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Abstract: This paper presents an engineering system approach using a 2D model of conservation of mass to study the dynamics of ozone and concerned chemical species in the stratosphere. By considering all fourteen photolysis, ozone-generating, and -depleting chemical reactions, the model calculated the transient, spatial changes of ozone under different physical-chemical-radiative conditions. Validation against the measured data demonstrated good accuracy, close match of our model with the observed ozone concentrations at both 20 °S and 90 °N locations. The deviation in the average concentration was less than 1% and in ozone profiles less than 17%. The impacts of various chlorine- (Cl), nitrogen oxides- (NO_x), and bromine- (Br) depleting cycles on ozone concentrations and distribution were investigated. The chlorine catalytic depleting cycle was found to exhibit the most significant impact on ozone dynamics, confirming the key role of chlorine in the problem of ozone depletion. Sensitivity analysis was conducted with levels of 25%, 50%, 100%, 200%, and 400% of the baseline value. The combined cycles (Cl+NO_x+Br) showed the most significant influence on ozone behavior. The total ozone abundance above the South Pole could decrease by a small 3%, from 281 DU (Dubson Units) to 273 DU for the 25% level, or by a huge thinning of 60% to 114 DU for the 400% concentration level. When the level of chlorine gases increased beyond 200%, it would cause ozone depletion to a level of ozone hole (below 220 DU). The 2D Ozone Model presented in this paper demonstrates robustness, convenience, efficiency, and executability for analyzing complex ozone phenomena in the stratosphere.

Key words: Ozone depletion, 2-D model, chlorine, bromine, nitrogen oxides, sensitivity analysis, total ozone abundance, DU.

1. Introduction

Stratospheric ozone O_3 is considered a natural sunscreen that protects living beings from high energy UV (Ultraviolet) rays from the Sun for hundreds of millions of years. As a result of the extremely high temperature of the Sun, nuclear fusions occur where the hydrogen protons fuse to form helium. The reactions cause the Sun radiating heat and light to the Earth. This form of energy enters the atmosphere as UV, visible light, and infrared rays. About 9% of solar energy lies in UV spectrum that has short wavelength and is considered a harmful solar radiation. The protective ozone layer in the stratosphere can block about 90% of it from reaching the ground [1, 2]. A large proportion (~90%) of ozone

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is found in the stratosphere layer (from 10 km to 50 km above the sea level), while a small proportion (~10%) of it is found in the troposphere (from ground level to 10 km). A higher concentration of O_3 near the ground is regarded a criterion pollutant and a photochemical smog [1, 2]. According to NASA (National Aeronautics and Space Administration) Ozone Watch, ozone level of less than 220 DU (Dobson Units) can be a result of the ozone loss from chlorine, bromine, and nitrogen oxide compounds, and is called the ozone hole [3]. The normal concentration of ozone at any given point on Earth should be about 300-350 DU [1, 3].

By the mid-1980s, scientists had already discovered that there was an unusual thinning of the ozone layer over Antarctica. The discovery of this ozone hole caused a major concern for the scientists and governments all over the world. They identified more than 100 ODS (Ozone Depletion Substances) needing to be regulated in terms of production and consumption to reduce the depletion of the stratospheric ozone. ODS can be classified into three types: chlorine gases, bromine gases, and HFCs (Hydrofluorocarbons). Each of them has different concentrations in the atmosphere [4]. Some of these gases are photo-dissociated from traditional refrigerants, such as CFCs (Chlorofluorocarbons) and HCFCs (Hydrochlorofluorocarbons) used widely in billions of heating, ventilation, and air conditioning HVAC, and refrigeration devices.

After CFCs and HCFCs are released or accidentally leaked, they remain chemically inactive in the troposphere and do not dissolve in water, making it freely mix and transport with air in motion. Although the weights of CFC/HCFC molecules are heavier than air, the atmospheric process of air currents and mixing carry some of them up from the troposphere to the stratosphere. It enters the lower stratosphere where it is slowly mixed and transported into the upper stratosphere of higher latitudes, where the solar UV radiation photodissociates it into chlorine gases [5, 6]. For an average CFC molecule, it takes around a whole year to move from the tropical upper troposphere to the upper stratosphere. The scientific foundations of the Montreal Protocol to protect the ozone layer lie in the measurements and analysis of the chemistry in the ozone layer. Active chlorine is a major catalyst for ozone depletion [5, 6]. As per a group of scientists, the constantly emitted CFCs gases, the volatile derivatives of propane, ethane, and methane, and their accompanying pollution continue to cause an irreversible alteration to the ozone level [7].

In the study of Earth's atmosphere, researchers have used various modeling techniques. While much attention goes to 2D (Two-Dimensional) models, it is important to note the use of simpler 1D (One-Dimensional) models. These 1D models provided fundamental insights into ozone distribution, focusing on altitude and chemical processes' impact on ozone dynamics. For example, the convection-diffusion-reaction ozone model significantly advanced our understanding of 1D modeling [8, 9].

Various 2D models, including the 2D chemical model, play a pivotal role in unraveling Earth's atmospheric intricacies. On going research refines these models, incorporating three-dimensional elements for a more profound understanding and accurate predictions [6]. Combining 2D models with observational data remains crucial for a comprehensive grasp of the ozone layer's dynamics. The 2D chemical model excels in the high stratosphere but encounters accuracy challenges in the lower stratosphere, serving as a valuable tool for shedding light on physical-chemical-radiative interactions [1, 10].

Chemical box models provide a specialized lens into individual atmospheric processes, particularly those involving trace gases and human-made emissions. Integration with larger-scale models becomes imperative for a holistic understanding [11]. Chemical transport models strike a balance between simplicity and complexity, simulating both atmospheric chemistry and the transport of chemicals, contributing significantly to our understanding of ozone depletion and its interconnected factors in projects like MATCH [12].

