OZONE

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Scientist E

What is Ozone

- While oxygen molecule consists of two atoms, ozone molecule consists of three. Extra atom makes a big difference, in some ways that benefit us and in other ways that are harmful. Pale blue gas, slightly soluble in water, more soluble in inert non-polar solvents.
- Less stable than diatomic O_2. Unstable at high concentrations, decaying to ordinary diatomic oxygen (in ½ hour) $2\ O_3 \rightarrow 3\ O_2$, reaction proceeds more rapidly with increasing temperature and decreasing pressure.
- Tropospheric ozone has distinct roles depending upon its altitude - in upper troposphere it is GHG and radiative forcing of tropospheric ozone is about 25% that of carbon dioxide and is the third largest contributor to greenhouse radiative forcing after carbon dioxide and methane. In middle it acts as an atmospheric cleanser and in lower (boundary layer) ozone is criteria air pollutant that require control under NAAQS and it is major component of photochemical smog.
- Stratosphere ozone provide protective shield for life on earth. Exposure of passengers in jet aircraft to stratospheric ozone has recently a matter of concern.
- About 0.01 ppm of ozone in air can be detected through specific sharp odour resembling chlorine bleach. Exposure of 0.1 to 1 ppm produces headaches, burning eyes, and irritation to the respiratory passages.
- Powerful oxidizing agent.

Sources of Tropospheric or Ground-level ozone

Tropospheric Ozone is formed (i) In situ through photolysis of NO_2. Ozone is a secondary pollutant formed by sunlight driven chemical reactions between the O3 precursor gases: VOC, CO, NOX, and CH4 that arise from a wide range of natural and man made sources. and Ozone is also formed (ii) through transport from Stratosphere.

Since 1900 the amount of ozone near the earth's surface has more than doubled.

Average background O3 in the Northern Hemisphere is 35–40 ppb range and can reach as high as 400 ppb during smog episodes.

Ground-level Ozone Formation

$$N2(g) + O2(g) \text{ -----> } 2NO(g) \qquad (i)$$

$$2NO(g) + O2(g) \text{ -----> } 2NO_2(g) \qquad (ii)$$

When the NO2 concentration is well above clean air levels and there is plenty of sunlight, then an oxygen atom splits off from the NO2 molecule. At wavelengths <0.430 µm, NO2 is photolyzed:

$$NO2(g) \xrightarrow{\text{sunlight}} NO(g) + O(g), \qquad (iii)$$

which is quickly followed by:

$O + O_2 + M \longrightarrow O_3 + M$ (iv)

(only reaction that produces atmospheric ozone. M is any "body" with mass, primarily nitrogen or oxygen molecules. Also trace gas molecules/surfaces of objects. M absorbs energy from the reaction, without which combining of O & O2 into O3 cannot be completed.)

Nitric oxide can remove ozone by reacting with it to form NO_2 and O_2, completing the "nitrogen cycle." $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$ (v)

When the ratio of NO_2 to NO is greater than 3, the formation of O_3 is the dominant reaction. If the ratio is less than 0.3, then the NO reaction destroys the O_3 at about the same rate as it is formed, keeping the O_3 concentration below harmful levels.

The cycle time for the three reactions is only a few minutes. Reactions (iv) and (v) are comparatively fast.

Slower photolysis reaction (iii) is usually the rate-limiting reaction for the nitrogen cycle and the reason why ozone is not formed appreciably at night and concentrations are high during the summer months, when temperatures are high and solar radiation is intense.

Ozone accumulates over several hours, depending on emission rates and meteorological conditions. The nitrogen cycle by itself does not generate the high ozone concentrations observed in urban areas. The net effect of the nitrogen cycle is neither to generate nor destroy ozone molecules. ozone to accumulate, an additional pathway is needed to convert NO to NO_2; one that will not destroy ozone. The photochemical oxidation of VOCs, such as hydrocarbons and aldehydes, provides that pathway.

The VOC Oxidation Cycle.

$RH + OH = H_2O + R$ (1)

R can be hydrogen or virtually any organic fragment. The oxidation process usually starts with reaction 1, from OH attack on a hydrocarbon or other VOC. OH is formed by photolysis of ozone in the presence of water vapor, and also from nitrous acid, hydrogen peroxide and other sources and ever present in atmosphere.

This is followed by reaction with oxygen in air to generate the peroxy radical (RO2).

$R + O2 + M = RO2 + M$ (2)

The key reaction in the VOC oxidation cycle is the conversion of NO to NO2. This takes place through the fast radical transfer reaction with NO.

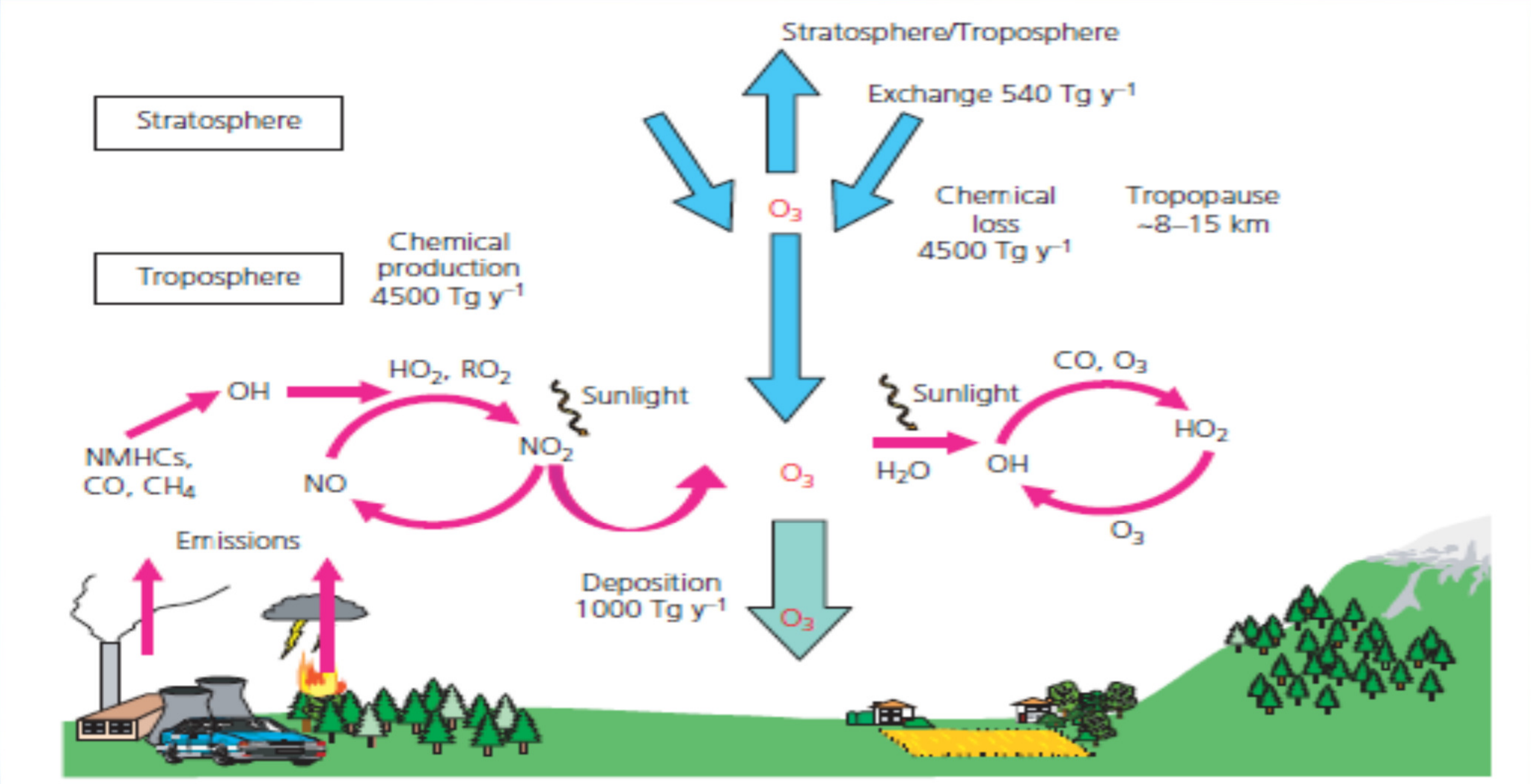
$RO2 + NO = NO2 + RO$ (3)

R can also be generated by photolysis, which usually involves only VOCs -molecules containing the carbonyl (C=O) bond. The simplest VOC molecule that contains carbonyl bond is formaldehyde (HCHO).

Formaldehyde oxidation cycle reaction sequence is as follows :

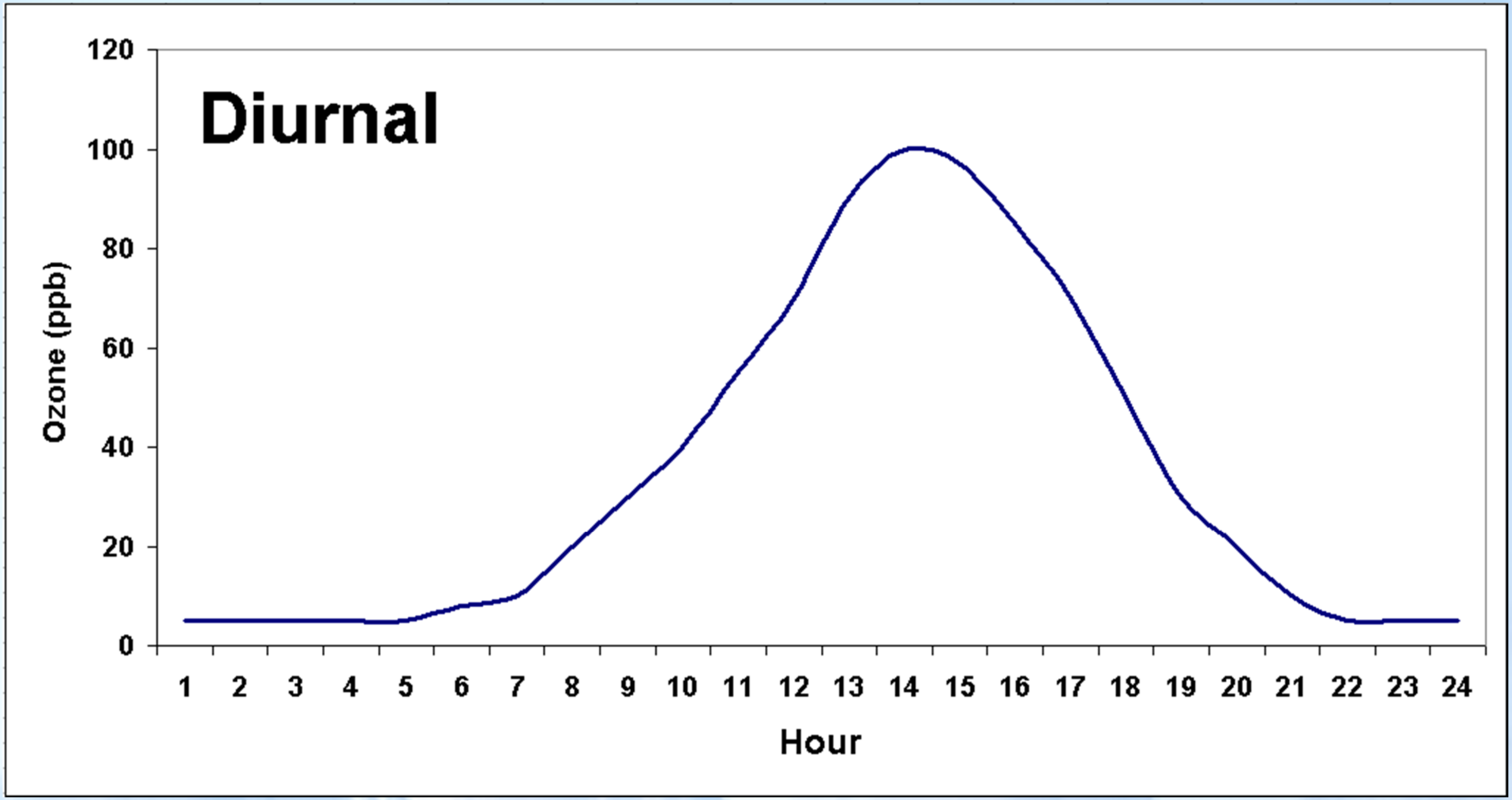
$OH + HCHO=H2O+HCO$ (4) $HCO+O2=HO2+CO$ (5) $HO2+NO=NO2+OH$ (6)

Hydroperoxyl radical (HO2) generated in 5, hydroxylradical consumed in 4 and returns in 6 to complete the cycle. In addition, reaction 6 produces the NO2 required for ozone formation, as described above.



A schematic view of the sources and sinks of O3 in the troposphere. Annual global fluxes of O3 calculated using a global chemistry–transport model have been included to show the magnitudes of the individual terms. These fluxes include stratosphere to troposphere exchange, chemical production and loss in the troposphere and the deposition flux to terrestrial and marine surfaces. Data source: IPCC Fourth Assessment Report

Diurnal Variation



In urban areas where ozone is generated, ozone concentrations tend to peak in the middle of the day and dip to their lowest concentrations during the middle of the night. This type of cycle is called diurnal

Stratospheric Ozone

- 90% of naturally occurring atmospheric ozone occurs in the stratosphere between 10-50 km, with maximum concentrations at 15-30 km - referred as Ozone layer - its height and intensity change with latitude, season, and meteorological conditions.
- It removes almost all incoming UVC (0.20-0.28µm), and 70% of the incoming UVB (0.28-0.32µm) at equator, 90% at poles.
- UV absorption by ozone gives the stratosphere its characteristic thermal structure.
- Atmospheric ozone is measured in Dobson Units (DU). 100 DU is equivalent to a one mm thick layer of pure ozone at surface pressure (1000 mbar). The average amount of ozone in the atmosphere is about 300 DU. Ozone layer is thinnest in the tropics (around the equator) and denser towards the poles.

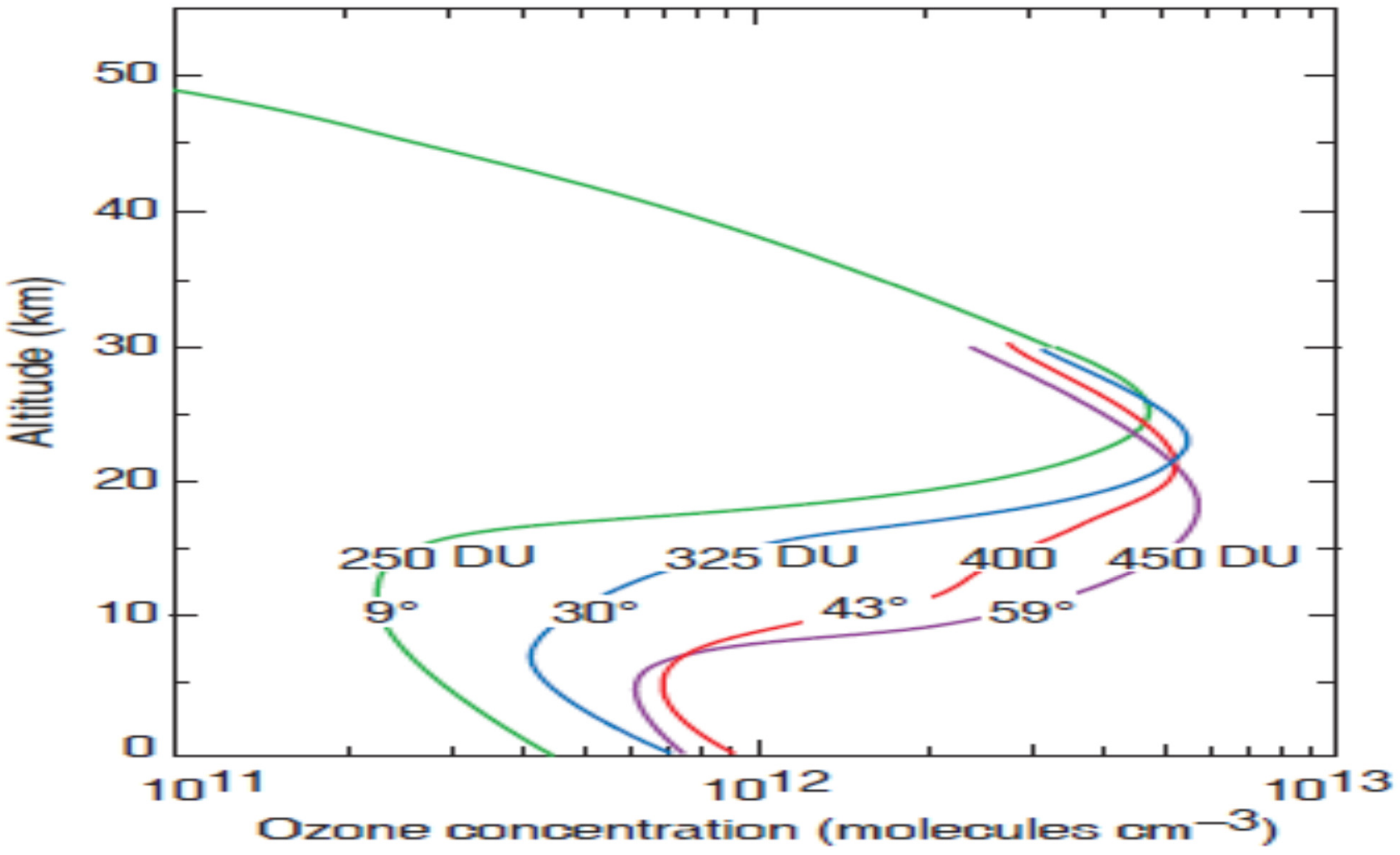
Vertical distribution at latitudes

Greatest column densities of O_3 in the northern hemisphere occur in polar latitudes in spring

In southern hemisphere the spring maximum is at mid-latitudes.

