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### **REVIEW ARTICLE An Overview of Stratospheric Ozone and Climate Effects**

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#### 1. Introduction

# Ozone, the triatomic allotrope of oxygen (chemical formula: $O_3$ ) is a chemical entity that is much less stable than its diatomic form $O_2$ . It is colourless, odourless gas at considerable concentrations. It exists as a pale blue gas at high concentrations which are weakly soluble in water and easily soluble in inert non-polar solvents. Also, ozone condenses to form a dark blue liquid at a temperature

#### ABSTRACT

Anthropogenic Chlorofluorocarbons (CFCs) compelled stratospheric ozone reduction is one of the significant global environmental issues of this era. Ozone acts as a life saviour in the stratosphere whereas the same plays a role as a secondary air pollutant at tropospheric levels. This review encompasses studies involving the science of ozone destruction with an emphasis on chemical processes involved, minimum ozone features, ozone hole area characteristics, various Ozone Depleting Substances (ODSs), consequences of reduced stratospheric ozone levels, and the different executed international commitments to restrain ozone depletion. It has been perceived that the decrease in stratospheric ozone volume gives away extensively to climate change such as through ozone chemistry fluctuations of polar annular modes and its Greenhouse Gas (GHG) features. Different international ozone layer protection agreements have been performing a major role in limiting stratospheric ozone depletion thereby its adverse effects, and specifically Montreal protocol has been a great success to this point.

of -112 °C. Throughout the Earth's atmosphere, ozone is present only in slight concentration and it makes up only 0.6 ppm of the entire atmosphere by volume. The chief irony is that ozone plays as a life saviour over the stratosphere whereas in the troposphere it acts as a secondary air pollutant. Around 90% of Earth's atmospheric ozone comes from the lower-mid stratosphere, that is in between 15 km and 35 km altitude (Figure 1)<sup>[1]</sup>. The rest 10% is only found at the tropospheric level<sup>[1,2]</sup>. The large-scale

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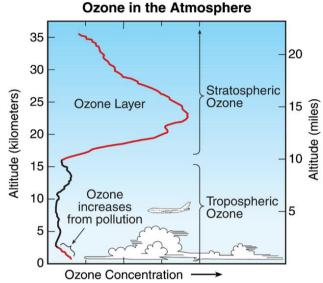
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quasi-horizontal exchange phenomena have a great contribution to making up the intricate vertical distribution of ozone <sup>[3]</sup>. Unlike the middle and high latitudes, the lower latitudes exhibit a less pronounced association of upper atmospheric waves with diurnal ozone variations <sup>[4]</sup>.



**Figure 1.** Vertical characteristics of ozone in Earth's atmosphere. Ozone concentration maximum is found at 23 to 25 km. And a tropospheric local maximum is noted at surface level which is attributed by pollution<sup>[1]</sup>.

A slight hike of ozone in the near-surface layer occurs as a consequence of anthropogenic emissions. Between 15 km and 35 km altitudes, a prolific amount of ozone is seen, and of which is present with maximum abundance at the 23 km to 25 km region. Therefore, the same region is often termed as an ozone layer <sup>[1,5]</sup>. It acts as a shielding layer for Earth from injurious solar Ultraviolet (UV) radiation effects. Even with energy-weak UV radiation, ozone gets split into molecular oxygen and free atomic oxygen. The production of atmospheric ozone is seriously connected with the dynamic equilibrium between ozone and oxygen. This equilibrium nowadays is badly affected by anthropologic halocarbon emissions. Human-induced surface ozone emissions make air polluted in the troposphere <sup>[6]</sup>. On a multi-annual temporal scale, extra-polar lower stratospheric ozone is regulated by distinct atmospheric dynamic processes <sup>[7]</sup>. By the manifestation of various photochemical reactions, maximum ozone mixing ratios are observed in the tropical middle stratosphere <sup>[1]</sup>. And that the maximum stratospheric ozone mixing ratio is present only in the range of ten molecules per one million air molecules. Nonetheless, it has found a profound significance in life on Earth. Also, there exists an assumption that the evolution of life on Earth became possible only after the set-up of the atmospheric ozone layer <sup>[1]</sup>. The

ozone layer care for life forms and various ecosystems on Earth <sup>[8]</sup>. The major objective of the article is to understand the stratospheric ozone condition under certain international commitments and evaluate it with its current circumstances. Also, the anthropogenic impression of the stratospheric ozone concentration will be examined along with some powerful chemical and dynamical processes involved in changing stratospheric ozone abundance. The annual worldwide casualties affected by air pollution are over 6 million, which is far more than that

