



# Ozone and Air Pollution

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**भारत मौसम विज्ञान विभाग**  
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# Air Pollution

- Primary Pollutants
- Secondary Pollutants
- Anthropogenic Sources
- Natural Sources

# Ozone

- Tropospheric Ozone
- Stratospheric Ozone
- Ozone Hole



# 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**

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# Air Pollution Classification (Contd.)

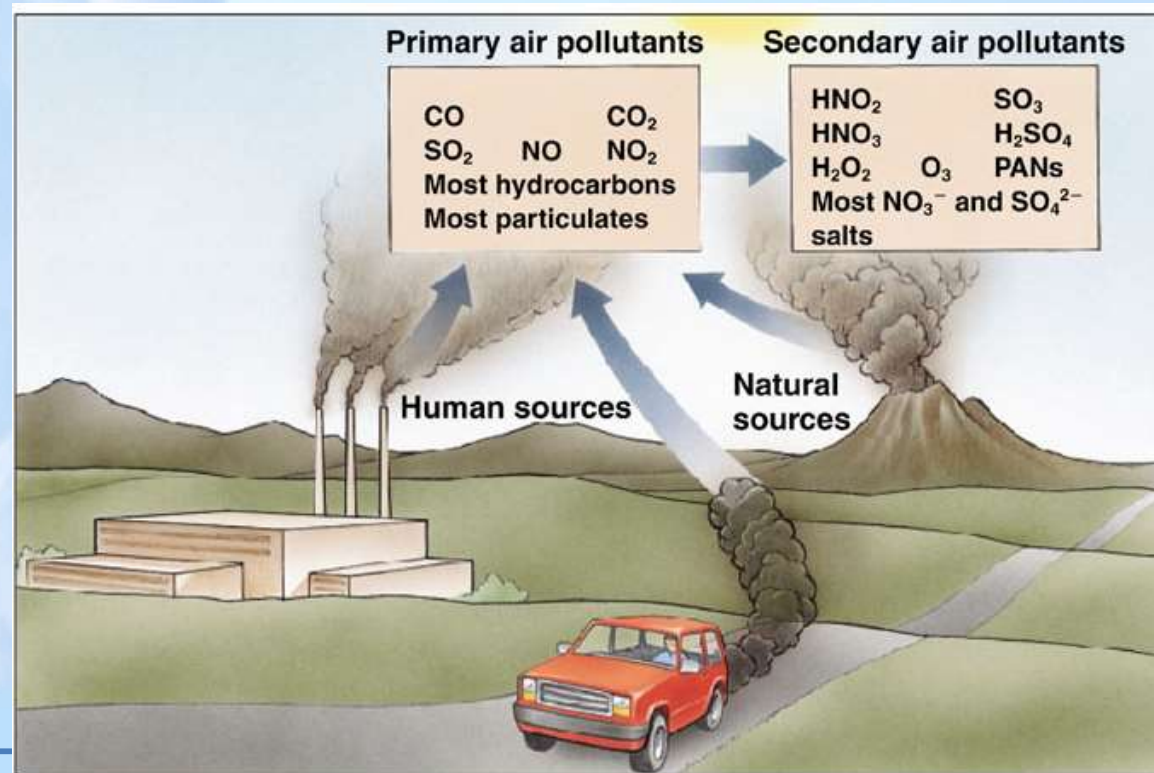
According to the manner in which they reach the atmosphere

## Primary Pollutants

products of natural events (e.g. fires and volcanic eruptions) and human activities which are emitted directly into the atmosphere, such as  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{NO}_2$  etc.

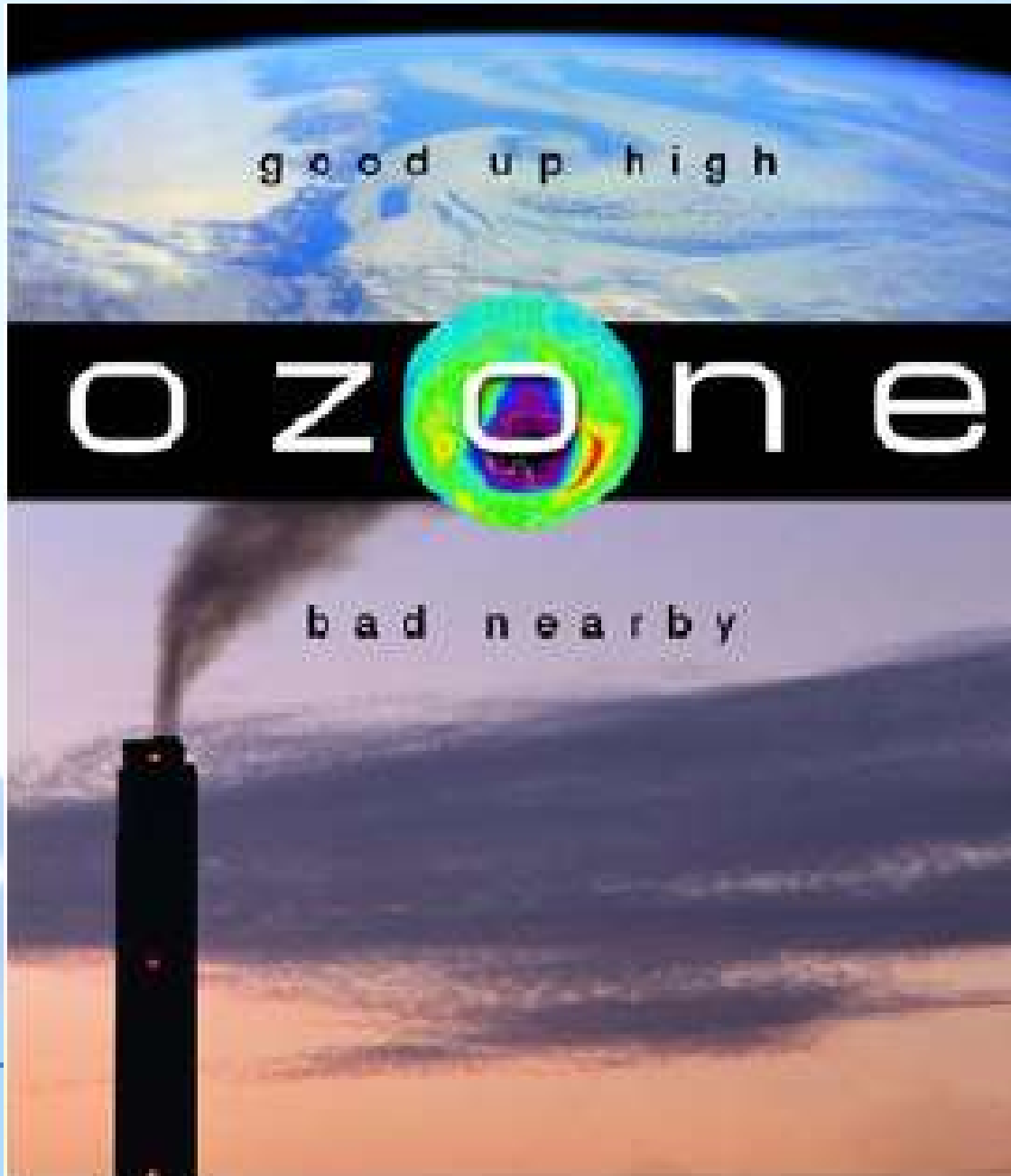
## Secondary Pollutants

formed by interaction of primary pollutants with each other or with normal components of the air e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{O}_3$  etc.



