

ATMOSPHERIC CHEMISTRY EXPERIMENT (ACE) MEASUREMENTS OF THE UPPER TROPOSPHERE AND STRATOSPHERE

Curtis. P. Rinsland¹, Peter Bernath², Chris Boone², Ray Nassar³,
Gaëlle Dufour⁴, Catherine Clerbaux⁵

¹NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-2199 U.S.A. c.p.rinsland@larc.nasa.gov,

²Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada bernath@uwaterloo.ca
cboone@uwaterloo.ca,

³Harvard University, Atmospheric Chemistry Modeling Group, Cambridge, MA ray@io.harvard.edu,

⁴Laboratoire de Météorologie Dynamique, Institut Pierre Simon Laplace, Palaiseau, France dufour@lisa.univ-paris12.fr,

⁵Service d'Aéronomie, Institut Pierre-Simon Laplace, Université Pierre et Marie Curie-Paris 6, Paris, France
catherine.clerbaux@aero.jussieu.fr.

ABSTRACT

We highlight chemistry and trend measurements from the Atmospheric Chemistry Experiment (ACE) which is providing precise middle troposphere to the lower thermosphere measurements of the Earth's upper troposphere to lower mesosphere with the solar occultation technique. The primary instrument is a 0.02 cm⁻¹ resolution Fourier transform spectrometer covering 750-4400 cm⁻¹ simultaneously. ACE also known as SCISAT 1 is a Canadian lead mission launched into a 74° inclined orbit at 650 km altitude on August 12, 2003 by a U.S.-supplied Pegasus vehicle. Additional measurements are obtained with a UV-visible

spectrometer and two imagers providing measurements at 0.525 and 1.02 microns.

2004 SOLAR FLARES

The Sun produced some of the most powerful solar flares ever recorded between 18 October and 5 November 2003. ACE measurements of Arctic NO_x vs. pressure from 0.07-2 hPa (~40-60 km) during February and March 2004 showed the dilution of NO_x resulting from photochemical loss in the sunlit atmosphere, and the time series of measurements were used to estimate the descent rate from the upper stratospheric NO_x time series [1].

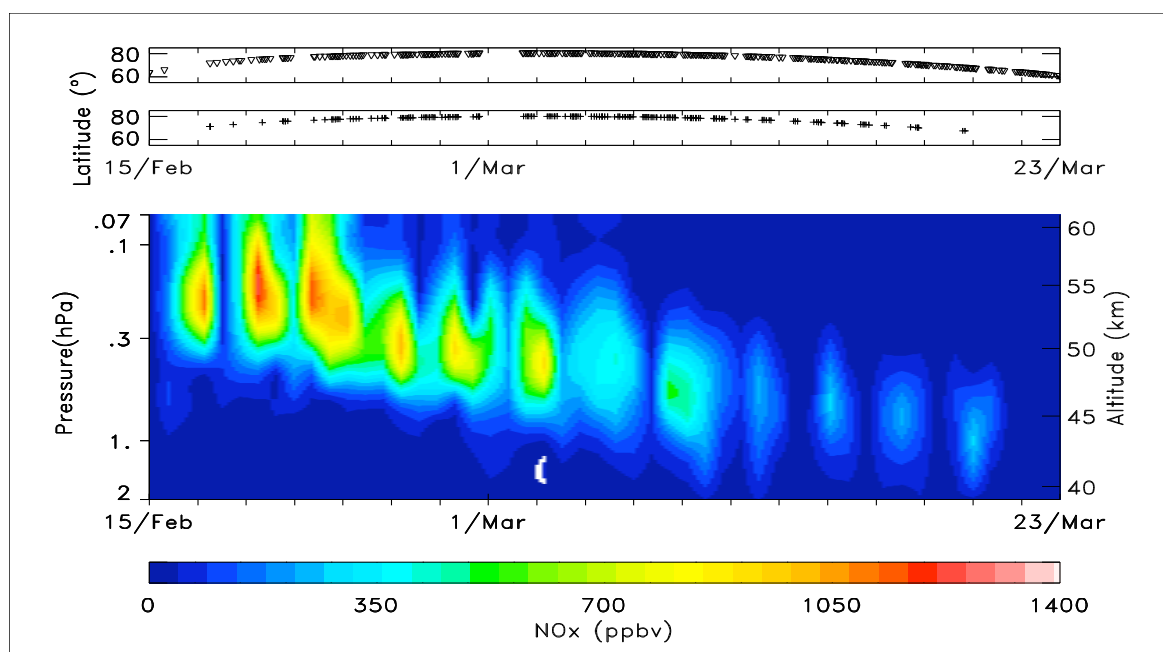


Figure 1. ACE time series of NO_x (NO+NO₂) measurements [Rinsland et al. [1]]