biologically detrimental Ultraviolet-B (UV-B) radiations

are largely absorbed by stratospheric ozone and thus the

pollution are over 6 million, which is far more than that of AIDS, Malaria, and Tuberculosis combined. Surface ozone is a Greenhouse Gas and a major pollutant harmful to humans, crops, and ecosystem productivity <sup>[9-13]</sup>. And it is not emitted straightaway. Instead it is produced by nitrogen oxide (NO<sub>x</sub>) chemical reactions and by Volatile Organic Compounds (VOCs)<sup>[9]</sup>. It is observed that a significant part of anthropogenic emission contribution has shifted from Europe and North America to Asian countries like India, China, the Republic of Korea, and Japan<sup>[14-17]</sup>. Furthermore, across these countries, surface emissions only dominate in the tropospheric ozone variations (Wang Wei-Chyung and Tanaka 2009). Surface ozone levels are found to be high in rural regions as there is forest agricultural production, and water supply <sup>[18]</sup>. Thus, their ozone production causes injuriously over ecosystems with effects like plant toxicity, cell damage, impacts on individual organisms, their ecological interactions, and effects on chemical and biological processes <sup>[14,19]</sup>. Superabundant intake of ozone can cause physiological alterations in photosynthesis, respiration, carbon allocation, stomatal functioning, and on volatile organic compound emissions. Also, it gives rise to growth reduction, seed production cutback, intensified senescence, and varied vulnerability toward biotic and abiotic stresses <sup>[14,20]</sup>. More extended ozone intake by plants can bring alteration in gene expression, species composition, and carbon sequestration <sup>[21]</sup>. Excessive exposure to ozone is capable of bringing leaf stipples, and leaf lesions<sup>[22]</sup>.

#### 2. Ozone Measurement Techniques

A corporal foundation for the development of optical estimation of ozone started in the second half of the nineteenth century. In 1920, Fabry and Buisson reported daily measurements of ozone effectively for the first in history by comparing wavelength parameters of sunlight with different intensities <sup>[23]</sup>. Afterward, several instruments came into the field of ozone measurement including electrochemical Ozonesondes <sup>[24,25]</sup>. Balloon-borne Ozonesondes have been carrying a significant role in measuring and verifying ozone and ozone-depleting chemicals [26].

The aggregate quantity of ozone present in a column that vertically extends from the Earth's surface up to the upper layer of the atmosphere is called Total Column Ozone (TCO). This can be calculated by ground-based and satellite measurement systems. These are reported in Dobson Units (DU). This unit can be defined as, "all the ozone over a confined volume is compressed down to a temperature of 0 °C and a pressure of 1 atm (STP), then it forms an ozone block of 3 mm thickness which is considered to be equal to 300 DU ozone" <sup>[27]</sup>.

#### 2.1 Dobson Spectrophotometer

In 1924, the British meteorologist Gordon Miller Dobson invented an ozone-measuring instrument called a Dobson spectrophotometer or simply a Dobson spectrometer. This instrument comprises a double quartz-prism monochromator which allows simultaneous measurements at two wavelengths over the UV region (Figure 2) <sup>[28]</sup>. At these two wavelengths the absorption rates will be different <sup>[29]</sup>. So this instrument measures a series of wavelength pairs <sup>[28]</sup>. And the Total Column Ozone (TCO) estimation is done by comparing the absorption of each pair of wavelengths. The final TCO can be determined by finding the weighted mean average of individual estimates. The double pair wavelengths can be utilised for the assessment, i.e., 305.5/325.4 and 317.6/339.8 nm <sup>[30]</sup>.

Bass-Paur ozone absorption coefficients are utilized for the estimation <sup>[31]</sup>. The two circumstances to be taken care of when performing individual observations are: (i) looking at the direct sun in a clear sky, and (ii) measuring Solar Zenith Angle (SZA) should be less than 84° <sup>[32]</sup>. The total evaluated error of Dobson spectrometer measurements was found to be 3% <sup>[33]</sup>.

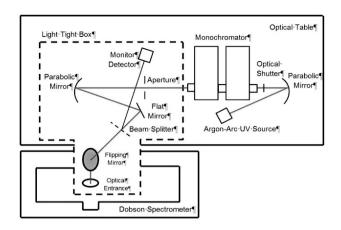


Figure 2. A schematic diagram of Dobson spectrophotometer<sup>[28]</sup>.

#### 2.2 Brewer Spectrophotometer

This instrument follows an analogous working principle to Dobson spectrophotometer to find out TCO (Figure 3)<sup>[34]</sup>. It comprises a focal plane mounted with five highly precise exit slits accompanied by a single diffraction grating. These slits are optimised for the assessment of ozone and SO<sub>2</sub> which are respective to five wavelengths namely 306.3 nm, 310.1 nm, 313.5 nm, 316.0 nm, and 320.0 nm. A Fabry lens is also placed after the exit slits through which a reduced image of a diffraction grating is produced on a 10 mm diameter photocathode of a photomultiplier tube. The sequential experimentation is carried out by moving a mask in front of each slit. When the slits are kept static, a stable wavelength calibration is achieved <sup>[34]</sup>. The instrumental resolution of the Dobson spectrometer was found to be in the range between 0.9 nm and 3.0 nm whereas the Brewer instrument has a much better resolution of 0.6 nm<sup>[35]</sup>.

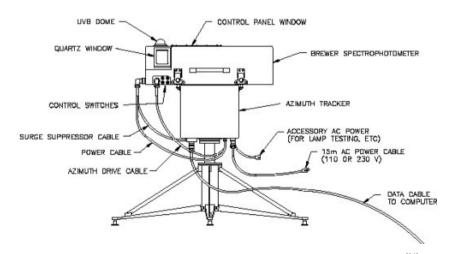


Figure 3. An experimental arrangement of Brewer spectrophotometer <sup>[34]</sup>.

## 2.3 SAOZ (System D'Analyse Par Observations Zenithales)

It is an UV-visible spectrometer with a resolution of 1 nm in that the observation is taken looking at sunlight scattered at Zenith during the dusk time. The ozone's Chappuis absorption (450-650 nm) is assessed by the instrument at an SZA between  $86^{\circ}$  and  $91^{\circ}$  <sup>[36,37]</sup>. As SAOZ instruments are capable of performing observations in visible wavelength range, the same are capable of undertaking measurements throughout the year <sup>[38]</sup>. As the air-mass factor is considered in retrieving observations, the error is found to be 3% and it may be higher in ozone-hole circumstances <sup>[39]</sup>.

