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

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[1] Springtime near-surface ozone depletion has been observed at northern high latitudes. Due to limited observations, the spatial and temporal extent of low $O_3$ concentrations near the surface is still unknown. A regional 3-D chemistry and transport model is applied to simulate surface $O_3$ 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 $O_3$ depletion events observed at two surface sites, Alert, Canada (82.5°N, 62.3°W) and Barrow, Alaska (71.3°N, 156.6°W), and by airborne in situ and DIAL instrument during the TOPSE experiments at northern high latitudes. Low $O_3$ events at Alert appear to be mostly driven by transport of $O_3$-poor air from high BrO regions. Model results indicate that low $O_3$ concentrations (<20 ppbv) near the surface cover ~60% of the northern high latitudes and that the depleted $O_3$ 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 $O_3$ concentrations (0–20 ppbv) near the surface [*Bottenheim et al.*, 1986; *Tarasick and Bottenheim*, 2002]. Low ozone events have also been found at Ny-Ålesund, Norway [*Solberg et al.*, 1996]. Surface $O_3$ measurements at Barrow, Alaska [*Oltmans and Levy*, 1994] are probably the longest continuous record with frequent low $O_3$ 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 $O_3$ air masses. In spring 2000, near-surface $O_3$ 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 $O_3$ loss is thought to be catalyzed by $BrO_x$ (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 $BrO_x$ level [*Fan and Jacob*, 1992; *McConnell et al.*, 1992; *Tang and McConnell*, 1996]. The chemical cycling of $BrO_x$ has been investigated using box models [*Tang and McConell*, 1996; *Sander et al.*, 1997; *Michalowski et al.*, 2000; *Evans et al.*, 2003]. However, the spatial and temporal distribution of near-surface low $O_3$ 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 $O_3$ concentrations at northern high latitudes in March and April 2000. Bromine catalyzed $O_3$ 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 $O_3$ 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 $O_3$ concentrations are available at Alert and Barrow. After evaluating the model simulations of low $O_3$ concentrations with the observations, we infer the spatial and temporal extent of the near-surface $O_3$ loss from the model results.

[5] The rate limiting step in bromine catalyzed $O_3$ loss is usually $BrO + BrO \rightarrow Br_2 + O_2$; under very low $O_3$ concen-

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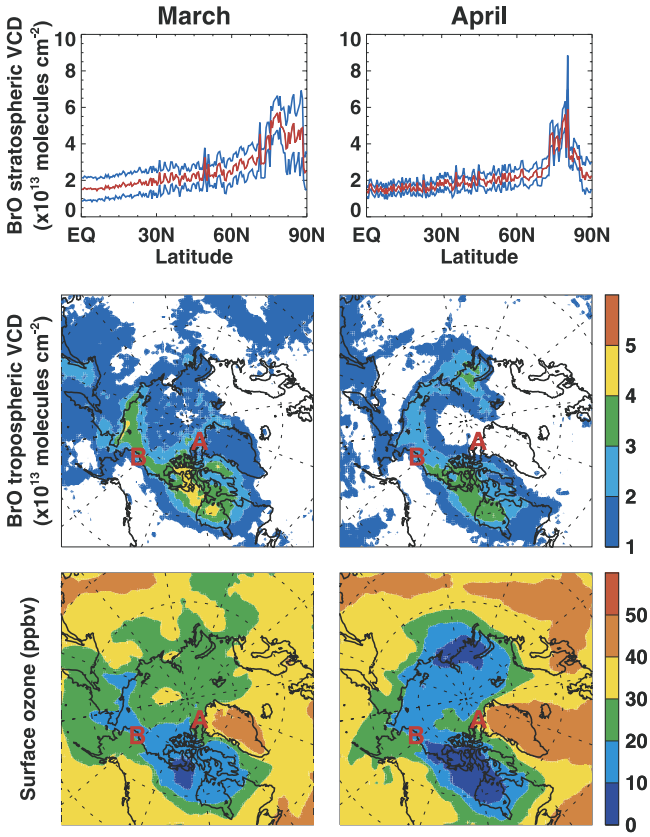


**Figure 1.** GOME BrO VCD and simulated near-surface $O_3$ concentrations in March and April, 2000. Upper: Daily stratospheric BrO VCD. Mean values are shown by the red lines. The values for mean ± the standard deviation are shown by the blue lines. Middle: Monthly mean tropospheric BrO VCD (at a thickness of 400 m, a column concentration of $1 \times 10^{13}$ 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°N, 62.3°W) (marked by "A") and Barrow, Alaska (71.3°N, 156.6°W) ("B"), are shown on the middle and bottom plots.

trations, the rate limiting step becomes $Br + O_3 \rightarrow BrO + O_2$ [*Haussmann and Platt*, 1994]. Once BrO concentrations are known, we can calculate Br concentrations by estimating the Br/BrO ratios (see Appendix) and compute the $O_3$ loss rates by bromine catalytic cycles. Therefore the key issue in the modeling is how to prescribe BrO concentrations.

