Widespread persistent near-surface ozone depletion at northern high latitudes in spring

Tao Zeng,1 Yuhang Wang,1 Kelly Chance,2 Edward V. Browell,3 Brian A. Ridley,4 and Elliot L. Atlas4,5

Received 9 September 2003; revised 28 October 2003; accepted 24 November 2003; published 31 December 2003.

[1] Springtime near-surface ozone depletion has been observed at northern high latitudes. Due to limited observations, the spatial and temporal extent of low O3 concentrations near the surface is still unknown. A regional 3-D chemistry and transport model is applied to simulate near-surface O3 depletion catalyzed by bromine radicals at northern high latitudes in March and April 2000. Satellite observations of BrO column by the ESA Global Ozone Monitoring Experiment (GOME) were processed to specify the BrO concentrations in the lower troposphere. In view of the GOME measurement and model uncertainties, the model results show an adequate agreement with the O3 concentrations near the surface. Model results indicate that low O3 concentrations (<20 ppbv) near the surface cover ~60% of the northern high latitudes and that the depleted O3 concentrations (<10 ppbv) cover ~20% of the region in April. The high BrO events tend to be large-scale and persistent (1–2 weeks). We find that they are correlated with low temperature, a condition conducive for heterogeneous reactions on frozen snow or aerosol surfaces. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1640 Global Change: Remote sensing. Citation: Zeng, T., Y. Wang, K. Chance, E. V. Browell, B. A. Ridley, and E. L. Atlas, Widespread persistent near-surface ozone depletion at northern high latitudes in spring, Geophys. Res. Lett., 30(24), 2298, doi:10.1029/2003GL018587, 2003.

1. Introduction

[2] A number of Canadian ozonesonde stations in the Arctic region, such as Churchill, Resolute, Eureka, and Alert, have reported low O3 concentrations (0–20 ppbv) near the surface [Bottenheim et al., 1986; Tarasick and Bottenheim, 2002]. Low ozone events have also been found at Ny-Alesund, Norway [Solberg et al., 1996]. Surface O3 measurements at Barrow, Alaska [Oltmans and Levy, 1994] are probably the longest continuous record with frequent low O3 events. Airborne observations during the 1992 Polar Sunrise Experiment [Leaitch et al., 1994] were conducted in small regions between Alert and Resolute to examine the characteristics of low O3 air masses. In spring 2000, near-surface O3 depletion was observed at two surface sites, Alert, Canada [K. Anlauf, personal communication, 2003] and Barrow, Alaska [e.g., Oltmans and Levy, 1994], and in the lower troposphere by airborne in situ instruments [Ridley et al., 2003] and differential absorption lidar (DIAL) [Browell et al., 2003] during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment [Atlas et al., 2003].

[3] The O3 loss is thought to be catalyzed by BrOx (Br + BrO) [Barrie et al., 1988; Haussmann and Platt, 1994]. Heterogeneous reactions on snow and aerosol surfaces appear to play an important role to sustain the high BrOx level [Fan and Jacob, 1992; McConnell et al., 1992; Tang and McConnell, 1996]. The chemical cycling of BrOx has been investigated using box models [Tang and McConnell, 1996; Sander et al., 1997; Michalowski et al., 2000; Evans et al., 2003]. However, the spatial and temporal distribution of near-surface low O3 concentrations is unclear due to the scarcity of the observations.

2. Methodology

[4] We have developed a regional 3-D chemistry and transport model to simulate the O3 concentrations at northern high latitudes in March and April 2000. Bromine catalyzed O3 loss is estimated in the model on the basis of BrO columns determined from GOME (ERS-2 satellite) spectral measurements [European Space Agency, 1995; Richter et al., 1998; Chance, 1998; Wagner and Platt, 1998]. The period was chosen because of the availability of in situ and DIAL measurements of lower tropospheric O3 concentrations extending from Colorado to north of Alert. The spatial coverage of the measurements, particularly that of DIAL, is substantially better than previous observations. In addition, surface observations of O3 concentrations are available at Alert and Barrow. After evaluating the model simulations of low O3 concentrations with the observations, we infer the spatial and temporal extent of the near-surface O3 loss from the model results.

