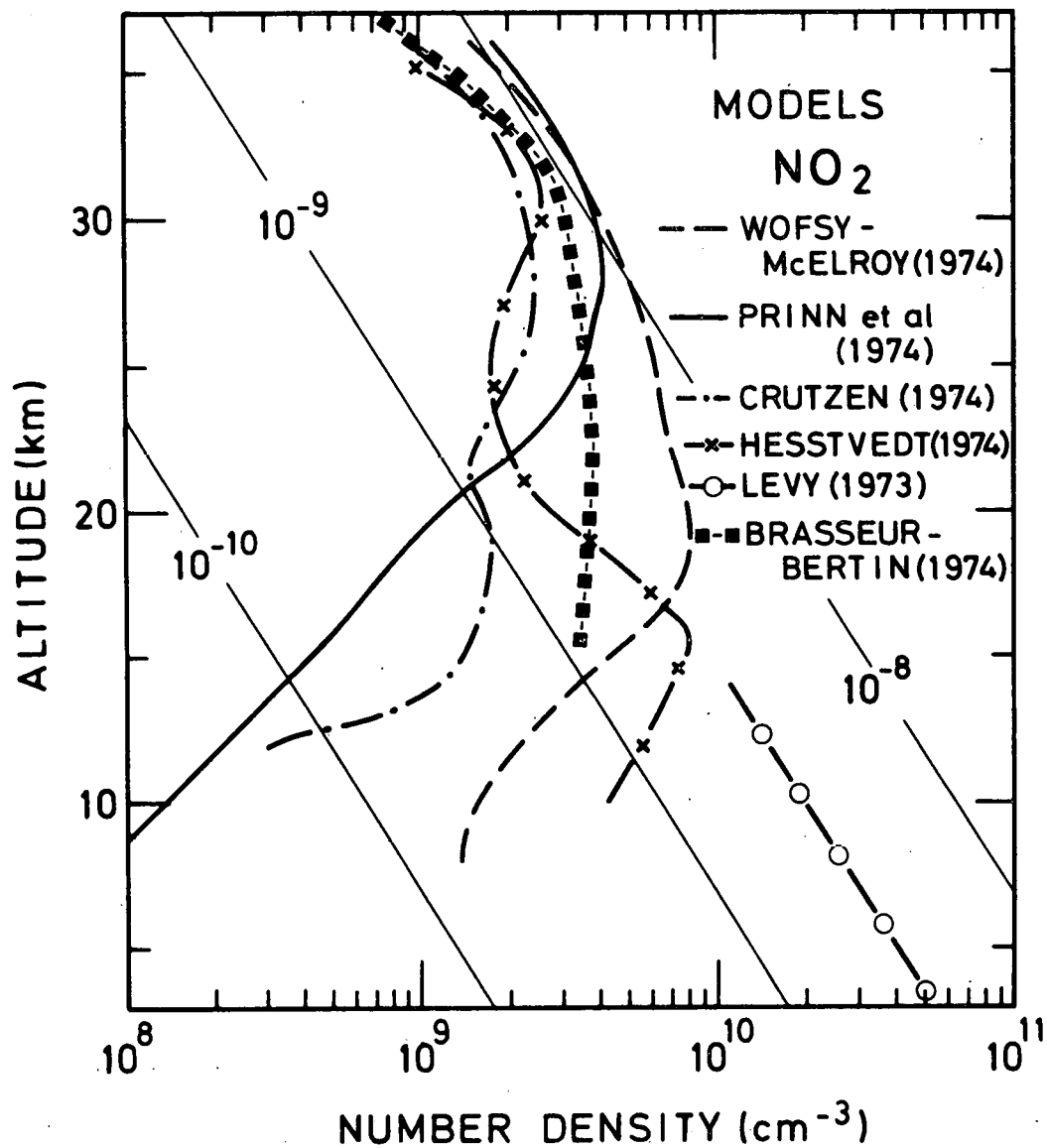
Fig. 5.- Theoretically evaluated NO_2 number densities versus altitude. Models yielding unique distributions have only been used. When various latitudes have been considered, the numbers for $45°$ latitude are represented. Levy·(1973) did not compute NO_2 but introduced a distribution to compute other parameters. Constant volume mixing ratios are represented by straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

represented by their sum currently called NO_x. This can be evaluated from experimental NO_2 and NO data available from ground level up to 36 km by

$$NO_x = NO_2 \left(\frac{1 + R}{R} \right) = NO(1 + R)$$

where $R = \dfrac{k_4 [O_3]}{J_5 + k_3 [O]}$

R has been evaluated by several authors, and measured once. The various values are represented versus altitude in Fig. 6. From the curve given by Brasseur and Nicolet (1973) and representing best the experimental data at the altitudes where they can be compared with the latter ones, and from the NO_2 and NO measurements shown in Fig. 1 and in Fig. 4 a possible envelope of NO_x values has been evaluated and is represented in Fig. 7. It will be discussed later.

