Seasonal Variations of NO and O\textsubscript{3} at Altitudes of 18.3 and 21.3 km

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ABSTRACT

Nitric oxide and ozone concentrations have been measured \textit{in situ} from a high-altitude research aircraft based at the NASA Ames Research Center. Data which show the variations of NO and O\textsubscript{3} with the time of year are presented for altitudes of 18.3 and 21.3 km. The extreme values of the observed NO concentrations at 21.3 km are \(1.2 \times 10^6\) cm\(^{-3}\) in summer and \(2 \times 10^5\) cm\(^{-3}\) in winter. At 18.3 km the extreme values are \(1.6 \times 10^5\) cm\(^{-3}\) in summer and \(1 \times 10^5\) cm\(^{-3}\) in winter. The smoothed NO seasonal data show a variation of about a factor of 2.5 at 21.3 km and a factor of 3 at 18.3 km. The ozone data show the generally expected magnitude and seasonal variation.

We have used a photochemical model employing the measured ozone concentrations, the mean solar zenith angle, and seasonal HNO\textsubscript{3} data reported by others to predict the seasonal NO variation at 20 km. The result is a summer-to-winter NO ratio of 2.5 which is in fair agreement with the observed ratios.

1. Introduction

The importance of the oxides of nitrogen in the chemistry of the atmospheric ozone layer has been discussed by Crutzen (1971) and Johnston (1971). Both authors pointed out the possibility of an effect on the ozone layer due to nitric oxide injection by supersonic transport operations in the lower stratosphere. The suggestion of such an effect has motivated various efforts in modeling and measurements of the ambient stratosphere. Recently, several workers (McElroy et al., 1974; Whitten and Turco, 1974) have presented one-dimensional atmospheric models including transport and chemistry in an attempt to provide a more realistic assessment of the effect of nitric oxide on the ozone layer.

The first NO\textsubscript{2} measurement (NO\textsubscript{2}=NO+NO\textsubscript{2}) in the lower stratosphere was reported in 1971 (Hale and Pontano, 1971). Since then, a number of workers have reported measurements of NO and NO\textsubscript{2} by various techniques at altitudes ranging from 15 to 30 km (Ackerman and Muller, 1972; Ackerman et al., 1973, 1975; Fontanella et al., 1975; Ridley et al., 1974a, b; Toth et al., 1974; Loewenstein et al., 1974a, b; Savage et al., 1974; Patel et al., 1974; Murcray et al., 1974). These authors measured only NO or NO\textsubscript{2} in a particular experiment, except for a simultaneous measurement of NO and NO\textsubscript{2} carried out by Ackerman et al. (1975).

Discrepancies which have existed between various NO measurements are now beginning to be resolved as a pattern of seasonal variations unfolds from our data. For example, Ackerman's measurements (Ackerman et al., 1973) which had appeared to disagree with our early measurements (Loewenstein et al., 1974a) now appear, because of the seasonal variation of NO, to agree well with our new data.

A measurement of stratospheric NO or NO\textsubscript{2} yields useful information because the NO/NO\textsubscript{2} ratio is given approximately by photochemical theory. The time constant for interconversion of NO and NO\textsubscript{2} is about 100 s at 20 km; therefore, these species are in photochemical equilibrium at this altitude. An additional factor in the photochemistry of NO\textsubscript{2} is its conversion to nitric acid by reaction with OH. Because the time constant for such conversion is \(\sim 10^6\) s at 20 km, HNO\textsubscript{3} is not in photochemical equilibrium with the other odd nitrogen compounds, NO and NO\textsubscript{2}. Hence, measurement of NO or NO\textsubscript{2} alone does not yield complete data on odd nitrogen abundance.

A continuing measurement program, which will also yield data on NO\textsubscript{2} and HNO\textsubscript{3} concentrations, is necessary in order to completely establish seasonal and geographical behavior of NO\textsubscript{2} concentrations in the lower stratosphere.

