Ozone and Air Pollution

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भारत मौसम विज्ञान विभाग

INDIA METEOROLOGICAL DEPARTMENT

New Delhi

Syllabus

Ozone and its importance in Meteorology, measurements of total ozone, vertical distribution of ozone and surface ozone, ozone sonde, Dobson and Brewer spectrophotometer Air Pollution measurement: AOD, Precipitation chemistry, PH meter, Conductivity meter, SO2/ Nox/ TSPM measurement

Why Should We Be Concerned About Air Pollution?

- Air pollution is a major environmental risk to health.

  Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause 4.2 million premature deaths worldwide. (Source: WHO)

The breathing frequency

Fig. 1 : AMOUNT OF AIR BREATHED BY CHILDREN

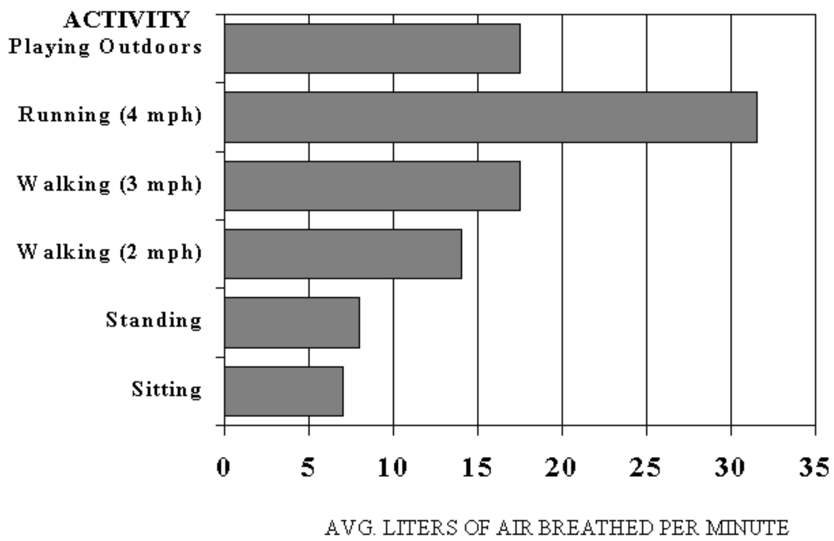


Fig. 2 : AMOUNT OF AIR BREATHED BY ADULT FEMALES

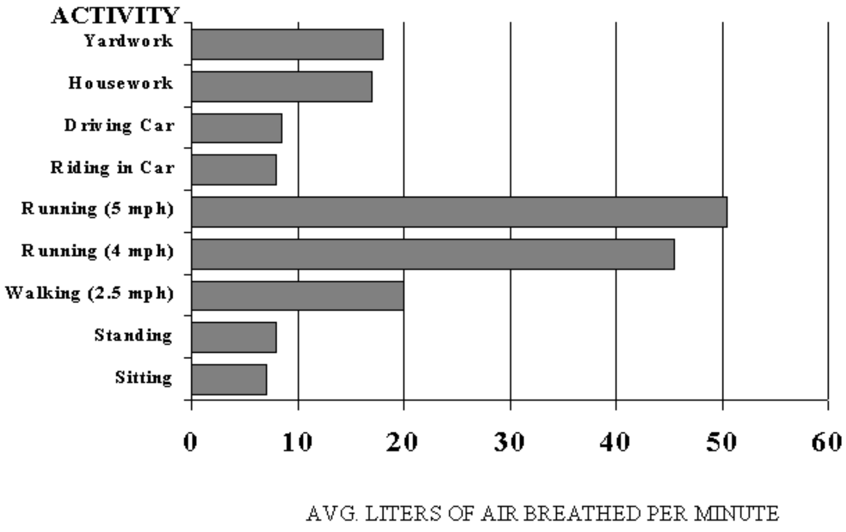


Fig. 3 : AMOUNT OF AIR BREATHED BY ADULT MALES

Source: California Environmental Protection Agency

Why Should We Be Concerned About Air Pollution?

•Air pollution is a major environmental risk to health.

Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause 3.7 million premature deaths worldwide in 2012. (Source: WHO)

How Much Air We Breath

The average breathing frequency (or respiratory rate) in a healthy adult at rest is 12-18 breaths per minute.

Average Volume of one breath (tidal volume) = 0.5 Liter

The average breathing frequency (or respiratory rate) in a healthy adult at rest is 12-18 breaths per minute (Let's work with an average of 15 breaths/minute).

An adult breaths about 21,600 times per day.

An average person will breathe 21600x0.5 = 10800 Liter = 10.8 m^3

Dry air has a density of 1.2754 kg/m^3

An average person will breathe 10.8x 1.2754 ≈ **14 Kg of Air**

Air Quality: A Definition

The term “air quality” means the state of the air around us. Good air quality refers to clean, clear, unpolluted air.

Ambient Air Quality

Ambient air quality refers to the quality of outdoor air in our surrounding environment. It is typically measured near ground level, away from direct sources of pollution.

Indoor Air Quality

The air in enclosed spaces, such as home, schools or workplaces, can also be polluted, from pollutants that have seeped in from the outdoors and pollutants emitted from indoor sources.

AIR POLLUTION

Air Pollution may be defined as presence in the atmosphere of one or more air contaminants or combinations of thereof in such concentrations and of such duration that are or may tend to be injurious to plant, animal, human kingdom or may unreasonably interfere with comfortable enjoyment of life.

Air pollution may be defined as any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation, or materials.

Presence of chemicals in the atmosphere in quantities and duration that are harmful to human health and the environment.

A pollutant is something that makes things foul or unclean; i.e., pollutants taint, contaminate and defile things.

Webster's Dictionary

Air Pollution Classification (Contd.)

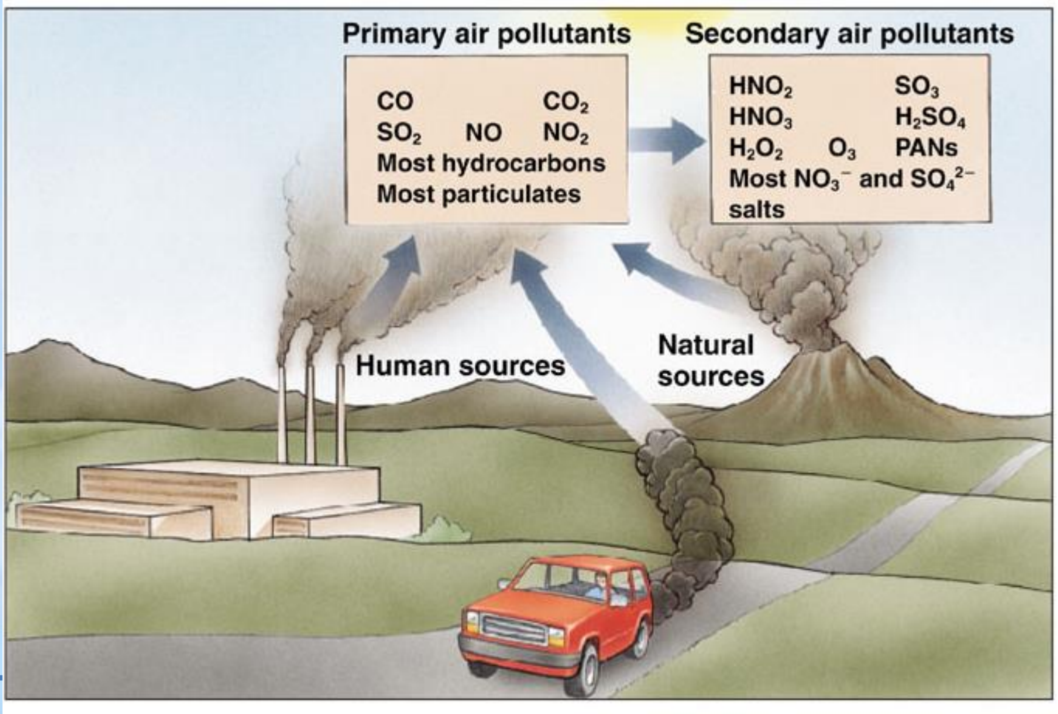
According to the manner in which they reach the atmosphere

Primary Pollutants

products of natural events (e.g. fires and volcanic eruptions) and human activities which are emitted directly into the atmosphere, such as SO_2, CO, NO_2 etc.

Secondary Pollutants

formed by interaction of primary pollutants with each other or with normal components of the air e.g. H_2SO_4, HNO_3, O_3 etc.



National Ambient Air Quality Standards

Environment (Protection) Seventh Amendment Rules, 2009

Pollutant	Time Weighted Average	Concentration in Ambient Air		
		Industrial, Residential, Rural and other area	Ecologically sensitive areas (notified by Central Govt.)	Methods of Measurement
SO_2 ($\mu g m^{-3}$)	Annual* 24 hours**	50 80	20 80	- Improved West and Goeke - UV - fluorescence
NO_2 ($\mu g m^{-3}$)	Annual* 24 hours**	40 80	30 80	- Modified Jacob & Hochheiser (Na-Arsenic) - Chemiluminescence
PM_{10}, ($\mu g m^{-3}$)	Annual* 24 hours**	60 100	60 100	- Gravimetric - TEOM - Beta Attenuation
$PM_{2.5}$, ($\mu g m^{-3}$)	Annual* 24 hours**	40 60	40 60	- Gravimetric - TEOM - Beta Attenuation
Ozone ($\mu g m^{-3}$)	8 hours 1 hour	100 180	100 180	- UV photometric - Chemiluminescence - Chemical Method
Lead ($\mu g m^{-3}$)	Annual* 24 hours**	0.5 1.0	0.5 1.0	- AAS/ICP method after sampling on EPM2000 or equivalent filter paper - ED-XRF using Teflon filter
CO ($\mu g m^{-3}$)	8 hours 1 hour	2000 4000	2000 4000	- Non-dispersive Infra Red (NDIR) spectroscopy

National Ambient Air Quality Standards

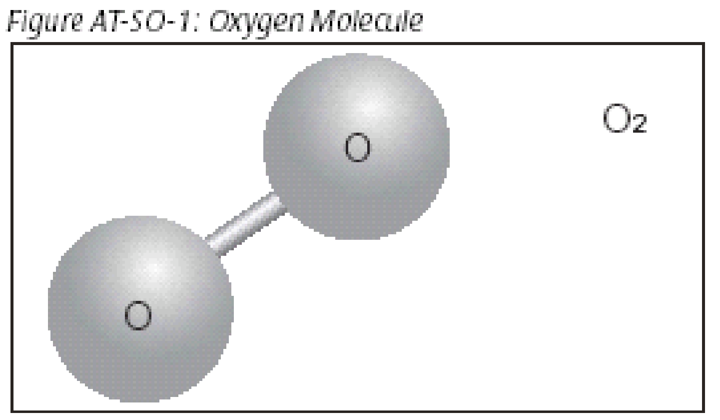
Environment (Protection) Seventh Amendment Rules, 2009

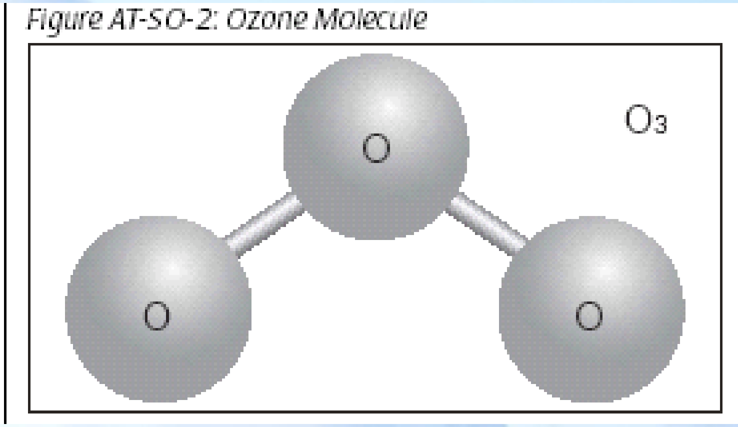
Pollutant	Time Weighted Average	Concentration in Ambient Air		
		Industrial, Residential, Rural and other area	Ecologically sensitive areas (notified by Central Govt.)	Methods of Measurement
NH3 (μgm^{-3})	Annual* 24 hours**	100 400	100 400	-Chemiluminescence -Indophenol Blue Method
Benzene (μgm^{-3})	Annual*	5	5	- Gas Chromatography based continuous analyzer - Absorption and Desorption followed by GC analysis
Benzo(a)Pyrene - particulate phase only (ngm^{-3})	Annual*	1	1	- Solvent extraction byHPLC/GC analysis
Arsenic (ngm^{-3})	Annual*	6	6	- AAS/ICP method after sampling on EPM2000 or equivalent filter paper
Nickel (ngm^{-3})	Annual	20	20	- AAS/ICP method after sampling on EPM2000 or equivalent filter paper

Sensitive Areas: Hill stations, health resorts, sancturies, national parks, national monuments and other areas where the nation conserves its clean environment even if that implies some curb on economic activity.