## 2.4 Differential Optical Absorption Spectrometer (DOAS)

This is a similar kind of instrument as SAOZ in which both UV and Visible channels are present in the spectrograph. And the ozone estimations are undergone at 490-555 nm wavelength range and at an SZA between 84° and 90°. This method brings an accuracy of 2%<sup>[40]</sup>.

#### **2.5 Satellite Measurements**

In addition to the ground-based measurements, there exist many artificial satellites for measuring columnar ozone and retrieving data; namely Total Ozone Mapping Spectrometer (TOMS), Ozone Monitoring Instrument (OMI), Global Ozone Monitoring Experiment (GOME), Microwave Limb Sounder (MLS), Indian National Satellite System 3D (INSAT-3D), Indian National Satellite System 3D Repeat (INSAT-3DR), etc. In comparison with ground- and aircraft-based instruments, satellite instruments have the potential to expand their working vicinity<sup>[41]</sup>. Alongside synoptic scale satellite measurements, groundbased, balloon-borne, models, and aircraft measurements with certain temporal and spatial resolutions are also incorporated in order to ease the analysis of polar ozone science [42,43]. Moreover, reanalysis model data like Modern-Era Retrospective analysis for Research and Applications (MERRA), Modern-Era Retrospective analysis for Research and Applications-2 (MERRA-2), Global Modelling and Assimilation Office (GMAO), etc. can also provide ozone columnar measurements.

#### 3. Life Cycle of Ozone

Stratospheric ozone is formed by photochemical reactions. It involves the interaction of solar radiation with different atmospheric gases specifically with oxygen. In 1930, Chapman put forward a theory of the formation of atomic oxygen which says the dissociation of  $O_2$  in presence of UV photons is responsible for the formation of atomic oxygen (Equation (1)). And these highly reactive oxygen atoms react with oxygen molecules to form ozone molecules (Equation (2)).

$$O_2 + O_2 \rightarrow O + O$$
  $\lambda \le 242 \text{ nm}$  (1)

$$O_2 + O + M \rightarrow O_3 + M \tag{2}$$

The M stands for any other molecule in the atmosphere most probably the abundant molecule like  $N_2$  or  $O_2$ . And for the energy equilibrium of the reaction, this neutral body is needed. The dissociation of ozone molecule into O and  $O_2$  is also undergone in the presence of UV photons (Equation (3)).

$$O_3 + hv \rightarrow O_2 + O \tag{3}$$

And the ozone is lost by reacting with free oxygen atoms (Equation (4)).

$$O_3 + O \to 2O_2 \tag{4}$$

The formation of ozone by solar UV photolysis is an endothermic reaction whereas the ozone dissociation reaction is an exothermic reaction. Since the presence of sunlight produces more ozone, Chapman's theory overestimates the tropics. With the help of meridional circulation, the transportation of tropically produced ozone to extra-tropics is taken place. This produced ozone gets destructed by particular highly reactive substances present over the stratosphere known as Ozone Depleting Substances (ODSs). These substances are majorly emitted at the surface of the Earth by various anthropogenic activities<sup>[1]</sup>.

The catalytic destruction cycles balance the stratospheric chemical ozone production of the Chapman cycle. One of such cycles (Cycle-1) is shown below:

$$XO + O \rightarrow X + O_2$$
$$X + O_3 \rightarrow XO + O_2$$

Cycle-1: Net:  $O + O_3 \rightarrow 2O_2$ 

X, the catalyst will get reproduced at the end of every cycle. A diatomic oxygen molecule is produced in the net reaction by the annihilation of one monoatomic oxygen and ozone molecule. In this way, thousands of ozone molecules get destructed and removed from the stratospheric layer. These catalyst gas molecules are produced by different anthropogenic actions occurring at the surface of Earth, and then these get reactive once reach stratosphere by some photochemical reactions<sup>[1]</sup>.

There are certain common radical families which cause the depletion of ozone.  $HO_x$  family is one such family which involves atomic hydrogen H, hydroxyl radical OH, and the hydroperoxyl radical HO<sub>2</sub>. Likewise, another radical nitric oxide (NO) also causes large ozone destruction. Furthermore, the reactive halogen gases

namely chlorine (Cl and ClO) and bromine (Br and BrO) also contribute to ozone destruction <sup>[1,44,45]</sup>.

