



A three-dimensional model study on the production of BrO and Arctic boundary layer ozone depletion

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Received 19 June 2008; revised 17 September 2008; accepted 22 October 2008; published 27 December 2008.

[1] A three-dimensional model (GEM-AQ/Arctic) was developed to study the chemistry and processes involved in the ozone depletion events (ODEs) in the Arctic boundary layer (ABL), which included a comprehensive mechanism of multiphase halogen chemistry in the ABL and our current understanding of the ODEs. Assuming that frost flower-derived aerosols were the primary halogen source, the areas potentially covered by frost flowers were determined. The carbonate precipitation scheme was taken into account for triggering the bromine explosions in the model. A comparison of the simulations with GOME satellite measurements in springs of 2000 and 2001 showed that the spatial structure and temporal evolution of tropospheric BrO clouds were well predicted by the model. The majority of the springtime ODEs observed at three arctic stations was reasonably reproduced. An analysis on the model results indicated that most periods of simulated ozone depletion ($O_3 < 1 \text{ nmol mol}^{-1}$) occurred in a layer 300 to 400 m deep at the Arctic sites. It is found that the halogen chemistry in the marine boundary layer (MBL) contributed substantially to the spring time ODEs, but atmospheric temperature and circulations as well as the transported air pollution in the ABL were also responsible for the ODEs. For springs of 2000 and 2001, two source regions with low surface O_3 levels were identified: the Siberian/Beaufort Arctic and the Canadian Arctic, broadly corresponding to areas of enhanced BrO levels and accompanied by the Arctic anticyclones. Dominant trans-Arctic transport pathways were also investigated for the ODEs at Alert, Barrow and Zeppelinfjellet.

Citation: Zhao, T. L., S. L. Gong, J. W. Bottenheim, J. C. McConnell, R. Sander, L. Kaleschke, A. Richter, A. Kerkweg, K. Toyota, and L. A. Barrie (2008), A three-dimensional model study on the production of BrO and Arctic boundary layer ozone depletion, *J. Geophys. Res.*, 113, D24304, doi:10.1029/2008JD010631.

1. Introduction

[2] The Arctic boundary layer (ABL) ozone depletion events (ODEs) in spring were first discovered in the 1980s, when it was observed that the surface ozone levels dropped from around 40 nmol mol^{-1} to below 10 nmol mol^{-1} or even below detection limit at Alert ($82^\circ 27'N$, $62^\circ 31'W$) in Canada [Bottenheim *et al.*, 1986; Barrie *et al.*, 1989] and at Barrow ($71^\circ 19'N$, $156^\circ 36'W$) in Alaska [Oltmans, 1981; Oltmans and Komhyr, 1986]. Barrie *et al.* [1988] were the

first to propose a catalytic photochemical ozone destruction mechanism including reactive bromine based on a negative correlation between surface ozone and bromine compounds. In subsequent years, knowledge on ODEs has advanced through intensive field campaigns, laboratory and modeling studies [Barrie *et al.*, 1994; Simpson *et al.*, 2007b; von Glasow and Crutzen, 2007]. The ODEs are a common phenomenon in both the remote Arctic and Antarctic [Kreher *et al.*, 1996; Wessel *et al.*, 1998] occurring several times every spring [Wennberg, 1999; Tarasick and Bottenheim, 2002; Bottenheim and Chan, 2006]. Satellite measurements found that BrO clouds were widespread in spring throughout the Arctic and also the Antarctic [Richter *et al.*, 1998; Wagner *et al.*, 2001], presenting a major advancement in our capability to monitor bromine radicals and hence ODEs in the polar regions. It is now generally accepted that ODEs are largely the results of bromine-catalyzed reactions occurring in the multiphase [Foster *et al.*, 2001]. The key gas-phase reactions of halogen atoms involved in ozone depletion are summarized into three reaction cycles [Sander *et al.*, 1999; Platt and Hönninger 2003; von Glasow and Crutzen, 2007]. The reactive halogens for these three reaction cycles could be sustained by a reaction sequence in the aqueous aerosol phase [Fan and Jacob, 1992; Vogt *et al.*,

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1996]. Since the reaction sequence in the aqueous aerosol phase is acid-catalyzed, it has been a scientific puzzle how it is able to proceed in particles derived from alkaline sea water [Sander *et al.*, 2006]. On the basis of the acid-catalyzed aerosol-phase reactions, a special sequence of multiphase and photochemical reactions is thought to be the likely mechanism for the production of the majority of reactive halogens for ODEs. This sequence of the heterogeneous and photochemical reactions, as an autocatalytic reaction cycle leading to the exponential release of reactive bromine gas, often referred to as “bromine explosions”, can theoretically produce reactive halogen gases for ODEs by consuming halogen ions (Bromide and Chloride) and protons (acidity) [McConnell *et al.*, 1992; Tang and McConnell, 1996]. Ocean water, the source of the brine layer on top of new sea ice and aqueous aerosols, is strongly buffered with HCO_3^- to a pH of about 8.2 [Riley and Skirrow, 1965]. This pH may be too high to support bromine explosions due to the pH dependence of the key step of the heterogeneous reactions in the bromine explosion mechanism. The recent studies by Sander *et al.* [2006] proposed the precipitation process of calcium carbonate (CaCO_3) out of brine layer due to thermodynamic phase change to reduce the buffering capacity of residual brine. The pH of the residual brine can thus drop significantly by a relatively small amount of acid uptake. The carbonate precipitation is a crucial process for facilitating aerosol acidification and then triggering bromine explosions in aerosols [Sander *et al.*, 2006; Piot and von Glasow, 2008].

[3] Frost flowers growing on young sea ice may play an important role in sustaining the bromine explosion [Rankin *et al.*, 2002]. Frost flowers are intricate crystals that grow in the water vapor saturated air environment over open leads and polynyas in recently frozen sea ice where they may persist for several days and have very large surface areas. Upon freezing of salt water, brine pockets are expelled while being concentrated and therefore the top of young sea ice and the overlying frost flowers become highly concentrated in salt content. Although the precise mechanisms of their involvement as a reactive halogen source is still an active area of research, it is currently believed that frost flowers may directly act as a reactive halogen source with the degassing of halogens (e.g., as Br_2 and BrCl) to the atmosphere [Rankin *et al.*, 2002], or may produce frost flower-derived aerosol as a reactive halogen source. Aerosols produced from frost flowers will contain high concentrations of halogen ions, and thus could be the predominant surface on which heterogeneous reactions occur, undergoing halogen activation and releasing photolabile halogen species to the atmosphere [Fan and Jacob, 1992; McConnell *et al.*, 1992; Tang and McConnell, 1996; Sander *et al.*, 1997]. The measured surface area of frost flowers may be much less than assumed, which suggests a less important role as a direct bromine source [Domine *et al.*, 2005]. This does not exclude a role of frost flowers in bromine release and may in fact imply that more likely frost flowers are a source of aerosol bromine from which gas-phase bromine can be emitted through acid-catalyzed reactions in aerosol form [Kalnajs and Avallone, 2006]. An analysis of multiple satellite-derived data sets showed a correlation between the tropospheric BrO loading and the potential for frost flower occurrence diagnosed by atmospheric and sea ice conditions [Kaleschke *et al.*, 2004]. In this analysis, the

areas potentially covered by frost flowers, which were referred to as potential frost flowers (PFF), were calculated by using a thermodynamic model of frost flower formation based upon the combination of open water fraction, the regions that soon freeze over forming new ice, and the ambient air temperature. Using back-trajectories, Kaleschke *et al.* [2004] revealed that areas of PFF impacted air matched spatial patterns of satellite GOME derived enhanced vertical column densities (VCDs) of tropospheric BrO . This suggested a link between frost flowers as the activation site for reactive bromine compounds and subsequent depletion of ozone [Jacobi *et al.*, 2006], and young ice regions with PFF seem to be the source of bromine for ODEs. Furthermore, reactive halogen sources for ODEs have been recently argued with the potential importance of frost flowers, snow pack processes and first-year sea ice for ODEs [Simpson *et al.*, 2007b; von Glasow and Crutzen, 2007; Piot and von Glasow, 2008]. Snow pack processes including halogen recycling on snow could be an additional source of reactive halogens, as brine-derived aerosol particles or brine wicking contaminate snow with halogen ions which are then activated and emitted from snow to the air (e.g., as Br_2 and BrCl).

