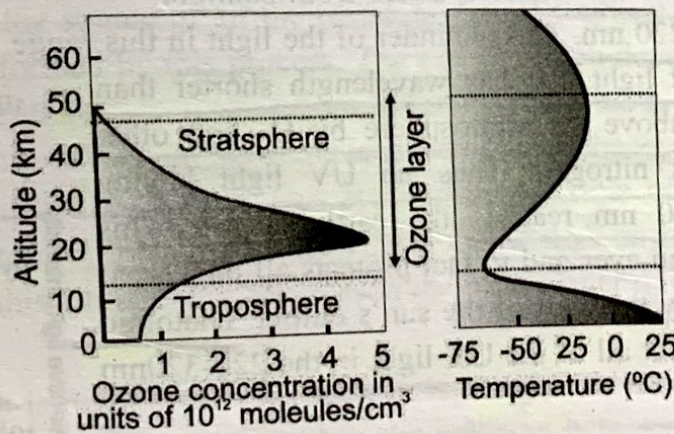
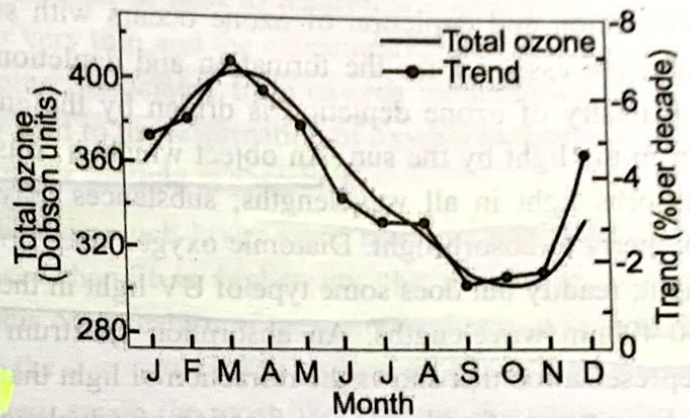


OZONE DEPLETION

OZONE DEPLETION

It is a pale blue gas with pungent odour. The total amount of atmospheric ozone that lies over given point is measured in terms of Dobson units (DU). 1DU is equal to 0.01mm or 0.001cm thickness of pure ozone at the density, it would possess if it were brought to ground level pressure (1atm) and 0°C temperature. On average this total overhead ozone at temperate latitude amounts to about 350 Dobson units which will be equivalent to 3.5mm if brought down to ground level. Because of stratospheric winds, ozone is transported from tropical regions where most of it is produced towards Polar Regions. Thus closer to the equator you live the less of total amount ozone that protects you from UV light. Ozone concentration in the tropics usually average 250 DU whereas those in sub polar region averages 450 DU. There is some natural variation of ozone concentration with season with highest level in the early spring and lowest in the fall.

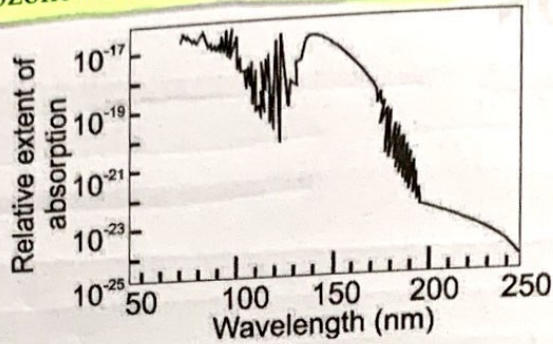


Troposphere ozone

Its average concentration is 0.05 ppm which varies from 0.01 in winters and 0.07 ppm in summers. In troposphere it acts as pollutants. In plants it causes stunted growth and can affect metabolic processes. It is also toxic to animals including human and has an acceptable intake value of 0.1 ppm. If humans are exposed to high concentration of ozone, it causes breathing disorders like bronchitis, hypertension etc.

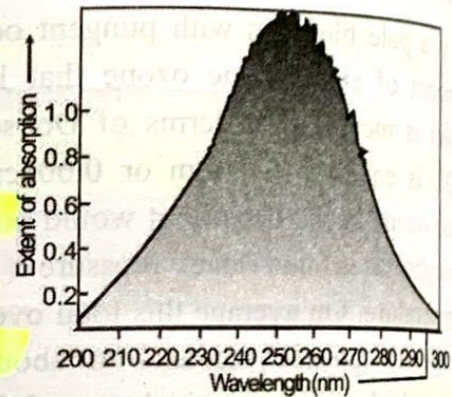
Stratosphere ozone

Average concentration is about 0.1 ppm. However within stratosphere it shows vertical variation with maximum intensity at about 25 km over tropical areas, 21 km over mid latitude and 18 km over arctic region. Collectively, most of the ozone is located in the region from 15-35 km known as ozone layer.

