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Sources of Reactive Nitrogen in the Upper Troposphere During SONEX

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Abstract. The relationship among NOy, O_3, N_2O, ultra-fine condensation nuclei (CN), and other trace gases in the upper troposphere (UT) and lower stratosphere (LS) observed during SONEX are analyzed with the goal to identify and quantify the sources of NOy in the UT. We use N_2O to separate upper tropospheric air from stratospheric influenced air and focus our analysis to the former. The distributions of NOy and O_3 show remarkable similarity when they are plotted as a function of N_2O. The only difference between NOy and O_3 is found in upper tropospheric air where a large number of data points have high values of both NOy and the NOy/O_3 ratio. Major sources contributing to these high NOy values are found to be emissions from lightning and surface sources transported to the UT by convection.

Introduction

Nitrogen oxides, i.e. NOx ($NO+NO_2$) are key trace gases in the tropospheric photochemistry. Photochemical reactions involving NOx, CO and CH_4 are a major source of tropospheric O_3. Because the lifetime of NOx is short and the sources are small, NOx concentrations in most parts of the troposphere are extremely low. As a result, NOx is usually the rate-limiting precursor of O_3.

As O_3 in the UT is an effective greenhouse gas (Fishman et al., 1979), an environmental concern is the possible increase of O_3 in the UT due to NOx emissions from subsonic aircraft (e.g. Singh et al., 1999). However, a quantitative evaluation of the increase in O_3 has turned out to be difficult and highly uncertain. A major contributor to the uncertainty is the lack of knowledge about the budget of NOx and other reactive nitrogen species in the UT.

Concurrent observations of total reactive nitrogen or NOy ($NO + NO_2 + N_2O_5 + NO_3 + HNO_3 + HO_2NO_2$ + PAN + other organic nitrates), NO and tracers such as N_2O, O_3, CN, CH_4, CO and others in the stratosphere have been shown to be valuable for studying the budgets of NOy and O_3 (e.g. Murphy et al., 1993; Ridley et al., 1994). The study by Murphy et al. (1993) is particularly interesting in addressing NOy sources in the UT. By examining the ratio of NOy to O_3 as a function of potential temperature observed from ER-2 aircraft over Punta Arenas, Stavanger, and Darwin during various airborne experiments, they were able to deduce that lightning was a major source of NOy in the tropical UT and LS, confirming findings of modeling studies (Tuck, 1976; Kley et al., 1981; Ko et al., 1986).

In this work, we study the budget of NOy by examining the relationship among NOy, O_3, CN, N_2O, and other trace gases in the UT and LS observed on board the NASA DC-8 aircraft during SONEX. SONEX was an airborne field campaign conducted in October-November 1997 in the vicinity of the North Atlantic Flight Corridor to study the impact of aircraft emissions on NOx and ozone (Singh et al., 1999). Following the work of Murphy et al. (1993), we will take advantage of the near-inert characteristics of O_3 and NOy in the LS and UT. In these regimes, the O_3 lifetime against photochemical sink is on the order of a year, except inside the polar vortex (Brasseur and Solomon, 1986; Liu and Trainer, 1988).

Characteristics of NOy and O_3 as a Function of N_2O

Figures 1a-1c depict the mixing ratios of NOy and O_3, and the NOy/O_3 ratio as a function of N_2O for all observations above 7 km. The observations used here are those from the 10 second merged data set as described by Singh et al. (1999). N_2O is used because it is a tracer that gives a good measure of the influence of stratospheric air. The smaller the N_2O mixing ratio is, the larger is the stratospheric influence. This is reflected clearly by the excellent anti-correlation between O_3 and N_2O in Fig. 1a which is typical for mid-latitude air observed near the tropopause (e.g. Murphy et al., 1993). In this study, 312 ppbv is chosen to represent the mixing ratio of N_2O at the tropopause based on an examination of the vertical distributions of N_2O, H_2O and O_3. The regime with mixing ratio of N_2O greater than 312 ppbv will be called upper tropospheric air (UTA) and below the value as the stratospheric influenced air (SIA). There is an uncertainty of about 1 ppbv in the determination of this tropopause value of N_2O. The uncertainty is small enough that it has a negligible effect on the major results of this work.

The relationship between NOy and N_2O (Fig. 1b) is similar to that of O_3 and N_2O, especially when the stratospheric influence is significant. This can be seen in Fig. 1b for the regime below 312 ppbv of N_2O where the distribution of NOy is very similar to that of O_3. The similarity between NOy and O_3 in the SIA was observed consistently in a number of experiments before (e.g. Fahey et al., 1990; Murphy et al., 1993; Weinheimer et al., 1993) and is expected as both O_3 and NOy have their major stratospheric sources in the upper stratosphere. In addition, the ratio of NOy to N_2O in the SIA is in good agreement with previous observations (e.g.

