

## **LECTURE NOTES: Ozone and Air Pollution**

### **Composition of the Atmosphere**

Atmospheric constituents can be classed in two groups: (i) well mixed, and (ii) variable. Nitrogen and oxygen, which account for roughly 99% of the atmosphere, are examples of the former. These constituents have long residence times—they enter and leave the atmosphere much more slowly than the typical time it takes for turbulence to mix them up thoroughly throughout the atmosphere. As a result, their number fraction is essentially constant in space and time.

The most important variable constituent is water vapour. At any given instant, water vapour can account for anything between 5% of the atmosphere (near the surface in the tropics) and almost zero (in the stratosphere).

Table: Composition of the atmosphere. Number fractions (other than for water vapour) are specified with respect to dry tropospheric air at a pressure of 1 atm.

Constituent	Number fraction (%)	Residence Time
Nitrogen (N <sub>2</sub> )	78.084	10 <sup>6</sup> -10 <sup>7</sup> years
Oxygen (O <sub>2</sub> )	20.946	3000-10,000 years
Argon (Ar)	0.93	Forever
Neon (Ne)	0.001818	Forever
Helium (He)	0.000524	10 <sup>6</sup> years
Methane (CH <sub>4</sub> )	0.0001745	2-10 years
Krypton (Kr)	0.000114	Forever
Hydrogen (H <sub>2</sub> )	0.000055	4-8 years
Water vapour (H <sub>2</sub> O)	0—5	
Carbon dioxide (CO <sub>2</sub> )	0.038	
Ozone (O <sub>3</sub> )	0—0.00001	

Every deep breath fills our lungs mostly with gaseous nitrogen and oxygen. Also inhaled, in minute quantities, may be other gases and particles, some of which could be considered pollutants. These contaminants come from car exhaust, chimneys, forest fires, factories, power plants, and other sources related to human activities. Virtually every large city has to contend in some way with air pollution, which clouds the sky, injures plants, and damages property. Some pollutants merely have a noxious odor, whereas others can cause severe health problems. The cost is high. Estimates are that, worldwide, nearly 1 billion people in urban environments are continuously being exposed to health

hazards from air pollutants.

### **Brief History of Air Pollution**

Strictly speaking, air pollution is not a new problem. More than likely it began when humans invented fire whose smoke choked the inhabitants of poorly ventilated caves. In fact, very early accounts of air pollution characterized the phenomenon as “smoke problems,” the major cause being people burning wood and coal to keep warm. To alleviate the smoke problem in old England, King Edward I issued a proclamation in 1273 forbidding the use of sea coal, an impure form of coal that produced a great deal of soot and sulfur dioxide when burned. One person was reputedly executed for violating this decree.

In spite of such restrictions, the use of coal as a heating fuel grew during the fifteenth and sixteenth centuries. As industrialization increased, the smoke problem worsened. In 1661, the prominent scientist John Evelyn wrote an essay deploring London’s filthy air. And by the 1850s, London had become notorious for its “peasoup” fog, a thick mixture of smoke and fog that hung over the city. These fogs could be dangerous. In 1873, one was responsible for as many as 700 deaths. Another in 1911 claimed the lives of 1150 Londoners. To describe this chronic atmospheric event, a physician, Harold Des Voeux, coined (around 1911) the word smog, meaning a combination of smoke and fog. Little was done to control the burning of coal as time went by, primarily because it was extremely difficult to counter the basic attitude of the powerful industrialists: “Where there’s muck, there’s money.” London’s acute smog problem intensified. Then, during the first week of December, 1952, a major disaster struck. The winds died down over London and the fog and smoke became so thick that people walking along the street literally could not see where they were going. This particular disastrous smog lasted 5 days and took nearly 4000 lives, prompting Parliament to pass a Clean Air Act in 1956. Additional air pollution incidents occurred in England during 1956, 1957, and 1962, but due to the strong legislative measures taken against air pollution, London’s air today is much cleaner, and “pea soup” fogs are a thing of the past. Air pollution episodes were by no means limited to Great Britain. During the winter of 1930, for instance, Belgium’s highly industrialized Meuse Valley experienced an air pollution tragedy when smoke and other contaminants accumulated in a narrow steep-sided valley. The tremendous buildup of pollutants caused about 600 people to become ill, and ultimately 63 died. Not only did humans suffer, but cattle, birds, and rats fell victim to the deplorable conditions.

The industrial revolution brought air pollution to the United States, as homes and coal-burning industries belched smoke, soot, and other undesirable emissions into the air. Soon, large industrial cities, such as St. Louis and Pittsburgh (which became known as the “Smoky City”), began to feel the effects of the everincreasing use of coal. As early as 1911, studies documented the irritating effect of smoke particles on the human respiratory system and the “depressing and devitalizing” effects of the

constant darkness brought on by giant, black clouds of smoke. By 1940, the air over some cities had become so polluted that automobile headlights had to be turned on during the day. The first major documented air pollution disaster in the United States occurred at Donora, Pennsylvania, during October, 1948, when industrial pollution became trapped in the Monongahela River Valley. During the ordeal, which lasted 5 days, more than 20 people died and thousands became ill.\* Several times during the 1960s, air pollution levels became dangerously high over New York City. Meanwhile, on the West Coast, in cities such as Los Angeles, the ever-rising automobile population, coupled with the large petroleum processing plants, were instrumental in generating a different type of pollutant—one that forms in sunny weather and irritates the eyes. Toward the end of World War II, Los Angeles had its first (of many) smog alerts. Air pollution episodes in Los Angeles, New York, and other large American cities led to the establishment of much stronger emission standards for industry and automobiles. The Clean Air Act of 1970, for example, empowered the federal government to set emission standards that each state was required to enforce. The Clean Air Act was revised in 1977 and updated by Congress in 1990 to include even stricter emission requirements for autos and industry. The new version of the Act also includes incentives to encourage companies to lower emissions of those pollutants contributing to the current problem of acid rain. Moreover, amendments to the Act have identified 189 toxic air pollutants for regulation.

### **Air Act in India**

The Air (Prevention and Control of Pollution) Act was enacted in 1981 and amended in 1987 to provide for the prevention, control and abatement of air pollution in India. WHEREAS decisions were taken at the United Nations Conference on the Human Environment held in Stockholm in June, 1972, in which India participated, to take appropriate steps for the preservation of the natural resources of the earth which, among other things, include the preservation of the quality of air and control of air pollution;

### **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. Good air quality refers to clean, clear, unpolluted air. Clean air is essential to maintaining the delicate balance of life on this planet — not just for humans, but wildlife, vegetation, water and soil. Poor air quality is a result of a number of factors, including emissions from various sources, both natural and “human-caused.” Poor air quality occurs when pollutants reach high enough concentrations to endanger human health and/or the environment. Our everyday choices, such as driving cars and burning wood, can have a significant impact on air quality.