[4] Numerical models have been used to test and improve our understanding of the chemical mechanisms and processes involved in the ODEs and the consequences for the chemistry of the atmosphere. All exploratory modeling studies used box models or one-dimensional models. The box model of McConnell *et al.* [1992] focused on gas-phase chemistry and showed that heterogeneous cycling of bromine is key to maintain high gas-phase BrO concentrations without considering details about the heterogeneous processes. Fan and Jacob [1992] explicitly included heterogeneous reactions in their box model and found that known aqueous-phase reactions in aerosol particles are sufficient to convert HBr , HOBr , and BrONO_2 back into Br and BrO radicals. In their box model study, Tang and McConnell [1996] treated heterogeneous and aqueous phase reactions as pseudo second-order reactions and proposed the bromine to be released autocatalytically from the snowpack on Arctic sea ice. The box model study of Sander *et al.* [1997] included an explicit treatment of multiphase processes and reproduced the measured total inorganic Br by assumed emissions of already activated bromine. One-dimensional models focused on the vertical structure of ODEs [Gong *et al.*, 1997b; Lehrer *et al.*, 2004; Piot and von Glasow, 2008; Saiz-Lopez *et al.*, 2008] have also been developed. Three-dimensional models have so far only used very simple approaches regarding the chemical processes, such as estimating ozone destruction based on satellite-derived vertical BrO columns with no aqueous-phase chemistry considered [Zeng *et al.*, 2003]. In the studies of Zeng *et al.* [2003, 2006], BrO -concentrations were prescribed based on the BrO -VCDs from GOME. Bromine concentrations were calculated by estimating the Br/BrO ratios. The O_3 loss rates were computed by bromine reaction cycles to simulate the ODEs within a 3-D chemical transport model. Compared with the surface observations at Alert and Barrow, Zeng’s modeling captured most of the ODEs in spring 2000 with some discrepancies. A major limitation of all previous model studies on ODEs was the lack of direct quantification

of the reactive halogen sources or source regions for ODEs and the process of triggering the acidity-dependent bromine explosions.

[5] In this work, a global 3-D chemistry and transport model GEM-AQ/Arctic for studying the halogen chemistry and processes involved in the ABL ozone depletion has been developed, which includes the recent advances in our understanding of the mechanisms and processes of the ODEs. These new advances are (1) a comprehensive chemical mechanism of gas- and aerosol-phase reactions as well as heterogeneous processes for halogen chemistry [Sander et al., 2005], (2) the frost flower aerosols released from PFF-areas to air being the major source of reactive halogens [Kaleschke et al., 2004], (3) a parameterization for frost flower aerosol production based on the modified sea salt generation scheme [Gong et al., 1997a], and (4) the carbonate precipitation out of the brine layer for the acidification of the liquid phase by acid uptake triggering bromine explosions [Sander et al., 2006]. With the 3-D model, the potential importance of these mechanisms and processes was evaluated, and the understanding of chemical and physical processes for the ODEs was examined in this study.

2. Model Description and Setup

2.1. Global Environmental Multiscale Model With Air Quality Processes (GEM-AQ)

[6] The host meteorological model used in this study is the Global Environmental Multiscale (GEM) model developed by the Meteorological Service of Canada (MSC) for operational weather prediction [Côté et al., 1998]. GEM can be configured to simulate atmospheric processes from the global scale down to the meso-gamma scale. With the integration of a gas phase chemistry module (ADOM) [Venkatram et al., 1988] and an aerosol module (CAM) [Gong et al., 2003] into GEM, the Global Environmental Multiscale model with air quality processes (GEM-AQ) [Kaminski et al., 2008] was designed to provide a consistent framework between the meteorological and air quality aspects of the atmospheric system. The chemical and aerosol modules are included in the host meteorological model “online”, so that the chemical and aerosol species are advected at each dynamical time step and the meteorological information can be used in the chemical and physical process calculations. The standard emission data set used for global simulations was compiled using EDGAR2.0 [Olivier et al., 1996]. Transport of the chemically active tracers and aerosol species by the resolved circulation is realized by a semi-Lagrangian advection scheme native to the GEM. The vertical transfer of trace species due to subgrid-scale turbulence is parameterized using eddy diffusion calculated by GEM.

2.2. MECCA Module

[7] The chemical module MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) was implemented on-line within GEM-AQ/Arctic. MECCA [Sander et al., 2005] contains a comprehensive atmospheric reaction mechanism including (1) the basic O_3 , CH_4 , HO_x and NO_x chemistry; (2) non-methane hydrocarbon (NMHC) chemistry; (3) halogen (Cl, Br, I) chemistry; and (4) sulfur

chemistry. Not only gas-phase chemistry but also aqueous-phase chemistry and heterogeneous reactions in the marine boundary layer (MBL) are considered in the MECCA [Sander and Crutzen, 1996; Sander et al., 1999; von Glasow et al., 2002]. A detailed listing of reactions, rate coefficients, and their references can be found in the electronic supplement of MECCA [Sander et al., 2005]. On the basis of our research objectives, an arbitrary subset of the comprehensive mechanism of halogen chemistry in the MBL together with tropospheric chemistry from MECCA were selected to form a complete set of chemistry mechanisms that were applicable to not only the general tropospheric chemistry but also the ABL ozone depletion. The final chemistry mechanism from MECCA used in this modeling study was composed of the heterogeneous and photochemical reactions of halogen (Cl and Br) chemistry, which replaced the ADOM-chemical mechanism and solver [Venkatram et al., 1988] in GEM-AQ. Unchanged were, the transport schemes for diffusion and convection from GEM-AQ, the emissions from EDGAR2.0 [Olivier et al., 1996], and the dry deposition and wet scavenging for gas species from ADOM [Venkatram et al., 1988]. The dry and wet deposition of gaseous HBr, HOBr and Br₂ were parameterized by analogy to the deposition of HNO₃, SO₂ and O₃ in ADOM [Venkatram et al., 1988] respectively. The halogen aerosol species were removed along with the sea salt aerosols by dry and wet deposition given in CAM [Gong et al., 2003]. In GEM-AQ/Arctic the precipitation process of calcium carbonate (CaCO₃) was introduced for frost flower aerosol acidification and the acidity-dependent bromine explosions by adjusting the HCO₃⁻ concentration in the chemical module [Sander et al., 2006; Dieckmann et al., 2008]. On the basis of the study of Richardson [1976], the removal rate of calcium carbonate due to CaCO₃ precipitation was calculated with the fitting function of air temperatures, which were online modeled from GEM.

2.3. Frost Flower Aerosol Emission Scheme

[8] It was assumed that particles released from liquid brine layers present on frost flowers constitute frost flower aerosols [Piot and von Glasow, 2008], a type of sea salt aerosols but with very high concentrations of halogen ions. On the basis of laboratory simulations, halides are concentrated in the surface brine layer by a factor of 11 for Cl⁻ and 38 for Br⁻ compared to seawater [Koop et al., 2000]. These numbers for Cl⁻ and Br⁻ of frost flower aerosols were adopted in GEM-AQ/Arctic. The amount of Br⁻ in sea salt aerosols from open oceans is too small to account for the BrO- and Br⁻ measurements during ODEs [Lehrer et al., 1997; von Glasow and Crutzen, 2007]. Therefore, in this study of Arctic halogen chemistry for ODEs, frost flower aerosols were assumed to be the source of reactive halogens.