NITRIC ACID

Absorption spectra have led to the detection (Murcray et al., 1969) of HNO_3 in the stratosphere and to several determinations. A rather large number of measurements make this odd nitrogen molecule the most measured in the stratosphere of the three that are considered here. High resolution absorption spectroscopy performed from ground level (Vigroux, 1973) has indicated on the basis of the narrowness of the observed lines that HNO_3 is more in the upper than in the lower layers of the atmosphere. By means of aircraft borne emission spectroscopy (Harries, 1974), the sharp increase of nitric acid has been observed above the tropopause. The same method used at shorter wavelengths on board of balloon gondolas (Murcray et al., 1974) has yielded vertical distributions of the abundance of nitric acid in the stratosphere at various latitudes. The chemical analysis of in situ collected samples (Lazrus and Gandrud, 1974) has also demonstrated the variability of nitric acid with time and latitude with higher values towards the pole than towards the equator. The results obtained by this method tend to be the lowest, particularly at low altitude while
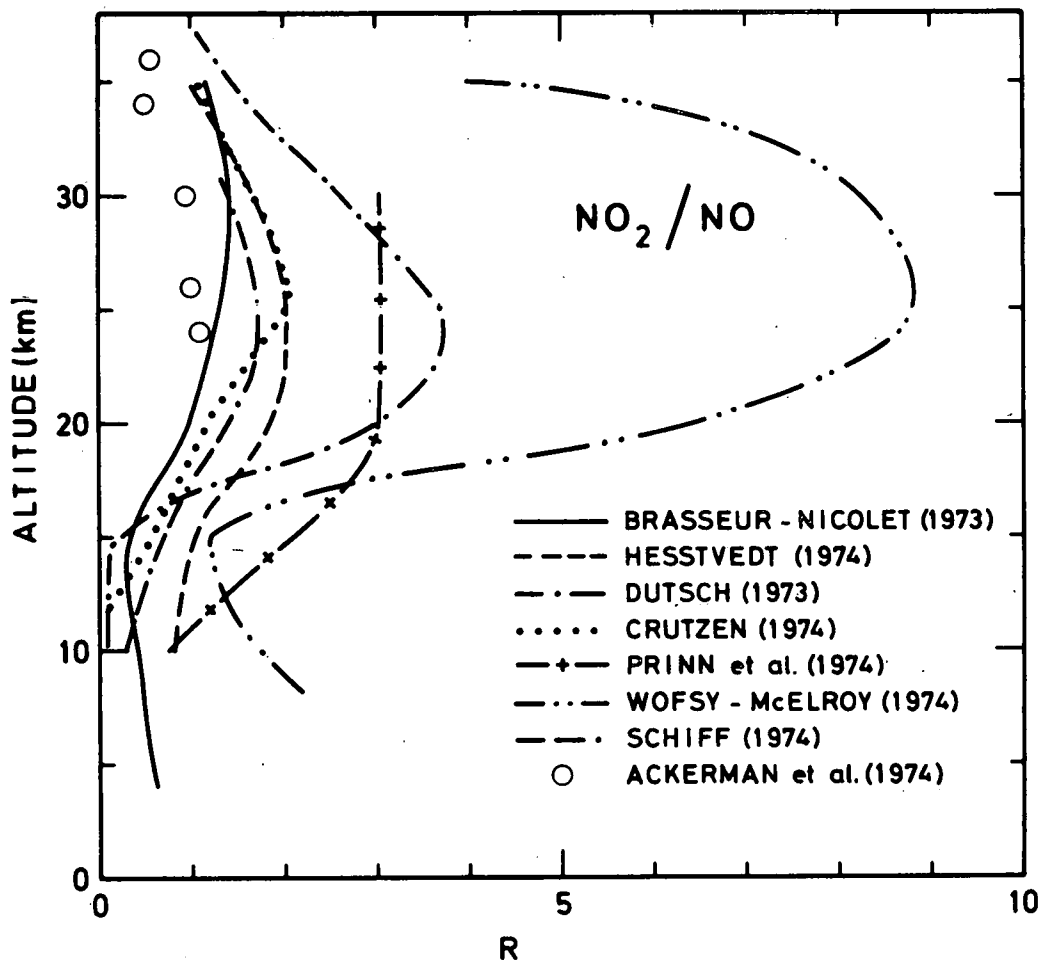
Fig. 6.- NO_2 over NO ratios versus altitude computed in various models. The circles represent measurements taken at low solar elevation but that have been considered by the authors to represent day time values.
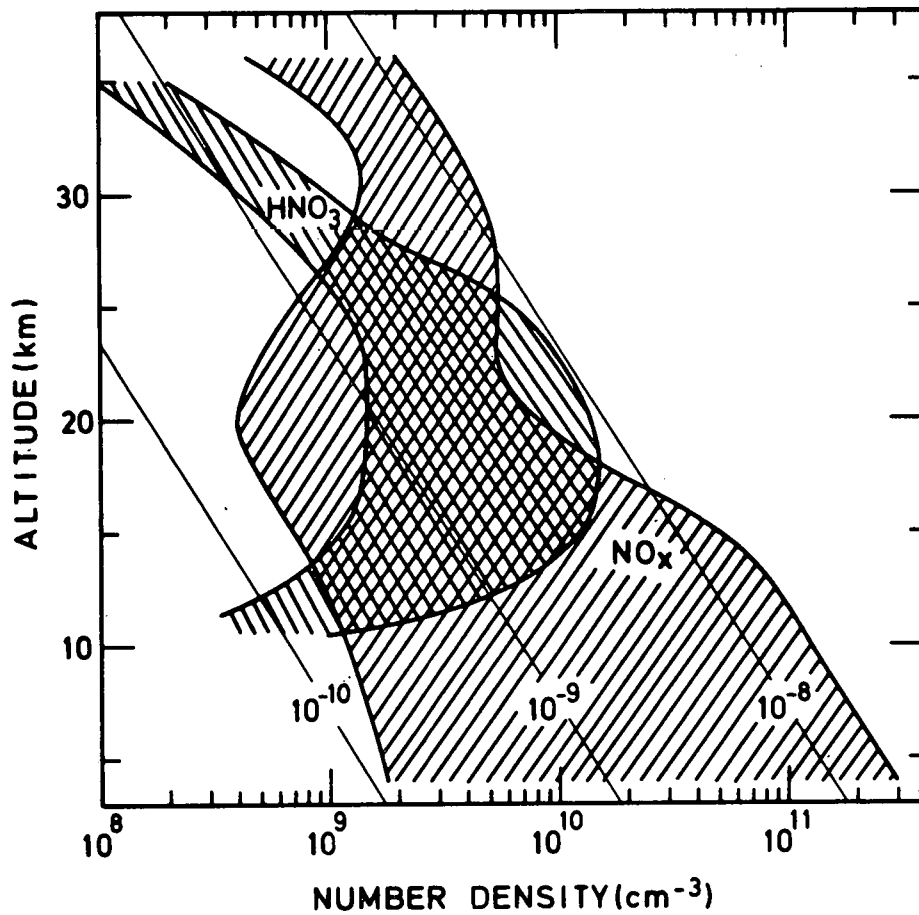
Fig. 7.- Envelopes including the available data on NO_x $(NO + NO_2)$ and on HNO_3. Constant volume mixing ratios are roughly represented by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.