In wintertime across polar regions, the low-temperature circumstances at Polar Stratospheric Clouds (PSCs) assist in the large concentration of ClO. And it decreases the atomic oxygen concentrations there suppressing the occurrence of Cycle-1. Instead, the situation enhances two other cycles namely Cycle-2 and Cycle-3 which are shown below:

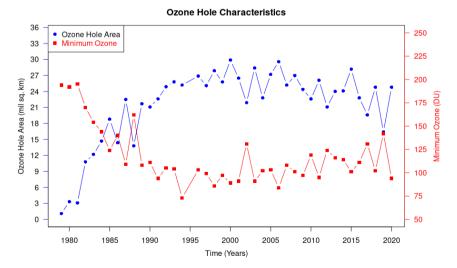
 $\begin{array}{c} \text{CIO} + \text{CIO} + \text{M} \rightarrow (\text{CIO})_2 + \text{M} \\ (\text{CIO})_2 + \text{hv} \rightarrow \text{CIOO} + \text{CI} \\ \text{CIOO} + \text{M} \rightarrow \text{CI} + \text{O}_2 + \text{M} \\ 2(\text{CI} + \text{O}_3 \rightarrow \text{CIO} + \text{O}_2) \\ \text{Cycle-2:} \quad \text{Net:} \qquad \text{O}_3 + \text{O}_3 \rightarrow 3\text{O}_2 \\ \text{CIO} + \text{BrO} \rightarrow \text{CI} + \text{Br} + \text{O}_2 \\ \text{CI} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\ \text{Cycle-3:} \quad \text{Net:} \qquad \text{O}_3 + \text{O}_3 \rightarrow 3\text{O}_2 \end{array}$ 

Noticeably, Cycle-2 and Cycle-3 only occurred when there is enough ClO production come about. And more ClO abundance is detected in wintertime. Accordingly, Cycles 2 and 3 are responsible for the majority of Antarctic and Arctic ozone destruction. Also, the losses from these catalytic destruction cycles are controlled by temperature variations<sup>[46]</sup>.

## 4. Role of Ozone Hole and Stratospheric Aerosols

It was noticed the declination within stratospheric ozone in the early 1970s across the extra-tropics <sup>[47]</sup>. All through the same decades, an investigation into the ozone trend in association with Supersonic Transport (SST) fleets and Chlorofluorocarbons (CFCs) was undertaken <sup>[48]</sup>. By the 1990s, the ozone destruction in both hemispheres got boosted up forward. Surprisingly, the Ozone Mass Deficiency (O<sub>3</sub>MD) in the northern hemisphere exceeded the spring deficiencies of Antarctica in 1993 and 1995. Generally, winter-spring deficiencies are observed to be more than summer deficiencies <sup>[48]</sup>. And this ozone-depleted area is often referred to as an "Ozone Hole". This area became the minimum till date in 1994 with an ozone measurement of about 73 DU (Figure 4) (https://ozonewatch.gsfc.nasa.gov/).

This rapid spring stratospheric ozone decline over Antarctica caused the onset of different hypotheses in the 1980s. Then came forward two major hypotheses on unmeasured chemical reactions and on a dynamical concept consisting of a potential systematic variation in Antarctic circulation. Then this dynamical hypothesis got wide acceptance because of the intense correlation between lower stratospheric temperature and column ozone variations. Nonetheless, soon later this dynamic theory got rejected by the innovative integrated ground-based and aircraft measurements. And that observation led to the successful explanation of the significant correlation between chemical reactions happening at the lower stratosphere with the ozone depletion. Thus this chemical hypothesis prevails over the rejected dynamic hypothesis <sup>[49]</sup>. Consequently, both hemispheric ozone depletions are all noticed to be accompanied by a cold temperature of around 192 K and polar stratospheric cloud chemistry<sup>[49]</sup>. In recent past decades, during austral spring, it is comprehended that certain chemical reactions which involve chlorine, bromine, hydrogen, and nitrogen cause the depletion of ozone severely over the polar region<sup>[1,50]</sup>. Distinct maps of TCO exhibit the disparity and advancement in the ozone hole area during October



**Figure 4.** Southern hemispheric ozone hole area variation and minimum ozone features from 1979 up to 2020. Source: https://ozonewatch.gsfc.nasa.gov/.

month for the period 1979 up to 2022 (Figure 5). The specific area is measured by representing a constant line of ozone of 220 DU (https://ozonewatch.gsfc.nasa.gov/). This particular value is selected because historic observations of pre-1979 have not shown a value of less than 220 DU. The 1979 evolving ozone hole characteristics continue till the end decade of the twentieth century. In the year 2002, it was observed that the particular Antarctic ozone hole is getting healed, but then again it resumed depletion but at a reduced pace. Similarly, in the year 2019, the ozone layer was expressing a recovery phase which further again went in vain by 2020 October.

In addition to that, recent direct Antarctic measurements have revealed the significant influence of bromine and chlorine compounds on columns with less than 220 DU ozone levels <sup>[51]</sup>. When the ozone level declines under 220 DU, it is investigated an upsurge in biologically vigorous UV radiation from 80 to 400% over the tropical, Arctic, and Antarctic regions <sup>[52]</sup>. The southern hemispheric climate change has been occurring in accordance with its ozone depletion throughout the recent past decades <sup>[53]</sup>. Around the previous 40 years, a poleward shift of extratropical circulation happened due to ozone depletion along the polar region. Subsequently, the subtropical precipitation and thereby hydrological cycle over the region has also become substantially disturbed <sup>[54]</sup>. In spring, the inert halide salts across the polar boundary layer got converted into highly reactive halogen species which deplete the ozone around the region up to an extent of nearly zero level <sup>[55]</sup>.