[9] The frost flower coverage over the frozen Arctic Ocean as the PFF was calculated by using a thermodynamic model of frost flower formation based upon the combination of open water fraction, the regions that soon freeze over forming new ice, and the ambient air temperature [Kaleschke et al., 2004]. With this model, the global daily fractional coverage of frost flowers by $0.5^\circ \times 0.5^\circ$ was preprocessed from satellite-derived sea-ice fraction maps (from SSM/I passive microwave images) and NCEP-reanal-

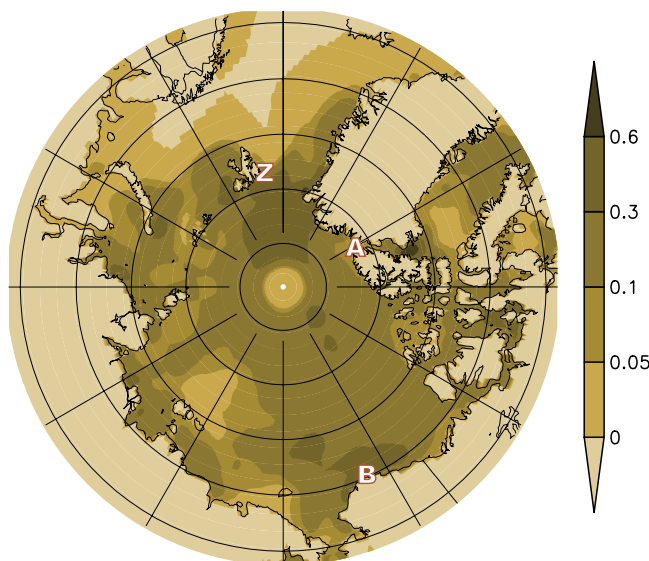


Figure 1. Averaged coverage (%) of potential frost flower (PFF) in springs (March, April and May) for 2000 and 2001. A, B and Z stand for the locations of three Arctic sites Alert, Barrow and Zeppelinfjellet, respectively.

ysis surface air temperatures. Figure 1 shows the mean coverage of PFF in the Arctic region for the two spring periods of 2000 and 2001. Considering a typical lifetime of frost flowers of up to five days [Kaleschke and Heygster, 2005], the PFF coverage for each day are obtained from the sum of PFF from the current day and the four previous days as the input-data for the daily fractional coverage of frost flowers in GEM-AQ/Arctic.

[10] The mechanism for the generation of frost flower aerosols is not known. As a first approximation, the parameterization for the productions of sea-salt aerosols from Gong *et al.* [1997a] was used in the scheme of frost flower aerosol emission. In the parameterization of Gong *et al.* [1997a], the source of sea-salt aerosols to the atmosphere is the open ocean under high wind speed conditions, so the emissions are proportional to the wind speed at 10 m to the power of 3.41 [Gong *et al.*, 1997a; Gong, 2003]. Mahowald *et al.* [2006] included a source of sea-salt aerosols (frost flower aerosols in this work) from new sea ice formation, as postulated by Kaleschke *et al.* [2004] in their modeling study. Except for the source of frost flower aerosols in the GEM-AQ/Arctic, their transport, scavenging and deposition were assumed to be identical to those for open ocean sea salt aerosols in the integrated aerosol module CAM, but with a proportionality factor to take into account the fractional coverage of frost flowers derived from the PFF areas. Furthermore, a scaling factor was estimated in the expression for the frost flower aerosol production from the best match to the measured Arctic atmospheric bromine loadings [Piot and von Glasow, 2008]. To give the best scaling factor for the production scheme of frost flower aerosols in GEM-AQ/Arctic, We also compared the atmospheric loadings of BrO simulation with the daily BrO-tropospheric VCD measured by GOME. The best representation was obtained by the addition of 10 to the wind speed for the frost flower aerosol emission in GEM-AQ/Arctic.

2.4. Simulation Setup

[11] The GEM-AQ/Arctic used in the current study was configured with 28 hybrid vertical levels with the model top at 10 hPa. Physical parameterizations employed in the model followed those presented by Mailhot *et al.* [2006]. The horizontal model grid was configured as global uniform resolution of 2 by 2 degrees with an integration time step of 15 minutes for dynamics, physics and air quality processes. Meteorological initial conditions were taken from the Canadian Meteorological Centre (CMC) global assimilation system [Gauthier *et al.*, 2007; Laroche *et al.*, 2007]. GEM-AQ/Arctic was run with the fully nudged meteorology of CMC-reanalysis every 24 hours. This setup resulted in the meteorological fields with 24-hour forecast segments starting from the reanalysis meteorology. Initial chemical conditions were generated by GEM-AQ running in the same global uniform configuration [Kaminski *et al.*, 2008].

[12] Observed depths of ODEs can extend from the surface to several hundred meters [Anlauf *et al.*, 1994; Gong *et al.*, 1997b; Tarasick and Bottenheim, 2002]. Zeng *et al.* [2006] found that the thickness of ODEs with 300 m yielded the best comparison of model results with surface ozone observations at Alert and Barrow and aircraft ozone vertical profiles measured during the TOPSE (Tropospheric Ozone Production about the Spring Equinox) experiment from February to May in 2000. In GEM-AQ/Arctic, therefore the aerosol-phase reactions of halogen chemistry in the ABL were set to occur in a 300 m deep surface layer for modeling of ODEs. Without this setting for the thickness of ODEs, the model runs lead to unrealistic O₃ background and vertical structure in the Arctic lower troposphere, possibly because the simulated boundary layer could not be rigid enough to prevent unwanted emanation of halogens and frost flowers to the free troposphere. Furthermore, the liquid water content in sea salt particles was calculated for frost flower aerosols on-line from the integrated aerosol module CAM [Gong *et al.*, 2003]. The inclusion of aerosol phase chemistry could lead to a very stiff set of ordinary differential equations in the reaction solver with decreasing liquid water content. For this reason the halogen chemistry calculations in the aerosol phase were applied with a limited range for the liquid water content of frost flower aerosol exceeding 10⁻¹² m³ (aq)/m³ (air) in the modeling [Kerkweg *et al.*, 2007].

[13] The GEM-AQ/Arctic simulations were conducted for 4 months from 1 February to 31 May 2000 and 2001, respectively. The results reported in this paper were obtained with one month of spin-up runs in February for each year. The last three months of modeling results during March, April and May were used in this study to compare with the chemical measurements in springs of 2000 and 2001 and to investigate the ODEs and springtime ABL halogen chemistry. For the sensitivity runs without halogen chemistry, the GEM-AQ/Arctic was run in the same configuration but with switching off multiphase halogen chemistry in the MBL.

[14] The primary objective of this 3-D modeling study was to examine our current understanding of the chemical and physical processes for ODEs, and to characterize the spatial structures and temporal variations of ODEs taking advantage of a 3-D modeling framework. In the following section, the simulation results on halogen chemistry of springtime ABL ozone depletion in 2000 and 2001 are presented with a comparison with the observations of

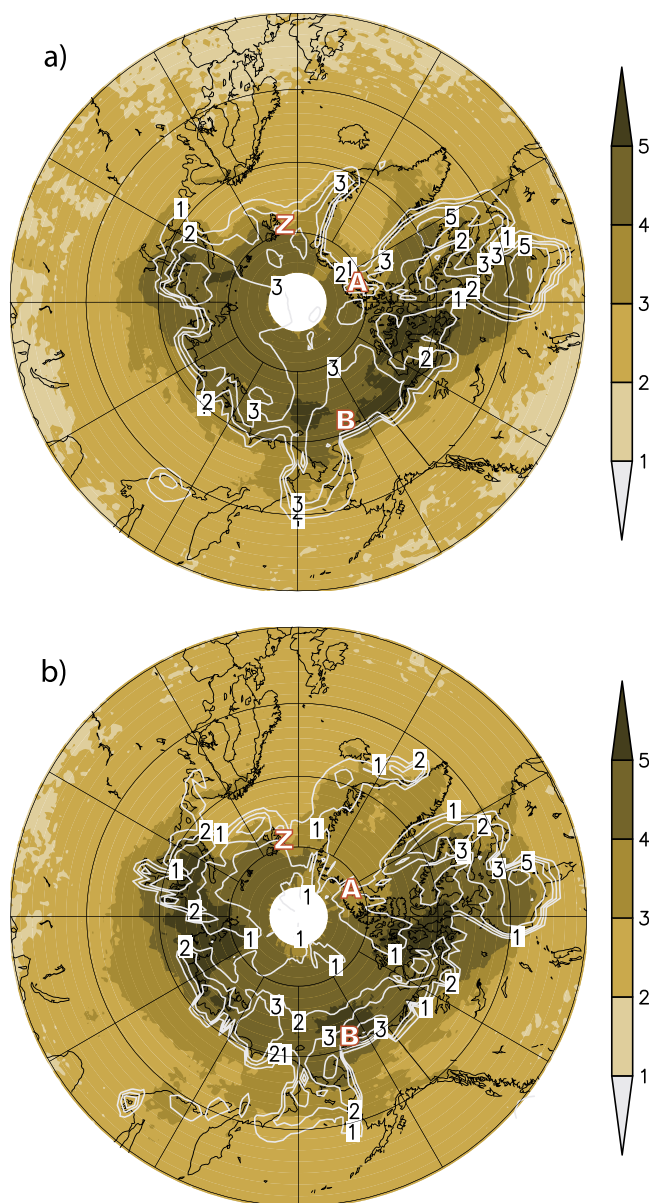


Figure 2. Comparisons of BrO-tropospheric VCD ($\times 10^{13}$ molecules/cm²) simulated by GEM-AQ/Arctic (contour lines) and measured by GOME (filled contours) averaged in springs of (a) 2000 and (b) 2001.

surface ozone and tropospheric BrO loading. Finally, the distributions and transport patterns of Arctic ozone and BrO associated with the springtime ODEs are investigated.

