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VARIABLES ACROSS THE TROPOPAUSE

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## ABSTRACT

The downward transport of air through the tropopause can bring substantial amounts of ozone and reactive nitrogen into the upper troposphere. In this cold region of the atmosphere,  $O_3$  is particularly effective as a greenhouse gas. As part of the North Dakota Thunderstorm Project in June 1989, the NCAR Sabreliner made five flights through the tropopause. We measured ozone, nitric oxide (NO), total reactive nitrogen ( $NO_y$ ), carbon monoxide (CO), and water vapor ( $H_2O$ ), and took grab samples for hydrocarbon (HC) analysis. Hydrocarbons, CO, and  $H_2O$ , species with sources primarily at the Earth's surface, showed a strong concentration decrease with increasing altitude, while  $O_3$  and  $NO_y$ , species with a source in the stratosphere showed a strong concentration increase with increasing altitude. Stratospheric concentrations of  $NO_x$ ,  $NO_y$ , and  $H_2O$  were all high relative to winter observations made during NASA's AASE. We suggest that mid latitude thunderstorms may inject wet, NO-rich air into the lower stratosphere. Calculation based on measured ratios of  $NO_x$  and  $NO_y$  to  $O_3$ , yield a total flux of reactive nitrogen from the Northern Hemisphere stratosphere into the troposphere of 1 to 2 Tg(N)  $yr^{-1}$  with about 8% in the form of  $NO_x$ . This value is higher than reported estimates of total stratospheric nitrogen fixation.

## 1. INTRODUCTION

The principal natural source of tropospheric ozone is downward transport from the stratosphere in extratropical regions (Junge, 1962). Much of this transport is associated with tropopause folding events occurring on the cyclonic (generally poleward) side of the jet streams (see WMO, 1986 for a review). Carried along with this ozone are reactive nitrogen compounds that can lead to in situ photochemical ozone production in the upper troposphere (Liu et al., 1980). Ozone is particularly effective at greenhouse warming at this altitude because it is the coldest part of the troposphere.

Published estimates of the flux of ozone from the stratosphere into the troposphere range from about 4 to  $8 \times 10^{10}$  molec.  $cm^{-2}s^{-1}$  for the Northern Hemisphere (see Fishman, 1985 and WMO, 1986 for reviews). From measured ratios of reactive nitrogen to ozone, one can estimate the flux of nitrogen species to the troposphere. Nitric oxide, NO and nitrogen dioxide,  $NO_2$ , (together referred as

$NO_x$ ) play the most active role in photochemical ozone production.  $NO_x$  can exist as several reservoir species; total reactive nitrogen,  $NO_y$ , is composed of NO,  $NO_2$ ,  $NO_3$ ,  $2xN_2O_5$ , HONO,  $HNO_3$ ,  $HO_2NO_2$ , ClONO<sub>2</sub>, PAN (peroxy acetylnitrate), RONO<sub>x</sub> (organo nitrates and nitrites), and small nitrate particles. In several recent NASA programs (see Murphy et al., 1993), ozone and reactive nitrogen species were measured in the lower stratosphere, but data are still sparse and there are no reports in the literature of simultaneous measurements of NO, or  $NO_y$  and  $O_3$  in this region of stratospheric egress. Here we report such measurements and use the results to estimate the flux of  $NO_x$  and  $NO_y$  from the stratosphere into the Northern Hemisphere troposphere.

## 2. EXPERIMENTAL METHODS

The research aircraft, the NCAR Sabreliner, is a small, twin engine jet, the capabilities of which are described by Pickering et al. (1989) and Luke et al. (1992).

Ozone was measured with a modified UV absorption instrument that gives a response time of about 10 s (Model 49, ThermoEnvironmental Corp. Franklin, MA). Water vapor was measured with a liquid nitrogen-cooled dew point detector developed at NCAR (Spyres-Duran, 1990).

Nitric oxide was measured by chemiluminescence (Dickerson et al., 1984) with a detection limit ( $\pm 2\sigma$ ) of about 10 ppt (parts per  $10^{-12}$  by volume) for a 20 s integration time. Total reactive nitrogen,  $NO_y$ , is detected by reduction to NO on  $375^\circ C$  Mo. The converter housing, attached directly to the top of the aircraft, has a very short (ca 5 cm) quartz inlet that prevents loss of reactive species such as  $HNO_3$  (Luke et al., 1992).