[5] The rate limiting step in bromine catalyzed O3 loss is usually BrO + BrO → Br2 + O2; under very low O3 concen-
Figure 1. GOME BrO VCD and simulated near-surface O$_3$ concentrations in March and April, 2000. Upper: Daily stratospheric BrO VCD. Mean values are shown by the red lines. The values for mean ± the standard deviation are shown by the blue lines. Middle: Monthly mean tropospheric BrO VCD (at a thickness of 400 m, a column concentration of $1 \times 10^{11}$ molecule cm$^{-2}$ is equivalent to a mixing ratio of 10 pptv). Bottom: Simulated monthly near-surface O$_3$ concentration. The locations of the two surface sites, Alert, Canada (82.5$^\circ$N, 62.3$^\circ$W) (marked by “A”) and Barrow, Alaska (71.3$^\circ$N, 156.6$^\circ$W) (“B”), are shown on the middle and bottom plots.

3. Results and Discussion

[9] Figure 1 shows the model simulated monthly mean O$_3$ concentrations near the surface and GOME BrO VCD in March and April. Regions around the Arctic Ocean with high tropospheric BrO VCD, such as northern Hudson Bay, Canadian archipelago, southern Chukchi Sea, and Kara Sea, have low O$_3$ concentrations. Despite lower BrO loading, more severe O$_3$ depletion is simulated in April than in March due to longer daylight.

[10] The model captures some important features of the surface O$_3$ variations, including some O$_3$ depletion events, observed at Alert and Barrow (Figure 2). Three-day low pass filtered O$_3$ measurements are also shown since GOME BrO measurements used in the model are 3–5 day averages. The correlation coefficients between observed and simulated O$_3$ concentrations are 0.52 and 0.58 at Alert and Barrow, respectively. The low temporal resolution of BrO measurements may account for some phase lags between observed and simulated O$_3$ variations at Barrow. The better simulation at Barrow than Alert is due in part to fewer high-frequency O$_3$ depletion events at this site. Considering the poor temporal and spatial resolution of the BrO data used in the model in addition to inherent model uncertainties, the relatively good simulations at the two surface sites imply that the O$_3$ depletion events observed at these sites are largely part of the large-scale persistent O$_3$ depletion features in the Arctic spring.
To further investigate the dependency of O\textsubscript{3} depletion events on BrO concentrations at these sites, we conducted two sensitivity simulations in which only BrO concentrations above 10 or 20 pptv are included. In the case of >10 pptv BrO, the model simulations at Alert and Barrow show little change. In the case of >20 pptv BrO, the model slightly underestimates the ozone loss but still captures the same O\textsubscript{3} depletion events. Both sites are strongly affected by transport of O\textsubscript{3}-depleted air since they are located on the edges of high BrO regions (Figure 1). The O\textsubscript{3} depletion at Alert near the end of April exemplifies the transport effect. Our results suggest that transport of O\textsubscript{3}-poor air from areas with persistent high-BrO concentrations contributes significantly to the low O\textsubscript{3} episodes in the observations.

The model results cannot be reliably evaluated using ozonesonde measurements due to the low frequency of the observations. During the TOPSE experiments, both in situ and DIAL measurements showed episodically large regions of lower tropospheric O\textsubscript{3} depletion along the flight tracks of Churchill-Thule-Alert [Browell et al., 2003; Ridley et al., 2003]. The remote sensing DIAL instrument, in particular, provides high temporal and spatial resolution data to evaluate the model results. Figure 3 shows the O\textsubscript{3} measurements of flight 29 (10 April) by DIAL and in situ instruments over the northern Hudson Bay and the corresponding model simulations along the flight track. The model captures the observations reasonably well. Also shown is a scatter plot of observed O\textsubscript{3} concentrations and corresponding model results below 500 m for all available TOPSE measurements in March and April. The correlation coefficients between observed and simulated O\textsubscript{3} concentrations are 0.51 and 0.68 for DIAL and in situ measurements, respectively. It is unclear why the correlation coefficient is higher for the in situ measurements. Including data at 500 m–1 km improves the correlation coefficients due to the addition of higher O\textsubscript{3} data points, which are captured in the model. The fact that the model is able to reproduce the high-frequency in situ and DIAL measurements despite the coarse temporal resolution of the GOME data provides additional support that the lower tropospheric O\textsubscript{3} depletions in the Arctic are large-scale persistent events.