3. Simulation Results and Discussion

3.1. Comparison With Surface and GOME Observations

[15] Satellite measurements of BrO from the Global Ozone Monitoring Experiment (GOME) enable us to monitor the spatial and temporal BrO coverage in polar regions. The daily GOME tropospheric BrO data of version 1 were used for the tropospheric BrO columns [Richter *et al.*, 1998, 2002]. The modeled BrO-concentrations below 10 km were integrated to produce a tropospheric BrO column loading

from the GEM-AQ/Arctic simulations. There are many days with incomplete or missing measurement data of GOME BrO-VCDs, which prevents from a detailed daily comparison. Therefore 45 days with more complete GOME-measurements between 1 March and 31 May for 2000 and 2001 were selected to estimate the spring mean of tropospheric BrO loading and compared with the corresponding GEM-AQ/Arctic simulations in Figure 2. On the basis of the two-spring-mean of Figure 2, the correlation coefficient between the BrO VCD within the Arctic Circle from the GEM-AQ/Arctic simulation and the GOME measurement reached 0.6728. Generally, a good agreement was achieved between the GEM-AQ/Arctic modeling and the GOME-measurements for both the spatial distributions and temporal variations of tropospheric BrO column loading (Figure 2).

[16] Surface daily averaged O₃ data were obtained from three sites in the Arctic [Bottenheim and Chan, 2006]: Alert (82°27'N, 62°31'W), Canada; Barrow (71°19'N, 156°36'W), United States and Zeppelinfjellet (78°54'N, 11°53'E), Norway, to compare with the model predictions (Figure 3). There are two cases of predictions shown Figure 3: one with and one without multiphase halogen chemistry. It is evident that the modeling with halogen chemistry captured the majority of the springtime ODEs observed at each Arctic station with prominent O₃-depletions. The discrepancies that are apparent between modeling and observations are due to several factors including differences in the “real” and modeled meteorology, especially from the polar GEM-model assimilated wind fields, the spatial model resolutions of 2 by 2 degrees, complex topography and the assumed initial O₃-background with the limitation of multiphase chemical processes in the model. Another uncertainty in the model is the treatment of the unique boundary layer in polar regions. This is especially true in view of the dominant role played by the boundary layer in ODEs, especially in ozone recovery driven by the turbulent vertical mixing of free tropospheric ozone down to ground level [Gong *et al.*, 1997b; Zeng *et al.*, 2006].

3.2. Spatial Distributions and Time Series of Arctic O₃ and BrO

[17] Time series of the simulated vertical profile of O₃-mole fractions in Alert, Barrow and Zeppelinfjellet from 1 March to 31 May 2000 and 2001 are presented in Figure 4. The majority of the simulated ozone depletion episodes (O₃ < 1 nmol mol⁻¹) is in a layer 300 to 400 m deep agreed well with the vertical O₃-profile observed from the Polar Sunrise Experiment (PSE94) [Gong *et al.*, 1997b]. It is well known that the Arctic lower troposphere in the winter and spring is characterized by a strong, stable stratification [Raatz, 1992]. The 9 years of 10-day trajectory investigation by Bottenheim and Chan [2006] revealed that much of ozone depletion occurred in the boundary layer. Figures 5 and 6 present two-spring-averages of the near-surface O₃- and BrO- mole fractions over March, April and May 2000 and 2001 simulated by GEM-AQ/Arctic. It was found that large areas of low ozone (O₃ < 20 nmol mol⁻¹) covered most Arctic region, especially centered around two areas in the coastal regions of Eurasia and North America and spreading over the Arctic Ocean (Figure 5). This simulated near-surface O₃ distribution in the Arctic is consistent with that of the computed O₃ from prescribed BrO concentrations based on

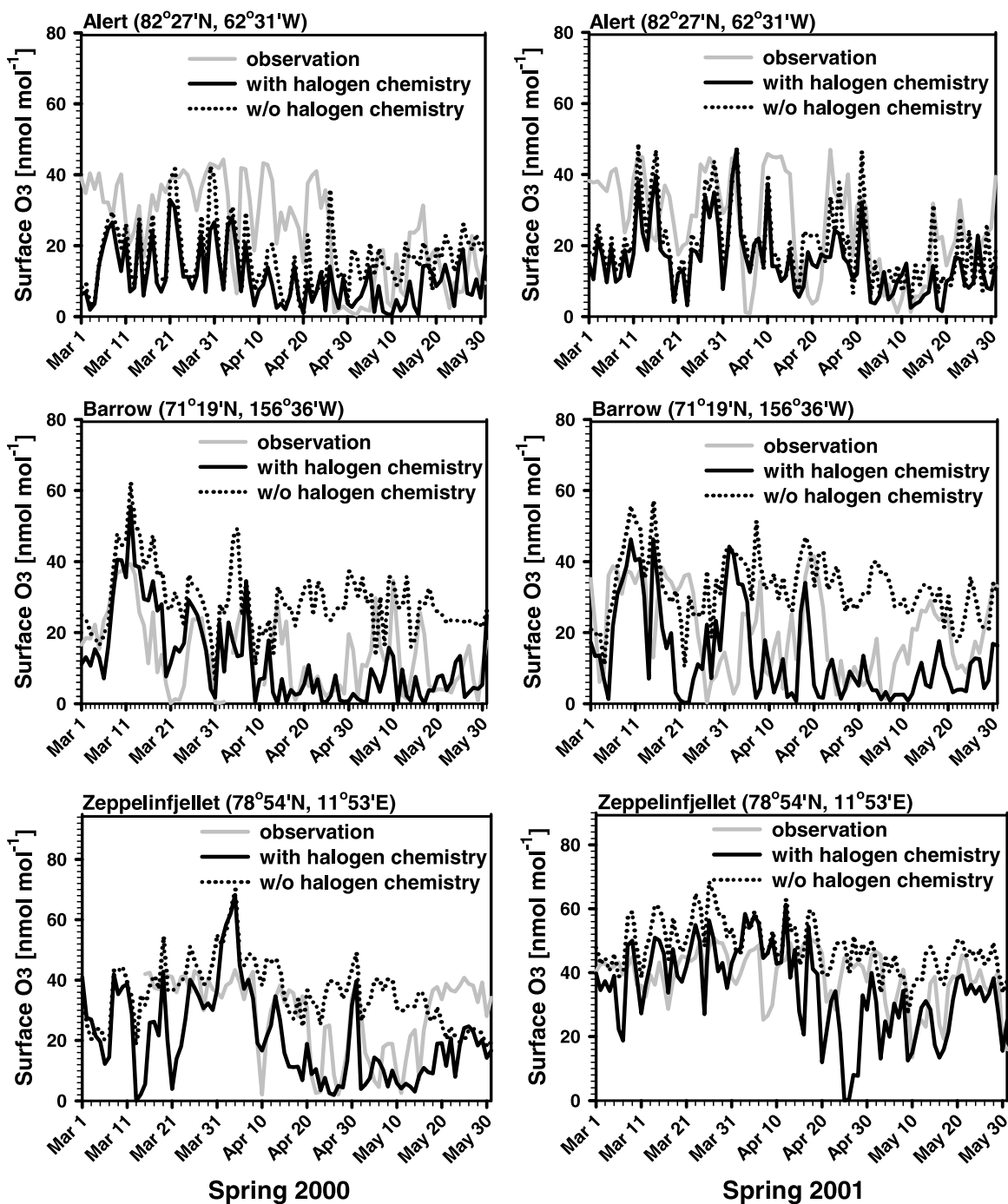


Figure 3. Comparisons of the observed and simulated daily near-surface O_3 -mole fractions at three Arctic sites from (left column) 1 March to 31 May 2000 and (right column) 1 March to 31 May 2001. The simulated near-surface O_3 -mole fractions were by GEM-AQ/Arctic with and without halogen chemistry, respectively.

