N95-11106

AIRCRAFT MEASUREMENTS OF NO AND NOy AT 12KM OVER THE PACIFIC OCEAN

M. Koike[1], Y. Kondo[1], Y. Makino[2], Y. Sugimura[2]

[1] Solar-Terrestrial Environment Laboratory, Nagoya University, Japan

[2] Meteorological Research Institute, Tsukuba, 305 Japan

Abstract. Measurements of nitric oxide (NO) and total reactive nitrogen (NOy) at altitudes about 12 km were made from two aircraft missions over the central and western Pacific Ocean at latitudes between 65°N and 65°S during the International Strato–Tropospheric Air Chemistry (INSTAC) program. NO measurements were performed during the first mission in late February and early March 1990, while NOy measurements were performed during the second mission in October 1990. Lowest NO and NOy mixing ratios in the upper troposphere were observed near the equator to be about 30~70pptv and 150~220pptv, respectively. NOy mixing ratios in the upper troposphere were higher in the northern middle latitude than in the southern middle latitude; 300~900pptv in 30°N~50°N and 250~400pptv around 25°S and 50°S possibly due to the transport of the polluted air from the boundary layer and the emissions from the commercial aircraft in the northern middle latitudes. Near the equator up to 40°S, the NO values showed very high variability and reached between 200 and 2000 pptv. NOy(pptv)/ozone(ppbv) ratios in the upper troposphere were between about 3 and 20 and these values seem to be higher in the lower latitude except for the polluted air in the northern middle latitude. These NOy/ozone ratios in the equatorial upper troposphere are higher than those in the lower stratosphere observed by others. These features of NO and NOy in the equatorial upper troposphere suggest that NOx is produced possibly by the lightning.

INTRODUCTION

Oxides of nitrogen ($NOx=NO+NO_2$) play important roles in the chemistry of the troposphere. NOx is one of the important precursors for photochemical production of tropospheric ozone. (Fishman et al., 1979; Liu et al., 1987). Since OH radical is produced mainly by the reaction between H_2O and $O(^1D)$ which is in balance with ozone, NOx also indirectly controls hydroxyl radicals. Since the hydroxyl radicals in turn control the chemical lifetime of a number of trace gases, such as CH_4, NOx impact the photochemistry of large number of trace gases in the troposphere.

The principal component species of total reactive nitrogen (NOy) in the troposphere are

$NOy = NO + NO_2 + NO_3 + 2\times N_2O_5 + HNO_3 + PAN + HO_2NO_2 + NO_3^- +$ other organic nitrates + ...

NOy is conserved against interchange reactions among the individual reactive nitrogen species. Therefore NOy has the chemical lifetime considerably longer than those for the individual species. NOy measurements could provide useful information for the source and transport processes of these reactive nitrogen species. Measurements of NO and NOy were made in the boundary layer and middle troposphere (Ridley et al., 1987, 1989; Carroll et al., 1990) and upper troposphere (Drummond et al., 1988; Murphy et al., 1992). Most of these data were obtained near and over the United States or over the Atlantic Ocean and coast of the South America.

We made measurements of NO and NOy at altitudes about 12 km from two aircraft missions over the central and western Pacific Ocean during the International Strato–Tropospheric Air Chemistry (INSTAC) program. NO concentration was measured during the first mission in late February and early March 1990, while NOy concentration was measured during the second mission in middle October 1990. Concentration of ozone and some other chemical species were also measured on the aircraft. The latitude range covered was from 65°S to 65°N in the both missions as shown in Figure 1. Since the cruise altitude was about 12km, most of the measurements were made in the upper troposphere or lower stratosphere at lower latitudes or higher latitudes, respectively.

INSTRUMENTATION

NO was measured by the chemiluminescence NO detector (Kondo et al., 1983, 1987). For measurements of NOy, NOy was catalytically converted to NO on a surface of the heated gold with the aid of added CO. The inner diameter and the length of the gold tube was 3.6mm and 55cm, respectively. About 30cm of this gold tube was kept at the temperature of 300±1 °C during the measurement. The conversion efficiency of this system was tested in the laboratory before the flights. For NO_2, a conversion efficiency of 99±2% was found.

