The NO_y Budget Above Eureka, Nunavut From Ground-based FTIR Measurements, Space-based ACE-FTS Measurements, and the CMAM-DAS, GEM-BACH, and SLIMCAT Models

R. Lindenmaier[1], R. L. Batchelor[2], K. Strong[1], S. Beagley[3], R. Ménard[4], A. I. Jonsson[1], M. Neish[1], S. Chabrillat[5], M. P. Chipperfield[6], G. L. Manney[7,8], W. H. Daffer[7], S. Polavarapu[4], T. G. Shepherd[1], P. F. Bernath[9], K. A. Walker[1]

[1]*University of Toronto, Department of Physics, Toronto, ON, Canada*
[2]*NCAR, Boulder, CO, USA*
[3]*York University, Department of Earth and Space Science and Engineering, York, ON, Canada*
[4]*Environment Canada, Atmospheric Science and Technology Directorate, Toronto, ON, Canada*
[5]*Belgium Institute for Space Aeronomy, Brussels, Belgium*
[6]*University of Leads, Institute for Atmospheric Science, School of Earth and Environment, Leads, UK*
[7]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*
[8]*New Mexico Institute of Mining and Technology, Socorro, NM, USA*
[9]*University of York, Department of Chemistry, Heslington, York, UK*
E-mail: rodica@atmosp.physics.utoronto.ca

1. Introduction

Reactive nitrogen species, collectively called NO_y, play an important role in the chemistry of the stratosphere. NO_y, shown in Equation 1, is responsible for significant ozone destruction in the mid-stratosphere and influences the partitioning of the hydrogen, chlorine, and bromine families in the lower stratosphere.

$$NO_y = NO + NO_2 + NO_3 + HNO_3 + 2 \times N_2O_5 + ClONO_2 + BrONO_2 + HO_2NO_2 \quad (1)$$

Approximately 97% of the NO_y budget can be accounted for by NO, NO_2, HNO_3, $ClONO_2$, and N_2O_5 [1]. Throughout the rest of this paper, we refer to the sum of these five nitrogen species as 5-NO_y.

The main source of stratospheric NO_y is oxidation of N_2O, which produces NO. NO is rapidly oxidized to NO_2 by reacting with ozone, O_3. NO_2, in turn, is subject to photolysis, regenerating NO. In the upper stratosphere (~40 km), where the timescale of exchange between NO and NO_2 is less than 100 s, a quasi-steady state is quickly established. NO and NO_2 have strong diurnal variability. As the sun sets, NO concentrations decrease, while the NO_2 concentrations increase. At sunrise, the process is reversed. This behavior is well described by photochemical box models [e.g., 2].

A much smaller and sporadic source of NO_y is the precipitation of energetic particles that form NO in the mesosphere and lower thermosphere, which can be transported downward into the polar stratosphere [e.g., 3-5]. This contribution constitute approximately 2% of the total budget of NO_y, thus being negligible compared to the stratospheric NO production.

The sinks of stratospheric NO_y include transport into the troposphere and photolysis in the upper stratosphere (usually above 40 km). During the polar night and early spring, HNO_3 may be removed from the gas phase and trapped in polar stratospheric clouds (PSCs) through heterogeneous reactions. If these particles grow sufficiently large, they undergo sedimentation resulting in NO_y being permanently removed from the stratosphere. This process is referred to as denitrification.

Recent studies have shown that N_2O is increasing at a rate of 2.6% per decade [6] and it has been described as the most important anthropogenic ozone-depleting substance emitted today [7]. Thus the impact of NO_y on ozone can be expected to increase in the future.

The goals of this work are to derive an NO_y partial column data product from ground-based measurements in the high Arctic, to use the resulting four-year time series to assess seasonal and interannual variability, and to compare the results with three atmospheric models and ACE-FTS satellite data.

2. Measurements

The Polar Environment Atmospheric Research Laboratory (PEARL) was established in 2005 by the Canadian Network for the Detection of Atmospheric Change (CANDAC) in the Canadian High Arctic. It is located on Ellesmere Island at Eureka, Nunavut, (80.05ºN, 86.42ºW) at 610 m above sea level. A

Bruker 125HR Fourier Transform infrared spectrometer (FTIR) was installed in July 2006. It is a high-resolution spectrometer that records solar absorption spectra throughout the sunlit part of the year (mid-February to mid-October).

Four years of measurements have been acquired using the Bruker FTIR. Altitude-dependent volume mixing ratio (VMR) profiles were retrieved from the spectra using SFIT2 [8], a profile retrieval algorithm that employs the Optimal Estimation Method (OEM) [9]. See [10] for a detailed description of the retrieval analysis. Partial column densities of NO, NO_2, HNO_3, and $ClONO_2$ from 15 to 40 km have been retrieved. This altitude range was chosen based on the averaging kernels and sensitivity (the amount of information coming from the measurement rather than the a priori [11]) for each of these four species.