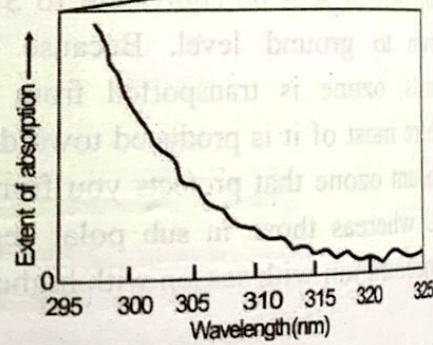


Stratospheric Ozone Depletion and Formation

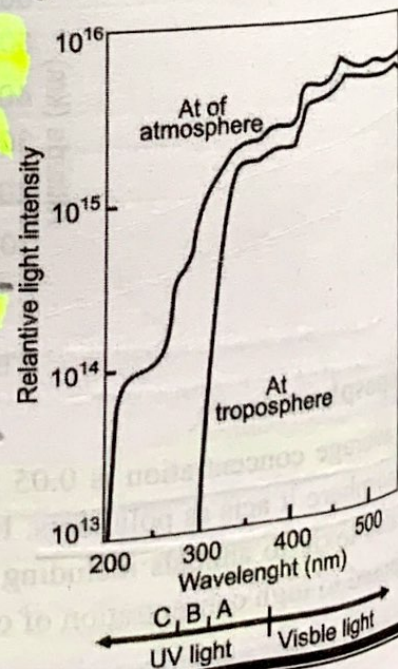
Formation and depletion of ozone occurs with sunlight and UV rays are essential for the formation and depletion of ozone. The chemistry of ozone depletion is driven by the energy associated from the light by the sun. An object which is considered as black absorbs light in all wavelengths; substances may differ in their property to absorb light. Diatomic oxygen does not absorb visible light; readily but does some type of UV light in the range between 50-400nm wavelengths. An absorption spectrum is a graphical representation that shows the refraction of light that is absorbed by a given types of molecule as a function of wavelength.



In the given graph, the efficient light absorbing behaviours of oxygen molecule for the UV region between 70-250nm is shown. The fraction of light absorbed by oxygen varies dramatically with wavelength. As a result of these absorption characteristics the oxygen gas that lies above the stratosphere filters from sunlight, most of UV light from 120-220 nm. The remainder of the light in this range is filter by the oxygen in the



stratosphere. The Ultraviolet light that has wavelength shorter than 120 nm is filtered in and above the stratosphere by O_2 and other constituents of air such as nitrogen. Thus no UV light having wavelength shorter than 220 nm reaches the earth surface. This screening protects our skin and eyes and in fact protects all biological life from extensive damage by this part of the sun's output. Diatomic oxygen also filters some but not all of the UV light in the 220-320nm range.



Ozone filters out all of the sun's UV light in the range 220-290 nm range which overlaps UV-C (220-280). However ozone can absorb only a fraction of sun's UV light in the 290-320 nm range. The remaining amount of sunlight of such wavelength, 10-30% depending upon latitude, penetrates the atmosphere to the earth's surface. Thus ozone is not completely effective in shielding or sealing us from light

in the UV-B region (280-320). Since, the absorption by ozone falls off in an almost exponential manner with wavelength in this region, the fraction of UV-B that reaches the troposphere increases with increasing wavelength.

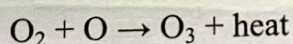
Because neither ozone nor any other constituent of the clean atmosphere absorbs significantly in the UV-A range (320-400nm), most of this, the least biologically harmful type of UV light penetrates to the earth surface, NO₂ does absorb UV.A light but is present in such a small concentration in clean air that its net absorption of sunlight is quite small.

What Maintains Ozone Concentration?