To check the zero level for NO measurement, ozone was added to the sample flow to convert NO into NO_2 which does not make signals in the reaction chamber. This zero level was checked carefully by sampling the purified air in the laboratory and by using night time ambient NO data obtained in this and other missions. As a result, 3.7pptv was subtracted from the measured NO concentration to correct the bias in the zero level. For NOy measurement, purified air was sampled to check the zero level. NOy concentration in the purified air used in this mission was found to be 41±10pptv in the laboratory experiment, and this value was added for measured NOy concentration. During the flights, the zero level was measured for two minutes in every four minutes. In every eighteen minutes the calibration was performed for two minutes to check the sensitivity of the instrument by adding the calibrated NO gas into the sample flow. In this paper two minutes

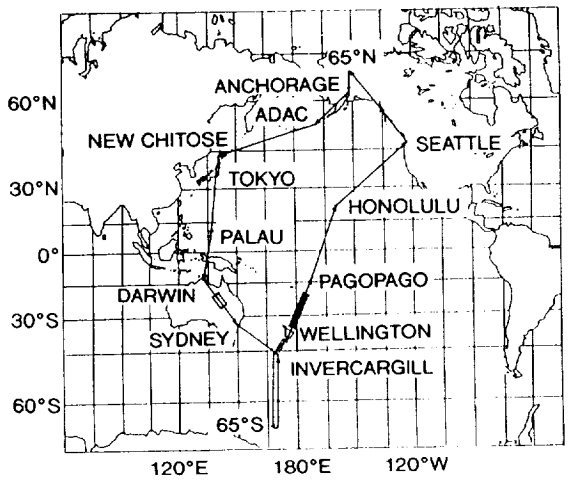

Fig. 1. Flight route of the two aircraft missions. The flight was started in the direction from Tokyo to Palau in the mission I and from Tokyo to Anchorage in the mission II. Open and closed squares on the flight route are the locations where enhanced NO mixing ratios were observed on February 21 (open square) and March 3 (closed square), respectively (see the text).

Table 1 Flight Schedule of Mission 1

Flight number	Date	Flight leg
1	Feb.20	Tokyo to Palau
2	Feb.20	Palau to Darwin
3	Feb.21	Darwin to Sydney
4	Mar. 2	Sydney to Invercargill
5	Mar. 2	Invercargill to 65°S to Invercargill
6	Mar. 2	Invercargill to Wellington
7	Mar. 3	Wellington to Pagopago
8	Mar. 3	Pagopago to Honolulu
9	Mar. 4	Honolulu to Seattle
10	Mar. 5	Seattle to 65°N to Anchorage
11	Mar. 7	Anchorage to Adac
12	Mar. 7	Adac to New Chitose
13	Mar. 7	New Chitose to Tokyo

averages of NO and NOy mixing ratios are presented.

Ozone concentration was also observed by UV photometer technique in both missions by Meteorological Research Institute. In this paper, data are shown at every one degree in latitude for the first mission and one minute average data are shown for the second mission.

RESULTS FROM MISSION I

Mission I was performed in late February and early March 1990 starting in the direction from Tokyo to Palau. Date of the each flight is given in Table 1 and the flight route is shown in Figure 1. In Figure 2 (a) and (b), NO mixing ratio is shown versus latitude with ozone data for northbound and southbound flight, respectively. In these