Pollutants are measured in one of two ways: either through continuous (real-time) or noncontinuous (discrete) monitoring. In continuous monitoring, air is constantly measured and the

data is automatically transmitted to a central database. In noncontinuous monitoring, pollutants collect on a filter or canister over a specified period of time (such as one, three or six days). Then a technician collects the filter or canister and sends it to a certified laboratory for measurement and analysis.

### **Air Pollutants**

"air pollutant" means any solid, liquid or gaseous substance present in the atmosphere in such concentration as may be or tend to be injurious to human beings or other living creatures or plants or property or environment;

### **Air pollution**

Definitions:

"Air pollution" means the presence in the atmosphere of any air.

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.

### **Types of air pollutants:**

- ♦ 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<sub>2</sub>, CO, NO<sub>2</sub> etc.
- ♦ Secondary pollutants - formed by interaction of primary pollutants with each other or with normal components of the air e.g. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, O<sub>3</sub> etc

**Criteria air pollutants** are major pollutants for which ambient air standards have been set to protect human health and welfare.

### National Ambient Air Quality Standards in India

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 <sub>2</sub> ( $\mu\text{gm}^{-3}$ )	Annual*  24 hours**	50  80	20  80	- Improved West and Goeke  - UV - fluorescence
NO <sub>2</sub> ( $\mu\text{gm}^{-3}$ )	Annual*  24 hours**	40  80	30  80	- Modified Jacob & Hochheiser (Na-Arsenic)  - Chemiluminescence
PM <sub>10</sub> , ( $\mu\text{gm}^{-3}$ )	Annual*  24 hours**	60  10  0	60  100	- Gravimetric  - TEOM  - Beta Attenuation
PM <sub>2.5</sub> , ( $\mu\text{gm}^{-3}$ )	Annual*  24 hours**	40  60	40  60	- Gravimetric  - TEOM  - Beta Attenuation
Ozone ( $\mu\text{gm}^{-3}$ )	8 hours  1 hour	100  180	100  180	- UV photometric  - Chemiluminescence  - Chemical Method
Lead ( $\mu\text{gm}^{-3}$ )	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 ( $\mu\text{gm}^{-3}$ )	8 hours  1 hour	2000  4000	2000  4000	Non-dispersive Infra Red (NDIR) spectroscopy

NH <sub>3</sub> (µgm <sup>-3</sup> )	Annual* 24 hours**	10 0 40 0	100 400	- Chemiluminescence - Indophenol Blue Method
Benze ne (µgm <sup>-3</sup> )	Annual*	5	5	- Gas Chromatography based continuous analyzer Absorption and Desorption followed by GC analysis
Benzo(a)Py rene - particulate phase only (ngm <sup>-3</sup> )	Annual*	1	1	Solvent extraction by HPLC/GC analysis
Arsen ic (ngm <sup>-3</sup> )	Annual*	6	6	AAS/ICP method after sampling on EPM2000 or equivalent filter paper
Nick el (ngm <sup>-3</sup> )	Annual	20	20	AAS/ICP method after sampling on EPM2000 or equivalent filter paper

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

### Major Classes of Air Pollutants:

#### **Carbon mono-oxide (CO)**

CO is a colorless, odorless, nonirritating, poisonous gas, major pollutant of an urban air, produced from incomplete combustion.

Anthropogenic sources: motor vehicles, industries, biomass burning

Natural sources: biomass burning

CO is also produced by atmospheric oxidation of methane gas and other hydrocarbons

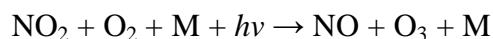
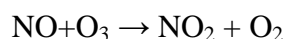
CO is highly poisonous to humans and most animals: when inhaled, CO attacks haemoglobin and displaces O<sub>2</sub> to form Carboxy-hemoglobin which reduces blood's capacity of carrying O<sub>2</sub>. (Red blood cells pick up CO instead of oxygen. Hemoglobin likes CO 250 times more than oxygen)

### **Sulfur oxides** (mainly SO<sub>2</sub>, or sulfur dioxide)

- ♦ Source = The burning of fossil fuels is mainly responsible for creation of SO<sub>2</sub> and oxides of nitrogen. Automobile exhaust fumes are partly to blame but the worst culprits are coal-burning thermal power plants and steel industry. Energy production in India mainly relies on coal, which accounts for about 71% of the total. In this context, power plants are the major source of wet and dry deposition of sulphur. SO<sub>2</sub> can react with gases in atmosphere to form sulfuric acid ('acid rain')
- ♦ Exposure to SO<sub>2</sub> can cause impairment of respiratory function, aggravation of existing respiratory disease (especially bronchitis), and a decrease in the ability of the lungs to clear foreign particles. It can also lead to increased mortality, especially if elevated levels of particulate matter (PM) are also present. Groups that appear most sensitive to the effects of SO<sub>2</sub> include asthmatics and other individuals with hyperactive airways, and individuals with chronic obstructive lung or cardiovascular disease. Elderly people and children are also likely to be more sensitive to SO<sub>2</sub>.

### **Nitrogen oxides (NO<sub>x</sub>)** - NO (nitric oxide) & NO<sub>2</sub> (nitrogen dioxide)

The oxides of nitrogen, NO (nitric oxide), and NO<sub>2</sub> (nitrogen dioxide), which together are referred to as NO<sub>x</sub>, play important roles in atmospheric chemistry. They 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. They are produced by fossil fuel combustion, biomass burning, and from soils, lightning, NH<sub>3</sub> oxidation, aircraft emissions, and transport from the stratosphere. All combustion processes account for only 5 % of NO<sub>2</sub> in the atmosphere, most is formed from reactions involving NO. NO<sub>x</sub> is emitted into the troposphere primarily as NO, but during the day NO rapidly establishes equilibrium with NO<sub>2</sub> through the following null cycle.



where M represents an inert molecule that absorbs excess molecular energies. Once NO is converted to NO<sub>2</sub>, a number of reaction paths are available. At night NO<sub>x</sub> is present only as NO<sub>2</sub> due to reaction.

