

Atmospheric Chemistry Experiment (ACE) Arctic stratospheric measurements of NO_x during February and March 2004: Impact of intense solar flares

Curtis P. Rinsland,¹ Chris Boone,² Ray Nassar,² Kaley Walker,² Peter Bernath,² John C. McConnell,³ and Linda Chiou⁴

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[1] Solar occultation measurements recorded in the Arctic by the Atmospheric Chemistry Experiment (ACE) Fourier transform spectrometer show elevated volume mixing ratios of NO and NO₂ in the upper stratosphere from mid-February to late March 2004. Mixing ratios of NO exceeded 1.3 ppmv (10^{-6} parts per million by volume) during mid-February and are higher than any values previously reported in the Arctic during late winter and early spring. The elevated NO_x (NO + NO₂) mixing ratios likely resulted from particle emissions by intense solar flares that occurred the previous October and November followed by NO_x production and downward transport to the upper stratospheric vortex where the elevated levels persisted due to the long lifetime of NO_x during darkness in polar winter and early spring. The descent and the NO_x decrease rates in the upper stratospheric vortex are estimated from an analysis of the time series. The measured descent rate is compared with previous observations and model predictions. **Citation:** Rinsland, C. P., C. Boone, R. Nassar, K. Walker, P. Bernath, J. C. McConnell, and L. Chiou (2005), Atmospheric Chemistry Experiment (ACE) Arctic stratospheric measurements of NO_x during February and March 2004: Impact of intense solar flares, *Geophys. Res. Lett.*, 32, L16S05, doi:10.1029/2005GL022425.

1. Introduction

[2] Significant photochemical ozone loss may occur in the upper stratosphere following periods of intense solar flares [Callis *et al.*, 1996, 1998]. The Sun produced some of the most powerful solar flare events ever recorded between 18 October and 5 November 2003 [Woods *et al.*, 2004]. The solar proton event, the associated coronal mass ejection, and energetic particle precipitation led to very large increases in energy deposition and the production of NO_x (NO + NO₂) over a range of altitudes and latitudes. The impact of the elevated solar activity on upper atmosphere ozone chemistry has been confirmed by analysis of solar occultation [Natarajan *et al.*, 2004; Randall *et al.*, 2005], stellar occultation [Seppälä *et al.*, 2004], and limb emission

measurements [Orsolini *et al.*, 2005]. NO_x volume mixing ratios of 99.1 ppbv (1 ppbv = 10^{-9} per volume) at 68°N latitude were reported from Halogen Occultation Experiment (HALOE) measurements inside the Arctic vortex, the highest ever measured by that experiment near 2 hPa. The purpose of this paper is to report and interpret a time series of solar occultation measurements of NO and NO₂ recorded in the Arctic upper stratosphere by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) from mid-February to late March 2004. The ACE-FTS time series show a maximum NO_x volume mixing ratio of 1361 ± 11.5 ppbv on February 18 at 0.173 hPa (~54 km altitude). We describe the ACE NO_x time series and their analysis to estimate the descent and NO_x decrease rates in the upper stratospheric Arctic vortex. The vortex descent rate is compared with previous measurements and model predictions.

2. ACE Infrared Observations

[3] The Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1, was successfully launched on 12 August 2003 into a 74° inclined orbit by a U.S.-supplied Pegasus XL at 650 km altitude [Bernath *et al.*, 2005]. The small Canadian-designed and built satellite contains three instruments with a shared field of view, and with the primary goal of recording high resolution atmospheric spectra taking advantage of the high precision of the solar occultation technique. The infrared instrument is a Fourier transform spectrometer (FTS) that records solar spectra below altitudes of 150 km at a spectral resolution of 0.02 cm^{-1} (maximum optical path difference of $\pm 25 \text{ cm}$). The spectral coverage is 750 to 4400 cm^{-1} . The instrument is self-calibrating as low Sun spectra are divided by exoatmospheric spectra from the same occultation. The ACE orbit yields tropical to high latitude occultations in both hemispheres with a vertical resolution of 3–4 km. Frequent Arctic occultation events are recorded during the winter and early spring period of maximum ozone depletion. Additional instruments onboard SCISAT-1 are the MAESTRO (Measurement of Aerosol Extinction in the Stratosphere and Troposphere by Occultation)- a two channel UV-visible spectrophotometer- and two imagers with optical filters at 0.525 and 1.02 μm to provide full disk solar images.

3. ACE Stratospheric Profile Measurements

[4] Routine ACE FTS science measurements began in February 2004, and we focus here on Arctic results from observations during that month and March 2004. We rely on

¹NASA Langley Research Center, Hampton, Virginia, USA.

²Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

³Department of Earth and Atmospheric Science, York University, Toronto, Ontario, Canada.

⁴Science Application International Corporation, Hampton, Virginia, USA.

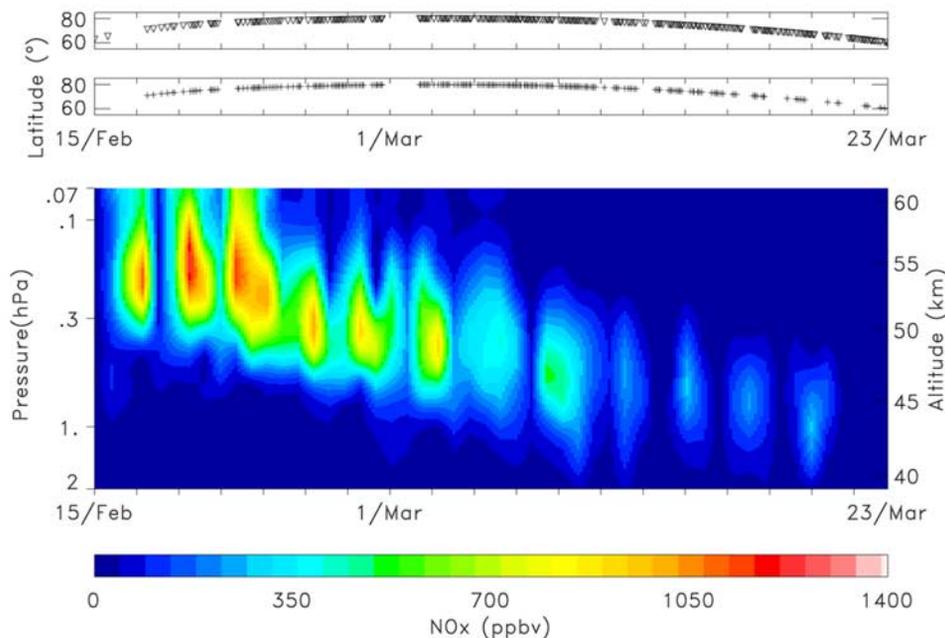


Figure 1. Time sequence of ACE-FTS Arctic volume mixing ratio measurements recorded from mid-February to late March 2004. Inverted triangles at top mark the latitude of each occultation. The panel beneath shows those occultations classified as inside the vortex based on scaled potential vorticity (SPV). Lower panels present corresponding contours of the volume mixing ratios of NO_x vs. pressure from 0.07 to 2 hPa with vertical lines marking two day time increments. Approximate altitude corresponding to each time series is indicated on the far right vertical axis.

version 1 retrievals (C. D. Boone et al., Retrievals for the Atmospheric Chemistry Experiment Fourier transform spectrometer, submitted to *Applied Optics*, 2005), which provide volume mixing ratios with statistical uncertainties from an algorithm that retrieves profiles of temperature and the volume mixing ratios of individual molecules from fits to multiple species in microwindows over pre-specified altitude ranges. Temperature profiles are retrieved from the occultation spectra assuming a realistic CO₂ volume mixing ratio profile. Profiles below 12 km altitude assume temperatures derived by the Canadian Meteorological Centre (CMC) for the location of the observation. Version 1 NO and NO₂ retrievals do not include line-of-sight diurnal corrections. Previous studies showed the impact of not including those corrections is relatively small from solar occultation spectra except in the lower stratosphere [see *Sen et al.*, 1998, Figure 1, and references therein]. Spectroscopic parameters and absorption cross sections are based on HITRAN 2004 [Rothman et al., 2005].

[5] We focus here on the ACE measurements of NO_x near the stratopause and their interpretation. Photochemical model calculations for the mid-February to late March time period of the ACE measurements indicate the lifetime of NO_x near the stratopause is 1–2 months for this time period with the lifetime increasing to lower altitudes (M. Natarajan, NASA Langley Research Center, Hampton, Virginia, private communication, 2005).

4. Observation Time Series

[6] Figure 1 presents contours of ACE-FTS measurements of Arctic NO_x in the upper stratosphere for the 15 February to 23 March 2004 time period. Inverted triangles and plus symbols at the top show latitudes and

observation dates for all occultations and those classified as inside the polar vortex, respectively. The lower panels present contours of NO_x vs. pressure from 0.07 to 2 hPa. Approximate altitudes corresponding to each measurement are indicated at the right. Vertical lines below each molecular sequence show 2 day time increments. The NO sequence spans the full altitude range, but the measurements for NO₂ do not extend to the highest altitude because of the weakness of the available absorption features in the upper atmosphere. We calculate NO_x above 58 km assuming a NO₂ volume mixing ratio of zero. Measurements for NO₂ extend to 58 km (~3 hPa). Objective criteria based on the measurement uncertainty were used to delete noisy measurements from the time series.