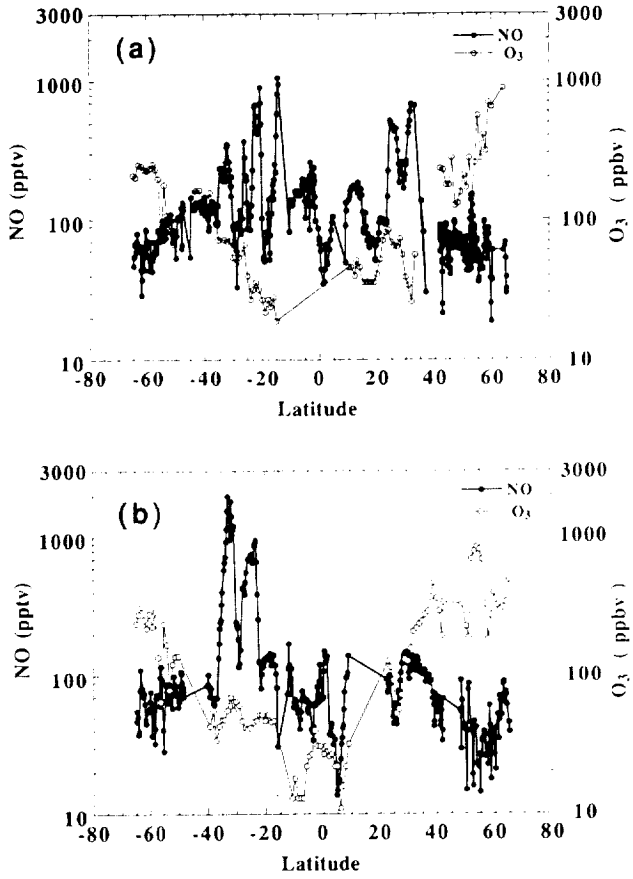

Fig. 2. NO (closed circle) and ozone (open circle) mixing ratio at altitude about 12km versus latitude. In Fig. 2 (a), southbound data obtained from Japan to 65°S point and from 65°N point to Japan are shown. In Fig. 2 (b), northbound data obtained from 65°S to 65°N (over the central Pacific) are shown.

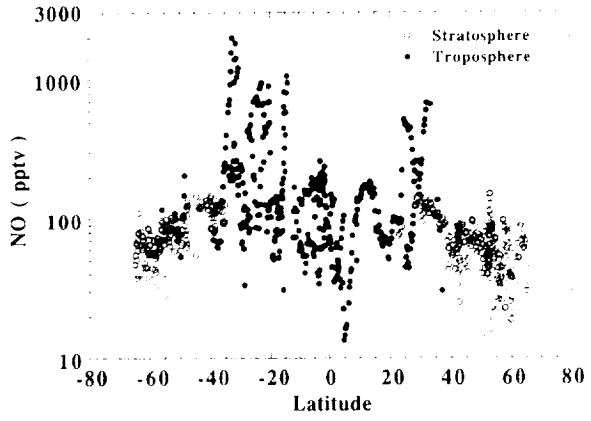

Fig. 3. All of the NO data obtained during the mission I. Closed circles and open circles represent the tropospheric and stratospheric data, respectively.

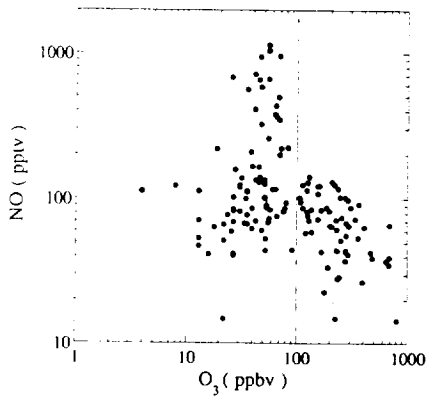

Fig. 4. NO mixing ratio versus ozone mixing ratio.

figures, data obtained at the altitude between 11km and 12km are shown. Also the data obtained at solar zenith angles smaller than 85 degrees are presented here.

In Figure 3, NO data obtained during the both southbound and northbound flight is shown versus latitude. The sampled air mass has been classified as tropospheric or stratospheric depending on the ozone mixing ratio smaller or larger than 100ppbv. In Figure 3 closed and open circles represent the tropospheric and stratospheric data, respectively.