The capability of solar occultation instruments to infer nearly all components of the stratospheric inventories of chlorine and fluorine from high spectral resolution solar occultation instruments was pioneered by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer. The ACE instrument improved on the ATMOS design, and has been used to infer the stratospheric trends of both chlorine and fluorine at a critical time when stratospheric chlorine is near its maximum. Figure 2 presents results for the trend of HCl obtained by comparing measurements near

molecular species not previously detected from space. Important new results are the detection of methanol (CH_3OH) [7], the most abundant organic molecule in the troposphere, and formic acid (HCOOH) [8]. ACE measures southern hemisphere lower to mid-latitudes during August to October when intense vegetative fires occur in tropical regions of Africa and South America. Convection from those fires results in transport of the pollutant emissions to the middle and upper troposphere, where molecules with a sufficiently long lifetime can be measured by ACE. Formic acid (HCOOH) is an

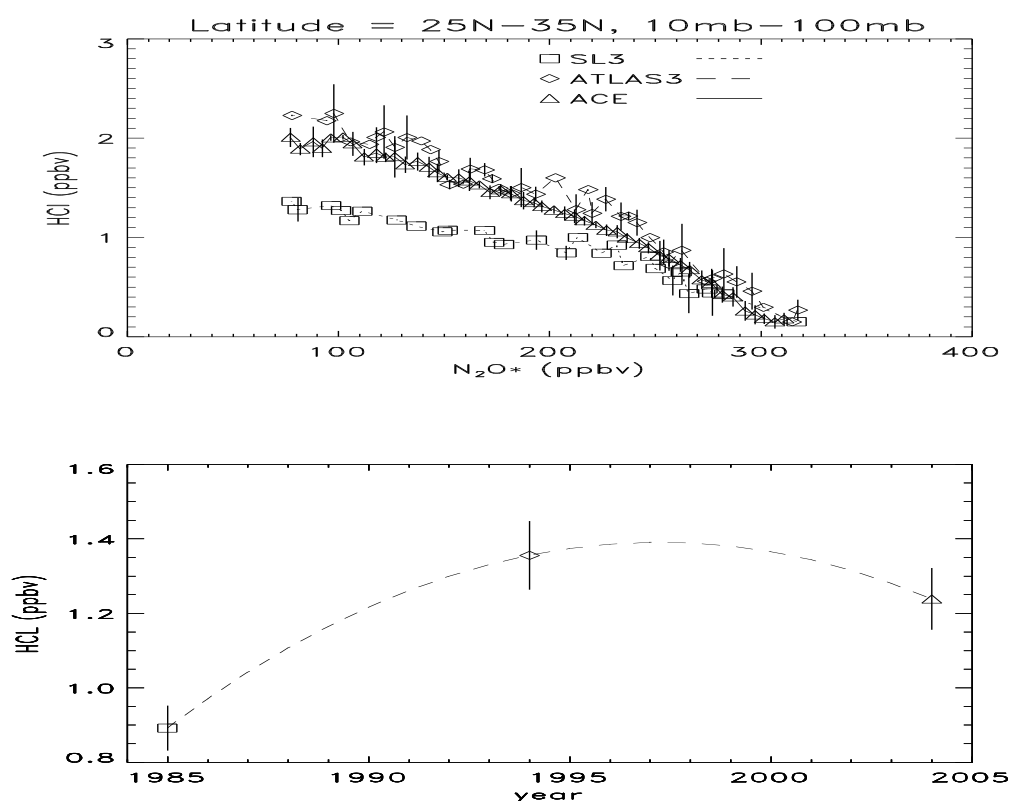


Figure 2. ATMOS-ACE measurements of HCl (upper panel) and trend (lower panel)

30°N latitude from ATMOS and ACE [2].

Additional ACE measurements include measurement of the trend of CF_4 [3] and the detections of HCFC-142b and CFC-113. Inventories for chlorine [4] and fluorine [5] in 2004 have been inferred and COCIF, a missing component in the chlorine and fluorine chemical families from coadded ACE spectra in the region of its strongest infrared band [6].

Frequent clear sky scenes occur in the middle and upper troposphere. ACE measured several

important oxygenated volatile organic compound (OVOC) with major limitations recognized in the ability of models to reproduce OVOC chemistry, particularly in the dry upper troposphere where OVOCs are a major source of HO_x in the background troposphere with ACE measurements showing elevated HCOOH in upper tropospheric plumes during both 2004 and 2005. Figure 3 illustrates a time series of ACE measurements that include HCOOH and other biomass burning emissions.

