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


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[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 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 springtime 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.


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°27’N, 62°31’W) in Canada [Bottenheim et al., 1986; Barrie et al., 1989] and at Barrow (71°19’N, 156°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; Wessler 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., 1992].
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 HCO₃⁻ 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 (CaCO₃) 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].

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 Br₂ 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., 2007; von Glassow and Crutzen, 2007; Piot and von Glassow, 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 Br₂ and BrCl).

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 BrONO₂ 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 O₃ 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 O3, CH4, HOx and NOx 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 MEC-CA [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 MEC-CA 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 chemical 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/Arcitic. 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° × 0.5° was preprocessed from satellite-derived sea-ice fraction maps (from SSM/I passive microwave images) and NCEP-reanal-
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
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

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).

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

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 2. Comparisons of BrO-tropospheric VCD (Ã10¹³ molecules/cm²) simulated by GEM-AQ/Arctic (contour lines) and measured by GOME (filled contours) averaged in springs of (a) 2000 and (b) 2001.
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 \(\text{O}_3\)-mole fractions simulated with and without halogen chemistry in the MBL could indicate halogen-driven ozone losses. In the
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 (O$_3 < 14$ 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

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
(O₃, CH₄, HOₓ, NOₓ and NMHC) chemistry to the Arctic springtime ozone depletions. Figure 7 shows the simulated near-surface O₃-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 O₃-production is positively correlated with air temperature based on tropospheric O₃-chemistry [von Kuhlmann et al., 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 O₃ distribution shown in Figure 7. Furthermore, the simulated near-surface O₃-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 O₃-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.

The ABL O₃ distribution with halogen chemistry in Figure 5 can be decomposed into two parts: (1) the O₃ 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-

Figure 5. Averaged distribution of the simulated near-surface O₃-mole fractions (nmol mol⁻¹) in springs (March, April and May) for 2000 and 2001.

Figure 6. Averaged distributions of the near-surface BrO-mole fractions (pmol mol⁻¹, filled contours) and the differences of the near-surface O₃-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 O₃-mole fractions (nmol mol⁻¹, filled contours) and air temperature (°C, contour lines) simulated by GEM-AQ/Arctic without halogen chemistry in springs (March, April and May) for 2000 and 2001.
ences of spring mean O$_3$-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 O$_3$ 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

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<th>Alert</th>
<th>Barrow</th>
<th>Zeppelinfjellet</th>
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<tr>
<td>Spring 2000</td>
<td>0.82</td>
<td>0.66</td>
<td>0.67</td>
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<tr>
<td>Spring 2001</td>
<td>0.88</td>
<td>0.62</td>
<td>0.76</td>
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Figure 8. Daily time series of the simulated near-surface O$_3$- 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.
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

Figure 8 shows the daily time series of the simulated near-surface O$_3$- and 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).

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

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<tr>
<td>Spring 2000</td>
<td>−0.29</td>
<td>−0.13</td>
<td>−0.21</td>
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<tr>
<td>Spring 2001</td>
<td>−0.20</td>
<td>−0.27</td>
<td>−0.32</td>
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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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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

[25] 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\textsubscript{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.

[26] 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 springtime ABL ozone depletion. Most periods of simulated ozone depletion (O\textsubscript{3} < 1 nmol mol\textsuperscript{-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\textsubscript{3} < 20 nmol mol\textsuperscript{-1}) covered most Arctic region, and high BrO with occasional BrO-peaks from 30 to 50 pmol mol\textsuperscript{-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\textsubscript{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\textsubscript{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.

[27] 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
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