This paper explores the impact of various ozone depletion cycles, involving substances like chlorine, bromine, and NO_x, on ozone distribution from an engineering perspective. The unique aspect of our model lies in its incorporation of different competing physical-chemical-radiative processes: wind convection, mass diffusion, UV photolysis, ozone-producing and ozone-depleting chemical reactions, within a cylindrical coordinate system, which distinguishes itself from existing literatures and offers advantages such as faster computation and improved capabilities for analyzing specific phenomena and regions, such as the ozone hole. Our extendable model allows for the easy addition of more reactions as needed, providing valuable insights into ozone behavior and dynamics, with a focus on simplicity and concentration on ozone distribution

compared to empirical data [1].

2. Modeling and Numerical Method

2.1 Mass Balance Equations

To investigate the ozone concentration, profile of the layer, and ozone depletion and ozone hole in the stratosphere, we employ a system of 2-D cylindrical mass balance equations [1, 13]. The conservation equations for various substances C_i (molecules per unit volume, or mass concentration, or parts per million, ppm), such as ozone O₃, atomic oxygen O, and various concerned chemical species, include the time change of concentration $(\frac{\partial C_i}{\partial t})$, convective transport by slow air

movement $(U, \nabla C_i)$, (U being the velocity vector of air motion), mass diffusion due to concentration gradients $(D_i \nabla^2 C_i)$ $(D_i$ being the diffusivity of species C_i), and change of concentration by various chemical reactions

 $\left(\frac{d[C_i]}{dt}\right)$, including the photolysis, ozone-generation and

ozone-depletion reactions. The mass balance equations below are coupled partial differential equations in a transient axisymmetric cylindrical coordinate (t, r, z), characterizing the change of a substance in the stratosphere due to five simultaneous, competing processes: convective transport, mass diffusion, photodissociation, ozone-generating reactions, and ozonedepleting reactions.

Conservation of mass equations:

$$\frac{\partial C_i}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[\left(D_i \frac{\partial C_i}{\partial r} r \right) - U_r C_i r \right] \\ + \frac{\partial}{\partial z} \left(D_i \frac{\partial C_i}{\partial z} - U_z C_i \right) + \frac{d[C_i]}{dt}$$

For the simplicity, the equation above encapsulates the key processes and parameters, but assumes axisymmetry (or $\partial C_i/\partial \phi = 0$). The concentration of a species C_i generally changes with time *t*, altitude *z*, and radial position *r*. The altitude or elevation of interests is the stratosphere, extending from z = 10-15 km to z =45-50 km, radial coordinate (*r*) being of different ranges and values, time (*t*) of interests being in seconds, days, or months, the slow wind speeds in the *z* and *r* directions being U_z and U_r , and diffusivity of C_i gases being D_i . The concentration C_i (in in molecules/volume or ppm) of species gases can be regular oxygen O₂, naturally available ozone O₃, active atomic oxygen O from photolysis, and various man-induced ozone depleting chemicals, such as Cl, ClO, ClOClO, ClOO, Br, BrO, BrCl, NO, and NO₂, as listed in Table 1. The mass balance equation sencapsulate the dynamic interplay of various factors that influence atmospheric chemistry, and can help understand the ozone behavior in the stratosphere.

2.2 Chemical Reactions and Ozone Depletion Cycles

In order to provide insight into various chemical reactions contributing to the change of ozone O₃, or in general, $\frac{d[C_i]}{dt}$, Table 1 lists a comprehensive compilation of 14 possible chemical reactions, its respective reaction rate constants k_i , initial concentrations C_i , and reaction expressions r_i , that are directly relevant to our study. The natural and three possible man-induced ozone-depleting cycles affecting ozone concentrations can be categorized into four groups, as delineated below [14-17]:

(1) Chapman (Natural) Mechanism of Ozone

Eqs. (1)-(3) in Table 1 illustrate the Chapman mechanism, first introduced in 1930 [14]. This mechanism elucidates the natural processes governing ozone generation and depletion in the absence of human-induced ozonedepleting substances. These processes involve photoexcitation, collision-induced transformation, and dissociation. The non-reactive species denoted as "M" serves as a random stabilizing intermediate, such as moleculeN₂ or O₂. In the stratosphere, ozone O₃ forms through multiple steps of chemical process initiated by sunlight's UV radiation. This high energy ray causes the dissociation of the abundant oxygen molecules O₂ into active oxygen atoms O + O, which subsequently collides with regular oxygen molecules to form ozone O_3 . Since the concentration of molecular oxygen O_2 is very large, constituting 20.95% or 2.095×10^5 ppm in

air, the generation of ozone O_3 primarily depends on the availability of active atomic oxygen O.

(2) Chlorine-Containing Catalytic Depleting Cycle

Eqs. (4)-(8) in Table 1describe how chlorinecontaining compounds, such as chlorine gas dissociated from traditional refrigerants CFCs and HCFCs, participating in converting ozone O_3 into regular oxygen molecule O_2 . Chlorine-containing gases act as a catalyst for ozone depletion reactions, including Cl, ClO, ClOO, and (ClO)², which are re-formed each time the depleting cycle is completed, and hence available for further destruction of ozone. Eqs. (4) and (5) are more important at tropical and middle latitude regions, where UV radiation is more intense. Eqs. (4) and (6)-(8) are more important for Antarctica, where ClO can reach large values during late winter and early spring, and the abundant ClO can react with another ClO to initiate the destruction of ozone [17].

(3) Nitrogen Oxides (NO_x) Depleting Cycle

Eqs. (9)-(11) in Table 1elucidate how nitrogen oxides NO_x (primarily NO and some NO₂), resulted from combustion of fossil fuels, both fuel NO_x and thermal NO_x [18, 19], or from natural processes, such

as wild forest fires, can react with ozone O_3 and reduce it to regular oxygen O_2 . NO_x is not as chemically stable as CFCs/HCFCs, and can react with water to be captured by rain and snow in troposphere. Some NO_x may be accumulated and transported from the ground level to the stratosphere via upward air motion.

(4) Bromine-Containing Catalytic Depleting Cycle

Also important for the polar region are Eqs. (12)-(14), that expound on how bromine-containing chemicals, such as CH₃Br (Methyl Bromide) and halons, initially developed for fire suppression and subsequently are used in large-scale applications like computer hardware and engine protection [17, 18], can similarly contribute to the destruction of ozone O₃ into regular oxygen O₂. Like chlorine, bromine also functions as an ozone-depleting catalyst, as active bromine-containing gases, including Br, BrO, and BrCl, reformed each time the depleting cycle is completed, and hence available for further destruction of ozone. Since the sunlight (UV) is required for both Eqs. (7) and (14), during polar night and other periods of darkness, ozone will not be destroyed by these reactions [17].