Ozone produced at tropical stratosphere through photochemical reaction is transported meridionally and downward leading to peaks in concentrations at polar and midlatitudes.

Much of the meridional contrast in the total column abundance of O_3 is due to differences in the profiles below 20 km, which are largely determined by transport.



Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees). Total ozone column abundance increased (given in DU) with increasing latitude.

Stratospheric Ozone formation

Major steps for stratospheric ozone formation (Chapman mechanism)

- Above about 30 km altitude, molecular oxygen absorbs solar radiation (wavelength < 242 nm) and photodissociates $O_2 + h\nu \text{----->} O + O$
- The oxygen atom O, reacts rapidly with O2 in presence of a third body, denoted M (M is usually another O2 or N2), to form ozone: $O_2 + O + M \text{->} O_3 + M$

  Above is the only reaction that produces ozone in the atmosphere!!!
- Ozone absorbs solar radiation (in the wavelength range of 240 to 320 nm) and decomposes back to O2 and O: $O_3 + h\nu \text{------>} O_2 + O$
- Additionally, ozone can react with atomic oxygen to regenerate two molecules of O2: $O_3 + O \text{------->} O_2 + O_2$

  Reactions (1)–(4) are called the *Chapman reactions*.

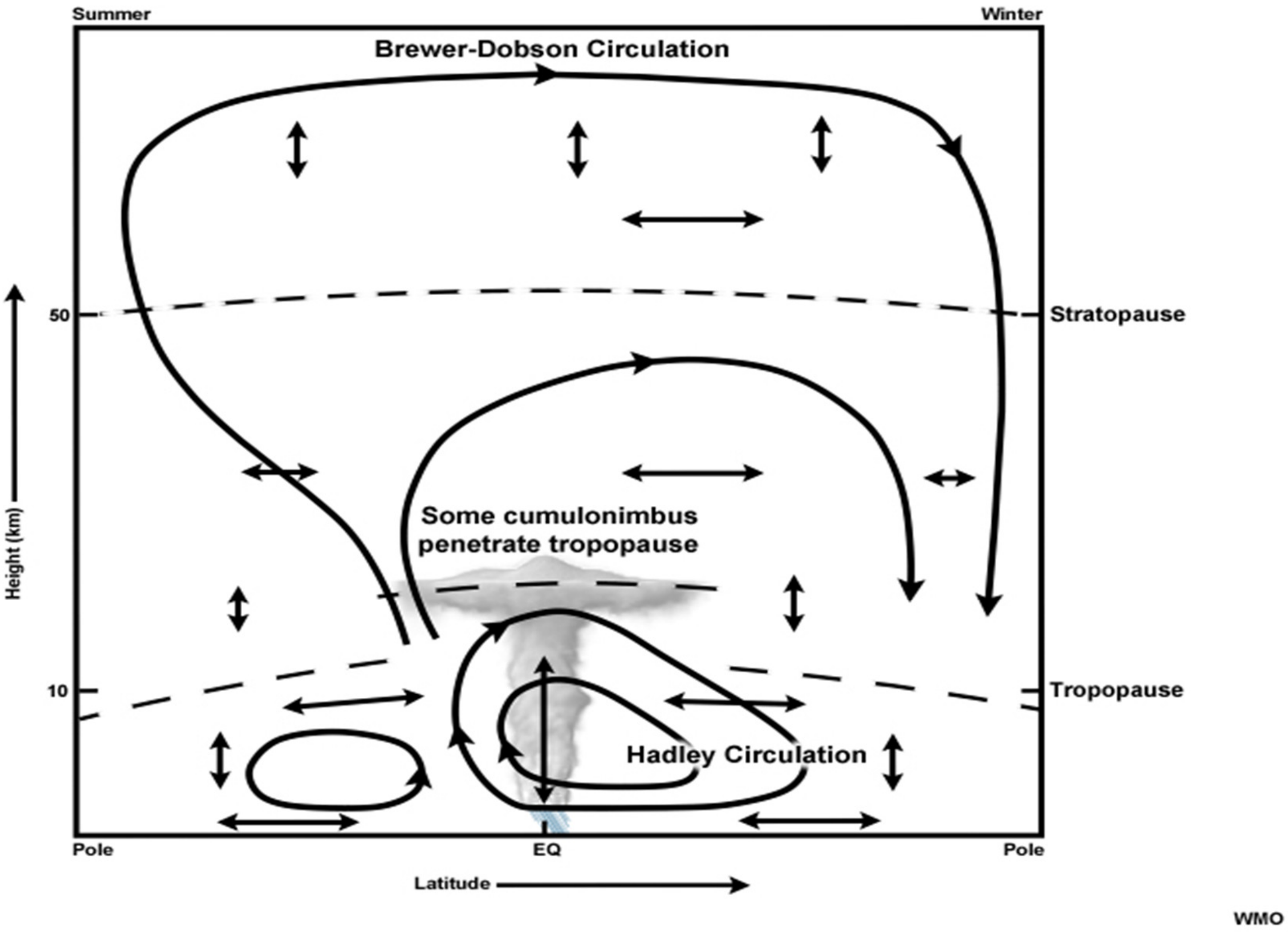
The mechanism for stratospheric ozone formation, photolysis of O2, does not take place in the troposphere because the strong UV photons needed for this photolysis have been totally absorbed by O2 and ozone in the stratosphere.

Stratospheric Ozone formation

Chapman reactions could predict the correct shape for vertical profile of O_3, over predict the concentrations by about a factor of two in the tropics and under predict O_3 concentration in middle to high latitudes.

Also, there is an equator-to-pole circulation in the stratosphere, sometimes referred to as the Brewer–Dobson circulation, which transports O3 from its primary source in the tropical stratosphere pole ward and downward into the extratropical lower stratosphere.

To explain observed stratospheric ozone concentrations, there is need to balance ozone production and loss. Ozone photolyzes to release O2 and O, but this is not an actual sink since O2 and O can just recombine to ozone. The main mechanism for ozone loss in the natural stratosphere is a catalytic cycle involving Nox, H, OH, Cl, and Br radicals that deplete O3 in the stratosphere, ***which speed up ozone loss but are not consumed in the process***.



Brewer–Dobson circulation

Most of the catalytic reactions that have been proposed for the removal of stratospheric odd oxygen are of the form

(5) $X + O_3 \rightarrow XO + O_2$

(6) $XO + O \rightarrow X + O_2$

(7) Net: $O + O_3 \rightarrow 2O_2$

where X represents the catalyst and XO the intermediate product. Provided that reactions (5) are fast, reaction (6) can proceed much faster than reaction (4). Also, because X is consumed in (5) but regenerated in reaction (6) and provided there is no appreciable sink for X, just a few molecules of X have the potential to eliminate large numbers of O3 molecules and atomic oxygen.

the main source in the stratosphere is oxidation of nitrous oxide (N_2O), which is emitted ubiquitously by bacteria at the Earth's surface. Nitrous oxide is inert in the troposphere and can therefore be transported up to the stratosphere, where much stronger UV radiation enables its oxidation. Nitrous oxide emissions have increased over the past century due to agriculture, but the rise has been relatively modest (from 270 to 327 parts per million by volume) and of little consequence for the ozone layer.

If concentration of catalysts X are increased significantly, the balance between the sources and sinks of atmospheric O3 will be disturbed and stratospheric O_3 concentrations can be expected to decrease.

Catalytic action of chlorine, from industrially manufactured chlorofluorocarbons (CFCs), in depleting stratospheric ozone has become greater concern. CFCs are compounds containing Cl, F, and C; CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) are the most common.

CFCs were spreading globally, due to inertness, expected residence times ranging to several hundred years in troposphere. Such long-lived compounds eventually find way into stratosphere where, about 20 km altitudes, they absorb UV radiation in wavelength interval 0.19–0.22 μm and photo dissociate.

$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl \text{ and}$$

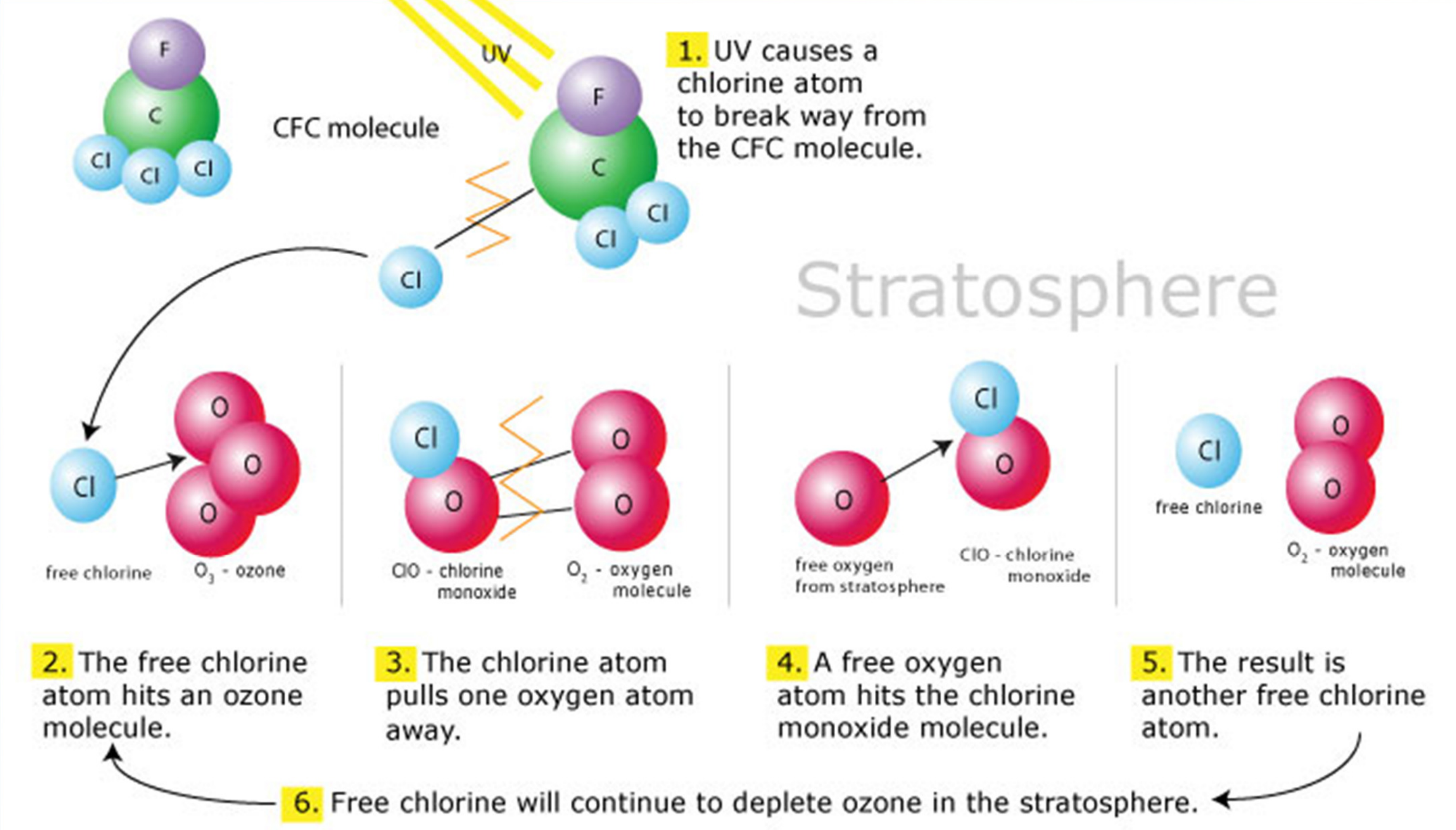
$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

The chlorine atom released by these reactions can serve as the catalyst X in cycle, thereby destroying odd oxygen in the cycle

$$Cl + O3 \rightarrow ClO + O2$$

$$ClO + O \rightarrow Cl + O2$$

$$\text{Net:} \quad O3 + O \rightarrow 2O_2$$

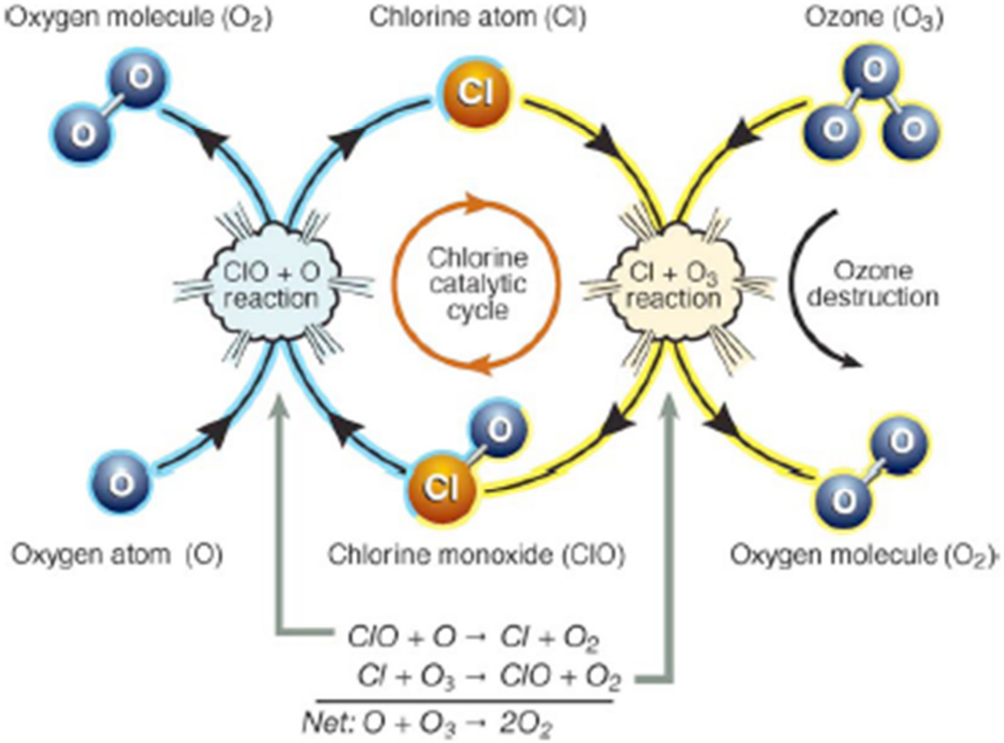


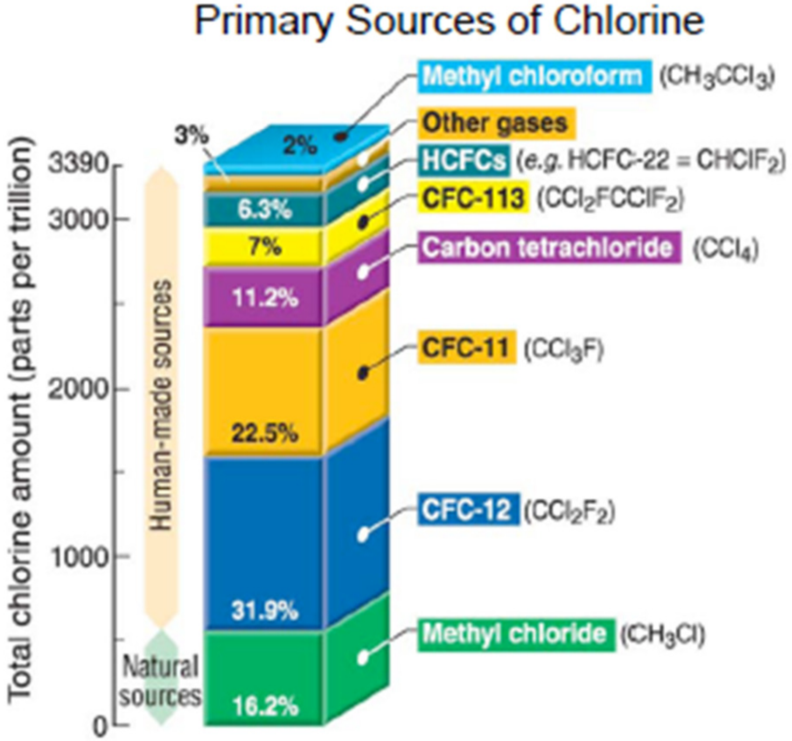
1. UV causes a chlorine atom to break way from the CFC molecule.
2. The free chlorine atom hits an ozone molecule.
3. The chlorine atom pulls one oxygen atom away.
4. A free oxygen atom hits the chlorine monoxide molecule.
5. The result is another free chlorine atom.
6. Free chlorine will continue to deplete ozone in the stratosphere.

What Causes Ozone Depletion?