# OZONE

*“Can't live with it, can't live without it”*



# 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

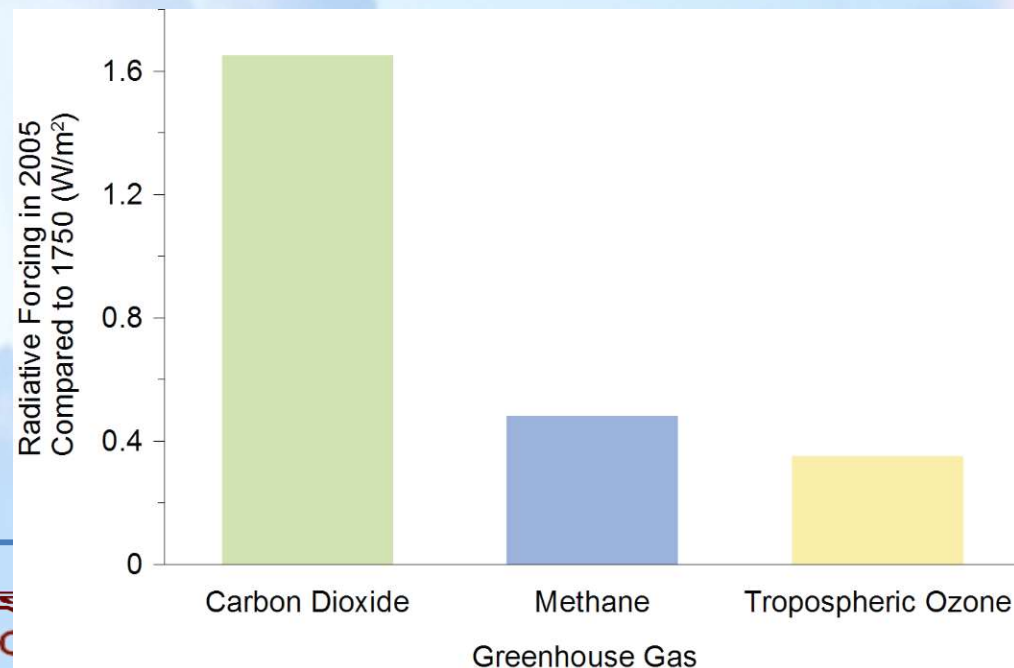


Lung lining inflamed by  $O_3$

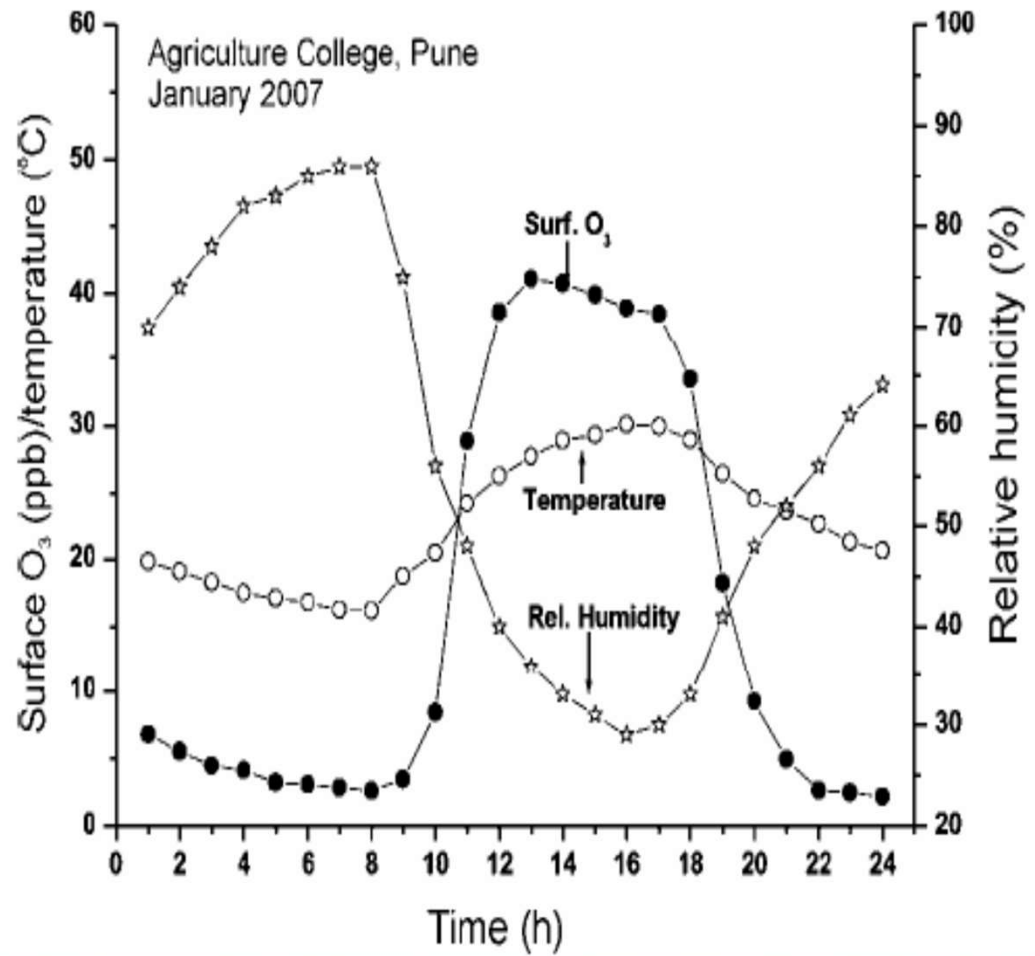
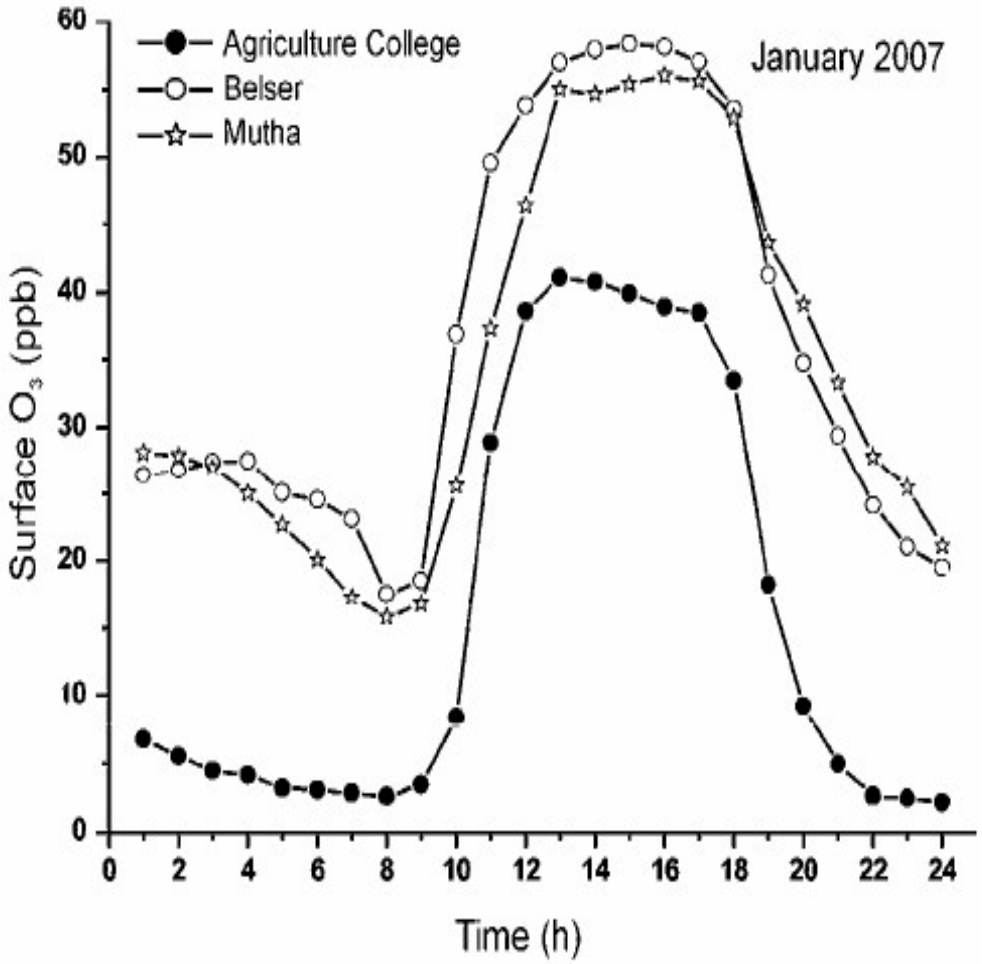


# Why Measure Surface Ozone Concentration?

- ❖ 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



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

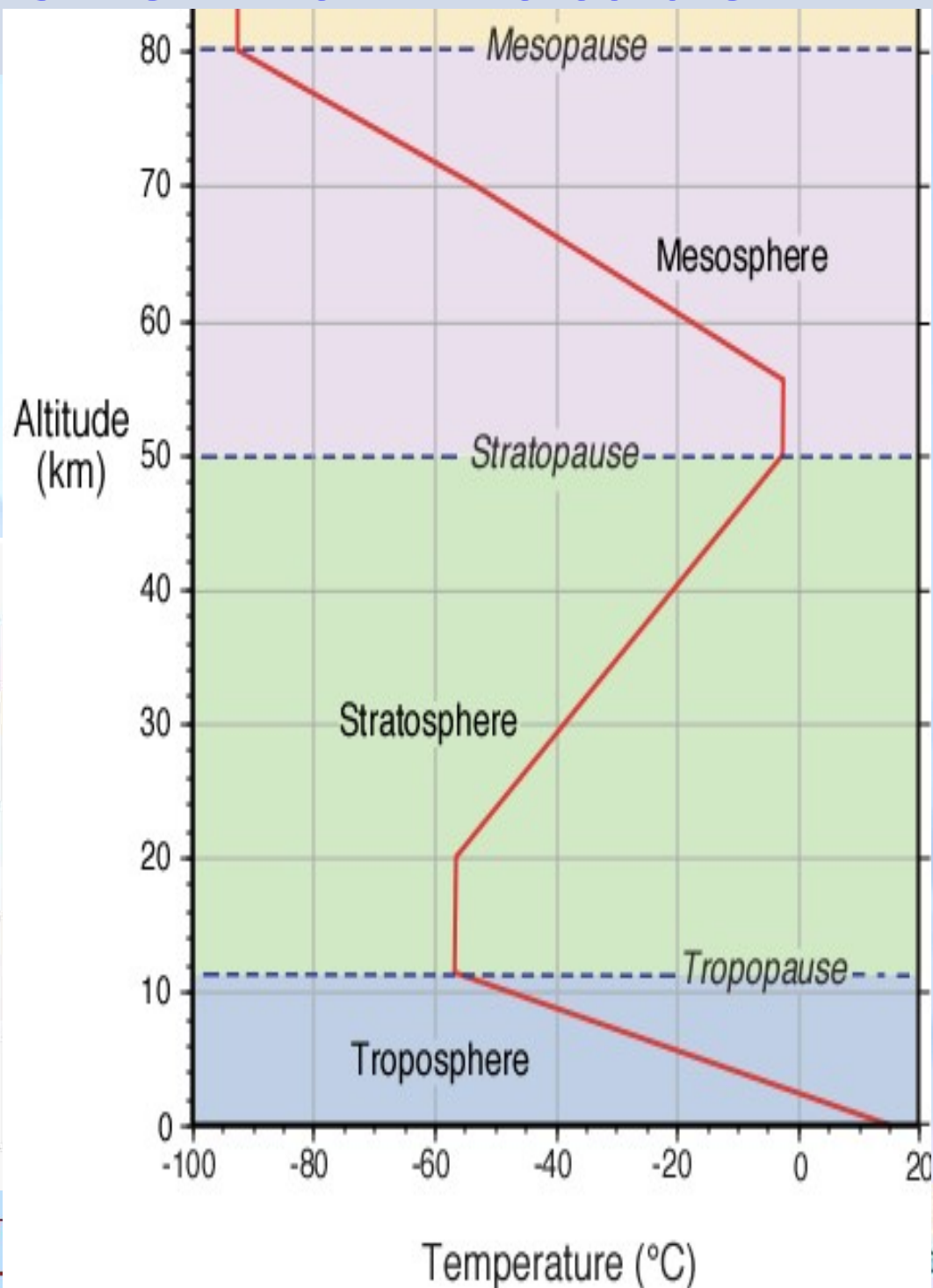
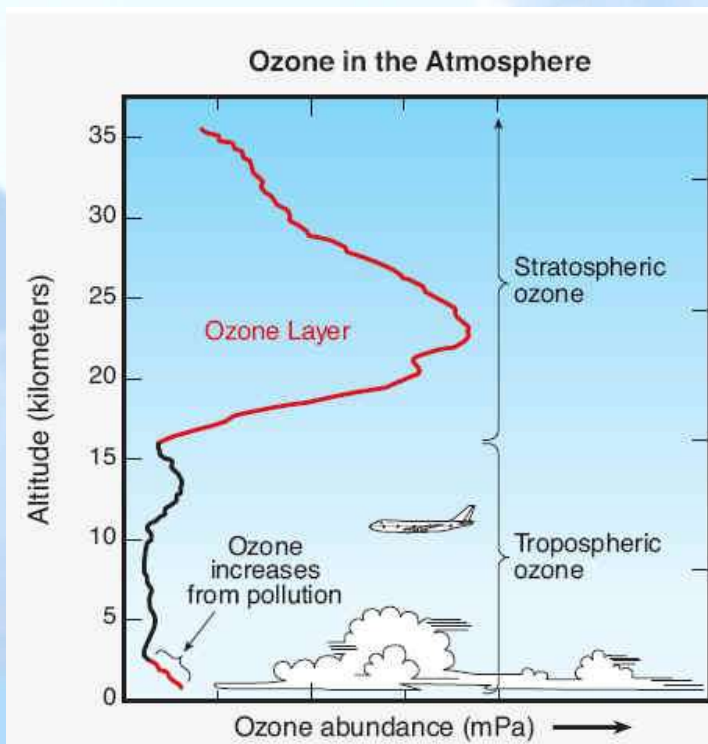




