

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

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Abstract. 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 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 depletion events observed at two surface sites, Alert, Canada (82.5N, 62.3W) and Barrow, Alaska (71.3N, 156.6W), and by airborne in situ and DIAL instrument during the TOPSE experiments at northern high latitudes. Low O₃ events at Alert appear to be mostly driven by transport of O₃-poor air from high BrO regions. 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.

Introduction

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-Ålesund, 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 [Leitch 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].

The O₃ loss is thought to be catalyzed by BrO_x (Br + BrO) [Barrie et al., 1988; Hausmann 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 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.

Methodology

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.

The rate limiting step in bromine catalyzed O₃ loss is usually $\text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2$; under very low O₃ concentrations, the rate limiting step becomes $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$ [*Hausmann and Platt, 1994*]. Once BrO concentrations are known, we can calculate Br concentrations by estimating the Br/BrO ratios (see Appendix) and compute the O₃ loss rates by bromine catalytic cycles. Therefore the key issue in the modeling is how to prescribe BrO concentrations.

GOME provides nadir-viewing backscattered radiances over the spectral range 240-800 nm with a spatial resolution of 320x40km² [*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] (Fig. 1). The tropospheric column is then computed by subtracting the stratospheric VCD from the total VCD and re-adjusting for the reduced tropospheric AMFs (Fig. 1).

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 80km (Fig. 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 O₃ concentrations, as well as O₃ production and loss tendencies by O₃-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].

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 500m [*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 300m, 400m, 500m, 1km, and the boundary layer height simulated by MM5, respectively. We find that a thickness of 400m gives the best comparison of model results with the observed O₃ concentrations at Alert and Barrow.

The chosen thickness is consistent with previous studies [*Leitch et al.*, 1994; *Michalowski et al.*, 2000].

Results and Discussion

Figure 1 shows the model simulated monthly mean O₃ 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 O₃ concentrations. Despite lower BrO loading, more severe O₃ depletion is simulated in April than in March due to longer daylight.

The model captures some important features of the surface O₃ variations, including some O₃ depletion events, observed at Alert and Barrow (Fig. 2). Three-day low pass filtered O₃ measurements are also shown since GOME BrO measurements used in the model are 3-5 day averages. The correlation coefficients between observed and simulated O₃ 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 O₃ variations at Barrow. The better simulation at Barrow than Alert is due in part to fewer high-frequency O₃ 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 O₃ depletion events observed at these sites are largely part of the large-scale persistent O₃ depletion features in the Arctic spring.

To further investigate the dependency of O₃ 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 >20pptv BrO, the model slightly underestimates the ozone loss but still captures the same O₃ depletion events. Both sites are strongly affected by transport of O₃-depleted air since they are located on the edges of high BrO regions (Fig. 1). The O₃ depletion at Alert near the end of April exemplifies the transport effect. Our results suggest that transport of O₃-poor air from areas with persistent high-BrO concentrations contributes significantly to the low O₃ 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 O₃ 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 O₃ measurements of flight 29 (April, 10) 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 O₃ concentrations and corresponding model results below 500m for all available TOPSE measurements in March and April. The correlation coefficients between observed and simulated O₃ concentrations are 0.51 and 0.67 for DIAL and in situ measurements, respectively. It is unclear why the correlation coefficient is higher for the in situ

measurements. Including data at 500m-1km improves the correlation coefficients due to the addition of higher O₃ 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 O₃ 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. The low temperature and high BrO regions (Fig. 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*].

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,

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

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 (J_{BrO}) is specified to be $4.51 \times 10^{-2} \text{ s}^{-1}$ [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 [Hausmann and Platt, 1994].

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Figure captions

Figure 1. GOME BrO VCD and simulated near-surface O₃ 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 400m, a column concentration of 1×10^{13} molecule cm⁻² is equivalent to a mixing ratio of 10pptv). Bottom: Simulated monthly near-surface O₃ concentration. The locations of the two surface sites, Alert, Canada (82.5N, 62.3W) (marked by “A”) and Barrow, Alaska (71.3N, 156.6W) (“B”), are shown on the middle and bottom plots.