the GOME-measurements [Zeng *et al.*, 2003]. BrO is regarded as an important indicator of Arctic ozone depletion chemistry. The mean of springtime simulation showed high BrO production near the surface of the Arctic Ocean with maximum values of BrO- mole fractions ranging from 5 to 10 pmol mol⁻¹ in the coastal regions (Figure 6), corresponding to the PFF coverage in spring (Figure 1). Enhanced BrO at the three Arctic observatories even reached levels of 30–50 pmol mol⁻¹ during ODEs in the ABL (Figure 8).

These values are comparable with surface BrO- measurements during the ALERT2000 Polar Sunrise Experiment [Hönninger and Platt, 2002]. It is generally accepted that Arctic ozone depletions are largely the result of bromine-catalyzed reactions occurring in the gas phase and sustained by heterogeneous reactions in the condensed phase [Foster *et al.*, 2001]. In Figure 6 the differences of O_3 -mole fractions simulated with and without halogen chemistry in the MBL could indicate halogen-driven ozone losses. In the

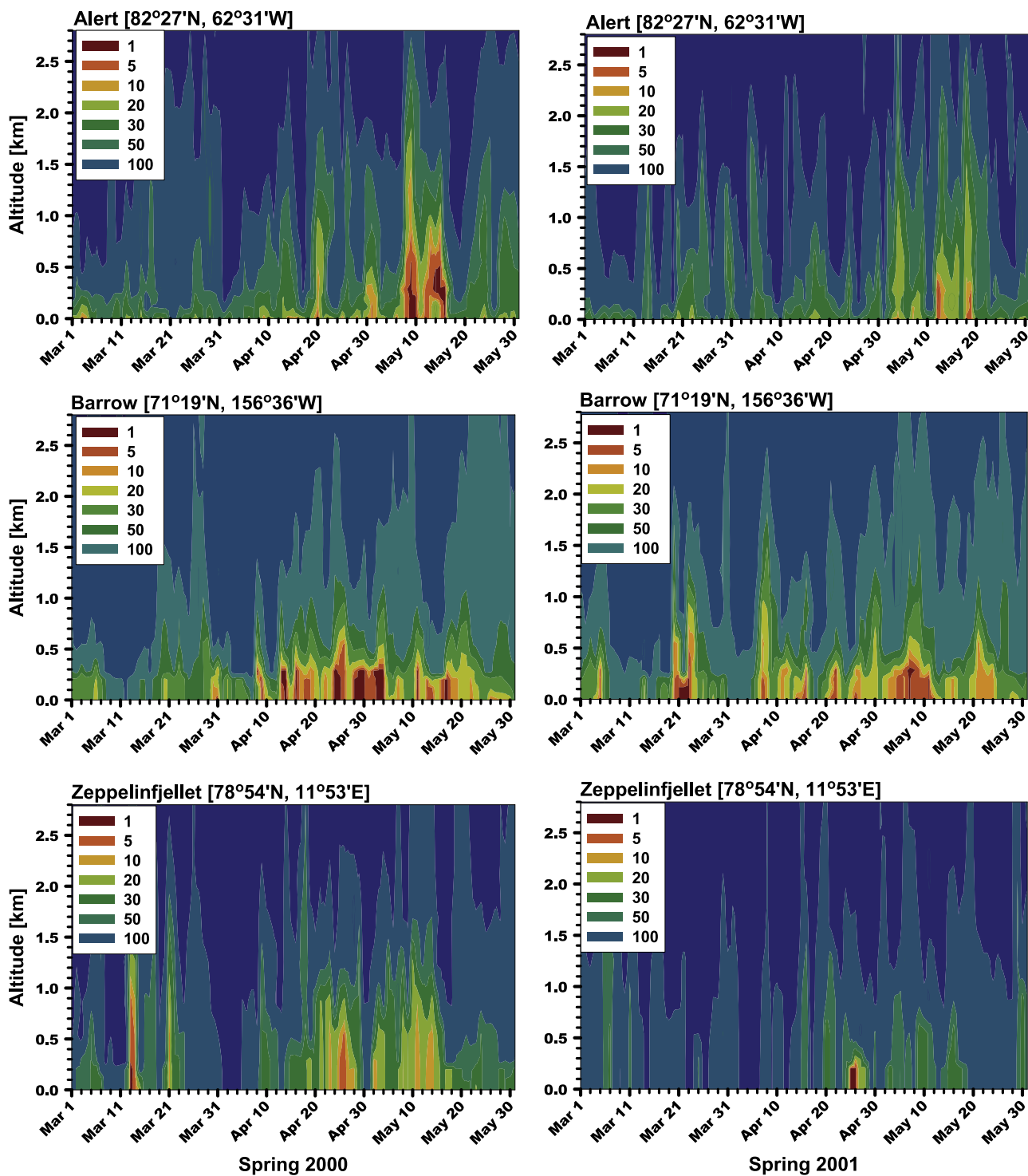


Figure 4. Time series of the vertical O_3 -profiles (nmol mol^{-1}) simulated by GEM-AQ/Arctic for three Arctic sites from (left column) 1 March to 31 May 2000 and (right column) 1 March to 31 May 2001.

model, the source of reactive halogens is from frost flower aerosols released mainly from coastal new-ice areas to the air. Halogen-driven ozone losses there spread over the Arctic with large amounts of O_3 removed ($\text{O}_3 < -14 \text{ nmol mol}^{-1}$) near the surface of the ocean in the spring mean (Figure 6). It can be concluded that halogen chemistry in the polar boundary layer made a great contribution to the simulated springtime ABL ozone depletion.

3.3. Mechanism for ABL Ozone Depletion

[18] As mentioned in the chemical module MECCA in the section 2.2, a complete set of the comprehensive mechanisms of halogen chemistry in the MBL together with tropospheric O_3 , CH_4 , HO_x , NO_x and non-methane hydrocarbon (NMHC) chemistry was implemented in the GEM-AQ/Arctic. To investigate the contribution of tropospheric non-halogen

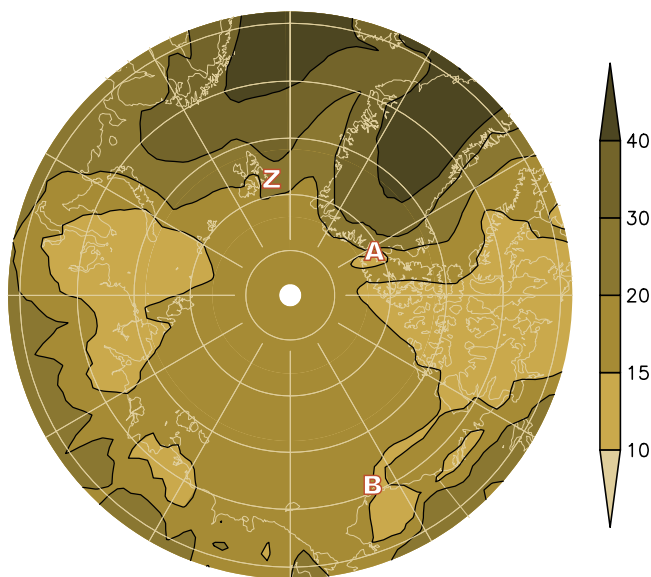


Figure 5. Averaged distribution of the simulated near-surface O_3 -mole fractions (nmol mol^{-1}) in springs (March, April and May) for 2000 and 2001.