# Variation of Ozone with Altitude

The Ozone layer can be divided into two main parts :

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



# Stratospheric Ozone Production

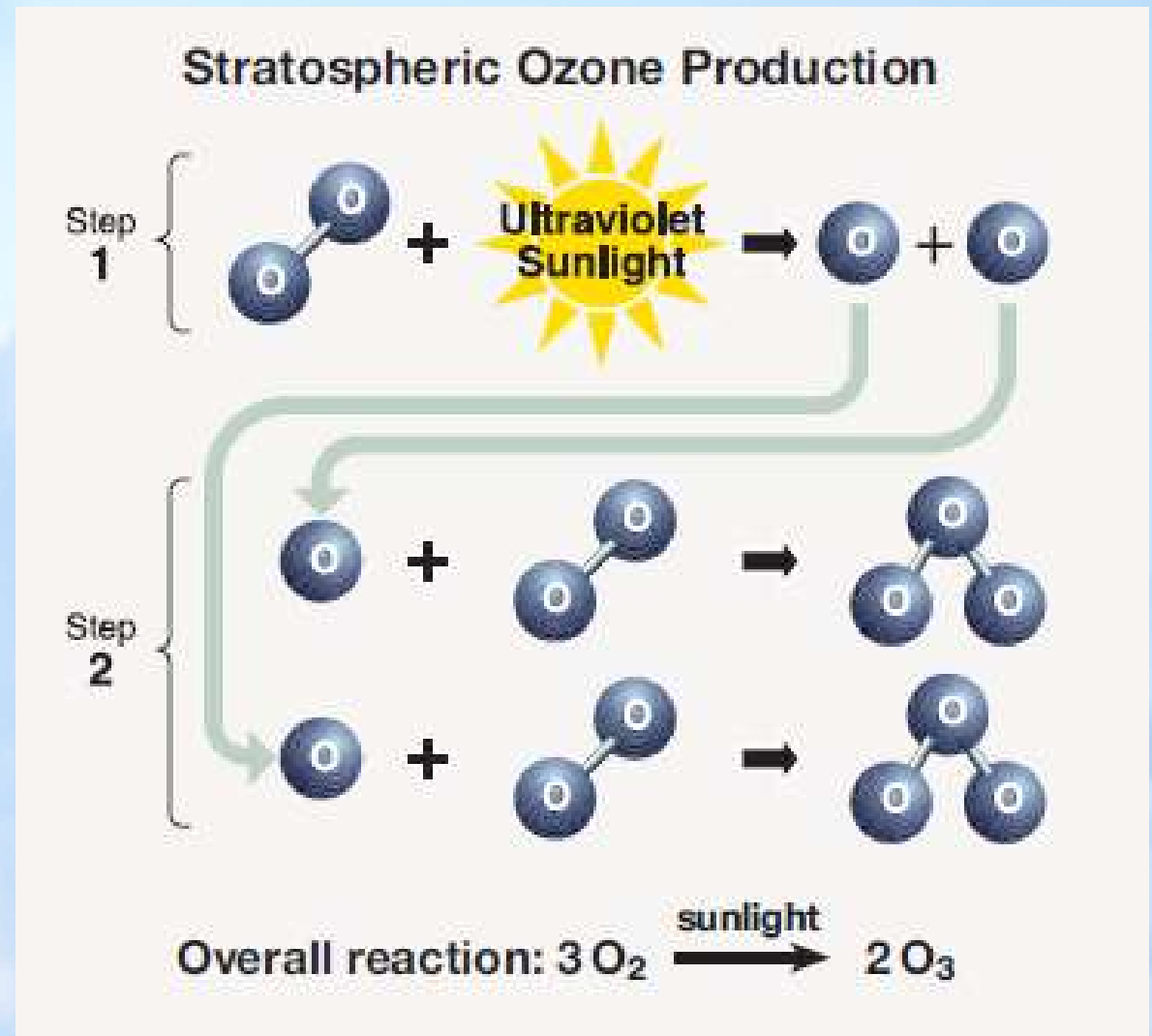
Stratospheric ozone is naturally formed in chemical reactions involving ultraviolet sunlight and oxygen molecules. In the first step, sunlight breaks apart one oxygen molecule (O<sub>2</sub>) to produce two oxygen atoms (2 O).



In the second step, each atom combines with an oxygen molecule to produce an ozone molecule (O<sub>3</sub>) in the presence of a third body (usually O<sub>2</sub> or N<sub>2</sub>).



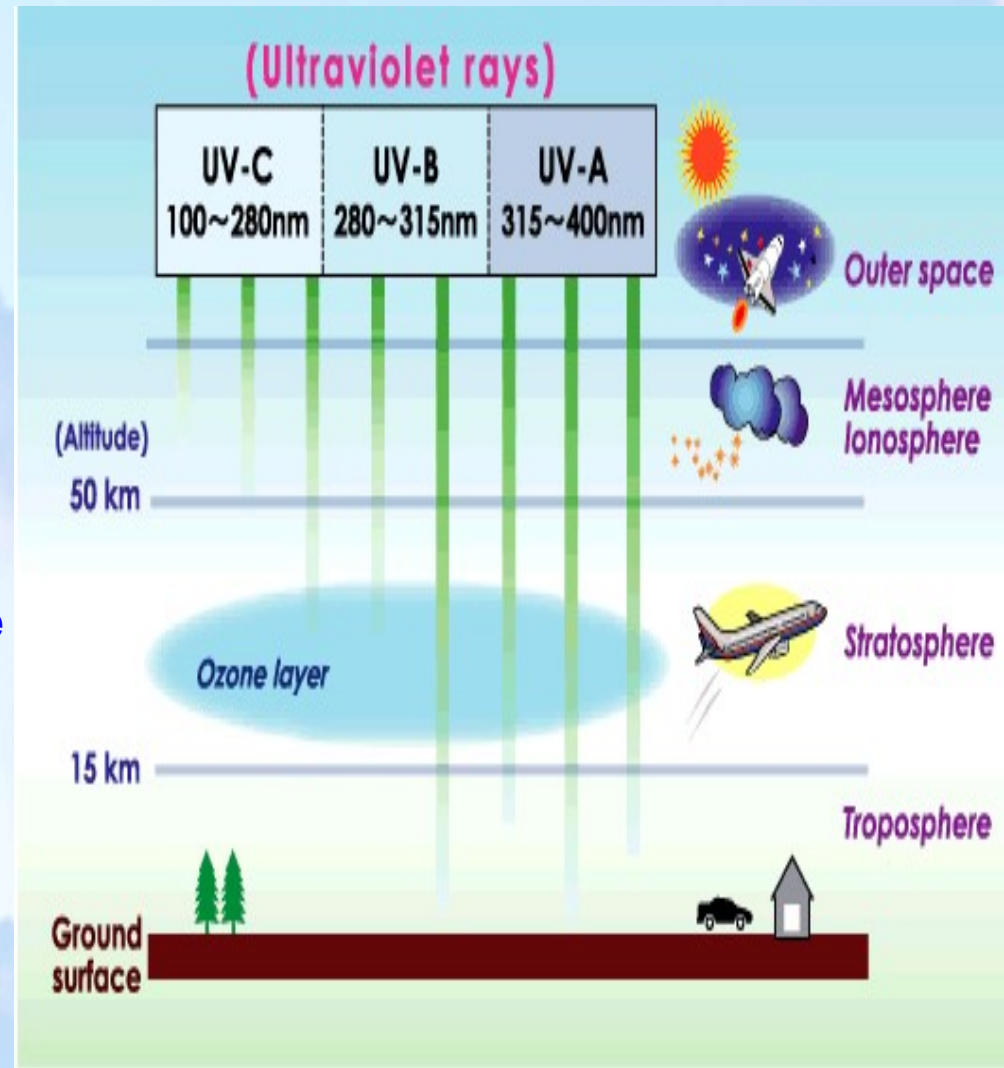
ozone is continually being created in the stratosphere by the combination of molecular oxygen and sunlight.