Table 1 List of a total of 14 natural and man-induced chemical equations, reaction rate constants k_i , initial concentrations of different species C_i , and reaction expression r_i of Eqs. (1)-(14) [1, 14, 15, 20].

Eq.	Chemical reaction equation	Reaction rate constant (k_i) (cm ³ /molecule * s)	Initial concentration (C_i) (molecules/cm ³)	Reaction expression (r_i)	
Chap	man (Natural) Mechanism				
1	$0_2 + hv(\text{sunlight}) \rightarrow 2 \ 0^*$	$k_1 = 1.03 \times 10^{-94}$	$O_2 = 2.00 \times 10^{17}$	$r_1 = k_1 [O_2]$	
2	$0^* + 0^2 + M \rightarrow 0_3 + M$	$k_2 = 5.92 \times 10^{-34}$	$O = 1.00 \times 10^{-6}$	$r_2 = k_2 [O_2] [O]$	
3	$0_3 + hv(\text{sunlight}) \rightarrow 0_2 + 0^*$	$k_3 = 4.38 \times 10^{-26}$	$O_3 = 5.00 \times 10^{12}$	$r_3 = k_3 [O_3]$	
Chlo	rine Catalytic Depleting Cycle				
4	$Cl + O_3 \rightarrow ClO + O_2$	$k_4 = 1.22 \times 10^{-11}$	$Cl = 6.46 \times 10^4$	$r_4 = k_4 [O_3] [C1]$	
5	$Cl0 + 0 \rightarrow Cl + 0_2$	$k_5 = 3.80 \times 10^{-11}$	$ClO = 7.22 \times 10^{7}$	<i>r</i> ₅ = <i>k</i> ₅ [O] [ClO]	
6	$ClO + ClO + M \rightarrow (ClO)_{2+}M$	$k_6 = 2.16 \times 10^{-32}$	$(C(0)) = 1.00 \times 10^{-6}$	$r_6 = k_6 [\text{ClO}]^2$	
7	$(ClO)2 + hv(sunlight) \rightarrow Cl + ClOO$	$k_7 = 8.53 \times 10^{-15}$	$(CIO)_2 = 1.00 \times 10^{-3}$	$r_7 = k_7 [(ClO)_2]$	
8	$ClOO + M \rightarrow Cl + O_2 + M$	$k_8 = 6.51 \times 10^{-13}$	$ClOO = 1.00 \times 10^{-6}$	$r_8 = k_8$ [ClOO]	
Nitrogen Oxides Depleting Cycle					
9	$NO + O_3 \rightarrow NO_2 + O_2$	$k_9 = 1.78 \times 10^{-14}$	$NO = 1.00 \times 10^9$	<i>r</i> 9= <i>k</i> 9 [O ₃] [NO]	
10	$NO_2 + O \rightarrow NO + O_2$	$k_{10} = 1.05 \times 10^{-11}$	$NO = 1.00 \times 10^9$	$r_{10} = k_{10} [NO_2] [O]$	
11	$NO_2 + O_3 \rightarrow NO + 2O_2$	$k_{11} = 1.00 \times 10^{-18}$	$NO_2 = 1.00 \times 10^{-5}$	$r_{11} = k_{11} [NO_2] [O_3]$	
Bron	ine-Catalytic Depleting Cycle				
12	$Br + O_3 \rightarrow BrO + O_2$	$k_{12} = 1.18 \times 10^{-12}$	$Br = 3.2 \times 10^5$	$r_{12} = k_{12} [Br] [O_3]$	
13	$BrO + ClO \rightarrow BrCl + O_2$	$k_{13} = 1.02 \times 10^{-12}$	$BrO = 6.4 \times 10^6$	<i>r</i> ₁₃ = <i>k</i> ₁₃ [BrO] [ClO]	
14	$BrCl + hv(sunlight) \rightarrow Br + Cl$	$k_{14} = 1.06 \times 10^{-8}$	BrCl = 1.00×10^{-6}	$r_{14} = k_{14} [BrCl]$	

Table 1 provides pertinent published data, including streaction rate constants (k_i) and initial concentrations for sicchemical species in Eqs. (1)-(14) for the tropical regions [15, 20]. It should be noted that these values may vary with factors such as latitude, time, and signature environment conditions. From the reaction expressions (r_i) in Table 1, we can derive for the total reaction rate for a species $\frac{d[C_i]}{dt}$, including ozone concentration $\frac{d[O_3]}{dt}$ and consequently the ozone layer characteristics, atomic oxygen O, and various ozone depleting the chemicals: Cl, ClO, Br, BrO, NO, NO₂, etc. For instance, $\frac{d[O_3]}{dt} = r_2 - r_3 - r_4 - r_9 - r_{11} - r_{12}$ and $\frac{d[O]}{dt} = 2r_1 - \frac{c_i}{r_2} + r_3 - r_5 - r_{10}$. As we add the reaction terms $\frac{d[C_i]}{dt}$ to the mass balance equations, along with the transient

 $(\frac{\partial c_i}{\partial t})$, diffusion and convection terms in cylindrical coordinate, we get the complete governing equations for solving concentrations and changes of ozone and other concerned species in the stratosphere. Our 2D ozone model enables the study of the ozone dynamics, ozone layer and ozone hole under various natural and man-induced depletion reactions at different geographical locations, times of the day or months of the year, and environment and boundary conditions [1, 17].

2.3 Numerical Method and Model Validation

In the mass balance equations, the concentrations of ozone and other species are a function of time (t), radial position (r), and altitude/elevation (z), denoted as $[C_i]$ or $[O_3] = f(t, r, z)$.For the mass balance calculations, we will select material properties and environment condition, k_i , D_i , U_z , U_r from the published measured or known data, and consider at different boundary and initial conditions at different latitudes in the stratosphere. The axisymmetric assumption provides acceptable results for a region of smaller radius on the globe and produces good results for the

stratosphere above the polar region of varying sizes/radius.