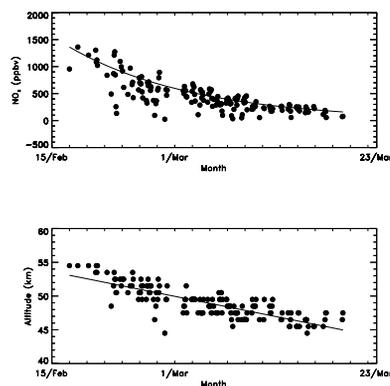


Figure 2. ACE-FTS Arctic upper stratospheric NO_x vortex volume mixing ratios vs. time. Solid lines show fit to the measurements to derive the rate of volume mixing ratio decrease and the descent rate assuming equations (1) and (2), respectively.

[7] Classifications of individual occultation events as sampling vortex, edge of vortex, or outside the vortex air were derived from scaled potential vorticity (sPV) [Manney *et al.*, 2005] values for the location, time, and altitude of individual ACE measurements derived from United Kingdom (UK) Met Office (MetO) measurements provided for a 1 km altitude grid from 0.5 to 65.5 km by G. Manney (Jet Propulsion laboratory, private communication, 2004). Empirically, we classified a measurement as a vortex observation if the sPV value exceeded 2.0 at ~35–50 km altitude. Stratospheric meteorology during winter 2003–2004 and other recent warm winters in the Arctic has been described by Manney *et al.* [2005].

5. Descent and Mixing of NO_x in the Upper Stratosphere

[8] Figure 2 presents results of an analysis to determine (top) the rate of upper stratospheric NO_x decrease and (bottom) the rate of descent as a function of time in vortex air. The NO_x volume mixing ratio time series was fitted with the empirical expression

$$[\text{NO}_x](t) = [\text{NO}_x](t_{\text{ref}}) \exp(-k(t - t_{\text{ref}})) \quad (1)$$

where $[\text{NO}_x](t)$ is the NO_x vortex volume mixing ratio at time t , t_{ref} is the time of the first measurement, and k is the NO_x decrease rate. The best fit with equation (1) indicates the vortex volume mixing ratios decreased from 1361.0 ppbv at the beginning of the time series (February 15, 2004) to 159.2 ppbv at the end (March 23, 2004) during the 5 week measurement time period. The best fit yields a coefficient k equal to $0.0689 \pm 0.00582 \text{ day}^{-1}$.

[9] Figure 2 (bottom) shows a fit to the vortex observation time series with the expression

$$Z(t) = Z(t_{\text{ref}}) + d(t - t_{\text{ref}}) \quad (2)$$

where $Z(t)$ is the altitude (km) of the vortex at time t and d is the vortex descent rate (km day^{-1}), assumed to be linear with time.

[10] The statistical uncertainties obtained from the analysis of the vortex measurements with equations (1) and (2) provide lower limit estimates of the total error as they do not include the impact of sources of systematic error such as uncertainties in the meteorological parameters which increase to large values in the mesosphere and uncertainties in the version 1 ACE retrievals including the impact of the finite measurement vertical resolution and temperature profile and pointing knowledge uncertainties.

[11] The NO_x vortex mixing ratio decreased as a result of the combined effects of photochemical loss in the sunlit atmosphere, dilution, and mixing. Consistent with Figure 1, our measurements and analysis show the NO_x mixing ratios in the vortex decreased to values close to those measured in the background upper stratosphere by the end of the time series while the vortex descended by 9 km in altitude from 54 to 45 km. The best fit coefficient d equals $(-0.2600 \pm 0.0144) \text{ km day}^{-1}$, a descent of ~8 km/month, close to the model descent rate of 7.8 km/month for the 1992–1993 Arctic winter stratospheric vortex for a starting altitude of 47 km [Manney *et al.*, 1994]. There have been several other

attempts to estimate Arctic vortex descent rates from models with a variety of approaches and assumptions as discussed, for example, by Greenblatt *et al.* [2002] and Nassar *et al.* [2005].