Carbon monoxide, CO, was measured by IR absorption (Dickerson and Delany, 1988) that provided a detection limit ( $\pm 1\sigma$ ) of about 12 ppb (parts per billion by volume) with a response time of 60 s. For the low mixing ratios encountered in the stratosphere, several 1-min values were averaged together. Mixing ratios were corrected for a 1.4 % interference from ozone. Nonmethane hydrocarbons (NMHC), were measured in grab samples taken during the flights. These samples were later analyzed by gas chromatography with a flame ionization detector (Greenberg and Zimmerman, 1984). The  $NO_2$  and  $O_3$  photolysis rate coefficients were derived from Eppley UV radiometer signals as described by Dickerson et al. (1982). Experimental uncertainty is discussed in the Appendix.

### 3. RESULTS

The aircraft experiment described here was conducted as part of the North Dakota Thunderstorm Project (NDTP) with the primary objective of understanding convective clouds. On two ferry flights between NCAR/RAF in Broomfield, CO and Bismarck, ND, and on three flights over North Dakota we were able to characterize the air in the upper troposphere and lower stratosphere (Fig. 1). North Dakota is frequently located north of the jet stream where the tropopause is relatively low and stratospheric intrusions are common.

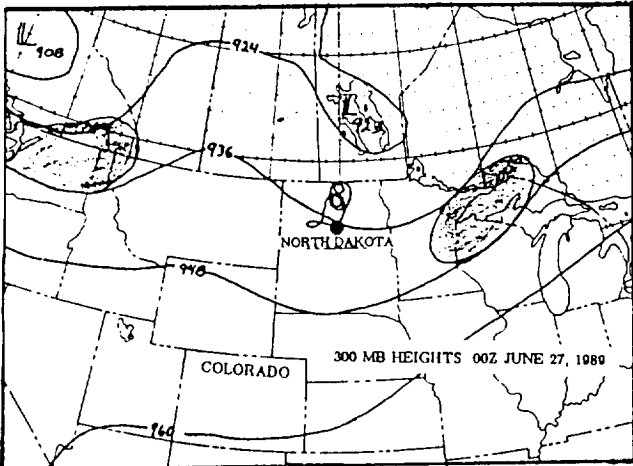


Fig. 1. Analysis of 300 mb heights (dm) for 00 UCT 27 June 1989. Operations were based in Bismarck, ND (indicated by a filled circle). The flight track for R7, conducted between 1612 and 1838 CDT (2112 and 2338 UCT) June 26, 1989, is shown north of Bismarck. The jet stream is indicated by the shaded areas. Skies over the flight region were cloud-free at this time -- note the region of upper level divergence over Montana.

The flight conducted on June 26, 1989 provides a good case study. Four constant-altitude legs were flown to the north of Bismarck (Fig. 1). Above the tropopause, located at about 10.5 km,  $O_3$  and  $NO_y$  showed a rapid increase, reflecting strong sources in the stratosphere. Water vapor and carbon monoxide showed the opposite effect, reflecting their origin at the Earth's surface (Table 1). In the upper troposphere leg (260 mb), the NO and CO mixing ratios are relatively high. A thin cirrus cloud was present just below this altitude, suggesting outflow from a thunderstorm upstream. Examination of flow fields and radar summaries confirms the existence of convective clouds over the northwestern US at the appropriate time.

Details of the flight leg at 216 mb (11.3 km) show considerable variation in potential temperature ( $\Theta$ ),  $O_3$ , and dew point with time, even though the altitude was constant to within about 20 m (Fig. 2). Ozone and  $\Theta$  are positively correlated, and dewpoint is anticorrelated. This shows that transport of air occurs more along levels of constant potential temperature (entropy) than along constant altitude, (e.g. WMO, 1986). Even the fine structure shows the strong correlative nature of these three variables. Each symbol represents a 10-s average, and the peak at 17:20 has a half width corresponding to about 1.5 km.

Correlation coefficients for all level flight legs (Table 2) generally show that species with an origin in the stratosphere,  $O_3$  and  $NO_y$ , have strong positive correlations with each other and with  $\Theta$ .