# What does the ozone layer do for us?

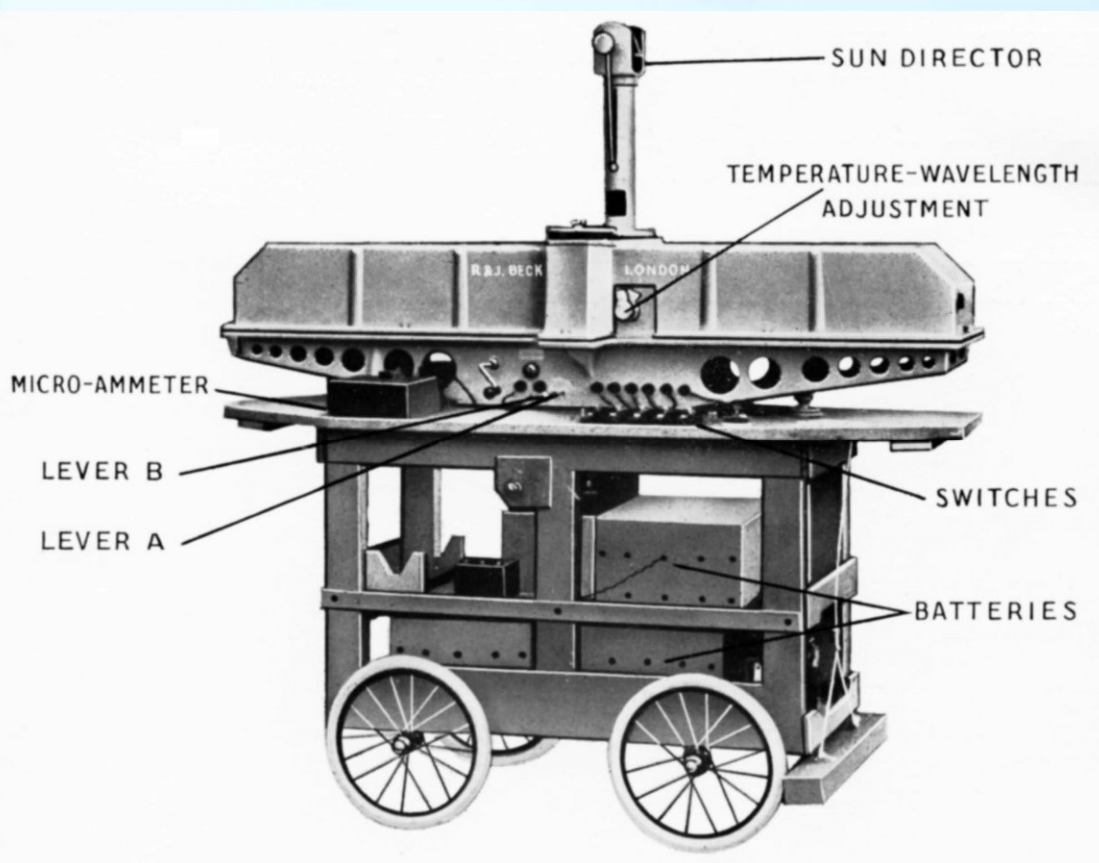
## Ozone Absorption in the UV Band

- ❖ 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<sub>3</sub>
- ❖ UV-A
  - Not strongly absorbed by the atmosphere



# Columnar Ozone Measurement

1. Dobson Ozone Spectrophotometer
2. Brewer spectrophotometers



# 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.



# Consequences of ozone layer depletion

## Increased UV

### Biological effects

Basal and squamous cell carcinomas

Malignant melanoma

Cortical cataracts

## Increased tropospheric ozone

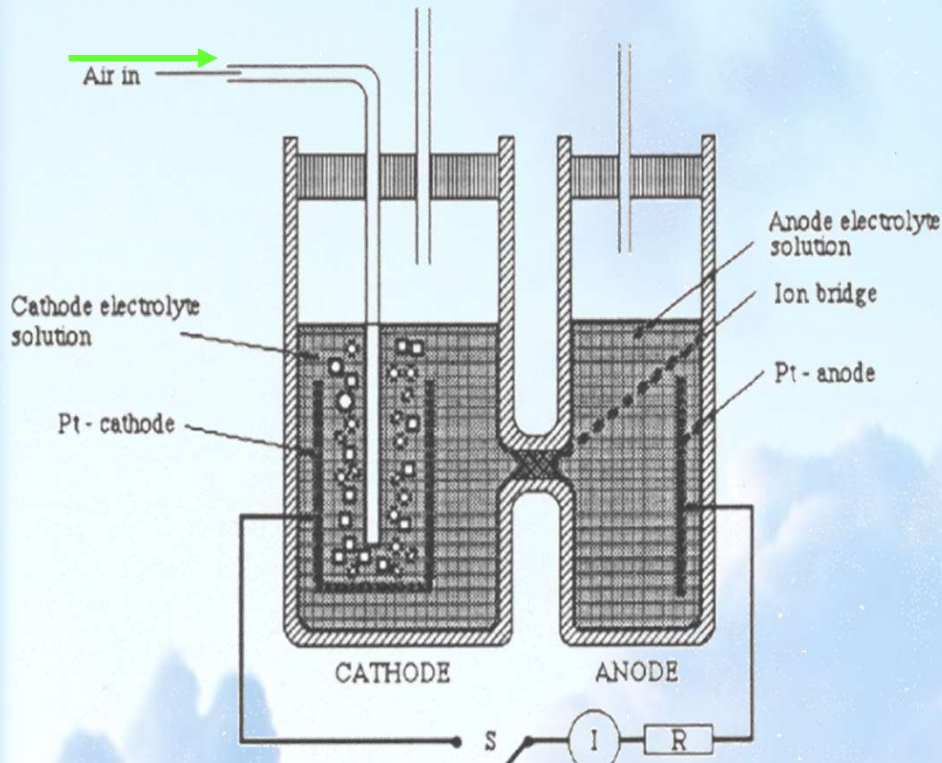
### Increased production of vitamin D

### Effects on animals

### Effects on crops



# Electrochemical Conductivity Cell (ECC)

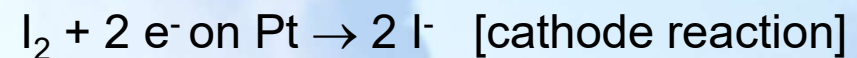


## Idea:

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



Measurement of "free" iodine ( $\text{I}_2$ ) 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:



- 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  $\text{O}_3$  distribution up to the stratosphere, Surface  $\text{O}_3$

**Problems:** interference by  $\text{SO}_2$  (1:1 negative) and  $\text{NO}_2$  (5-10% positive)

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



# Mitigation Strategies

**Vienna Convention**

**Montreal Protocol**





## **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 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.



# Sulfur Oxides ( $\text{SO}_2$ )



# Sulfur Oxides (mainly SO<sub>2</sub>)

SO<sub>2</sub> is a colorless gas with a sharp odor like a struck match, primary pollutant, has anthropogenic and natural sources.

## Anthropogenic sources

Industries burning sulfur-containing fossil fuels, ore smelters, oil refineries, coal-burning thermal power plants.

Sulfur is present in many fuels (e.g., coal, crude oils) over a wide range of concentrations. Combustion causes its oxidation to sulfur dioxide.

## Natural sources

Marine plankton, sea water, plants, volcanic eruption.



# Effects of Sulfur Dioxide

- At relatively high concentrations  $\text{SO}_2$  causes severe respiratory problems. Groups that appear most sensitive to the effects of  $\text{SO}_2$  include asthmatics and other individuals with hyperactive airways, and individuals with chronic obstructive lung or cardiovascular disease.
- Sulfur dioxide is an acid precursor, which is a source of acid rain produced when  $\text{SO}_2$  combines with water droplets to form sulfuric acid,  $\text{H}_2\text{SO}_4$ .
- Sulfur dioxide is an precursor of sulfate particulates which affect the radiation balance of the atmosphere and can cause global cooling



# **SO<sub>2</sub>: Measurement Methods and Sampling Frequency**

SO<sub>2</sub> concentrations can be measured continuously using a **pulsed-fluorescence analyser**. Its ease of calibration, dependability, accuracy, and SO<sub>2</sub> specificity make it preferable. More sensitive gas chromatographic techniques are also available.