- UV-Rays
- Concentration of ozone

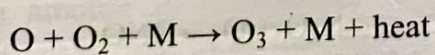
Formation of ozone in the stratosphere and destruction depends upon both catalytic and non-catalytic processes. The formation reaction generates sufficient amount of heat to determine temperature of this region of atmosphere. Above the stratosphere, the air is very thin and the concentration of molecule is so low that most oxygen exists in atomic form having being dissociated from oxygen molecule by UV-C. The eventual collisions of oxygen atom with each other lead to the reformation of oxygen molecule which subsequently dissociates photo chemically again when more sunlight is absorbed.

In the stratosphere itself, the intensity of UV-C light is much lower since much of it is filtered by oxygen that lies above. In addition the air is denser than it is higher up; the molecular oxygen concentration is much higher in the stratosphere. For this combination of most stratospheric oxygen exist as O₂ molecule rather than as atomic oxygen. Because the concentration of oxygen molecule is relatively high and the concentration of atomic oxygen is relatively small, the most likely fate of the stratospheric oxygen atom created by the photochemical decomposition of oxygen is not their mutual collision to reform oxygen molecule rather they are more likely to collide and react with undissociated intact diatomic oxygen molecule that results in the production of ozone.



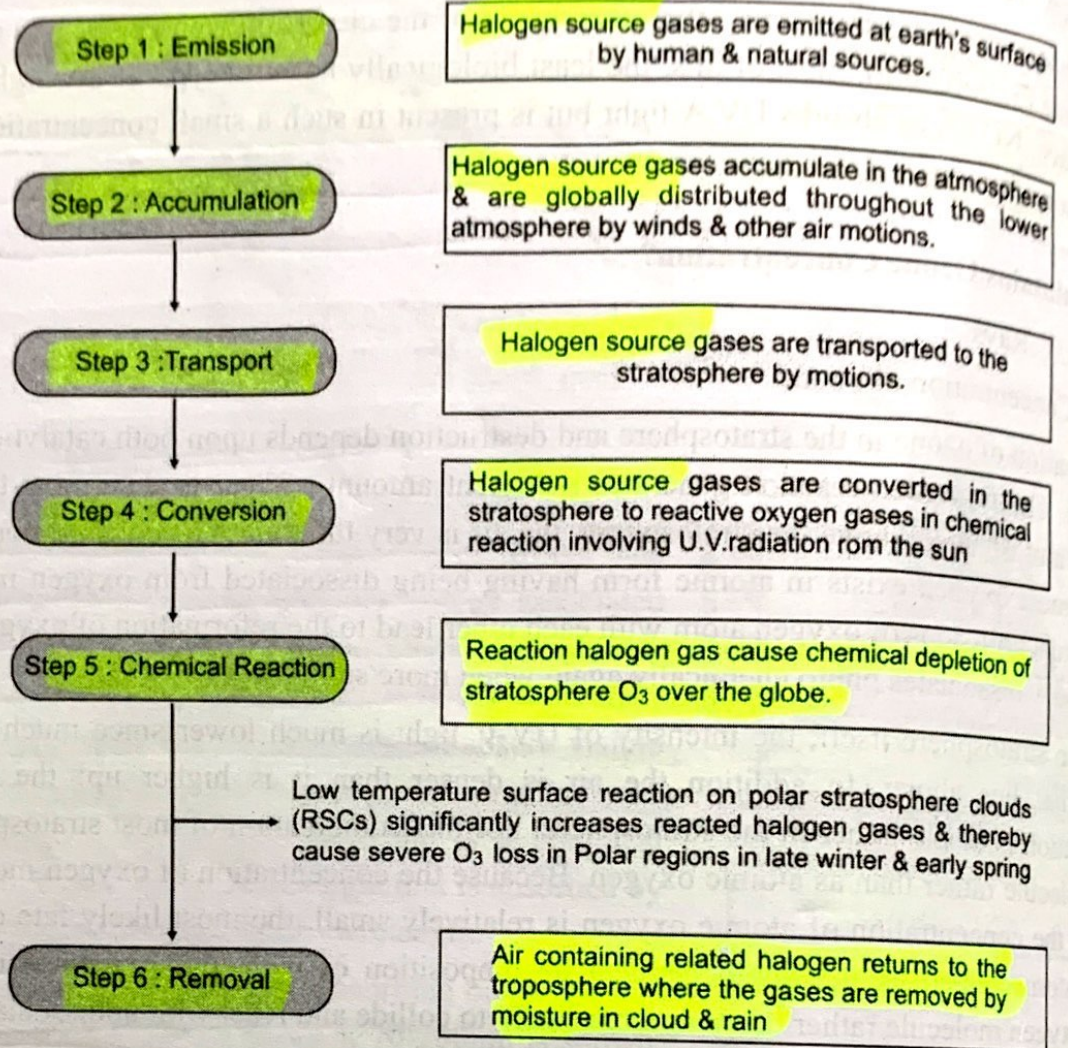
Indeed, this reaction is the source of all the ozone in the stratosphere. During day light hours, the ozone is consistently being formed by this process. The rate of which depends upon the amount of UV light and therefore, the concentration of oxygen atom and molecule at the given altitude. At the bottom of the stratosphere, the abundance of oxygen molecule is greater than at the top because air density increases progressively as one approach like surface. However, relatively little of the oxygen at this level is dissociated and thus little ozone is formed because almost all the high energy UV has been filtered from sunlight before it descends this altitude. For this reason the ozone layer does not extend much below the stratosphere.