Ozone

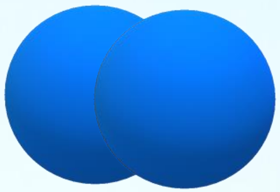
a regional and global problem



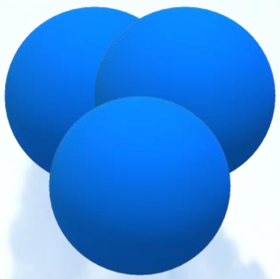


WHAT IS OZONE

OXYGEN ATOM

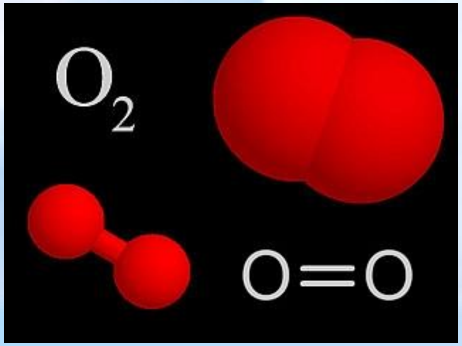


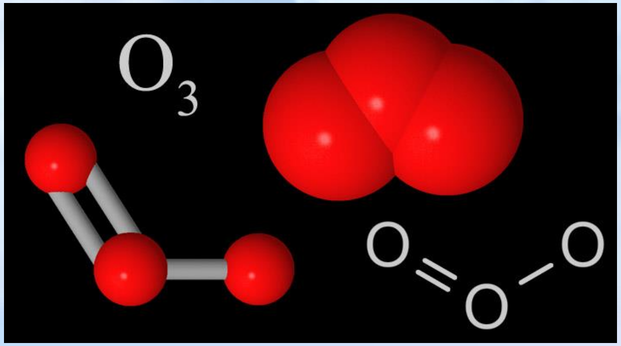
OXYGEN O_2



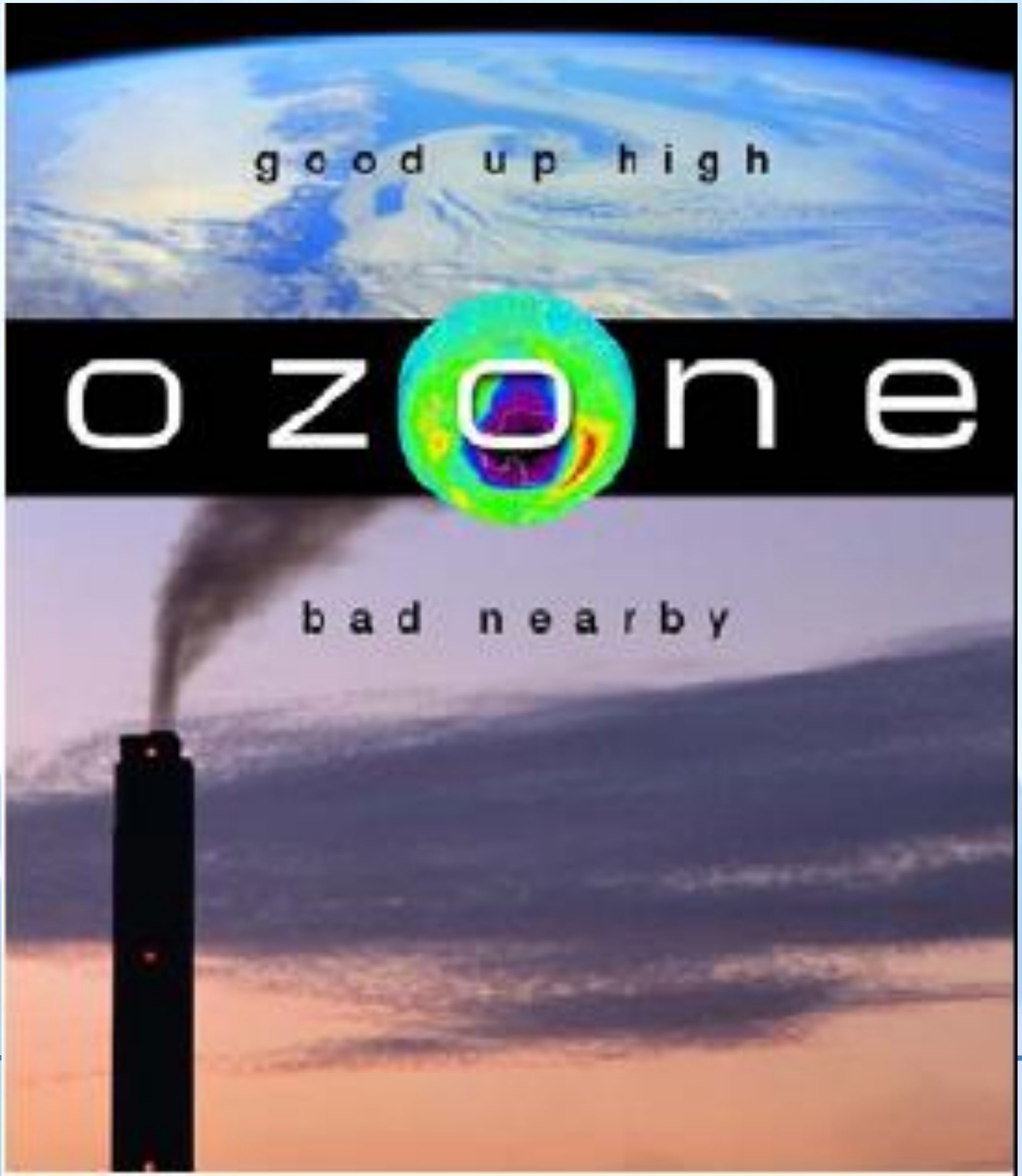
OZONE O_3

- **Ozone (O_3) or Trioxygen is an allotrope of oxygen that is much less stable than the diatomic allotrope (O_2).**
- **O_3 is a colourless, odourless gas at ambient concentrations.**
- **At high concentration, it is a pale blue gas, slightly soluble in water and much more soluble in inert non-polar solvents. At −112 °C temperature, it condenses to form a dark blue liquid.**
- **Ozone is present in low concentrations throughout the Earth's atmosphere. In total, ozone makes up only 0.6 parts per million of the atmosphere.**





OZONE *“Can’t live with it, can’t live without it”*



TROPOSPHERIC OZONE FORMATION CHEMISTRY

The basis for ozone formation is the photolysis of nitrogen dioxide (NO2), by the following reactions

$$NO_2 + h\upsilon \xrightarrow{k_1} NO + O \qquad (1)$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \qquad (2)$$

Where hv represents photochemical energy from UV radiation (λ<400nm)

k represents a rate constant for the reaction of NO and *M represents* N_2 *or* O_2 *or another molecule* that absorbs the reaction's excess vibrational energy.

Once formed, ozone is rapidly dissociated by reaction with NO, as follows:

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \qquad \text{................ (3)}$$

The NO_2 molecule is regenerated, and in the absence of other species a steady state is achieved through reactions (1) through (3) in which the ozone concentration can be estimated by the following relationship:

$$[O_3] = \frac{k_1[NO_2]}{k_2[NO]}$$

In the natural troposphere, these reactions normally result in a background O_3 concentration of 15 to 45 ppb (Altshuller and Lefohn, 1996).

Altshuller A.P. and Lefohn A.S. (1996) "Background ozone in the planetary boundary layer over the United States". *J. Air & Waste Manag. Assoc.* ***46, 134-141.***

This equilibrium is disturbed by the oxidation of NO to NO_2 by peroxy radicals (HO_2) formed in the course of oxidation of carbon monoxide (CO) and hydrocarbons by OH radicals:

For CO:

$CO + OH$ -----> $CO_2 + H$

$H + O_2$ ------> HO_2

$HO_2 + NO$ ------> $OH + NO_2$

For hydrocarbons (e.g., CH_4):

$CH_4 + OH$ ------> $CH_3 + H_2O$

$CH_3 + O_2$ ------> CH_3O_2

$CH_3O_2 + NO$ -------> $CH_3O + NO_2$

$CH_3O + O_2$ --------> $CH_2O + HO_2$

$HO_2 + NO$ ------> $OH + NO_2$

The net result of this chemistry is to produce NO_2 from NO by other means than by reaction (3), thus leading to enhanced ozone concentrations following reactions (1) and (2).

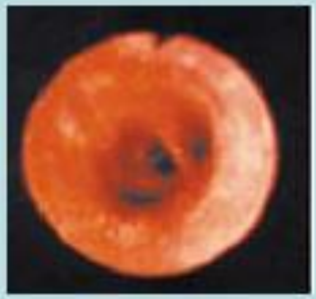
SURFACE OZONE

Ground-level O_3 is a pollutant that is harmful to living organisms. Levels of surface ozone exceeding 80 ppb for 8 hours or longer are considered harmful for most living things

- **Ozone can inflame and damage cells that line your lungs.** Within a few days, the damaged cells are replaced and the old cells are shed-much in the way your skin peels after a sunburn.
- **Ozone may aggravate chronic lung diseases** such as emphysema and bronchitis and reduce the immune system's ability to fight off bacterial infections in the respiratory system.
- **Ozone may cause permanent lung damage.** Repeated short term O_3 damage to children's developing lungs may lead to reduced lung function in adulthood.

Ozone can inflame the lung's lining.

Healthy lung



Lung lining inflamed by O_3

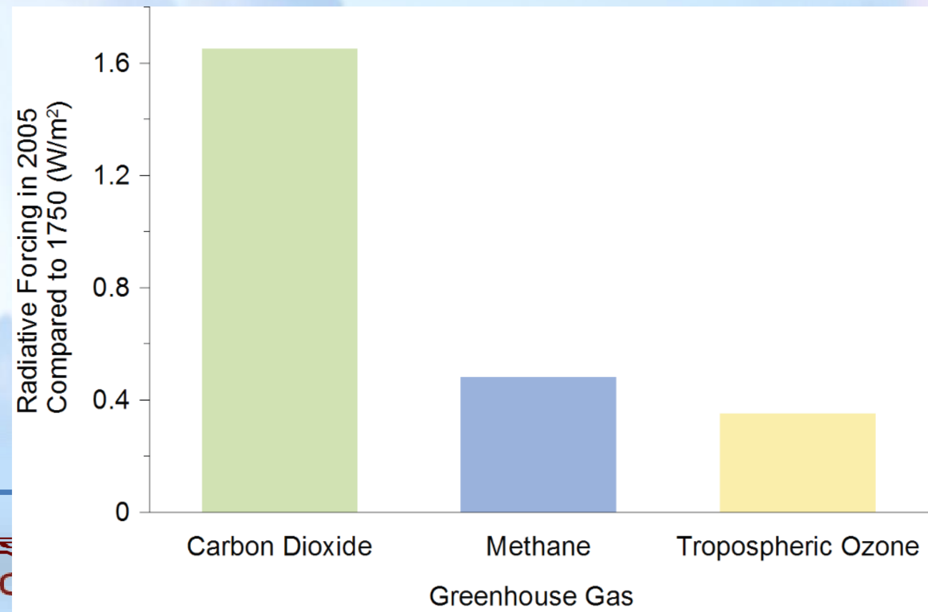
Why Measure Surface Ozone Concentration?