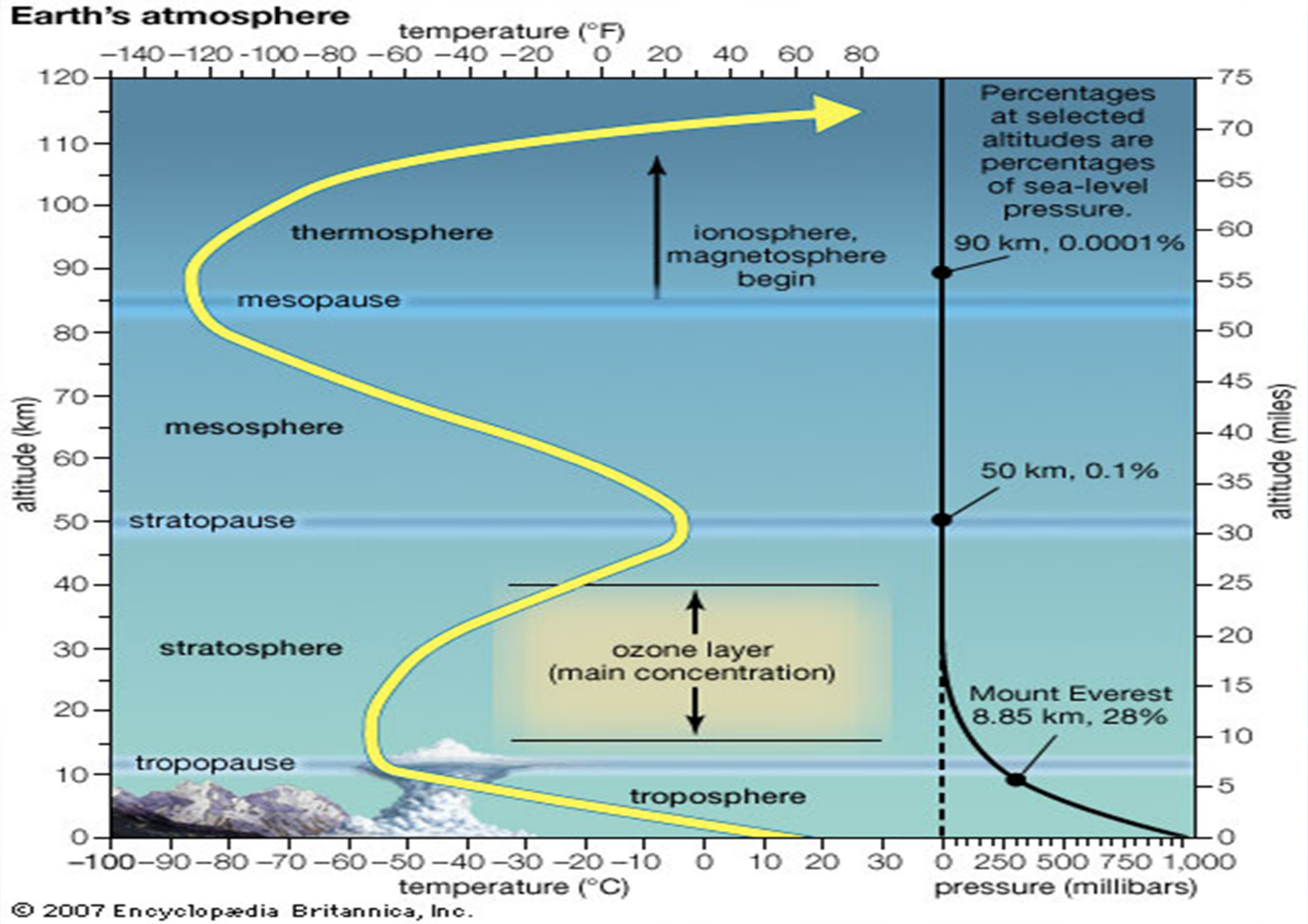
Reactive chlorine- and bromine-containing gases in the stratosphere

“Catalytic” cycles allow a single chlorine or bromine atom to destroy many hundreds of ozone molecules





Figures from WMO, 2006



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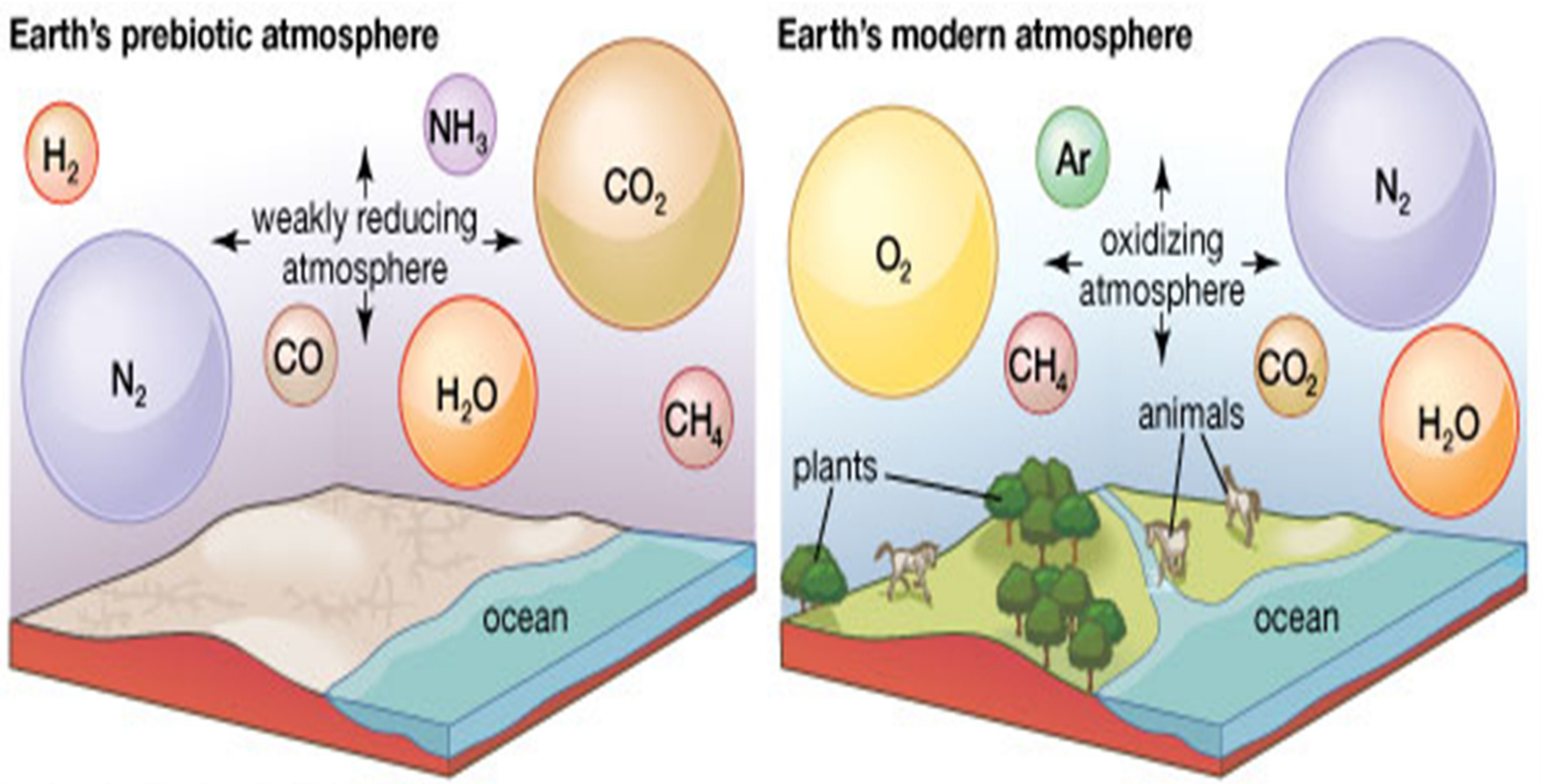
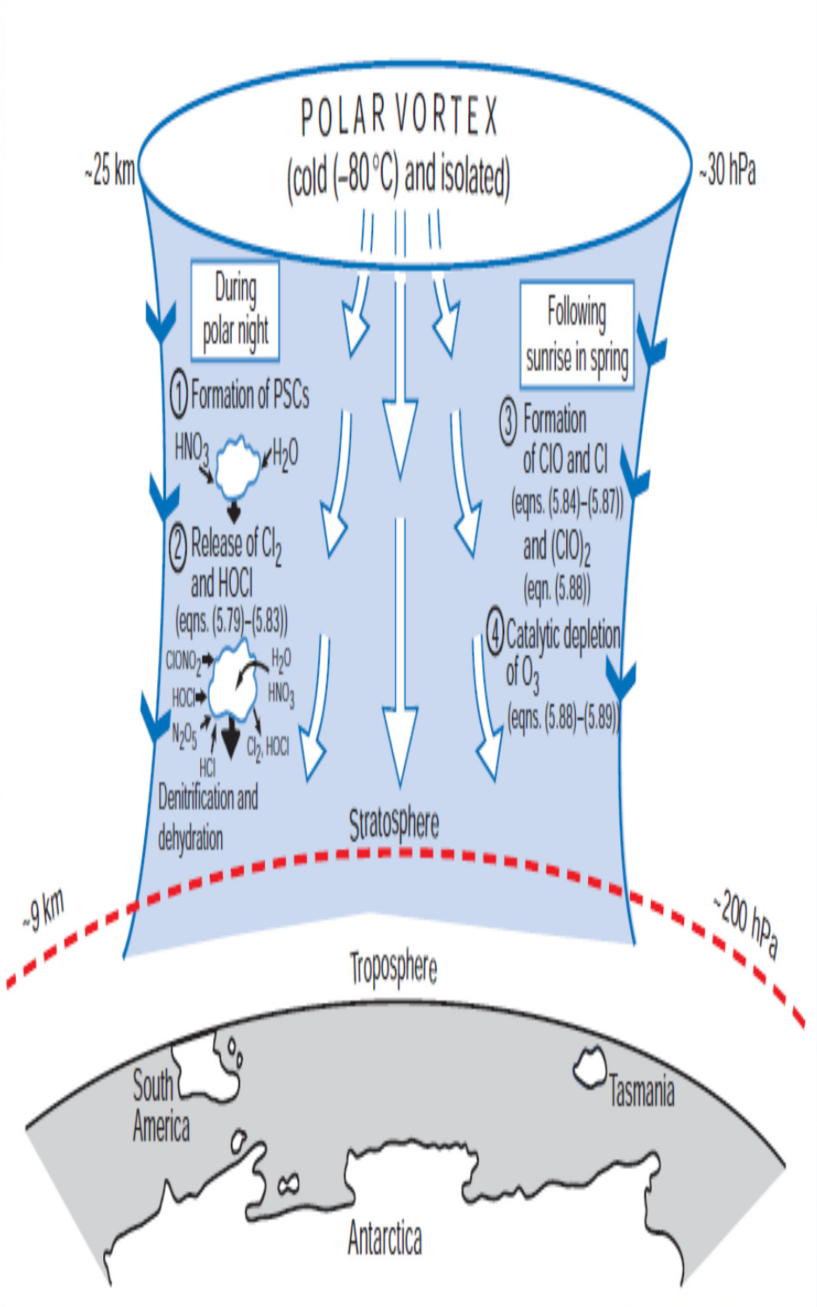


Comparison of Earth's prebiotic and modern atmospheres. Before life began on the planet, Earth's atmosphere was largely made up of nitrogen and carbon dioxide gases. After photosynthesizing organisms multiplied on Earth's surface and in the oceans, much of the carbon dioxide was replaced with oxygen.

Ozone Hole

The ozone "hole" is literally not a hole; rather, the phenomenon is the area where concentration of ozone depletes below the historical threshold of 220 DU. Phenomenon is seasonal, starting each year during the Antarctic spring and peaking between mid-September and early October. The first evidence of a significant depletion in stratospheric O_3 produced by anthropogenic chemicals, came surprisingly, from measurements in the Antarctic in spring. The areal extent of the Antarctic ozone hole, derived from satellite measurements shows that since 1979 ozone hole grew progressively and occupies 4th largest area in year 2015.

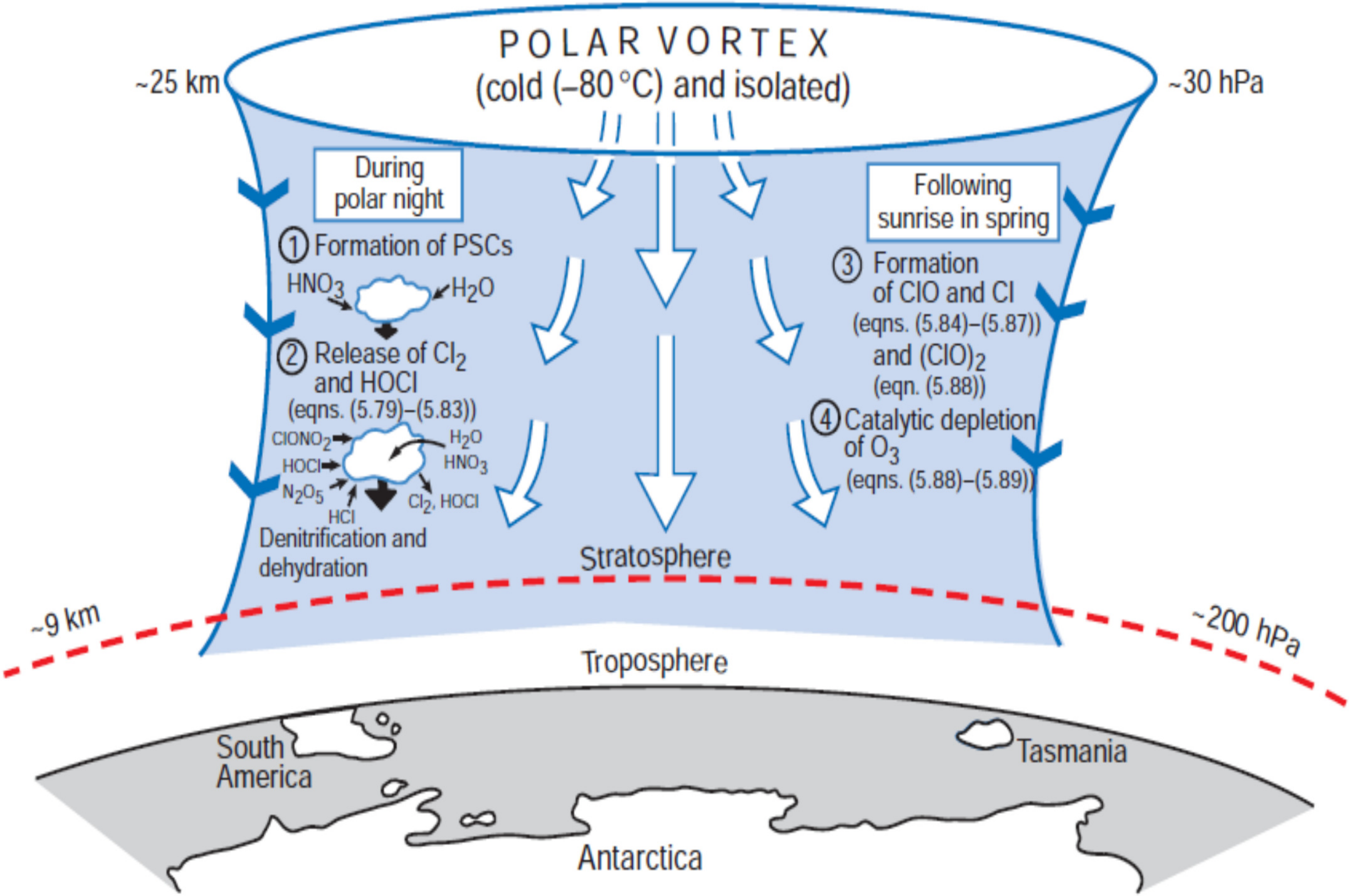
- During the austral winter (June–September), stratospheric air over the Antarctic continent is restricted from interacting with air from lower latitudes by a large-scale vortex circulation, which is bounded at its perimeter (called the vortex collar) by strong westerly winds encircling the pole.
- Because of the lack of solar heating in the austral winter, the air within the vortex is extremely cold and it lies within the sinking branch of the Brewer–Dobson circulation. High-level clouds, called polar stratospheric clouds (PSCs), form in the cold core of the vortex, where temperatures can fall below -80 °C.
- Vortex serves as a giant and relatively isolated chemical reactor in which unique chemistry occur. Although the concentrations of O_3 in the vortex are normal, the concentrations of ClO in the vortex are 10 times greater than just outside the vortex collar.



Polar stratospheric clouds (PSCs) are fundamental to an understanding of Antarctic ozone hole. PSCs form in the extremely cold and dry conditions that exist in the polar night regions of the stratosphere. PSC cloud particles are composed of mixtures of nitric acid (HNO_3), water vapor (H_2O) and sulfuric acid (H_2SO_4).

Denitrification and Dehydration of the Stratosphere

PSCs convert non reactive chlorine species, i.e hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$) into reactive Cl_2 (molecular chlorine) and HOCl (hypochlorous acid), compounds through Heterogeneous Reactions that take place on the solid surfaces of the PSC cloud particles. The Cl_2 is released as a gas. The HOCl is likewise released off the surface of the PSC cloud particle in gaseous form. Both Cl_2 and HOCl are subsequently photolyzed by sunlight, initiating the catalytic ozone loss cycle. These processes determine the location and timing of the ozone hole. PSC particles settle out of the stratosphere . This sedimentation transports reactive nitrogen and water that are on the particles out of the lower stratosphere. The removal of reactive nitrogen is known as **denitrification** and the removal of water vapor is known as **dehydration**. These denitrification and dehydration processes occur inside the Antarctic polar vortex over the course of the very cold winter.