(O_3 , CH_4 , HO_x , NO_x and NMHC) chemistry to the Arctic springtime ozone depletions, Figure 7 shows the simulated near-surface O_3 -mole fractions and air temperature in the Arctic averaged for springs of 2000 and 2001 without the halogen chemistry. It is clearly seen that overall low (high) ozone regions are collocated with low (high) air temperatures in most Arctic regions (Figure 7), confirming that chemical O_3 -production is positively correlated with air temperature based on tropospheric O_3 -chemistry [von Kuhlmann *et al.*,

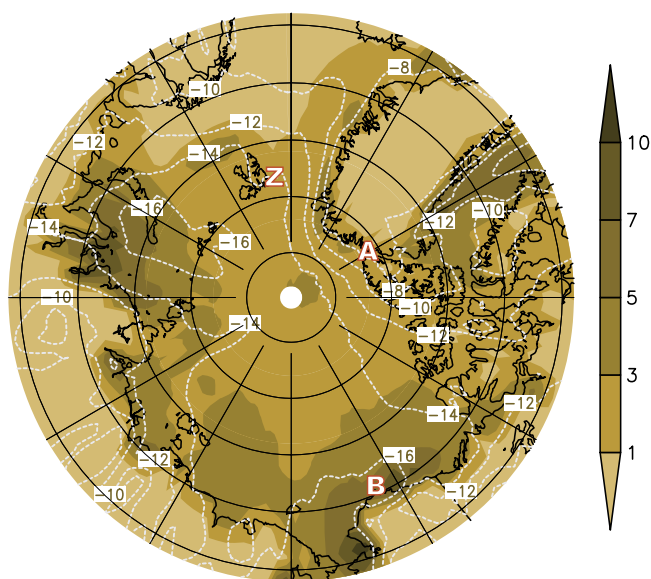


Figure 6. Averaged distributions of the near-surface BrO-mole fractions (pmol mol^{-1} , filled contours) and the differences of the near-surface O_3 -mole fractions (nmol mol^{-1} , contour lines) simulated by GEM-AQ/Arctic with and without halogen chemistry in springs (March, April and May) for 2000 and 2001.

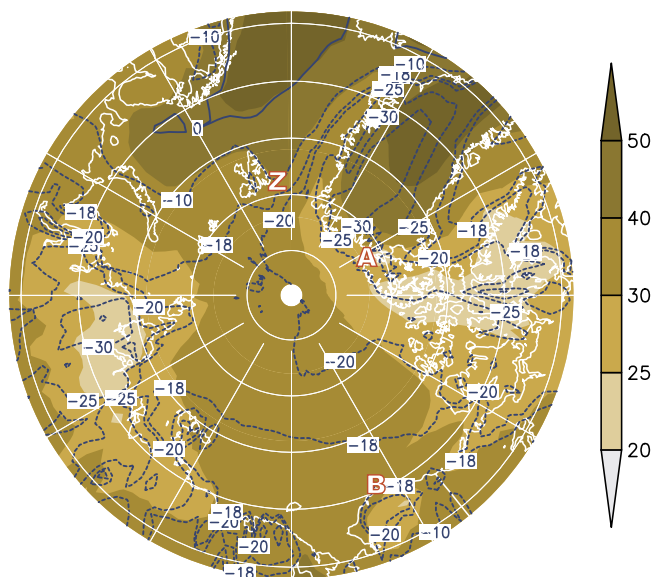


Figure 7. Averaged distributions of the near-surface O_3 -mole fractions (nmol mol^{-1} , filled contours) and air temperature ($^{\circ}\text{C}$, contour lines) simulated by GEM-AQ/Arctic without halogen chemistry in springs (March, April and May) for 2000 and 2001.

2003; Zeng *et al.*, 2008]. The climatology of springtime distributions of Arctic surface air temperature (Figure 7) is characterized with the cold regions in the interior of northern Russia and Canada caused by the continental conditions and the warm regions in the northeastern part of the Atlantic Ocean, exerting a significant influence on the near-surface O_3 distribution shown in Figure 7. Furthermore, the simulated near-surface O_3 -mole fractions in the Arctic are only correlated with nitrogen oxides and reactive hydrocarbons in tropospheric non-halogen chemistry (Figure 7). The Arctic nitrogen oxides and reactive hydrocarbons were mainly imported from polluted midlatitude regions. Air masses move from Eurasian midlatitude regions into the Arctic gyre due to the evolution of the Siberian high [Bottenheim *et al.*, 2004], and air pollution originating from North America, Asia and Europe can be transported into the Arctic along different pathways in spring [Klonecki *et al.*, 2003; Stohl, 2006]. The transport pathways to the Arctic are governed by both the zonal and meridional atmospheric circulation patterns between northern mid- and high-latitude regions [Worthy *et al.*, 1994; Huang *et al.*, 2007]. From the above discussion, the near-surface O_3 -distributions simulated with non-halogen chemistry in Figure 7 were therefore modulated by the air temperature, the atmospheric circulation and the associated air pollution transport in the Arctic region.

[19] The ABL O_3 distribution with halogen chemistry in Figure 5 can be decomposed into two parts: (1) the O_3 levels (Figure 7) modeled without halogen chemistry in the ABL and (2) the halogen-driven ozone losses (Figure 6). It can be revealed that not only halogen chemistry in the ABL but also air temperature, atmospheric circulation in the Arctic and the levels of the transported air pollution from the northern mid- and high-latitudes are all responsible for causing ABL ozone variations. From Figure 6, the differ-

Table 1. Regression Correlation Coefficients Between Daily Near-Surface O₃ Simulated by GEM-AQ/Arctic With and Without Multiphase Halogen Chemistry at Three Arctic Sites in Springs 2000 and 2001

	Alert	Barrow	Zeppelinfjellet
Spring 2000	0.82	0.66	0.67
Spring 2001	0.88	0.62	0.76

ences of spring mean O₃-mole fractions simulated with and without multiphase halogen chemistry were estimated to be about -8 , -14 and -16 ppbv for the halogen-driven ozone losses in Alert, Zeppelinfjellet and Barrow respectively. Nevertheless, it is surprising that remarkably high positive correlations between near-surface O₃ simulations with and without halogen chemistry were derived for the three Arctic sites especially at Alert in cold northern Canada (Table 1). These correlations could be explained by the occurrence of episodes in long-range transport of pollution and air mass change closely associated with Arctic air circulation, which