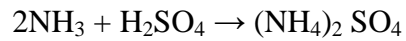
The principal sink for NO<sub>x</sub> in the daytime is  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$

The nitric acid (HNO<sub>3</sub>) is removed in about 1 week by dry and wet deposition. At night, NO<sub>2</sub> is oxidized by O<sub>3</sub> to NO<sub>3</sub>, the NO<sub>3</sub> then reacts with NO<sub>2</sub> to produce N<sub>2</sub>O<sub>5</sub>, and the N<sub>2</sub>O<sub>5</sub> reacts with water on particles to produce HNO<sub>3</sub>. The resulting residence time of NO<sub>2</sub> is about 1 day.

- ♦ Visibility decreases due to yellowish color of NO<sub>2</sub>. It contributes to heart and lung problems, NO<sub>2</sub> can suppress plant growth, may encourage the spread of cancer, decreases resistance to infection. can react with other gases in atmosphere to form nitric acid (HNO<sub>3</sub>)

### **Ammonia**

Ammonia (NH<sub>3</sub>) originates from soils, animal waste, fertilizers, and industrial emissions. It is the principal basic gas in the atmosphere. Ammonia neutralizes acid species by reactions of the form



The primary removal mechanisms for NH<sub>3</sub> involve its conversion to ammonium-containing aerosols by reactions such as given above. The aerosols are then transported to the ground by wet and dry deposition. The residence time of NH<sub>3</sub> in the lower troposphere is about 10 days.

### **OZONE**

#### **What Is Ozone**



Ozone (O<sub>3</sub>) is a reactive oxidant gas produced naturally in trace amounts in the Earth's atmosphere. **Ozone** is a relatively colorless gas at typical mixing ratios. It appears faintly purple when its mixing ratios are high because it weakly absorbs green wavelengths of visible light and transmits red and blue, which combine to form purple. Ozone exhibits an odor when its mixing ratios exceed 0.02 ppmv. Ozone is considered an air pollutant in the boundary layer (lower troposphere) because of the harm that it does to humans, animals, plants, and materials. In India, it is one of the criteria air pollutants that require control under NAAQS. In the stratosphere, ozone's absorption of UV radiation provides a protective shield for life on Earth. Although ozone is considered to be "good" in the stratosphere and "bad" in the boundary layer, ozone molecules are the same in both cases.

The increase in ozone is a concern because ozone present in the upper troposphere acts as a GHG, absorbing some of the infrared energy emitted by the earth. The radiative forcing of tropospheric ozone is about 25% that of carbon dioxide (IPCC Third Assessment Report). The annual global warming potential of tropospheric ozone is between 918-1022 tons carbon dioxide equivalent / tons tropospheric ozone. This means on a per-molecule basis, ozone in the troposphere has a radiative forcing effect roughly 1,000 times as strong as carbon dioxide. However, tropospheric ozone is a short-lived greenhouse gas, which decays in the atmosphere much more quickly than carbon dioxide. This means that over a 20 year horizon, the global warming potential of tropospheric ozone is much less, roughly 62 to 69 tons carbon dioxide equivalent / tons tropospheric ozone. Ozone plays a controlling role in the oxidizing capacity of the troposphere.

### **Sources of Tropospheric or Ground-level ozone**

Ozone is not directly emitted into the atmosphere. Ozone is a secondary pollutant formed in the atmosphere by sunlight driven chemical reactions between the O<sub>3</sub> precursor gases: VOC, CO, NO<sub>x</sub>, and CH<sub>4</sub>. Emissions of O<sub>3</sub> precursor gases arise from a wide range of sources that are either natural in origin or driven by human activities. Energy generation, transport, agriculture, industrial processes, biomass burning and land use changes such as deforestation are significant sources of O<sub>3</sub> precursor gases. In addition small amounts of stratospheric ozone, which occasionally migrate down to the earth's surface also, contribute. With increasing populations, more automobiles, and more industry, there is more ozone in the lower atmosphere. Since 1900 the amount of ozone near the earth's surface has more than doubled. When referring to ground-level O<sub>3</sub>, a distinction is usually drawn between baseline, hemispheric background, or peak/episodic O<sub>3</sub> concentrations. Background O<sub>3</sub> in the Northern Hemisphere is now in the range of 35–40 ppb. High O<sub>3</sub> concentrations occur episodically throughout the year depending on the weather. During such episodes, O<sub>3</sub> concentrations can reach as high as 200 ppb. Even larger values, of up to 400 ppb, can be observed during the smog episodes.

In urban areas in the Northern Hemisphere, high ozone levels usually occur during the warm, sunny summer months (from May through September). Typically, ozone levels reach their peak in mid to late afternoon, after the sun has had time to react fully with the exhaust fumes from the morning rush hours. A hot, sunny, still day is the perfect environment for ozone pollution production. In early evening, the sunlight's intensity decreases and the photochemical production process that forms ground level ozone begins to subside.

Stratosphere-Troposphere Exchange accounts for about 18% of Ozone in the troposphere (with a range of 8-44% -- large amount of error!). Although photochemistry in the lower troposphere is the major source of tropospheric ozone, the stratosphere-troposphere transport of ozone is important to the overall climatology, budget and long-term trends of tropospheric ozone.

### **The Lifetime and Sinks**

Sinks of ozone include reaction, transfer to soils and ice caps, and dissolution in ocean waters. Because ozone is relatively insoluble, its dissolution rate is relatively slow. The lifetime of O<sub>3</sub> is determined by removal processes (or sinks) which lead to loss of O<sub>3</sub> from the atmosphere. The average lifetime of O<sub>3</sub> in the troposphere has been estimated at 22 (±2) days; however, it varies with altitude and ranges from 1–2 days in the boundary layer where dry deposition is the major sink, to several weeks in the upper troposphere. This, in combination with the potential for O<sub>3</sub> to be produced from precursors long after they have been emitted, makes O<sub>3</sub> a global pollutant.

### **Health Effects of Ozone**

Ozone causes headaches at mixing ratios greater than 0.15 ppmv, chest pains at mixing ratios greater than 0.25 ppmv, and sore throat and cough at mixing ratios greater than 0.30 ppmv. Ozone decreases lung function for people who exercise steadily for more than an hour while exposed to concentrations greater than 0.30 ppmv. Symptoms of respiratory problems include coughing and breathing discomfort. Small decreases in lung function affect people with asthma, chronic bronchitis, and emphysema. Ozone may also accelerate the aging of lung tissue. At levels greater than 0.1 ppmv, ozone affects animals by increasing their susceptibility to bacterial infection.