A third molecule which is described as M, such as N₂ or H₂O or even another oxygen molecule is required to carry away the heat energy generated in the collision between atomic oxygen and diatomic oxygen that produces ozone. Thus, the reaction is written more realistically as;



Within the stratosphere, the air at a given altitude is cooler than that which lies above it. The general name for this phenomenon is temperature inversion, because cool air is denser than hot air, it does not

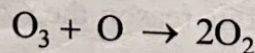
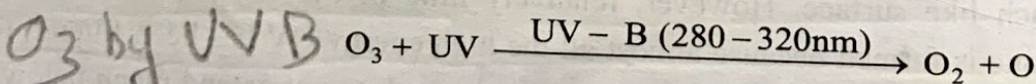
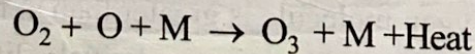
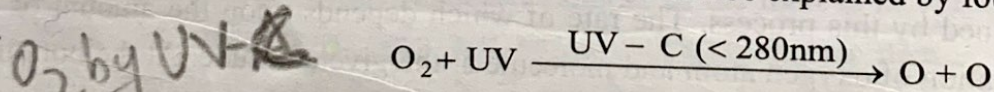
raise simultaneously due to force of gravity consequently the vertical mixing of air in the stratosphere is a very slow process composed of mixing in the troposphere. The air in this region is therefore stratified hence, the name stratosphere.



Steps of depletion of stratospheric ozone

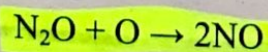
Classical Chapman Theory

According to this, natural sink and source of ozone can be explained by four reactions:

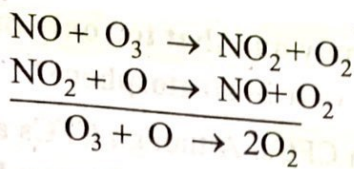


Catalytic Ozone Destruction by Nitrous Oxides

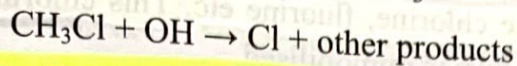
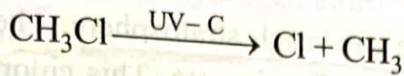
It is produced when molecules of nitrous oxide rise from the troposphere to the stratosphere where they may collide with an excited oxygen atom produced by photochemical decomposition of ozone.



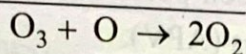
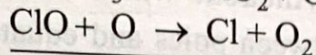
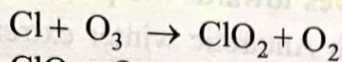
The nitrous oxide molecule formed above catalytically destroys ozone by extracting oxygen atom from ozone and forming Nitrogen dioxide.



Catalytic Activity of Chlorine



Chlorine is extracted from methyl chloride by following above reactions:

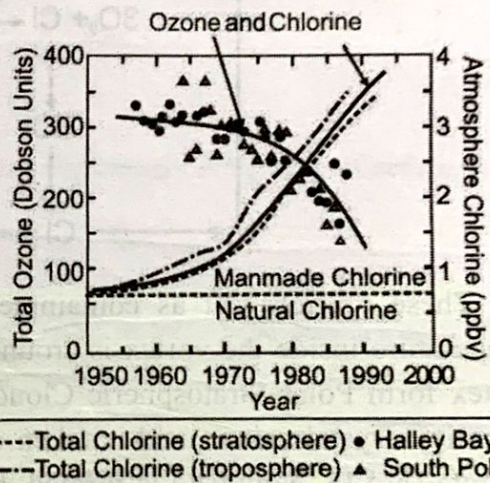


Cl & N₂O
catalyze O₃
destruction

Thus, one molecule of chlorine can undergo this cycle for about 10,000 times causing destruction of about 1 lakh ozone molecules. Another important catalyst in stratosphere is the hydroxyl free radical (-OH), which originates in the reaction of excited oxygen atom with water or methane molecule.