Since SO<sub>2</sub> has a short atmospheric lifetime, understanding the sulphur cycle requires knowledge of the source and sink terms. This is best accomplished with sampling frequencies of less than 1 hour.



# SO<sub>2</sub>

## Siting Requirements

1. The sources for SO<sub>2</sub> in the atmosphere include the sea, volcanic activity, anthropogenic emissions, and biomass decay processes. Measurements to monitor the background concentration of SO<sub>2</sub> should be made far away from sources.
2. Careful placement of the SO<sub>2</sub> monitoring lines should be considered in order to reduce contamination from local sources.
3. SO<sub>2</sub> is a reactive gas with an atmospheric lifetime of hours to days. It may stick to intake lines or oxidize within water drops condensed in the lines. Thus, intake lines should be made of inert material (Teflon, stainless steel) and be as short as possible.

## QA/QC

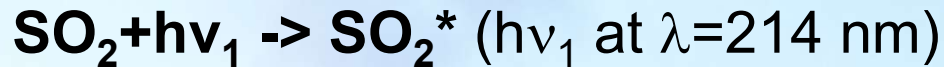
Zero checks and calibrations should be performed at regular intervals. Raw data should be inspected by a trained operator to facilitate flagging of erroneous measurements and data validation. All maintenance procedures and intervals as recommended by the manufacturer of the instrumentation should be carefully observed.



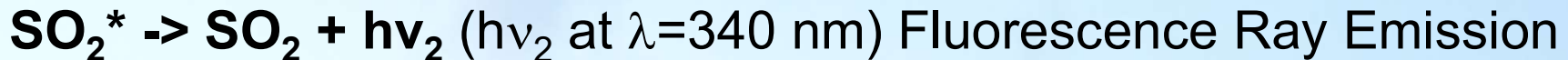
# SO<sub>2</sub>

## Ultraviolet Fluorescence Method

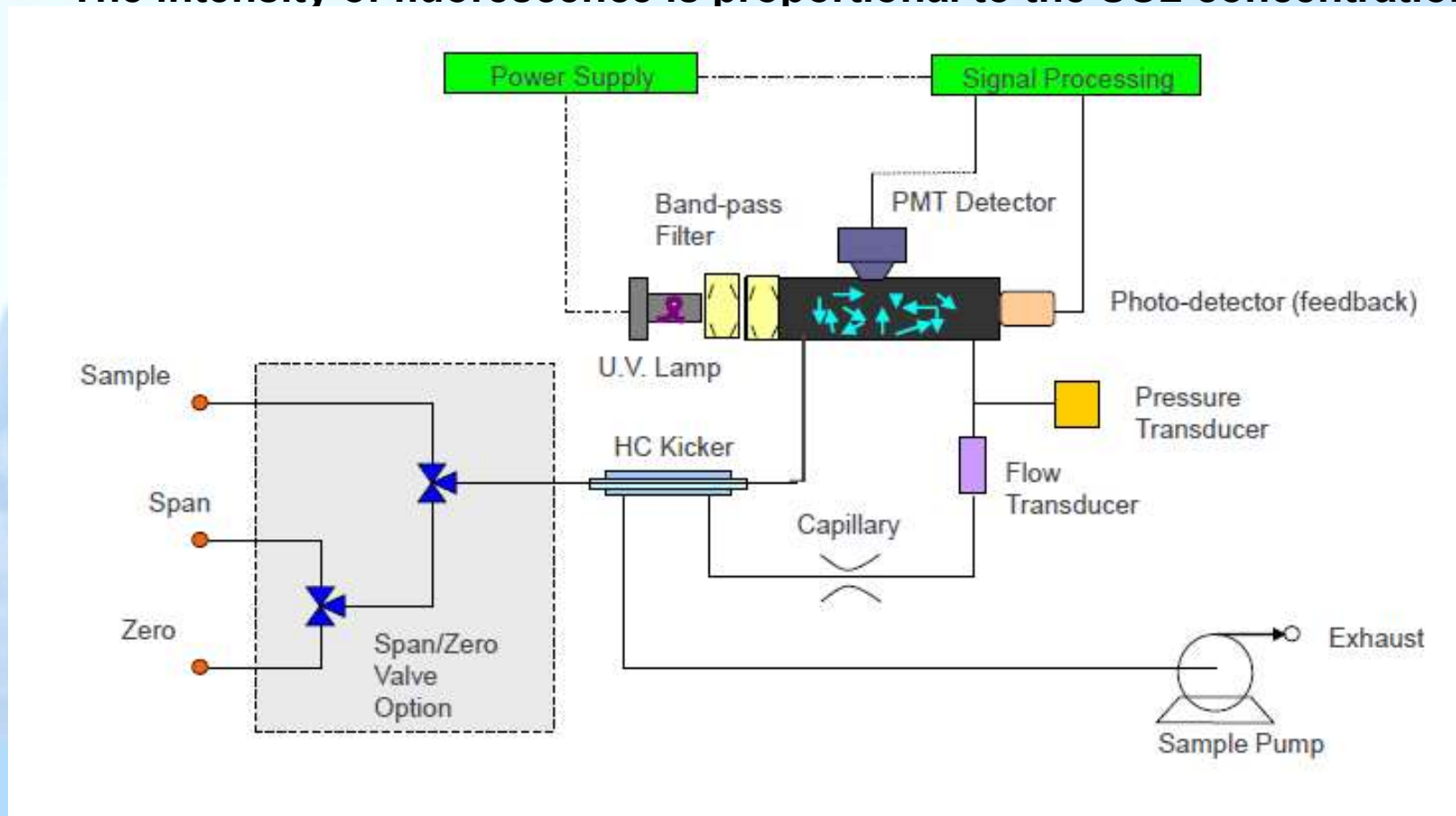
This method is based on the principle that SO<sub>2</sub> molecules absorb ultraviolet(UV) light and become excited at one wavelength,



then decay to a lower energy state emitting UV light at a different wavelength.



The intensity of fluorescence is proportional to the SO<sub>2</sub> concentration.



# Nitrogen oxides (NO<sub>x</sub>)

NO (nitric oxide) & NO<sub>2</sub> (nitrogen dioxide)

Nitrogen oxides are formed in every combustion processes (at high temperature) from the nitrogen that forms part of the combustion air and is pretty much independent of kind of fuel used. With growing energy consumption, concentration of nitrogen oxides will continue to rise.

**Anthropogenic sources:** motor vehicles, industries, biomass burning

**Natural sources:** bacteria, lightning, biomass burning

About 40% of nitrogen oxides come from transportation, about 25% from thermoelectric generating stations, and the balance from other industrial, commercial, and residential combustion processes.





NO (nitric oxide) & NO<sub>2</sub> (nitrogen dioxide)

## NOx effects

- Causes the reddish-brown haze in city air, which contributes to heart and lung problems and may be carcinogenic.
- NOx is an acid precursor, which is a source of acid rain produced when nitrogen oxides combines with water to produce nitric acid, HNO<sub>3</sub>, and other acids.
- Nitrogen oxides are the precursors of nitrate particulates (nitrates) which affect the radiation balance of the atmosphere and can contribute to global cooling.
- Nitrogen oxides are major contributors to the formation of ground level 'bad' ozone.



# Nitrogen Oxides (NO<sub>x</sub>)

## ***Nitrogen Oxides***

Nitrogen oxides play a crucial role in determining the ozone concentration in the air; they can also contribute to acid precipitation. NO and NO<sub>2</sub> (sum of these is called NO<sub>x</sub>) are the initial compounds emitted, while the others are secondary products resulting from atmospheric conversions.

## **Methods of Measurements**

Reliable measurements of these compounds at background levels have only been possible with instruments that are based on **chemiluminescence** of NO (with ozone)

## **Siting Requirements**

Obvious precautions related to human interference with the measurements have to be taken. Since the levels are so low even at less remote locations, great care has to be taken to minimize potential contamination from any form of motorized transportation, which is a principal source of NO<sub>x</sub>.