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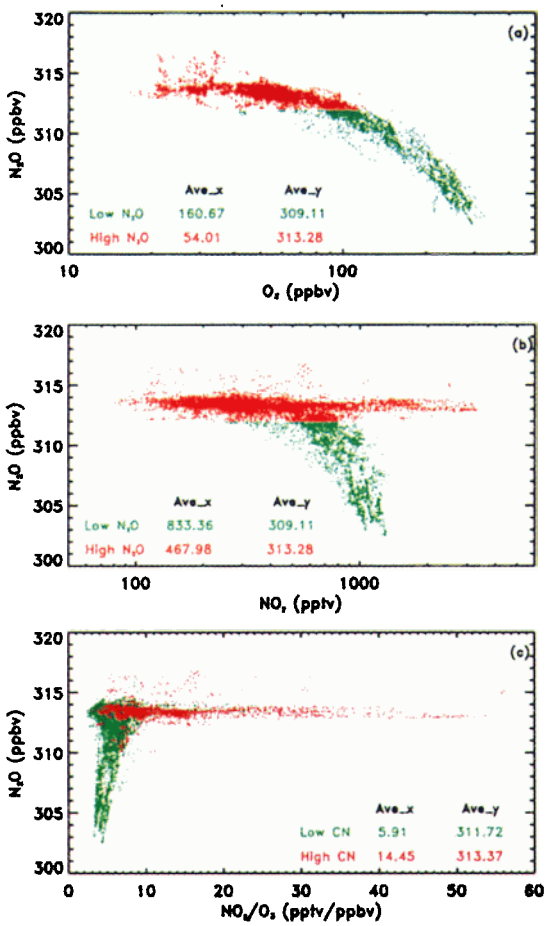

Figure 1a. Correlation between O_3 and N_2O for all data points above 7 km; 1b, same as 1a except for NOy and N_2O; 1c, same as 1a except for NOy/O_3 and N_2O.

Loewenstein et al., 1993; Murphy et al., 1993). The only significant difference between NOy and O_3 is in the UTA where NOy deviates from the smooth profile of SIA by having significant number of data points with large mixing ratios. Both the difference and the similarity between NOy and O_3 are highlighted by the plot of the NOy/O_3 ratio against N_2O in Fig. 1c. The ratio is nearly a vertical straight line in the SIA. In contrast, there is a long horizontal tail of high NOy/O_3 ratio in the UTA as a result of large increases in NOy mentioned above.

The nearly vertical distribution of NOy/O_3 ratio in Fig. 1c is substantiated by the fact that the median value of NOy/O_3 ratio increases by only about 70% from the lowest 10% of N_2O to the highest 10% of N_2O. In contrast, corresponding changes in the median values of O_3 (Fig. 1a) and NOy (Fig. 1b) are greater than a factor of five. This drastic reduction in the variability suggests that NOy and O_3 distributions in the UTA and the SIA are controlled by common factors or processes. One of the processes may be the exchange process between the UT and the LS that may have a strong influence on the O_3 and NOy distributions in both the SIA and the UTA.

Identifying the Sources of NOy in the UTA

What is the NOy source(s) in the UTA? In order to address this question, an obvious approach is to examine data points with high NOy/O_3 ratio. Fig. 1c indicates that NOy/O_3 ratio of $10x10^{-3}$, above which about 20% of the data points reside, is a reasonable cut-off value for high NOy/O_3 because it is close to the top quartile cut-off value and it clearly separates the high NOy/O_3 tail from the rest of the data. The time periods and flight numbers of these points are plotted and examined (not shown). The major contributing flights listed in decreasing importance are flights 14, 12, 10, 3, and 9. A general description of the flight tracks and characteristics of these flights is presented in Singh et al. (1999). These five flights contribute to about 80% of the total points with $NOy/O_3 > 10x10^{-3}$. An examination of the lightning frequency observed and back trajectories during each flight indicates that these were the very flights with significant occurrences of lightning or convective activities upwind. This strongly suggests that NO emissions from lightning or some other NOx sources related to convection are the predominant sources of NOy. This notion is also supported by the fact that most of the points with $NOy/O_3 > 10x10^{-3}$ have high concentrations of CN (> 5000 cm^{-3}, red points in Fig. 1c) which are known to be produced in the convection (Ridley et al., 1997; Wang et al., 1999). Of course, high CN may also indicate emissions from aircraft (e.g. Schlarger et al., 1997; Anderson et al., 1999). However, aircraft contrails are characterized by short pulses/spikes of CN and NOy of several seconds to a few minutes (e.g. Zheng et al., 1996; Wang et al., 1999) rather than the long pulses evident in flights 10, 12 (Fig. 2), and 14.