The FTIR data are compared with satellite measurements made by the Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS), which was launched on the Canadian SCISAT satellite in August 2003 [12]. Providing coverage from 85ºN to 85ºS and working in solar occultation, the ACE-FTS provides profile information for temperature, pressure, and more than 30 different atmospheric species. It has a similar spectral range to the Bruker FTIR, but considerably higher vertical resolution due to the limb-sounding geometry [12] The satellite has overpasses above Eureka during polar sunrise (February – March), when ozone depletion chemistry can be observed, and again near polar sunset in September-October.

3. Models

The Canadian Middle Atmosphere Model (CMAM) is an upward extension of the Canadian Centre for Climate Modelling and Analysis (CCCma) third-generation coupled general circulation model (CGCM3). The middle atmosphere component includes comprehensive interactive treatments of stratospheric chemistry, radiative processes and wave-driven dynamics. Detailed descriptions are given by [13] and [14]. We use results from the special IPY simulation for February 2007 to August 2009 performed with the CMAM-DAS (Data Assimilation System).

The GEM-BACH model consists of the Canadian Global Environmental Multiscale (GEM) model in combination with the Belgium Atmospheric Chemistry module (BACH). A detailed description of the model is given by [13]. The model is based on the stratospheric version (GEM-Strato) of the Canadian GEM model [15] which has been coupled online with a comprehensive module of stratospheric chemistry developed at BIRA-IASB. For GEM-BACH the special IPY run was also used, for March 2007 to February 2009.

SLIMCAT is a three-dimensional off-line chemical transport model (CTM) [16]. It differs from a general circulation model in that the model dynamics uses winds and temperatures from meteorological analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF). Also, the chemistry is calculated off-line or performed separately for each dynamical time-step and is thus not integrated into the dynamical model. SLIMCAT has been used for many studies of ozone and ozone related gases in the polar regions [e.g., 17-19]. The model calculates the abundances of chemical species in the troposphere and stratosphere. For SLIMCAT, data are shown for August 2006 to March 2010.

4. Results

Four components of the NO_y budget were measured by the Bruker FTIR (NO, NO_2, HNO_3, $ClONO_2$), while N_2O_5 was derived using model ratios of N_2O_5/NO_x (NO_x=NO+NO_2) for the closest grid point to Eureka. The resulting 5-NO_y partial columns were compared with the three atmospheric models. The model profiles were first smoothed to the vertical resolution of the Bruker FTIR using the FTIR averaging kernels and a priori profiles [20]. The comparison showed that the CMAM-DAS 5-NO_y partial columns were smaller than the Bruker FTIR partial columns, the mean percentage difference being (16.2±0.6)% (where the uncertainty represent the standard error of the mean). GEM-BACH showed a difference of (-5.2±1.0)%, with the model partial columns being slightly larger than the Bruker FTIR columns. The SLIMCAT partial columns were slightly smaller than the Bruker FTIR columns, the mean percentage difference being (5.8±0.4)%.

The Bruker FTIR measurements were further compared with springtime measurements by ACE-FTS. Data from four Canadian Arctic ACE Validation Campaigns at Eureka were compared using strict coincidence criteria to constrain time, distance, temperature, and sPV (scaled potential vorticity) at altitudes along the line-of-sight for both instruments for the compared air masses. A mean percentage difference of (-5.7±2.3)% was found, showing that the ACE-FTS partial columns are slightly larger than the Bruker FTIR columns. The small difference shows that the two instruments are in good agreement, despite their different viewing geometries and the high variability of the spring-time Arctic stratosphere.

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The seasonal and interannual variability of 5-NO_y above Eureka was also investigated. The 5-NO_y partial column was approximately constant through the sunlit part of the year, from mid-February to mid-October, with greater variability during the spring. The mean partial column averaged over the period including julian days greater than 140 was $(2.3\pm0.1)\times10^{16}$ molec cm^{-2}, while for the spring period (up to julian day 140) the mean partial column was $(2.5\pm0.2)\times10^{16}$ molec cm^{-2} (where the uncertainty values represent one standard deviation). The springtime evolution of 5-NO_y and its family members, along with that of the scaled potential vorticity, was examined for all four years. The 5-NO_y partial column variability was seen to be dominated by that of HNO_3. In conclusion, the evolution of the individual nitrogen species was found to be consistent with the current understanding of the chemical and dynamical processes that occur in the polar stratosphere.

5. References

[1] Brohede, S., C. A. McLinden, J. Urban, C. S. Haley, A. I. Jonsson, and D. Murtagh (2008), Odin stratospheric proxy NOy measurements and climatology, *Atmos. Chem. Phys., 8,* 5731 – 5754.

[2] McLinden, C. A., J. C. McConnell, E. Griffioen, and C. T. McElroy (2002), A vector radiative transfer model for the Odin/OSIRIS project, *Can. J. Phys., 80*(4), 375–393, doi:10.1139/p01-156.