A new parameter termed Equivalent Effective Stratospheric Chlorine (EESC) got introduced so as to particularize the ease of ozone variability investigation. A temporal examination of this EESC together with the Freon-11 (CFC-11) is conducted and got to find a strong

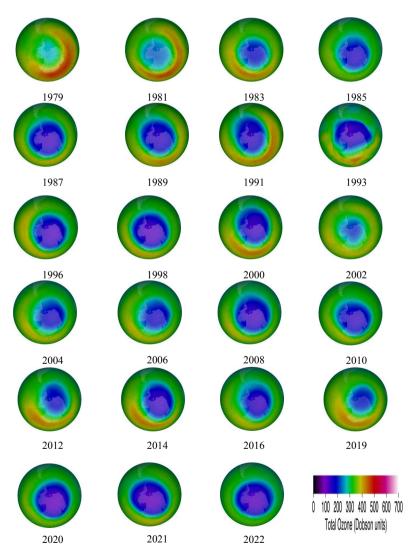
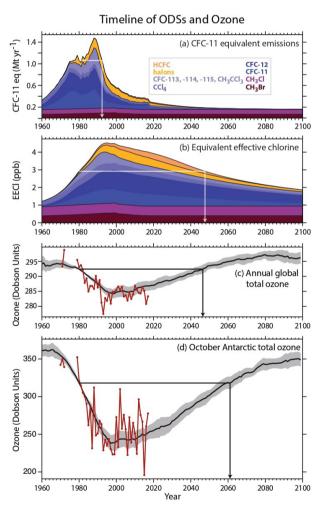


Figure 5. Antarctic ozone hole monthly mean characteristics for October from 1979 up to 2022 (with intermediate year intervals; https://ozonewatch.gsfc.nasa.gov/).

peak during the late 1990s and early 2000s (Figure 6) <sup>[56]</sup>. And the corresponding ozone levels experienced a considerable decline. A strong recovering tendency of the ozone hole is also observed from the projected analysis <sup>[56]</sup>.

Since the 1980s, the Antarctic ozone layer has been experiencing a significant decline in the ozone mixing ratio of 0.01 to 0.1 ppm during spring seasons. And this corresponds to a regional chemical loss of around 95% to 99%. On the contrary, the north-polar stratospheric ozone loss has been considerably better than that of the south with a maximum value of only 0.5 ppm. Nevertheless, in spring 2020 a huge ozone loss happened over the Arctic at an altitude of around 18 km. The Ozonesondes observations reveal a local chemical loss of about 93%. A strong and long lasted cold polar vortex was observed to be the major cause of this unforeseen Arctic chemical loss <sup>[57]</sup>.



**Figure 6.** Characteristic temporal variation of Ozone and Ozone Depleting Substances (ODSs). An ozone hole restorative condition is witnessed after a profound decline during the late 1990s and early 2000s<sup>[56]</sup>.

The progress of recent three-dimensional stratospheric

ozone models has helped extensively in predicting reliable ozone level fluctuations in comparison with the onedimensional models of the 1970s. Flawless computational model development and refined prediction obviously come from impeccable observation data [58]. These are majorly produced by volcanic eruptions, and infrequently by aerosols formed from other natural and anthropogenic actions <sup>[59]</sup>. Highly vigorous volcanic eruptions in the tropics cause the ejection and transport of large quantities of gases like sulphate, hydrogen halides, etc. into the stratosphere from where they spread globally by the action of large-scale meridional circulations [52,60]. The 1991 Mount Pinatubo volcanic eruption incident caused an explosive injection of sulphate aerosols into the stratosphere. It was observed that this event had resulted in polar region ozone depletion in the following few years. Though it caused the ozone layer destruction, the "Earth cooling effect" contributed by those sulphate aerosol ejections was praised and suggested as a remedial tool to defend against global warming. On the other hand, the assessment of the required quantity of sulphates in order to compensate with the amount for surface warming CO<sub>2</sub> and its ozonedepleting action made that trial impossible <sup>[61]</sup>. Similarly, another study on aerosols of polar regions revealed that the Solar Proton Events (SPEs) caused short-term ozone depletion events by the production of nitrate aerosols would also result in significant impacts on our biosphere <sup>[62]</sup>. The aerosol optical depth (AOD) spectral variations triggered by anthropogenic actions are found to be playing a key role in ozone variations and Earth-Atmosphere radiation balances over the Arctic which in turn will affect the regional and global climate change <sup>[63]</sup>.

Many human activities are observed transcending natural processes and causing precarious aftermaths in the environment. Production of high-risk chemical compounds like CFCs is also observed to be contributing to certain dangerous events such as ozone layer depletion. Furthermore, these human activities have currently levelled up to consider profound geological forces. The activities like fossil fuel burning, land-use changes, and deforestation are some examples. Therefore, an assignment of a new term "Anthropocene" has come into the limelight compulsorily in order to represent the current geological epoch. And it is considered that the epoch started in the year 1784 when the designing of James Watt's steam engine has got taken place <sup>[64]</sup>.

## 5. Polar Vortex and Polar Stratospheric Clouds

The area in the atmosphere at which the rotational motion of fluid occurs with respect to a particular axis is called an atmospheric vortex. And the Polar Vortex is one such vortex observed over polar regions where an eastward movement of fluid (gaseous atmosphere) takes place. The northern hemispheric polar vortex will be centred at the Arctic and the southern hemisphere will have a vortex with a rotation axis around Antarctica <sup>[65]</sup>.

1) Arctic Polar Vortex: In the northern hemisphere, the Arctic air being the coldest in comparison with its southward air circulation will undergo a cold temperate vortex flowing from west to east. And as the zone of the interface of cold Arctic air with warm subtropical air, there at the margin of intersection witnesses the polar front jet stream <sup>[66]</sup>. In the year 2019-2020, the winter-spring seasons experienced a remarkably low temperature and an established boreal polar vortex which led to widespread ozone depletion in the Arctic region <sup>[57]</sup>. And these ozone depletions are only localized over polar vortex regions <sup>[67]</sup>.

