Modeling of Auto-Catalytic Halogen Release and Ozone Depletion in Polar Regions

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Abstract. This article concerns the modeling of the tropospheric ozone depletion event in polar spring where the aim is an improved understanding of the underlying physical and chemical processes. For this purpose, a model based on OpenFOAM 1.7.1 is developed, where two-dimensional compressible Navier-Stokes equations are solved numerically by finite volume method to predict the effects of turbulent mixing, advection of the fluid, and detailed chemical reactions. The present chemical reaction mechanism consists of 53 chemical reactions among 33 species to model the auto-catalytic process considering halogen species X, X₂, XY, XO, HOX, where X and Y denote halogen atoms - here Br is studied. Large eddy simulation is applied to account for the turbulence and the Smagorinsky model is employed as sub-grid model. Good agreement with literature and experimental data is obtained for the profiles of the chemical species. In particular, the correct time scale of the phenomenon is captured. It is confirmed that the mixing ratio of ozone in the troposphere drops to a value near zero within several days. Moreover, it is shown that the well-mixed air is confined inside the boundary layer. A parameter study shows that the ozone depletion event happens even at reduced initial values of molecular bromine. Also, the study of coupled transport and chemistry shows that the turbulent mixing enhances the ozone depletion in the lowest layer above the earth’s surface.

1. Introduction

Enhanced ozone depletion in tropospheric layer during spring time has been reported in polar regions since the mid-1980s (Oltmans, 1981; Barrie et al., 1989). It is found that within a few hours or days, the mixing ratio of ozone in the atmosphere drops from the background level which is tens of ppb to the amount of less than 1 ppb or even below the detection limit (Barrie et al., 1988). These episodes are called ”ozone depletion events” (Oltmans et al., 1989).

Previous research has confirmed that reactive halogen species (X, X₂, XY, XO, HOX, where X and Y denote halogen atoms such as Cl or Br) are responsible for those depletion events, where especially bromine compounds play an important role. It is suggested that the reactive bromine species are involved in an autocatalytic chemical reaction cycle (Wayne et al., 1995; Platt & Janssen, 1995; Platt & Höhninger, 2003),
\[ \text{Br}_2 \xrightarrow{h\nu} 2 \text{Br} \quad (1) \]
\[ 2 \text{Br} + 2 \text{O}_3 \rightarrow 2 \text{BrO} + 2 \text{O}_2 \quad (2) \]
\[ \text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2 \quad (3) \]
\[ 2 \text{O}_3 \xrightarrow{h\nu} 3 \text{O}_2 \quad (4) \]

Under photolysis conditions, the reactive bromine species act as catalysts. The overall effect is that the ozone in the tropospheric layer is destructed without any loss of bromine in the atmosphere. However, based on the previous model results (Fan & Jacob, 1992), it is verified that the natural atmospheric bromine concentration is inadequate for causing such a rapid ozone depletion event, and the source of the larger amount of the reactive bromine is still unclear. Sea ice, which covers most of the area in polar regions, is suggested to be one of the possible sources (Rankin & Wolff, 2003). GOME (global ozone monitoring equipment) observation has also confirmed the correlation between the large amount of the BrO and the existence of newly formed ice (Wagner et al., 2001). Thus, the following heterogeneous chemical reaction occurring at the ice surface was suggested (Fan & Jacob, 1992; Tang & McConnell, 1996)

\[ \text{HOBr} + \text{H}^+ + \text{Br}^- \rightarrow \text{H}_2\text{O} + \text{Br}_2. \quad (5) \]

The bromine ions in the saline surfaces are activated via this heterogeneous reaction when HOBr molecules contact the ice surface, producing the reactive bromine species Br\(_2\). In this activation process, one molecule of HOBr is consumed while molecular Br\(_2\) is produced, which may lead to two new bromine atoms released into the air by the photochemical reaction shown in Eq. (1). Thus, the bromine concentration in the atmosphere grows exponentially, speeding up the destruction rate of the ozone. This effect is known as the ”bromine explosion” (Platt & Lehrer, 1991).

2. Mathematical Model

A two-dimensional model to describe the tropospheric ozone depletion in polar regions is developed based on OpenFOAM version 1.7.1. Figure 1 shows a schematic of the configuration. The size of the computational domain is 1000 m \( \times \) 1000 m. The initial wind speed is set to 8 m/s along the horizontal direction. The vertical velocity is set to zero at the ice surface while the top boundary condition is free slip. Periodic boundary conditions are applied to the left and right side of the calculation domain. When the air, which is taken by the wind, flows across the colder ice surface, a temperature inversion layer with hundreds of meters height will be generated. The temperature inversion will suppress the turbulent mixing while the wind shear enhances the mixing. Therefore, a stable boundary layer develops, where turbulent mixing leads to eddies reversing the position of the air parcel, which again is influenced by buoyancy tending to force the displacement of the air parcel to its original position. Thus, these two overlying processes cause a reduction of the size of the eddies inside the boundary layer.

