Evidence of convection as a major source of condensation nuclei in the northern midlatitude upper troposphere

Y. Wang[1,2], S. C. Liu[1], B. E. Anderson[3], Y. Kondo[4], G. L. Gregory[3], G. W. Sachse[3], S. A. Vay[3], D. R. Blake[5], H. B. Singh[6], and A. M. Thompson[7]

Abstract. We examine concurrent measurements of CN (size > 8 nm), NO, and NO_y in the upper troposphere over the North Atlantic during the SONEX Experiment (Oct.-Nov., 1997). High CN and NO_y observations are attributed largely to the enhancement in convective outflow. Using the ratio of NO/NO_y as a chemical clock, we estimate that dilution of convective high-CN plumes is rapid (on a time scale of < 2 days) and accounts for a large fraction of elevated CN concentrations above the background. We estimate that less than 7% of observed high-CN (> 10000 cm^{-3}) plumes may be attributed to aircraft emissions. The contribution by aircraft emissions to upper tropospheric CN concentrations is estimated to be significantly higher than 7% because aircraft plumes dilute much faster than convective plumes and hence are sampled less frequently.

1. Introduction

Atmospheric aerosols originate from a variety of primary sources including mineral dust, sea spray, and soot from combustions, and secondary sources from gas to particle conversion of sulfate, nitrate, ammonia, and organic compounds. The presence of large amounts of tiny aerosol particles with myriad chemical compositions and sizes ranging from few nm to a few hundred μm has important impact on climate and chemistry of the atmosphere [*Andreae and Crutzen*, 1997].

Primary aerosols are generally orders of magnitudes larger in size than secondary condensation nuclei (CN) [*Slinn*, 1975]. They provide abundant surface area for condensation of soluble gases and thus suppress new particle formation in continental and marine boundary layer [*Clarke*, 1993]. In the middle and upper troposphere, where concentrations of primary aerosols are low, new particle formation characterized by bursts of high CN concentrations has been observed [e.g., *Clarke*, 1993; *Perry and Hobbs*, 1994; *Schröder and Ström*, 1997; *de Reus et al.*, 1998; *Clarke et al.*, 1998; *Ström et al.*, 1999]. The formation of particles is generally attributed to the homogenous nucleation process. Observational evidence, however, cannot be used to exclude heterogeneous processes [e.g., *Schröder and Ström*, 1997].

A growing source of CN for the upper troposphere is aircraft emissions. Near-field observations of aircraft exhaust plumes show high concentrations of soot and ultra fine particles composed mostly of sulfuric acid [*Fahey et al.*, 1995; *Schumann et al.*, 1996; *Anderson et al.*, 1998; *Schröder et al.*, 1998]. Using long-term balloonborne observations of CN in Laramie, Wyoming, *Hoffmann et al.* [1998] suggested a 10% aircraft enhancement on background CN concentrations between 9 and 13 km at the site.

We analyze 10 second averages of CN (size > 8 nm), NO and total reactive nitrogen (NO_y) measurements in the upper troposphere over the North Atlantic during the SASS (Sub-

sonic Assessment) Ozone and NO_x Experiment (SONEX). An overview of the SONEX Experiment is described by *Singh et al.* [1999]. We will show that convection stands out as a major CN source for the upper troposphere at northern midlatitudes and will attempt to assess the contribution by aircraft emissions.

2. Association of High CN Concentrations with Convection

Near-field observations of fresh aircraft plumes show CN concentrations over 10^7 cm^{-3} [e.g., *Anderson et al.*, 1998] and NO_y concentrations exceeding 5 ppbv [*Zhang et al.*, 1994; *Campos et al.*, 1998]. Encounters with aircraft plumes can therefore contribute significantly to high CN and NO_y populations in observations. Since the cruise altitude of aircraft is at 10-12 km, near the tropopause region at midlatitudes, we would expect aircraft imprints in both the lower stratosphere and the upper troposphere. Figure 1 compares the percentage probability distributions of CN and NO_y in these two regions. The population density of high concentration CN is much higher in the upper troposphere than the stratosphere. Whereas 14% of the tropospheric data points have CN concentrations > 10000 cm^{-3}, only 0.4% of the stratospheric data points have concentrations that high. The lack of fresh aircraft plumes in the stratosphere is also evident in the probability distribution of NO_y. Hardly any stratospheric data (3 out of 3100) have NO_y concentrations > 1.5 ppbv in comparison to a much larger fraction of 2% in the upper troposphere (400 out of 17000) despite that the median stratospheric NO_y concentration of 0.9 ppbv is three times larger than that of the troposphere. If they are not observed in the lower stratosphere, fresh aircraft plumes are less likely to be observed in the more turbulent troposphere to account for the observed high CN and NO_y concentrations in the upper troposphere. A plausible explanation for the lack of aircraft plume observations is rapid dilution of these plumes (section 4).

