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Comment on "Middle atmospheric O_3, CO, N_2O, HNO_3, and temperature profiles during the warm Arctic winter 2001–2002" by Giovanni Muscari et al.

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[1] In a recent paper, *Muscari et al.* [2007] presented measurements of stratospheric constituents in Arctic winter 2001–2002 from mid-January to early March that were obtained using the ground-based millimeter-wave spectrometer (GBMS) and a Lidar system at Thule, Greenland (76.5°N, 68.7°W). Among the recent Arctic winters, winter 2001–2002 is one of the warmest winters on record [e.g., *Tilmes et al.*, 2004; *Manney et al.*, 2005; *Rex et al.*, 2006]. Using the GBMS stratospheric O_3, CO, N_2O, and HNO_3 measurements together with Lidar temperature observations, *Muscari et al.* [2007] characterized the polar stratosphere over Thule in the altitude range between $\sim$17–45 km focusing on two issues. First, they found low ozone concentrations in the Aleutian high at 900 K to be well correlated with low solar exposure and, secondly, they quantified ozone loss in the polar vortex in the lower stratosphere.

[2] Here, we discuss statements by *Muscari et al.* [2007] with regard to the lower stratosphere: "using correlations between GBMS O_3 and N_2O mixing ratios, in early February a large ozone deficiency owing to local ozone loss is noted inside the vortex. GBMS O_3-N_2O correlations suggest that isentropic transport brought a O_3 deficit also to regions near the vortex edge, where transport most likely mimicked local ozone loss".

[3] We will first discuss possible uncertainties in the way that the chemical ozone loss was derived by *Muscari et al.* [2007] as a result of the selection criteria used to sort GBMS profiles into different vortex regions. Then, considering the reported ozone loss values, we argue that, for the warm Arctic winter 2001–2002, chemical ozone loss to the extent suggested by *Muscari et al.* [2007] cannot be reconciled with the current understanding of halogen-driven chemical ozone destruction in the Arctic [e.g., *Solomon*, 1999; *World Meteorological Organization*, 2007].

[4] To distinguish between data points inside, outside, and at the edge of the polar vortex, *Muscari et al.* [2007] used GBMS N_2O measurements instead of considering meteorological fields such as potential vorticity gradients and horizontal wind speed [e.g., *Nash et al.*, 1996; *Bodeker et al.*, 2001; *Tilmes et al.*, 2006b; *Manney et al.*, 2007]. The authors state that they "trust the GBMS N_2O observations (O_3 and N_2O measurements were carried out within a total of 4 to 5 h) more than the temporally and spatially coarser Potential Vorticity data analysis". Indeed, *Greenblatt et al.* [2002] developed a technique to accurately determine the edge of the polar vortex from in situ (aircraft and balloon) measurements of a long-lived trace gas like N_2O. They found that for high-resolution aircraft data, a potential vorticity analysis may misidentify the inner edge by more than 400 km. However, GBMS measurements have a much coarser spatial and temporal resolution than the in situ data employed by *Greenblatt et al.* [2002]. Although the width of the instantaneous field of view of the GBMS is $\sim$10 km in the lower stratosphere, the integration time of the measurements ($\sim$1.5 h for O_3, $\sim$3 h for N_2O) means that the GBMS samples an air mass of a certain horizontal extent. Assuming wind speeds of 20–40 km/h at 10 hPa, *Muscari et al.* [2007] estimated an effective horizontal resolution of 90–180 km. Considering typical wind speeds for the lower polar stratosphere at approximately 480 K [e.g., *Chan et al.*, 1990] between 40 km/h (vortex core) and 180 km/h (toward the vortex edge), we obtain a conservative estimate of the range of horizontal resolution of 180 km to 810 km, a range that includes earlier estimates for GBMS measurements of a single species (about 200–300 km [*Muscari et al.*, 2002]). The vertical resolution of the GBMS is about 7 km in the Arctic lower stratosphere [*Muscari et al.*, 2007]. Current meteorological analyses reach higher spatial resolutions, for example in 2000 the European Centre for Medium-Range Weather Forecasts (ECMWF) introduced a T511/L60 system with a horizontal resolution of about 40 × 40 km and a vertical resolution of about 1 km in the upper troposphere and lower stratosphere [e.g., *Jung and Leutbecher*, 2007].

