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The temporal evolution of the ratio HNO₃/NOₓ in the Arctic lower stratosphere from January to March 1997

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Abstract. Aircraft-based measurements of HNO₃, NOy, N₂O, and O₃ have been performed in the Arctic lower stratosphere in January (POLSTAR I) and March (STREAM III) of 1997. The two projects employed different aircraft platforms. In addition, NOy and O₃ were measured using different instruments in the two campaigns. HNO₃ and NOy were found strongly correlated with correlation coefficients of 0.84 (POLSTAR I) and 0.69 (STREAM III), respectively. The fraction of HNO₃ within NOy decreased from 96% in January to 59% in March. The decrease is consistent with the lifetime of HNO₃ due to photolysis after polar sunrise. The relationship of NOy and HNO₃ with N₂O shows that in January NOy and HNO₃ values were markedly higher than expected, which may indicate nitrification by PSC-II particle sedimentation and evaporation. Contradictory, the ratios NOy/O₃ observed in January are only slightly elevated. In March, NOy/N₂O and NOy-O₃ relations agree well with others reported in the literature. The difference between the NOy/O₃ and NOy-N₂O relationships is partly explained by an observed O₃ decrease of about 30% between January and March.

Introduction

Nitric acid (HNO₃), which plays a key role in polar ozone chemistry, is the major component of reactive nitrogen (NOₓ) in the lower stratosphere. So far only few simultaneous measurements of NOy and HNO₃ in the lower stratosphere have been reported [Singh et al., 1997; Fischer et al., 1997], yielding HNO₃/NOy ratios of about 70 – 80%. Calculated HNO₃/NOy ratios [Fahey et al., 1989; Kawa et al., 1992] indicate the rather low range of the fraction HNO₃/NOy of 40 to 90%. The main source of HNO₃ and NOy in the stratosphere is thought to be the reaction of nitrous oxide (N₂O) with O(D) yielding two NO molecules which are further oxidized to NO₂ and HNO₃. In the stratosphere, nitric acid is destroyed mainly by photolysis, leading to the formation of NO₂. The latter is important for the chlorine deactivation via ClO + NO₂ + M → ClONO₂ + M.

When reactive nitrogen (mainly HNO₃) is removed from high altitudes (around 20 km) and released at lower altitudes (11 to 15 km) by PSC-II particle sedimentation and evaporation, the efficiency of chlorine deactivation is reduced. These so-called denitrification/nitrification events have been regularly observed in the Antarctic winter stratosphere [cf. Fahey et al., 1990a], but only rarely in the Arctic stratosphere. For example, in February 1995, substantial denitrification was observed at altitudes around 19 km [Sugita et al., 1998], while renitrification was observed between 10 and 13 km [Fischer et al., 1997; Arnold et al., 1998].

In late winter/early spring, sunrise after the polar night, followed by photodissociation of HNO₃ leads to formation of NO and, via reaction (1), of ClONO₂. This is expected to shift the partitioning within NOy towards NOy and ClONO₂ and to a decrease of the HNO₃ fraction within NOy.

This paper reports on measurements of HNO₃, NOy, N₂O, and O₃ during two aircraft campaigns in winter 1997 in the Arctic lower stratosphere. We focus on a strong reduction of the ratio HNO₃/NOy observed from January to March.

Measurements

The POLSTAR I (Polar Stratospheric Aerosol Experiment I) included 7 measurement flights between January 24 and February 06, 1997. The STREAM III (Stratosphere-Troposphere Experiment by Aircraft Measurements III) included 5 flights between March 9 and 25, 1997. The operational base for both campaigns was Kiruna, Sweden (69°N, 20°E). During the POLSTAR I mission the German research aircraft Falcon, owned and operated by DLR (Deutsches Zentrum für Luft- und Raumfahrt) was used, while the STREAM mission used the Dutch Cessna Citation research aircraft, operated by Delft University of Technology. Both research aircraft are twin-jets with a maximum flight altitude of approximately 14 km.