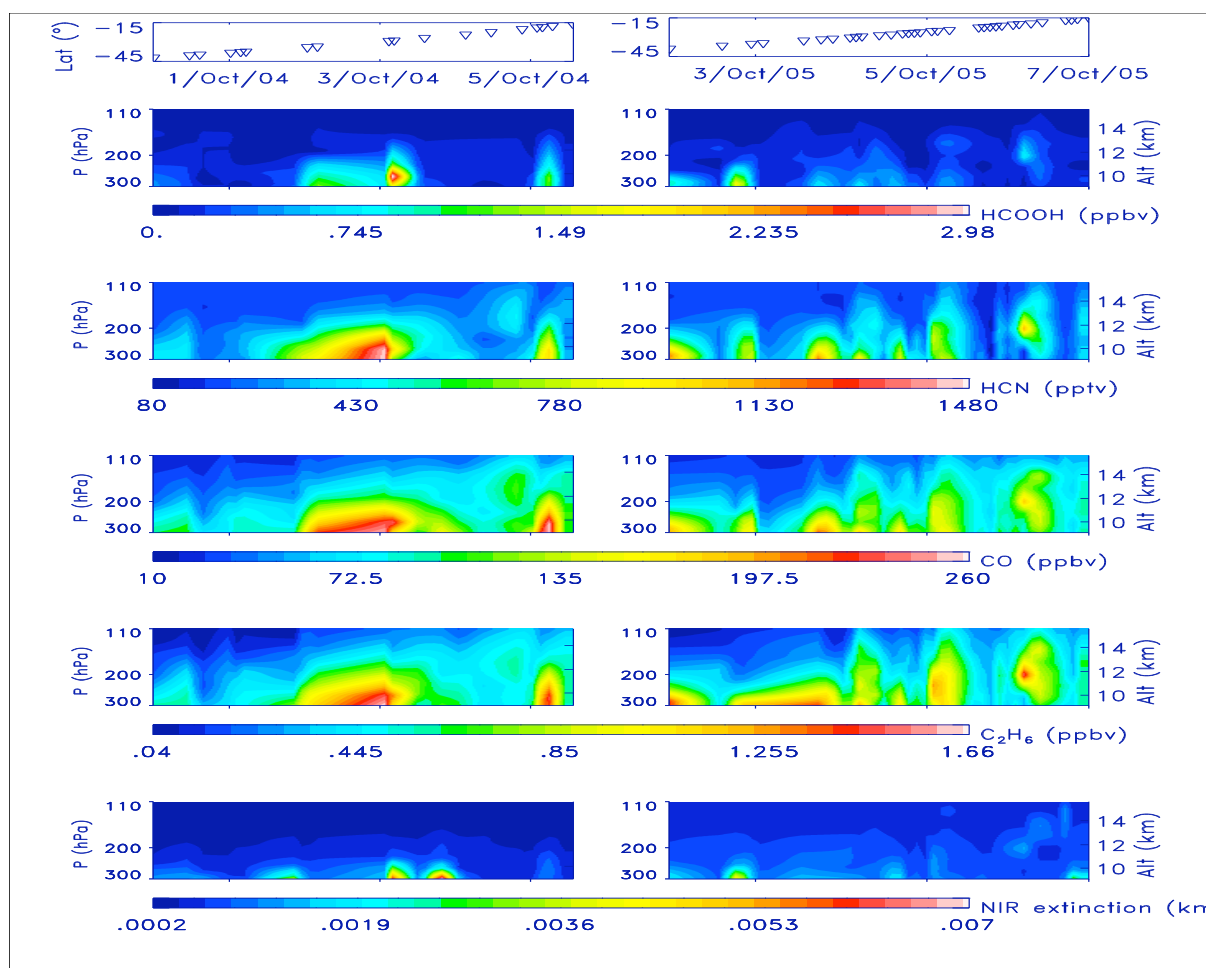


Figure 3. ACE Austral springtime series of HCOOH and other biomass burning emissions. Latitude of the measurements are indicated at top.

Additional tropospheric measurements include the detection of elevated upper tropospheric mixing ratios of H_2O_2 (hydrogen peroxide) in the subtropics [9]. ACE also measures boreal regions which are frequently impacted during summer by biomass burning. Summer 2004 measurements show elevated upper tropospheric CO, C_2H_6 , HCN, CH_3Cl , CH_4 , C_2H_2 , CH_3OH , HCOOH, and OCS mixing ratios in plumes up to 189 ppbv (10^{-9} per unit volume) for CO, 1.40 ppbv for C_2H_6 , 830 pptv (10^{-12} per unit volume) for HCN, 1.78 ppbv for CH_3Cl , 2.16 ppmv (10^{-6} per unit volume) for CH_4 , 0.118 ppbv for C_2H_2 , 3.89 ppbv for CH_3OH , 0.843 ppbv for HCOOH, and 0.543 ppbv for OCS in western Canada and Alaska at 50°N - 68°N latitude between 29 June and 23 July 2004. Emission factors have been inferred for several molecules and compared with previously reported values [10].