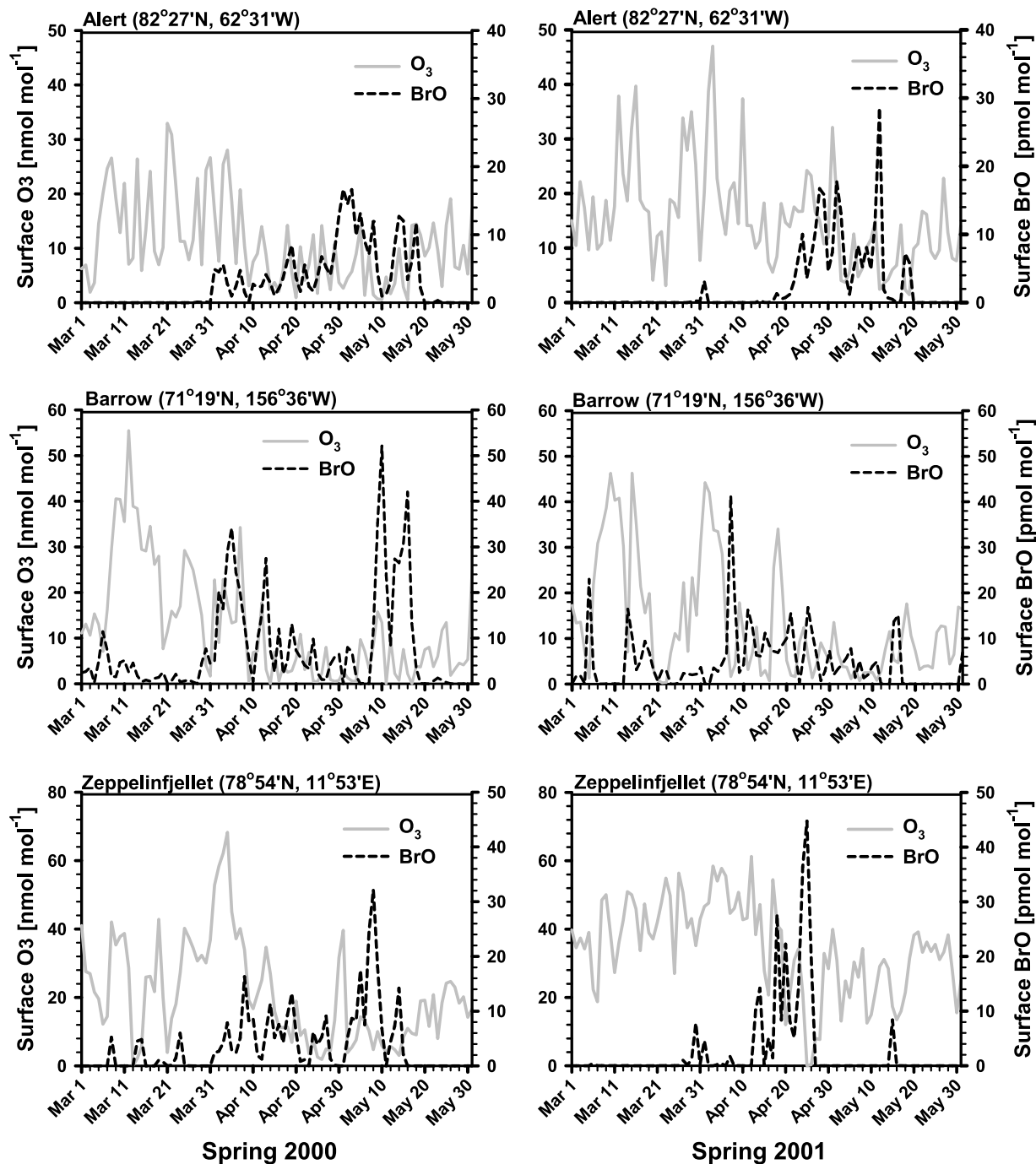


Figure 8. Daily time series of the simulated near-surface O₃- and BrO-mole fractions at three Arctic sites from (left column) 1 March to 31 May 2000 and (right column) 1 March to 31 May 2001.

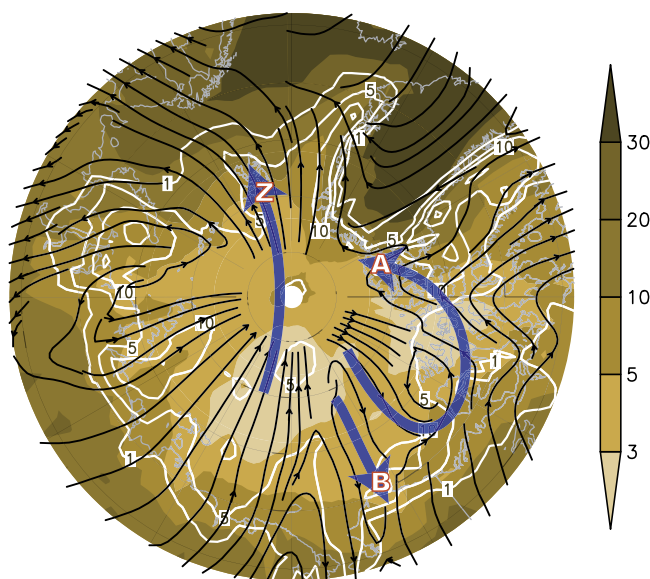


Figure 9. Averages of the modeled near-surface O_3 -mole fractions (nmol mol^{-1} , filled contours), BrO-mole fractions (pmol mol^{-1} , contour lines) and wind streamlines (black color) from 16 April to 15 May 2000. The thick lines with arrows stand for the transport pathways starting from the depleted O_3 source regions to Alert (A), Barrow (B) and Zeppelinfjellet (Z).

could play an important role in the periodicity of O_3 -concentration changes with the depletion and recovery in spring at these sites.

3.4. Sources and Transport Patterns of the ABL Ozone Depletion

[20] Figure 8 shows the daily time series of the simulated near-surface O_3 - and BrO-mole fractions at the three Arctic sites from 1 March to 31 May 2000 and 2001. As expected [Bottenheim et al., 1990; Morin et al., 2005], weak negative correlations between the near-surface O_3 - and BrO-mole fractions were found for Alert, Barrow and Zeppelinfjellet (Table 2), suggesting that local bromine-catalyzed reactions are of minor importance for ozone loss at these sites. Near-surface ozone variations at these three Arctic sites seem more sensitive to transport. Meteorological transport of ozone depleted boundary layer air from the Arctic Ocean has been identified as the cause of observed ozone depletion at Alert, a site located inland in the Arctic [Barrie et al., 1989; Bottenheim et al., 2002]. Air mass changes and associated horizontal advection were dominant factors in controlling ozone change during the PSE94 experiment [Gong et al., 1997b]. According to the daily time-series of simulated near-surface O_3 - and BrO-mole fractions at the three Arctic sites in Figures 3 and 8, sustained episodes of simulated ODEs occurred mostly during the periods from 16 April to 15 May 2000 and 21 April to 20 May 2001 respectively. The averaged near-surface O_3 - and BrO-mole fractions as well as wind streamlines are shown in Figures 9 and 10, respectively, for these two periods of 2000 and 2001, representing the horizontal advection of O_3 -mole fractions by winds and the BrO-connection to ABL ozone depletion. This is to characterize the sources and transport

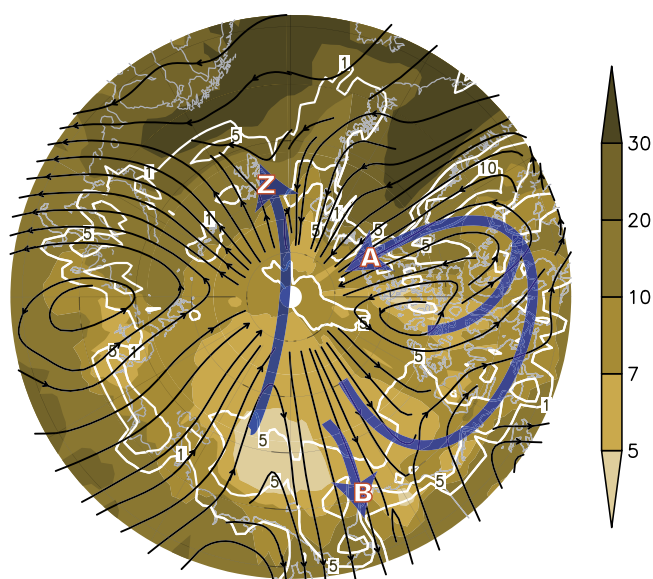


Figure 10. Same as Figure 9 but averages from 21 April to 20 May 2001.

patterns of ABL ozone depletion in springs of 2000 and 2001 and to elucidate the mechanisms of ODEs at three Arctic observation sites. In Figures 9 and 10 the transport pathways starting from the depleted O_3 source regions to the Arctic sites of Alert, Barrow and Spitsbergen were also marked.

[21] Apparent source regions of ABL ozone depletions in springs of 2000 and 2001 could be identified as areas of lower O_3 -mole fractions [Bottenheim and Chan, 2006]. For the ODEs in spring 2000, the two source regions with lower O_3 were centered over the Siberian/Beaufort Arctic and the Canadian Arctic, in agreement with locations derived from 9 year observations of ODEs [Bottenheim and Chan, 2006]. Two lower O_3 source regions for the ODEs in spring 2001 were located over the same regions but with weaker strengths and smaller areas compared to spring 2000. It is interesting to note that these source regions of ODEs broadly corresponded to areas with increased BrO levels, and were accompanied by the Arctic anticyclones or the strong south wind over the Eastern Siberian Sea and Canadian Arctic (Figures 9 and 10), implying that halogen-driven O_3 losses with the influence of atmospheric circulation over the Arctic together built up the source regions of ODEs. The atmospheric circulation patterns controlling air temperature variations and governing air mass change and pollution transport could impact on the ABL ozone distributions.