NO mixing ratio in the lower stratosphere at the middle latitudes decreases toward higher latitude in the both hemispheres; 80~130pptv at 35°N/S and 30~90pptv at 65°N/S. NO mixing ratio in the troposphere at low and middle latitudes varies significantly. Minimums of NO values are between about 30pptv and 70pptv depending on the latitude. The lowest values were observed near the equator to be about 30pptv. The lowest ozone mixing ratios less than 20ppbv were also often observed near the equator. On the other hand, some enhancements of NO mixing ratios were often observed in the troposphere. Rapid changes more than 100pptv were seen even within a few hundred kilometer. Two quite large enhanced NO mixing ratio about 2000pptv and 900pptv were observed between 20°S and 40°S over the ocean, north of New Zealand on March 3. On February 21, two other enhancements of about 900pptv were also observed at similar latitudes over Australia. The location of these enhancements observed on the different days are shown in the Figure 1 by an closed and open squares, respectively. As seen in Figure 2 (a) and (b), the ozone mixing ratio did not change associated with the two enhancements of NO. The areal extent where NO values are larger than 500pptv is about 300km~400km in both cases.

In Figure 4, NO mixing ratio are plotted versus ozone mixing ratio. No clear correlation between NO and ozone is seen for both stratospheric and tropospheric data. It is clearly seen that the NO values has a higher variability in the troposphere than in the stratosphere.

RESULTS FROM MISSION II

Mission II was performed in mid October 1990 and the flight route was similar to that in Mission I except that the flight started in the direction from Tokyo to Anchor-

Table 2 Flight Schedule of Mission 2

Flight number	Date	Flight leg
1	Oct.15	Tokyo to Cold Bay
2	Oct.15	Cold Bay to Anchorage
3	Oct.16	Anchorage to 65°N to Seattle
4	Oct.17	Seattle to Oakland
5	Oct.17	Oakland to Honolulu
6	Oct.18	Honolulu to Pagopago
7	Oct.18	Pagopago to Invercargill
8	Oct.20	Invercargill to 65°S to Invercargill
9	Oct.21	Invercargill to Melbourne
10	Oct.21	Melbourne to Darwin
11	Oct.22	Darwin to Palau
12	Oct.22	Palau to Tokyo

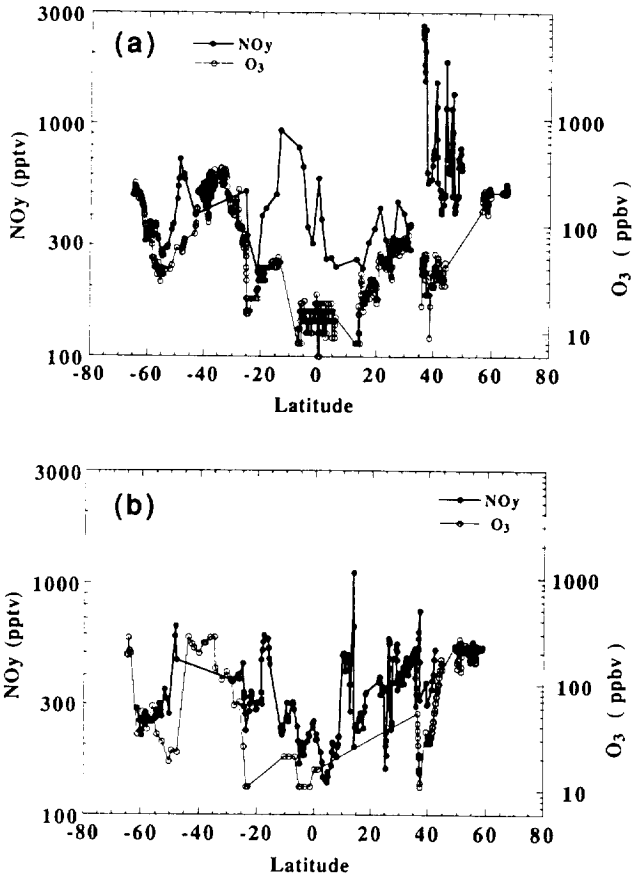

Fig. 5. NOy (closed circle) and ozone (open circle) mixing ratio at altitude about 12km versus latitude. In Fig. 5 (a), northbound data obtained from Japan to 65°N point and from 65°S point to Japan are shown. In Fig. 5 (b), southbound data obtained from 65°N to 65°S (over the central Pacific) are shown. In these figures only the tropospheric data are plotted for NOy.