POLAR VORTEX
(cold (–80 °C) and isolated)
~25 km
~30 hPa
During polar night
① Formation of PSCs
HNO_3
H_2O
② Release of Cl_2 and HOCl
(eqns. (5.79)–(5.83))
$ClONO_2$
HOCl
N_2O_5
HCl
H_2O
HNO_3
Cl_2, HOCl
Denitrification and dehydration
Following sunrise in spring
③ Formation of ClO and Cl
(eqns. (5.84)–(5.87))
and $(ClO)_2$
(eqn. (5.88))
④ Catalytic depletion of O_3
(eqns. (5.88)–(5.89))
Stratosphere
~9 km
~200 hPa
Troposphere
South America
Tasmania
Antarctica

Because of this nitrogen loss, there is no NO2 to react with ClO to form the reservoir ClONO2, hence denitrification results in a maintenance of high levels of active chlorine that can continuously destroy ozone.

Principal Heterogeneous Reactions .

- ClONO2 (g) + HCl(s) --> Cl2 (g) + HNO3 (s)
- HOCl(g) + HCl(s) --> Cl2 (g) + H2O(s)
- ClONO2(g) + H2O (s) --> HOCl(g) + HNO3 (s)
- N2O5 (g) + H2O (s) --> 2 HNO3 (s)
- N2O5 (g) + HCl(s) --> ClNO2 (g) + HNO3 (s)

The key point here is the conversion of relatively benign reservoir species ClONO2 and HCl into Cl2, which can then be photolyzed by visible and ultraviolet wavelengths. Also formed is HOCl, another reactive chlorine compound that can be photolyzed by ultraviolet wavelengths. These processes determine the location and timing of the ozone hole.

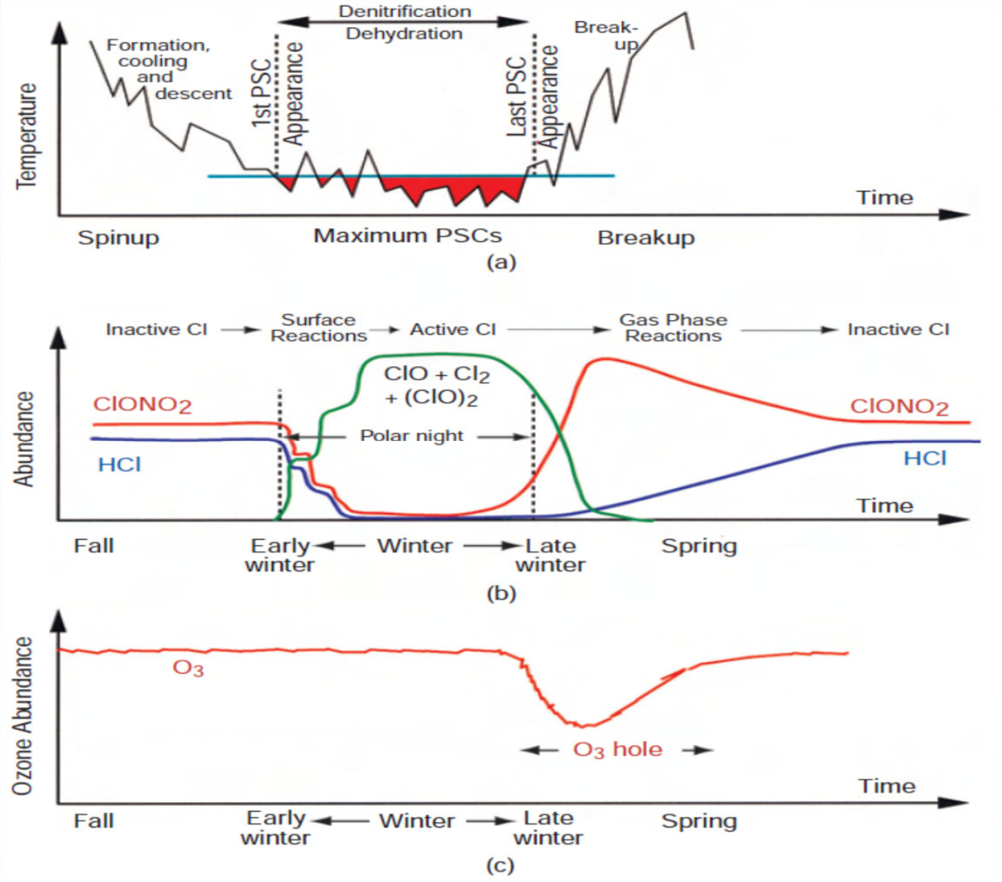
Denoxification of the Antarctic stratosphere.

These same reactions also remove nitrogen from the stratosphere in a process known as denoxification. These heterogeneous reactions simultaneously act to remove nitrogen from gas phase compounds such as N2O5 (dinitrogen pentoxide) and ClONO2 and sequester reactive nitrogen as HNO3, a reservoir species for nitrogen. HNO3 (nitric acid) produced is retained on the PSC cloud particle surfaces. This process of sequestering nitrogen is known as denoxification (as opposed to denitrification which carries reactive nitrogen out of the stratosphere.

By mid-October, the photolysis time scale for HNO3 in the lower stratosphere is over a month, making HNO3 a relatively inert trace gas during the ozone hole period. Furthermore, since PSC particles slowly settle, the particle denitrification process will carry HNO3 to lower altitudes. In short, the reactive chlorine compounds are able to destroy ozone without reacting with reactive nitrogen, which is locked up in HNO3 form. HNO3 must be photolyzed by sunlight to form reactive nitrogen compounds. There is no sunlight in Antarctic during the wintertime polar night. The lifetime of HNO3 therefore becomes very long.

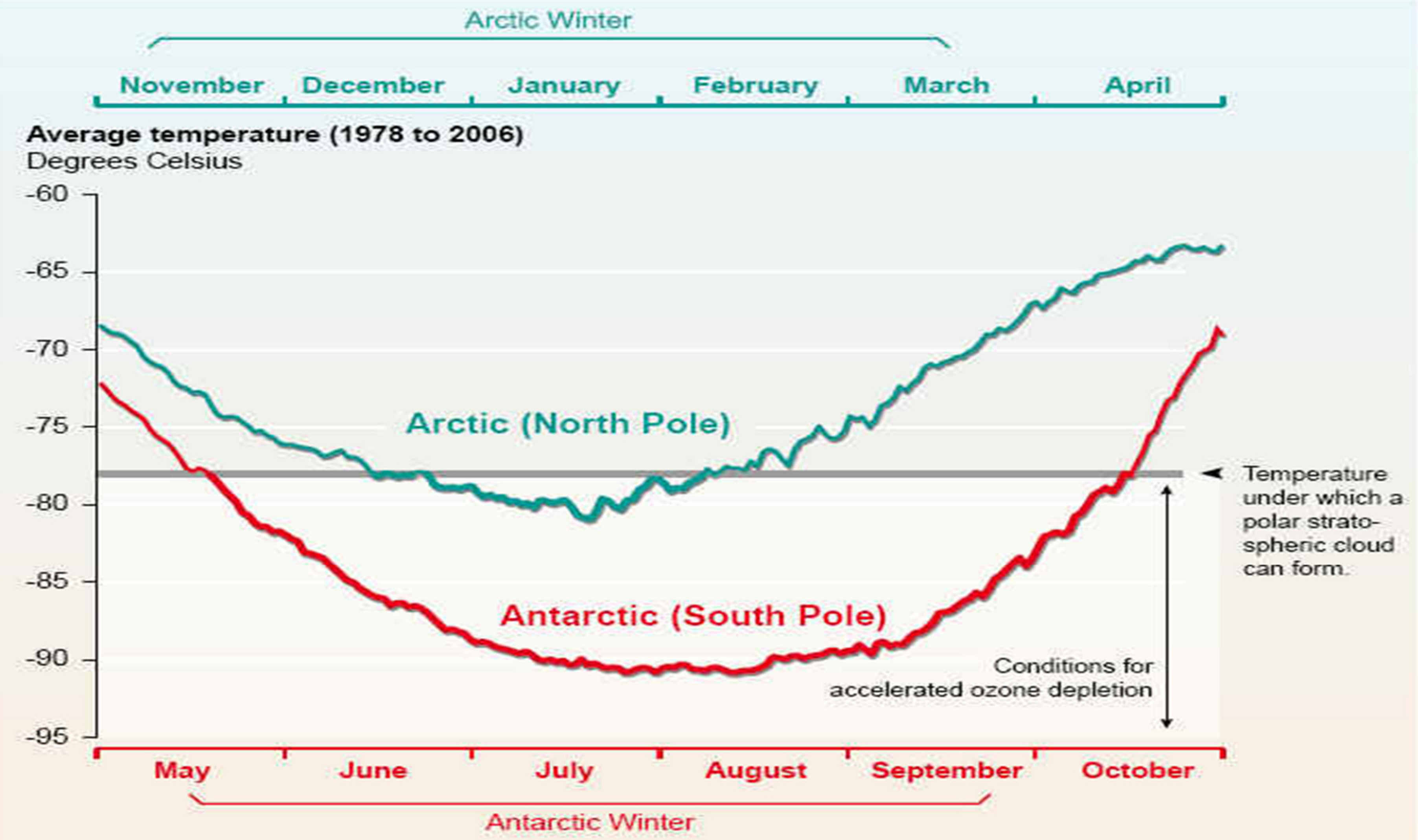
Return of Sunlight : The next step occurs when sunlight first returns to the Antarctic stratosphere in early spring, which photolyzes hypochlorous acid, HOCl, and marks the end of cold temperatures.

Homogeneous (chemical reactions in the gas phase only).



Schematic time evolution development of the Antarctic ozone hole. (a) The Antarctic vortex. Polar stratospheric clouds (PSCs) form, and reactions occur on the PSC particles when stratospheric temperatures fall into the region colored red. (b) Chlorine reservoirs in the Antarctic vortex. The inactive reservoir species ClONO2 and HCl are converted into the active chlorine species Cl_2, ClO, and $(ClO)_2$ when the temperature falls below the value required for the formation of PSCs. The reservoir species return after the disappearance of the PSCs. (c) Ozone in the Antarctic vortex. Ozone is depleted rapidly by photolysis when the sun rises in September. As the active chlorine species are depleted, and the vortex breaks up, the concentration of O3 rises.

THE COLDER ANTARCTIC WINTER DRIVES FORMATION OF THE HOLE IN THE SOUTH



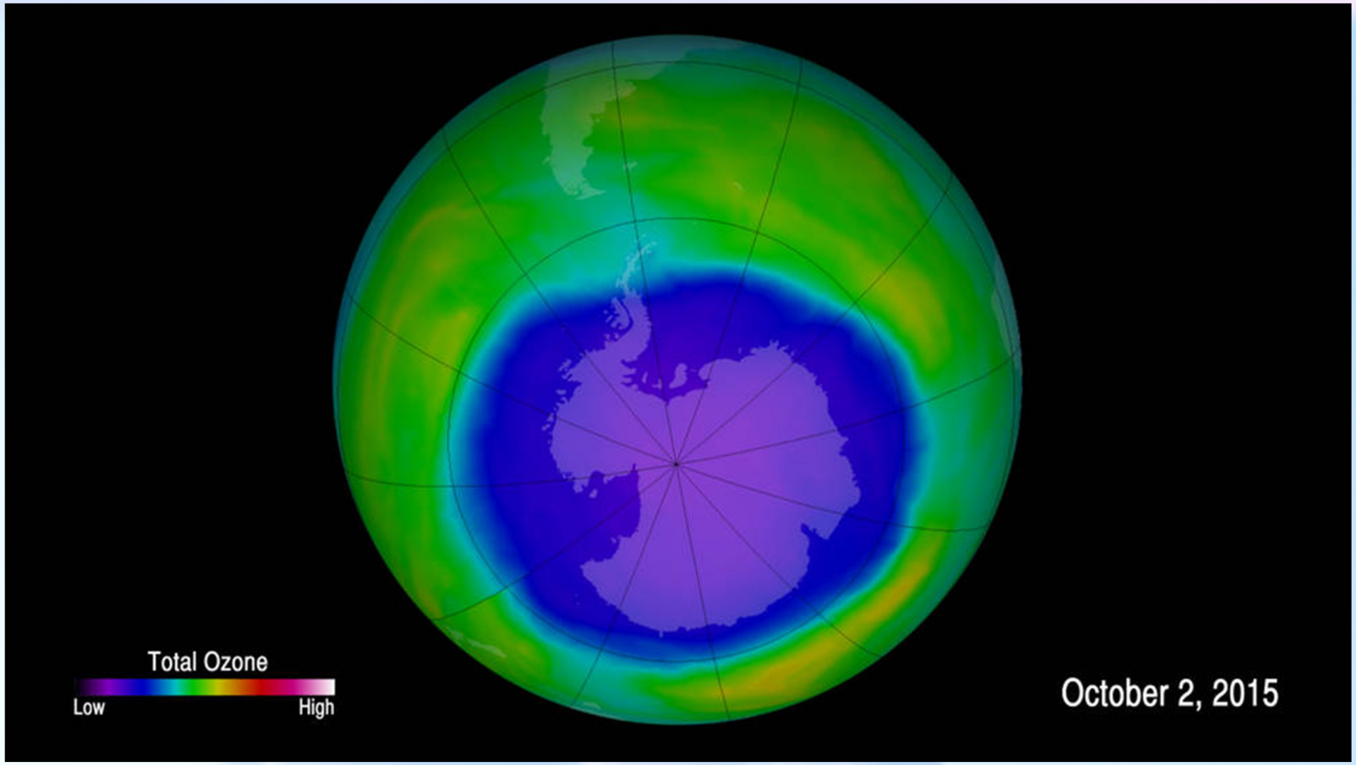
Source: *Twenty Questions and Answers about the Ozone Layer: 2006 Update*, Lead Author: D.W. Fahey, Panel Review Meeting for the 2006 ozone assessment.

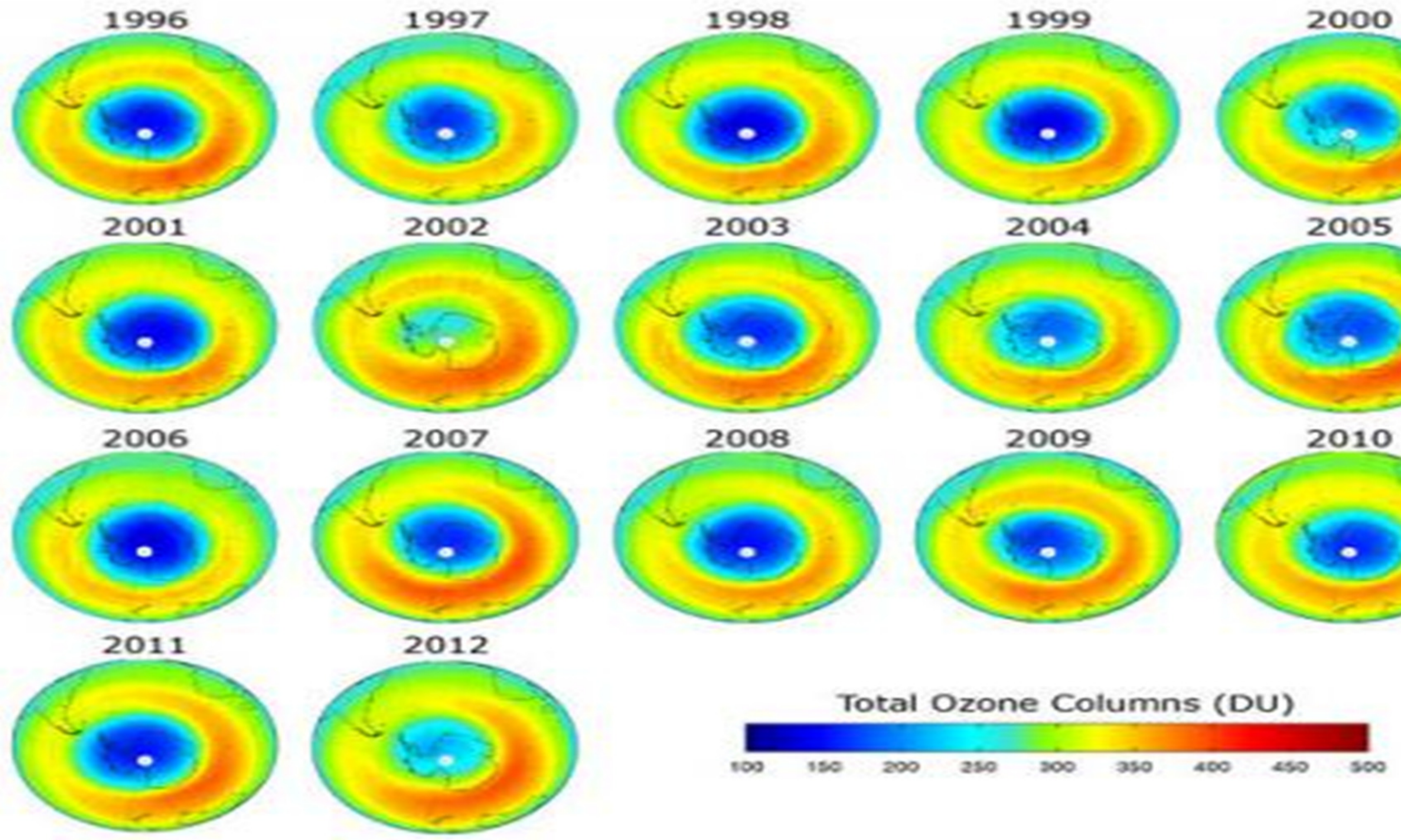
On October 2, 2015, OMI on NASA’s Aura satellite and Ozone Monitoring and Profiler Suite (OMPS) on the NASA-NOAA Suomi NPP satellites observed that **ozone hole** over Antarctica reached its **largest single day area for the year, spanning 28.2 million square kilometers**. Also **average size in September–October 2015 was 25.6 million square kilometers**. Both are the **fourth largest since the start of the satellite record**. This phenomena in 2015 was consistent with known ozone depletion and chemistry. According to NASA there are still plenty of ozone depleting chlorine and bromine compounds present in the stratosphere. Moreover, the lower stratosphere was colder than in previous years, which creates favorable conditions for ozone depleting chemical reactions.