# Nitrogen Oxides (NOx)

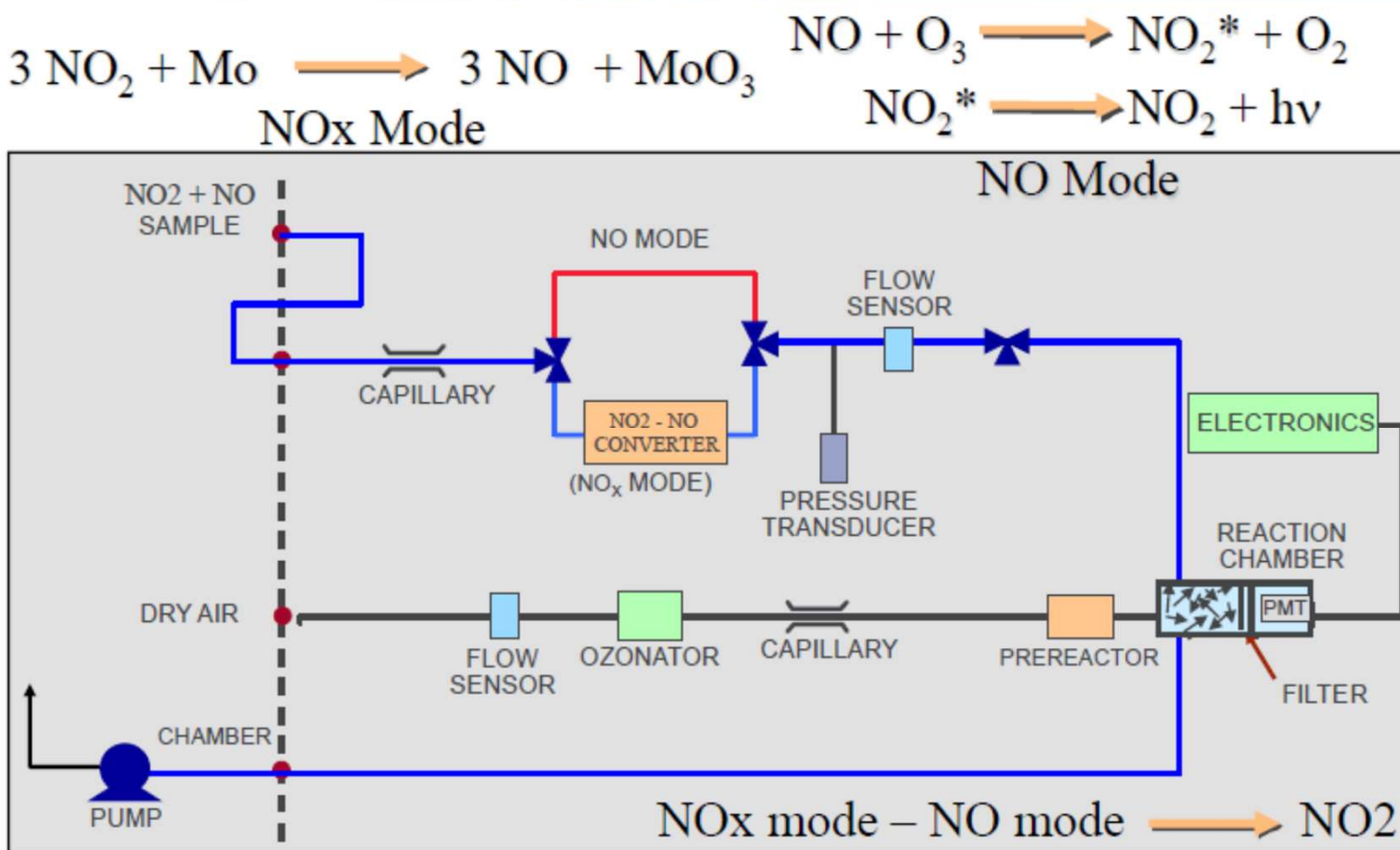
## NOx : Chemiluminescence Method

Chemiluminescence corresponds to an oxidation of NO molecules by O<sub>3</sub> molecules



NO is a relatively unstable molecule which will oxidize to NO<sub>2</sub> in the presence of O<sub>3</sub>. This reaction produces a quantity of light for each NO molecule which is reacted. This light can be measured using a photomultiplier tube or solid state device.

If the volumes of sample gas and excess ozone are carefully controlled, the light level in the reaction chamber is proportional to the concentration of NO in the gas sample.



# Atmospheric Particulates

**Particulate matters** (aerosols) are solid or aqueous particles composed of one or several chemicals and small enough to remain suspended in the air

**Examples:** dust, soot, smoke, sulfates, nitrates, asbestos, pesticides, bioaerosols (e.g., pollen, spores, bacterial cells, fragments of insects, etc.)

**Anthropogenic sources:** various (biomass burning, gas to particle conversion; industrial processes; agriculture's activities)

**Natural sources:** various (sea-salt, dust storm, biomass burning, volcanic debris, gas to particle conversion)

**Total Suspended Particulate Matter (TSP):** particle size 0.01 - 100  $\mu\text{m}$

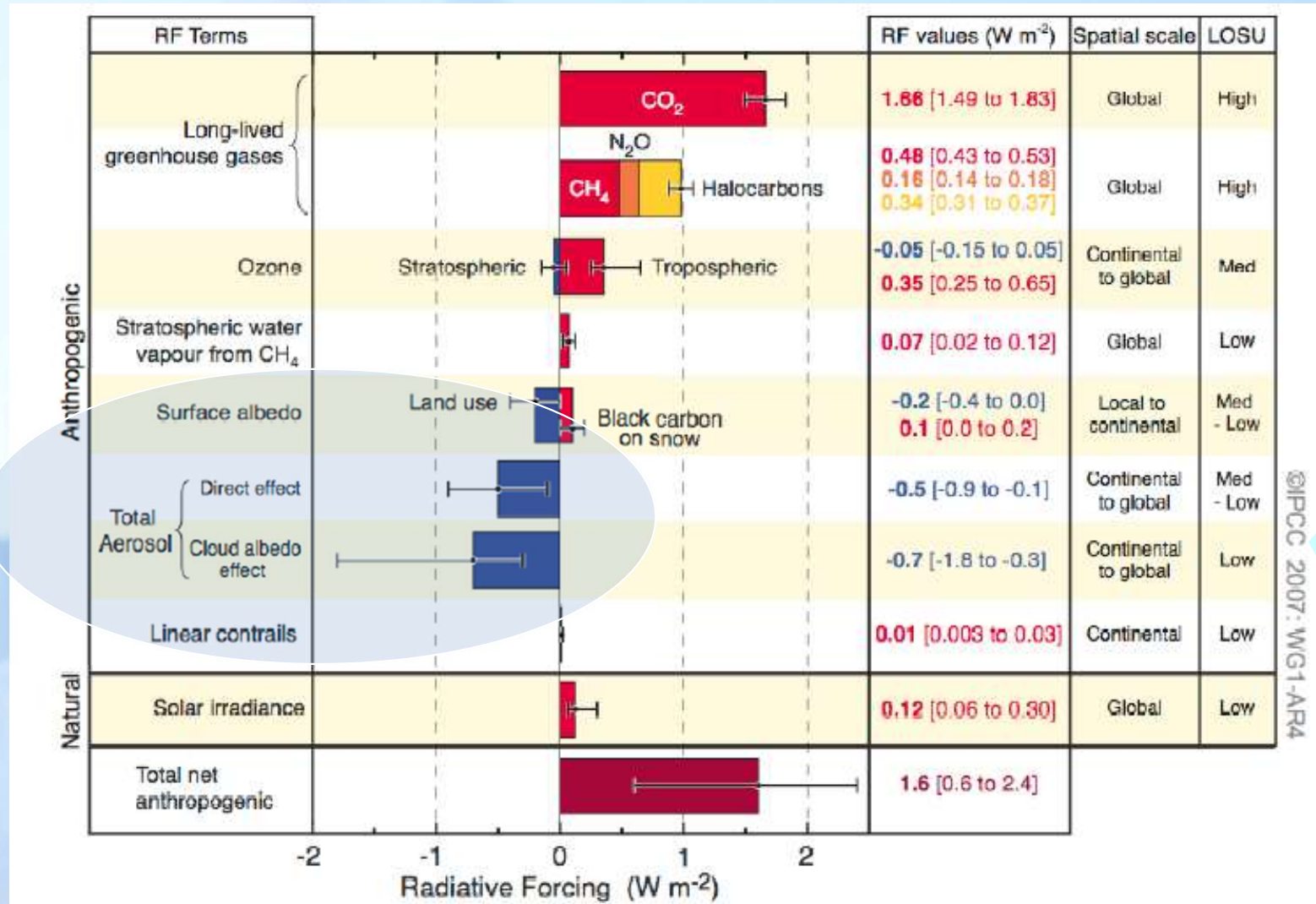
**PM10 =** particulate matter  $\leq 10\mu\text{m}$  in diameter;

**PM2.5 =** mass of particulate matter  $\leq 2.5 \mu\text{m}$  in diameter  
these particles enter the smallest spaces in the lungs

**PM1 =** mass of particulate matter  $\leq 1 \mu\text{m}$  in diameter



# Anthropogenic Radiative Forcing (IPCC)



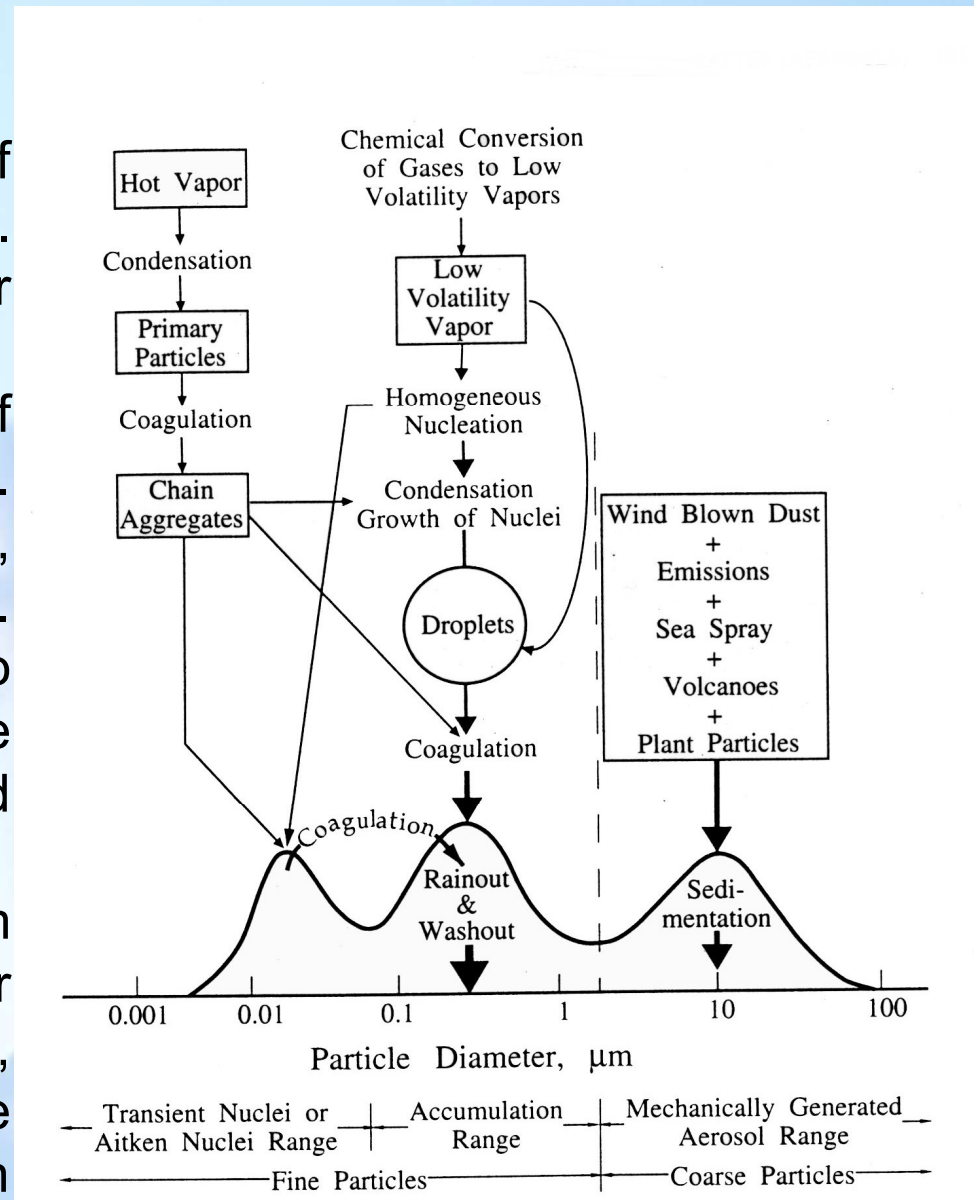
**Level Of Scientific Understanding still LOW**