Figure 2. Near-surface BrO concentrations derived from GOME columns and observed and simulated O₃ concentrations at Alert, Canada, and Barrow, Alaska in March and April, 2000. Three-day low pass filtered O₃ observations are also shown. The frequency of O₃ data at Alert is every 5 min.; it is hourly at Barrow. The correlation coefficients are calculated using 4-hour averages.

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 O₃ 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.

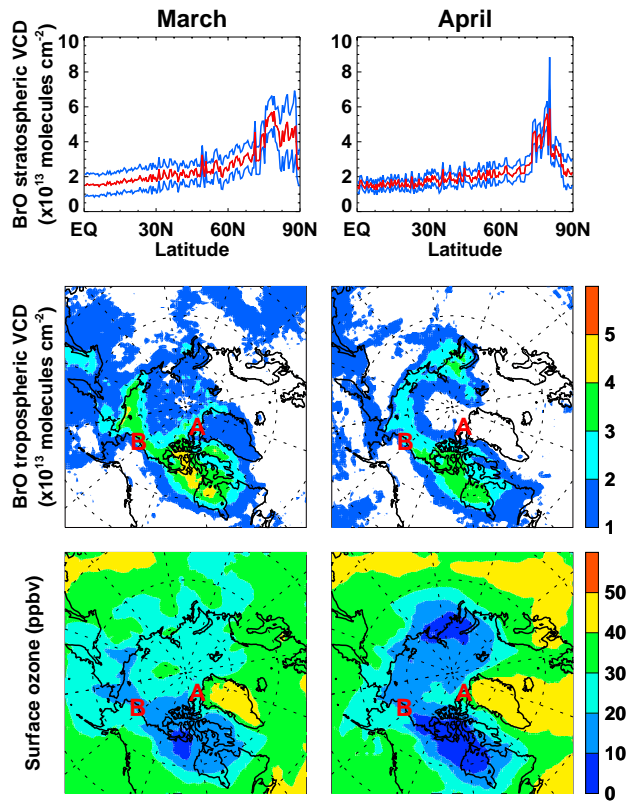


Figure 1

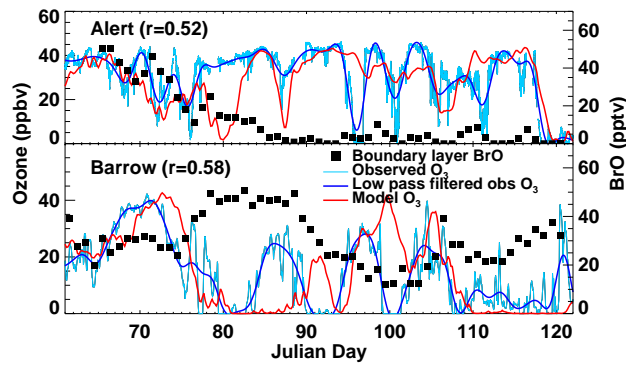


Figure 2

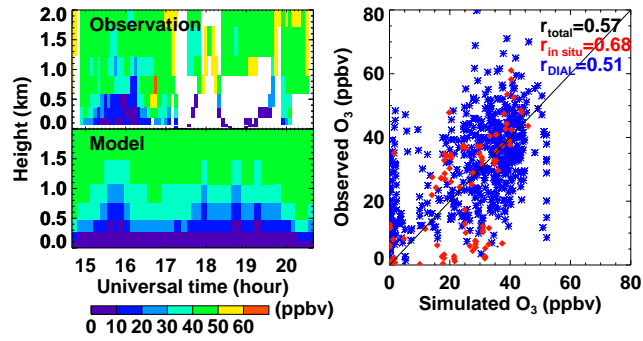


Figure 3

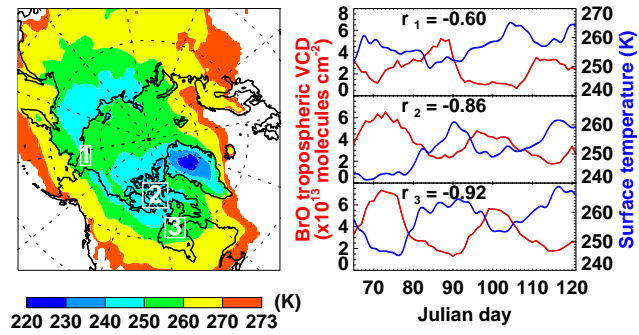


Figure 4