- Ozone is a major product of air pollution and globally its abundance is unknown

- Ozone at the earth's surface plays a key role in the chemical cycling of many other trace gases in the troposphere.

- Knowing the amount of ozone helps assess the degree to which it is an environmental problem

- Ozone is a GHG



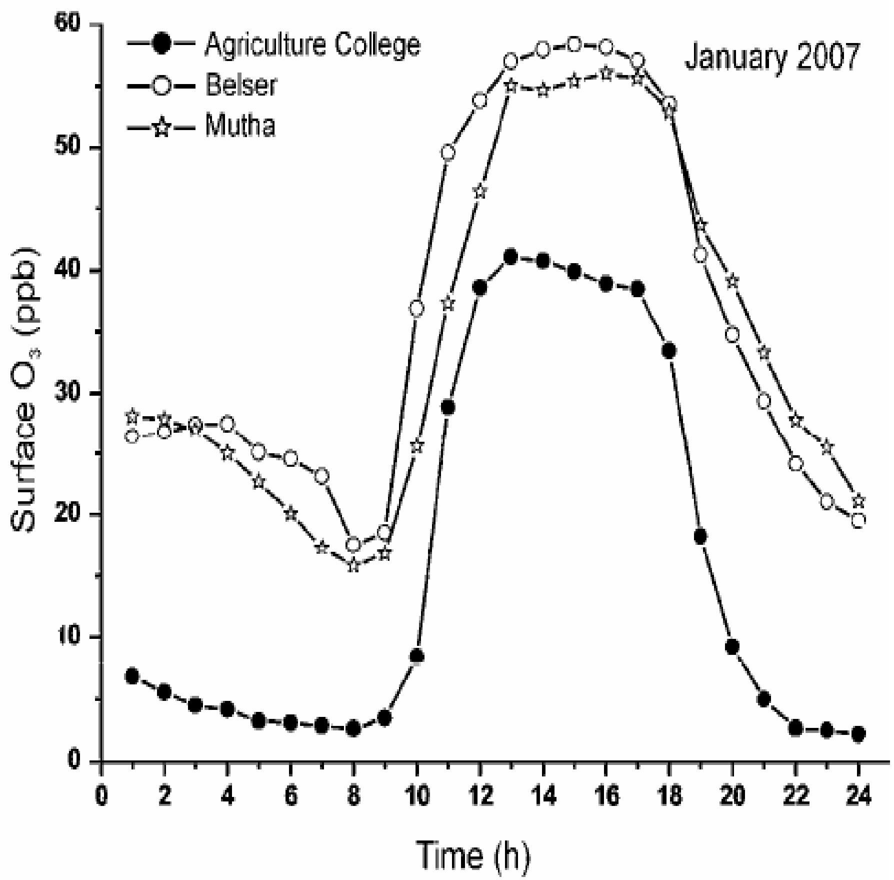
Significant Values

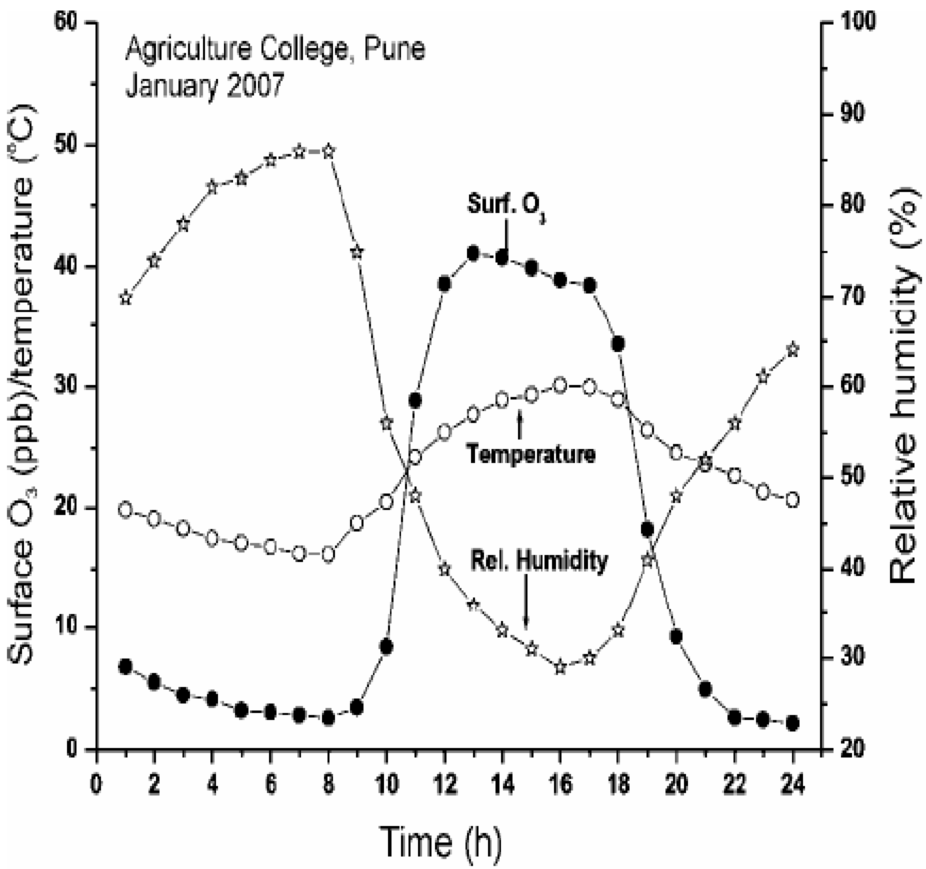
- ❖ Average concentrations range from almost 0 ppb to over 100 ppb depending on time of year and geographic location

- ❖ In extremely polluted conditions ozone can reach 200 ppb and more

- ❖ Levels of surface ozone exceeding 80 ppb for 8 hours or longer are considered harmful for most living things

Diurnal variation of surface ozone at the urban and rural locations.

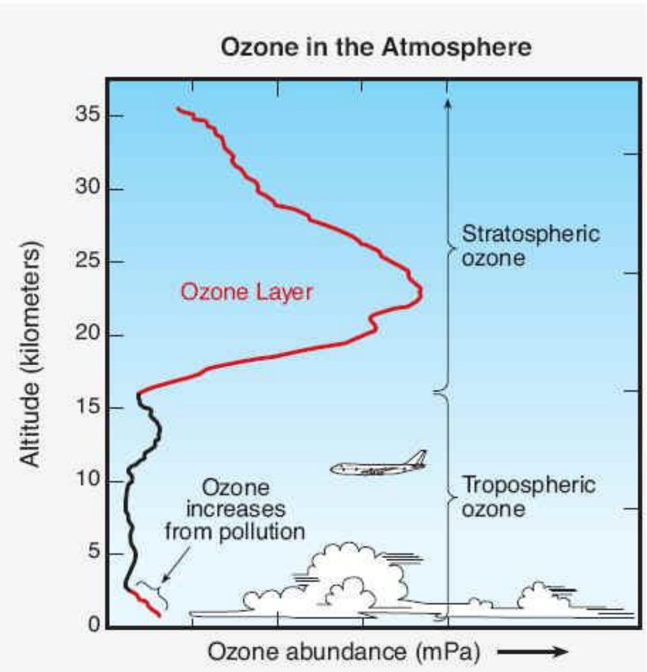


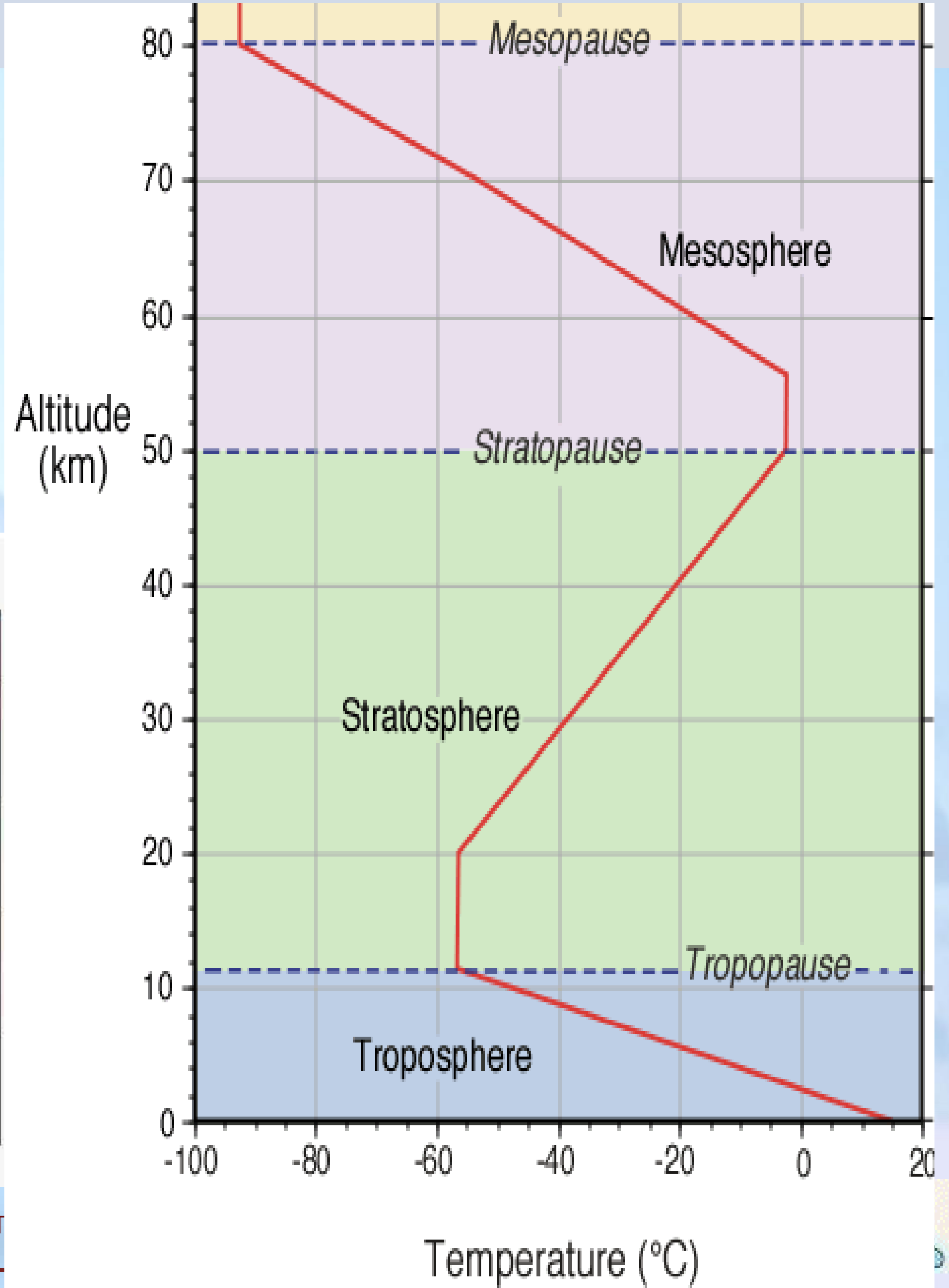


Variation of Ozone with Altitude

The Ozone layer can be divided into two main parts :

- **Tropospheric Ozone**
  - **Surface Ozone**
  - **Upper Tropospheric Ozone**
- **Stratospheric Ozone**