absorption spectroscopy from aircraft (Fontanella *et al*, 1974) has a tendency to give the highest concentrations as well as some interpretations of emission measurements (Fried and Weinman, 1970).

No optical measurement seems to have been reported for HNO_3 in tropospheric air. We have used spectra taken by absorption spectrometry during balloon ascents and published by Murcray *et al.* (1969) to evaluate one tropospheric upper limit corresponding to a volume mixing ratio smaller than 10^{-10}. The result is shown in Fig. 8 with enveloppes representing the data obtained by means of the various methods at various times and locations. All results are included in the broad envelope illustrated in Fig. 7.

Examples of theoretically deduced vertical distributions of HNO_3 are shown in Fig. 9. Values given for altitudes higher than 15 km represent rather well the experiments while below 12 km, the theory appears to generate overestimated abundances of HNO_3.

DISCUSSION

Nitric acid is known, as any very polar molecule, such as HCl for instance, to have an extremely low activity in dilute aqueous solutions. On the other hand Warneck (1974) has shown that the time constant for collisions of trace constituants with cloud elements is shorter than 5 seconds. These considerations would explain a low concentration of HNO_3 in the tropospheric gas phase. They have not been taken into account in models where rain out times not shorter than a few days have been introduced to represent the evacuation of odd nitrogen from the stratosphere to the troposphere. They would however possibly improve the agreement between theories and experiments in the region of the tropopause and below. This would probably require adjustments to maintain the computed concentrations of NO_2 at the level indicated by the observations requiring other sources of odd nitrogen in the low stratosphere.

NO_x presents obviously an important variability with time in the stratosphere. Seasonal variations have been considered in models as well as the possibility (Ruderman and
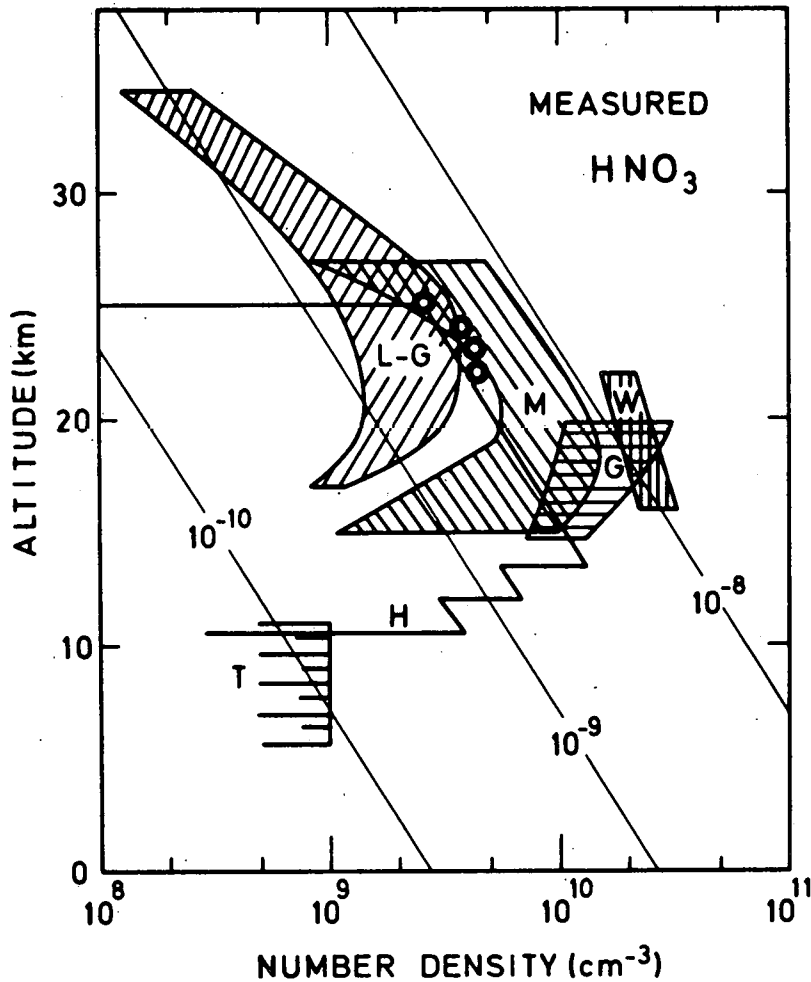
Fig. 8.- Envelopes representing the measured nitric acid number densities versus altitude. L-G corresponds to the data of Lazrus and Gandrud (1974), M to those of Murcray et al. (1974), G to those of Fontanella et al. (1974), W to those of Fried and Weinman (1970) and H to those of Harries (1974). The values represented by the circles and by the upper limit marked T have been evaluated on the basis of the atmospheric experiments of Murcray et al. (1969) and of the laboratory data published by Fontanella et al. (1974). Constant volume mixing ratios are roughly illustrated by the straight lines marked 10^{-8}, 10^{-9} and 10^{-10}.
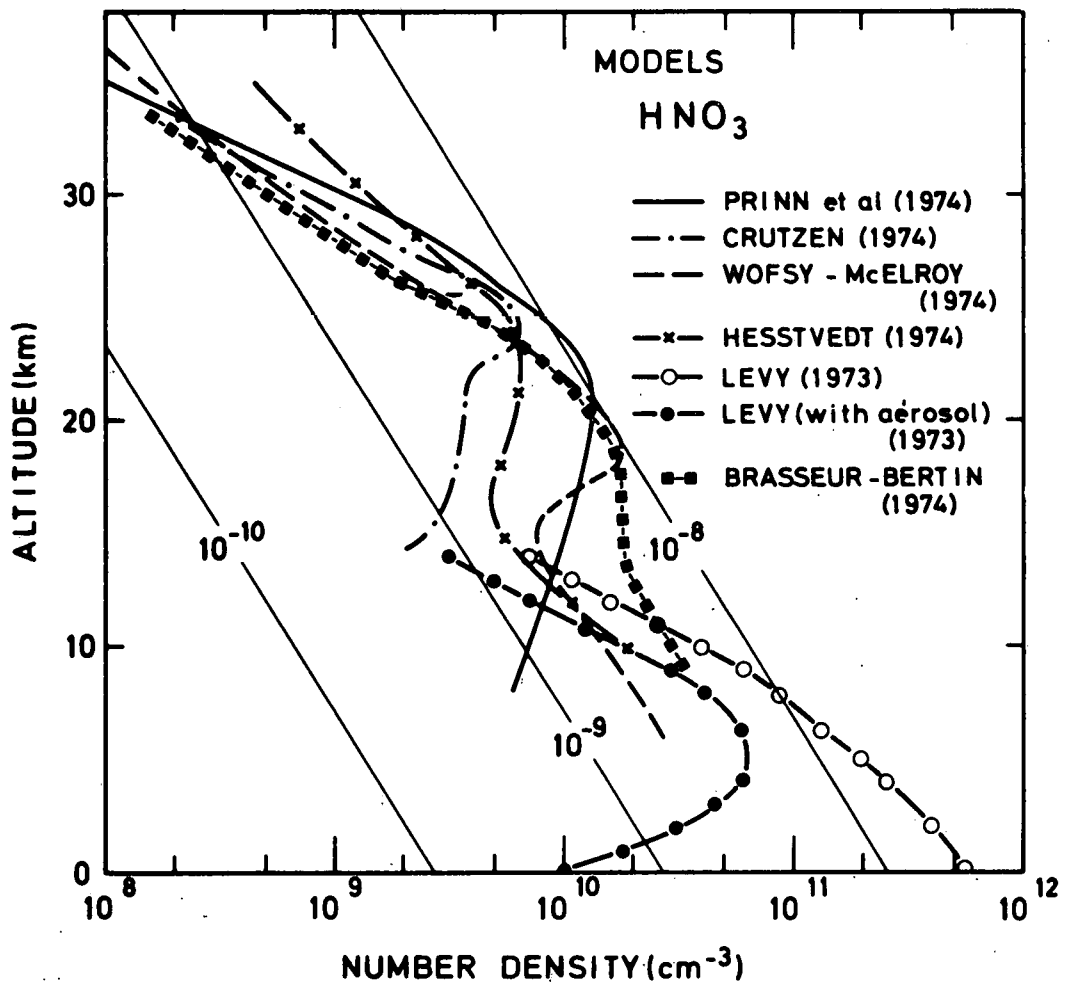
Fig. 9.- Theoretically evaluated HNO_3 number densities versus altitude. Models yielding unique distributions have only been used. When various latitudes were considered, the numbers for 45° have been represented.