The following two dimensional compressible Navier-Stokes equations to describe the physical domain are solved:

- Mass:
  \[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0 \quad (6) \]

- Momentum:
  \[ \frac{\partial (\rho \vec{U})}{\partial t} + \nabla \cdot (\rho \vec{U} \vec{U}) + \nabla \cdot \tau = -\nabla p + \rho \vec{g} \quad (7) \]
• Energy:

\[
\frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{U} h_s) - \nabla \cdot (\alpha \nabla h_s) = \frac{\partial p}{\partial t} + \dot{Q}
\]  

(8)

• Species:

\[
\frac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{U} Y_i) - \nabla \cdot (\rho D_i \nabla Y_i) = \dot{\omega}_i,
\]  

(9)

where \(\rho\) is the air density, \(\mathbf{U}\) is the gas velocity, \(\mathbf{g}\) is the gravitational acceleration, \(h_s\) is the sensible enthalpy, \(\alpha\) is the thermal diffusivity, and \(p\) denotes the pressure, \(\dot{Q}\) is the reaction enthalpy, \(Y_i\) is the mass fraction of species \(i\), \(D_i\) is the diffusion coefficient for species \(i\), \(\omega_i\) is the specific reaction rate of species \(i\), and \(\tau\) is the stress tensor,

\[
\tau_{ij} = -\frac{1}{3} \tau_{kk} \delta_{ij} - 2\mu (\epsilon_{ij} - \frac{1}{3} \epsilon_{kk} \delta_{ij}),
\]

(10)

where \(\delta\) is the Kronecker symbol, and \(\epsilon\) is given as

\[
\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).
\]

(11)

Large eddy simulation is used to account for the turbulence. The effective viscosity is calculated as

\[
\mu_{eff} = \mu_l + \mu_t,
\]

(12)

where \(\mu_l\) and \(\mu_t\) are the laminar and eddy viscosity, respectively. The Smagorinsky model is used as the sub-grid model in which the eddy viscosity is modeled by

\[
\mu_t = \rho C_l \Delta \sqrt{k}.
\]

(13)

The filter width, \(\Delta\), equals (Grid size) \(\frac{1}{3}\). \(k\) denotes the sub-grid kinetic energy, and the constant \(C_l\) is set to 0.02.

The detailed reaction mechanism given by Lehrer et al. (2004) is used involving 53 chemical reactions among 33 species, and the rate constants are taken from Atkinson et al. (2006). Temperature dependent physical properties of the chemical species including heat capacity, enthalpy, and entropy are computed following JANAF tables (Chase, 1996).

Figure 1. Schematic depiction of the model
3. Results

First, a box model study over a period of 50 days is studied by turning off both the turbulence model and the convection terms in the two dimensional model described above. Thus, time-dependent equations considering diffusion and chemical reactions are used to investigate the chemical reactions.

Time-dependent profiles of the chemical species are displayed in Figure 2, where the process is observed between day 25 and day 50. Enhanced ozone depletion occurs after day 30 where the most rapid decrease is found between day 35 and day 40. These values agree with previous numerical results by Michalowski et al. (2000) and Lehrer et al. (2004), who found the ozone to be completely destructed within approximately five days. Initially, HOBr is the major bromine-containing species: Its mole fraction reaches the maximum value of approximately 20 ppt after about 35 days. The rapid decrease of HOBr between day 35 and 40 coincides with the rapid

![Figure 2. Time variation of ozone and bromine species with 0.3 ppt initial bromine concentration](image)

![Figure 3. Time variation of ozone and bromine species with 0.1 ppt initial bromine concentration](image)

![Figure 4. Contour of mean vertical velocity](image)

![Figure 5. Vertical distribution of O₃, BrO, and HOBr at day 30](image)
ozone depletion during that period of time. As HOBr decreases, BrO builds up reaching a peak value of 23 ppt, which again compares well with experimental data (Hausmann & Platt, 1994; Höninger & Platt, 2002). BrO decreases rapidly as ozone is depleted before day 40. The ozone mole fraction falls to a value of less than 1 ppb after day 40, after which the only remaining Br-containing species is the less reactive HBr. The total amount of bromine at the end of the depletion process is stable at around 40 ppt.

Figure 3 shows the time variation of ozone and bromine species, where the initial gas-phase bromine concentration was reduced from 0.3 to 0.1 ppt. The ozone depletion event occurs about 10 days later than in the first case. The principal profiles of bromine species concentrations are similar whereas the peak values are somewhat lower.

In a second step, the full set of equations shown in the previous chapter including convection, turbulent transport and chemical reactions are investigated. Figure 4 shows that the reactive halogen species, which are generated at the ice surface by the heterogeneous reactions, are taken upwards by the turbulence induced by the wind shear. Thus, the air is well mixed within the boundary layer, the top of which is located at some hundred meters above the earth’s surface. This is consistent with previous findings (Anderson & Neff, 2007). Under the present conditions, the concentration of surface emissions would accumulate within the boundary layer, leading to the amplification of the halogen-related chemistry in this layer, which is displayed in Figure 5. However, more parameter studies are needed to quantitatively analyze the effects of turbulence and temperature inversion.

4. Conclusions

The results demonstrate that the present model is capable of simulating the spring time bromine release and ozone depletion in polar regions. The detailed chemical reaction mechanism including heterogeneous reactions is implemented to numerically study the phenomenon of ozone depletion. Moreover, variation of initial bromine concentration in the gas phase shows that the ozone depletion event occurs even for reduced initial concentration. It is also shown that the reactive bromine species generated at the ice surface are well mixed within the boundary layer because of the wind shear.

An extension of the model to consider the effect of parameters such as wind speed, ice surface, and temperature inversion will be beneficial to study ozone depletion under more realistic conditions. Moreover, the influence of other halogens such as chlorine or iodine will be studied.

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