[12] Arctic profile measurements of long-lived tracers were reported previously inside and outside of the April 1993 Arctic vortex by the Atmospheric Trace Molecule Spectroscopy experiment by comparing vertical separations between measured late winter vortex and extra-vortex tracer profiles for similar tracer mixing ratios [Abrams *et al.*, 1996]. The altitude-dependent descent rates reported from that work relied on assumptions of unmixed descent, an assumed vortex formation starting date, and an initial altitude for the vortex and were limited to altitudes below 35 km as the vortex had broken down at higher altitudes. Our factor of three higher descent rate compared to their rate at their highest altitude is likely due in part to the large difference in the altitude range. Our descent rate is also substantially higher than the upper stratospheric vortex descent rate of 4.5 km/month for February and March 2004 estimated with a similar analysis approach from ACE N₂O and CH₄ measurements for that time period when a strong vortex existed at those altitudes [Nassar *et al.*, 2005; Manney *et al.*, 2005]. A vortex descent rate of a few km in 10 days was reported at 30–50 km altitude from NO₂ early winter 2004–2005 GOMOS (Global Ozone Monitoring by Occultation of Stars) NO₂ measurements and latitudes above 45°N [Seppälä *et al.*, 2004, Figure 2], prior to the warming and upper vortex breakup in early January that was followed by recovery and formation of a record strong upper stratospheric vortex [Manney *et al.*, 2005]. Although our descent rate estimate is consistent with the approximate value derived from the early winter GOMOS measurements for a similar altitude range, those results correspond to an early season time period when descent is known to be rapid. The differences in the reported descent rates (both measured and simulated) highlight the difficulty with applying assumptions for quantifying altitude and seasonal dependent vortex descent rates in the Arctic, where year-to-year variability in vortex strength is much greater than in the Antarctic, and the limitations of seasonal averaged rates. Our Arctic vortex descent rate is also higher than inferred for the cold 1999/2000 winter [Greenblatt *et al.*, 2002, Table 3] based on balloon and aircraft N₂O and CH₄ measurements mostly for the middle to lower stratosphere.

6. Discussion and Conclusions

[13] Elevated NO_x initially originated directly from particle precipitation during powerful coronal mass ejections associated with the X-class solar flares of October and November 2003 [Orsolini *et al.*, 2005; Randall *et al.*, 2005; Seppälä *et al.*, 2004; Semeniuk *et al.*, 2005]. As noted by Natarajan *et al.* [2004], mechanisms for production of NO_x in this region involve solar x-rays in the lower latitudes and auroral disturbances with energetic particle precipitation at high latitudes. The solar storms resulted in dissociation of N₂ and NO_x production through subsequent reaction of atomic nitrogen with molecular oxygen. Model calculations [Semeniuk *et al.*, 2005] suggest thermospheric NO_x levels resulting from the enhanced auroral activity

from the flares consistent with GOMOS stratospheric measurements and HALOE stratospheric and mesospheric measurements from the same time period, although there were no ACE NO_x measurements covering a similar range of latitudes and a comparable time period to provide confirmation.

[14] As prevailing transport during winter and early spring at high northern latitudes is downward at all levels in the mesosphere and upper stratosphere, ACE observations show residual elevated NO_x levels remained where downward transport from the high altitude source region to the upper stratosphere occurred possibly with enhancements due to the unusually strong upper stratospheric vortex in late February–March 2004 [Manney et al., 2005; Randall et al., 2005]. A strong mesospheric vortex would have helped any NO_x in its interior at middle mesosphere levels in January to stay confined to the polar night despite a reversal of the circulation and a major warming that occurred earlier in the Arctic during January–February 2004, hindering downward transport at that time [Manney et al., 2005; Semeniuk et al., 2005]. The elevated NO_x levels measured by ACE remained as a result of the long lifetime of NO_x against photochemical loss at high latitudes during polar winter darkness [Solomon et al., 1982]. ACE measurements show the NO_x enhancements in the Arctic upper stratospheric vortex air masses first observed during mid-February persisted throughout the time period with gradual reductions accompanied by descent through mid-March 2004. Randall et al. [2005] further showed NO_x enhancements persisted at least into July. Additional modeling work is needed to quantify the transport and the production mechanism that gave rise to the enhanced NO_x levels measured by ACE and quantify their impact on O₃ levels.

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References

Abrams, M. C., et al. (1996), Trace gas transport in the Arctic vortex inferred from ATMOS ATLAS-2 observations during April 1993, *Geophys. Res. Lett.*, **23**, 2345–2348.

- Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, **32**, L15S01, doi:10.1029/2005GL022386.
- Callis, L. B., et al. (1996), A 2-D model simulation of downward transport of NO_y into the stratosphere: Effects on the 1994 austral spring O₃ and NO_y, *Geophys. Res. Lett.*, **23**, 1905–1908.
- Callis, L. B., M. Natarajan, J. D. Lambeth, and D. N. Baker (1998), Solar atmospheric coupling by electrons (SOLACE): 2. Calculated stratospheric effects of precipitating electrons, 1979–1988, *J. Geophys. Res.*, **103**, 28,421–28,438.
- Greenblatt, J. B., et al. (2002), Tracer-based determination of vortex descent in the 1999/2000 Arctic winter, *J. Geophys. Res.*, **107**(D20), 8279, doi:10.1029/2001JD000937. (Correction, *J. Geophys. Res.*, **108**(D5), 8307, doi:10.1029/2002JD001597, 2003.)
- Manney, G. L., et al. (1994), On the motion of air through the stratospheric polar vortex, *J. Atmos. Sci.*, **51**, 2973–2994.
- Manney, G. L., et al. (2005), The remarkable 2003–2004 winter and other recent warm winters in the Arctic stratosphere since the late 1990s, *J. Geophys. Res.*, **110**, D04107, doi:10.1029/2004JD005367.
- Nassar, R., P. F. Bernath, C. D. Boone, G. L. Manney, S. D. McLeod, C. P. Rinsland, R. Skelton, and K. A. Walker (2005), ACE-FTS measurements across the edge of the winter 2004 Arctic vortex, *Geophys. Res. Lett.*, **32**, L15S05, doi:10.1029/2005GL022671.
- Natarajan, M., E. E. Remsburg, L. E. Deaver, and J. M. Russell III (2004), Anomalous high levels of NO_x in the polar upper stratosphere during April, 2004: Photochemical consistency of HALOE observations, *Geophys. Res. Lett.*, **31**, L15113, doi:10.1029/2004GL020566.
- Orsolini, Y. J., G. L. Manney, M. L. Santee, and C. E. Randall (2005), An upper stratospheric layer of enhanced HNO₃ following exceptional solar storms, *Geophys. Res. Lett.*, **32**, L12S01, doi:10.1029/2004GL021588.
- Randall, C. E., et al. (2005), Stratospheric effects of energetic particle precipitation in 2003–2004, *Geophys. Res. Lett.*, **32**, L05802, doi:10.1029/2004GL022003.
- Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopy database, *J. Quant. Spectrosc. Radiat. Transfer*, in press.
- Semeniuk, K., J. C. McConnell, and C. H. Jackman (2005), Simulation of the October–November 2003 solar proton event in the CMAM GCM: Comparison with observations, *Geophys. Res. Lett.*, **32**, L15S02, doi:10.1029/2005GL022392.
- Sen, B., et al. (1998), Measurements of reactive nitrogen in the stratosphere, *J. Geophys. Res.*, **103**, 3571–3585.
- Seppälä, A., P. T. Verronen, E. Kyrölä, S. Hassinen, L. Backman, A. Hauchecorne, J. L. Bertaux, and D. Fussen (2004), Solar proton events of October–November 2003: Ozone depletion in the Northern Hemisphere polar winter as seen by GOMOS/Envisat, *Geophys. Res. Lett.*, **31**, L19107, doi:10.1029/2004GL021042.
- Solomon, S., P. J. Crutzen, and R. G. Roble (1982), Photochemical coupling between the thermosphere and the lower atmosphere: 1. Odd nitrogen from 50 to 120 km, *J. Geophys. Res.*, **87**, 7206–7220.
- Woods, T. N., F. G. Eparvier, J. Fontenla, J. Harder, G. Kopp, W. E. McClintock, G. Rottman, B. Smiley, and M. Snow (2004), Solar irradiance variability during the October 2003 solar storm period, *Geophys. Res. Lett.*, **31**, L10802, doi:10.1029/2004GL019571.

P. Bernath, C. Boone, R. Nassar, and K. Walker, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada N2L 3G1. (bernath@uwaterloo.ca; cboone@acebox.uwaterloo.ca; ray@acebox.uwaterloo.ca; kwalker@uwaterloo.ca)

L. Chiou, Science Application International Corporation, 1 Enterprise Parkway, Mail Stop 927, Hampton, VA 23666, USA. (l.s.chiou@larc.nasa.gov)

J. C. McConnell, Department of Earth and Atmospheric Science, York University, 4700 Keele Street, Toronto, ON, Canada M3J 1P3. (jcmcc@yorku.ca)

C. P. Rinsland, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681–2199, USA. (c.p.rinsland@larc.nasa.gov)