**2)** *Antarctic Polar Vortex:* Analogous to the Arctic vortex system, in the southern hemisphere, a cold vortex formation establishes which interface with southern hemispheric mid-latitude air where causing the formation of the austral polar frontal jet stream <sup>[66]</sup>. In general, these polar vortices comprise a large low-pressure area that circulates in an anti-clockwise direction in the northern hemisphere and in a clockwise direction southern hemisphere. More importantly, it is an eastward rotation of atmospheric fluid in both hemispheres. The vortex shape can vary from a circle to some irregular meanders extending up to the equator <sup>[65]</sup>.

Polar Stratospheric Clouds (PSC) are clouds present at an elevation range of 15 km up to 25 km. They are well witnessed during winter time over polar regions at twilight. It is found that these high-altitude clouds cause ozone depletion in the stratosphere. These PSCs are formed at very lower temperatures. PSCs are associated with ozone destruction mainly in two ways; PSCs provide a surface for the establishment of reactive ozone-depleting chlorine, and these PSCs will take part in the removal of nitrogen compounds that regulate the destructive nature of chlorine <sup>[59,68]</sup>. In the 2019-2020 winter, a massive loss of Arctic stratospheric ozone occurred. Other analogous exceptional Arctic stratospheric ozone depletions happened in 2015-2016, 2010-2011, and 1996-1997 winter times. All these events owe to the lowest polar vortex temperatures which made it easy for the formation of PSCs. This resulted in the denitrification and dehydration of the Arctic polar vortex that further caused the enhancement of ozone depletion [69].

#### 6. Ozone and Climate Change

There exists a convincing association between stratospheric ozone chemistry and annular modes <sup>[70]</sup>. An annular mode is a significant pattern of climatic variability observed over northern and southern hemispheres. Northern Annular Mode (NAM) is intense during boreal winter and Southern Annular Mode (SAM) is larger during austral summer. Both the annular modes play a strategic responsibility in climate change <sup>[71]</sup>.

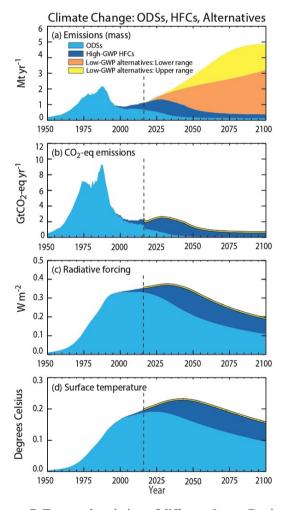
The significant causes of the impact of ozone layer depletion on climate change are due to solar radiation absorption characteristics of ozone, its GHG features, and alteration of tropopause height <sup>[72]</sup>. In order to retrieve a better quantification of UV radiation, since the 1990s several stations have been operating for the continuous measurement of radiation. The UV radiation quantification depends on factors namely latitude, longitude, height, incident angle, azimuth angle, wavelength, and polarisation <sup>[73]</sup>. For the sake of reversal of climate change effects, the Paris Accord-2016 has put forward certain suggestions to phase out the usage of hazardous synthetic refrigerants. Currently, the GHGs used in refrigeration, air-conditioning, and heatpumping systems are regulated under Kyoto protocol-1997<sup>[74]</sup>. By choosing natural refrigerants, further intensification in GHGs can be regulated <sup>[74]</sup>.

In 1992, so as to provide a comprehensive scientific base and plan for World Meteorological Organization (WMO)—UNEP ozone assessments, a project named Stratospheric Processes And Role in Climate (SPARC) was implemented by World Climate Research Programme (WCRP)<sup>[75]</sup>. There originated three ozone assessment panels of experts under UNEP namely the Environmental Effects Assessment Panel (EEAP), Scientific Assessment Panel (SAP), and Technology and Economic Assessment Panel (TEAP). The EEAP works on the impacts of UV rays on human health, global climate change, terrestrial and aquatic ecosystems, and on air quality attributes<sup>[76]</sup>.

By the comparison of UV measurements with model simulations, UV-B radiation is found to be decreasing at the Earth's surface. Therefore, the Montreal Protocol is observed to be showing its efficacy. On the contrary, though the ozone layer over Antarctica is getting recovered, the corresponding reduction in UV-B radiation has not been witnessed <sup>[77]</sup>. During the summer season, it is perceived that the Antarctic ozone depletion strongly controls climate change in the southern hemisphere <sup>[78]</sup>. Also, in another analysis, it has been shown that the Arctic ozone inter-annual variability makes modifications in the climate of northern hemispheric mid-latitudes. In the course

of positive Arctic ozone anomaly events, it is found that it strengthens the precipitation over central China. And during its negative phase, the precipitation along the same region is suppressed <sup>[79]</sup>. The concept of potentials namely Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) has been widely used in policymaking by integrating them with ozone and climate issues <sup>[80]</sup>. A comparative study between the emissions, radiative forcing, and surface temperature by integrating all these with variations of ODSs, high GWP HFCs, and low GWP HFCs has been conducted (Figure 7). Throughout the observations, a co-existing feature of high GWP HFC is noticed along with ODS to a considerable extent <sup>[56]</sup>.