NOy and O₃ in the POLSTAR I project were measured by DLR, Oberpfaffenhofen [Feigl, 1998]; NOy in the STREAM III campaign was measured by the Max Planck Institute for Chemistry (MPI-CH), Mainz [Wienhold et al., 1998]; O₃ during STREAM III was measured by the Institute for Marine and Atmospheric Research, Utrecht University (IMAU); in both campaigns N₂O was measured by MPI-CH; during the STREAM II project, additionally, N₂O was measured on two flights of the STREAM III campaign by the Institute for Stratospheric Chemistry, Forschungszentrum Jülich (FZJ) [Bujok et al., 1998]; in both campaigns HNO₃ was measured by the Max Planck Institute for Nuclear Physics (MPIK), Heidelberg [Schneider et al., 1998a].

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tem for stratospheric NO\textsubscript{y} measurements. N\textsubscript{2}O was measured during two flights of the STREAM III campaign by two different techniques (gas chromatograph, FZJ, and tunable diode laser, MPI-CH). The mean deviation (2\sigma) between both instruments was 1% (Flight #1) and 1.8% (Flight #2). Also, the calibration standards of both measurement systems have been compared, yielding agreement of \( \leq 1\% \). Note also that the accuracy of the NO\textsubscript{y} measurements is \( \pm 25\% \) [Fischer et al., 1997; Feigl, 1998], while that of HNO\textsubscript{3} is only \( \pm 40\% \), due to the accuracy of the rate coefficient of the calibration reaction [Möhler and Arnold, 1991; Schneider et al., 1998b]. IMRMS measurements of gaseous HNO\textsubscript{3} in the Arctic lower stratosphere can be affected by sampling and evaporation of cloud and aerosol particles containing HNO\textsubscript{3}. During the residence time of the probe gas inside the flow tube (approximately 50 ms) small particles are able to evaporate. Since the sampling is not isokinetic, an enhancement factor of particle sampling of about 4 is to be expected. During the POLSTAR I campaign where occasionally high cirrus clouds were observed in the tropopause region, an overestimation of HNO\textsubscript{3} can not be excluded. However, this does not affect the present data discussion since it focuses only on stratospheric data, selected by the criterion N\textsubscript{2}O < 300 ppbv. In the STREAM III campaign the HNO\textsubscript{3} measurements suffered from an additional uncertainty due to collision induced ion dissociation. A correction has been applied relying on the measured ion ratio O\textsuperscript{-}/CO\textsuperscript{-}, yielding a correction factor of about 1.1. This increased the overall uncertainty to \( \pm 50\% \).

Results and discussion

Figure 1 presents the nitric acid volume mixing ratios measured during the POLSTAR I (a) and STREAM III (b) campaigns. The entire data sets are shown (sampling frequency: 13 s) as a function of potential temperature \( \Theta \). The error bars indicate the accuracy (POLSTAR I: 40%, STREAM III: 50%) of the measurements. During the POLSTAR I mission, slightly higher potential temperatures of up to 365 K were reached. Highest nitric acid mixing ratios of up to 4 ppbv were observed at a \( \Theta \) level of about 357 K. During the STREAM III campaign maximum HNO\textsubscript{3} mixing ratios reached only 2.5 ppbv at a \( \Theta \) level of 352 K.

For further analysis, the data were averaged over 5 minutes, and a subset was selected by the criterion N\textsubscript{2}O < 300 ppbv to exclude tropospheric air masses. This rather conservative criterion led to the rejection of 3 flights so that only 4 flights from the POLSTAR I mission (28-01-97, 30-01-97, 01-02-97, 04-02-97) are included in the data discussion. We note that NO\textsubscript{y} was not measured on the flight of 04-02-97.