[22] Transport of ABL ozone depletion from the lower O_3 regions to the fixed observational points (Alert, Barrow and

Table 2. Regression Correlation Coefficients Between Daily Near-Surface O_3 - and BrO-Mole Fractions Simulated by GEM-AQ/Arctic at Three Arctic Sites in Springs 2000 and 2001

	Alert	Barrow	Zeppelinfjellet
Spring 2000	-0.29	-0.13	-0.21
Spring 2001	-0.20	-0.27	-0.32

Zeppelinfjellet) is controlled by the atmospheric circulation in the Arctic. The Arctic is climatologically characterized by patterns of anticyclone and cyclone circulations or of high- and low-pressure systems (<http://nsidc.org/arcticmet/>). On average for major ODEs of 2000, one anticyclone or high-pressure ridge, known climatologically as the Siberian High was located over the Eastern Siberian Sea and a second anticyclone called the Arctic High was located over the Canadian Archipelago and surroundings. Concurrently a cyclone corresponding to the Icelandic Low was established in the Barents and Kara Seas region, and a second cyclone or a depression over the Beaufort Sea existed between the two anticyclones in the Eastern Siberian Sea and the Canadian Archipelago (Figure 9). The most remarkable features of near-surface air circulations in the Arctic during the major ODEs of spring 2001 were two well developed cyclones in association with the split of the Icelandic Low into two centers: one over the Eurasian Arctic, the Barents and Kara Seas regions; and another one over the North American Arctic. The Siberian High also persisted over the Eastern Siberian Sea and the surrounding regions for spring 2001 (Figure 10). Transport patterns and pathways were created through the interaction and evolution of Arctic near-surface anticyclone (High) and cyclone (Low) circulations [Hopper and Hart, 1994]. Between the two source regions for the springtime ODEs, the stronger source region in the Siberian/Beaufort Arctic was located just upwind to the north of Barrow. The depleted O_3 from this source was directly advected to Barrow by the north wind between the anticyclone (the Siberian High) over the source regions and the cyclone over the Beaufort Sea for 2000 (Figure 9) or over the North American Arctic for 2001 (Figure 10). Following the cyclone circulation stretched over the Eurasian Arctic, the Barents and Kara Seas regions, the lower O_3 air from the source regions of the Siberian/Beaufort Arctic traversed the Arctic Ocean and reached Zeppelinfjellet in a southerly direction for both the springtime ODEs 2000 and 2001 (Figures 9 and 10). The transport pathway from the source regions of the Siberian/Beaufort Arctic was quite different for ODEs at Alert in spring between 2000 and 2001. The lower O_3 air blew to Alert along the pathway connected by the cyclone circulations over the Beaufort Sea and the anticyclone circulation over the Canadian Archipelago in spring 2000 (Figure 9), while the pathway for the ODEs at Alert in spring 2001 was circulated by the cyclone centered in the North American Arctic (Figure 10). The major ODEs at Alert, Barrow and Zeppelinfjellet in spring 2000 and 2001 originated from the same source regions, and ozone depleted air flowed downwind to Barrow in a short time, but to Alert and Zeppelinfjellet in a longer time simply due to the lengths of the transport pathways (Figures 9 and 10). These trans-Arctic transport characteristics are consistent with the results from a 9-year trajectory analysis [Bottenheim and Chan, 2006], which identified the dominant transport pathways starting from the source regions in the Siberian/Beaufort Arctic across the Arctic Ocean to Alert, Barrow and Zeppelinfjellet. A secondary transport pathway linked the ozone depleted source regions in the Canadian Arctic and Alert. Controlled by the atmospheric circulations over the North American Arctic, low- O_3 air traveled along this pathway with a southerly flow from the direction of continental North America (Figures 9 and

10). The secondary transport pathway was also verified by the 1992 Polar Sunrise Experiment [Hopper and Hart, 1994].

4. Summary

[23] A global 3-D chemistry and transport model GEM-AQ/Arctic, based on current understanding of the chemical reaction cycles, the halogen sources and the triggering of bromine explosions involved in ODEs was established and applied to simulate the ABL ozone depletion and BrO production in springs of 2000 and 2001. This is the first attempt in a global model to study the full Arctic ODE cycle by simulating the halogen sources, i.e., frost flower from newly-formed sea ice, multiphase chemistry and transport. The evaluation of model simulations with available GOME satellite BrO observations and surface O_3 measurements at Alert, Barrow and Zeppelinfjellet generally demonstrated a good agreement. In particular the spatial structure and temporal evolution of tropospheric BrO clouds, the timing of ODEs observed at the three arctic stations was reasonably captured. This 3-D modeling study highlighted the potential importance of several processes in ODE occurrence including: (1) the heterogeneous processes of halogen chemistry in the MBL and tropospheric chemistry [Sander *et al.*, 2005], (2) aerosols released from frost flowers to air comprising major source of reactive halogens [Kaleschke *et al.*, 2004], (3) a parameterization for frost flower aerosol production based on a modified sea salt generation scheme [Gong *et al.*, 1997a], and (4) the carbonate precipitation out of the brine layer for the reduction of buffer capacity of frost flower aerosols triggering bromine explosions [Sander *et al.*, 2006] in the model.

[24] The 3-D modeling of the spatial structure and temporal evolution of Arctic halogen chemistry for ODEs has led to a better understanding of the mechanisms for spring-time ABL ozone depletion. Most periods of simulated ozone depletion ($O_3 < 1 \text{ nmol mol}^{-1}$) remained in a layer 300 to 400 m deep at the Arctic sites. It is found that on average large areas of reduced ozone mole fractions ($O_3 < 20 \text{ nmol mol}^{-1}$) covered most Arctic region, and high BrO with occasional BrO-peaks from 30 to 50 pmol mol^{-1} were in the coastal regions. In addition to the ABL halogen chemistry, atmospheric circulation and the associated air pollution transport in the Arctic are found to have an impact on the ABL ozone depletion. Weak negative correlations between the near-surface O_3 - and BrO-mole fractions were obtained for Alert, Barrow and Zeppelinfjellet, indicating that local ozone destruction is less relevant than transport. For the ODEs in springs of 2000 and 2001, two source regions with lower surface O_3 were identified namely the Siberian/Beaufort Arctic and the Canadian Arctic. These regions broadly corresponded to areas with enhanced BrO levels, and were accompanied by the Arctic anticyclones and the strong south wind from the continents. The trans-Arctic transport pathways for the major ODEs at Alert, Barrow and Zeppelinfjellet in springs of 2000 and 2001 were also identified from the same source region over the Siberian/Beaufort Arctic.

[25] Many uncertainties remain in the modeling. One important aspect is the sources of reactive halogens involved in ODEs. In this model, only frost flower-derived

aerosols as the principle source for reactive halogens were assumed, which may be too restrictive in view of more recent suggestions that snow pack processes and first-year sea ice for ODEs may be large contributors as well. One central point of this study is the inclusion of aerosol formation from frost flower areas. Since an unclear and fundamentally different process, as compared to the sea salt aerosol from the open ocean, is responsible for the frost flower aerosol production, the mechanism for the generation of frost flower aerosol in this study was highly approximated by a size segregated sea salt production scheme from open oceans applying a changed wind speed dependency and needs to be evaluated and improved. The incorporation of the sources of first-year sea ice [Simpson et al., 2007a] and the snow pack processes including halogen recycling on snow [Piot and von Glasow, 2008] in the 3-D models is left as a challenge for the further research, which requires a quantitative physical and chemical understanding of these sources and processes involved in ODEs. Another uncertainty in the model simulation is the unique polar boundary layer, which is believed to play a dominant role in ODEs, especially in ozone recovery and the associated turbulent vertical mixing of free tropospheric ozone down to ground level [Gong et al., 1997b; Zeng et al., 2006]. Other uncertainties exist regarding the modeled meteorology especially for the polar model assimilated wind fields with the spatial model resolutions of 2 by 2 degrees, the initial O₃-background and multiphase halogen chemistry. A more sophisticated model with a more detailed treatment of polar boundary layer and data assimilation for Arctic meteorology and chemistry is in progress.

[26] **Acknowledgments.** The authors wish to thank The Canadian Foundation for Climate and Atmospheric Sciences (CFCAS) for its financial support.

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