Chamberlain, 1974) of the interpretation of the apparent correlation of ozone variation with the eleven years cycle of solar activity in terms of the effect of nitrogen oxides modulation by cosmic rays. Even if doubts have been casted on the significance of such correlations (London and Oltmans, 1973) such investigations are very interresting. There is however no peremptory demonstration of the direct role of oxides of nitrogen as an intermediate on these phenomena that would allow to make now firm assessments (Johnston, 1974) about the possible effects of stratospheric aircrafts on ozone. Large variations of NO have been observed as described in a previous section. The NO abundances observed by Ackerman *et al.* in May 1973 and in May 1974 differ markedly. Total ozone data for the two months are shown in Fig. 10. In May 1973, total ozone appears to vary from day to day randomly around mean values larger at high latitudes as currently observed. The latitudinal variation is also present in May 1974, but a well pronounced decrease of 10 to 20% appears over one week. The observations indicate the occurance of a well organized modification of large geographic extent from at least 51^0 North to 39^0 North including the area of high NO observations. The decrease in total ozone is suggested to be due to the replacement of ozone rich air below 20 km by ozone poor air. This suggestion stems from the observed vertical profiles observed over Switzerland and shown in Fig. 3a and b. The Umkehr observations made over Lisbon show the same trend, that is not unique near the end of the ozone sping maximum at this station (Figueira, 1973) namely, during the minimum of total ozone in the month of May 1974, levels 2 and 3 (12 and 16.5 km) exhibit minimum values while maximum values for the whole month are observed at levels 5,6 and 7 corresponding respectively to 25, 30 and 35 km.