NO\textsubscript{y} partitioning

Figure 2 presents the overall relationships between HNO\textsubscript{3} and NO\textsubscript{y} during both campaigns, i.e. for all flight tracks characterized by N\textsubscript{2}O < 300. The accuracy of the measurements is indicated by the error bars (HNO\textsubscript{3}: 40% and 50%, respectively; NO\textsubscript{y}: 25%). The dotted lines indicate HNO\textsubscript{3} fractions within NO\textsubscript{y} of 50% and 100%. The solid lines represent linear regressions through the data points. Both species are well correlated with a correlation coefficient \( r^2 \) of 0.84 during POLSTAR I and 0.69 during STREAM III. The most remarkable feature evident from Figure 2 is the different HNO\textsubscript{3} fraction comparing January and March 1997. While the mean ratio HNO\textsubscript{3}/NO\textsubscript{y} (for N\textsubscript{2}O < 300 ppbv) of the three POLSTAR I flights is 0.96 \( \pm 0.18 \), it is only 0.59 \( \pm 0.05 \) (mean and standard deviation) during the five STREAM III flights.

Figure 3 shows the temporal evolution of the HNO\textsubscript{3}/NO\textsubscript{y} ratio between January 28 and March 25, 1997. The thick bars indicate mean values and standard deviations for the individual flights, the thin error bars indicate the absolute accuracy of the measure-
ments: 25% for NOy, 40% for HNO3 during POLSTAR I, 50% for HNO3 during STREAM III. These errors were added linearly, resulting in a "worst case" scenario (i.e. the upper error bar limit, for example, is reached when HNO3 was overestimated by 40% and NOy was underestimated by 25%). The accuracy of the HNO3 measurements of 40-50% is mainly determined by the error in the rate coefficient of the calibration reaction [Mohler and Arnold, 1991; Schneider et al., 1998b]. The HNO3 fraction measured in January (96%) is very high, and the mean value of flight #1 (97-01-28) is even larger than 1. Thus, an overestimation of HNO3 is rather likely, while an underestimation of NOy during POLSTAR I is unlikely, since the values are already much higher than the calculated NOy* (see below). Any systematic error in HNO3 or NOy, however, does not change the observed decrease of the ratio HNO3/NOy.

Nitric acid is destroyed by photochemical conversion, either by photolysis (HNO3 + hv → OH + NO2) or by reaction with OH (OH + HNO3 → H2O + NO2). A decrease of the HNO3 fraction inside the NOy at the end of the polar night is not completely unexpected, although, to our knowledge, neither measurements or model calculation showing this feature were reported up to now. From January to March, solar exposure is markedly increasing at the polar regions. The diurnally averaged photodissociation rate of HNO3 for 70øN and 12 km altitude is increasing from about 0.2x10^-7s^-1 on January 20 to 2.5x10^-7s^-1 at the end of March. The dashed line in Figure 3 represents the functional fit $y = a \times \exp(\alpha/t)$ through the data, yielding a time constant $\tau$ of 86 days. This decrease agrees with the time constant for HNO3 photolysis. Although the measurements discussed here have not encountered the same air masses, air masses sampled in March have seen longer periods of sunlight than those encountered at the end of January.

Also shown in Figure 3 is the ratio HNO3/NOy measured during the STREAM II project in February 1995 [Fischer et al., 1997] which yielded an average value of 69%. Although this pertains to measurements two years before the presently discussed data sets, in an environment presumably influenced by nitrification, the values fit rather well to the 1997 picture.