REFERENCES

1. Rinsland, C. P., C. Boone, R. Nassar, K. Walker, P. Bernath, J. C. McConnell and L. S. Chiou, 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, 2005.
2. Rinsland, C., C. Boone, R. Nassar, K. Walker, P. Bernath, E. Mahieu, F. Zander, J. C. McConnell, and L. Chiou, Trends of HF, HCl, CCl_2F_2 , CCl_3F , CHClF_2 (HCFC-22) and SF_6 in the lower stratosphere from Atmospheric Chemistry Experiment (ACE) and Atmospheric Trace Molecule Spectroscopy (ATMOS) measurement near 30°N latitude, *Geophys. Res. Lett.*, **32**, L16S03, doi: 10.1029/2005GL022415, 2005.
3. Rinsland, C.P., E. Mahieu, R. Zander, P. Bernath, C. Boone, and L.S. Chiou, Long-Term Stratospheric Carbon Tetrafluoride (CF_4) Increase from 1985-2004 Infrared Solar

- Occultation Measurements, *Geophys. Res. Lett.*, **33**, L02808, doi:10.1029/2005GL024709, 2006.
4. Nassar, R., B.F. Bernath, C.D. Boone, C. Clerbaux, B.F. Coheur, G. Dufour, L. Froidevaux, E. Mahieu, J.C. McConnell, S. D. McLeod, D.P. Murtagh, C.P. Rinsland, K. Semeniuk, R. Skelton, and R. Zander, The global inventory of stratospheric chlorine in 2004, *J. Geophys. Res.*, **111**, D22312, doi:10.1029/2006JD007073, 2006.
 5. Nassar, R., P.F. Bernath, C.D. Boone, S.D. McLeod, C.P. Rinsland, R. Skelton, K.A. Walker, R. Zander, A global inventory of stratospheric fluorine in 2004 based on ACE-FTS measurements, *J. Geophys. Res.*, **111**, D22313, doi:10.1029/2006JD007395, 2006.
 6. Rinsland, C.P., R. Nassar, C.B. Boone, P. Bernath, L. Chiou D. Weisenstein, Spectroscopic Detection of COClF in the tropical and mid-latitude lower stratosphere from Atmospheric Chemistry Experiment Infrared Solar Spectra: Preliminary Retrievals and Comparison with Previous Measurements and Model Calculations, *J. Quant. Spectrosc. Radiat. Transfer*, **105**, 467-475, 2007 (doi: 10.1029/jqsrt.2006.11.013).
 7. Dufour, G., C. D. Boone, C. P. Rinsland, and P. F. Bernath, First space-borne measurements of methanol inside aged tropical biomass burning plumes using the ACE-FTS instrument, *Atmos. Chem. Phys. Discuss.*, **6**, 3945-3963, 2006.
 8. Rinsland, C. P., C. D. Boone, P.F. Bernath, E. Mahieu, R. Zander, G. Dufour, C. Clerbaux, S. Turquety, L.S. Chiou, J. C. McConnell, L. Neary, and J.W. Kaminski, and, First Space-based Measurements of Formic Acid (HCOOH): Atmospheric Chemistry Experiment austral spring 2004 and 2005 Southern Hemisphere tropical-mid-latitude upper tropospheric measurements, *Geophys. Res. Lett.*, **33**, L23804, doi: 10.1026/2006GL027128, 2006.
 9. Rinsland, C. P., P.F. Coheur, H. Herbin, C. Clerbaux, C. Boone, P. Bernath, and L. S. Chiou, Detection of elevated tropospheric H₂O₂ (hydrogen peroxide) mixing ratios in ACE (Atmospheric Chemistry Experiment) Subtropical Infrared Solar Occultation Spectra, *J. Quant. Spectrosc. Radiat. Transfer*, 2006, doi: 10.1029/jqsrt.2006.11.013).
 10. Rinsland, C.P., S. Turquety, C. Clerbaux, G. Dufour, P.-F. Coheur, C. D. Boone, P. F. Bernath, and L.S. Chiou, Satellite boreal measurements over Alaska and Canada during June-July 2004: Simultaneous measurements of upper tropospheric CO, C₂H₆, HCN, CH₃Cl, CH₄, C₂H₂, CH₃OH, HCOOH, OCS, and SF₆, *Global Biogeochemical Cycles*, submitted, 2006.