### **Effect of Ozone on Plants**

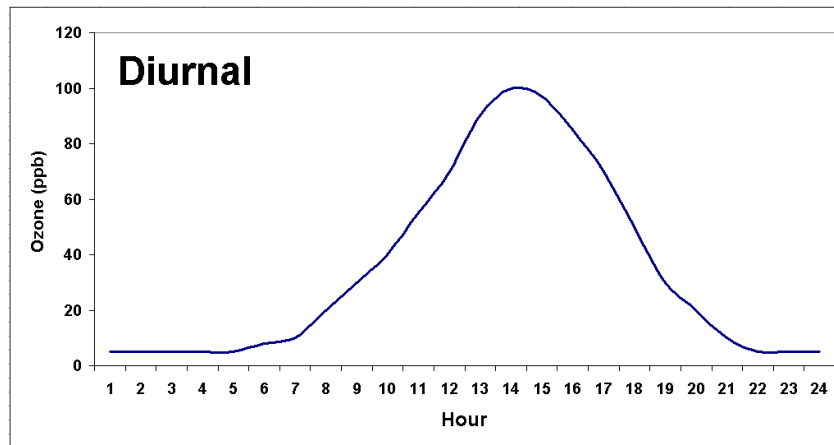
O<sub>3</sub> is considered the most damaging air pollutant for plants. O<sub>3</sub> enters the leaf through stomata, and its primary site of injury is the cells of the mesophyll or palisade layer on the upper leaf surface. This tissue contains chloroplasts (chlorophyll containing plastids) and is responsible for photosynthesis. Therefore, a primary effect of O<sub>3</sub> is on photosynthesis, and exposure to sufficient O<sub>3</sub> can produce a variety of injury symptoms associated with chlorophyll breakdown.

O<sub>3</sub> reacts with O<sub>2</sub> and produces reactive oxygen species, including H<sub>2</sub>O<sub>2</sub>, superoxide (O<sub>2</sub><sup>-</sup>), singlet oxygen (<sup>1</sup>O<sub>2</sub>\*), and the hydroxyl radical. These denature proteins, damage nucleic acids and thereby give rise to mutations, and cause lipid peroxidation, which breaks down lipids in membranes.

O<sub>3</sub> injury on plant leaves is 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. The most extensive research on crop loss was performed from 1980 to 1987 at five locations in the USA as part of the National Crop Loss Assessment Network (NCLAN). At each location, numerous chambers were used to expose plants to ozone treatments spanning the range of concentrations that occur in different areas of the world. The results show that dicot species (soybean, cotton, and peanut) are more sensitive to yield loss caused by O<sub>3</sub> than monocot species (sorghum, field corn, and winter wheat).

### **When are ozone concentrations highest?**

Ozone concentrations vary over different scales of time. 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.

### **Diurnal Variation of Surface Ozone**

#### **The ozone layer and Stratospheric Ozone**

The atmosphere modifies solar energy as it passes through by acting as a filter, reducing certain types of incoming radiation by absorption. One of the most important filtering effects for life on earth is the reduction of **ultraviolet radiation (UV)**: this is radiation of shorter wavelength than the visible spectrum. Low levels of UV are useful to life: it is used in Vitamin D synthesis, for example. However, high levels of UV are harmful, causing skin cancers, genetic damage and climate change.

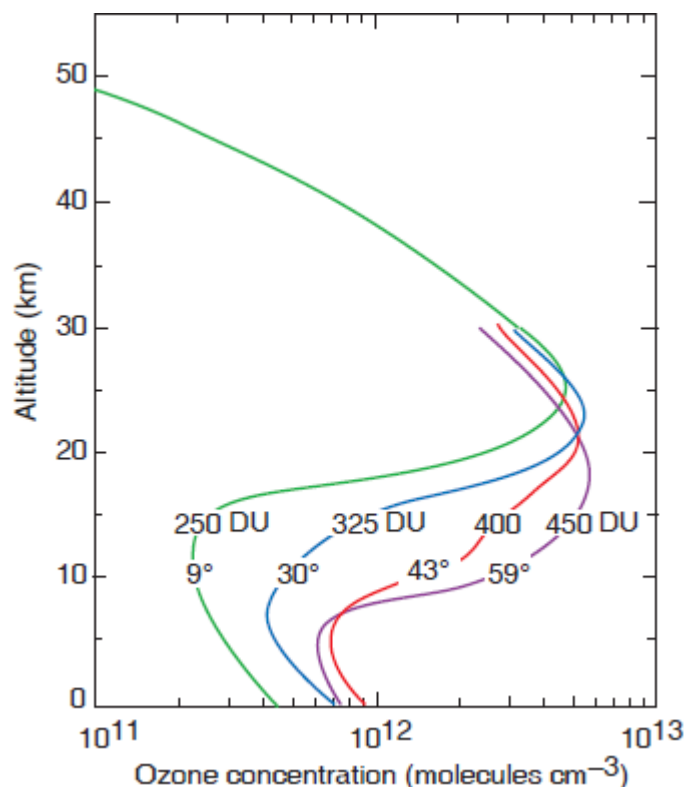
UV radiation can be subdivided into three bands:

- UVA: 0.32-0.40 microns,
- UVB: 0.28-0.32 microns,
- UVC: 0.20-0.28 microns.

UVC is entirely filtered out by the atmosphere, and of the UV that reaches sea-level, organisms are most sensitive to UVB.

90% of naturally occurring atmospheric ozone occurs in the stratosphere between 10-50 km, with maximum concentrations at 15-30 km - it is this part of the atmosphere that is referred to as the Ozone layer. Stratospheric ozone is very important: it removes almost all incoming UVC, and 70% of the incoming UVB at equator, 90% at poles. It is processes of UV absorption by ozone that gives the stratosphere its characteristic thermal structure: in the stratosphere, temperature increases upward (due to energy acquired during UV absorption), unlike the lower part of the atmosphere (troposphere) in which temperature usually decreases upwards. Ozone layer is thinnest in the tropics (around the equator) and denser towards the poles. Atmospheric ozone is measured in **Dobson Units** (DU). 100 DU is equivalent to a 1mm thick layer of pure ozone at surface pressure (1000 mbar). The average amount of ozone in the atmosphere is about 300 DU.

The presence of an *ozone layer* between heights of 15–30 km is clear. However, the O<sub>3</sub> layer is highly variable: its height and intensity change with latitude, season, and meteorological conditions.

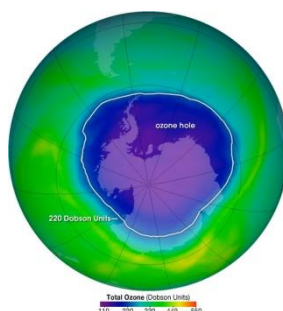


**Figure:** Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees). Note the increase in the total ozone column abundance (given in DU) with increasing latitude.