[5] An appropriate criterion to determine whether profiles are measured inside or outside the vortex is essential for the application of ozone-tracer relations to calculate polar ozone loss because the characteristics of air outside the vortex are very different to those of vortex air. A criterion that leads to using a mixture of profiles measured inside and outside of the vortex could cause the chemical ozone loss in the vortex to be underestimated [*Tilmes et al.*, 2004].

[6] We will now discuss the chemical ozone loss in Arctic winter 2001–2002. On the basis of correlations between

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GBMS O_3 and N_2O mixing ratios, *Muscari et al.* [2007] reported large chemical ozone loss values for early February in the polar vortex. The ozone deficiency reported is ~1.5 ppm at 480 K (40 ppb N_2O) for the vortex core. A chemical ozone loss of this magnitude disagrees with the ozone loss values deduced from ozone tracer (HF) relations in this winter which were measured by HALOE; for March 2002, *Tilmes et al.* [2004] report a maximum local loss of 0.5 ± 0.2 ppm, a vortex average column ozone loss of 12 ± 10 DU, and very little (5 ± 10 DU) ozone loss in the vortex core. On the basis of an analysis of SAOZ measurements, *Goutail et al.* [2005] report an Arctic column ozone deficit of 10% for the end of March 2002, however the reported ozone deficit for mid-January is only about 5%. There are observations [e.g., *Tilmes et al.*, 2004; *Rex et al.*, 2004] of an accumulated chemical ozone loss in the lower stratosphere reaching and exceeding 1.5 ppm, but only for late winter (that is for "established ozone loss" conditions) and only for much colder winters than 2001–2002 (e.g., 1995–1996 or 1999–2000). For comparison, the accumulated column ozone loss reported by *Goutail et al.* [2005] is 30% for 1995–1996 and 23% for 1999–2000.

[7] Owing to the fact that the last polar stratospheric clouds were observed in mid-January in winter 2001–2002 and no enhancement of ClO was detected by Odin/SMR after 8 January, *Muscari et al.* [2007] concluded that the ozone deficiency deduced from the GBMS measurements in early February (~1.5 ppm) was caused by chemical loss in the first half of January. They state that "because of the long lifetime of ozone in the lower stratosphere, the deficiency could have persisted at least until the beginning of February". Indeed, the rate of photochemical ozone production in the polar lower stratosphere in spring is slow (and zero in complete darkness). Therefore, it is highly likely that chemical ozone loss occurring in early January was still detectable a couple of weeks later. Nevertheless, mixing between air masses that have been subject to chemical loss and surrounding air masses that are richer in ozone would reduce the signature of ozone loss to a certain extent.

[8] However, an accumulated chemical ozone loss of about 1.5 ppm in the lower stratosphere between mid-December and mid-January 2002 means that ozone loss rates of ~50 ppb per day were sustained for a month (and during a period of very low solar elevation in the Arctic). For comparison, ozone loss rates of 50 ppb per day were observed only on one occasion to date, namely for about two weeks at the end of January 1992 [*von der Gathen et al.*, 1995; *Rex et al.*, 1998]. Loss rates of this magnitude are greater than can be explained by model simulations [*Becker et al.*, 1998; *Rex et al.*, 2003].