History of Ozone Hole

Antarctic ozone hole was discovered by Joe C. Farman around 1985, who worked with British Antarctic Survey. CFC production and use started around 1930s and they became important industrial product by 1950. By 1970s, James Lovelock noticed that CFC level are increasing in the atmosphere, as there was belief that CFCs are inert molecule, so they are harmless. Mario Molina and Sherwood Rowland (got Nobel Prize along Paul Curzon) has around 1974 shown that ozone could be destroyed by chlorine released from CFCs. Thereafter many models were made to predict the effect of chlorine on ozone, but no one ever predicted the presence of ozone hole.



In 1992, a team of British Antarctic Survey lead by Joe C. Farman at a station called Halley bay found that over Antarctic ozone level decrease by 40% during September-October (Antarctic spring). In 1995 they published a paper in 'Nature' and also contacted NASA, which with the help of NIMBUS, measuring the level of ozone with the machine called TOMS (Total Ozone mapping spectrometer), confirmed the presence of ozone hole. In 1986, US launched NOZE-I (National Ozone Expedition-I). In 1987, NOZE-II was launched which was an international effort in which India also took part. It included ground based systems, weather balloon, satellite measurement and aeroplane flying right through the ozone hole. All these efforts proved the existence of ozone hole and the experiment also measured the levels of other compounds like chlorine, fluorine, hydroxyl radicals etc.

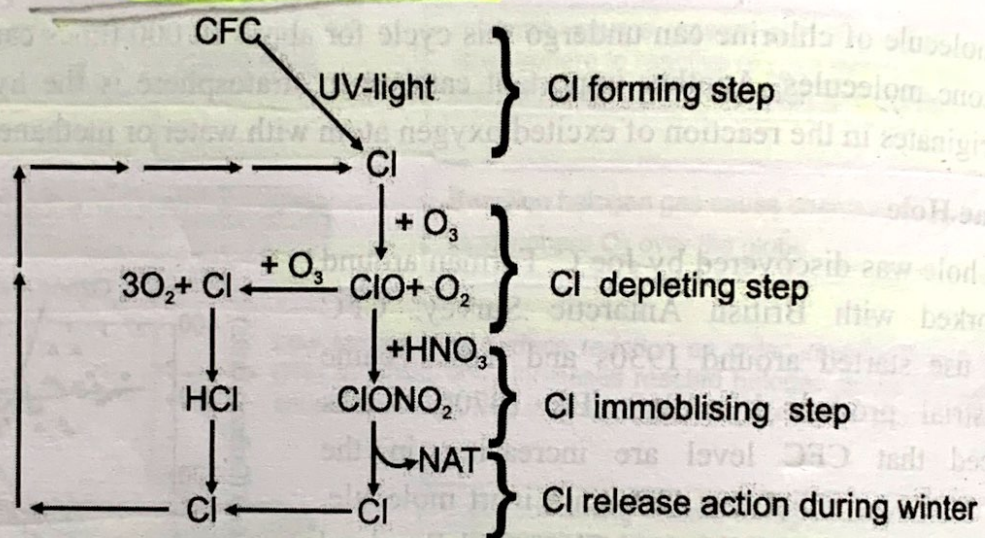
Observations reveal that as the amount of chlorine increased in the atmosphere, there was a consequent decrease in the amount of ozone. The chlorine monoxide was traced to CFCs; the two main catalytically inactive molecules containing chlorine in the stratosphere are chlorine nitrate (ClONO₂) and Hydrogen chloride gas. ClO is produced from chlorine nitrate by removing nitrite as nitric acid.

Why ozone hole appears in Antarctic only and that too only during spring seasons. Despite the fact that ozone is produced throughout the year in stratosphere?

Discovery of ozone hole was linked with CFCs. Although CFCs are produced throughout the world, they caused most of the ozone destruction in the Antarctica and ozone hole also found in Antarctica, the reason being the presence of special conditions in the Antarctica.