TABLE 1. MEAN PROPERTIES OF THE ATMOSPHERE MEASURED NEAR THE TROPOPAUSE

Pres. mb	Date mo/day	Temp. K	$\Theta$ K	$H_2O$ ppmv	CO ppb	NO ppb	$NO_y$ ppb	$O_3$ ppb	Alt. km
198	6/13	221.0	352.6	21	37	0.188	NA	454	11.3
198	6/26	221.4	351.5	6.5	34	0.189	5.15	417	11.8
216	6/26	219.3	340.0	24	76	0.202	3.75	236	11.3
217	6/13	228.2	338.6	80	55	0.180	NA	267	11.3
218	6/12	219.5	339.1	NA	75	0.330	2.54	182	11.2
237	6/26	219.8	331.6	41	113	0.163	1.52	126	10.7
238	6/30	229.4	345.5	31	83	0.100	4.40	171	10.7
238	6/22	227.3	342.4	8	38	0.093	9.51	383	10.7
239	6/13	217.4	327.4	80	113	0.151	4.86	88	10.7
260	6/26	223.1	328.3	55	119	0.309	1.51	88	10.1
350	6/13	240.8	322.7	336	119	0.016	2.84	66	7.9
378	6/22	237.1	313.6	130	101	0.032	2.43	56	7.6

Dates are month/day of 1989. Each entry represents a flight segment of approximately 20 min. duration.

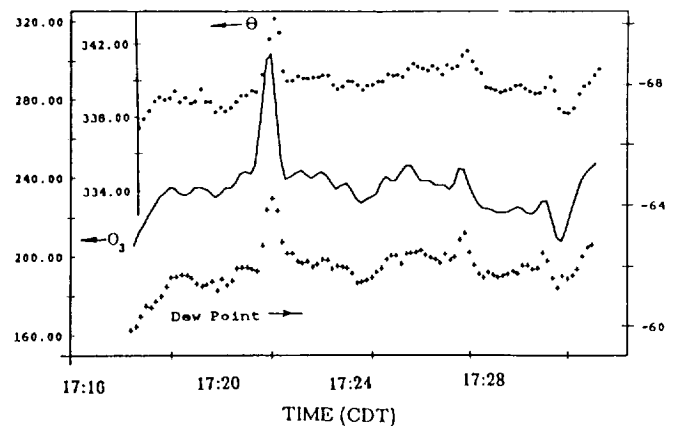


Fig. 2. Time series of in lower stratosphere June 26, 1989 at a constant altitude of  $11.29 \pm 0.02$  km (216 mb) about 800 m above the tropopause. Equivalent potential temperature (top) in K, with the scale on the insert. Ozone, continuous line in middle, in ppb. Dew point, bottom in  $^{\circ}C$ ; note sign. These results demonstrate that potential temperature rather than altitude defines chemically coherent layers in the lower stratosphere.

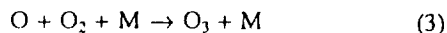
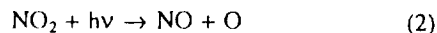
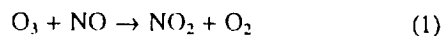
TABLE 2. CORRELATION COEFFICIENTS FOR FLIGHTS NEAR THE TROPOPAUSE

	$H_2O$	CO	NO	$NO_y$	$O_3$
$\Theta$	-.60	-.70	.37	.48	.85
$H_2O$		.53	-.60	-.18	-.55
CO			-.12	-.83	-.95
NO				-.40	.19
$NO_y$					.76

Species with an origin at the Earth's surface, CO and  $H_2O$ , show a positive correlation with each other, but a negative correlation with  $\Theta$ . Both the stratosphere and lightning are strong sources for NO in this data set; if the points showing greatest NO production by lightning (260 mb on 6/26) are omitted, the NO/ $NO_y$  correlation coefficient changes from -0.40 to 0.04. The strongest correlation coefficient, -0.95, is observed for CO and  $O_3$ . The product of the mixing ratios (in ppb) of CO and  $O_3$  is remarkably constant at about  $15 \times 10^3$ ; analysis of stratospheric data reported by Hipskind et al. (1987) shows the same value.

#### 4. DISCUSSION

In order to calculate the fraction of NO<sub>y</sub> in the form of NO<sub>x</sub>, we must convert measured concentrations of NO into NO<sub>x</sub>. This is achieved through the assumption of a photostationary state in which the following reactions dominate.