The **largest single-day ozone hole recorded by satellite was 29.9 million square kilometers on September 9, 2000 while the largest September–October average on record was 26.6 million square kilometers in 2006**.

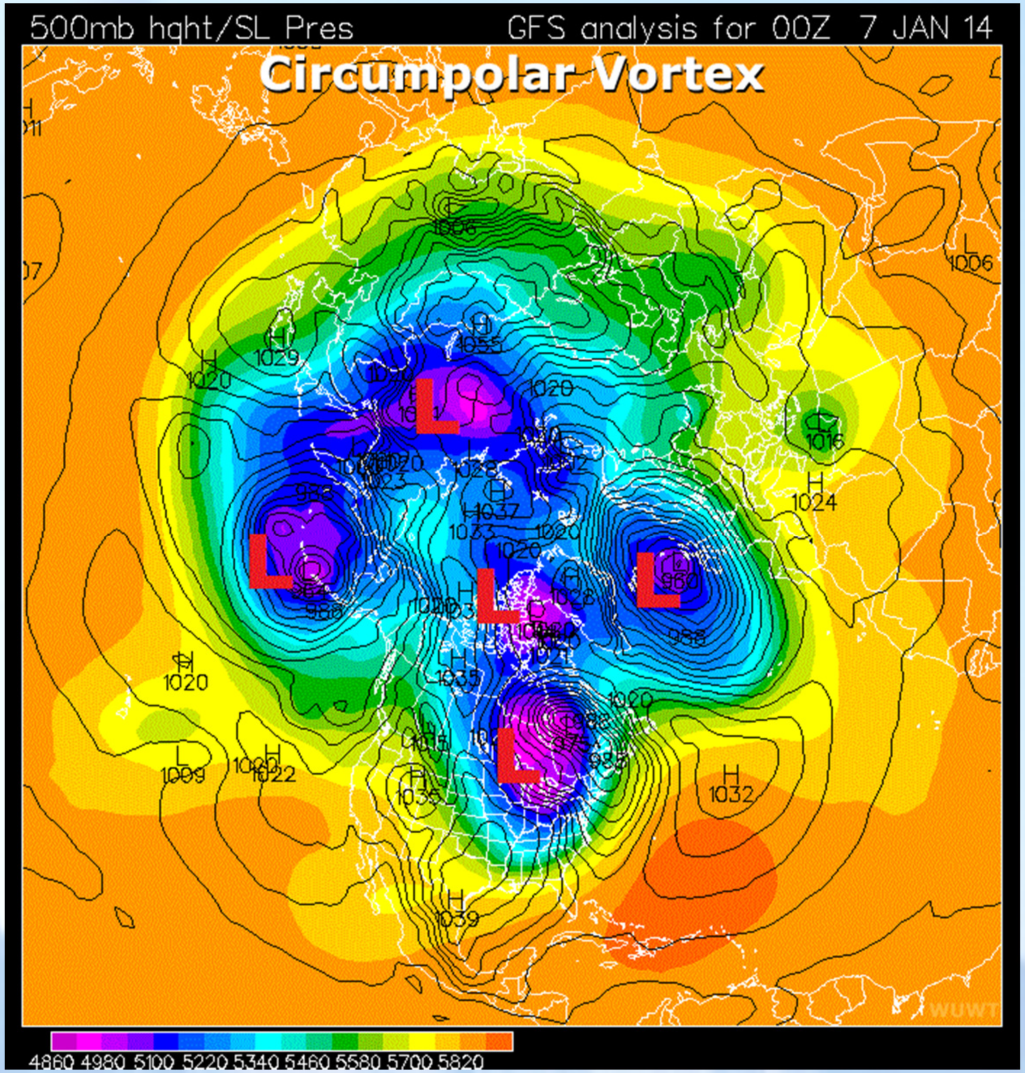
In 2015, ozone concentrations also plunged lower than in recent years. **On October 4, ozone reached an annual minimum concentration of 101 Dobson Units**.

In the images follow ozone areas are purple and blue.


Total Ozone
Low
High
October 2, 2015



Time-series (1996 to 2012) of total polar ozone mean values over the months of September, October and November as measured by GOME, SCIAMACHY and GOME-2 flown on ERS-2, Envisat and MetOp-A, respectively. the hole over Antarctica in 2012 was the smallest in the last 10 years.


500mb hght/SL Pres
GFS analysis for 00Z 7 JAN 14
Circumpolar Vortex
L
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1006
1029
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1024
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980
988
1020
1009
1022
1035
1032
1039
4860 4980 5100 5220 5340 5460 5580 5700 5820

International Efforts to protect Ozone hole

In September 1987, the Montreal Protocol on Substances that Deplete the Ozone Layer (the Protocol) was signed by **25** nations and the European Community. The Protocol was the first international environmental agreement, and its signing by so many nations represented a major accomplishment, and a major shift in the approach to handling global environmental problems. The Protocol called for a **freeze on the production of halons and a requirement to reduce the production of CFCs by 50% by 1999.**

The principal provisions of the Montreal Protocol as it now stands are as follows:

- Production of CFCs, halons, methyl chloroform, and CTC ceased at the end of 1995 in industrial countries and will cease by 2010 in developing countries. Developing countries are defined in the Protocol as those that use less than 0.3 kilograms (kg) of ODS per capita per year. They are often called Article 5 countries in reference to the defining article in the Montreal Protocol.
- HCFCs, originally developed as a less harmful class of CFC alternatives, will be phased out by 2020 in industrial countries, with some provisions for servicing equipment to 2030. Developing countries are to freeze consumption by 2016 (base year 2015) and phase out use by 2040.

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International Efforts to protect Ozone hole

Consumption and production of methyl bromide will end in 2005 in industrial countries (subject to phase-out stages and exemptions) and in 2015 in developing countries.

Ozone Depletion Potential (ODP) of the Principal Ozone-Depleting Substances (ODSs)

ODS	ODP
CFC-11	1.0
CFC-12	1.0
CFC-113	0.8
CFC-114	1.0
CFC-115	0.6
CFC-111, -112, -13, -211, -212, -213, -214, -215, -216, -217	1.0
Halon 1211	3.0
Halon 1301	**10.0**
Halon 2402	**6.0**
Carbon tetrachloride (CTC)	1.1
Methyl chloroform (MCF); 1,1,1-trichloroethane	0.1
HCFC-22	0.05
HCFC-123	0.02
HCFC-124	0.02
HCFC-141b	0.15
HCFC-142b	0.06
HCFC-225ca	0.01
HCFC-225cb	0.04
Methyl bromide	0.7

International Efforts to protect Ozone hole

HCFC Phaseout Schedule

- All developed (i.e., non-Article 5) countries that are Parties to the Montreal Protocol are subject to caps on their consumption and production of hydrochlorofluorocarbons (HCFCs). Consumption is calculated by the following formula:
- Consumption = production plus imports minus exports.
- The cap is set at 2.8% of that country's 1989 chlorofluorocarbon consumption + 100% of that country's 1989 HCFC consumption. The cap on production is set at the average of i) 1989 HCFC production + 2.8% of 1989 CFC production and ii) 1989 HCFC consumption + 2.8% of 1989 CFC consumption. (Quantities of chemicals measured under the cap are ODP-weighted, which means that each chemical's relative contribution to ozone depletion is taken into account.)

Montreal Protocol	
Year to be Implemented	% Reduction in Consumption and Production Using the Cap as a Baseline
2004	35.0%
2010	75.0%
2015	90.0%
2020	99.5%
2030	100.0%

International Efforts to protect Ozone hole

India:

The Ozone Cell, MoEF The Ozone Cell, which has been the given the responsibility for carrying out all tasks relating to phaseout. It governs day-to-day operations, promulgation of relevant policies and monitoring implementation of all phaseout projects. The Ozone Cell reports to the Secretary, MoEF on key issues relating to ODS phaseout and to the Executive Committee on the overall progress of all MLF-funded activities. The Quota and Licensing system, on CFC production, imports and exports of ODS, is primarily handled by Ozone Cell. The Ozone Cell receives MLF support for its operations through the UNDP. It is the main interface between GOI, Montreal Protocol Secretariat and ODS consuming industries in India.

India's Commitment to the Montreal Protocol

India became party to the Montreal Protocol on 17.9.92

Ozone Measurement in India

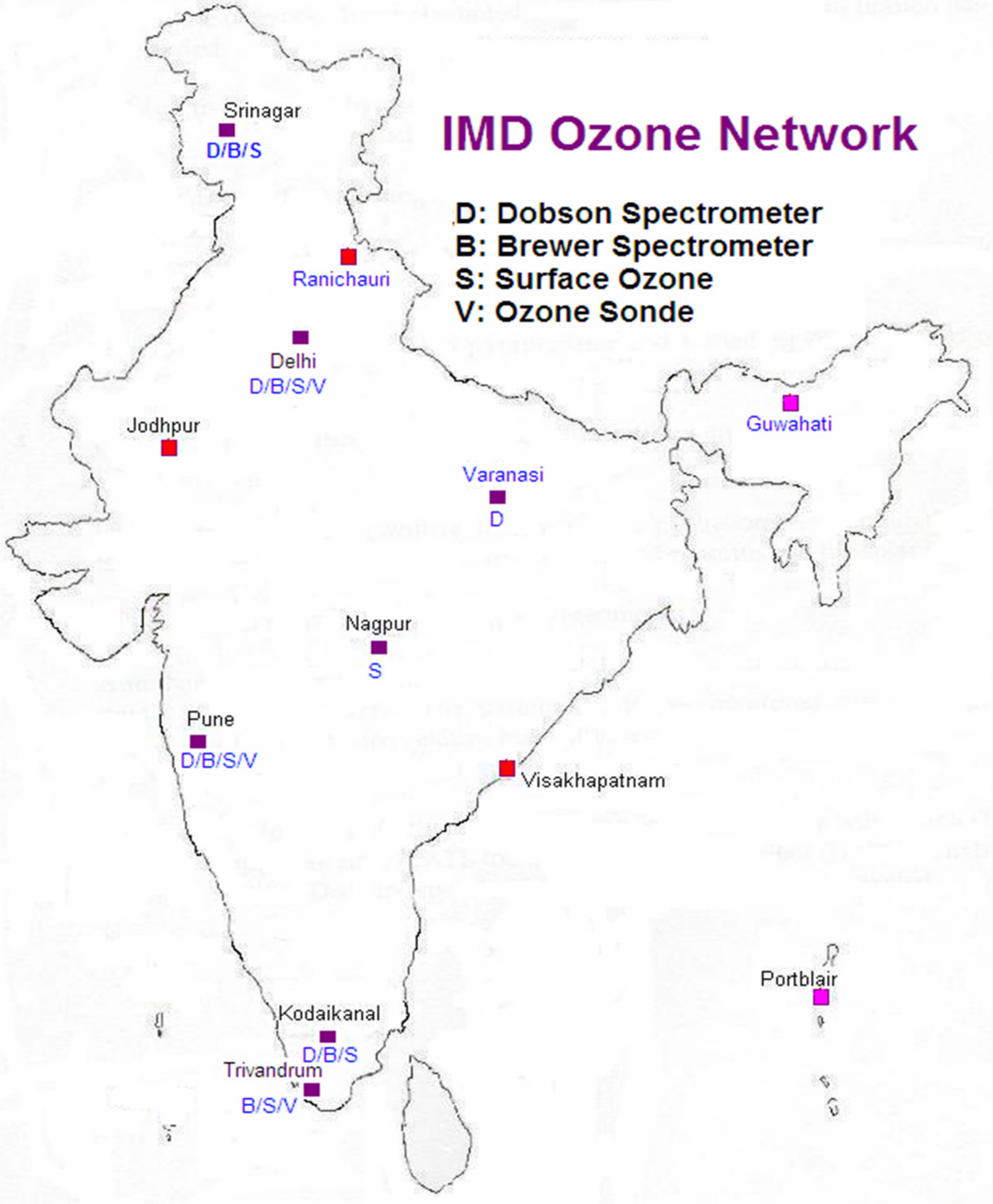
- The first Columnar Ozone Observations made in 1928-29 at Kodaikanal as part of Dobson's worldwide Total Ozone Measurements.
- IMD acquired first Dobson Spectrophotometer in 1940.
- Development of Indian Ozone sonde by Instrument division of IMD in 1964. Vertical ozone profiles using indigenous balloon-borne ozone-sondes are observed fortnightly at 4 stations including Maitri.
- IMD's National Ozone Centre at New Delhi is designated as Secondary Regional Ozone Centre for Regional Association II (Asia) of the World Meteorological Organisation.
- The centre maintains and controls a network of ozone monitoring stations including Maitri (Antarctica).
- Total ozone is measured with Dobson/Brewer Ozone Spectrophotometer from five locations including Maitri (Antarctica).
- Surface ozone measurements using electrochemical method are recorded continuously at 7 stations Srinagar, Pune, Nagpur, New Delhi, Kodaikanal, Trivandrum and Maitri.
- IMD has installed Serinus 10 Surface UV Ozone Analyzers at nine locations DLH, PNE, NGP, KDK, GHT, PBL, Ranichouri, TRV, Antarctica and VNS.

Ozone Measurement in India

- Ozone data is being regularly sent to World Ozone Data Centre, Canada for archival. The data is available in the Internet on: http://www.woudc.org .
- IMD is collaborating at both the national and international levels through international inter comparison of instruments, conducting experiments to study tropospheric ozone over the Indian ocean, comparing satellite data with ground truth and studying diurnal and seasonal variations in the ozone layer over Indian and Russian stations.

MODERNIZATION OF IMD OZONE NETWORK

Surface Ozone Measurement using UV-Absorption Photometer **(Srinagar, Delhi, Pune, Kodaikanal, Trivandrum, Nagpur, Ranichauri, Guwahati, Visakhapatnam, Jodhpur)**	**10** **(6+4)**
Ozone sonde **(Delhi, Pune, Trivandrum, Portblair, Guwahati)**	**5** **3+2**


IMD Ozone Network

D: Dobson Spectrometer
B: Brewer Spectrometer
S: Surface Ozone
V: Ozone Sonde

Techniques for Measuring Atmospheric Ozone

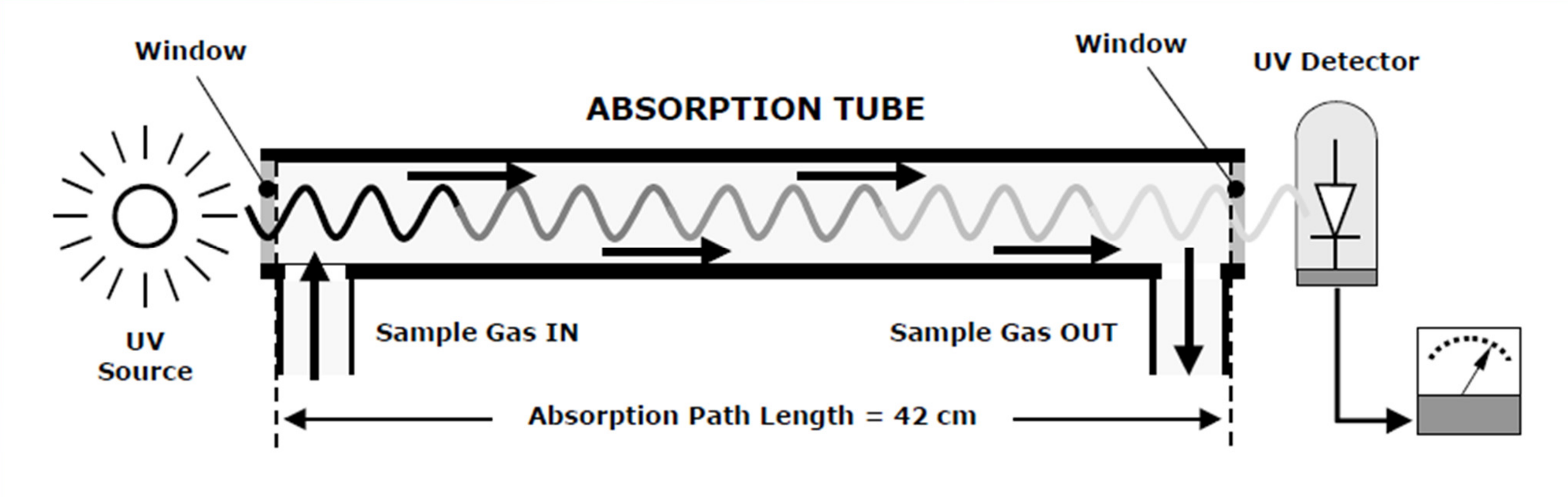
IMD's National Ozone Centre at New Delhi is designated as Secondary Regional Ozone Centre for Regional Association II (Asia) of the World Meteorological Organisation. The centre maintains and controls a network of ozone monitoring stations including Maitri (Antarctica). The following parameters of ozone are being measured at IMD stations:

- Surface Ozone Measurement using UV Photometer / UV Ozone Analyzer
- Surface Ozone Measurement using Electrochemical Concentration Cell (ECC)
- Total Columnar Ozone using Dobson/ Brewer Spectrophotometer
- Vertical Distribution of Ozone using Electrochemical Ozone-sonde

Surface Ozone Measurement by UV Absorption method

- IMD has installed Serinus 10 Surface UV Ozone Analyzers at ten locations e.g. New Delhi, Pune, Nagpur, Kodaikanal, Guwahati, Portblair, Ranichouri, Thiruvananthpuram, Antarctica and Varanasi.
- UV photometer determines the concentration of Ozone in a sample gas at ambient pressure by detecting the absorption of UV radiation in a glass absorption tube. The Serinus 10 ozone analyzer follows these principles and techniques:
- Ozone shows strong absorption of UV light at 254 nm
- Sample air is passed into the glass absorption tube (measurement cell). Within the measurement cell a single beam of UV radiation passes through the sample and is absorbed by the Ozone. The solar blind vacuum photodiode detects any UV that is not absorbed. **SO2 and aromatic compounds also absorb radiation at 254 nm wavelength**. Sample air is passed through an ozone scrubber which allows all interfering gases through but eliminates ozone thereby accurately measuring interfering gases effects on signal and removing them from the sample measurement signal.
- The strength of the UV signal being detected is proportional to the amount of UV light being absorbed by Ozone.
- The Ozone analyzer uses the Beer-Lambert relationship to calculate the ozone concentration.