CFCs because of their inert nature can reach stratosphere. They are broken down by wavelength of 220 nm or less and thus produce chlorine, fluorine etc. This chlorine immediately combines with nitric acid to form chlorine nitrate and thus is immobilised.

This ClONO_2 along with CFCs moves towards the polar region but it will not cause destruction of ozone as it is present in inert form. With Antarctic winter extreme, dark and cold conditions set in and their temperature developed difference between poles and equator. Cyclone like storms developed over Antarctic is known as Antarctic Polar Vortices (APV).



These vortices act as containment well and separate area inside the vortex from outside. The temperature inside the vortex is around -70 to -80°C, and it contains, O₃, Cl, NO₃, CFCs etc. Inside the vortex form Polar Stratospheric Clouds (PSCs) which are made up of ice crystals. In the formation of these icy crystals nitric acid is taken out which combines with water to form crystals of nitric acid trihydrate (NAT). Now ClO is formed, but for breakdown of ozone light is required so ClO remains non-reactive during Antarctic winter.

With the arrival of spring season and sunlight, ClO reacts with ozone to form molecular oxygen and thus causes the breakdown of ozone. When temperature become warmer in spring, this vortex disappear and the surrounding air comes in which is more nitrified. The mixing of outside air with denitrified air of vortex helps in locking of ClO into ClONO₂.

Ozone Depleting Substances

1. CFCs

They are totally synthetic compounds containing C, H, F, Cl etc. They were discovered in 1928 by Thomas Midgley of General Motors Corporation. Their commercial production started in 1930 by Du-point with the trade name Freon.

Nomenclature of CFCs

1. Conversion of chemical name into commercial name:

Where, X = no. of carbon -1
Y = no. of hydrogen +1
Z = no. of fluorine

2. Conversion of commercial name into chemical name: Add 90 in the numeric value of formula
Number of Cl = $(2n+2) - (\text{number of hydrogen atom} + \text{number of fluorine atom})$

Where, n = Number of carbon atom.

The two most important properties of CFCs are:

- Inertness
- Stability

Uses of CFCs

- As a propellant in aerosol (Perfumes)
- As a refrigerant in Air conditioner and Refrigerators
- In manufacture of foam (Hard foam or Soft foam)
- In manufacture of insulating material
- In disposable food packaging material
- In cleaning electronic circuit
- As a sterilant for medical equipment.

ODP (Ozone Depleting Potential)

It is measure of cumulative effect on ozone for each unit of ozone depleting chemicals released in the atmosphere calculated against the effect of CFC₁₁.

Halons

Discovered in December, 1993. These are extinguishing substances, used in fire fighting machines, they do not contain Chlorine rather they contains Bromine. Br is an element those 100 times more potent in causing ozone destruction than chlorine.

Chemical names of Halons

Example; Halon ABCD

Where, A = no. of carbon atom

B = no. of fluorine atom

C = no. of chlorine atom

D = no. of bromine atom

- Halon 1211 = CF_2ClBr
- Halon 1302 = CF_3Br
- Halon 2402 = $\text{C}_2\text{F}_4\text{Br}_2$

Methyl chloroform (CHCCl₃)

- Used as an industrial solvent and metal cleaning agent
- ODP = 0.12

3. Residence time = 0.7 years

Carbon Tetrachloride (CCl₄)

1. Industrial solvent and grain fumigant
2. ODP = 1.08

CH₃Br (Methyl bromide)

1. Used as soil fumigants against insect pests
2. To certain extent ozone depletion is caused by supersonic flights of N₂ fertilizers

Effect of Ozone Depletion

1. More of the UV in the same range
2. UV of even shorter wavelength will also be reached earth surface

UV rays divided in 3 types

1. UV-A (400-320 nm): They are not harmful and have no mutagenic effect.
2. UV-B (320-280 nm): It converts 7-dihydrocholesterol in vitamin D₃ due to cholecalciferol. Vitamin D helps in fighting with skin rashes and infection but can cause some DNA damage
3. UV-C (less than 280 nm): These are normally absent in UV radiation reaching earth surface as they are absorbed in stratosphere, they are highly mutagenic.

Biological action spectrum (BAS)

It is a series of measurement of a particular biological function across a range of wavelength. It also helps in establishing the relationship between different phenomenon of UV light. BAS helps in calculation of Random Amplification Factor (RAF).