Stratospheric Ozone Production

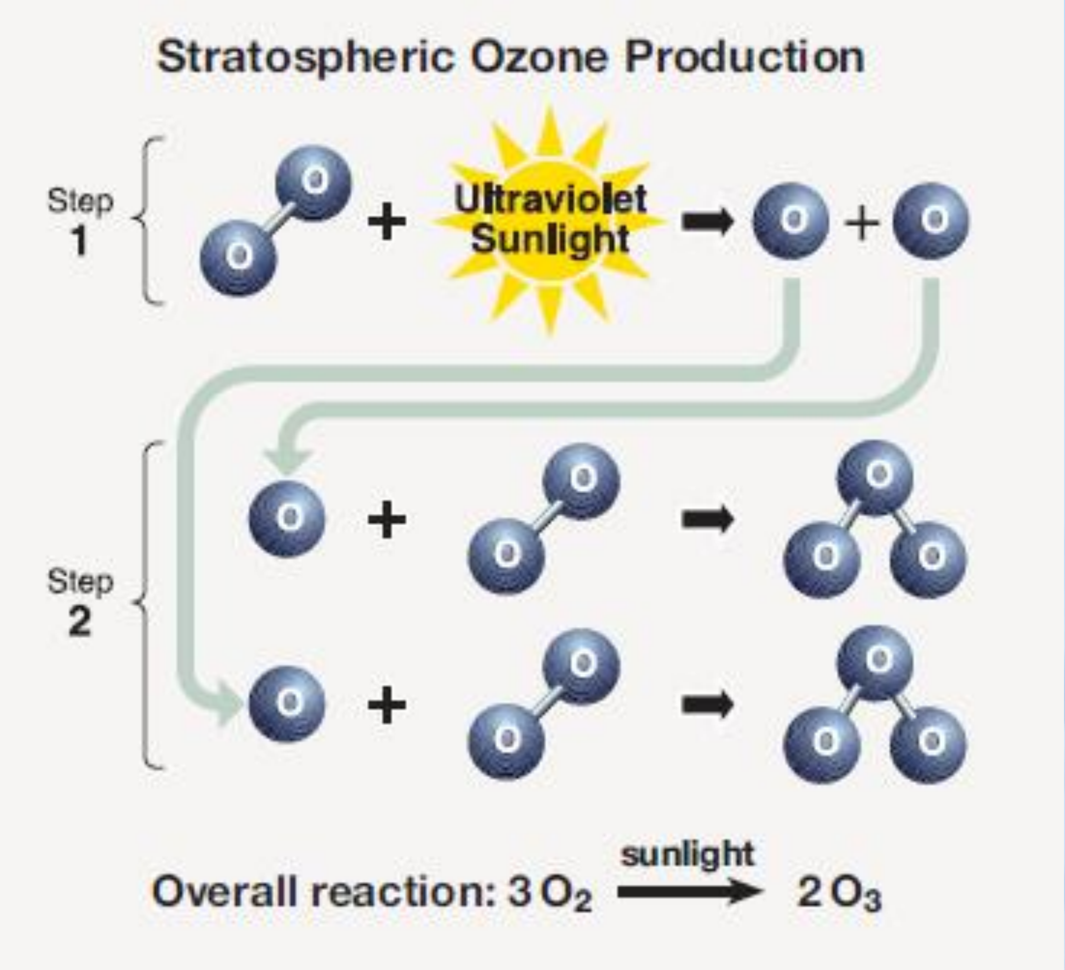
Stratospheric ozone is naturally formed in chemical reactions involving ultraviolet sunlight and oxygen molecules. In the first step, sunlight breaks apart one oxygen molecule (O2) to produce two oxygen atoms (2 O).

O2 + UV photon --> O + O

In the second step, each atom combines with an oxygen molecule to produce an ozone molecule (O_3) in the presence of a third body (usually O_2 or N_2).

O + O2 + third body --> O3 + third body

ozone is continually being created in the stratosphere by the combination of molecular oxygen and sunlight.



Ozone Absorption in the UV Band

Ozone is also destroyed naturally in the stratosphere, being dissociated by ultraviolet radiation:

O_3 + UV photon --> O_2 + O

O + O_3 --> $2O_2$

The O_3 formation and destruction are normally in a steady state in the stratosphere, such that the rate of its formation is equal to the rate of its removal. (Ozone is also destroyed by odd nitrogen and hydrogen radicals in catalytic cycles which won't go into, but which have generally been in balance with rates of formation)

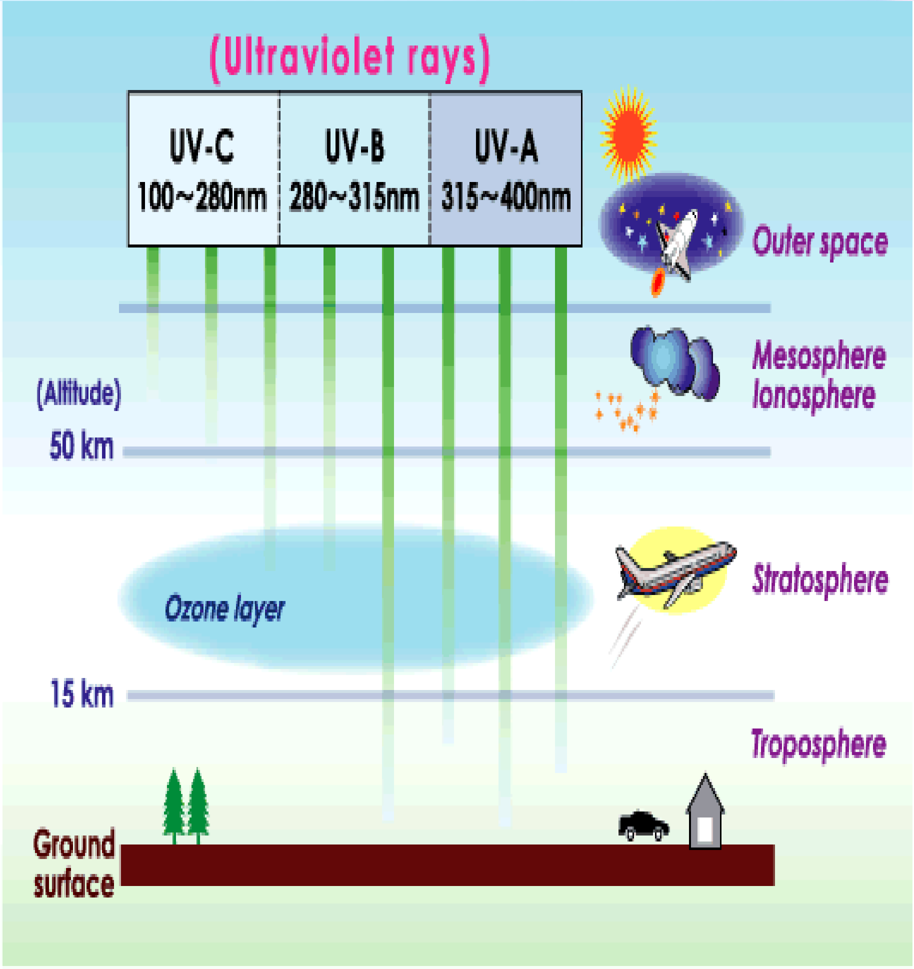
What does the ozone layer do for us?

Ozone Absorption in the UV Band

- UV radiation includes wavelengths from 200 to 400 nm

- UV-A 315 ~ 400 nm
- UV-B 280 ~ 315 nm
- UV-C 100 ~ 280 nm

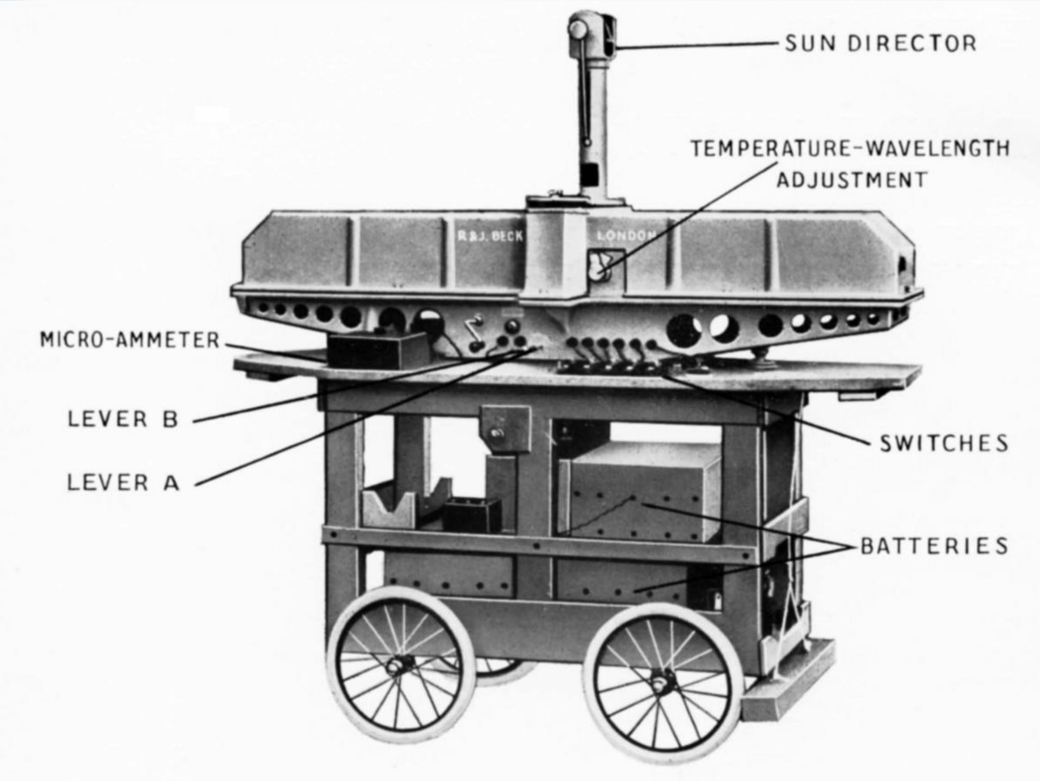
- UV-C
  - Nearly all UV-C is absorbed in the upper atmosphere
- UV-B
  - 90% of UV-B is absorbed by the atmosphere, mostly by O_3
- UV-A
  - Not strongly absorbed by the atmosphere



Columnar Ozone Measurement

1. Dobson Ozone Spectrophotometer

2. Brewer spectrophotometers



Details of Dobson Spectrophotometers in India

S.No.	Name of Station	Lat.	Long.	since when	Status
1	New Delhi (D36)	28°35'N	77°12'E	Jan. 1955 – till date	Working
2	New Delhi (D112) Standard	28°35'N	77°12'E	Apr, 1969 – till date	Working
3	Varanasi (D55)	25°18'N	83°01'E	Dec, 1963 – May, 2019	Working,need maintenance and calibration
4	Pune (D39)	18°32'N	73°51'E	Mar, 1973 – May 2003	Not Working, Repairable
5	Kodaikanal (D45)	10°14'N	77°28'E	Jul, 1957 – Apr, 1998	Not Working, Repairable
6	Srinagar (D10)	34°05'N	74°50'E	Nov, 1955 – Aug, 1989	Not Working.