[9] Moreover, for the vortex edge region at 480 K (at 120 ppb N_2O), *Muscari et al.* [2007] found a significant O_3 deficit of about 1.2 ppm in late January to mid-February 2002. They offer as an explanation that air masses subject to strong ozone loss in the vortex core were mixed with air masses in the vortex edge region, where chemical ozone loss is considered to be unlikely. *Muscari et al.* [2007] state that "transport brought a O_3 deficit also to regions near the vortex edge, where transport most likely mimicked local ozone loss". It is important to note that the mixing of vortex core and vortex edge air masses leads to a reduction in the apparent ozone loss in the vortex core air at the same time when the signature of chemical ozone loss is exported from the core to the vortex edge. In reply to the present comment, *Muscari and de Zafra* [2008] correctly point out that mixing in ozone tracer space may affect chemical ozone loss estimates in a nonlinear way; that is, a mixed air parcel does not generally show the mean chemical ozone loss of its two parent particles (see also *Lemmen et al.* [2006] for a detailed discussion of the impact of different mixing scenarios on an ozone-tracer relation in the vortex showing significant ozone loss). *Muscari and de Zafra* [2008] assume a difference of 80 ppb in N_2O between the vortex core and vortex edge. However, the polar isentropic tracer gradient between the vortex core and the vortex edge is rather small up to a few degrees of the vortex edge [e.g., *Loewenstein et al.*, 1990; *Riese et al.*, 2002; *Manney et al.*, 2006; *Tilmes et al.*, 2006b] so that mixing between core and edge air masses occurs for roughly constant tracer values. Therefore, relative to the 'early vortex reference', the mixed air parcel will show approximately the same ozone loss as the mean of the two original air parcels. Thus, the vortex average chemical ozone loss does not change significantly by mixing between vortex core and vortex edge air masses. This process, therefore, will not lead to an overestimation of chemical ozone loss. As a clearer, more appropriate description of such conditions, we suggest that ozone loss is homogenized in the vortex.

[10] A homogenization of the ozone loss signal in the vortex was observed in winter 1996–1997. In March 1997, ozone loss in the vortex was strongly inhomogeneous, noticeable both in observations and simulations [*Schulz et al.*, 2000; *McKenna et al.*, 2002; *Tilmes et al.*, 2003]. The ozone-tracer relation in March was not compact because of a chemical reason, namely stronger chemical ozone loss in the vortex core than at the edge of the vortex [*McKenna et al.*, 2002; *Tilmes et al.*, 2003]. In early May 1997, compact ozone-tracer relations were observed again in the remaining vortex indicating that mixing in the vortex had, by that time, rehomogenized the vortex air mass and thus the ozone loss signal.

[11] *Muscari et al.* [2007] emphasized that chemical ozone loss in Arctic winter 2001–2002 must have taken place in a limited region of the vortex. However, none of the six vortex observations or the four vortex edge observations of the GBMS instrument (with a horizontal resolution of 180–810 km) in early 2002 sampled air masses that were not affected by chemical loss.

[12] In summary, we argue that the magnitude of Arctic chemical ozone loss and the implied ozone loss rates reported by *Muscari et al.* [2007] are very difficult to reconcile with the current understanding of chemistry in the polar vortex [e.g., *Solomon*, 1999; *World Meteorological Organization*, 2007]. However, we agree with the conclusion of *Muscari et al.* [2007] that if noticeable chemical ozone loss occurred in the polar vortex in 2001–2002, it can only have occurred locally in restricted areas of the vortex. Therefore, their findings do not call into question the notion that the average chemical ozone loss in the Arctic vortex shows a very close relation to temperature conditions and thus to the potential for chlorine activation in the vortex [e.g., *Rex et al.*, 2004, 2006; *Tilmes et al.*, 2006a, 2008; *World Meteorological Organization*, 2007].

References

Becker, G., R. Müller, D. S. McKenna, M. Rex, and K. S. Carslaw (1998), Ozone loss rates in the Arctic stratosphere in the winter 1991/92: Model calculations compared with Match results, *Geophys. Res. Lett.*, *25*(23), 4325–4328.