# Atmospheric Particulates (Contd.)

## Typical spectrum of particles

- **Ultrafine** (0.01-0.1 $\mu\text{m}$ ) = nucleation of saturated vapors ( $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ ). Affected by coagulation (gather together) and condensation.
- **Fine** (0.1-2.5  $\mu\text{m}$ ) = condensation of gases onto pre-existing particles. Major constituents are  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ , EC, OC and many trace metals. Too small to settle out and too large to coagulate into larger particles so have a long residence time (days) and travel great distances.
- **Coarse** (2.5-100 $\mu\text{m}$ ) = particles from sea and soil (natural). Major constituents are Si, Al, Ca, Fe, Mn, Sr, Na, and K. Particles  $\geq 10 \mu\text{m}$  settle from the atmosphere by sedimentation



# Example of PM as “Source”?: Primary and Secondary

**Primary** PM is composed of material in the same chemical form as when they were emitted into the atmosphere including windblown dust, sea salt, road dust, mechanically generated particles and combustion-generated particles such as fly ash and soot.

PM also includes particles formed from the condensation of high temperature vapors formed during combustion (e.g., As, Se, Zn). Concentrations of primary PM are a function of emission rate, transport and dispersion, and removal rate.

**Secondary** particles are formed from condensable vapors generated by chemical reactions of gas-phase precursors. Secondary processes can result in either the formation of new particles or the addition of PM to pre-existing particles.

Sulfate in PM is mostly formed by atmospheric oxidation of  $\text{SO}_2$ . Also, oxides of nitrogen react in the atmosphere to form nitric acid vapor which in turn may react with  $\text{NH}_3$  to form particulate ammonium nitrate. A portion of the organic aerosol is also due to secondary processes. Secondary formation is a function of many factors including: concentrations of precursors, concentrations of other gaseous reactive species (e.g., ozone, hydroxyl radical), atmospheric conditions, and cloud or fog droplet interactions.



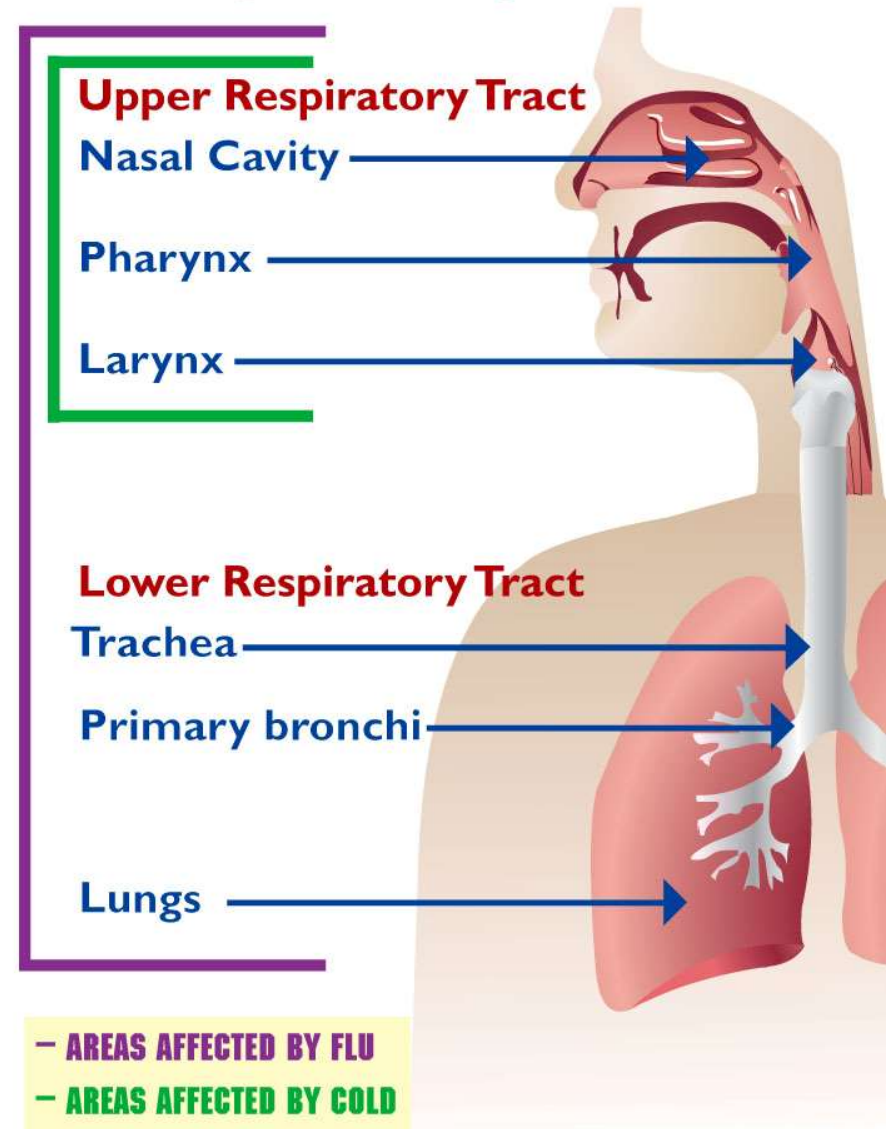
# Effect of Atmospheric Particulates

- Premature death
- Respiratory related hospital admissions and emergency room visits
- Aggravated asthma
- Acute respiratory symptoms, including aggravated coughing and difficult or painful breathing
- Chronic bronchitis
- Decreased lung function that can be experienced as shortness of breath

## Who is Most at Risk from Exposure to Fine Particles?

- The Elderly
- Individuals with Preexisting Heart or Lung Disease
- Children
- Asthmatics and Asthmatic Children

## Respiratory Tract





# MONITORING ISSUES

- ❖ ALL KINDS
- ❖ SPM
- ❖ PM10
- ❖ PM 2.5
- ❖ PM 1
- ❖ ULTRA-FINES



# MONITORING ISSUES

- **Sampling and analysis of  $PM_{2.5}$  is most important area of research because without accurate measurement and speciation of fine particles, source apportionment and dose-response studies will not be valid.**
- **Identifying important species in  $PM_{2.5}$  will help in suggesting control strategies.**
- **The findings will assist the researcher and the gaps identified in current knowledge could be addressed in future research.**



# Instruments used in PM Sampling

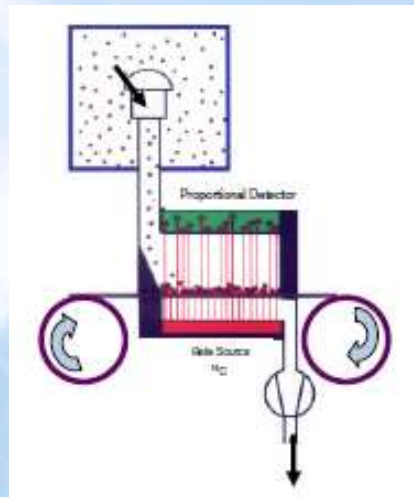
- ❖ Advance instrument
- ❖ Speciation
- ❖ Mass concentration
- ❖ Number concentration
- ❖ Size fractionation
- ❖ Configuration measurements
- ❖ Mobility and aggregation



# Beta-Attenuation Mass Monitor

Continuous Ambient Particulate Monitor continuously measures the mass concentration of suspended and refined particulates (e.g., TSP, PM10, PM2.5, and PM1) by the use of beta attenuation.