To approximate the simultaneous partial differential equations into a large, but manageable system of simultaneous algebraic equations, we employ finite difference formulas to represent the first- and second-order partial derivatives in both spatial coordinate, *r* and *z*, and temporal coordinate, *t*. The discretization of the solution domain results in a grid-based representation with chosen values of Δt , Δr , and Δz in the stratosphere [21-24]. For example, the first-order partial derivatives can expressed as $\frac{\partial C_i}{\partial t} = \frac{C_i (i,j,n+1) - C_i (i,j,n-1)}{2\Delta t}$, while the second-order partial

derivatives expressed as, $\frac{\partial^2 C_i}{\partial z^2} =$

 $\frac{C_{i(i,j+1,n)-} 2C_{l(i,j,n)} + C_{i(i,j-1,n)}}{\Delta z^2}$. The numerical solution process involves formulating time-dependent convection-diffusion finite difference equations, which are applied separately to ozone O₃, molecular oxygen O₂, atomic oxygen O, and other concerned chemical species. Notably, we can safely omit the mass balance equation for molecular oxygen O₂ due to its large and stable concentration of 20.95% in the atmosphere, which remains largely unaffected by changes in small gas concentrations, typically measured in several ppm. To account for chemical reactions, we add the last term, $\frac{d[C_i]}{dt}$, representing the overall chemical reaction of

linear algebraic equations, as listed in Table 1.

We set up a large set of simultaneous finite difference algebraic equations for all grid meshes within the stratosphere, as given in equation below, with the term on the left and the 1st term on the right representing the transient change of ozone concentration, the 2nd, 3rd, and 6th terms on the right representing the mass diffusion due to concentration gradients, the 4th, 5th, and 7th on the right representing the transport by convection from slow air movement, and the last (8th) term on the right representing the overall change of ozone by various ozone-depleting and ozone-generating chemical reactions as seen in Table 1. The numerical solution entails formulating a convection-diffusion-reaction equation for O_3 , expressed as:

$$O_{3}^{n+1}{}_{i,j} = O_{3}^{n}{}_{i,j} + \Delta t * \left\{ \frac{1}{r} \left[\frac{D_{i}}{\Delta r^{2}} r \left(O_{3}^{n}{}_{i+1,j} - \right. \right. \right] \right\} \\ = O_{3}^{n}{}_{i,j} + O_{3}^{n}{}_{i-1,j} + \left. \frac{D_{i}}{2\Delta r} \left(O_{3}^{n}{}_{i+1,j} - O_{3}^{n}{}_{i-1,j} \right) - \frac{U_{r}}{2\Delta r} r \left(O_{3}^{n}{}_{i+1,j} - \left. O_{3}^{n}{}_{i,j+1} - 2O_{3}^{n}{}_{i,j} \right] + \left[\frac{D_{i}}{\Delta z^{2}} \left(O_{3}^{n}{}_{i,j+1} - 2O_{3}^{n}{}_{i,j} + O_{3}^{n}{}_{i,j-1} \right) - \frac{U_{z}}{2\Delta r} \left(O_{3}^{n}{}_{i,j+1} - 2O_{3}^{n}{}_{i,j} + O_{3}^{n}{}_{i,j-1} \right) - \frac{U_{z}}{2\Delta r} \left(O_{3}^{n}{}_{i,j+1} - 2O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} \right) - \frac{U_{z}}{2\Delta r} \left(O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} \right) - \frac{U_{z}}{2\Delta r} \left(O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} - O_{3}^{n}{}_{i,j+1} \right) - \frac{U_{z}}{2\Delta r} \left(O_{3}$$

The equation above accounts for the overall changes in ozone concentration due to various natural and maninduced chemical reactions in the stratosphere, including both generation and depletion mechanisms. For our numerical solutions, we utilized Python Solvers, which provide a robust environment for solving complex systems of simultaneous equations. Python, with its extensive libraries for numerical computations. served as the ideal software for executing our code. In our simulations, we discretize the altitude (elevation) zinto intervals of Δz ranging from 1 km to 2 km, or as dimensionless altitude either using $z^* = (z - 15)/(45-15)$ or using $z^* = (z - 10)/(50-10)$, depending on the available measured or known data for comparison. The dimensionless radial coordinate, r*, was selected within a range of 50 km or larger, with discretization of Δr between 1 km, 2 km, or larger. The time step Δt has been tested with different values, ranging from 0.1 s to 10 s, to ensure computational convergence, efficiency, and stability. A value of $\Delta t = 1$ s was ultimately chosen to capture the dynamic changes in ozone concentration

with a good temporal resolution. Consequently, most of the results presented in this paper were obtained using $\Delta t = 1$ s, $\Delta z = 2$ km (or 20 grids), and 20 grids along the radial direction ($r^* = 0$ to 1.0).

To validate our model against the published measured data [25], we calculated ozone concentrations and distribution at two selected geographical locations: the North Pole (90 ° N) and a tropical region (20 ° S, such as S ão Paulo, Brazil), which is known for an intense and long radiation from the Sun. A comparative analysis of ozone depletion caused by NO_x and CFCs was carried out, as shown in Fig. 1. A visual comparison is presented between the calculated ozone concentrations and distribution, depicted by solid curves, alongside the measured data in shallower dotted curve, at two distinct locations: the North Pole (90 °N, green curve) and atropical region (20 °S, orange curve).

At 20° S, where solar radiation is particularly intense. the ozone distribution demonstrates interesting dynamics. The solid orange curve showing calculated ozone concentration exhibits a symmetrical pattern along the altitude, peaking at 8.69 ppm near z= 30 km, as seen in Fig. 1. Similarly, the measured ozone concentration of the dotted orange curve reveals a similar symmetrical trend, with a peak concentration of 9.31 ppm near z = 30 km. The calculated results closely align with the measured concentrations, vielding an average ozone concentration of 5.53 ppm in the stratosphere, which closely resembles the measured average of 5.58 ppm. However, the ozone distribution profiles exhibit a coefficient of variation of 14.1%.