Figure 1

Figure 1 also shows that the probability distributions of upper tropospheric CN and NO_y are very similar in contrast to the drastically different distributions in the lower stratosphere. The latter difference reflects different sources of CN and NO_y in the lower stratosphere. Stratospheric NO_y is largely from upper stratospheric oxidation of N_2O [*McElroy and McConnell*, 1971]. Mixing with tropospheric air tends to decrease NO_y concentrations. In contrast, stratospheric CN is mainly from condensation of sulfuric acid in the lower stratosphere [e.g., *Andreae and Crutzen*, 1997]. Mixing with tropospheric air tends to increase CN concentrations. The similarity of probability distributions between CN and NO_y in the upper troposphere implies similar source and sink distributions.

Using concurrent measurements of chemical species, we find that high CN data are largely associated with convection. All data shown hereafter are daytime (solar zenith angle < 85°) upper tropospheric observations. We analyzed the observations with CN concentrations > 15000 cm^{-3} for each SONEX flight. Aircraft CN plumes show up in observations as spikes, whereas convective CN plumes are broad plateaus (Figure 2). We find that aircraft plumes characterized by spikes of high NO, NO_y and CN concentrations are apparent only in flights

Figure 2

on Oct. 18, 23, 25, and Nov. 5 and 10, when high CN data points encountered per flight are less than 10. All the other high CN plumes are largely associated with two types of convective plumes. A large fraction of convective plumes shows high NO/NO_y ratios and elevated concentrations of NO_y and CO. These plumes explain almost all the high CN points observed on Oct. 29 and Nov. 3 and some on Oct. 13 and Nov. 9. These plumes appear to be influenced strongly by lightning [*Liu et al.*, 1999]. A particularly interesting convective plume was sampled on Nov. 9. at 19-21 UT. Unlike the high CN plumes on Oct. 29 (Figure 2), elevated CN concentrations in this broad plume show much more variability. The scatter plot of CN and NO_y concentrations shows a clear positive correlation (Figure 3).

Figure 3

The remaining convective plumes, which appear not to be influenced by lightning, show NO/NO_y ratios much closer to the background and somewhat higher concentrations of NO_y and CO than the background. Concentrations of C_2H_2, alkanes (up to C_5), and organic nitrates in these plumes are elevated. These plumes account for nearly all the high CN observations on Oct. 20 and 28 and some on Oct. 13 and Nov. 9. The majority of convective plumes therefore appears to be continental air. An apparent marine convective event was observed during the flight on October 20, when highest CH_3I concentrations (0.6-1 pptv) in the upper troposphere were recorded during SONEX. Concentrations of CN during this flight often exceeded 10000 cm^{-3} but were less than 15000 cm^{-3}; corresponding NO_y concentrations were below 150 pptv.

3. Dilution of Convective Plumes

We examine here the evolution of CN and NO_y concentrations in convective plumes. Previously, hydrocarbon enhancement ratios have been used to determine the age of the plumes [*McKeen and Liu*, 1993]. However, during SONEX, large enhancements of hydrocarbons were not observed. Another difficulty of using hydrocarbon enhancements in our analysis is that the sampling frequency of hydrocarbons of 2-4 minutes is much longer than the sampling frequencies of NO_y and CN (< 5 s). We use observed daytime NO/NO_y ratios as an indicator for the age of the plumes. We choose NO/NO_y ratio rather than the ratio of NO_x ($NO+NO_2$) to NO_y to maximize available data points; the difference is small because 80% of NO_x is NO in the upper troposphere. Aircraft plumes are removed from the data using the criteria discussed in the next section.