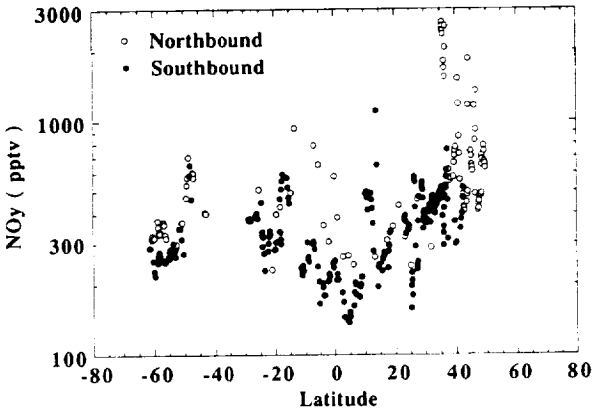

Fig. 6. All of the tropospheric NOy data obtained during the mission II. Closed circles and open circles represent the southbound and northbound data, respectively.

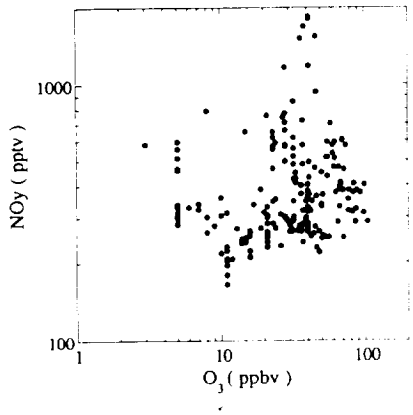

Fig. 7. NOy mixing ratio versus ozone mixing ratio.

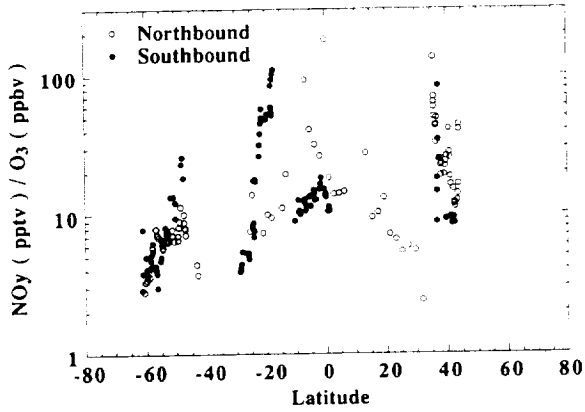

Fig. 8. NOy(pptv)/ozone(ppbv) ratio versus latitude. Closed circles and open circles represent the southbound and northbound data, respectively.

age. Date of each flight is given in Table 2. In Figure 5 (a) and (b), volume mixing ratios of NOy at the altitude between 11km and 12km are shown versus latitude with ozone data. In Figure 6, both northbound and southbound NOy data are shown. The air mass, in which the ozone mixing ratio is smaller than 100ppbv, has been classified as tropospheric. In Figures 5 and 6, only the tropospheric NOy data are shown.

NOy mixing ratios in the upper troposphere show a clear variation with latitude. Lowest values of NOy were observed near the equator to be 150~220pptv. Small enhancements with maximum between 500pptv and 1000pptv were observed at latitudes between 30°N and 30°S, however these features are not as pronounced as those found in NO values shown in Figure 3. In the northern Pacific NOy mixing ratio increases with the latitude until up to 50°N. At latitudes between 40°N and 50°N, NOy mixing ratio is about 300~900pptv. Also enhancements up to more than 1000pptv were often observed at these latitude. On the other hand, at southern middle latitudes, NOy mixing ratio are about 250~400pptv around 25°S and 50°S. Though the tropospheric NOy data was not obtained between 30°S and 45°S, NOy value over the Pacific in the southern hemisphere seems to have only small variation with the latitude. As a result, in the upper troposphere, NOy values in the northern hemisphere is systematically higher than those in the southern hemisphere.