The cases of UV radiation-caused cutaneous malignant melanoma are showing an increasing trend in northern European countries. Even though, Australia and New Zealand are the leading countries in terms of melanoma affected. The same countries are showing a good recovery rate as well<sup>[81]</sup>.



**Figure 7.** Temporal variation of different Ozone Depleting Substances (ODSs) and their co-existence with emissions, radiative forcing, and surface temperature <sup>[56]</sup>.

#### 7. Consequences of Ozone Layer Depletion

- As ozone is an effective absorber of UV radiation, its depletion will cause a substantial increase in ground-level abundance of UV radiation <sup>[82]</sup>.
- The decline in stratospheric ozone will cause an upsurge in extratropical tropospheric ozone level <sup>[80]</sup>. When the precursor molecules such as NOX, and VOCs react with sunlight, surface ozone is produced. And this is a key air pollutant. And these precursor molecules can be formed by biomass burning, etc. <sup>[83]</sup>. Such processes are enhanced by the tropospheric oxidizer OH <sup>[84]</sup>.
- Increased production of Vitamin D because of the extensive solar UV radiation availability over the Earth's surface <sup>[85]</sup>.
- Cataract is the major reason for blindness in the world. And it is frightening that a 1% decrease in the ozone layer would cause a 0.3% to 0.6% increased chance of cataracts <sup>[86,87]</sup>. Because of the oxidative agents like oxygen produced by UV radiation, the cornea and lens of the eye would get damaged. In addition to cortical cataracts, photokeratitis, pterygium, and macular degeneration can also be caused <sup>[88]</sup>.
- Overexposing to UV due to the depletion of the ozone layer would cause sunburns and skin cancers. There are mainly two categories of skin cancers. One is melanoma cancer and the second one is non-melanoma. The former is more detrimental than the latter. In non-melanoma, there includes basal cell carcinoma and squamous cell carcinoma<sup>[89]</sup>.
- The fatal UV-B radiations can damage DNA. It can harm biomolecules like lipids, proteins, and nucleic acids. It can even enhance mutations in DNA <sup>[90]</sup>.
- As a consequence of ozone layer depletion, reduced oxygen production got enhanced in the Earth's atmosphere which further initiate the formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). This produced hydrogen peroxide is toxic and a water pollutant. Thus it adversely affects human health <sup>[91]</sup>.
- UV radiation exposure would also result in some deadly lungs related health issues like Emphysema, Asthma, and Bronchitis <sup>[90]</sup>.
- Furthermore, the ozone layer depletion affects other terrestrial and aquatic ecosystems very dangerously and it would alter various biogeochemical cycles <sup>[91]</sup>.
- Due to the stratospheric ozone destruction, the mean age of Antarctic summer air in the lower stratosphere has become increased. This is mainly because of intense Antarctic downwelling that fetches older

air from the upper to lower stratosphere. Also, a seasonal obstruction in austral polar vortex breakup stops new mid-latitude air from mixing up with the internal old air of the vortex <sup>[92]</sup>.

#### 8. International Commitments

The necessary monitoring of the deterioration of the ozone layer has been of primary importance since the beginning of the 1980s <sup>[93]</sup>. From the early 1980s, there have been several international ozone assessments that paved the foundation for the Vienna convention and Montreal protocol <sup>[23]</sup>.

*Vienna Convention—1985:* By the initiative of the United Nations Environment Programme (UNEP), the conciliation of the Vienna convention began in January 1982. And all these initiatives were taking place under the leadership of a UNEP council formed in May 1981 to protect the ozone layer <sup>[94]</sup>. The Vienna convention was just a preamble and legal foundation for the Montreal protocol. It does not depend on some particular chemical compound's legitimate regulation at a global level. The Vienna ozone convention was one of the first international agreements on environmental protection <sup>[94]</sup>.

Montreal Protocol-1987: It is an international trea-

tv signed on 26th August 1987 to reduce the production and emission of ODSs. But it came into effect on 26th August 1989. Since then many amendments and adjustments to this protocol have entered into force. Around nine revisions have come into operation till 2018 (Table 1). Many modifications have been implemented to the Montreal protocol to date [95]. In the 1992 revisions, CFCs have got substituted by relatively less depleting Hydrochlorofluorocarbons (HCFCs) <sup>[96]</sup>. Later on, HCFCs have also got replaced by Hydrofluorocarbons (HFCs) as those were noticed to be having an ozone-depleting potential of nearly zero. Although, HFCs have got turned up to be causing global warming as per the 1997 Kyoto protocol assessments <sup>[95]</sup>. Kigali amendment on 15th October 2016 came into a decision to phase down HFCs under the Montreal protocol. Then attended 197 countries came into an agreement to cut down the manufacturing and consumption of HFCs by greater than 80% by the next 30 years. To date, we can consider this Montreal Protocol a success and it is one of the greatest successful multilateral environmental agreements in history. United States National Oceanic and Atmospheric Administration (NOAA) observed that the concentration of various ODSs has fallen below 1980 levels after an increase in the early 2000s. They also predicted that the concentration of