Further insight into the ozone concentration dynamics at 20 °S can be gained by considering the top boundary of the stratosphere, approximately at z = 45 km. Here, the ozone concentration stands at 3 ppm, indicating the initiation of ozone formation processes. High-energy UV-C and UV-B radiation from the Sun initiates the breakdown of oxygen molecules (O₂) into atomic oxygen (O), leading to ozone (O₃) formation. This process continues until the ozone concentration peaks



Fig. 1 Comparison of calculated ozone concentrations and distribution (solid curves) with the measured data (dotted curves) at two geographical locations: $20 \,^{\circ}$ S (orange curves) and the $90 \,^{\circ}$ N (green curves).

at 8.69 ppm around z = 30 km. However, the intensity of UV radiation diminishes as it penetrates through the upper stratosphere, resulting in a reduced generation of atomic oxygen and ozone. Ozone-depletion reactions, particularly in the presence of man-induced ozonedepleting chemicals, remain active, consume ozone and lead to the reduced ozone in the lower stratosphere. Physical processes like diffusion and slow air movement also play a significant role in shaping the ozone distribution. As shown in Fig. 1, ozone concentration declines rapidly from its peak in the midstratosphere to a lower boundary value of 0.5 ppm at z= 15 km with a transition to the tropopause and the troposphere below.

In contrast, at locations near 90 ° N latitude, ozone concentrations and distribution shown in Fig. 1 exhibit a distinct feature compared to those observed at 20 °S. Both calculated (solid green curve) and measured (dotted green curve) ozone concentrations and profile showcase variations. The calculated ozone concentrations peak at 7.25 ppm around z = 31.5 km,

while the measured ozone concentrations peak at 6.45 ppm at a higher altitude of z = 36 km. Despite these disparities, the calculated average ozone concentration in the stratosphere of 4.66 ppm closely approximates the measured average of 4.55 ppm. The variation in ozone profile is larger, with a coefficient of variation of 16.7%. This is believed to reflect the natural differences in atmospheric conditions and material properties across different locations.

3. Results and Discussions

3.1 Effect of Ozone-Depleting Reactions on Ozone Distribution

We conducted a comparative analysis to quantify and rank the influences of different ozone-depleting reactions and cycles. Our simulating calculations last for a four-month period using our 2D ozone model, with a specific focus on isolating the effects of respective reactions within different cycles. For instance, we kept reactions Eqs. (4)-(8) for chlorine (Cl) in effect, while deactivating by setting all other reaction

constants k_i being zero, including reactions in Eqs. (9)-(11) for NO_x and (12)-(14) for bromine (Br). This allows us to quantify the contribution from respective ozone-depleting reactions cycle. For a fair and accurate comparison, we evaluate the impact of ozone-depleting cycles on ozone concentrations and distribution in the South Pole (Antarctic)region. Notably, we observed a distinctive peak in measured ozone distribution at higher altitudes (typically around 35 to 40 km) for this region, contrasting to that at lower latitudes, in the equatorial and mid-latitudinal regions. At higher latitudes, the reduced angle of sunlight hitting the Earth's surface results in less direct solar penetration into the air mass of the lower stratosphere. Consequently, there is a decrease in the photolysis of molecular oxygen and a subsequent reduction in ozone production, particularly at lower altitudes.

Fig. 2 illustrates the effects of chlorine- (yellow curve), NO_{x} - (red curve), and bromine- (green curve) depleting cycles on ozone distribution, alongside initial ozone distribution measured data depicted by black dotted curve. The initial data, obtained from measurements using ozone concentrations from the Microwave Limb Sounder [25], served as a reliable baseline for our analysis. Over a four-month period

involving approximately 10,000,000 time steps ($\Delta t = 1$ s), our analysis revealed distinct influences of chlorine-, NO_x-, and bromine-depleting cycles on ozone concentrations and distribution. Notably, chlorine(Cl) curve exhibited a greater impact on ozone concentrations and distribution, compared to nitrogen oxides (NO_x) and bromine (Br).As seen in Fig. 2, the peak of all four ozone distribution curves remained at the same location close to z = 39 km, with the original, measured concentration of 5.33 ppm, and a slightly decreased peak concentration of 5.24 ppm for Cl cycle, 5.12 ppm for NO_x cycle, and 5.32 ppm for Br cycle. The averaged concentration showed a smaller value of 3.87 ppm for Cl cycle, 3.88 ppm for NO_x cycle, and 4.0 ppm for Br cycle, as compared to the original, measure averaged of 4.01 ppm. As for the variations of the ozone profile, the Cl cycle showed the largest change (reduction) of -3.21% from the measured profile, as compared to -3.12% for NO_x cycle, and only -0.10% for Br cycle. For the overall ozone abundance above the Antarctica, the original, measured value was 281 DU, the Cl-depleting cycle caused a reduction to a thinner 275 DU, NO_x-depleting cycle to 276 DU, and Brdepleting cycle remained at 281 DU and did not cause any reduction.



Effect of Ozone-Depleting Chemical Reactions On Ozone Distribution

Fig. 2 Impact of ozone-depleting chemical reactions on ozone concentrations and distribution: comparison of chlorine cycle (yellow curve), NO_x cycle (red curve), and bromine cycle (green curve), with the measurement (dotted black curve).

Following the respective impact of ozone-depleting cycles on ozone concentrations and distribution, we further examined how these depleting cycles interact when combined (co-existed) in the stratosphere. Fig. 3 illustrates how different chemical reactions affect ozone levels when they combined. Again, we studied this over a four-month period to see their long-term effects. Starting with measured data as the baseline [25] plotted in black dotted curve, the red curve presents the combined impact of all chlorine-, nitrogen oxides-, and bromine-depleting cycles (Cl+NO_x+Br), while the orange curve shows the combined effect of both chlorine- and nitrogen oxides-cycles (Cl+NO_x). The vellow curve represents the combined influence of chlorine- and bromine-cycles (Cl+Br), and the green line shows the collective effect of nitrogen oxides- and bromine-cycles (NO_x+Br). It can be seen that combined cycles compounded the effects, leading to additive ozone depletion. Detailed calculation results along the altitude of the stratosphere are listed in Table 2. Interestingly, despite the intensification of ozone depletion, the peak location of ozone distribution remains unchanged, suggesting that the combined depletion cycles will not alter the overall distribution pattern.