A strong piece of evidence supporting lightning or some other NOx sources related to convection as the dominant sources of the high NOy/O_3 data points can be seen in Fig. 1c. In this figure there are a total of 1,241 data points with $NOy/O_3 > 10x10^{-3}$, 1239 of them in the UTA but only 2 points in the SIA. This large disparity is also seen in the distribution of the absolute levels of NOy (Fig. 1b), e.g. there are significant number of points with NOy increments of 1000 pptv or more above the median value (325.5 pptv) in the UTA (red points), but not a single point with such increment in the SIA (green points). Such a large disparity can only be explained by sources of NOy that reside only in the troposphere. These sources can be lightning and/or surface sources, but not emissions from aircraft, because the North Atlantic Flight Corridor often cross into the LS in this season (Baughcum et al., 1996). This was confirmed by back-trajectory study of Koike et al., (1999) and Kondo et al. (1999) who showed a large number of aircraft flights occurred in the SIA.

The absolute value of NOy can be used to calculate an upper limit of the aircraft contribution to the high NOy values in the UTA. This is done by first calculating the occurrence of data points with NOy increments of 325.5 pptv (median UTA NOy) above the median NOy level of each 1 ppbv bin of N_2O. We find that 29 points occur in the SIA while 877 points occur in the UTA, i.e. a ratio of 3.3%. The value 3.3% is more than a factor of ten smaller than the ratio of number of data points in the SIA vs. that in the UTA (2532/6158 = 0.41 or 41%). By assuming all the high NOy values observed in the SIA are from aircraft emissions, we can calculate an upper limit of the aircraft contribution to the high NOy values in the UTA to be 3.3%/0.41 = 8%.

Once the aircraft emissions are excluded as a major source of data points with $NOy/O_3 > 10x10^{-3}$, the major contributing sources can be identified relatively easily as they each tend to

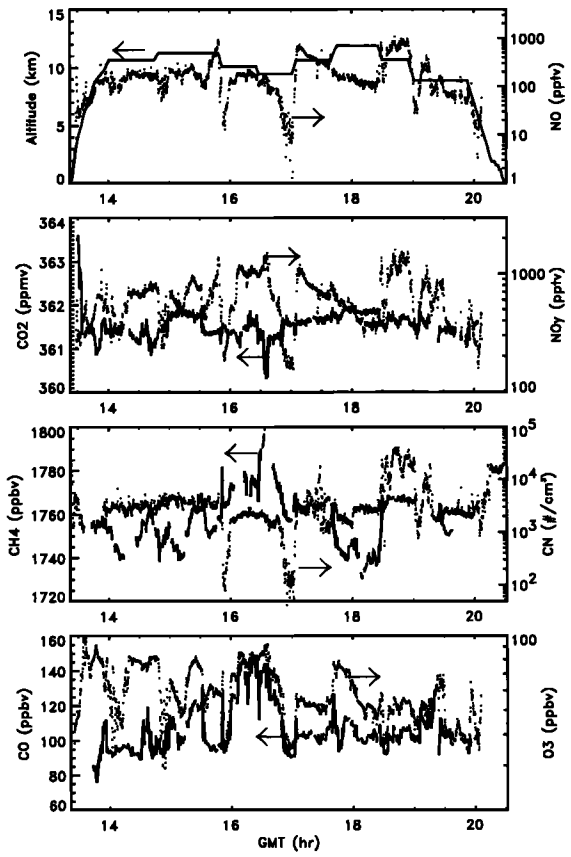

Figure 2. Time series of mixing ratios of key trace species and altitude observed during flight 12, November 3, 1997. The y-coordinates are denoted by arrows.

have unique characteristics in their relationship with various tracers. Zheng et al. (1995) was successful in using the correlation between NOy and other trace gases such as CO, CO_2, CH_4, O_3, and H_2O to identify surface sources, lightning emissions, and stratospheric influence. We apply their method in the following analysis and an example is illustrated in Fig. 2 for flight 12 on November 3, 1997. Surface pollution can be clearly identified for the time period from about 1610 to 1645 Universal Time (UT). During this period the CO mixing ratio reached more than 145 ppbv. CH_4 was also above normal and the CN levels were also below normal. Interestingly the NOx/NOy ratio was low at 0.23, suggesting extensive atmospheric processing and significant production of O_3. Indeed, O_3 was high at about 85 ppbv. In contrast, a lightning source of NOy can be seen between 1830 to 1850 UT during which NOy, NO, and CN were all substantially elevated. The ratio of NOx/NOy was about 0.7, while O_3 was at a moderate level of about 55 ppbv, as expected from fresh emissions of NOx. In addition, both CO and CH_4 were substantially lower than those of the surface pollution case.