		· ·
Year	Policy Decisions	Scientific Reports
1981		The Stratosphere 1981: Theory and Measurements. WMO No. 11.
1985	Vienna Convention	Atmospheric Ozone 1985. Three volumes. WMO No. 16
1987	Montreal Protocol	
1988		International Ozone Trends Panel Report 1988. Two volumes. WMO No. 18.
1989		Scientific Assessment of Stratospheric Ozone: 1989. Two volumes. WMO No. 20
1990	London Adjustment and Amendment	
1991		Scientific Assessment of Ozone Depletion: 1991. WMO No. 25.
1992		Methyl Bromide: Its Atmospheric Science, Technology, and Economics (Montreal Protocol Assessment Supplement). UNEP (1992)
1992	Copenhagen Adjustment and Amendment	
1994		Scientific Assessment of Ozone Depletion: 1994. WMO No. 37.
1995	Vienna Adjustment	
1997	Montreal Adjustment and Amendment	
1998		Scientific Assessment of Ozone Depletion: 1998. WMO No. 44.
1999	Beijing Adjustment and Amendment	
2002		Scientific Assessment of Ozone Depletion: 2002. WMO No. 47.
2006		Scientific Assessment of Ozone Depletion: 2006. WMO No. 50.
2007	Montreal Adjustment	
2010		Scientific Assessment of Ozone Depletion: 2010. WMO No. 52.
2014		Scientific Assessment of Ozone Depletion: 2014. WMO No. 55.
2016	Kigali Amendment	
2018		Scientific Assessment of Ozone Depletion: 2018. WMO No. 58.

 Table 1. International commitments on ozone layer depletion

CFCs would also decrease below 1980 levels by 2050 <sup>[95]</sup>. Furthermore, ODS manufacturing sank from 1.2 million tons in 1986 to 23000 tons in 2016. By the same token, its consumption also has got plunged to 22000 tons in 2016 from 86000 tons in 1986 <sup>[76]</sup>. The UNEP Ozone Secretariat investigated that the global usage of CFC would have been more than 3 million tons in 2010 and would have become 8 million tons by 2060. if it happens to result in the depletion of half of the ozone layer by 2035. In 2018, a study revealed that the cut down of chlorine from ODSs caused healing of ozone hole <sup>[97,98]</sup>.

#### 9. Conclusions

At surface and tropospheric levels warming is instigated by the ozone hole formation whereas at the stratosphere it provides a cooling effect <sup>[99]</sup>. Being the major side-effect of ozone layer depletion, increased UV-B on the surface of Earth caused substantial health issues for humans and other living beings. Over the Arctic, the earlier chlorine activation and the depletion occurred by 2010 and 2019 Novembers respectively for 2011 and 2020. In addition, it longed till the end of spring. These events are attributed to the weak polar vortices of corresponding seasons. Contrary to ozone destruction, the primary impact of ODS on the Arctic is observed to be affected by the effect of radiative warming <sup>[100]</sup>.

All the international treaties for the protection of the ozone layer have their own participation in restraining the production of ODSs. Nearly all ODSs fall under the category of GHGs. Therefore they too broadly contribute to global warming <sup>[101]</sup>. Remarkably the Montreal protocol has been a great success so far, the inorganic chlorine level was noticed to be decreasing and the ozone hole reinvigoration was found to be happening over the Antarctic stratosphere. The long lifespan of the precursor molecules delays the expected speedy recovery of the ozone layer up to the rest of the twenty-first century. However, by the mid-century, the mid-latitude ozone will come back to the 1980s level. In addition to that, the UV-B irradiance at mid-latitudes is also getting declined even though it has some attributions with aerosols and clouds. Nonetheless, polar latitudes show a substantial increase in the same. Overall, specific uncertainties exist with respect to the rate of recovery of the ozone layer. Unexpected hike in the emission of natural ODSs namely CH<sub>3</sub>Cl and CH<sub>3</sub>Br along with the climate change-induced stratospheric structural-changes which further will obstruct the ozone depletion recovery <sup>[102]</sup>. The world without a Montreal protocol would have been having tripled UV radiation of current time by 2065 across the mid-latitudes [8]. A robust interaction between GHG-induced climate change and ozone destruction scenarios has been contemplated throughout recent past decades. Self-awareness in reducing ODS partly benefited in decreasing GHG emissions globally. The projected decline in radiative forcing with respect to CFC cut-down has been underestimated. Although ozone shows tendencies for recovery, the future evolution of UV-B radiation will be determined by the ongoing climate change and the decreasing ODSs. Recent studies show cloud cover generally decreases, leading to increased solar radiation, apart from the high latitudes, where no significant changes are observed. Total ozone shows an increasing trend due to the reduction in ODSs, while a decrease is observed after 2050 on a near-global scale due to the increasing GHGs. UV trends are a combination of changes in ozone and cloud cover, while at high latitudes, the decreasing surface albedo in the second half of the 21st century has a significant influence on the surface UV radiation.

Rather than the frequent variants in the usage of synthetic refrigerants, natural refrigerants are the long-term alternatives <sup>[103]</sup>. The present-day anticipated annual global total ozone recovery to 1980s levels is approximated to the mid-2040s. The Antarctic ozone layer restoring noticed to be happening every September <sup>[104]</sup>. The climate change—ozone depletion association would be a challenging task for the scientific world to project the future ozone scenario flawlessly. Persistent high quality ground-based and satellite ozone measurements only will assure the errorless projections <sup>[69]</sup>.

#### **Authors' Contribution**

M. M. Karadan: Conceptualization of the study, data archiving and preparation of the initial draft of the manuscript; P.V.S. Raju: Interpretation of the concept and finalization of the manuscript; P.C.S. Devara: Guidance and help in finalization of manuscript.

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#### **Conflicts of Interest**

No potential conflict of interest was reported by the author(s).

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