[6] GOME provides nadir-viewing backscattered radiances over the spectral range 240–800 nm with a spatial resolution of $320 \times 40$ $km^2$ [*European Space Agency*, 1995]. Analyses of GOME spectra have shown high BrO concentrations at northern and southern high latitudes in spring [*Richter et al.*, 1998; *Chance*, 1998; *Wagner and Platt*, 1998]. The BrO slant column density (SCD) is obtained here from direct fitting to the radiance measurements [*Chance*, 1998]. Stratospheric [*Chance*, 1998] and tropospheric [*Wagner et al.*, 2001] air mass factors (AMFs) are applied to convert the SCD to vertical column density (VCD = SCD/AMF). Three-day BrO averages are mainly used in the present study. Five-day averages are used in the case of missing and highly biased data (in late March). The resulting daily 10th percentile column for each half-degree latitude band is used to determine the stratospheric column, the values of which are consistent with previous estimates [*Fitzenberger et al.*, 2000; *Wagner et al.*, 2001] (Figure 1). The tropospheric column is then computed by subtracting the stratospheric VCD from the total VCD and re-adjusting for the reduced tropospheric AMFs (Figure 1).

[7] A previous 3-D regional chemistry and transport model [*Mckeen et al.*, 1991] is updated with an efficient and accurate transport scheme [*Walcek*, 2000]. The model has a horizontal resolution of 80 km (Figure 1). There are 19 vertical layers in the terrain following σ-coordinate, of which eight are located in the lowest 1 km. The polar version of the Penn State/National Center for Atmospheric Research mesoscale model MM5 [*Cassano et al.*, 2001] is used to generate the meteorological fields. Four-dimensional data assimilation is conducted with the 6-hour National Center for Environmental Prediction reanalysis, rawinsonde and surface observations. The initial and boundary conditions of $O_3$ concentrations, as well as $O_3$ production and loss tendencies by $O_3$-$NO_x$-hydrocarbon chemistry, are taken from the spring-2000 simulation of the global 3-D chemistry and transport model, GEOS-CHEM [*Bey et al.*, 2001].

[8] The vertical distribution of BrO concentrations in the lower troposphere is unknown. Ozonesonde observations in this period show that the ozone loss mainly occurred below 500 m [*Tarasick and Bottenheim*, 2002]. We assume that BrO is evenly distributed in the lower troposphere and conduct 5 test simulations by specifying the BrO-layer thickness as 300 m, 400 m, 500 m, 1 km, and the boundary layer height simulated by MM5, respectively. We find that a thickness of 400 m gives the best comparison of model results with the observed $O_3$ concentrations at Alert and Barrow. The chosen thickness is consistent with previous studies [*Leaitch et al.*, 1994; *Michalowski et al.*, 2000].

## 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.

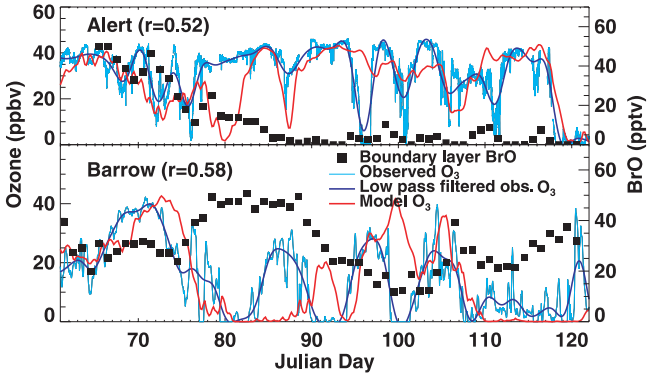


**Figure 2.** Near-surface BrO concentrations derived from GOME columns and observed and simulated $O_3$ concentrations at Alert, Canada, and Barrow, Alaska in March and April, 2000. Three-day low pass filtered $O_3$ observations are also shown. The frequency of $O_3$ data at Alert is every 5 min.; it is hourly at Barrow. The correlation coefficients are calculated using 4-hour averages.

[11] To further investigate the dependency of $O_3$ 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 $O_3$ depletion events. Both sites are strongly affected by transport of $O_3$-depleted air since they are located on the edges of high BrO regions (Figure 1). The $O_3$ depletion at Alert near the end of April exemplifies the transport effect. Our results suggest that transport of $O_3$-poor air from areas with persistent high-BrO concentrations contributes significantly to the low $O_3$ episodes in the observations.