Although the detailed mechanism for high BrO concentrations cannot be investigated in our model, we find that the regions with high BrO tend to have low temperature. Figure 4 shows the monthly mean surface temperature simulated in MM5. Three regions, (1) southern Chukchi Sea, (2) Canadian archipelago, and (3) northern Hudson Bay, have BrO concentrations >40 pptv. Right: GOME derived BrO tropospheric VCD and MM5 simulated surface air temperature in the three regions. The correlation coefficients are calculated using daily averages.
of the high BrO region coincides with the movement of cold air. High BrO events in these regions last 1–2 weeks. Freezing of snow or aerosols at low temperature therefore appears to be a necessary condition for releasing and sustaining high BrO concentrations [e.g., Mozurkewich, 1995].

GOME observations of BrO column were used in a regional 3-D chemistry and transport model to simulate bromine catalyzed near-surface O₃ loss in March and April 2000. Despite the relatively low temporal and spatial resolution of the BrO observations, the model captures reasonably well the O₃ depletion events observed during TOPSE and at two surface sites. Model results indicate widespread persistent regions of lower tropospheric O₃ depletion due to O₃ loss catalyzed by high BrO concentrations and transport of the resulting O₃-poor air. High BrO events last 1–2 weeks and occur in low temperature episodes.

Appendix

[Bromine radical concentrations are estimated by scaling to BrO concentrations [Tuckermann et al., 1997]. The BrO/Br ratio is estimated as,

$$[\text{BrO}] = \frac{k_{\text{exp}} [\text{O}_3]}{2k_{\text{exp}} + k_{\text{BrO}} [\text{ClO}]} + \frac{k_{\text{exp}} [\text{NO}]}{2k_{\text{exp}} + k_{\text{BrO}} [\text{NO}]} + \frac{k_{\text{exp}}}{2k_{\text{exp}}}$$

Nitric oxide (NO) concentrations from TOPSE are averaged according to the different O₃ concentration bands. The concentration of chlorine monoxide (ClO) is assumed to be equal to the concentration of BrO [Tuckermann et al., 1997]. The photolysis rate of BrO (U_{\text{BrO}}) is specified to be 4.51 × 10⁻² s⁻¹ [Michalowski et al., 2000]. Ozone loss takes place only during daytime and is calculated on the basis of the lower rate of the BrO-BrO and Br-O₃ reactions [Haussmann and Platt, 1994].

Acknowledgments. We thank Kurt Anlauf for providing the surface O₃ data at Alert and Louisa Emmmons for her help on ozonesonde data. We also thank Daniel Jacob and Robert Yantosca for providing the GEOS-CHEM model and data. Assimilated GEOS-3 meteorological data for spring 2000 are provided by the NASA Global Modeling and Assimilation Office. The European Space Agency and the German Aerospace Center provided invaluable cooperation with GOME data. This work was supported by the National Science Foundation and by the National Aeronautics and Space Administration.

References


Y. Wang and T. Zeng, School of Earth and Atmospheric Science, Georgia Institute of Technology, Atlanta, GA 30332, USA. (ywang@eas.gatech.edu)

K. Chance, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA.

E. V. Browell, Atmospheric Sciences, NASA Langley Research Center, Hampton, VA 23681, USA.

E. L. Atlas and B. A. Ridley, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307, USA.