Surface Ozone analyzer
UV Absorption Ozone Analyzer



- **UV photometer determines ozone concentration by measuring the attenuation of light due to ozone in the absorption cell.**

Absorption wavelength is 254 nm.

The concentration of ozone is directly related to the absorbance.

Problem – other gases absorb at 254 nm.

Solution: Add a reference cycle to the sample cycle - use a manganese dioxide scrubber to selectively remove ozone from the sample gas, measure absorbance due to interferants, and subtract interferants from sample cycle.

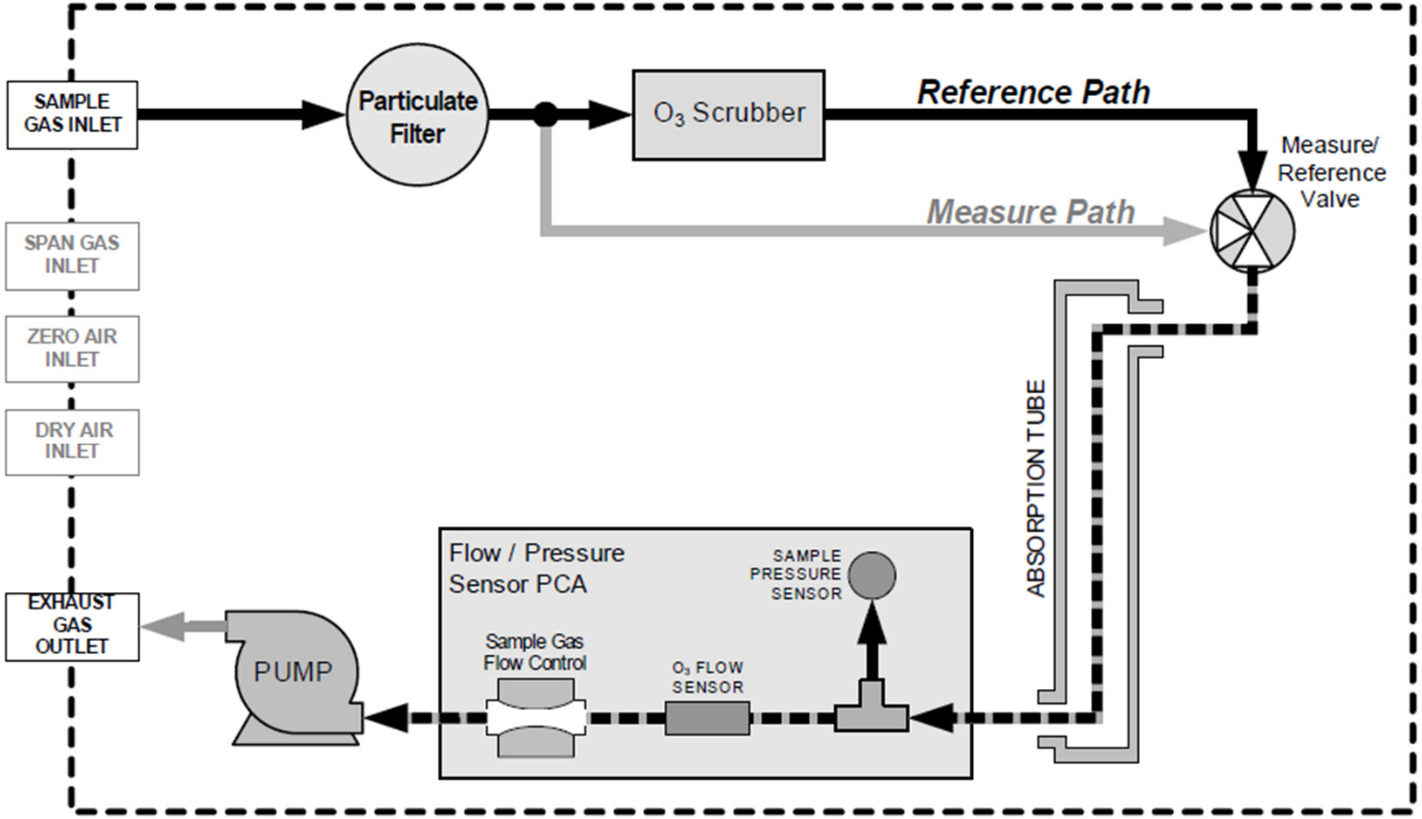


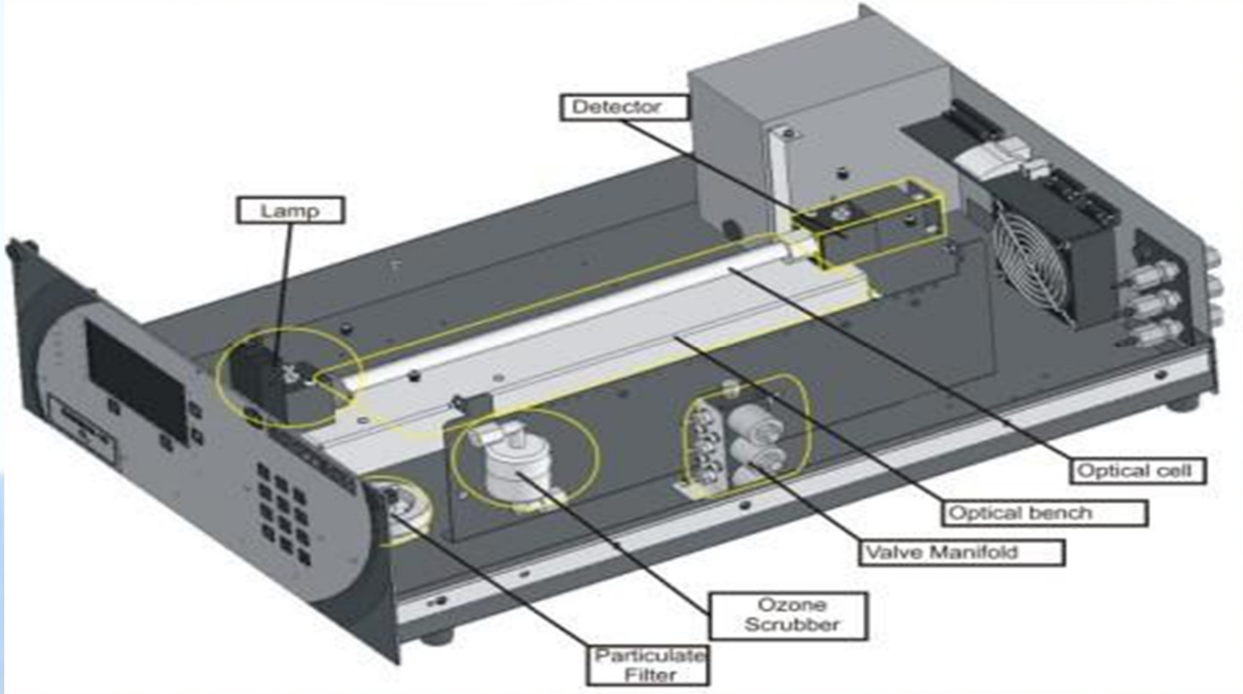
Figure 11-2: Reference / Measurement Gas Cycle

UV Photometer

- The Serinus 10 Ozone analyzer uses non-dispersive ultraviolet (UV) absorption technology and sensitivity is less than 0.5ppb in the range of 0-20ppm. The Ozone analyzer contain following components

Mercury vapour lamp, Photodiode detector & Ozone scrubber

The Ozone (O3) concentration is automatically corrected for gas temperature and pressure changes and referenced to 0°C, 20°C or 25°C at 1 atmosphere.



Serinus 10 Surface Ozone UV Photometer

Electrochemical Concentration Cell (ECC)

- The surface ozone is measured by Brewer Bubbler.
- The bubbler ozone sensor is based on electrochemical reaction of ozone with potassium iodide in solution.
- A glass bubbler containing about 3 ml of buffered potassium iodide solution is surrounded by a reservoir of the same solution. A small hole at the bottom of bubbler allows the solution from the reservoir to enter the chamber.
- Air is aspirated through the bubbler using a suction pump. When ozone enters the sensor, iodine is formed in the cathode half cell. The cell then converts the iodine to iodide, a process during which electrons flow in the cell's external circuit.

Titration of ozone in a potassium iodide (KI) solution according to the redox reaction:

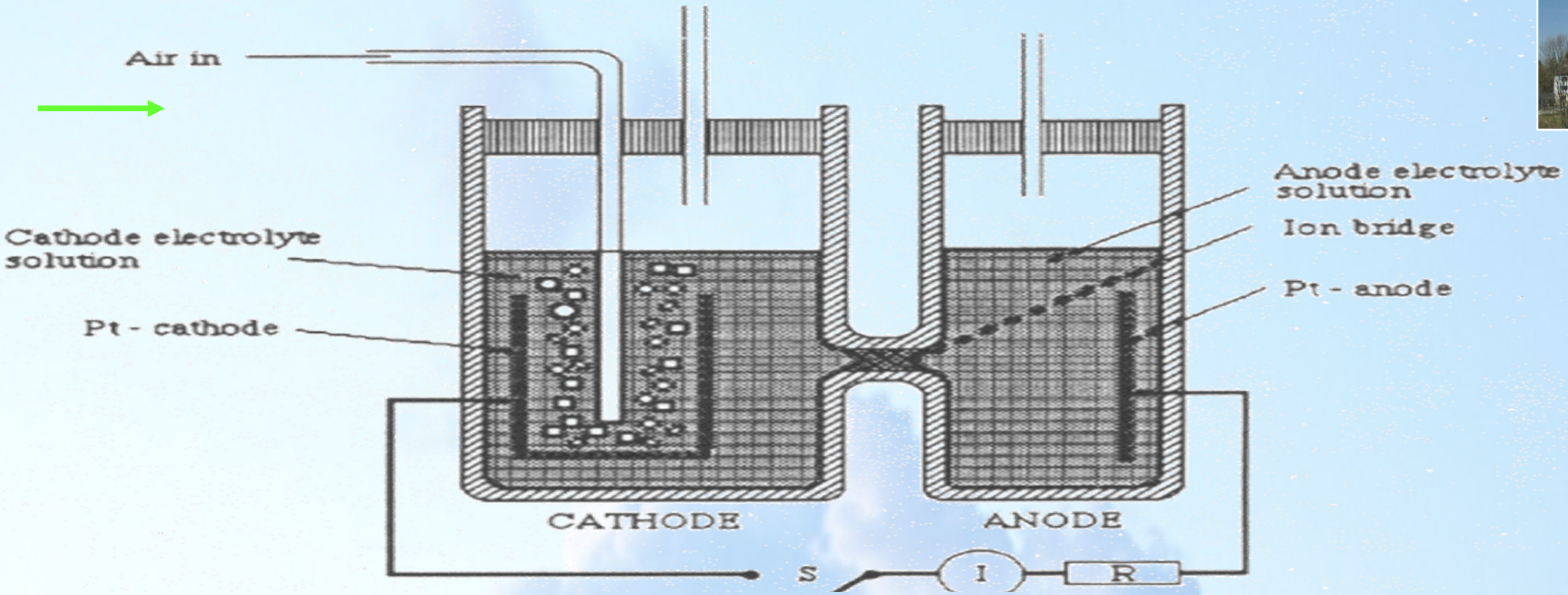
$\mathrm{2\ KI + O3 + H2O = I2 + O2 + 2\ KOH}$

- The iodine makes contact with a platinum cathode and is reduced back to iodide ions by the uptake of 2 electrons per molecule of iodine:
- $\mathrm{I2 + 2\ e^- \ on\ Pt = 2\ I^-}$ [cathode reaction]
- By measuring the electron flow (i.e., the cell current) and the rate at which ozone enters the cell per unit time, ozone concentrations can be calculated.

Electrochemical Concentration Cell (ECC)

- The ozone recording system consists of a modified bubbler sensor, a suitable miniature pump, a network for supplying a polarising potential to the bubbler and a recorder capable of full scale deflection for a current of 2mA. The recorder is calibrated by a micro ampere current source. From the record, the ozone current in mA is determined and the partial pressure P of ozone is calculated from the formula:
- $P(mb) = 4.31 \times 10^{-3} iTt$
- where i is the ozone sensor current in mA, T is the temperature of the air in Kelvin and t is time in seconds for pumping 100 ml of air.
- The system has a response time of few seconds and has a resolution capability of 0.1 part of ozone per 100 million parts of air. The overall accuracy is about 5%

Electrochemical Conductivity Cell (ECC)