In Figure 7 NOy mixing ratios are plotted versus ozone mixing ratios. Weak positive correlation between NOy and ozone can be seen.

In Figure 8, NOy(pptv)/ozone(ppbv) ratio is shown. The ratio in the upper troposphere is between about 3 and 20, and it seems to be higher in the lower latitude. The ratios more than 50 were observed in a few cases in the middle latitude both in the northern and southern hemispheres. These values agree well with the values of between 3 and 15 observed in the troposphere at Darwin (12°S), Stavanger (59°N), and Punta Arenas (53°S) presented by Murphy et al. (1992).

DISCUSSION AND SUMMARY

NOy mixing ratios in the upper troposphere over the Pacific Ocean are higher in the northern hemisphere than in the southern hemisphere at mid latitudes. In the northern hemisphere, enhancements of NO and NOy values were also often observed. These high NO and NOy values are possibly caused by a fast vertical transport of the polluted air from the planetary boundary layer and by emissions from commercial aircraft. Ehhalt et al. (1992) estimated the importance of several NOx sources and showed that fast transport from the planetary boundary layer makes a major contribution in the upper troposphere at latitudes between 40°N and 50°N as well as the aircraft emission.

In the upper troposphere, the lowest values of NO and NOy mixing ratio were observed near the equator. This is considered to be due to the transport of NOy poor tropical maritime air from the lower troposphere to the upper troposphere by the strong convections. This is supported by the observed low ozone mixing ratios at low latitudes.

High variabilities of NO and NOy in the upper troposphere at latitudes between 20°N and 40°S may be caused by NOx production by the lightning activities. Potential

importance of the NO production by the lightning activities in the equatorial region has been presented from several model calculations (Liu et al., 1983; Ko et al., 1986; Chameides et al.,1987). Evidence of NO production was reported by Ridley et al. (1987) and Davis et al. (1987). In that case two spikes of NO mixing ratio up to 700 and 900pptv were measured in a cumulus cloud at altitude of 9.3km over the ocean near Hawaii. The spatial scale was about 3km. Murphy et al. (1992) discussed that the most plausible source of NOy in the tropical upper troposphere is lightning production of NOx. As an evidence they showed a larger NOy/ozone ratio in the troposphere than that in the stratosphere observed near Darwin. Sources of NO or NOy in the upper troposphere are, (1) transport from the stratosphere, (2) transport from the planetary boundary layer, where NOx is produced by combustion of the fossil fuel and other processes, (3) emission of NOx from the commercial aircraft and (4) lightning. As shown in Figure 8, NOy(pptv)/ozone(ppbv) ratios in the equatorial upper troposphere of about 5~20 are higher than that in the lower stratosphere at Darwin of about 3 reported by Murphy et al. (1992). A higher ratio in the upper troposphere than that in the lower stratosphere is consistent with the results presented by Murphy et al. (1992). This means that these high NOy air is not stratospheric origin. Also NO or NOy sources (2) and (3) are unlikely to be cause of enhanced NO and NOy values at low latitude. As a result the lightning is most likely source of NO and NOy in the upper troposphere at low latitudes. The lightning activities near the Australian continent is known to be very high especially between January and March (Turman and Edgar, 1982). In October the activity is less. This is consistent with the higher variability of NO value observed in late February and early March than that of NOy observed in middle October (see Figure 3 and 6). Because of the large areal extent of these high NO and NOy region, NO production by the lightning is important for NO and NOy budget in the upper troposphere.

Acknowledgments. The INSTAC aircraft missions were funded by the Science and Technology Agency of Japan. M.K. and Y.K. acknowledge supports by the Japanese Ministry of Education, Science and Culture. M.K. and Y.K. wish to thank N. Toriyama, M. Kaneda, and H. Jindo for their assistance with the aircraft observations.