As seen in Table 2, the peak of all five cases remained at the same location close to z = 39 km, with the measured concentration of 5.33 ppm, and a slightly decreased peak concentration of 5.23 ppm for Cl+Br cycles, 5.11 ppm for NO_x+Br cycles, 5.03 ppm for Cl+NO_x cycles, and 5.02 ppm for Cl+NO_x+Br cycles. The averaged concentration of the measured 4.01 ppm decreased from a small change of 3% to 3.88 ppm for Cl+Br cycles to a large change of 8% to 3.69 ppm for Cl+NO_x+Br cycles. As for the thinning of the overall ozone abundance above the Antarctica, it reduced from the measured 281 DU, to a small change of 2% to 275 DU with co-existing Cl+Br depleting cycles to a large change of 9% to 256 DU for all combined Cl+NO_x+Br depleting cycles. As expected, the most depleting combination was when all depleting reactions were in

Combined Influence of Ozone-Depleting Chemical Reactions on Ozone Distribution



Fig. 3 Combined impacts of ozone-depleting chemical reactions on ozone concentrations and distribution: comparison of different combination of chlorine cycle, NO_x cycle, and bromine cycle, with the initial measured data.

Ozone-depletion cyc	les						
A 14: to a J = (1)	Ozone concentration (ppm)						
Altitude(km)	Measured O ₃	(Cl+NO _x Cycles)	(Cl+Br Cycles)	(NO _x +Br Cycles)	(Cl+NO _x +Br Cycles)		
45	3.912	3.912	3.912	3.912	3.912		
43.5	4.469	4.377	4.442	4.388	4.370		
42	4.882	4.740	4.839	4.764	4.732		
40.5	4.923	4.723	4.859	4.764	4.712		
39	5.332	5.031	5.229	5.107	5.019		
37.5	5.308	4.930	5.163	5.038	4.913		
36	5.066	4.609	4.843	4.782	4.588		
34.5	4.761	4.281	4.488	4.499	4.257		
33	4.561	4.096	4.267	4.336	4.071		
31.5	4.175	3.757	3.888	3.995	3.733		
30	3.962	3.556	3.658	3.811	3.530		
28.5	3.952	3.523	3.604	3.817	3.492		
27	3.951	3.482	3.537	3.827	3.438		
25.5	3.953	3.589	3.621	3.847	3.535		
24	3.952	3.849	3.859	3.873	3.785		
22.5	3.800	3.701	3.672	3.724	3.602		
21	3.437	3.347	3.265	3.368	3.204		
19.5	3.322	3.235	3.030	3.256	2.979		
18	2.862	2.788	2.456	2.805	2.425		
16.5	2.006	1.953	1.848	1.966	1.816		
15	1.550	1.494	1.453	1.503	1.425		
Avg.	4.01	3.76	3.81	3.88	3.69		
DU	281	269	261	275	256		
Change of O ₃ profile		-6.54%	-5.26%	-3.38%	-8.15%		

Table 2Combined influences of ozone-depleting cycles on ozone concentrations and distribution: averaged concentration,total ozone abundance (DU), and percentage changes of the distribution profile (%).

effect, or the combined $Cl+NO_x+Br$ cycles. Notably, depleting cycles involving chlorine (Cl) exhibited a more significant impact compared to those without Cl, as seen in both Fig. 3 and Table 2.

3.3 Sensitivity Analysis of Cl-, NO_x-, and Br-Depleting Cycles on Stratospheric Ozone

Calculations and sensitivity analysis for various ozone-depletion cycles were conducted with varied initial concentrations for each cycle, by adjusting the concentrations at intervals of 25%, 50%, 100%, 200%, and 400% of the baseline value (100%, at time = 0), along the altitude from 15 to 45 km in the stratosphere. Our calculations were carried out over a four-month period to assess a longer term impact of different depleting cycles on ozone concentrations and distribution, if such a change from as low as 25% to as

high as 400% does happen. It is noted that the initial ozone distribution data were taken from the average of actual measurements spanning from June 2005 to 2019, serving as a reference baseline of 100% for the planned comparison [25].

3.3.1 Sensitivity Analysis of Combined Depleting Cycles (Cl+NO_x+Br)

Fig. 4 shows the impact of combined depleting cycles of $Cl+NO_x+Br$ on ozone concentrations for a four-month period of calculations, starting with a low concentration of 25% for each depleting chemical species (Cl, NO_x, and Br) measured in the stratosphere. The curves represent different concentration levels: blue curve for 25%, green curve for 50%, yellow curve for 100%, light blue curve for 200%, and red curve for 400%. The detailed results of calculation in Table 3showedthatthe blue curve for 25% exhibited a lower

Sensitivity Analysis: Comparative Impact of Cycles (Cl+NOx+Br) on Ozone Distribution and Profile at 25%, 50%, 100%, 200%, and 400%



Fig. 4 Sensitivity study: Impact of combined depleting cycles (Cl+NO_x+Br) on ozone concentrations and distribution at various concentration levels of 25%, 50%, 100%, 200%, and 400% of the depleting chemical species (Cl, NO_x, and Br) measured.

impact on ozone depletion with a peak of 5.179 ppm at around z = 39 km. With increasing concentration to 50%, ozone depletion dropped to 5.125 ppm and further to 5.019 ppm, 4.809 ppm, and 4.408ppm at 100%, 200%, and 400% respectively, all around z =39km.This shows that increasing the depleting chemical concentrations does cause increased thinning (depletion) of ozone concentrations, but the peak of the ozone layer remains at the same location.

Additionally, we further assess the impact and quantify the change of total ozone abundance expressed in DUs above the South Pole. The original, measured total ozone abundance of 281 DU decreased over a four-month period by 3% to 273 DU for the 25% interval, by 5% to 268 DU for the 50% case, by 9% to 256 DU for the 100% case, by 27% to 206 DU for the 200% case, and to a maximal depletion of thinning by 60% to 114 DU for the 400% level. It is evident that increasing chlorine beyond 200% may cause substantial depletion of ozone over a four-month period

that may drop the total ozone abundance to below 220 DU, defined as the "ozone hole". Both Fig. 4 and Table 3 showed clearly the relationship between the concentration levels of combined ozone-depleting gases (Cl+NO_x+Br) and ozone concentrations, ozone layer profile, ozone depletion and hole.