RAF is a measure biological significance of a solar radiation change over a specific wavelength region brought about by particular amount of ozone depletion.

Effect of ozone depletion on Public health

1. Skin cancers

In skin there are two kinds of cell:

- Keratin forming
- Melanin forming cells.

Melanin forming cells absorb UV radiation so they are first to show the effect of UV radiation. The two types of cancers associated with UV radiation are;

- a) Malignant melanoma affects pigment cell
- b) Non melanomas carcinoma affects keratin forming cell.

Malignant melanoma

Its incidence depends on the melanin in the skin, as the concentration of melanin is less in white population than black, so they have 10 times greater chance of having this cancer. Among whites, the people inhabiting Finland, Denmark and Norway are more prone to it. The symptoms include red hair, green eyes, pale and pink skin. It shows sexual variation that is survival rate is about 65% in females and 45% in males. But the incidence rate is higher in...

Non melanomas carcinoma

- Squamous cell carcinoma
- Basal cell carcinoma

According to EPA, 3% decrease in ozone can lead to 200 thousand additional skin cancer cases.

Three other disorders related to UV radiation are-

- a) Xeroderma pigmentosum (which occurs because of inefficiency of DNA repair mechanism)
- b) Sunburns (Erithrima)
- c) Skin rashes and disorders.
- d) Cataract:
 - In this lens become translucent
 - Cornea is damaged and sometimes even retinal detachment can occur.

Other problems related to eye are Photokeratitis (Snow blindness) and symptoms include reddening and swelling of areas around the eyes.

1. Effect on immune system

Increased UV radiation will cause down regulation of Immune system. Generally immune system has two types of cells;

- T-lymphocyte: which cause cell mediated immunity
- B- lymphocyte: which help in formation of antibodies

T-cells are of different types:

- T_4 cells (control AIDS virus)
- Effector cells (Identify and Display the antigen)
- Suppressor cell (T_s): which identify self or non-self

Thus, the lowering immune system in response to UV radiation is because of increase in T_s - cells. In stratum corneum, a substance called uroconic acid is responsible for increase in T_s cells. The uroconic acid occurs in cis and trans form. On exposure to UV-B, this trans form changes into cis form which somehow triggers increase in T_s cells.

2. Effect on environment

Such impact is studied more in case of marine planktons. They are the primary producer in the marine ecosystem. They live in photic zone to carry out the process of photosynthesis. If the UV incidence increases then the initial response of these organisms would be to go deeper and it will have an adverse impact on photosynthesis. According to some estimates of 65% world protein requirements are fulfilled by phytoplankton and in lasts 50-60 years, it has been found that phytoplankton productivity has decreased by 6-12%.

3. Effect on terrestrial environment

- Plants differ in their sensitivity to UV radiation. The initial response of the plants is to produce more of sunscreen like flavanoids, caretenoids, phenols etc.
- There will be reduction in leaf surface area

- Bronzing of leaves
- Change in bud burst and flowering time

GREENHOUSE EFFECT V/S OZONE DEPLETION

Ozone depletion will lead to increase in incidence of shorter wavelength UV rays which will have two impacts:

1. Reduction in photosynthesis and consequent decrease in the amount of carbon dioxide being fixed, so more accumulation of CO₂ which will lead to more global warming.
2. The shorter wavelength UV rays will cause formation of ozone in the troposphere and ozone itself is a GHG. So, formation of more ozone will increase more of global warming.

S. No.	Gases	Atmospheric Life time (years)	Global emission in 2008 (KT/year)	ODP	GWP
1	CFC11	45	52-91	1	4750
2	CFC12	100	41-99	0.82	10900
3	CFC113	85	3-8	0.85	6130
4	CCl ₄	26	40-80	0.82	1400
5	HCFC	1-17	385-481	0.01-0.12	77-2220
6	Halon 1301	65	1-3	15.9	7140
7	Halon 1211	16	4-7	7.9	1890
8	HFC 134a	13.4	149±29	0	1370
9	HFC 23	222	12	0	14200

MONTREAL PROTOCOL

In 1985, a treaty called the Vienna Convention for the protection of the Ozone layer was signed by 20 nations in Vienna. In response to growing concerns, the Montreal Protocol on substances that depletes the Ozone layer was signed in 1987 and entered into force in 1989, in establishing legally binding control for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion.