Ozone and NO are measured directly, thus we can express NO<sub>x</sub> as follows.

$$[\text{NO}_x] = [\text{NO}] + \frac{k[\text{NO}][\text{O}_3]\text{M}}{j(\text{NO}_2)} \quad (\text{E1})$$

Where  $k$  is the rate coefficient for Reaction 1 ( $2.0 \times 10^{-12} e^{-1400/T} \text{ cm}^3 \text{ s}^{-1}$ ); the ambient temperature, is measured directly. The coefficient for NO<sub>2</sub> photolysis,  $j(\text{NO}_2)$ , is obtained from the output of upward- and downward-looking Eppley UV radiometers (Dickerson et al., 1982).

Our observations (Table 3) can be profitably compared to those obtained on the Airborne Arctic Stratospheric Expedition (AASE). We observed stratospheric NO<sub>x</sub> mixing ratios range from about 0.17 to 0.44 ppb. Carroll et al. (1990) measured fairly constant stratospheric mixing ratios of 0.10 ppb during winter near 40° N, and even less in the Arctic.

TABLE 3. RATIOS OF REACTIVE NITROGEN TO OZONE MEASURED NEAR THE TROPOPAUSE

Pres. mb	Date mo/day	$j(\text{NO}_2)$ s <sup>-1</sup> × 10 <sup>3</sup>	NO <sub>x</sub> ppb	NO <sub>x</sub> /NO <sub>y</sub> ppb/ppb	O <sub>3</sub> /NO <sub>x</sub> ppb/ppm	O <sub>3</sub> /NO <sub>y</sub> ppb/ppm
198	6/13	10.2	0.293	NA	0.65	NA
198	6/26	11.6	0.346	0.067	0.83	12.3
216	6/26	12.0	0.296	0.079	1.25	15.9
217	6/13	18.4	0.238	NA	0.89	NA
218	6/12	13.3	0.441	0.173	2.42	13.9
237	6/26	12.0	0.209	0.137	1.66	12.0
238	6/30	5.5*	0.205	0.046	1.20	26.3
238	6/22	15.2	0.168	0.018	0.44	25.0
239	6/13	19.3	0.168	NA	1.92	NA
260	6/26	12.6	0.378	0.250	4.29	17.2
359	6/13	19.2	0.019	NA	0.29	NA
376	6/22	14.4	0.040	0.016	0.71	43.6

See text for explanation of how NO<sub>x</sub> is calculated.  
\*Zenith angle greater than 80° and  $j(\text{NO}_2)$  highly uncertain.

On the NDTP, NO<sub>y</sub> values range from about 1.5 to 9.5 ppb. On AASE Kawa et al. (1990) measured 1-2 ppb at similar potential temperatures near 60° N in December. Hübner et al. (1990) measured 1.5 to 1.9 ppb NO<sub>y</sub> with occasional excursions to over 10 ppb attributed to nitric acid-containing falling from above. Kondo et al. (1990) measured 2 to 3.5 ppb at about 15 km ( $\Theta = 380 \text{ K}$ ).

Ratios of trace gas concentrations can also be instructive. If we consider only flights on the cyclonic side of the jet stream, and clearly in the stratosphere as indicated by ozone mixing ratios above 100 ppb, we arrive at the following mean (median) ratios.

$$[\text{NO}_x]/[\text{O}_3] = 0.83(.89) \text{ ppb/ppm}$$

$$[\text{NO}_y]/[\text{O}_3] = 14.9(13.9) \text{ ppb/ppm}$$

$$[\text{NO}_x]/[\text{NO}_y] = .075(.079) \text{ ppb/ppb}$$

The range of values for the NO<sub>x</sub> ratios is about a factor of two, while that for NO<sub>y</sub> is about 30%. On the AASE project, stratospheric NO<sub>x</sub>/NO<sub>y</sub> ratios measured near 40° N were very similar to those reported here. Both data sets show higher ratios in the troposphere, and ASSE showed lower ratios in the Arctic. AASE ratios of NO<sub>y</sub>/O<sub>3</sub>, however, were lower (4 to 10 ppb/ppm) than those observed in the NDTP.