D36 calibrated at Regional Dobson Calibration Center (RDCC) at the Meteorological Observatory Hohenpeissenberg, Germany

D112 calibrated at Irene / South Africa (2019)

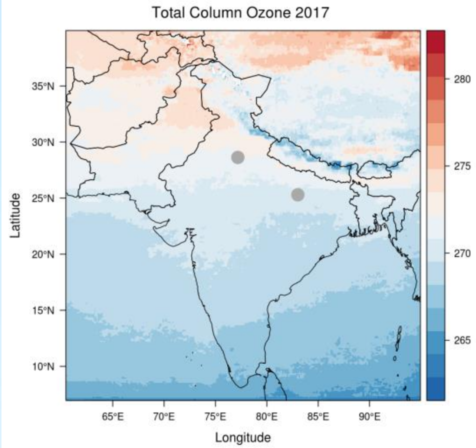
*Details of *Brewer Spectrophotometers in India*

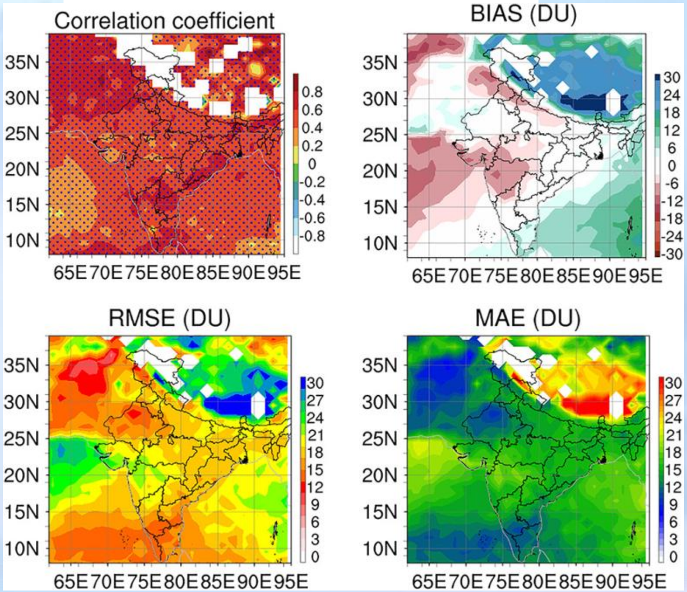
S.No.	Name of Station	Lat.	Long.	since when	Status
	New Delhi (#89)	28°35'N	77°12'E	Aug, 1994 - Oct, 2002	Not Operational
	New Delhi (#164)	28°35'N	77°12'E	Jan, 2006 - Feb, 2011	
	Pune (#170)	18°32'N	73°51'E	Oct, 2005-Jul, 2010	
	Kodaikanal (#94)	10°14'N	77°28'E	Mar, 1994 - Nov, 2005	
	Maitri, Antarctica (#153)	70°45′S	11°43′E	Jan, 1994 - Nov, 2011	

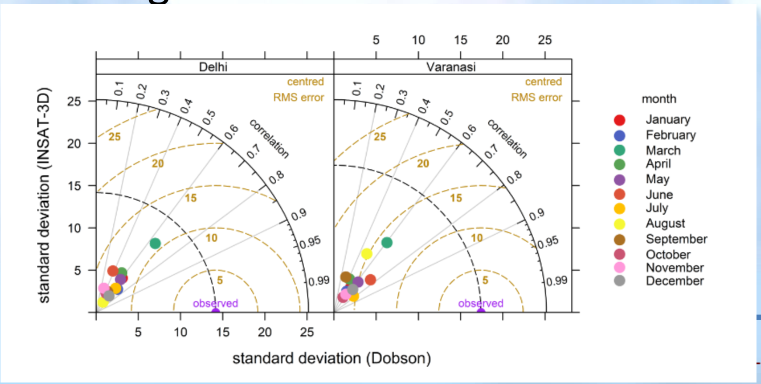
Satellite measurements

The geostationary meteorological satellite INSAT-3D launched in July 2013 and INSAT-3DR launched in August 2016 by Indian Space Research Organisation (ISRO)

19 channel sounder
9.67 µm ozone absorption band provides the total columnar ozone during the clear sky conditions on hourly basis at
spatial resolution 10 km x 10 km
coverage 5-40^{o}N and 60-100^{o}E over the Indian region.







Comparison with AIRS

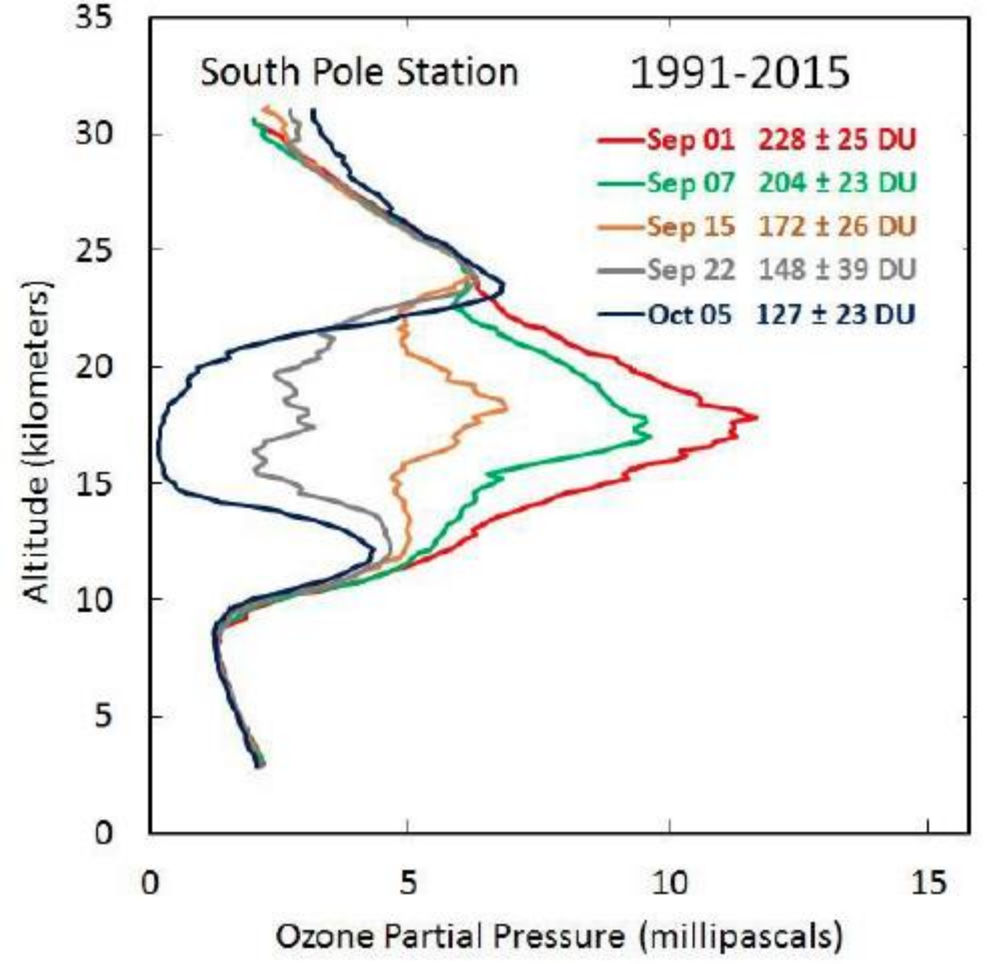
The “Ozone Hole”

Questions

- What is the “ozone hole?”
- When did it first appear?
- How does it form?

The **ozone hole** is not technically a “hole” where no ozone is present, but is actually a region of **depleted ozone** in the stratosphere over the Antarctic that happens at the beginning of Southern Hemisphere spring (August-October).

The average concentration of ozone in the atmosphere is about 300 Dobson Units; any area where the concentration drops **below 220 Dobson Units** is considered part of the ozone hole.



Average ozone profiles over South Pole for specific days prior to the onset of springtime ozone depletion (September 1); in the middle of the depletion events (September 15): and at their peak (October 5).

THE STORY OF THE OZONE HOLE

The appearance of a hole in the earth's ozone layer over Antarctica, first detected in 1976, was so unexpected that scientists didn't pay attention to what their instruments were telling them; they thought their instruments were malfunctioning. When that explanation proved to be erroneous, they decided they were simply recording natural variations in the amount of ozone.

It wasn't until 1985 that scientists were certain they were seeing a major problem.

The Antarctic Ozone Hole was discovered in 1985 by British scientists Joseph Farman, Brian Gardiner, and Jonathan Shanklin of the British Antarctic Survey.

Key ingredients to make an Ozone Hole

1. <u>Chlorine</u>: supplied by manmade CFCs
2. <u>Cold Temperature</u>: Antarctic Polar Vortex
3. <u>Seasons</u>: Dark and Light seasons
4. <u>Clouds</u>: Polar Stratospheric Clouds
5. <u>UV radiation</u>: Springtime sunlight

Chloro-fluoro-carbons

Thomas Midgley, Jr. (1889-1944) an industrial chemist, developed Freon, a nonflammable, nontoxic compound (CFC-12) to replace the hazardous compounds then used as refrigerants.

- These chemicals have been extensively used since the 1960s as
  - Air conditioning
  - Refrigerants
  - Aerosol sprays
    - hair spray, deodorants, paints
  - Styrofoam insulation
  - Furniture and carpet padding
  - Computers
  - Fire extinguishers (Halons)
  - Dry cleaning
- As the use of CFCs has increased, however, so has their concentration in the atmosphere. Scientists could detect 100 parts per trillion (ppt) of CFC-12 in the atmosphere by the 1960s, 200 ppt by 1975, and more than 400 ppt by 1987. By 1990, they detected more than 750 ppt of CFC-11 and CFC-12, the two most destructive and persistent CFCs.
- Once in the atmosphere, CFCs drift slowly upward to the stratosphere.

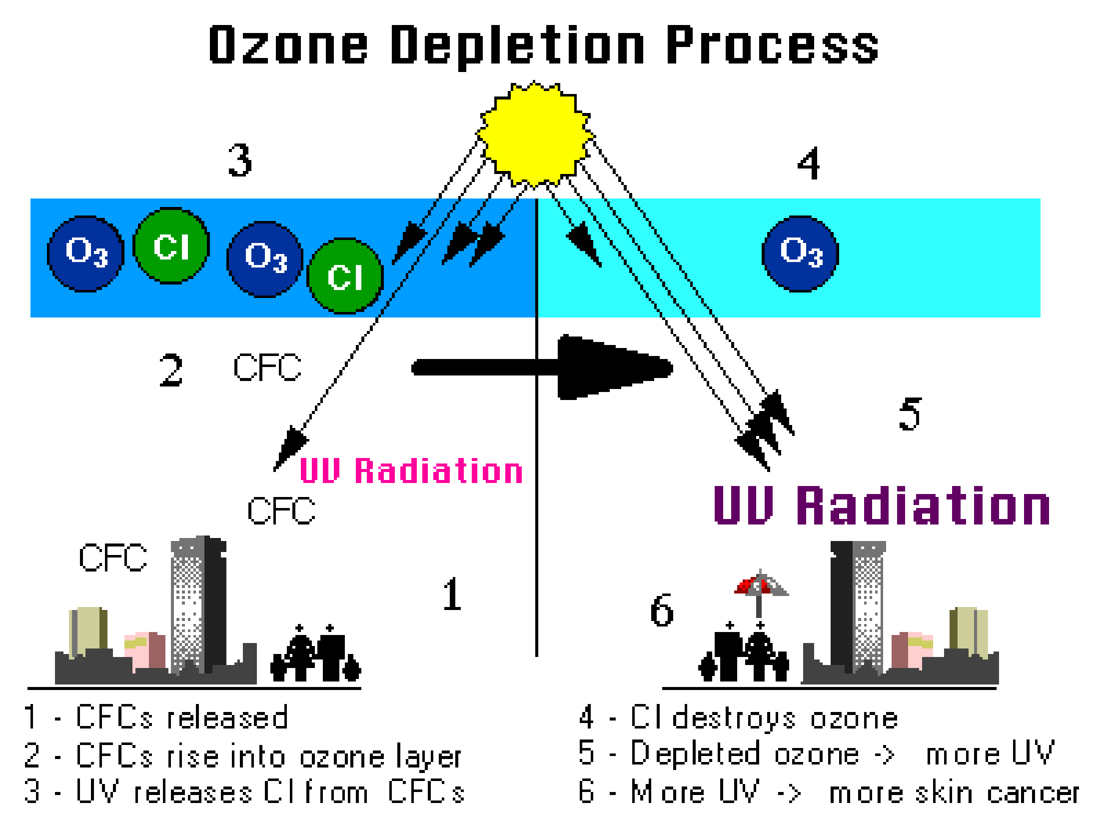
Nitrogen-, Chlorine-, and Bromine-Ozone Chemistry