Bodeker, G. E., J. C. Scott, K. Kreher, and R. L. McKenzie (2001), Global ozone trends in potential vorticity coordinates using TOMS and GOME intercompared against the Dobson network: 1978–1998, *J. Geophys. Res.*, *106*(D19), 23,029–23,042.

Chan, K. R., S. W. Bowen, T. P. Bui, S. G. Scott, and J. Dean-Day (1990), Temperature and wind measurements and model atmospheres of the 1989 Airborne Arctic Stratospheric Expedition, *Geophys. Res. Lett.*, *17*(4), 342–344.

Goutail, F., et al. (2005), Early unusual ozone loss during the Arctic winter 2002/2003 compared to other winters, *Atmos. Chem. Phys.*, *5*, 665–677.

Greenblatt, J. B., et al. (2002), Defining the polar vortex edge from an N_2O: Potential temperature correlation, *J. Geophys. Res.*, *107*(D20), 8268, doi:10.1029/2001JD000575.

Jung, T., and M. Leutbecher (2007), Performance of the ECMWF forecasting system in the Arctic during winter, *Q. J. R. Meteorol. Soc.*, *133*, 1327–1340, doi:10.1002/qj.99.

Lemmen, C., R. Müller, P. Konopka, and M. Dameris (2006), Critique of the tracer-tracer correlation technique and its potential to analyze polar ozone loss in chemistry-climate models, *J. Geophys. Res.*, *111*(D18), D18307, doi:10.1029/2006JD007298.

Loewenstein, M., J. R. Podolske, and K. R. Chan (1990), N_2O as a dynamical tracer in the Arctic vortex, *Geophys. Res. Lett.*, *17*(4), 477–480.

Manney, G. L., K. Krüger, J. L. Sabutis, S. Amina Sena, and S. Pawson (2005), The remarkable 2003–2004 winter and other recent warm winters in the Arctic stratosphere in the late 1990s, *J. Geophys. Res.*, *110*, D04107, doi:10.1029/2004JD005367.

Manney, G. L., M. L. Santee, L. Froidevaux, K. Hoppel, N. J. Livesey, and J. W. Waters (2006), EOS MLS observations of ozone loss in the 2004–2005 Arctic winter, *Geophys. Res. Lett.*, *33*, L04802, doi:10.1029/2005GL024494.

Manney, G. L., et al. (2007), Solar occultation satellite data and derived meteorological products: Sampling issues and comparisons with Aura Microwave Limb Sounder, *J. Geophys. Res.*, *112*, D24S50, doi:10.1029/2007JD008709.

McKenna, D. S., J.-U. Grooß, G. Günther, P. Konopka, R. Müller, G. Carver, and Y. Sasano (2002), A new Chemical Lagrangian Model of the Stratosphere (CLaMS): 2. Formulation of chemistry scheme and initialization, *J. Geophys. Res.*, *107*(D15), 4256, doi:10.1029/2000JD000113.

Muscari, G., and R. L. de Zafra (2008), Reply to comment by Rolf Müller and Simone Tilmes on "Middle atmospheric O_3, CO, N_2O, HNO_3, and temperature profiles during the warm Arctic winter 2001–2002," *J. Geophys. Res.*, *113*, D18304, doi:10.1029/2008JD010292.

Muscari, G., M. L. Santee, and R. L. de Zafra (2002), Intercomparison of stratospheric HNO_3 measurements over Antarctica: Ground-based millimeter-wave versus UARS/MLS Version 5 retrievals, *J. Geophys. Res.*, *107*(D24), 4809, doi:10.1029/2002JD002546.

Muscari, G., A. G. di Sarra, R. L. de Zafra, F. Lucci, F. Baordo, F. Angelini, and G. Fiocco (2007), Middle atmospheric O_3, CO, N_2O, HNO_3, and temperature profiles during the warm Arctic winter 2001–2002, *J. Geophys. Res.*, D14304, doi:10.1029/2006JD007849.