Unlike NO_x and CN which are subject to losses by oxidation to HNO_3 and by coagulation, respectively, NO_y is generally a conserved tracer in the upper troposphere. The change of NO_y as a function of NO/NO_y ratio therefore provides a gauge for the effect of dilution. Figure 4 shows the probability distributions of NO_y and CN for data groups with NO/NO_y ratios of <0.2, 0.3-0.5, and > 0.6 mol/mol. The population distributions of NO_y and CN show a clear shift from one populated in high NO_y and CN concentrations in fresh convective plumes (NO/NO_y ratio > 0.6 mol/mol) to one populated in low concentrations in aged plumes, reflecting the effect of dilution.

Figure 4

To assess the time scale of dilution (defined as the time for mixing from the environment to double the air mass in convective plumes), we plot median NO_y concentration as a function

of NO/NO_y ratio in Figure 5. We also plot a mixing line. We use the median concentration of the whole dataset to represent the environmental air mixed into fresh convective plumes (NO/NO_y ratio > 0.6 mol/mol). For comparison, we show the evolution of the fresh plumes isolated from the environment (hence the NO_y concentration is conserved) using a chemical lifetime of 7 days for NO_x [*Jaeglé et al.*, 1998]. The mixing line for the fresh plumes after a 2-day isolation is also shown. Although the variability in the data prevents a precise estimate, it is apparent that the dilution time scale is unlikely to be longer than 2 days to account for the observed decrease of NO_y concentrations with decreasing NO_x/NO_y ratios. By examining the decrease of water vapor concentrations with time in tropical convective plumes, *McCormack et al.* [1999] estimated a time scale of 20-30 hours for dilution. Based on our results, this estimate appears to be reasonable for the convective plumes at northern midlatitudes.

We also show in Figure 5 the median concentrations of CN and NO_y grouped by NO/NO_y ratio. As previously, we draw a mixing line between the fresh plumes and the environmental air. The mixing line again closely tracks the observed medians. Dilution therefore appears to be much more important than the coagulation loss of CN. We can estimate the time scale against coagulation by $2/(K_c N_0)$, where K_c is the coagulation kernel and N_0 is the initial concentration [*Turco and Yu*, 1997]. Applying a K_c of 6×10^{-10} cm^3 s^{-1} [*Turco and Yu*, 1997] and an N_0 of 5000 cm^{-3} at ambient pressure (corresponding to 20000 cm^{-3} at sea level for fresh convective plumes), the time scale against coagulation is about 8 days. Observations by *Anderson et al*. [1999] showed that the ratios of CN to NO_y in aircraft plumes was invariant for 6 hours, which is the time period when aircraft plumes are identifiable, consistent with a low value of K_c and a lifetime much longer than the dilution time scale of less than 2 days. A large fraction of the observed CN concentrations for NO/NO_y ratio of 0.3-0.6 mol/mol therefore can be accounted for by dilution of large amounts of CN in fresh convective plumes.

Figure 5

4. Relative CN Source Strength of Aircraft versus Convection

Anderson et al. [1999] found that aircraft plumes with CN concentrations > 10000 cm^{-3} account for 1% of the observations. Since 14% of the data points during SONEX have CN concentrations > 10000 cm^{-3}, we can estimate that the aircraft contribution to high CN plumes is about 7%. Based on the aircraft plume characteristics found by *Anderson et al.* [1999], we use a different approach and diagnose aircraft exhaust plumes as data groups with NO/NO_y ratios > 0.6 mol/mol and with time durations shorter than 40 s. We diagnose data groups with longer time durations as convective plumes. Changing the time duration criterion to 60 s has a 20% effect on our results. Using our criteria, we find that only about 6% of high CN plumes may be attributed to aircraft emissions in agreement with the former estimate of 7%.

We can compare the emissions ratios of CN to NO_y in aircraft and convective plumes. Assuming median concentrations of the dataset (300 pptv NO_y and 2700 cm^{-3} CN) as the background, we find that the average CN to NO_y emission ratio is

27 cm^{-3} $pptv^{-1}$ for aircraft plumes, similar to a ratio of 23 cm^{-3} $pptv^{-1}$ found by *Anderson et al.* [1999]. The average CN to NO_y enhancement ratio for fresh convective plumes (apparently influenced by lightning) is 17 cm^{-3} $pptv^{-1}$, only 30-40% less than the aircraft emission ratio.