- **In 1962 Harry Wexler warned about Cl and Br catalytic reactions that could destroy Ozone.**
- **In 1970, while examining the potential impact of supersonic transports (SSTs) on the stratosphere, atmospheric chemist Paul Crutzen identified an ozone-destroying catalytic cycle involving oxides of nitrogen.**
- **In 1974 Mario Molina and F. Sherwood Rowland linked this cycle to the chlorine in CFCs.**

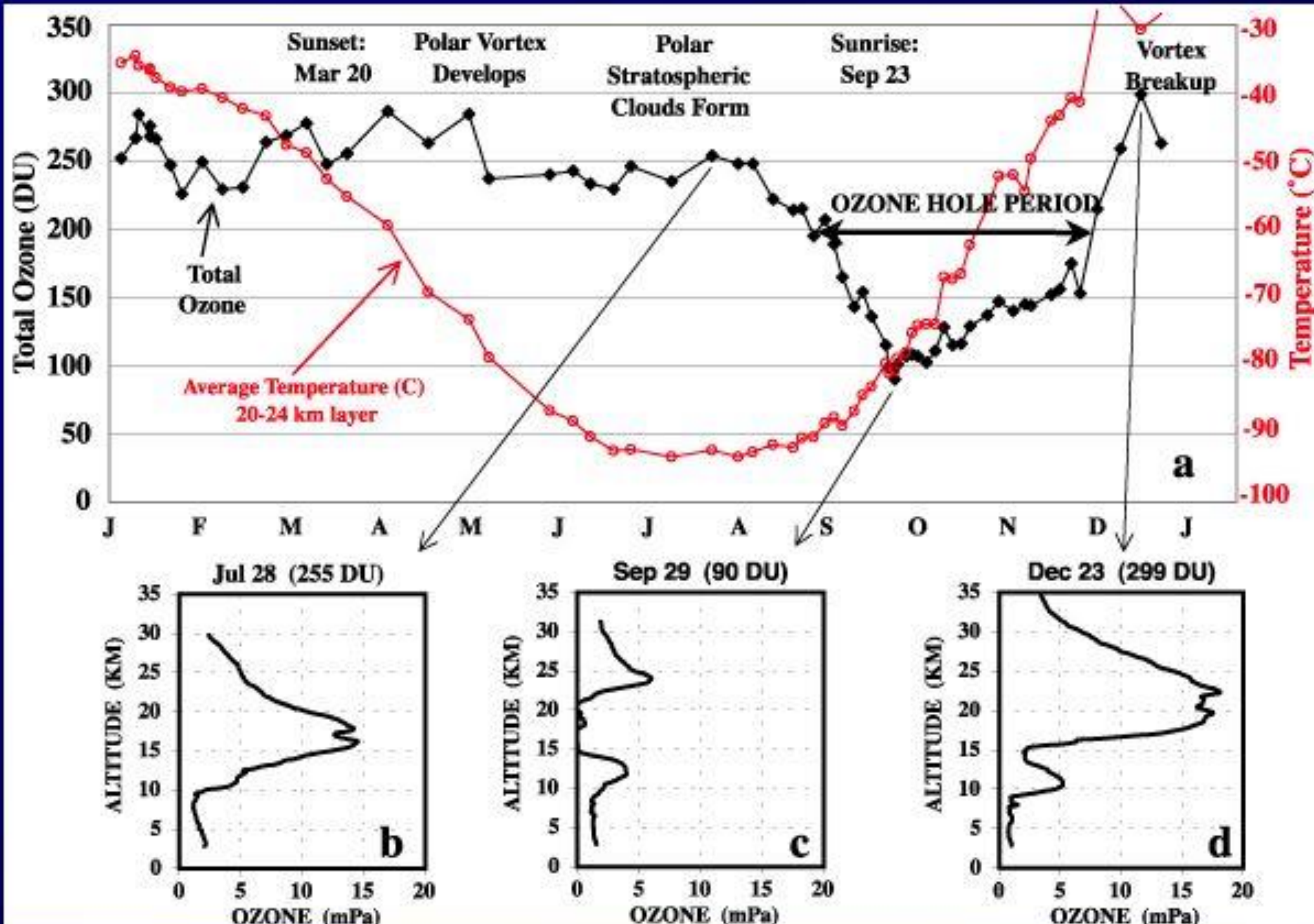
Paul J. Crutzen | Mario J. Molina | F. Sherwood Rowland

Mario Molina, Sherwood Rowland and Paul Crutzen, who jointly received the Nobel Prize in 1995 for their work on stratospheric ozone depletion.

UV Radiation and CFCs

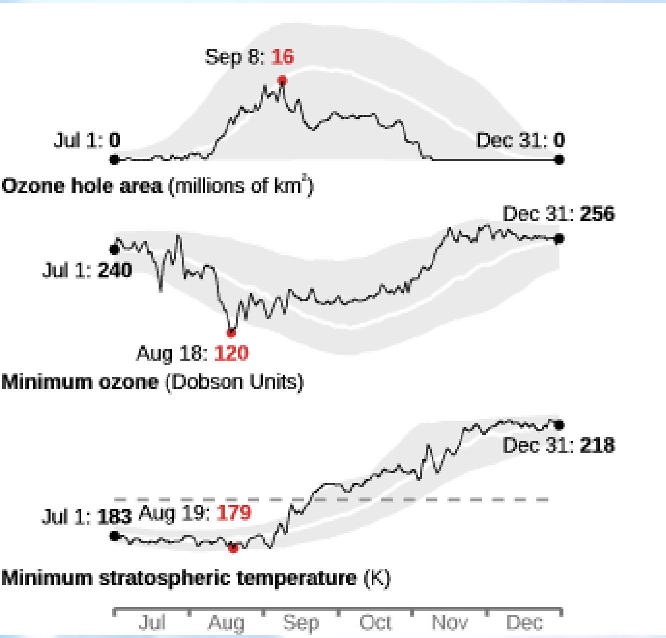


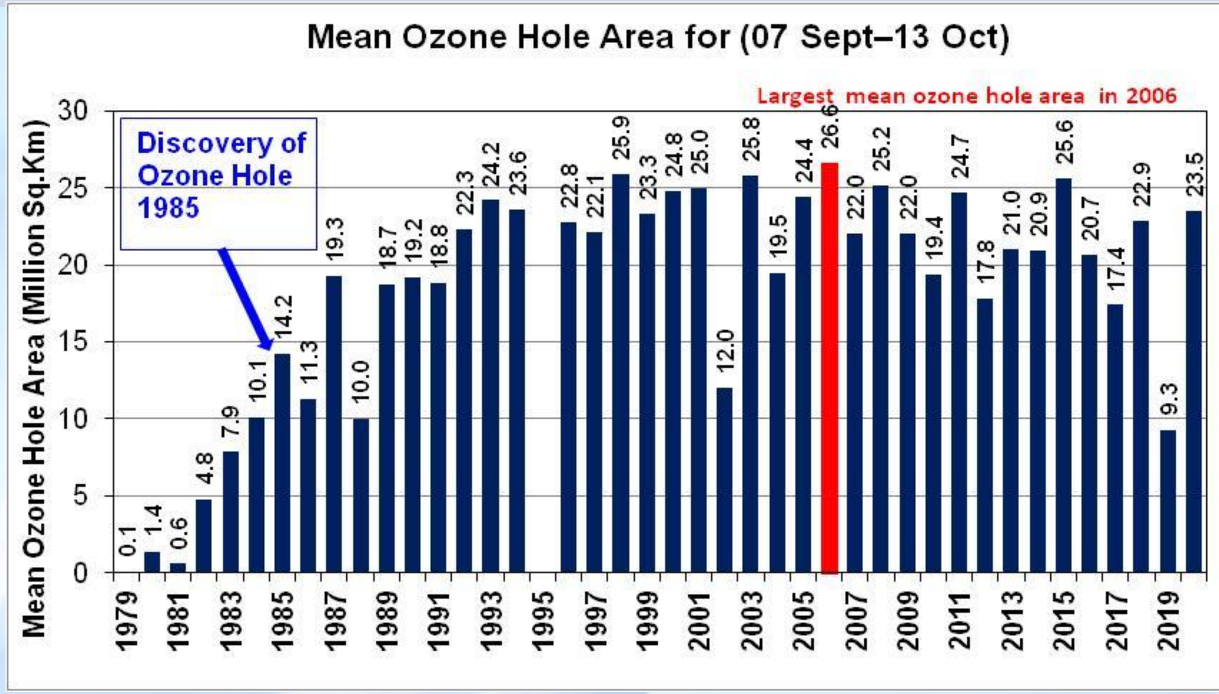
Seasonality of the Antarctic Ozone Hole

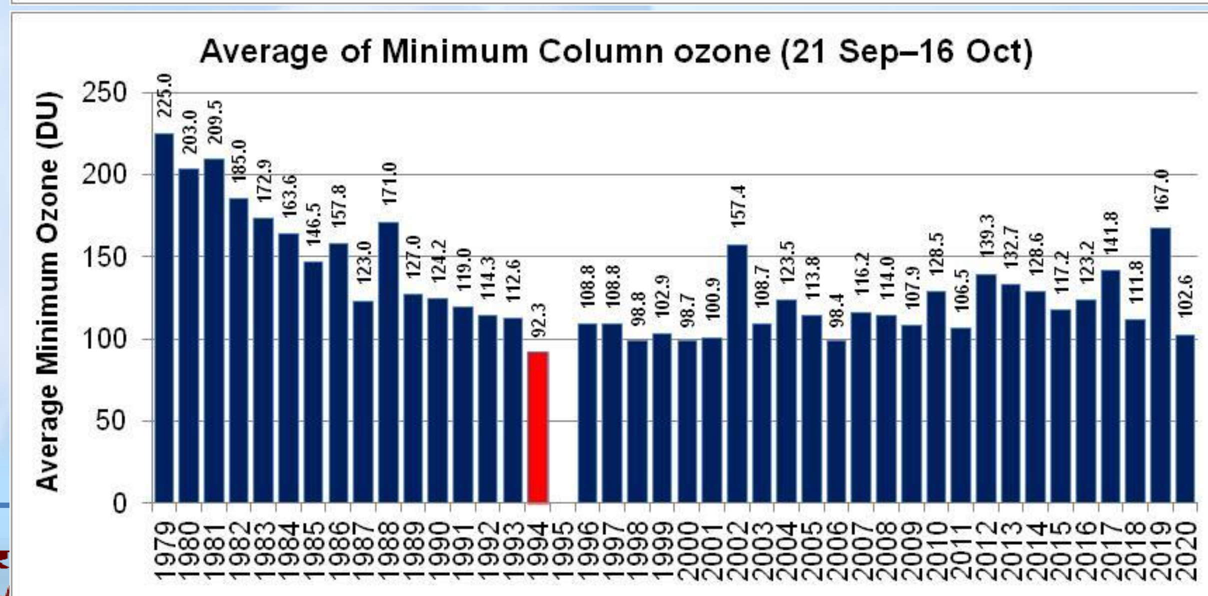


Climate Variability & Predictability - World Climate Research Programme (www.clivar.org)