3.3.2 Sensitivity Analysis of Chlorine Catalytic Depleting Cycle (Cl)

In this Section, we focus on the sensitivity test solely on the chlorine catalytic depleting cycle, delineated in Eqs. (4)-(8) in Table 1. We assume that all other ozonedepletion cycles exhibited no impact on ozone behavior in the stratosphere by setting the reaction rate constants of Eqs. (9)-(14) in Table 1equal to zero. With the same hypothetical approach of ozone depletion testing in the previous Section, we vary the initial, measured concentration (100%) of chlorine gas in the stratosphere [16] to a lower value of 25% and 50%, or to a higher value of 200% and 400%, and observe the ozone dynamics and changes over a four-month period.

Ozone sensit	Ozone sensitivity for combined cycles (Cl+NO _x +Br)							
Altitude	Ozone concentration (ppm)							
(km)	Initial O ₃	25%	50%	100%	200%	400%		
45	3.912	3.912	3.912	3.912	3.912	3.912		
43.5	4.469	4.408	4.395	4.370	4.321	4.224		
42	4.882	4.795	4.774	4.732	4.648	4.484		
40.5	4.923	4.811	4.778	4.712	4.583	4.333		
39	5.332	5.179	5.125	5.019	4.809	4.408		
37.5	5.308	5.126	5.055	4.913	4.631	4.110		
36	5.066	4.859	4.773	4.588	4.226	3.584		
34.5	4.761	4.556	4.467	4.257	3.862	3.174		
33	4.561	4.369	4.283	4.071	3.676	2.992		
31.5	4.175	4.006	3.928	3.733	3.369	2.736		
30	3.962	3.807	3.724	3.530	3.167	2.527		
28.5	3.952	3.801	3.700	3.492	3.095	2.379		
27	3.951	3.794	3.675	3.438	2.953	2.105		
25.5	3.953	3.822	3.726	3.535	3.125	2.427		
24	3.952	3.886	3.852	3.785	3.655	3.396		
22.5	3.800	3.727	3.685	3.602	3.440	3.029		
21	3.437	3.358	3.307	3.204	2.907	1.951		
19.5	3.322	3.223	3.152	2.979	2.081	0.167		
18	2.862	2.763	2.685	2.425	0.696	0.018		
16.5	2.006	1.948	1.908	1.816	1.390	0.103		
15	1.550	1.493	1.467	1.425	1.346	0.246		
Avg.	4.01	3.89	3.83	3.69	3.33	2.68		
DU	281	273	268	256	206	114		

Table 3Quantification of combined cycles (Cl+NOx+Br) impact on ozone distribution above the Antarctica over a four-monthperiod at different concentration level of respective chemical species (Cl, NOx, and Br) measured.

Fig. 5 plots the calculated results of ozone concentrations and distribution profile under different levels of chlorine gas over a four-month period. The impact of chlorine gas on ozone depletion was evidently large, particularly in the upper stratosphere from z = 25 km to z = 40 km, while the peaks of the distributions remained around the same altitude of z =39 km. The averaged ozone concentration in the stratosphere for the initial case was 4.01 ppm, which decreased slightly to 3.97 ppm for the 25% case (navy blue curve), to 3.94 ppm for the 50% case (green curve), to 3.88 ppm for 100% case (yellow curve), to 3.75 ppm for the 200% case (light blue curve), and to 3.51 ppm for the 400% case (red curve), respectively. Consequently, this ozone depletion led to a reduction in total ozone abundance above the South Pole from 281 DU to a small ozone thinning of 280 DU for the 25% concentration level, and to a maximal thinning of 9%

of ozone, or 257 DU, for the 400% case. Moreover, the large change of ozone concentrations for different amount of chlorine gases was clearly observed in the mid-stratosphere with altitudes from z = 25 km to z = 39 km. This increased sensitivity correlates directly with the higher level of chlorine concentrations in the mid-stratosphere [26].

3.3.3 Sensitivity Analysis of Nitrogen Oxides (NO_x) Depleting Cycle

In this section, we conducted a sensitivity analysis on the influence of ozone concentration from the NO_xdepleting cycle in Eqs. (9)-(11) in Table 1. Similar to the previous analysis of chlorine influence, we set the reaction rate constants of chemical equations of both Cl- and Br- depleting cycles to zero, and adjust the concentrations of NO_x along the altitude of the stratosphere to be at the intervals of 25%, 50%, 100%, 200%, or 400% of its original value derived from

Sensitivity Analysis: Comparative Impact of Chlorine Cycle (Cl) on Ozone Distribution and Profile at 25%, 50%, 100%, 200%, and 400%



Fig. 5 Sensitivity study: Impact of chlorine catalytic depleting cycles (Cl) on ozone concentrations and distribution above the South Pole at various concentration levels of 25%, 50%, 100%, 200%, and 400% of the initial, measured Cl concentrations over a four-month period.





Fig. 6 Sensitivity study: Impact of NO_x- depleting cycles on ozone concentrations and distribution above the South Pole at various concentration intervals of 25%, 50%, 100%, 200%, and 400% of the initial, measured NO_x concentrations over a four-month period.

measured data [16]. Using the transient mass balance equations in Eq. (15), we calculated the concentrations of ozone, atomic oxygen, and other concerned chemical species along the altitude of the stratosphere for a fourmonth period to assess the impact of NO_x -depleting cycle, as shown in Fig. 6.