The greatest column densities of  $O_3$  in the northern hemisphere occur in polar latitudes in spring; in the southern hemisphere the spring maximum is at mid-latitudes. Because  $O_3$  is produced by photochemical reactions, the production is a maximum in the stratosphere over the tropics. The peaks in concentrations at polar and midlatitudes are attributed to meridional and downward transport of  $O_3$  away from the equator, although at any given point in the atmosphere the balance between the production and loss of  $O_3$ , and its flux divergence, determines the  $O_3$  concentration at that point. It is clear from above figure that 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.

### Ozone Hole:

The ozone hole is not technically a “hole” where no ozone is present, but is actually a region of exceptionally depleted ozone in the stratosphere over the Antarctic that happens at the beginning of Southern Hemisphere spring (August–October). Satellite instruments provide us with daily images of ozone over the Antarctic region. The ozone hole image below shows the very low values (blue and purple colored area) centered over Antarctica on 4 October 2004. From the historical record we know that total column ozone values of less than 220 Dobson Units were not observed prior to 1979. From an aircraft field mission over Antarctica we also know that a total column ozone level of less than 220 Dobson Units is a result of catalyzed ozone loss from chlorine and bromine compounds. For these reasons, we use 220 Dobson Units as the boundary of the region representing ozone loss. Using the daily snapshots of total column ozone, we can calculate the area on the Earth that is enclosed by a line with values of 220 Dobson Units (the white line in the figure below).



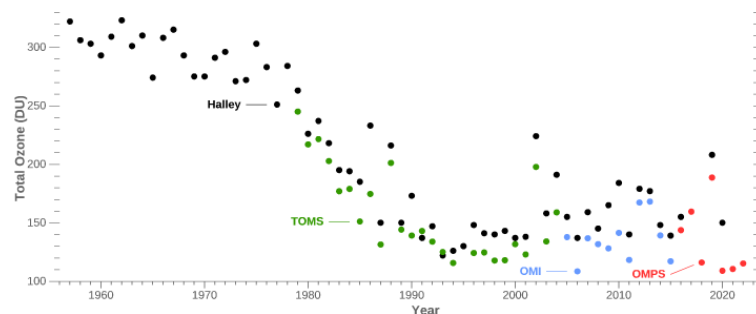
*The ozone hole is the region over Antarctica with total ozone of 220 Dobson Units or lower. This map*

shows the ozone hole on October 4, 2004. The data were acquired by the [Ozone Monitoring Instrument](#) on NASA's [Aura](#) satellite.

## History of the Ozone Hole

Throughout the 20th century, discoveries and observations trickled in that would allow scientists to understand how human-made chemicals like chlorofluorocarbons create a hole in the ozone layer over Antarctica each spring. As early as 1912, Antarctic explorers recorded observations of unusual veil-type clouds in the polar stratosphere, although they could not have known at the time how significant those clouds would become. In 1956, the British Antarctic Survey set up the Halley Bay Observatory on Antarctica in preparation for the International Geophysical Year (IGY) of 1957. In that year, ozone measurements using a Dobson Spectrophotometer began.

These measurements gave the first clues that there was trouble in the ozone layer. In 1985, a group of scientists (J. C. Farman, B. G. Gardiner, and J. D. Shanklin) published in the journal *Nature* the first paper on observations of springtime losses of ozone over Antarctica. In 1986, NASA scientists used satellite data from the Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscatter Ultraviolet (SBUV) instrument to demonstrate that the ozone hole is a regional-scale Antarctic phenomenon.



*Instruments on the ground (at Halley) and high above Antarctica (Total Ozone Mapping Spectrometer [TOMS], Ozone Monitoring Instrument [OMI], and Ozone Mapping and Profiler Suite [OMPS]) measured an acute drop in total atmospheric ozone during October in the early and middle 1980s. (Halley data supplied by [J. D. Shanklin, British Antarctic Survey](#)).*

## Anthropogenic Perturbations to Stratospheric Ozone: The Ozone Hole

The ozone hole is not technically a “hole” where no ozone is present, but is actually a region of exceptionally depleted ozone in the stratosphere over the Antarctic that happens at the beginning of Southern Hemisphere spring (August–October). Satellite instruments provide us with daily images of ozone over the Antarctic region. The ozone hole image below shows the very low values (blue and purple colored area) centered over Antarctica on 4 October 2004. From the historical record we know that total column ozone values of less than 220 Dobson Units were not observed prior to 1979. From an aircraft field mission over Antarctica we also know that a total column ozone level of less than 220 Dobson Units is a result of catalyzed ozone loss from chlorine and bromine compounds. For these reasons, we use 220 Dobson Units as the boundary of the region representing ozone loss. Using the daily snapshots of total column ozone, we can calculate the area on the Earth that is enclosed by a line with values of 220 Dobson Units (the white line in the figure below).

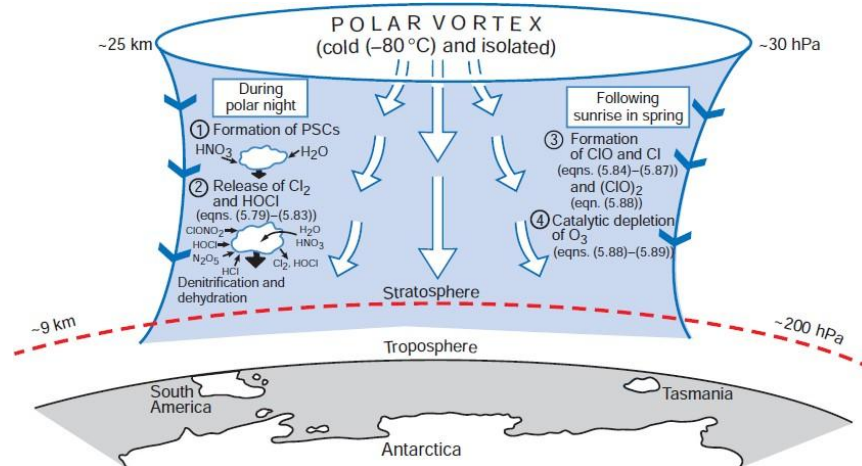
The first evidence of a significant depletion in stratospheric  $O_3$  produced by anthropogenic chemicals in the stratosphere came, surprisingly, from measurements in the Antarctic. In 1985, British scientists, who had been making ground-based, remote sensing measurements of  $O_3$  at Halley Bay in the Antarctic for many years, reported a 30% decrease in springtime (October) total column  $O_3$  since 1977. These observations were subsequently confirmed by remote sensing measurements from satellite and by airborne *in situ* measurements. The areal extent of the Antarctic ozone hole, derived from satellite measurements shows that from 1979 to 2001 the ozone hole grew progressively until it occupied an area (approx. 25 million  $km^2$ ). However, in 2002 the area occupied by the ozone hole decreased dramatically, but returned to its former size in 2003.