Antarctic Ozone Hole Trend

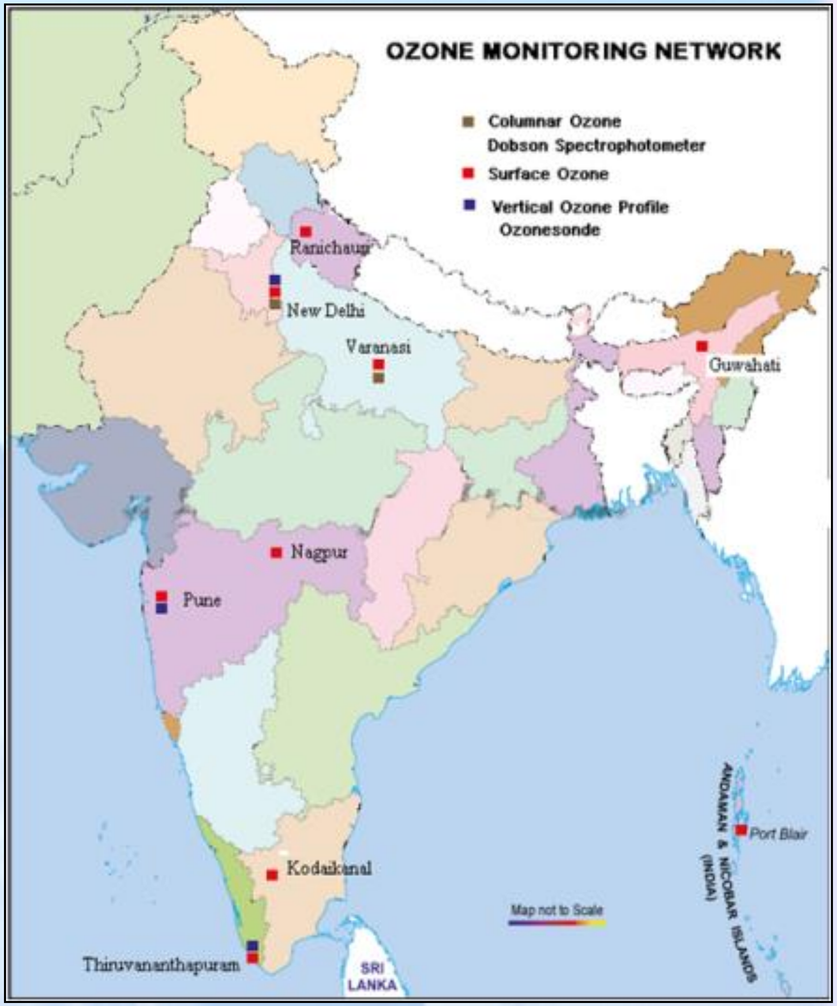




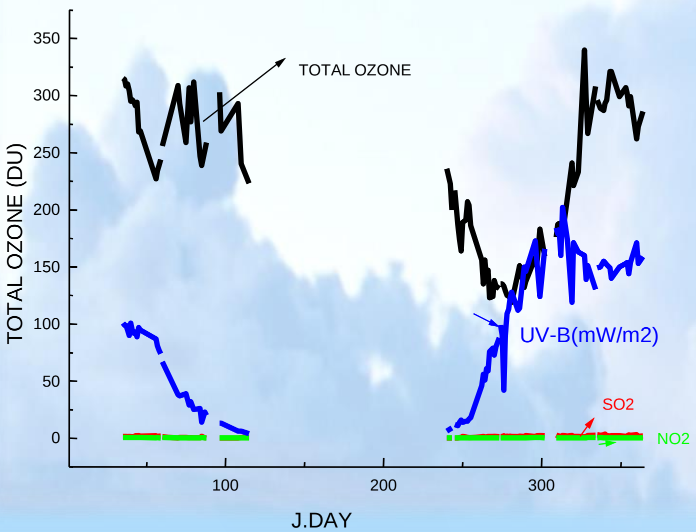


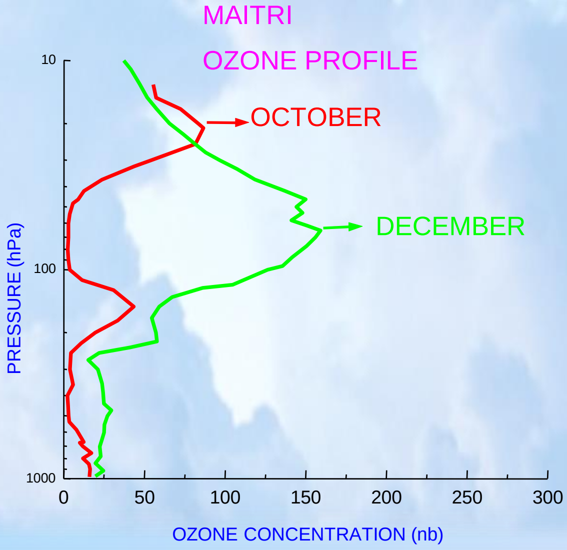
Ozone Measurement in India

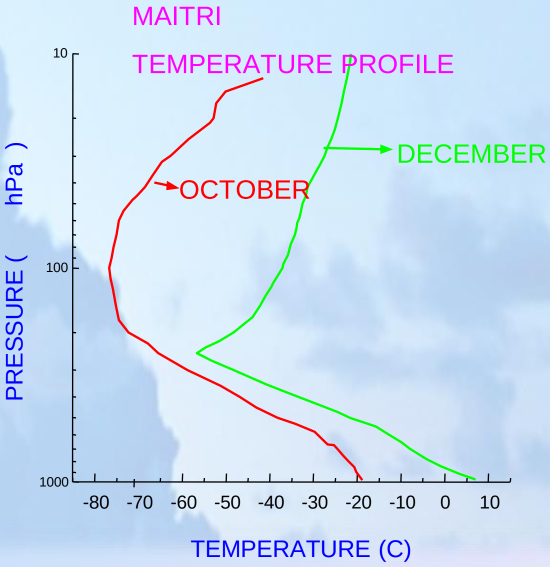
- The first Ozone Observations were made in 1928-29 at Kodaikanal as part of Dobson's worldwide Total Ozone Measurements.
- IMD acquired first Dobson Spectrophotometer in 1940
- Surface Ozone Network of IMD
- Development of Indian Ozone sonde by Instrument division of IMD in 1964



Brewer Ozone Spectrophotometer and Ozonesonde Observations at Maitri (Antarctica)







भारत मौसम विज्ञान विभाग

INDIA METEOROLOGICAL DEPARTMENT

Indian Antarctica Stations

Observations at Bharati Antarctica (Indian Station)

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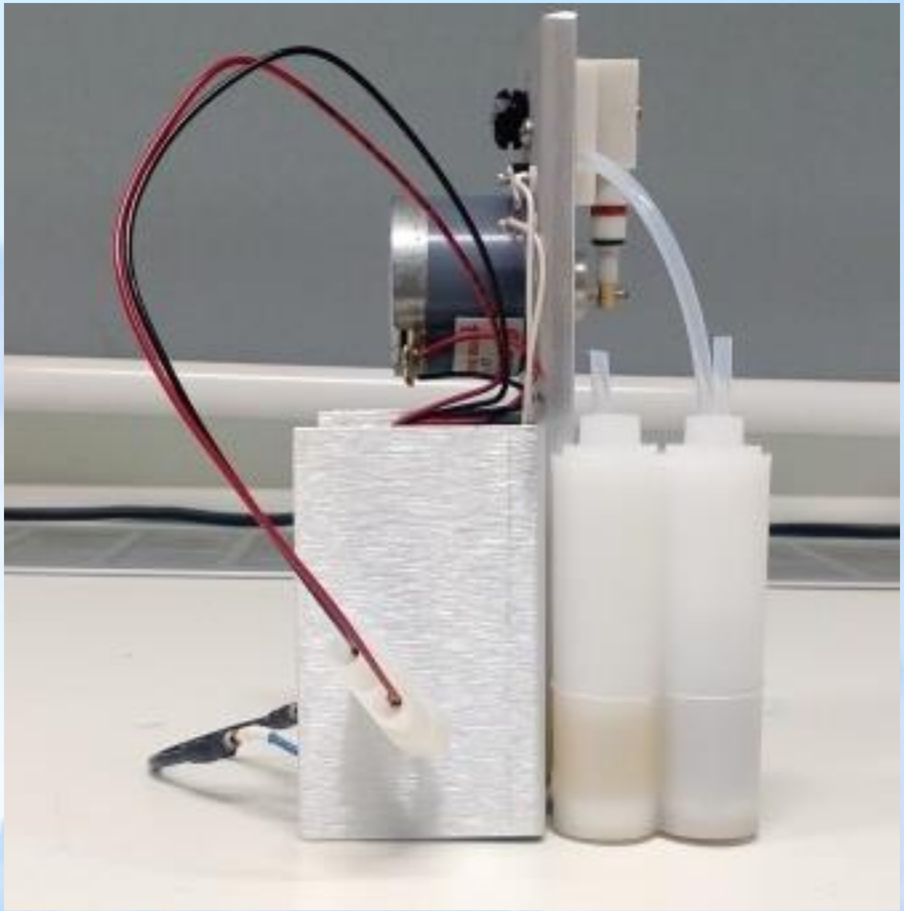
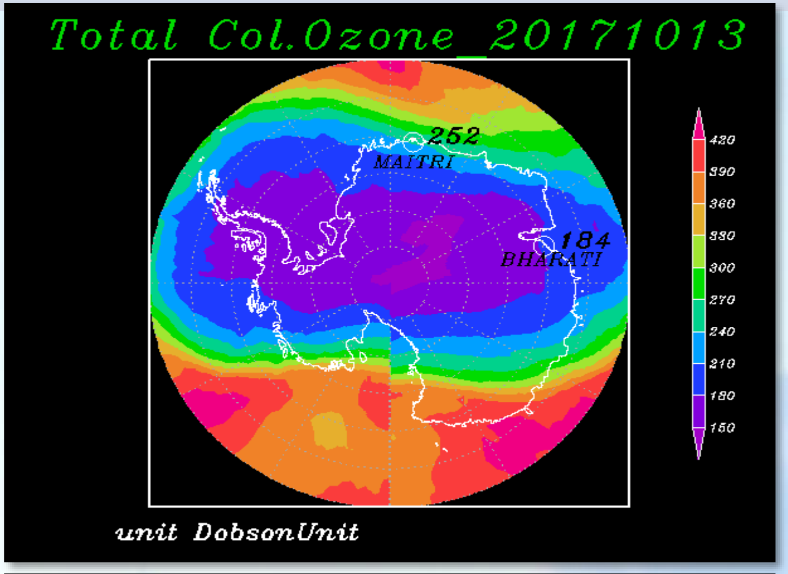
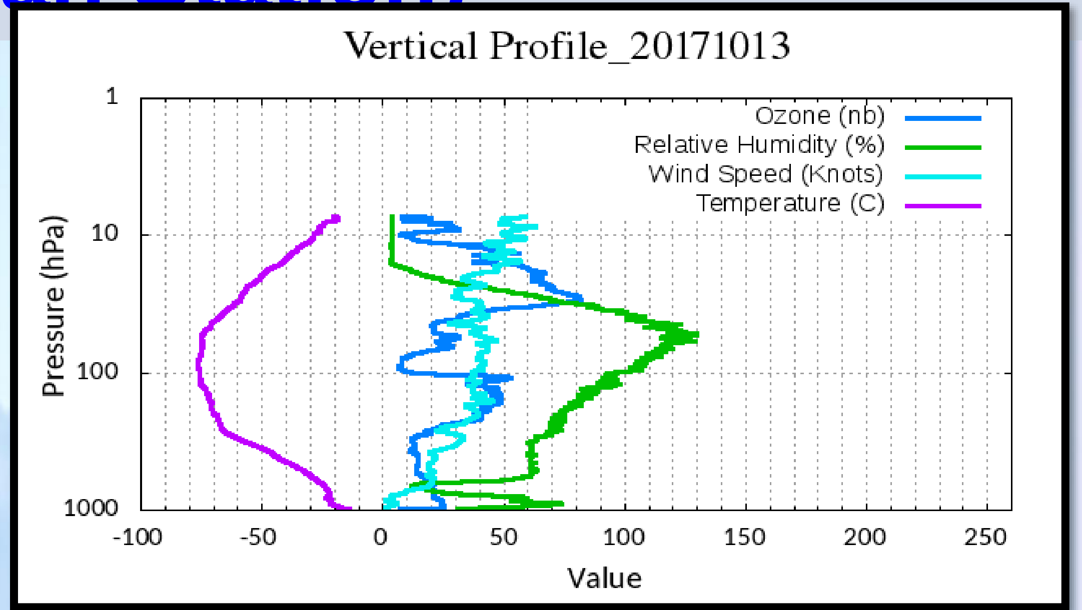
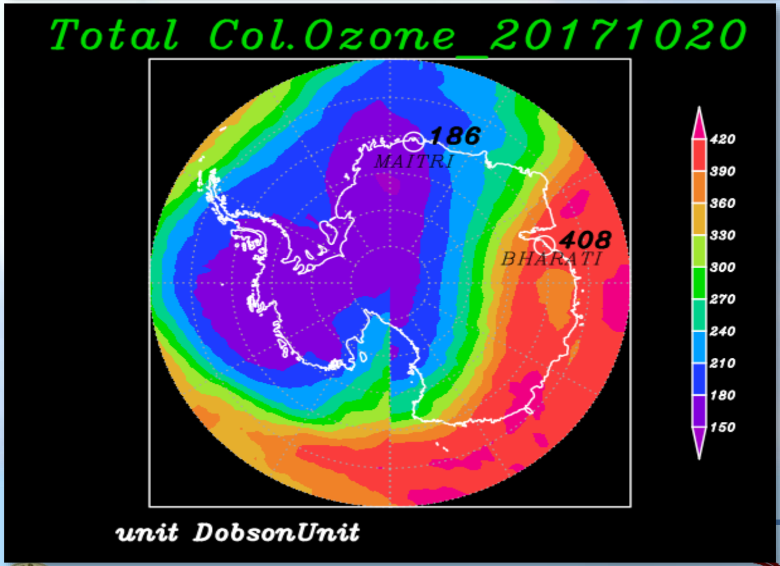
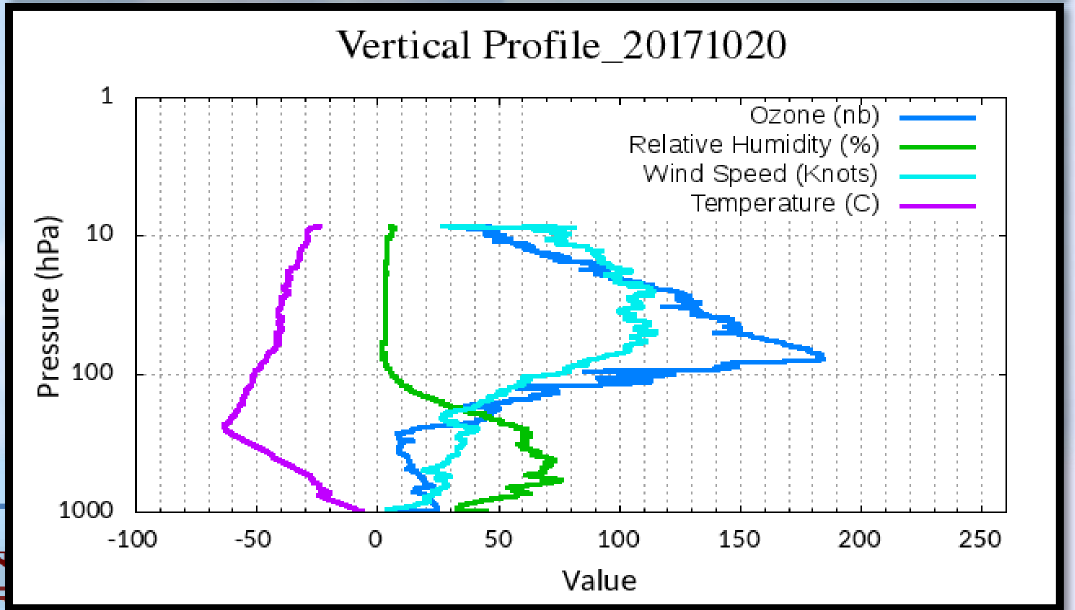