[3] Randall, C. E., V. L. Harvey, G. L. Manney, Y. Orsolini, M. Codrescu, C. Sioris, S. Brohede, C. S. Haley, L. L. Gordley, J. M. Zawodny, and J. M. Russell III (2005), Stratospheric effects of energetic particle precipitation in 2003–2004, *Geophys. Res. Lett., 32,* L05802, doi:10.1029/2004GL022003.

[4] Randall, C. E., V. L. Harvey, C. S. Singleton, S. M. Bailey, P. F. Bernath, M. Codrescu, H. Nakajima, and J. M. Russell II (2007), Energetic particle precipitation effects on the Southern Hemisphere stratosphere in 1992–2005, *J. Geophys. Res., 112,* D08308, doi:10.1029/2006JD007696.

[5] Randall, C. E., V. L. Harvey, D. E. Siskind, J. France, P. F. Bernath, C. D. Boone, and K. A.Walker (2009), NO_x descent in the Arctic middle atmosphere in early 2009, *Geophys. Res. Lett., 36,* L18811, doi:10.1029/2009GL039706.

[6] Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. Fahey, J. Haywood, J. Lean, D. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz, and R. V. Dorland (2007), *Changes in Atmospheric Constituents and in Radiative Forcing, in: Climate change 2007: The physical scientific basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[7] Ravishankara, A. R., J. S. Daniel, and R. W. Portmann (2009), Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century, *Science, 326*, 123-125.

[8] Pougatchev, N. S., B. J. Connor, and C. P Rinsland (1995), Infrared measurements of the ozone vertical distribution above Kitt Peak, *J. Geophys. Res., 100*(D8), 16689–16697.

[9] Rodgers, C. D. (2000), *Inverse Methods for Atmospheric Sounding: Theory and Practice*, World Scientific Publishing Co. Pte. Ltd, pp 238.

[10] Batchelor, R.L., K. Strong, R. Lindenmaier, R. Mittermeier, H. Fast, J. R. Drummond, P. F. Fogal (2009), A new Bruker IFS 125HR FTIR spectrometer for the Polar Environment Atmospheric Research Laboratory at Eureka, Canada- measurements and comparison with the existing Bomem DA8 spectrometer, *J. Atmos. Oceanic Technol., 26*(7), 1328-1340, doi:10.1175/2009JTECHA12151.

[11] Vigouroux, C., M. De Mazière, P. Demoulin, C. Servais, F. Hase, T. Blumenstock, I. Kramer, M. Schneider, J. Mellqvist, A. Strandberg, V. Velazco, J. Notholt, R. Sussmann, W. Stremme, A. Rockmann, T. Gardiner, M. Coleman, and P. Woods (2008), Evaluation of tropospheric and stratospheric ozone trends over Western Europe from ground-based FTIR network observations, *Atmos. Chem. Phys., 8*, 6865–6886.

[12] Bernath, P. F., C. T. McElroy, M. C. Abrams, C. D. Boone, M. Butler, C. Camy-Peyret, et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission Overview, *Geophys. Res. Lett., 32,* L15S01, doi:10.1029/2005GL022386, 2005.

[13] de Grandpré, J., R. Ménard, Y. J. Rochon, C. Charette, S. Chabrillat, and A. Robichaud (2009), Radiative impact of ozone on temperature predictability in a coupled chemistry-dynamics data assimilation system, *Amer. Meteorol. Soc., 137,* 679-692, doi:10.1175/2008MWR2572.1.

[14] Scinocca, J. F., N. A. McFarlane, M. Lazare, J. Li, and D. Plummer (2008), The CCCma third generation AGCM and its extension into the middle atmosphere, *Atmos. Chem. Phys., 8,* 7055–7074.

[15] Côté , J., S. Gravel, A. Méthot, A. Patoine, M. Roch, and A. Staniforth (1998), The operational CMC–MRB Global Environmental Multiscale (GEM) model. Part I: Design considerations and formulation. *Mon. Wea. Rev., 126*, 1373–1395.

[16] Chipperfield, M. P. (2006), New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric traces experiments, *Q. J. R. Meteorol. Soc., 132,* 1179-1203, doi:10.1256/qj.05.51.

[17] Chipperfield, M. P., and R. L. Jones (1999), Relative influences of atmospheric chemistry and transport on Arctic ozone trends, *Nature, 400*, 551–554.

[18] Manney, G. L., R. S. Harwood, I. A. MacKenzie, K. Minschwaner, D. R. Allen et al. (2009), Satellite observations and modeling of transport in the upper troposphere through the lower mesosphere during the 2006 major stratospheric sudden warming, *Atmos. Chem. Phys., 9*, 4775–4795.

[19] Solomon, P., B. Connor, J. Barrett, T. Mooney, A. Lee, and A. Parrish (2002), Measurements of stratospheric ClO over Antarctica in 1996-2000 and implications for ClO dimer chemistry, *Geophys. Res. Lett., 29*(15), doi: 10.1029/2002GL015232.

[20] Rodgers, C. D. and B. J. Connor (2003), Intercomparison of remote sounding instruments, *J. Geophys. Res., 108*(D3), 4116, doi:10.1029/2002JD002299.