More NO<sub>x</sub> in the mid latitude summer than in the Arctic winter is expected due to more active photochemistry. Higher NO<sub>y</sub>, however, cannot be explained on the basis of stratospheric photochemistry. The origin of the relatively high NO<sub>x</sub> and NO<sub>y</sub> concentrations observed in the lower stratosphere on the NDTP may be the active convection characteristic of summer on the Great Plains. As evidence, consider the water vapor mixing ratios (Table 1.). In AASE the mean value was near 5 ppm, typical of the stratosphere (WMO, 1986), but on the NDTP, water vapor mixing ratios were several times higher. The injection of NO must have occurred a day or more before we sampled the air, because under these conditions the lifetime of NO<sub>x</sub> with respect to HNO<sub>3</sub> is about a day, and the observed ratio of NO<sub>x</sub>/NO<sub>y</sub> is not unusually high.

The NO<sub>y</sub> is unlikely to result from upward transport of polluted boundary layer air — the CO levels were typical of the stratosphere. Hydrocarbon levels were likewise low; on the 11.8 km (198 mb) on 6/13 we detected ethane (0.320 ppt), propane (60 ppt), and i-butane (10 ppt). When high NO<sub>y</sub> comes from convective transport of boundary layer air, CO and NMHC are elevated (e.g. Dickerson et al., 1987).

From the estimated flux of O<sub>3</sub> into the Northern Hemispheric troposphere of 4 to 8 × 10<sup>10</sup> molec. cm<sup>-2</sup>s<sup>-1</sup> we estimate the range of NO<sub>x</sub> flux as 0.06 to 0.13 Tg(N) yr<sup>-1</sup>, and the range of NO<sub>y</sub> flux as from 1.1 to 2.2 Tg(N) yr<sup>-1</sup>. These values exceed the rate of nitrogen fixation in the global stratosphere calculated by Kasibhatla et al. (1991) of 0.64 Tg(N) yr<sup>-1</sup>, and may be inflated by lightning-produced NO. The results indicate clearly that downward transport of reactive nitrogen can be important for the photochemistry of the upper troposphere, but not for the lower troposphere over the continents or for nitrogen deposition to the continents.

#### 5. CONCLUSIONS

- O<sub>3</sub>, and NO<sub>y</sub> are positively correlated.
- CO and H<sub>2</sub>O are anticorrelated with O<sub>3</sub> and O<sub>3</sub>.
- High NO<sub>x</sub>, NO<sub>y</sub>, and H<sub>2</sub>O concentrations were observed in the stratosphere on the cyclonic side of the jet stream.
- Implied NO<sub>x</sub> flux into Northern Hemisphere troposphere is 1 to 2 Tg(N) yr<sup>-1</sup> with 8% as NO<sub>x</sub>; this exceeds some estimates of global stratospheric NO<sub>y</sub> production.
- Observed trace gas concentrations suggest that thunderstorms inject water and NO produced by lightning into the lower stratosphere.

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#### APPENDIX: EXPERIMENTAL UNCERTAINTY

Several factors contribute to the uncertainty in the calculated  $[\text{NO}_x]$ . Our technique for calculating  $j(\text{NO}_2)$  gives results equivalent within experimental uncertainty to those obtained using the technique described by Madronich (1987), however no direct calibration of radiometers with chemical actinometers has ever been performed for these conditions. We have ignored other species such as  $\text{HO}_2$  that can oxidize  $\text{NO}$  to  $\text{NO}_2$ , but these should play a relatively minor role in the lower stratosphere. Measurements of  $\text{NO}$  under field conditions carry an uncertainty of about  $\pm 15\%$ , and errors in the other factors in Equation 1 are small. Calculation of  $j(\text{NO}_2)$  at the surface can be performed with an uncertainty of about  $\pm 10\%$ , but for our aircraft observations, the uncertainty is more likely  $\pm 20\%$ . The calculation of  $[\text{NO}_x]$  is still robust, however, because  $\text{NO}$  is typically about 70% of  $\text{NO}_x$ ; an error of 20% in the estimate of  $j(\text{NO}_2)$  would lead to an error of only about 7% in  $[\text{NO}_x]$ .

The estimated absolute accuracy (95% confidence) of the  $\text{NO}_y$  measurements in the stratosphere is about  $\pm 30\%$ . The molybdenum converter releases  $\text{NO}$  when first exposed to high levels of ozone, and the low ambient pressures reduce the flow and thus the sensitivity of the instrument. The estimated absolute accuracy in the  $\text{CO}$  measurements is  $\pm 10$  ppb or  $\pm 5\%$  whichever is greater. Total uncertainty ( $\pm 1\sigma$ ) in the reported frost points is  $\pm 0.43$  K (Spyres-Duran, 1990)

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