Correlations with N2O and O3

Figure 4 shows the volume mixing ratios of HNO3 and NOy as a function of N2O for both measurement campaigns. Linear regressions through the HNO3 data are represented by the solid lines, the dashed lines refer to the NOy data. The STREAM III data fit well to a linear regression with correlation coefficients of 0.66 (NOy) and 0.76 (HNO3), while the POLSTAR I data only yield a correlation coefficient of 0.44 (both HNO3 and NOy). The functional relationships given by the linear regressions are:

POLSTAR I: $NOy = -0.1081 \times (N2O - 318.4) \quad r^2 = 0.44$

HNO3: $-0.0827 \times (N2O - 324.7) \quad r^2 = 0.44$

STREAM III: $NOy = -0.0598 \times (N2O - 318.7) \quad r^2 = 0.66$

HNO3: $-0.0339 \times (N2O - 319.2) \quad r^2 = 0.76$

All values are ppbv. Also indicated, by the dotted line, is NOy* which is a measure of the expected NOy [Fahey et al., 1990b]. NOy* was calculated using the expression $NOy* = \text{slope} \times (N2O_{\text{meas}} - N2O_{\text{trop}})$. We adopted the slopes measured in the AASE-II project [Weinheimer et al., 1993] for January (-0.0778) and March (-0.0765) and the mean tropospheric N2O values measured during the POLSTAR I campaign (310 ± 4 ppbv) and STREAM III (312 ± 3 ppbv) campaigns. The NOy data from the STREAM I data set are in very good agreement with calculated NOy*, indicating that no denitrification or nitrification occurred. The POLSTAR I NOy and HNO3 data are higher than the calculated NOy* by up to 2 ppbv. This finding might indicate nitrification by PSC-II particle sedimentation in January 1997, although 2 ppbv of renitrification seem to be very much, since that would require an almost complete removal of NOy from the 20 km region. A calibration error of N2O, however, can be excluded, since tropospheric values of both campaigns were equal inside the error limits of 4 ppbv (see above). A systematic overestimation of HNO3 and NOy might explain part of the difference (see error bars in Figure 4a), but then NOy and HNO3 would have been measured too low during the STREAM III campaign.

Figure 5 gives HNO3 and NOy as a function of O3 for both campaigns. The dashed lines give the linear regressions to the NOy-O3 relationships, while the solid lines refer to HNO3. The functional relationships are:

POLSTAR I: $NOy = 5.217 \times 10^5 \times O3 - 0.141, \quad r^2 = 0.82$

HNO3: $4.157 \times 10^3 \times O3 + 0.264, \quad r^2 = 0.87$

STREAM III: $NOy = 3.833 \times 10^3 \times O3 + 0.077, \quad r^2 = 0.77$

HNO3: $1.793 \times 10^3 \times O3 + 0.215, \quad r^2 = 0.60$

All values are ppbv. Also shown, by the dotted line, is the relationship NOy/O3 measured in AASE I [Murphy et al., 1993] in January/February 1989 at 59°N (Stavanger, Norway). The POLSTAR I NOy data are slightly higher than the AASE I data, but the NOy enhancement is smaller than that deduced from the N2O reference. If substantial renitrification had taken place, the
ratio NO$_2$/O$_3$ should be enhanced by the same value (about 2 ppbv at the highest O$_3$ levels) as the NO$_2$-N$_2$O relationship. This finding is not consistent with the explanation in terms of netrification.

The STREAM III data agree well with the AASE I data. However, there are also higher HNO$_3$/O$_3$ ratios reported in the literature: Weinheimer et al. [1993] report a ratio of HNO$_3$ to O$_3$ of about 5x10$^{-3}$ ppbv/ppbv, measured in AASE II in January and March 1992. This value is nearly identical to the POLSTAR I data and higher than the STREAM III data. We also observe a decrease in O$_3$ from January to March: The loss in ozone between the POLSTAR I and the STREAM III measurements is about 30% at N$_2$O < 275 ppbv, corresponding to about 1% per day. This value is comparable to measurements from 1993 [Bregman et al., 1997] and data deduced from ozonesonde measurements for 1997 [Kraus et al., 1998]. This O$_3$ decrease does partly compensate the response of the observed NO$_2$/O$_3$ ratio to the NO$_y$ decrease between January and March, in a way that the ratio NO$_y$/O$_3$ does not change substantially.

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