The similarity in the emission ratios of CN to NO_y for aircraft and convection implies that aircraft contributions to high-CN and high-NO_y plumes are alike. We found that only 6-7% of high CN plumes are due to aircraft emissions; *Liu et al.* [1999] suggested that less than 10% of high NO_y plumes are from aircraft and that most of high NO_y plumes are associated with convection. The small percentages do not imply an insignificant contribution by aircraft. Aircraft plumes dilute rapidly [*Schumann et al.*, 1998]. Their faster dilution relative to that of convective plumes leads to more frequent observations of convective plumes. *Anderson et al.* [1999] found that observable aircraft plumes last about 6 hours after emission. We can only estimate that the dilution time scale of convective plumes is less than 2 days (Figure 5). For our estimate, we adopt the result by *McCormack et al.* [1999] that the dilution time scale is about 1 day. The time duration of observable convective plumes with CN concentrations >10000 cm^{-3} is therefore about 1 day, since the average CN concentration of fresh convective plumes is about 20000 cm^{-3}. Taking the observation frequency into account, the contribution by aircraft should be increased by about a factor of 4 (1 day/6 hours), making aircraft a significant contributor (about 30%) to upper tropospheric CN and NO_y. The uncertainty of this factor hinges on the estimate of the dilution time scale of convective plumes.

5. Conclusions

We analyzed observations of CN (size > 8nm), NO, and NO_y during SONEX. The contrast in probability distributions of CN and NO_y between the upper troposphere and lower stratosphere suggests observed high CN and NO_y concentrations in the upper troposphere cannot be explained by aircraft emissions. Close examination of these high CN plumes reveals close association with convection and air of continental origin. The high CN plumes reflect most likely new particle formation in convective outflow [e.g., *Schröder and Ström*, 1997; *de Reus et al.*, 1998; *Clark et al.*, 1998; *Ström*, 1999]. We use NO/NO_y ratio as a chemical clock. The probability distribution of NO_y shows a clear population shift by dilution from high concentrations in fresh plumes to low concentrations in aged plumes. A similar shift is found for CN. Rapid dilution of high CN and NO_y in convective plumes appears to contribute significantly to observed above-background concentrations. The dilution time scale of fresh convective plumes is estimated to be less than 2 days. We find a 6-7% contribution by aircraft to high-CN plumes similar to the previous estimate of < 10% contribution by aircraft to high-NO_y plumes. The impact of aircraft on upper tropospheric CN and NO_y is larger than 6-10% because convective plumes have a longer time scale against dilution than aircraft plumes and are therefore sampled more frequently in observations. We estimate a factor of 4 increase from the observed fractions. The uncertainty in this estimate is, however, large at present.

Acknowledgments. We thank L. Jaeglé, G. M. Gardner, and D. J. Jacob for providing the 10-second merged data files. This work was supported by the National Aeronautics and Space Administration (AEAP /SASS Program). We thank the anonymous reviewers for their helpful comments. We also thank R. Friedl, S. Kawa, and D. Anderson who are SASS project scientists and J. A. Eilers who is the SONEX project manager.

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Figure Captions (Single Column)

Figure 1. Percentage probability distributions for CN (binned per 1000 cm^{-3}) and NO_y (binned per 100 pptv) above 8-km altitude, respectively. The percentage probability is plotted as a function of the mean concentration of each bin. Observations are diagnosed as tropospheric if O_3 concentrations are less than 100 ppbv. The CN concentrations are in the unit of particles cm^{-3} at sea level.

Figure 2. Time series of CN observed during flights on Oct. 29 (12-18 UT hours) and Nov. 5 (19-20 UT hours). The observations shown are upper tropospheric samples (altitude > 8 km and O_3 concentrations < 100 ppbv). Four broad CN convective plumes were observed on Oct. 29 and typical aircraft CN spikes were observed on Nov. 13. The time duration of aircraft spikes was less than 30 s.

Figure 3. The correlation between CN and NO_y in the convective plume observed at 19:10-20:30 UT on Nov. 9. A least-squares fitting line is shown.