2. Instrumentation

Our measurements of nitric oxide and ozone are made \textit{in situ} with instruments carried on a U-2 aircraft flying at altitudes of 18.3 and 21.3 km. A flow of ambient air is brought into the experiment bay of the aircraft by an air scoop extending beyond the aircraft boundary layer. At a 21.3 km cruise altitude, where the true airspeed of the aircraft is 206 m s\(^{-1}\), the pressure developed at the inlet scoop is 12 mm Hg in excess of ambient pressure. Inside the experiment bay, a flexible line carries the airflow to a manifold.
The linear relationship between signal and mixing ratio expressed by Eqs. (4) and (5) is assured by using a large excess of ozone reactant relative to the nitric oxide being measured.

In the chemiluminescence instrument (Fig. 1) the atmospheric sample and ozone reactant are introduced through concentric injector tubes into a cylindrical flow reactor which is 20 cm long and 5 cm in diameter. The reactor is glass with an interior gold plating to enhance light collection by the detector. The reaction chamber end window opposite the gas injector is a Corning 2-62, 6200 Å long-pass filter. An EMI 9659 photomultiplier, which has a photocathode with “extended red” sensitivity, views the reaction chamber through the 2-62 filter. The photomultiplier tube is operated at Dry Ice temperature. Pulse counting electronics are used to process the output from the tube, and linear count-rate circuits provide analog outputs equivalent to 10⁴ and 3×10⁴ counts per second full scale each with a 1 s electronic time constant.

Ozone reactant is provided from a 1-liter stainless steel bottle containing a mixture of nominally 8 mole percent ozone in liquid Freon 13. Typical reactant flow is 30–50 g h⁻¹ of the O₂–Freon solution. NO calibrator gas is carried in a 500 cm³ stainless steel bottle which is filled to 500 psi from a master calibrator gas cylinder prior to each flight. The NO mixing ratio of the calibrator currently being used is 6.7 ppm in nitrogen. Calibrator gas flows of 4 and 10 cm³ min⁻¹ STP are used for the periodic instrument calibration. Air sample flow through the instrument is typically 19×10⁶ cm³ min⁻¹ STP at a 21.3 km cruise altitude.

The NO instrument has three operating modes: calibrate, null, and measure. Each mode is allotted 3 min, which yields a 9 min cycle for one complete atmospheric NO measurement. Alternate 9 min cycles employ the high- and low-calibrator flow as a check on the linearity of the instrument response.

In the calibrate mode, the calibrator gas flow is added into the atmospheric gas flow upstream of the mixing manifold. In the null mode, the ozone reactant is added into the atmospheric flow upstream of the mixing manifold. To check the nulling of the atmospheric NO in this mode, an overlap of 1 min between high-calibrator and null modes is provided. This gives a direct measurement of the nulling efficiency once every 18 min. If less than 99% nulling is observed, the NO data are corrected correspondingly. The minimum detectable NO mixing ratio is dependent on the instrument operating conditions and is generally in the range 0.02 to 0.04 ppb, which is 3×10⁷ to 6×10⁷ molecules cm⁻³ at 21.3 km.

b. Ozone sensor

Ozone is measured in a commercial ultraviolet photometer (Bowman and Horak, 1972) by monitoring the transmission of the 2537 Å Hg line radiation
Table 1. Summary of the flight parameters.

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<th>End run (GMT)</th>
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<th>Average temperature (°K)</th>
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through a 71 cm airpath. This wavelength lies close to the peak of the strong Hartley continuum absorption of O₂. A temperature-controlled Hg lamp is used as the 2537 Å source, and the absorption cell is continuously flushed with ambient air at a flow of 250 cm³ min⁻¹ STP. A vacuum photodiode with a CsTe cathode is used to detect the transmitted 2537 Å radiation. A second identical photodiode detector viewing the Hg source directly is incorporated into a servo loop to control the output intensity of the lamp.

The instrument operates in two modes, measure and null. In the null mode, an MnO₂ scrubber removes O₂ from the airflow and a signal I₀, proportional to the unattenuated 2537 Å intensity, is measured and stored. In the measure mode, a signal I, proportional to the attenuated 2537 Å intensity, is measured and stored. The I and I₀ values are used to obtain the ratio

\[
\frac{I - I₀}{I₀} = 1 - e^{-αpl},
\]

where \(α=306 \text{ cm}^{-1} \text{ atm}^{-1}\) is the ozone absorption coefficient at 2537 Å, \(p\) is the STP partial pressure of ozone, and \(l=71\) cm is the absorption tube length.