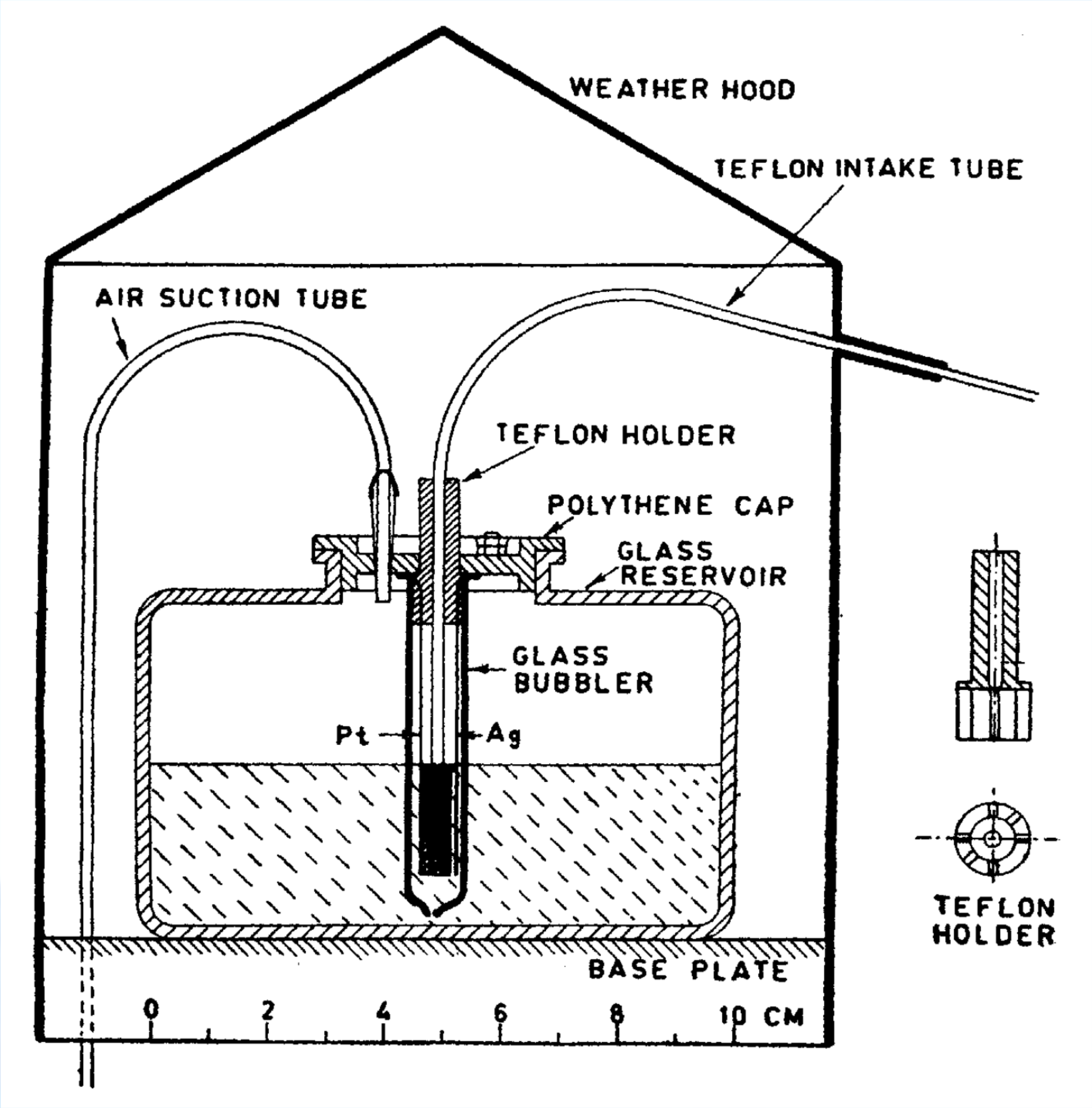


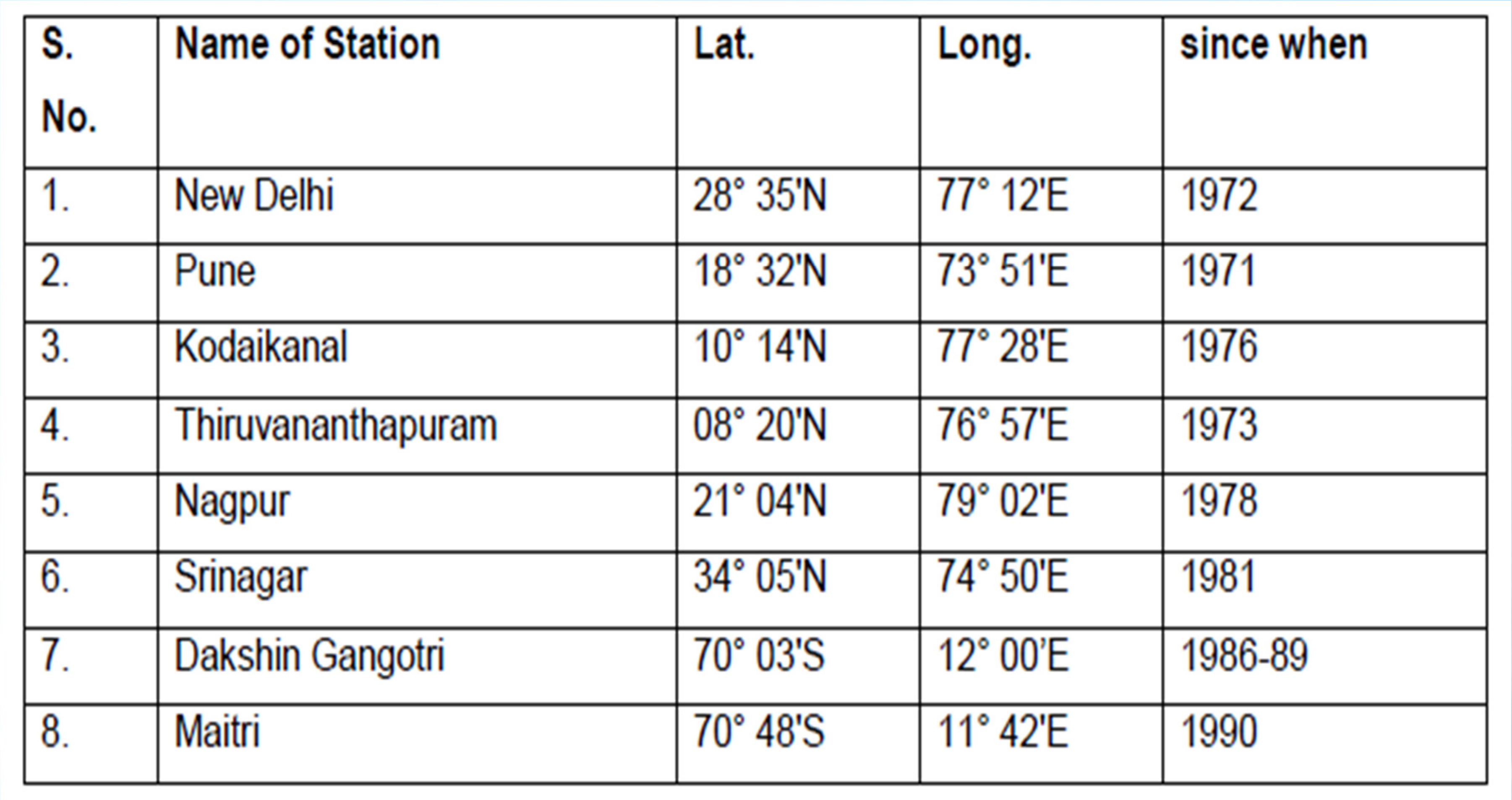
- Electrical current generated is proportional to the mass flow of ozone through the cell
- Continuous operation through pumping of air through the solution

Applications: Measure vertical O_3 distribution up to the stratosphere, Surface O_3

Problems: interference by SO_2 (1:1 negative) and NO_2 (5-10% positive)

- solution preparation has large impact on measurement accuracy
- pump efficiency is reduced at high altitudes


WEATHER HOOD
TEFLON INTAKE TUBE
AIR SUCTION TUBE
TEFLON HOLDER
POLYTHENE CAP
GLASS RESERVOIR
GLASS BUBBLER
Pt
Ag
TEFLON HOLDER
BASE PLATE
0
2
4
6
8
10 CM



S. No.	Name of Station	Lat.	Long.	since when
1.	New Delhi	28° 35'N	77° 12'E	1972
2.	Pune	18° 32'N	73° 51'E	1971
3.	Kodaikanal	10° 14'N	77° 28'E	1976
4.	Thiruvananthapuram	08° 20'N	76° 57'E	1973
5.	Nagpur	21° 04'N	79° 02'E	1978
6.	Srinagar	34° 05'N	74° 50'E	1981
7.	Dakshin Gangotri	70° 03'S	12° 00’E	1986-89
8.	Maitri	70° 48'S	11° 42'E	1990

Siting Requirements

- Because O_3 is a reactive gas, measurements in many locations are required to define its spatial and temporal variations. Near sources of industrial pollution or biomass burning, O_3 concentrations are generally elevated due to photochemical production. At sites more remote from these primarily anthropogenic influences, background measurements may be representative of broad geographic regions.
- The elevation of a site may be an important factor in determining the type of measurement obtained. For example, stations located at high elevation mountain sites are frequently representative of the free troposphere. At boundary layer sites in marine environments, photochemical losses usually dominate while stations downwind of pollution sources will measure higher values of O_3.

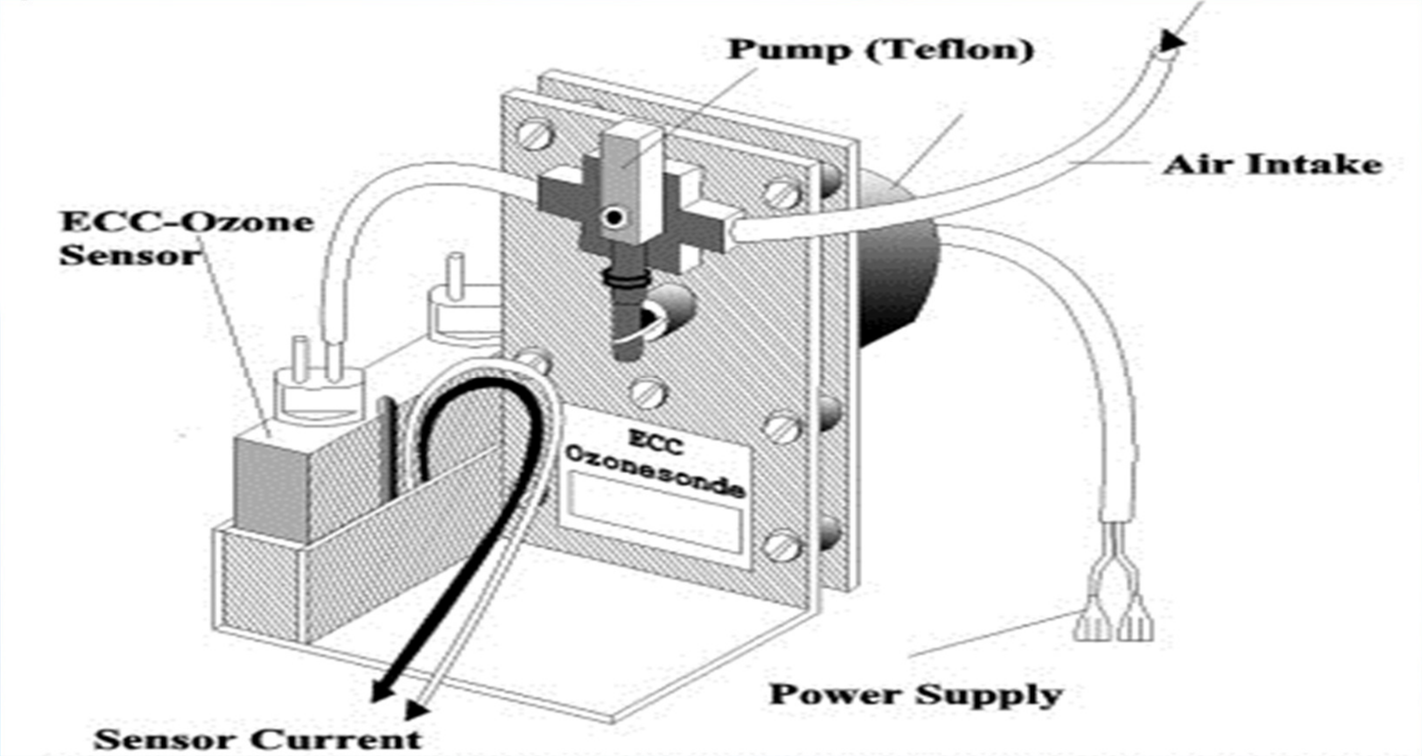
QA/QC

- On a daily to weekly schedule, the instrument is given a "zero" check by sampling air with ozone removed to determine the zero level of the instrument.
- A "span" concentration can also be provided to the instrument to check its operation.
- All data should be routinely inspected by the trained operator in order to flag erroneous measurements.
- Internal intercomparisons by the station operator with a NIST-traceable O_3 calibrator are recommended every 6 months to determine possible instrument malfunction. Periodic intercomparisons between an instrument maintained as a network standard and the station instrument provides one means of ensuring an instrument's accuracy and making corrections to station instrument records.

MEASUREMENT OF VERTICAL DISTRIBUTION OF OZONE (OZONE SONDE)

- Vertical ozone profiles using indigenous balloon-borne ozone-sondes are observed fortnightly at 3 stations namely New Delhi, Trivendrum, Pune and 2 new station at Guwahati and Portblair will be opened this year.
- The heart of the ozone-radiosonde is an electrochemical concentration cell (ECC) that senses ozone as is reacts with a dilute solution of potassium iodide to produce a weak electrical current proportional to the ozone concentration of the sampled air.
- Ozonesondes are composed of an ozone sensor, a battery, a small gas pump, and some electronic circuit boards.
- The ozone-radiosonde is a lightweight, balloon-borne instrument that is mated to a conventional meteorological radiosonde.
- As the balloon carrying the instrument package ascends through the atmosphere, the ozone-radiosonde telemeters to a ground receiving station information on ozone and standard meteorological quantities such as pressure, temperature and humidity.
- The balloon will ascend to altitudes of about 115,000 feet (35 km) or about 3 hPa before it bursts.

The ozone sensor is connected to a meteorological radiosonde. This radiosonde transmits values of air temperature, air pressure, relative humidity, detector current, detector temperature, and pump speed to a ground receiving station. The air containing the ozone sample is pumped through a solution which is oxidized by this ozone producing an electrical current. The electrical current is proportional to the flow of ozone. By knowing the flow (pump speed), the ozone concentration can be deduced. The result is an ozone partial pressure vertical profile.

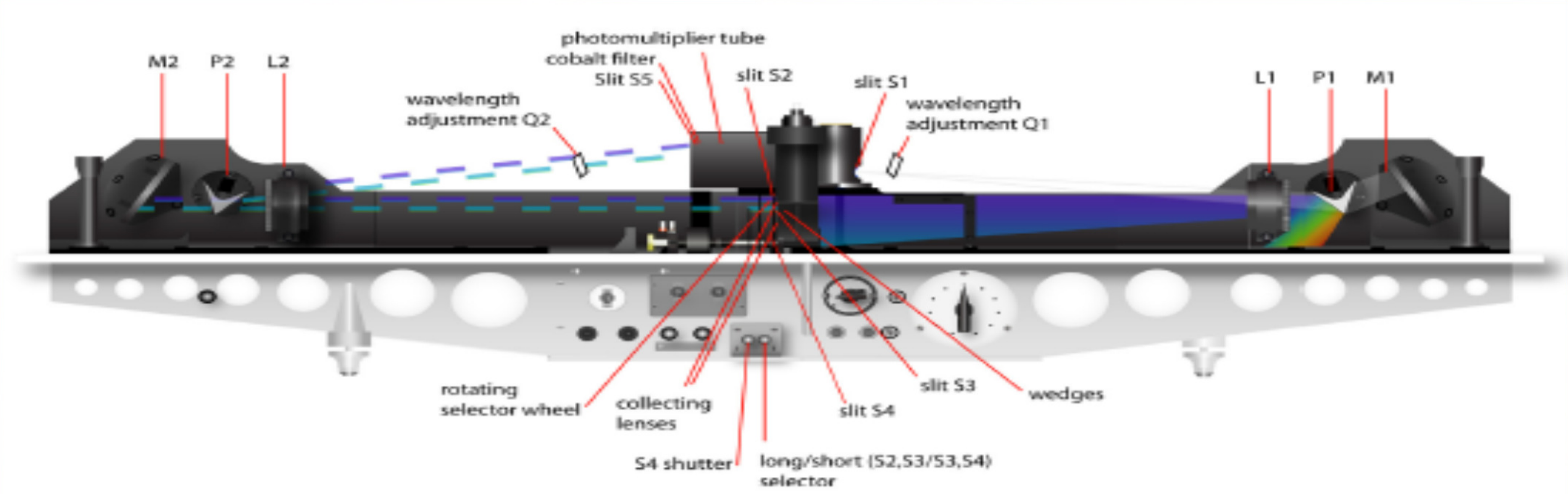


Schematic of an electrochemical concentration cell (ECC) Ozone sonde

MEASUREMENT OF TOTAL COLUMN OZONE BY DOBSON SPECTROPHOTOMETER

- IMD is taking measurements of total ozone by Dobson Spectrophotometer at two stations e.g. New Delhi and Varanasi.
- The Dobson Spectrometer measures the total ozone by measuring the relative intensity of the dangerous UVB radiation that reaches the Earth and comparing it to that of UVA radiation at ground level. If all of the ozone were removed from the atmosphere, the amount of UVB radiation would equal the amount of UVA radiation on the ground. As ozone does exist in the atmosphere, the Dobson Spectrometer can use the ratio between UVA and UVB radiation on the ground to determine how much ozone is present in the upper atmosphere to absorb the UVC radiation.

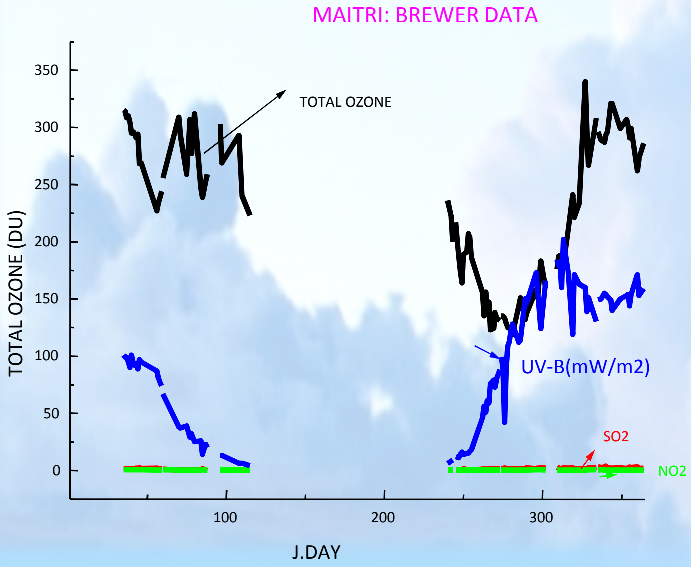
The ratio is determined by turning the R-dial, which can be rotated a full 300°, on the instrument. The spectrometer compares two different wavelength intensities, UVB (305 nm) and UVA (325 nm), in order to calculate the amount of ozone. When turned, the R-dial filters and blocks out the light of the UVC wavelength until the intensity of the two wavelengths of light are equal. The ratio of the two wavelengths at incidence can be deduced once the filtered intensities are the same. The results are measured in Dobson Units.