The ozone reduction below 20 km responsible for the reduction in total ozone cannot be attributed to NO_x chemistry since the currently accepted atomic oxygen content at these altitudes implies a caracteristic reaction time larger than a year. It should also be remarked that ozone decrease in the lower stratosphere occured concurrently with an increase at higher altitudes. All these observations suggest that the variability with time of total ozone that could, in a simple minded correlation, be related in this case with NO_x on the basis of chemical interactions was entirely under the control of transport processes.

Determinations of tropospheric NO_2 indicate a wide range of NO_x values tentatively
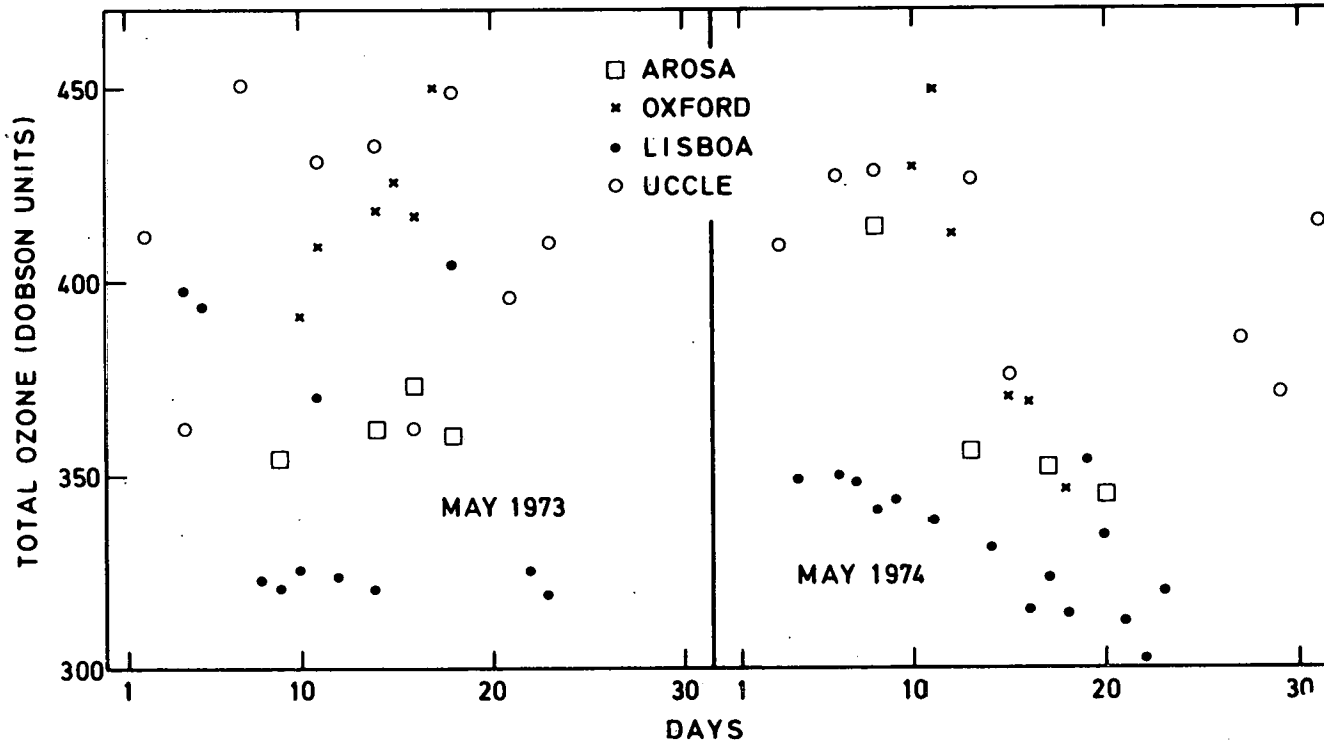
Fig. 10.- Total ozone versus time measured over various european stations in May 1973 and in May 1974. The beginning of the summer minimum occurs in this latter case while May 1973 is still in the spring maximum.