References

Chameides, W.L., D.D. Davis, J. Bradshaw, M. Rodgers, S. Sandholm, and D.B. Bai, An estimate of the NOx production rate in electrified clouds base on NO observations from the GTE/CITE I fall 1983 field operation, *J. Geophys. Res.*, *92*, 2153–2156, 1987.

Carroll, M.A., D.R. Hastie, B.A. Ridley, M.O. Rodgers, A.L. Torres, D.D. Davis, J.D. Bradshaw, S.T. Sandholm, H.I. Schiff, D.R. Karecki, G.A. Harris, G.I. Mackay, G.L. Gregory, E.P.Condon, M. Trainer, G. Hübler, D.D. Montzka, S. Madronich, D.L. Albritton, H.B. Singh, S.M. Beck, M.C. Shipham, and A.S.Bachmeier, Aircraft measurements of NOx over the eastern Pacific and continental United States and implications for ozone production, *J. Geophys. Res.*, *95*, 10205–10233, 1990.

Davis, D.D, J.D. Bradshaw, M.O. Rodgers, S.T. Sandholm, and S. KeSheng, Free tropospheric and boundary layer measurements of NO over the central and eastern North Pacific Ocean, *J. Geophys. Res.*, *92*, 2049–2070, 1987.

Drummond, J.W., D.H Ehhalt, and A.Volz, Measurements of nitric oxide between 0-12km altitude and 67°N to 60°S latitude obtained during STRATOZ III, *J. Geophys. Res.*, *93*, 15831–15849, 1988.

Ehhalt, D.H., F. Rohrer, and A. Wahner, Sources and distribution of NOx in the upper troposphere at northern mid-latitudes, *J. Geophys. Res.*, *97*, 3725–3738, 1992.

Fishman, J., S. Solomon, and P.J. Crutzen, Observational and theoretical evidence in support of a significant in-situ photochemical source of tropospheric ozone, *Tellus*, *31*, 432–446, 1979.

Ko, M.K.W., M.B. McElroy, D.K.Weisenstein and N.D.Sze, Lightning: A possible source of stratospheric odd nitrogen, *J. Geophys. Res.*, *91*, 5395–5404, 1986.

Kondo, Y., W.A. Matthews, A. Iwata, Y. Morita, and M. Takagi, Aircraft measurements of oxides of nitrogen along the eastern rim of the Asian continent: winter observation, *J. Atmos. Chem.* , *5*, 37–58, 1987.

Kondo, Y., H. Muramatsu, W.A. Matthews, N. Toriyama, and M. Hirota, Tropospheric ozone and oxides of nitrogen over the north-western Pacific in summer, *J. Atmos. Chem.* , *6*, 235–250, 1988.

Liu, S.C., M. McFarland, and D. Kley, O. Zafiriou, B. Huebert, Tropospheric NOx and O_3 budgets in the Equatorial Pacific, *J. Geophys. Res.*, *88*, 1360–1360, 1983.

Liu, S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parrish, E.J.Williams, D.W. Fahey, G. Hübler, and P.C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, *92*, 4191–4207, 1987.

Murphy, D.M., D.W. Fahey, M.H. Proffitt, S.C. Liu, K.R. Chan, C.S. Eubank, S.R. Kawa, and K.K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, in press, 1992.

Ridley, B.A, M.A. Carroll, and G.L. Gregory, Measurement of nitric oxide in the boundary layer and free troposphere over the Pacific Ocean, *J. Geophys. Res.*, *92*, 2025–2047, 1987.

Ridley, B.A, M.A. Carroll, D.D. Dunlap, M. Trainer, G.W. Sachse, G.L. Gregory, and E.P.Condon, Measurement of NOx over the eastern Pacific Ocean and southwestern United States during the spring 1984 NASA GTE aircraft program, *J. Geophys. Res.*, *94*, 5043–5067, 1989.

Turman, B.N., and B.C Edgar, Global lightning distribution at dawn and dusk, *J. Geophys. Res.*, *87*, 1191–1206, 1982.