The measure and null modes are of 5 s duration each; thus, an O₃ measurement is completed in 10 s.
The instrument sensitivity is 3 nb STP of ozone, or 8×10^10 molecules cm^-2.

c. Atmospheric temperature sensor

Outside air temperature is measured with a resistance thermometer and is recorded by the pilot every 15 min during the flight. The accuracy of the measurements is ±2 K, and the average temperatures measured are listed in Table 1.

3. Measurements and calibrations

One complete nitric oxide measurement is made every 9 min of flight; therefore, the spatial resolution of the NO measurements is 110 km. The mean mixing ratio of NO is calculated using Eqs. (4) and (5):

\[ X_{NO} = \frac{S_{ATM}}{S_{CAL}} \cdot \frac{F_{CAL}}{F_{ATM}} X_{CALo} \]  

where \( S_{ATM} \) and \( S_{CAL} \) are the signals from the atmospheric nitric oxide and the nitric oxide calibrator as derived from the flight data. The uncertainty in the ratio of these signals is due to the counting statistics of the measure, null, and calibrate determinations. This uncertainty ranges from 1% to 20% depending upon the size of the NO signals being detected on a particular flight.

\( F_{CAL} \), the nitric oxide calibrator flow rate, is measured by monitoring the differential pressure across a calibrated capillary, and the pressure and temperature in the capillary. Calibrator flows are fixed by a pressure regulator and critical orifices. \( F_{ATM} \) is determined by measuring the differential pressure across the NO instrument, and the pressure and temperature in the reaction chamber. The uncertainty in the ratio of these flows is estimated to be ±10%.

\( X_{CAL} \) is the mixing ratio of nitric oxide in nitrogen of the calibrator gas used in the flight experiments. The mixing ratio of the master calibrator bottle has been determined recently (January 1975) using an NOx analyzer which was calibrated against an NOx permeation tube. The result is \( X_{CAL} = 6.7 \pm 0.7 \) ppm NO in N\(_2\). A previous determination of the mixing ratio in the same bottle was made by the manufacturer in February 1974 and found to be 6.34 ± 0.13 ppm. The agreement of these two measurements indicates that the NO in N\(_2\) mixture we are using is stable, and we have adopted our own measurement and uncertainty estimate of \( X_{CAL} \) for the calculations in this paper.

A number of systematic effects on the atmospheric NO determinations have been identified and are accounted for in the data analysis. Briefly, these are:

1) Depletion of NO in the flight calibrator bottle has been measured to be 3% day\(^{-1}\); this bottle is normally filled within 24 h prior to a flight, and a correction for the depletion is made to the data.

2) When incomplete nulling is observed, a correction is made as discussed in the previous section.

3) Loss of NO due to reaction with ambient O\(_3\) in the inlet lines to the NO detector has been computed and a correction amounting to about 2% is made.

4) Wall losses within the system have been measured and are found to be negligible.

After correcting the data for these systematic effects there remains a residual systematic uncertainty in the NO data of ±3%.

Combining the error estimates above, we can give a range of uncertainties for the data presented here. When the counting statistics contribute much less than 10% uncertainty, the flows and the NO calibrator mixing ratio fix, the uncertainty at ±15%. For a statistical uncertainty as large as 20%, which is sometimes observed, the overall uncertainty becomes ±25%.

Since one complete ozone measurement is made every 10 s of flight, the spatial resolution is 2 km. The data from the ozone ultraviolet photometer are corrected for line losses which have been determined to be stable at 15% after a system conditioning time of 30 min under simulated atmospheric conditions. The estimated uncertainty in the ozone data is ±15%.

4. Results

Figs. 2 and 3 and Table 1 summarize the results of flights made between November 1973 and January 1975 and show the seasonal variations of O\(_3\) and NO at altitudes of 18.3 and 21.3 km. Each plotted point for NO and O\(_3\) is the average value observed at that

![Graph](image)

**Fig. 2.** Average NO and O\(_3\) concentrations at 18.3 km altitude versus time of year. See Table 1 for range of latitude and longitude. Symbol size for the NO data is determined by actual spread of values (not uncertainty).
Figure 3. As in Fig 2 except at 21.3 km altitude.