National consumption of an ODS is defined as the amount that production and imports of the substance exceed its export to other nations. The Protocol provisions are structured for developed countries to act first and for developing countries to follow with some financial assistance. In 2010, the Montreal Protocol becomes the first International treaty to achieve universal ratification by all 196 United Nations Members.

Montreal Protocol was strengthened with amendments and adjustments. Each amendment is named after the city in which the meeting of the Parties to the Montreal Protocol took place and by the year of the meeting.

The initial Protocol called for a 50% reduction in CFC production and a freeze on Halon production. The 1990 London Amendment called for a phase-out of the production and consumption of the most damaging ODS, in developed nations by 2000 and in developing nations by 2010. Copenhagen Amendment accelerated the phase-out date to 1996 in developed nations.

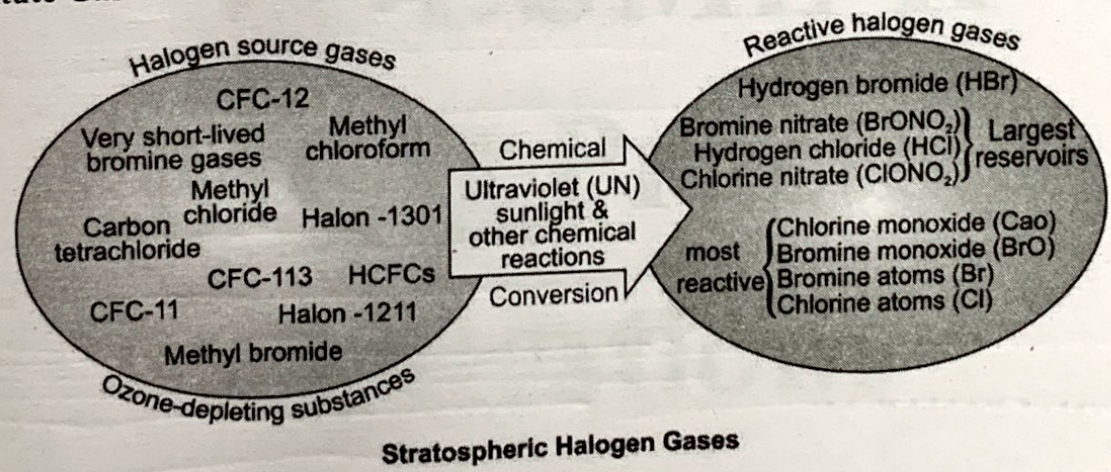
HCFC Substitute Gas

The Montreal Protocol provides for the use of HCFCs as transitional short-term substitute compound for ozone depleting substance with higher ODP such as CFC₁₂. HCFCs are used for refrigeration, in making insulating forms and as solvents. HCFCs are generally more reactive in the troposphere than other ODS, because they contain hydrogen in addition to Cl, F, and C.

HCFCs are 83-98% less effective than CFC₁₂ in depleting stratospheric ozone because their chemical removal occurs primarily in the troposphere. This removal protects stratospheric ozone from most of the halogen content of HCFC emission.

Under the provision of the Montreal Protocol developed and developing countries may continue to use HCFCs as ODS substitutes in the coming decades before they are ultimately phased out. In the most recent adjustment to the protocol, the phase out of HCFCs for all parties was accelerated, so that it will be complete in 2030.

HFCs substitute Gas



Stratospheric Halogen Gases

HFCs are used as long term substitute compounds for CFCs, HCFCs and other ODSs. HFCs contain hydrogen, Fluorine and carbon. HFCs do not contribute to ozone depletion because they contain no Cl, Br or I. As a consequence HFCs are not ODS, and are not subject to the provisions of Montreal Protocol. HFCs and all ODS are relatively active gases that contribute to human induced climate change based on their accumulation in atmosphere. HFCs are included in the basket of gases being control by the Kyoto Protocol of the UNFCCC. The Kyoto Protocol is an international treaty designed to protect climate by controlling emissions from HFCs, CO₂, CH₄, N₂O, PFCs, SF₆. HFC emissions are expected to grow substantially in coming decades as the demands for their use as substitute gases and in new applications increases in developed and developing countries. The climate change contribution from future HFC emission will be minimized when HFCs will very low GWP (less than 100) are chosen to meet growing demands.