Figure 4. Percentage probability distributions for CN (binned per 5000 cm^{-3}) and NO_y (binned per 500 pptv) in the upper troposphere for data with NO/NO_y ratios of <0.2, 0.3-0.5, and >0.6 mol/mol. Aircraft plumes are filtered out.

Figure 5. Median values of NO_x/NO_y molar ratio and CN concentration as a function of the median concentration of NO_y. Data are binned into 0.1 mol/mol intervals by NO/NO_y ratio. The NO/NO_y ratio is > 0.6 mol/mol for the last bin, representing fresh convective plumes. Concentrations of NO_x were computed from a diel steady state photochemical model by *Jaeglé et al.* [1999]. Mixing between the fresh plumes and the environment (represented by the median concentration for the whole dataset) is shown by the dotted line. Pluses represent the isolation of the fresh plumes by 1-4 days. Mixing between the fresh plumes after a 2-day isolation and the environment is shown by the dashed line. The horizontal bar represents the range between 25 and 75 percentile NO_y concentrations within each data bin. The vertical bar represents the range between 25 and 75 percentile CN concentrations within each data bin.

[1] Georgia Institute of Technology, Atlanta, Georgia
[2] Now at Rutgers University, New Brunswick, New Jersey
[3] NASA Langley Research Center, Hampton, Virginia
[4] Nagoya University, Toyokawa, Japan
[5] University of California, Irvine, California
[6] NASA Ames Research Center, Moffet Field, California
[7] NASA Goddard Space Flight Center, Greenbelt, Maryland

Yuhang Wang, Department of Environmental Sciences, Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901-8551. (e-mail: yhw@envsci.rutgers.edu)

(Received July 15, 1999; revised September 27, 1999; accepted November 30, 1999)

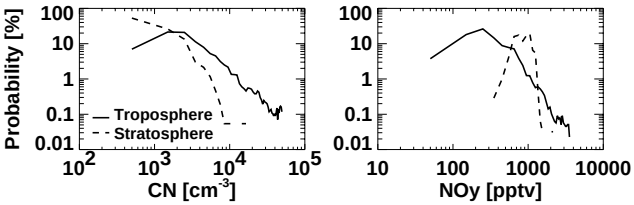

Figure 1

TOP

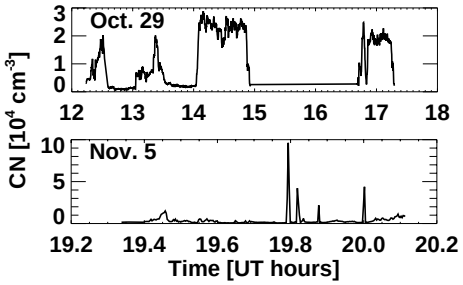

Figure 2

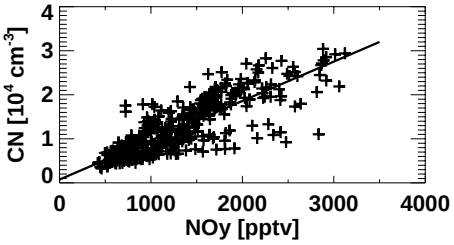

Figure 3

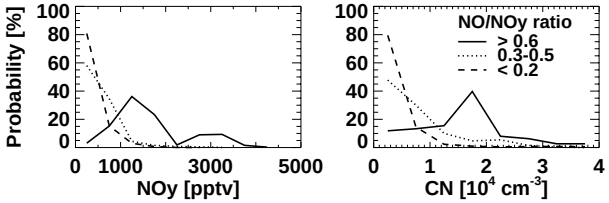

Figure 4

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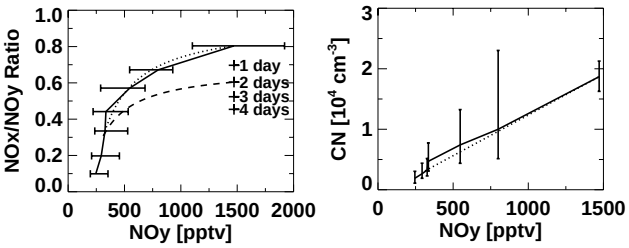

Figure 5