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  $-80^\circ C$ . In the austral spring, as temperatures rise, the winds around the vortex weaken, and by late December the vortex disappears. However, during winter, the vortex serves as a giant and relatively isolated chemical reactor in which unique chemistry can occur. For example, although the concentrations of  $O_3$  in the vortex are normal in August, the concentrations of ClO in the vortex are 10 times greater than just outside the vortex collar. In September, when sunlight returns to the polar cap region,  $O_3$  concentrations within the vortex decrease dramatically. There are also sharp decreases in the concentrations of oxides of nitrogen and water vapor when passing from the outside to the

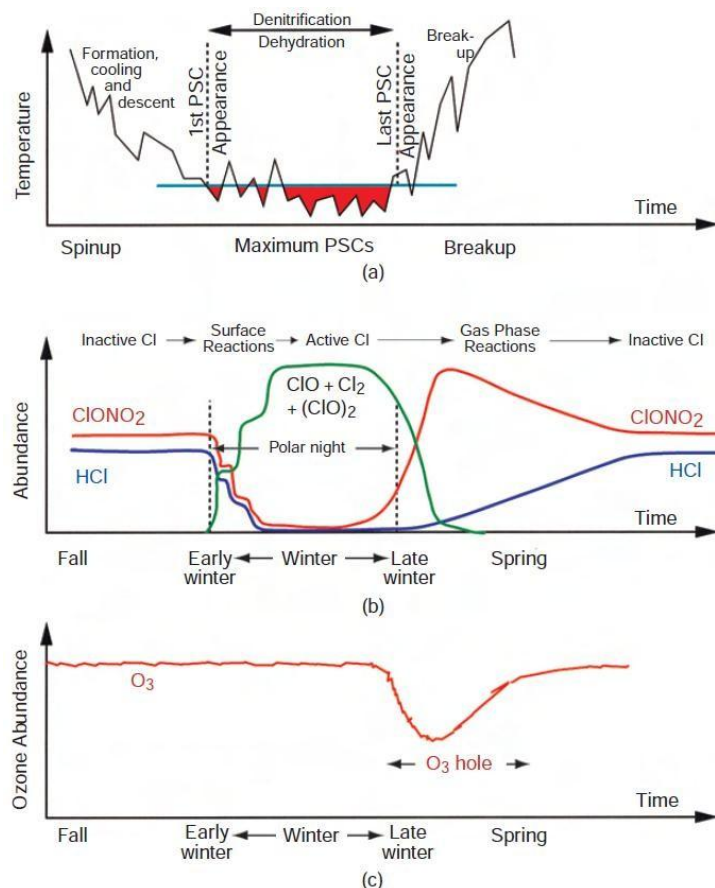


inside of the vortex collar. These decreases are due, respectively, to the formation of nitric acid ( $\text{HNO}_3$ ) and to the condensation of water at the very low temperatures inside the vortex.

As the particles in PSCs slowly sink, they remove both water and nitrogen compounds from the stratosphere, processes referred to as *dehydration* and *denitrification*, respectively. The chemical reactions involved in the removal of these two species play an important role in depleting  $\text{O}_3$  in the Antarctic vortex.



Schematic of the polar vortex (blue) over Antarctica. Large arrows indicate cold descending air



*Schematic illustrating time evolution of the main processes associated with the 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 ClONO<sub>2</sub> and HCl are converted into the active chlorine species Cl<sub>2</sub>, ClO, and (ClO)<sub>2</sub> 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 O<sub>3</sub> rises.*

### **Volatile organic compounds BTEX**

BTEX is the term used for benzene, toluene, ethylbenzene, and xylene-volatile aromatic compounds typically found in various organic chemical product formulations and petroleum product, such as gasoline and diesel fuel.

- ♦ BTX are potentially toxic air pollutants among volatile organic compounds (VOCs).
- ♦ The exposure to high level of BTX causes neuro-toxic symptoms. Persistent exposure to high level of toxic benzene, toluene and xylene may cause injury to human bone marrow, DNA damage in mammalian cells, damage to immune system. Mild exposure causes irregular heartbeat, headache, dizziness, nausea and even unconsciousness, if exposure is continued for long time.

Early manifestation of toxicity is anaemia, leucocytopenia and thrombocytopenia. Benzene is a known human carcinogen. WHO estimates 4 in one million risk of leukemia on exposure to a concentration of 1 microgram per cubic meter.

### **Suspended Particulate Matter**

- ♦ Solid or liquid particles suspended in ambient air are known as Suspended Particulate Matter or aerosol.
- ♦ Sources = power plants, iron/steel mills, land clearing, highway construction, mining, & other activities that disturb or disrupt the earth's surface. Fine particles (PM-2.5) result from fuel combustion from motor vehicles, power generation, and industrial facilities, as well as from residential fireplaces and wood stoves

- ♦ can aggravate heart/respiratory diseases, act as respiratory irritants, some are known carcinogens
- ♦ Particulates influence the climate through the formation clouds, rain and snow by acting as nuclei upon which water condensation can take place.

#### ♦ PM10 and PM2.5

PM10 means particulate mass of particles smaller than 10 µm in diameter and consequently PM2.5 means particulate mass of particles smaller than 2.5 µm in diameter. The reason for these two size categories is that particles smaller than 10 µm can be inhaled below the nasopharynx area (nose and mouth), and particles below 2.5 µm travels down below the tracheobronchial region (into the lungs). The PM2.5 cut off size also coincides with both the local minimum in particle concentration between coarse and fine particles and the natural and anthropogenic fractions.