Fig. 6 shows the impact of NO_x variations on ozone concentrations and depletion for different concentration levels, as depicted by navy blue curve (25%), green curve (50%), yellow curve (100%), light blue curve (200%), and red curve (400%). Similar to the influence of chlorine gas, a family of curves in Fig. 6 showed an evident depleting impact of NOx concentration shifts on the reduction of ozone concentrations (the ozone depletion). While the peak of the ozone distribution remained in the upper stratosphere, the average ozone concentration along the altitude of the stratosphere decreased from the original 4.01 ppm to 3.94 ppm for the 25% case, to 3.88 ppm for the 100% case, and further to 3.66 ppm for the 400% case for a four-month period. The ozone depletion by NO_x led to a reduction in total ozone abundance above the South Pole from 281 DU to a small ozone thinning of 278 DU for the 25% concentration level, and to a maximal thinning of 6% of ozone, or 263 DU, for the 400% case. It should be noted that nitrogen oxides NO_x have been one of the most problematic criterion pollutants in the world, primarily generated from burning fossil fuels, either in large-scale coal- and natural gas-fired electric utility power plants or in billions of gasoline- and diesel-fired cars and trucks [17, 18]. Should more such NO_x formed by human activities at the ground level are somehow escaping through the cleansing air of moisture and droplets in the troposphere, and manage to ascend to the stratosphere, there will be more ozone depleted. The ozone layer may thus be diluted and distorted by this man-induced NO_x .

3.3.4 Sensitivity Analysis of Bromine Catalytic Depleting Cycle (Br)

The impact of ozone concentration from bromine (Br) catalytic depleting cycles in Eqs. (12)-(14) of Table 1was explored in a similar sensitivity analysis, where reaction rate constants of Cl and NO_x, or k_3 to k_{11} , were all set to zero. The concentrations of bromine gas along the altitude of the stratosphere were selected to be 25%, 50%, 100%, 200%, or 400% of its original value derived from measured data [16]. The concentrations of ozone and other concerned species in the stratosphere were calculated for a four-month period to quantity the impact of Br catalytic depleting cycle, as shown in Fig. 7.

Sensitivity Analysis: Comparative Impact of Bromine Cycle (Br) on Ozone Distribution and Profile at 25%, 50%, 100%, 200%, and 400%



Fig. 7 Sensitivity study: Impact of bromine (Br) catalytic depleting cycles on ozone concentrations and distribution above the South Pole at concentration levels of 25%, 50%, 100%, 200%, and 400% of the measured Br concentrations over a four-month period.

The results in Fig. 7 exhibited much less variations compared to the depleting cycles of chlorine and NO_x . There was a very minor, negligible impact for Br gases on ozone concentrations and distribution in the stratosphere. The fluctuations of ozone reduction observed in the average ozone concentration ranged from the original 4.01 ppm to 4.004 ppm for the 25% case, and to a maximal thinning of 3.980 ppm for the 400% case. Similarly, there was only very minimal decrease in total ozone abundance, from the original 281 DU to 280 DU for all cases. Bromine gases were shown to be not important, nor sensitive for the ozone behavior above the South Pole in the stratosphere. Further investigation may be required to examine or confirm the role of bromine gases on ozone depletion.

4. Summary

This paper provides a thorough exploration of ozone dynamics in the stratosphere, employing an engineering system approach and a 2-D cylindrical model. Through rigorous validation against the measured data, our model demonstrates good accuracy, close match of the observed ozone concentrations at both 20 °S and 90 °N locations. The variation in ozone profiles was within a coefficient of change of less than 17%, while the deviation of the average ozone concentration in the stratosphere was within only 1%. This is believed to reflect the natural differences in atmospheric conditions on Earth.

The impacts of various ozone-depleting reactions and cycles on ozone concentrations and distribution were studied for a four-month period with our 2D ozone model. The focus was on the isolated impact of specific chemical reactions in chlorine (Cl), nitrogen oxides (NO_x), and bromine (Br) depleting cycles. Among these cycles, the chlorine depleting cycle had the most significant impact on ozone concentrations and distribution. While the peak of ozone layer of all depleting cycles remained at the same location close to z = 39 km, the averaged concentration showed a smaller value of 3.87 ppm for Cl cycle, 3.88 ppm for NO_x cycle, and 4.0 ppm for Br cycle, as compared to the original, measure averaged of 4.01 ppm. For the variations of the ozone profile, the Cl cycle showed the largest change (reduction) of -3.21% from the measured profile, as compared to -3.12% for NO_x cycle, and only -0.10% for Br cycle. For the overall ozone abundance above the South Pole, the original, measured value of 281 DU, decreased under the Cl-depleting cycle to a thinner 275 DU, to 275 DU for the NO_x-depleting cycle, and at the same 281 DU for Br-depleting cycle.

When examining the combined effects of Cl, NO_x , and Br cycles on ozone levels, it was found that the combination of these cycles had additive effects on ozone depletion, as expected. The combined cycles Cl+NO_x+Br resulted in the most significant depletion, lowering overall ozone abundance by 9% to 256 DU. The chlorine depleting cycle was found to cause the largest impact, confirming the key role of chlorine (Cl)among other chemical species in the problem of ozone depletion.

Sensitivity analysis was conducted to explore how variations in the initial concentrations of Cl, NO_x, and cycles affect ozone distribution. Br Initial concentrations were adjusted to levels of 25%, 50%, 100%, 200%, and 400% of the baseline value. The combined cycles (Cl+NO_x+Br) showed significant changes in ozone concentrations and distribution. At 25% concentration level, the peak ozone concentration was 5.179 ppm at 39 km altitude, but it dropped dramatically to 4.408 ppm at 400% concentration. The total ozone abundance similarly decreased from 281 DU by 3% to 273 DU for the 25% level, and by 60% to 114 DU for the 400% concentration level. If chlorine gases increase beyond 200%, it would cause substantial depletion of ozone and result in an ozone hole (below 220 DU).

In summary, the study in this paper illustrates that the chlorine catalytic depleting cycle plays the most significant role in ozone depletion, both on itself and in combined with NO_x and Br depleting cycles. Increased concentrations of Cl, NO_x, and Br cycles led to substantial reductions in ozone abundance over the four-month period, with peak reductions occurring around the peak of ozone layer at 39 km altitude. Understanding the impacts of these depleting cycles on ozone concentrations and distribution would help guide the efforts to mitigate ozone depletion and protect the ozone layer. Furthermore, this paper presents a robust 2D model for analyzing stratospheric ozone dynamics, validated well with the measurement data [25]. The model is convenient, efficient, and executable, providing valuable insights into complex ozone phenomena in the stratosphere.

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