Altitude on that day. Each NO point is typically the average of 8–12 observations. The size of the rectangles for each NO point shows the spread in the values measured on that day and is not related to the uncertainty of the individual observations. The small spread shown for some of the flights at 18.3 km is due to the small number of observations at that altitude. Also shown for comparison are the NO data of Ackerman et al. (1975) and Ridley et al. (1974a, 1974b). The spread of the O₅ data is not shown in Figs. 2 and 3, since many of the spreads are of the order of the size of the symbols.

Figs. 2 and 3 show a seasonal variation in nitric oxide concentrations at both 18.3 and 21.3 km. At 21.3 km NO concentrations are typically 1×10⁶ cm⁻³ in midsummer and 4×10⁸ cm⁻³ in winter, although extreme values range from 1.2×10⁶ cm⁻³ in summer to 2×10⁸ cm⁻³ in winter. At 18.3 km the same trend is observed, with 1.2×10⁶ cm⁻³ being a typical midsummer NO concentration, decreasing to 3×10⁵ cm⁻³ in winter. In this case the extremes observed are 1.6×10⁶ cm⁻³ in summer and 1×10⁵ cm⁻³ in winter.

The observed seasonal change of ozone concentration at both 18.3 and 21.3 km is in agreement with the well-known seasonal variation of ozone at mid-latitudes.

5. Discussion

From Figs. 2 and 3 it appears that NO varies over the year by about a factor of 3 at the altitudes studied. The effect is slightly larger at 18.3 km than at 21.3 km, and the variation is more clearly defined at the lower altitude.

We have considered various possible causes of an NO seasonal variation with the observed phase and magnitude. They are:

1) Increased oxidation of NO to HNO₃ due to increased winter ozone and decreased winter photolysis of HNO₃.

2) Increased oxidation of NO to HNO₃ due to increased water vapor in winter.

3) Increased transport of N₂O from the tropics in spring.

4) Increased transport of NOₓ and HNO₃ into the troposphere in winter.

Of the possible effects listed only the first one can account for the magnitude and phase of the NO variation as well as the observed ~35% winter increase of the nitric acid overburden (Murcray et al., 1975).

Production of nitric acid from NOₓ is related to the ozone concentration by the reactions:

\[ \text{O}_5 + hν \rightarrow \text{O}(^1\text{D}) + \text{O}_3, \]  \hspace{1cm} (7)

\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}, \]  \hspace{1cm} (8)

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}, \]  \hspace{1cm} (9)

whereas the principal destruction mechanism is photoysis:

\[ \text{HNO}_3 + hν \rightarrow \text{OH} + \text{NO}_2. \]  \hspace{1cm} (10)

Odd nitrogen equilibrium is established by the reactions:

\[ \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2, \]  \hspace{1cm} (11)

\[ \text{NO}_2 + hν \rightarrow \text{NO} + \text{O}. \]  \hspace{1cm} (12)

For an assumed condition of photochemical equilibrium in the 20 km altitude region, we can derive a proportionality between NO and HNO₃ from the foregoing six chemical reactions:

\[ [\text{NO}] \sim \frac{J_{10}[\text{HNO}_3]}{[\text{O}_3]^F}, \]  \hspace{1cm} (13)

where \( J_{10} \) is the photolysis rate for reaction (10).

From our ozone data we find about a 50% increase in midwinter O₃ concentration over the summer value. From some of our one-dimensional model results, we estimate the HNO₃ photolysis rate at 40°N to be about 1.5 times greater in summer than in winter. If we take the HNO₃ winter increase at 20 km to be 35%, as suggested by the data of Murcray et al. (1975), then by using Eq. (13) the summer-to-winter ratio of nitric oxide is 2.5, in rough agreement with our observations.

A more definitive treatment of the seasonal variation of stratospheric nitric oxide awaits further studies with our two-dimensional stratospheric model and simultaneous measurements of O₃, NO, NO₂, HNO₃ and OH.
REFERENCES