When the above method is applied to all UTA points with $NOy/O_3 > 10x10^{-3}$, we obtain the following results: about 50% of the points are due to NOx emissions from lightning, and about 20% due to convection of surface sources. The rest are not identified because of lack of clear signatures. They could be due to a mixture of sources, including lightning, surface sources, aircraft (< 8%) and other unknown sources. The average NOy mixing ratio of all points with $NOy/O_3 > 10x10^{-3}$ is 1017 pptv (1239 points). Assuming the median NOy mixing ratio (325.5 pptv) of the entire UTA data points (6158 points) as the background value of NOy, we can calculate the contribution of the points with $NOy/O_3 > 10x10^{-3}$ to the upper tropospheric NOy by calculating the average difference between the 1239 points with $NOy/O_3 > 10x10^{-3}$ and the background value, i.e. (1017 – 325.5) x 1239 / 6158 = 139.1 pptv. This is a lower limit because we include only the difference as the contribution. In reality, the points with $NOy/O_3 > 10x10^{-3}$ also contribute to the background NOy. This lower limit is highly significant, representing about 30% of the total NOy observed in the UTA (above 7 km) during SONEX. This translates to a lower limit of 21% (i.e. 30% x 70%) contribution by lightning and convection.

From the above discussion, aircraft emissions contribute less than 8% to the NOy increments with $NOy/O_3 > 10x10^{-3}$, which is equivalent to (30% x 8% = 2.4%) of the total NOy observed. Why the contribution is so low? Why are the contrails hardly noticed? If we can't see them in the data points with $NOy/O_3 > 10x10^{-3}$, can they still contribute significantly to the background NOy distribution? In the following, we attempt to address these questions.

Contrails of subsonic aircraft were observed frequently before, often with NOy spikes larger than several ppbv and time intervals of the spikes significantly greater than the 10 seconds data resolution used in this study (e.g. Zheng et al., 1995; Schlager et al., 1997). Therefore, the answer to the first two questions is most likely that the majority of aircraft contrails observed during SONEX were relatively old so that the NOy levels in the contrails were diluted too much to raise the NOy/O_3 ratio above $10x10^{-3}$. This suggests that aircraft emissions may contribute significantly to the data points with $NOy/O_3 < 10x10^{-3}$, including the background level of NOy/O_3 ($6.6x10^{-3}$ in the UTA). To address this problem, we have made a similar study of the contributing sources for the data points with NOy/O_3 between $7x10^{-3}$ and $10x10^{-3}$. A total of 1466 data points are found in the UTA. The previously identified convection/lightning flights (14, 12, 10, 3, and 9) and time periods contribute about 60% to the total number of these data points. Although this again suggests the importance of lightning and surface sources, it does not rule out aircraft emissions as a major contributor to the other 40% of the points. Unfortunately, it is difficult to even make a qualitative identification of the contributing sources of these 40% of points because most of the points are from aged emissions that are characterized by low values of NOx/NOy ratio, low CN (<5000 cm^{-3}), and small spikes. The average NOy level with NOy/O_3 between $7x10^{-3}$ and $10x10^{-3}$ is 434.5 pptv, merely 109 pptv above the median value. If we apply the earlier method of calculating the lower limit of contribution to the NOy abundance in the UTA, the 60% and 40% correspond to only 3.3% and 2.2% of the total NOy, respectively. Thus, even if all 40% of the data points with NOy/O_3 between $7x10^{-3}$ and $10x10^{-3}$ were from aircraft emissions, the contribution to the total NOy observed in the UT (above 7 km) during SONEX would be only 2.2%.

Conclusions

By examining the distributions of NOy, O_3, and NOy/O_3 ratio as a function of N_2O, we have found that the data points with NOy/O_3 ratio greater than $10x10^{-3}$ contribute more than 30% to the NOy abundance in the UTA observed during

SONEX. The major sources (> 70%) contributing to these points are emissions from lightning and surface sources transported to the UT by convection, while the contribution from aircraft emissions is < 8%. For data points with NOy/O_3 ratio between $7x10^{-3}$ and $10x10^{-3}$, lightning and surface sources also appear to be the major sources, but aircraft emissions may account for as much as 40%. However, this 40% corresponds to only about 2% of the total NOy abundance in the UTA. Finally, a few important points of caution are needed: first, our results apply only to the region sampled during SONEX; second, our method of analysis applies only to data points with relatively high ratios of NOy/O_3; third, the method used in this study cannot be applied to the background level of NOy which accounts for about 60% of the NOy abundance in the upper tropospheric air observed during SONEX.

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