[12] The model results cannot be reliably evaluated using ozonesonde measurements due to the low frequency of the

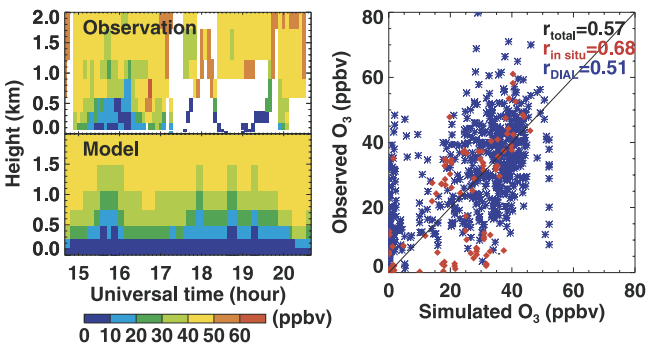


**Figure 3.** Model comparisons with TOPSE observations. (Left): TOPSE DIAL and in situ ozone concentrations for flight 29 (April 10, 2000), and the corresponding model simulation along the flight track. Area covered by clouds could not be measured by DIAL. (Right): DIAL and in situ $O_3$ measurements at 0–500 m above the surface for all TOPSE flights in March and April and the corresponding model results. Simulated and observed data points are 5-min averages. DIAL measurements below 1 km are reported at 14, 36, 72, 181, 365, 590, and 900 m.

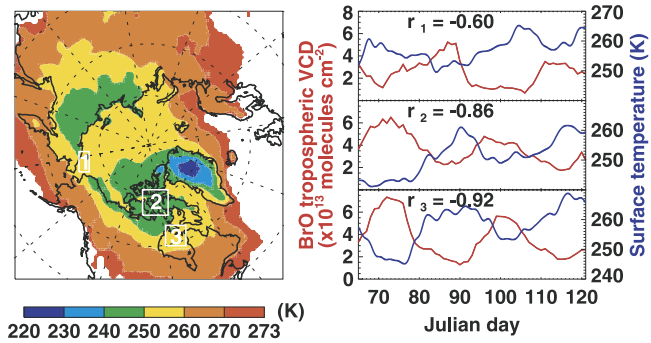


**Figure 4.** Correlation of BrO concentrations with surface temperature. Left: Monthly mean surface temperature (K) for March simulated in MM5. Three regions, (1) southern Chukchi Sea, (2) Canadian archipelago, and (3) northern Hudson Bay, have BrO concentrations >40 pptv. Right: GOME derived BrO tropospheric VCD and MM5 simulated surface air temperature in the three regions. The correlation coefficients are calculated using daily averages.

observations. During the TOPSE experiments, both in situ and DIAL measurements showed episodically large regions of lower tropospheric $O_3$ 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 $O_3$ 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 $O_3$ concentrations and corresponding model results below 500 m for all available TOPSE measurements in March and April. The correlation coefficients between observed and simulated $O_3$ 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 $O_3$ 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 $O_3$ depletions in the Arctic are large-scale persistent events.

[13] 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. The low temperature and high BrO regions (Figure 1) overlap. The low temperature in Greenland is due to its elevation. We examine three regions with high BrO concentrations (>40 pptv) and find a strong anti-correlation between GOME BrO tropospheric column and MM5 simulated surface temperature. Regions 2 and 3 are similar, showing a correlation coefficient of about −0.9. The anti-correlation in region 1 is weaker with a coefficient at −0.6. The BrO tropospheric column is also lower in this region than the other two. There is a 180° phase lag between region 1 and regions 2 and 3, indicating that the migration

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].

[14] GOME observations of BrO column were used in a regional 3-D chemistry and transport model to simulate bromine catalyzed near-surface $O_3$ loss in March and April 2000. Despite the relatively low temporal and spatial resolution of the BrO observations, the model captures reasonably well the $O_3$ depletion events observed during TOPSE and at two surface sites. Model results indicate widespread persistent regions of lower tropospheric $O_3$ depletion due to $O_3$ loss catalyzed by high BrO concentrations and transport of the resulting $O_3$-poor air. High BrO events last 1–2 weeks and occur in low temperature episodes.

## Appendix

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

$$\frac{[\mathrm{BrO}]}{[\mathrm{Br}]} = \frac{k_{\mathrm{Br+O_3}}[\mathrm{O_3}]}{2k_{\mathrm{BrO+BrO}}[\mathrm{BrO}] + k_{\mathrm{BrO+ClO}}[\mathrm{ClO}] + k_{\mathrm{BrO+NO}}[\mathrm{NO}] + J_{\mathrm{BrO}}}$$

Nitric oxide (NO) concentrations from TOPSE are averaged according to the different $O_3$ 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 ($J_{\mathrm{BrO}}$) is specified to be $4.51 \times 10^{-2}$ 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-$O_3$ reactions [*Haussmann and Platt*, 1994].

[16] **Acknowledgments.** We thank Kurt Anlauf for providing the surface $O_3$ data at Alert and Louisa Emmons 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.

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