Observations at Bharati Antarctica (Indian Station)









IMD, New Delhi

ENT

Mitigation Strategies

Vienna Convention

Montreal Protocol

Consequences of ozone layer depletion

Increased UV

Biological effects

- **Basal and squamous cell carcinomas**
- **Malignant melanoma**
- **Cortical cataracts**

Increased tropospheric ozone

Increased production of vitamin D

Effects on animals

Effects on crops

What We Can Do

Be an Ozone-friendly consumer
Buy products (aerosol spray cans, refrigerators, fire extinguishers, etc.) that are labelled "ozone friendly" or "CFC free".

Be an ozone-friendly homeowner
Dispose of old refrigerators and appliances with CFC and HCFC refrigerants should be should be properly recycled. Portable halon fire extinguishers that are no longer needed should be returned to your fire protection authority for recycling.

Ozone-friendly farming
If you use methyl bromide for soil fumigation, consider switching to effective and safe alternatives.

Be an ozone-friendly citizen
Read and learn more about the effects of ozone depletion on people, animals and the environment, your national strategy and policies to implement the Montreal Protocol, and what the phase out of ozone depleting substances means to your country.

Protect yourself from ozone layer depletion

Avoid excessive sun exposure

Take extra precautions because unprotected skin and eyes will be damaged and can burn quickly. Wear sunglasses on bright days.

When outdoors in the sun, use sunscreen, use umbrella or wear a wide-brimmed hat and protective clothing.

An easy way to tell how much UV exposure you are getting is to look for your shadow.
If your shadow is taller than you are (in the early morning and late afternoon), your UV exposure is likely to be lower.
If your shadow is shorter than you are (around midday), you are being exposed to higher levels of UV radiation. Seek shade and protect your skin and eyes.

Take care of your appliances to minimize ozone layer impact

Use refrigerators, air conditioners and other equipment responsibly to assist in protecting the ozone layer and climate

→ Dispose of appliances and equipment with refrigerants responsibly

Have your car and home air conditioner and refrigerator checked for leaks.

Insulate your walls, doors and windows properly for improved energy efficiency and prolonged life of your equipment.

Set the thermostat of your refrigerator and freezer at the right temperature (avoid too low temperatures) and switch equipment off when not in use, as even a standby mode consumes energy.

Keep rooms cool at night with ventilation, without air conditioning if possible and also remember that a higher setting of your air conditioner's thermostat saves a lot of energy.

Ozone Measurement in India

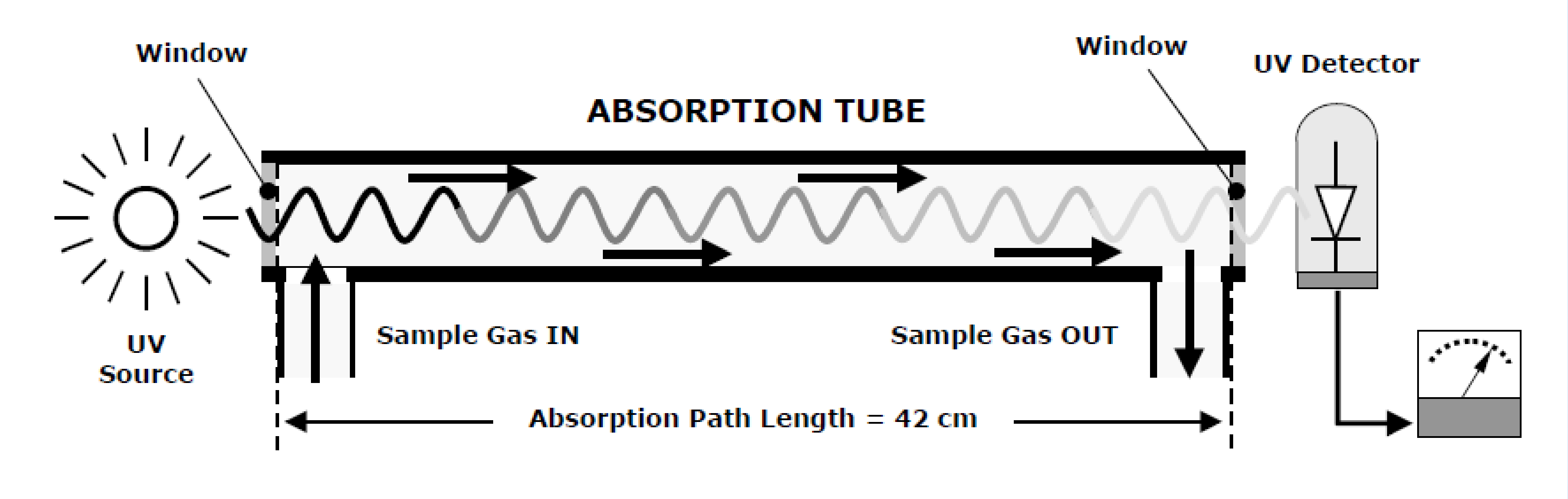
- The first Ozone Observations were made in 1928-29 at Kodaikanal as part of Dobson's worldwide Total Ozone Measurements.
- IMD acquired first Dobson Spectrophotometer in 1940
- Surface Ozone Network of six stations of IMD.
- Development of Indian Ozone sonde by Instrument division of IMD in 1964.

Methods of Measurement: Surface Ozone

- **Ultraviolet Absorption photometry is regarded as the preferred method because of its high accuracy, stability, freedom from interference, and ease of operation.**
- **The basic measurement principle is the attenuation of UV light at a wavelength of 254 nm due to the presence of ozone in a flowing air sample. The instruments measure the relative attenuation between an air sample in which only the ozone is removed and one in which ozone is present. With a knowledge of the sample path length and the UV absorption coefficient of ozone, the ozone concentration is determined. Measurements using a UV ozone monitor are virtually continuous.**

In principle, this method is highly accurate, but instrument defects or degradation of components, such as the catalyst used to destroy ozone in the reference portion of the

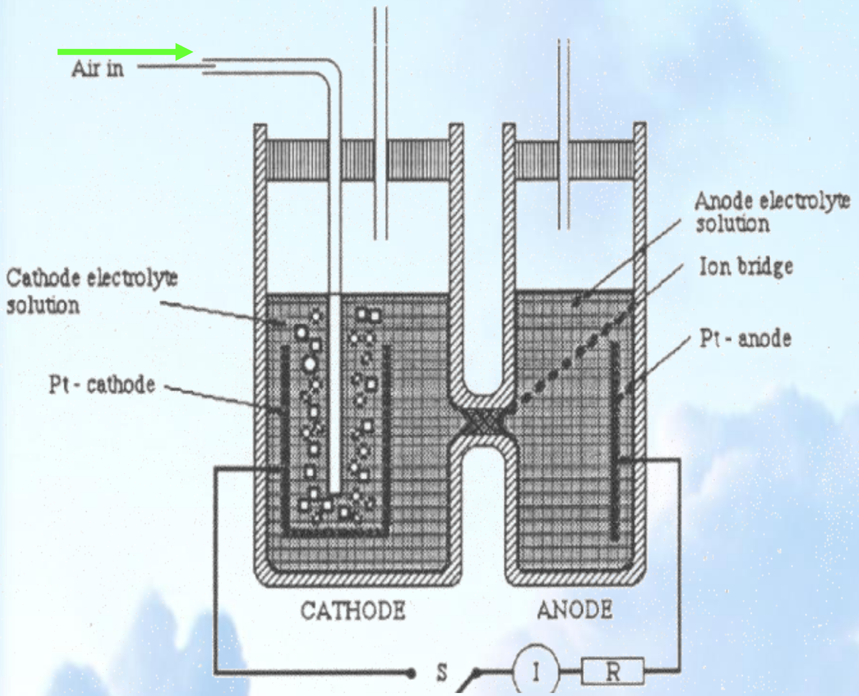
Surface Ozone analyzer
UV Absorption Ozone Analyzer



- **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.

Electrochemical Conductivity Cell (ECC)



Idea:

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

$$2\ KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2\ KOH$$

Measurement of "free" iodine (I_2) in electrochemical reaction cell(s). 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:

$$I_2 + 2\ e^- \text{ on Pt} \rightarrow 2\ I^- \quad \text{[cathode reaction]}$$

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

Applications: Measurement of 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