illustrated in Fig. 7. Low values are usually thought to be characteristic of unpolluted air and are much smaller than those used in models (Levy, 1973; Chameides and Walker, 1974). The reduction of NO_x in these models would reduce the production of HNO_3 that has been considered as being to high by Warneck (1974) on the basis of the observed global precipitation of nitric acid in rain. On the other hand high values of NO_x concentrations, suggested by the observations of Georgii and Jost who have indicated a seasonal variation (summer values higher than those observed in Winter) that could hardly be explained on the basis of human activities, could have consequences for the stratosphere. They could lead to injections of tropospheric NO_x into the stratosphere when its mixing ratio at the stratospheric heights is smaller than in the troposphere. This could be supported by the isotopic composition of HNO_3 observed between 21 and 27 km (Moore, 1974) showing about the same N^{14}/N^{15} ratio than for standard N_2. If stratospheric HNO_3 was all derived from N_2O that shows a marked N^{15} enrichment, this should also appear in nitric acid as a product of NO_x provided that reactions

$$N_2O + O^1D \rightarrow N_2 + O_2 \qquad (6)$$
$$\text{and} \quad N_2O + O^1D \rightarrow NO + NO \qquad (7)$$
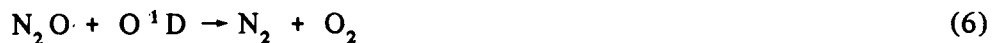
have no differential isotopic effects. This could be a reasonable assumption that should of course be check to allow a definite interpretation of the stratospheric isotopic measurements.

Considering the replacement time (Danielsen 1968) of stratospheric air by tropospheric air and the high HNO_3 amounts derived by absorption spectrometry (Fontanella et al., 1974) a downward flux of nitric acid larger than 5×10^8 cm^{-2} sec^{-1} should be accepted that would imply an other source of odd stratospheric nitrogen than reaction (7) that has led to odd nitrogen production equal to $(0.29 - 1.5) \times 10^8$, $(0.25 - 0.65) \times 10^8$, $(0.5 - 1.3) \times 10^8$ and $(0.8 - 1.0) \times 10^8$ cm^{-2} sec^{-1} respectively proposed by Crutzen (1974), Wofsy and McElroy (1974), Brasseur and Nicolet (1973) and Isaksen (1973).

On the other hand the low HNO_3 values of Fig. 8 would imply on the basis of the same interchange time between tropospheric and stratospheric air, a flux equal to .8 x 10^8 cm^{-2} sec^{-1}. The average value (2.9 ± 2.1) x 10^8 cm^{-2} sec^{-1} shows clearly that the actual uncertainty on HNO_3 measurements is unsatisfactory. If it was admitted that HNO_3 abundances derived from in situ sampling were systematically to low and if, on the basis of such an argument, they were rejected, an average flux value of (3 ± 2) x 10^8 cm^{-2} sec^{-1} would be derived excluding several theoretical values. An additionnal source of odd stratospheric nitrogen would have to be introduced, particularly if a first measurement was showing that the absolute quantum yield for the formation of $O\ ^1D$ by the O_3 photolysis, the value of which has always been assumed (Welghe, 1974), is in fact smaller than currently accepted.

CONCLUSION

Measurements of the chemically related odd nitrogen molecules in the atmosphere appear to be a particularly good test for models designed to predict the possible modifications of the stratosphere under natural and artificial constraints. Measurements are at present to sparse to provide a thorough check. They however indicate possibilities to improve the evaluation of vertical distributions and temporal variations of NO_x and HNO_3 particularly required for the lower stratosphere and for the troposphere.

A fundamental aspect such as the sources and fate of odd nitrogen above the *average* tropopause height as well as in the troposphere seems to require further priority investigations. Some experimental methods have contributed the most to the gathering of the available information. Their use should be intensified. The use of others has perhaps not been enough emphasized up to now.

As far as the prediction of a possible reduction of ozone by a factor of 2 is concerned, some models now predict that it could be 1% for a same fleet of stratospheric aircrafts. Present models can, however, hardly be used for natural stratosphere forecast.

ACKNOWLEDGMENTS

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