### Air Quality Index

Air Quality Index (AQI) or Air Pollution Index (API), a scale 0 - 500 is used to characterize the quality of the air at a given location:

$$I = \frac{I_{high} - I_{low}}{C_{high} - C_{low}}(C - C_{low}) + I_{low}$$

where:

$I$  = the (Air Quality) index,  
 $C$  = the actual ambient concentration of pollutant,  
 $C_{low}$  = the concentration breakpoint that is  $\leq C$ ,  
 $C_{high}$  = the concentration breakpoint that is  $\geq C$ ,  
 $I_{low}$  = the index breakpoint corresponding to  $C_{low}$ ,  
 $I_{high}$  = the index breakpoint corresponding to  $C_{high}$

AQI Index and breakpoint pollution concentration for India are as follows

Description	AQI Index	Ozone (8h avg) (ppb)	CO (8h avg) (ppm)	NO2 (24h avg) (ppb)	PM10 (24h avg) (µg/m <sup>3</sup> )	PM2.5 (24h avg) (µg/m <sup>3</sup> )
Good	0 -100	0 -50	0 - 1.7	0 - 42	0 – 100	0 - 60
Moderate	101 - 200	51 - 98	1.8 - 10.3	43 - 94	101 - 150	61- 90

Poor	201- 300	99 - 118	10.4 - 14.7	95 - 295	151 - 350	91 - 210
Very poor	301-400	119 - 392	14.8 – 30.2	296 - 667	351 - 420	211 - 252
Very Unhealthy	401  &above	393 & above	30.3 & above	668 & above	421 & above	253 & above

<b>Description</b>	<b>AQI Index</b>	<b>Colour Coding</b>
Good	0 -100	
Moderate	101 - 200	
Poor	201- 300	
Very poor	301-400	
Very Unhealthy	401 & above	

### **Deposition Processes**

Precipitation removes gases and particles from the atmosphere by two processes: (1) rainout, which is the incorporation of material into cloud drops that grow in size sufficiently to fall to the

ground, and (2) washout, which occurs when material below the cloud is swept out by rain or snow as it falls. Together, these two processes account for wet deposition of acidic material on the earth's surface.

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.

### **Acid Precipitation**

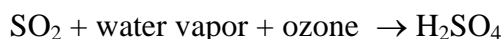
#### **The pH scale and acid rain:**

Acid rain is measured using a scale called "pH." The lower a substance's pH, the more acidic it is. Pure water has a pH of 7.0. Normal rain is slightly acidic because carbon dioxide dissolves into it, so it has a pH of about 5.65. Rainwater having pH below 5.65 is known as acid rain.

#### **What Causes Acid Rain?**

The oxides of sulphur and nitrogen are the main factor while organic acids and to an extent hydrochloric acid also contribute to acidic precipitation.

#### **Where do acids come from?**



### **Effects of Acid Deposition**

#### **On Vegetation**

- ♦ The plant's water uptake is most efficient with a soil pH value of 6 and above. For plant growth important nutrients are easily available and the most harmful metals are least absorbed at this pH.
- ♦ Direct effects may harm needles or leaves when the protective layer of wax is corroded by the dry/wet acidic deposition.
- ♦ There may be damage to stomata, which among other things regulate the evaporation of water. Membranes may also be injured inside the needle or leaf, causing loss of nutrients through leakage and upsetting the water balance.
- ♦ Acidic water dissolves the nutrients and helpful minerals in the soil and then washes them away before trees and other plants can use them to grow. At the same time, acid rain causes the release of substances that are toxic to trees and plants, such as aluminum, into the soil.
- ♦ Forests in high mountain regions often are exposed to greater amounts of acid than other forests because they tend to be surrounded by acidic clouds and fog that are more acidic than rainfall.

#### **On Human being**

- ♦ Acidic water liberates Hg from the soil.
- ♦ Where the ground water is highly acidic, metals such as Al and Cd may appear at elevated levels since they are released from the soil when pH is less than 5.

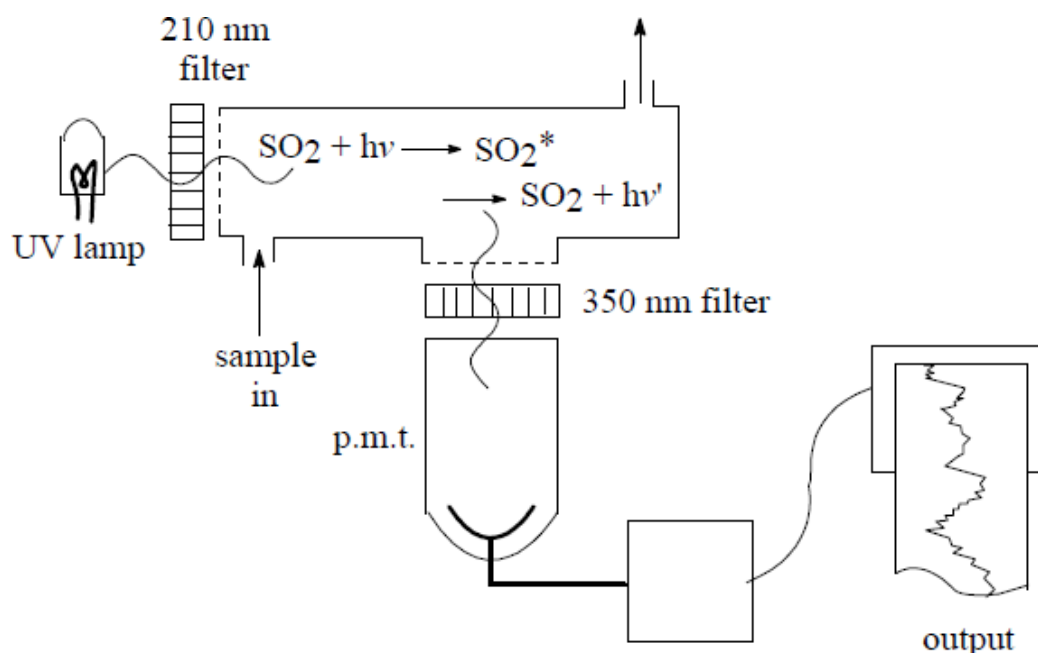
### **On Aquatic System**

- ♦ In acid lakes there are increasing concentrations of aluminium in ion form, which is highly toxic to many organisms. The disappearance of fish is due to the combination of a lowered pH and Al poisoning. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die.
- ♦ The levels of other metals also rise, among them Cd, Zn, and Pb are taken up to a greater extent by animals and plants. Not only the chemistry of water but biological changes also take place due to destabilisation of the Eco system.
- ♦ Accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage.

## MEASUREMENT METHODS

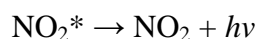
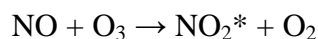
### Ultraviolet Fluorescence Analyzer for SO<sub>2</sub> Measurement

**SO<sub>2</sub>** concentration is measured by the **ultraviolet fluorescence method**, where the analysed sample is exposed to UV-lamp irradiation with energetic excitation of SO<sub>2</sub> molecule. With the backward conversion of the molecule into the basic energetic level, energy as fluorescing radiation is released. This radiation is proportional to the sulfur dioxide concentration and is detected by a photomultiplier. A typical layout of a **fluorescence** analyzer is given below; a UV lamp provides a source of radiation, either continuous or pulsed, which is filtered to admit a narrow band of light into the cell, centred at about 210 nm. The fluorescent radiation is measured at right angles to the incident beam, using a photomultiplier.