Nash, E. R., P. A. Newman, J. E. Rosenfield, and M. R. Schoeberl (1996), An objective determination of the polar vortex using Ertel's potential vorticity, *J. Geophys. Res.*, *101*(D5), 9471–9478.

Rex, M., et al. (1998), In situ measurements of stratospheric ozone depletion rates in the Arctic winter 1991/1992: A Lagrangian approach, *J. Geophys. Res.*, *103*(D5), 5843–5853.

Rex, M., R. J. Salawitch, M. L. Santee, J. W. Waters, K. Hoppel, and R. Bevilacqua (2003), On the unexplained stratospheric ozone losses during cold Arctic Januaries, *Geophys. Res. Lett.*, *30*(1), 1008, doi:10.1029/2002GL016008.

Rex, M., R. J. Salawitch, P. von der Gathen, N. R. P. Harris, M. P. Chipperfield, and B. Naujokat (2004), Arctic ozone loss and climate change, *Geophys. Res. Lett.*, *31*, L04116, doi:10.1029/2003GL018844.

Rex, M., et al. (2006), Arctic winter 2005: Implications for stratospheric ozone loss and climate change, *Geophys. Res. Lett.*, *33*, L23808, doi:10.1029/2006GL026731.

Riese, M., G. L. Manney, J. Oberheide, X. Tie, R. Spang, and V. Küll (2002), Stratospheric transport by planetary wave mixing as observed during CRISTA-2, *J. Geophys. Res.*, *107*(D23), 8179, doi:10.1029/2001JD000629.

Schulz, A., et al. (2000), Match observations in the Arctic winter 1996/97: High stratospheric ozone loss rates correlate with low temperatures deep inside the polar vortex, *Geophys. Res. Lett.*, *27*(2), 205–208, doi:10.1029/1999GL010811.

Solomon, S. (1999), Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, *37*(3), 275–316, doi:10.1029/1999RG900008.

Tilmes, S., R. Müller, J.-U. Grooß, D. S. McKenna, J. M. Russell, and Y. Sasano (2003), Calculation of chemical ozone loss in the Arctic winter 1996–1997 using ozone-tracer correlations: Comparison of Improved Limb Atmospheric Spectrometer (ILAS) and Halogen Occultation Experiment (HALOE) results, *J. Geophys. Res.*, *108*(D2), 4045, doi:10.1029/2002JD002213.

Tilmes, S., R. Müller, J.-U. Grooß, and J. M. Russell (2004), Ozone loss and chlorine activation in the Arctic winters 1991–2003 derived with the tracer-tracer correlations, *Atmos. Chem. Phys.*, *4*, 2181–2213.

Tilmes, S., R. Müller, A. Engel, M. Rex, and J. Russell III (2006a), Chemical ozone loss in the Arctic and Antarctic stratosphere between 1992 and 2005, *Geophys. Res. Lett.*, *33*, L20812, doi:10.1029/2006GL026925.

Tilmes, S., R. Müller, J.-U. Grooß, H. Nakajima, and Y. Sasano (2006b), Development of tracer relations and chemical ozone loss during the setup phase of the polar vortex, *J. Geophys. Res.*, *111*, D24S90, doi:10.1029/2005JD006726.

Tilmes, S., R. Müller, R. J. Salawitch, U. Schmidt, C. R. Webster, H. Oelhaf, J. M. Russell III, and C. C. Camy-Peyret (2008), Chemical ozone loss in the Arctic winter 1991–1992, *Atmos. Chem. Phys.*, *8*, 1897–1910.

von der Gathen, P., et al. (1995), Observational evidence for chemical ozone depletion over the Arctic in winter 1991–92, *Nature*, *375*, 131–134.

World Meteorological Organization (2007), Scientific assessment of ozone depletion: 2006, Global Ozone Res. and Monit. Proj. 50, 572 pp., Geneva.

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