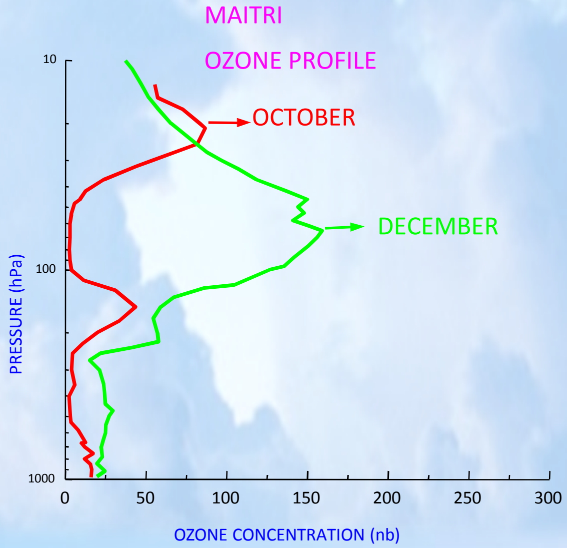


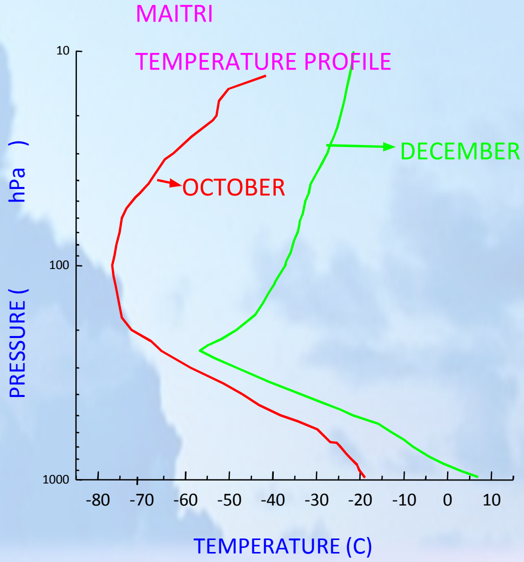
MEASUREMENT OF TOTAL COLUMN OZONE BY BREWER SPECTROPHOTOMETER

IMD is taking measurements of total ozone by Brewer Spectrophotometer at two stations e.g. New Delhi and Kodaikanal. The Brewer spectrophotometer measures ozone based on the same technique as the Dobson instrument. Unlike the Dobson instrument, however, the Brewer spectrophotometer is completely automated and can be programmed by a laptop computer to make measurements at any given time during the day. The absolute accuracy for a total ozone measurement made by a well calibrated Brewer instrument is estimated to be +/- 2.0%.

BREWER OZONE SPECTROPHOTOMETER AT MAITRI (ANTARCTICA)







- **Satellite Measurements**

Satellites measure ozone over the entire globe every day, providing comprehensive data. In orbit, satellites are capable of observing the atmosphere in all types of weather, and over the most remote regions on Earth. They are capable of measuring total ozone levels, ozone profiles, and elements of atmospheric chemistry. In the mid-1980s wide-ranging ozone depletion over the Antarctic was first recognized from satellite data.

Sinks and Lifetime

Sinks - reaction, transfer to soils and ice caps, and dissolution in ocean waters. Its dissolution rate is slow since it is relatively insoluble.

Lifetime - Determined by processes that lead to loss of O_3 from the atmosphere (sinks).

Average lifetime of ~ 22 (±2) days in troposphere varies with altitude. 1-2 days in the boundary layer where it is removed mainly by dry deposition to several weeks in the upper troposphere.

Health Effects :

at mixing ratios > 0.15 ppmv – headaches, > 0.25 ppmv chest pains, > 0.30 ppmv sore throat and cough, decreases lung function

Symptoms of respiratory problems –

coughing and breathing discomfort. Small decreases in lung function

Affect people with

asthma, chronic bronchitis, and emphysema.

At levels greater than 0.1 ppmv, ozone affects animals by increasing their susceptibility to bacterial infection.

It also interferes with the growth of plants and trees and deteriorates organic materials, such as rubber.

The Impacts of Ozone Depletion

- **Harm to human health**:
- More skin cancers, sunburns and premature aging of the skin.
- UV radiation can damage several parts of the eye, including the lens, cornea, retina and conjunctiva (more cataracts, blindness and other eye diseases).
- **Adverse impacts on agriculture, forestry and natural ecosystems:**
- Several of the world's major crop species are particularly vulnerable to increased UV, resulting in reduced growth, photosynthesis and flowering. These species include wheat, rice, barley, oats, corn, soybeans, peas, tomatoes, cucumbers, cauliflower, broccoli and carrots.
- Plant growth, especially in seedlings, is harmed by more intense UV radiation.
- **Materials**:
- Wood, plastic, rubber, fabrics and many construction materials are degraded by UV radiation.
- The economic impact of replacing and/or protecting materials could be significant.

Effects of Ozone on Plants

Most damaging air pollutant for plants.

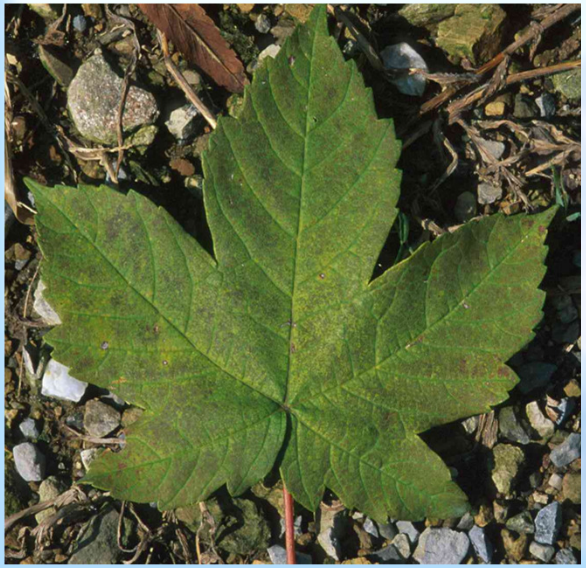
Enters the leaf through stomata, primary site of injury is the cells of the mesophyll or palisade layer on the upper leaf surface. This tissue contains chloroplasts (chlorophyll containing plastids) and is responsible for photosynthesis. So photosynthesis is effected. Exposure to sufficient O_3 produce a variety of injury symptoms associated with chlorophyll breakdown.

O_3 reacts with O_2 and produces reactive oxygen species, including H_2O_2, superoxide (O^{2-}), singlet oxygen ($^1O_2$*), and the hydroxyl radical (OH^-). These denature proteins, damage nucleic acids and thereby give rise to mutations, and cause lipid peroxidation, which breaks down lipids in membranes.

Visible symptoms arising from O_3-induced injury

Usually characterized by upper leaf surface chlorosis (yellowing), stippled or mottled markings or by a 'bronzed' appearance. At very high concentrations, the leaf tissue will show small dead areas (lesions).

Symptoms will vary among plants, and even among varieties within a single type of plant. Crop, landscape, trees and native vegetation can all be susceptible to ozone impact.



Acer pseudoplatanus

The small yellow, green mottled spots on this leaflet of Aran white clover were caused by ozone. Clover is one of the most sensitive species.

Morus nigra

Plant Commonly affected by O_3 & typical symptoms

Crop	Foliar Symptoms
Bean (Phaseolus sp.)	**Bronzing; chlorosis; bifacial isolated necrosis of small areas**
Cucumber (Cucumis sp.)	**White stipple**
Grape(Vitis sp.)	**Red to black stipple**
Morning glory (Ipomoea sp.)	**Chlorosis**
Onion (Allium sp.)	**White flecks; tip dieback**
Potato (Solanum sp.)	**Gray fleck; chlorosis; bronzing**
Soyabean (Glycine sp.)	**Red bornzing; chlorosis; purple stipple**
Spinach (Spinacia sp.)	**Gray to white fleck**
Tobacco (Nicotiana sp.)	**Metallic to white fleck**
Watermelon (Citrullus sp.)	**Gray fleck**

O_3induced injury on Nicotiana tobacum cv. BelW3

O3-induced cholorosis on a watermelon

Plant Commonly affected by O_3 & typical symptoms

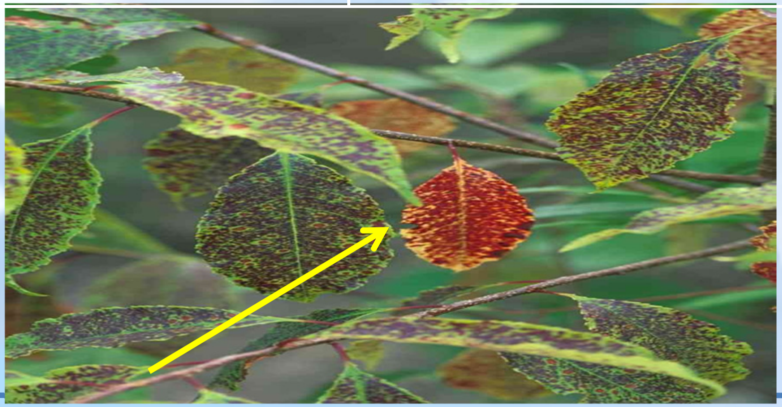
Conifers	Foliar Symptoms
Eastern white pine (Pinus strobus)	**Chlorotic fleck or mottle on older needles; red brown tipburn of current needles.**
Jeffrey pine (P. Jeffreyi)	**Chlorotic mottle of older needles (banding possible)**
Ponderosa pine (P. Ponderosa)	**Chlorotic fleck or mottle on older needles followed by needle dieback from tips (banding possible)**
White fir (Abies concolor)	**Chlorotic mottle on older needles**

Healthy plant of Pinus ponderosa – Left

Loss of needles and loss of tree vigor due to O_3 injury - Right

Plant Commonly affected by O_3 & typical symptoms

Deciduous trees	Foliar Symptoms
Black cherry (Prunus serotina)	Red black stipple; reddening and leaf chlorosis; premature defoliation
Green Ash (Fraxinus pennsylvanica)	Red purple stipple
Quaking aspen (Populus tremuloides)	Black stipple; chlorosis; premature defoliation
Sycamore (Platanus occidentalis)	Chlorosis; early senescence (fall coloring) and defoliation
Tulip Poplar (Liriodendron tulipifera)	Dark stipple (classic symptoms)



Prunus serotina

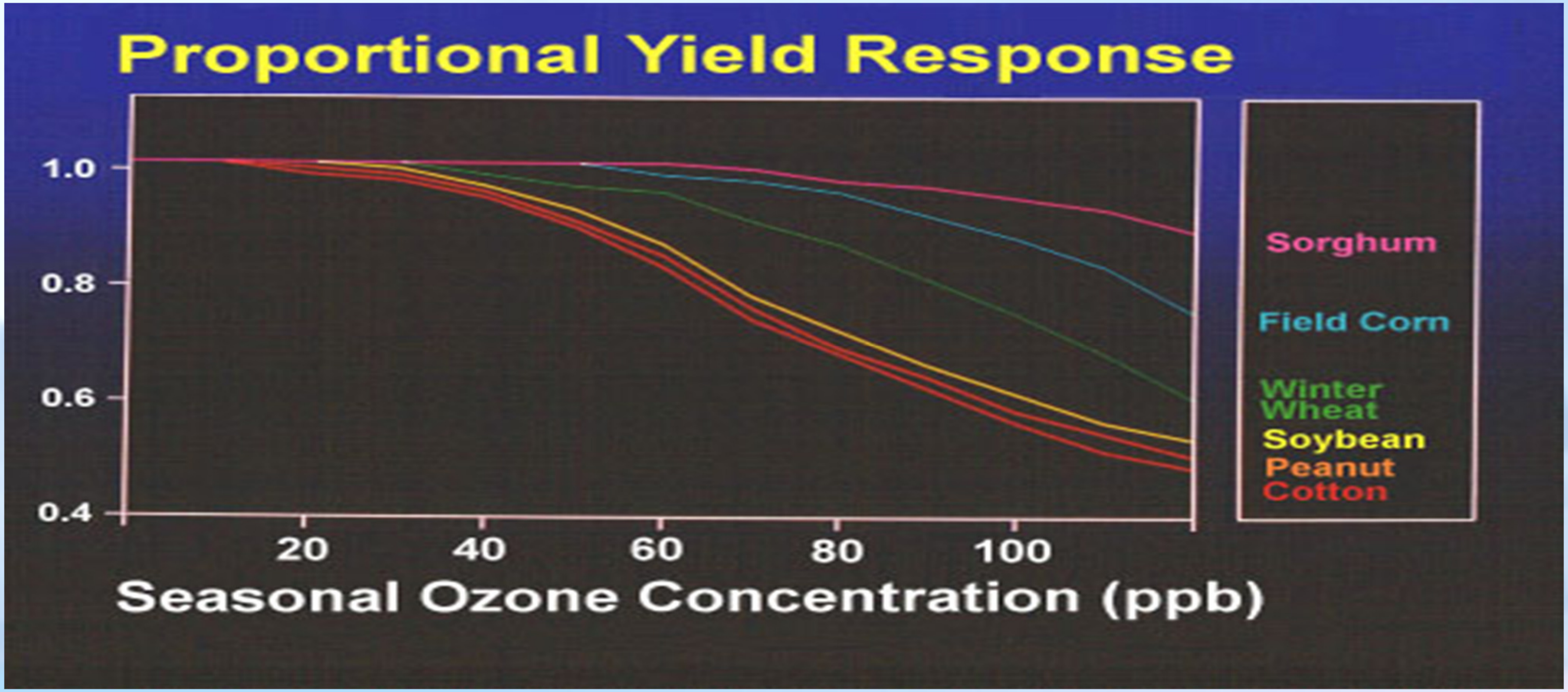
Effects of Ozone on Yield

With mean daily 40, 50, or 60 ppb O_3 concentration, the combined yields of soybean, maize, and cotton would be decreased by 5, 10, and 16%, respectively.


Ozone injury to soybean foliage

Yield Loss

Experiments at five locations using numerous chambers to expose plants to ozone treatments spanning the range of concentrations that occur in different areas of the world revealed dicot species (soybean, cotton, and peanut) are more sensitive to yield loss caused by O_3 than monocot species (sorghum, field corn, and winter wheat).



Open Top Chambers

OZONE PROTECTION IN PLANTS

Several chemical substances have been found to have the properties of a "protectant" – they cause the plant to become insensitive to ozone, or they react with ozone before the ozone can react with plant tissues.

The use of pesticides as ozone protectants

Fungicides

CHLOROFLUOROCARBONS

Freon represents several different chlorofluorocarbons or CFCs. CFCs are manufactured under the trade name Freon.

CFCs are colorless, odorless, nonflammable, noncorrosive gases or liquids and highly stable compounds

Used as propellants in spray cans and in refrigeration units.

They are several organic compounds composed of carbon, fluorine, chlorine, and hydrogen.

The most widely used CFCs are

Chlorofluorocarbons (CFCs) contain Carbon and some combination of Fluorine and Chlorine atoms.

Hydrofluorocarbons (HFCs) contain Hydrogen, Fluorine, and Carbon (no chlorine).

Hydrochlorofluorocarbons (HCFCs) contain Hydrogen, Chlorine, Fluorine, and Carbon atoms

Hydrobromofluorocarbons (HBFCs) contain Hydrogen, Bromine, Fluorine, and Carbon atoms.

Perfluorocarbons contain Fluorine, Carbon, and Bromine atoms, and some contain Chlorine and/or Hydrogen atoms.

These compounds are often designated by a combination of letters and numbers (e.g., CFC-11, HCFC-142).

chemical formula ($C2H3F2Cl$)

To find the number, given the chemical formula:

consider the number as consisting of 3 digits: a, b, and c. For 2-digit numbers (e.g., CFC-11) the a digit is zero (e.g., CFC-011).

a is the number of carbon atoms minus 1;
b is the number of hydrogen atoms plus 1;
c is the number of fluorine atoms.

For $CFCl3$: a=the number of carbon atoms (1) minus 1=0
b=the number of hydrogen atoms (0) plus 1=1
c=the number of fluorine atoms=1
and, the compound is CFC-011, or CFC-11.

Similarly: CCl_2F_2 is CFC-12 and $C_2Cl_3F_3$ is CFC-113

To find the chemical formula, given the number.

first add 90 to the abc number, to obtain a 3-digit def number, where:

- d is the number of carbon atoms;
- e is the number of hydrogen atoms;
- f is the number of fluorine atoms; and
- 2d + 2 - e - f = the number of chlorine atoms.

For CFC-11: 90 + 11 = 101, so the number of carbon atoms is 1, the number of hydrogen atoms is zero, the number of fluorine atoms is 1, and the number of chlorine atoms is (2 + 2 - 0 - 1 = 3).

So the chemical formula for CFC-11 is CFCl3.

Similarly:

CFC-12: 12 + 90 = 102; 4-2 = 2 Cl; the chemical formula is CCl2F2

CFC-113: 113 + 90 = 203; 6-3 = 3 Cl; the chemical formula is: C2Cl3F3

HCFC-142b: 142 + 90 = 232; 6-5 = 1 Cl; the chemical formula is: C2H3F2Cl

Halons : Fluorocarbons (not hydrofluorocarbons, i.e., no hydrogen atoms) with at least one bromine atom.

Nomenclature is relatively simple; each halon has an abcd number, where:

a = the number of carbon atoms
b = the number of fluorine atoms
c = the number of chlorine atoms
d = the number of bromine atoms.

C2F4Br2 is Halon 2402.

And other way: Halon 1211 is CF2ClBr.

i

Ozone Layer thickness____________with latitude. (Increases / decreases)

Ground level Ozone is ____________ pollutant (Primary / Secondary)

Ozone hole occurs in Antarctica in -----------------season (Summer / Winter)

100 DU is approximately --------------------- thickness (1mm / 100 mm)

Ozone shows absorption of UV light ----------- (254 / 454 nm)

- Halons contain Hydrogen atom.
- Freon is more dangerous than methyl chloride refrigerant
- For same Ozone concentration yield loss to Cotton is more than Sorghum

a) Derive the chemical formula of CFC -011 and CFC-113

b) Derive the number for CFC-12

c) Derive the number for Halon C2F4Br2.

d) Derive the chemical formula for Halon 1211

Write cycle of four reactions from photolysis of Chlorofluorocarbons to release of free chlorine atom.

THANK YOU