A known volume of air (16.7 lpm) is drawn through a size-selective inlet, which can be configured to measure PM-10, PM-2.5, PM-1 or TSP, and deposited onto the auto-advancing filter tape. The combined measurement of mass and air volume are used to obtain the mass concentration readings. Carbon-14 is used as a source of the beta rays. As a result, a continuous, realtime measurement of airborne particulate is provided.



$$C_{\beta} = \frac{A}{\mu_m Q t} (\ln f_0 - \ln f_f)$$

A = particle collection area

$\mu_m$  = mass attenuation coefficient

Q = sample volumetric flow rate

t = sampling time

$f_0$  = initial beta count (s-1)

$f_f$  = final beta count (s-1)



# AEROSOL OPTICAL THICKNESS (AOT) OR AEROSOL OPTICAL DEPTH (AOD)

Aerosol Optical Thickness is a convenient parameter frequently used to estimate the aerosol optical characteristics. These are important to monitor closely because of their daily, seasonal, and long-term variability as well as their link to global climate change, atmospheric pollution, visibility degradation and solar radiation extinction. Presently, the most accepted method of obtaining the AOT at different wavelengths is through the use of multi-wavelength sunphotometer or Skyradiometer.

AOT is a measure of spectral extinction of extra-terrestrial solar irradiance and is computed from ratio of irradiance measured to the corresponding extra-terrestrial values. Hence, the AOT can be computed for any arbitrarily chosen unit of radiation, may it even be the voltage recorded by the sensor.

$$AOT = \left[ \frac{\ln\left(\frac{V_o}{V * S}\right) - mr * \delta R * \left(\frac{P}{P_o}\right)}{mr} \right]$$

P = station pressure

Po = standard atmospheric pressure (= 1013.25 mb)

S = mean sun-earth correction factor

mr = relative optical airmass

$\delta R_1$  = Rayleigh scattering factor for wavelength  $\lambda_1$

Vo1 = Extraterrestrial constant for channel-1  
(wavelength  $\lambda_1$ ) in mV

V1 = signal in mV (meter value) for channel-1



# Sky-radiometer Network of IMD Skynet-India

Online Data Transfer on real time

Data processing at Central Data Processing System, EMRC, New Delhi



# How does it Work?

- Sun Photometers absorb *direct* sunlight energy and convert the intensity into a quantified voltage to measure aerosols in the atmosphere.
- The intensity of sunlight at the top of the earth's atmosphere is constant. While the sunlight travels through the atmosphere, though, aerosols can dissipate the energy by scattering (Rayleigh) and absorbing the light. More aerosols in the atmosphere cause more scattering and less energy transmitted to the surface.
- Knowing the sunlight's energy at the top of the atmosphere, the thickness of the atmosphere, and the amount of sunlight transmitted to the earth's surface and can allows us to determine the amount of scattering, and thus, the amount of aerosols.



# Aerosol Parameters measured and Estimated

❖ **Direct and Diffuse Spectral fluxes ( $Wm^{-2}$ ) measured**

$$AOT1 = \left[ \frac{\ln\left(\frac{V_{o_1}}{V_1 * S}\right) - m_r * \delta_{R1} * \left(\frac{P}{P_o}\right)}{m_r} \right]$$

❖ **Aerosol Optical Depth**

(Columnar load of Aerosols)

❖ **Ångström's Exponent ( $\alpha$ )**

a large Ångström exponent indicates more fine mode aerosol events. ( $\alpha$  generally range from greater than 2.0 for particles near combustion sources to values close to zero for coarse-mode-dominated desert dust aerosols).

• **Single Scattering Albedo**





# Single Scattering Albedo

$$\omega = \frac{\text{Scattering Coeff.}}{\text{Scattering Coeff.} + \text{Absorption Coeff.}}$$

**The single scattering albedo ( $\omega$ ), defined as a measure of the relative importance of scattering and absorption. Values of single scattering albedo range from 1.0 for nonabsorbing particles to below 0.5 for strongly absorbing particles.**



# Deposition Processes

There are two different mechanisms for removal of pollutants from the atmosphere:

## (i) Wet Deposition

Precipitation removes gases and particles from the atmosphere by two processes: (1) rainout and (2) washout

## (ii) Dry Deposition

Pollutants are also removed from the atmosphere in the absence of precipitation by direct contact with the ground and vegetation and by gravitational settling. This process is called dry deposition.

Both types are included in the determination of acid rain.



# Definition of pH

pH = pondus Hydrogenii, literally: hydrogen exponent

**Most common interpretation:**

pH is used to specify the degree of acidity or basicity (also called causticity) of an aqueous solution.

**Historical definition:**

pH is defined as the negative logarithm of the hydrogen ion concentration in solution

$$\text{pH} = -\log[\text{H}^+]$$

**Later definition:**

pH is defined as the negative logarithm of the hydrogen *ion activity* in solution

$$\text{pH} = -\log a_{\text{H}^+} = -\log \gamma[\text{H}^+]$$



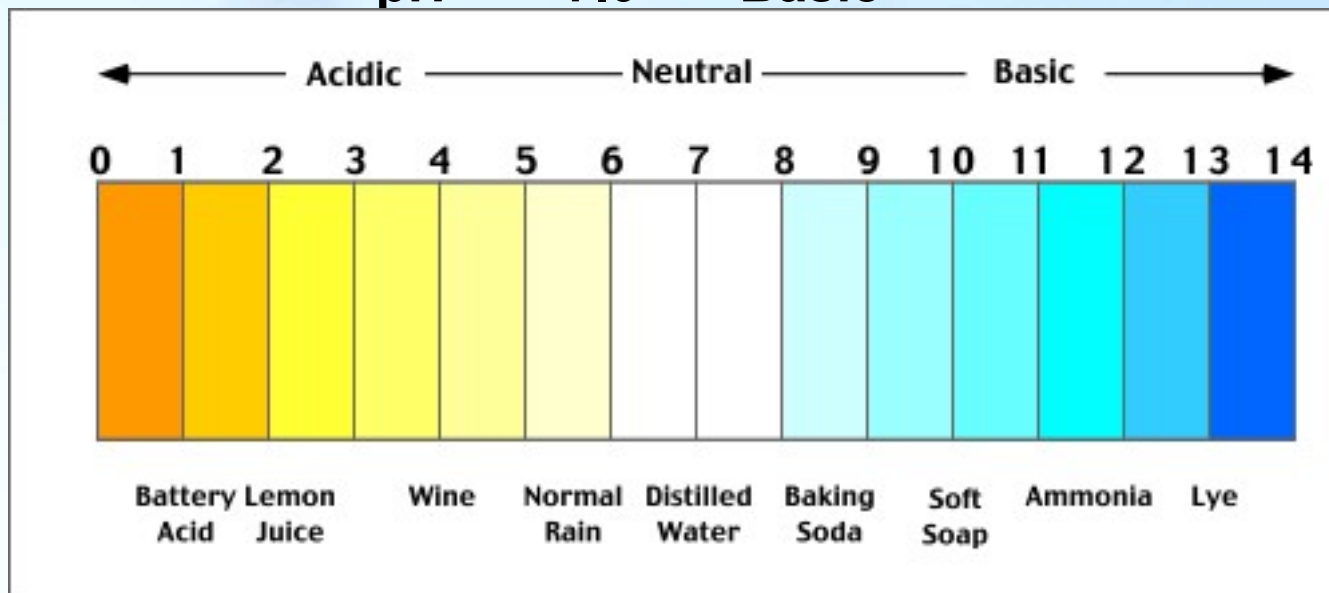
# The pH Scale

pH Scale ranges from 0 to 14.

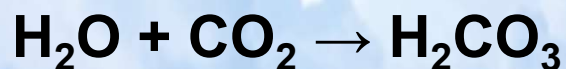
pH = 7.0      Neutral

pH < 7.0    Acidic

pH > 7.0    Basic



Rainwater having pH < 5.65 is known as Acidic. This is being due to pure water in equilibrium with CO<sub>2</sub> has pH of 5.65.



**ACID RAIN pH ≤ 5.65**



<b>Chembur</b>	<b>4.80 (1976)</b>		
<b>Santacruz</b>	<b>4.70 - 5.73 (2000)</b>		<b>IMD</b>
<b>Agra</b>	<b>9.1 (1965)</b>	<b>6.3 (1984)</b>	<b>Khemani et al (1989)</b>
<b>Delhi</b>	<b>7.0 (1965)</b>	<b>6.1(1984)</b>	
	<b>5.93 (1991)</b>	<b>5.0 (1997)</b>	
<b>Bhopal</b>	<b>6.00-7.10</b>		
<b>Calcutta (Kolkata)</b>	<b>5.90-7.30</b>		<b>Dass(1988)</b>
<b>Lucknow</b>	<b>6.55-8.15</b>		
<b>Jaipur</b>	<b>7.14-8.45 (1996-98)</b>		<b>Manoj et al (2000)</b>
<b>Kota</b>	<b>7.40-7.95 (1996-97)</b>		<b>Manoj et al (2000)</b>



**Q1. The pollutants such as NO<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub> dissolved in the moisture of air are the cause of \_\_\_\_\_.**

**Q2. The permissible concentration of PM<sub>10</sub> in the air on annual time weighted average as per NAAQS by CPCB of notification of year 2009 is**

**a) 60 µg/m<sup>3</sup>**

**b) 40 µg/m<sup>3</sup>**

**c) 50 µg/m<sup>3</sup>**

**d) 20 µg/m<sup>3</sup>**

**Q3: Clouds are present in**

**(a) stratosphere**

**(b) troposphere**

**(c) mesosphere**

**(d) thermosphere**

**Q4: Write down the at least two natural sources of air pollution?**

**Q5. Excessive release of carbon dioxide in the atmosphere is the cause of \_\_\_\_\_ effect which produces global warming.**