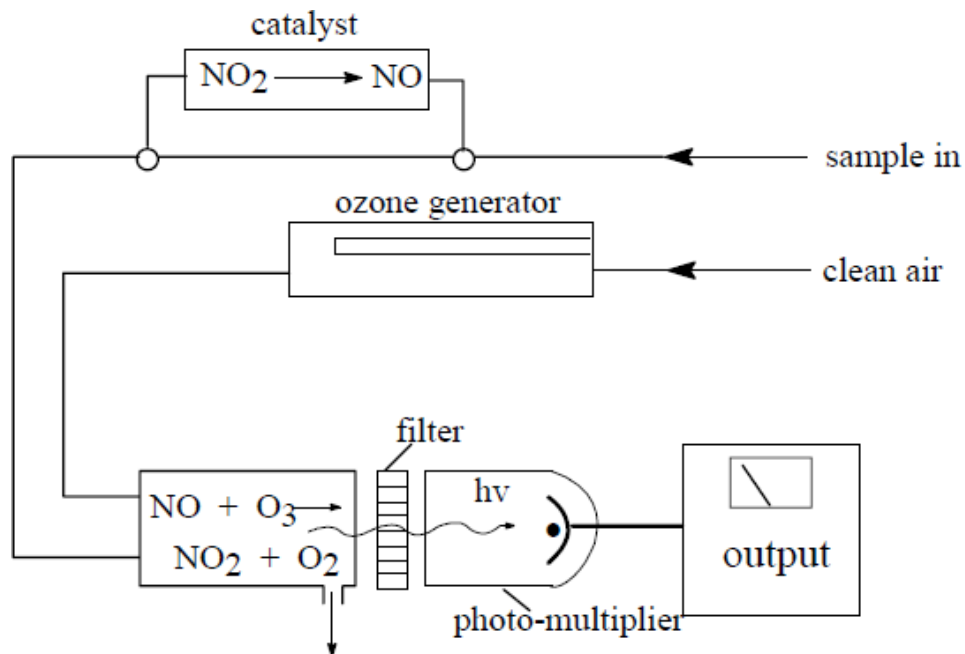


### Chemiluminescence Analyzer for NO<sub>x</sub> Measurement

**NO<sub>x</sub>** concentration is measured by a **chemiluminescence analyzer** for the NO, NO<sub>2</sub> and NO<sub>x</sub> concentration measurement. The principle of this method stands on the nitrogen molecule excitation by ozone. With the conversion of the molecule into the basic energetic level, liberation of radiation as chemiluminescence occurs. This radiation is detected by a photomultiplier. The analyzer design makes possible the acquirement of information on nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) concentrations. The reaction between NO and O<sub>3</sub> is an example:







A typical layout of a chemiluminescence analyser for NO<sub>x</sub>. Ozone is generated by the UV irradiation of clean air and mixed in a reaction chamber with the sample air. Light from the reaction passes through an optical filter and is detected with a photomultiplier tube. Clearly, NO<sub>2</sub> in the sample will not be detected in this system. However, this can be reduced to NO by means of a heated catalyst, such as a stainless steel or molybdenum. If this is included in the system the instrument can respond to NO and NO<sub>2</sub>, i.e. NO<sub>x</sub>.

### **Chemiluminescence Analyzer for NH<sub>3</sub> Measurement**

The Chemiluminescence NH<sub>3</sub> Analyzer operates using the same principles as a NO<sub>x</sub> analyzer, but with an ammonia converter. In operation, sample gas is passed through the converter, which converts NH<sub>3</sub> and NO<sub>2</sub> to NO, producing the total oxides of nitrogen (NO<sub>y</sub>). In the next cycle the sample is routed through a molybdenum/photolytic converter which converts nitrogen oxides (less NH<sub>3</sub>) to NO, producing the NO<sub>x</sub> reading. The difference between these readings (NO<sub>y</sub> — NO<sub>x</sub> = NH<sub>3</sub>) provides a reading proportional to the NH<sub>3</sub> concentration.

### **Suspended Particulate Monitoring (SPM) Methods**

The term 'suspended particulate matter' refers to particles which can remain suspended in air for significant periods of time, ranging from a few minutes for the larger particles through to several days for very fine material.

#### **Air Sampler**

Traditionally SPM is measured by sucking air through a filter and determining the weight of dust collected. The equipment used is known as a High-Volume Air Sampler (at high flow rates

(typically  $1.13 \text{ m}^3/\text{min}$  or  $40 \text{ ft}^3/\text{min}$ ). Air is drawn into the sampler and through a glass fiber or quartz filter by means of a blower, so that particulate material collects on the filter surface. Without a size-selective inlet, particles of  $100 \text{ }\mu\text{m}$  size and less enter the sampling inlet and are collected on the downstream filter. The results are referred to as total suspended particulate (TSP). The collection efficiencies for particles larger than  $20 \text{ }\mu\text{m}$  decreases with increasing particle size, and it varies widely with the angle of the wind with respect to the roof ridge of the sampler shelter. When glass fiber filters are used, particles  $100\text{-}0.1 \text{ }\mu\text{m}$  or less in diameters are ordinarily collected. With a size-select inlet, PM<sub>10</sub>, PM<sub>2.5</sub> or PM<sub>1</sub> are collected on the quartz filter. The volume of air sampled is determined by a flow-rate indicator. The high volume sampler is a compact unit consisting of a protective housing; an electric motor driven; a high-speed, high-volume blower; a filter holder; and a flow-controller for controlling the air-flow rate through the instrument. Air is drawn through a pre-weighed filter at a known rate, which collects any particles on the surface. The filter is weighed

again to determine the mass of particles collected, and by dividing the mass by the total volume of air, we can calculate the concentration of the particles.

$$TSP = \frac{(W_f - W_i) \times 10^6}{V}$$

Where:

TSP = mass concentration of total suspended particulate matter in  $\mu\text{g}/\text{m}^3$ ,

$W_i$  = initial weight of clean filter, in gram

$W_f$  = final weight of exposed filter, in gram

$V$  = air volume sampled, in  $\text{m}^3$ ,  $V = Q \times t$ ,  $Q$  = average sample flow rate at ambient temperature and pressure in  $\text{m}^3/\text{min}$ ,  $t$  = sampling time in minutes

$10^6$  = conversion of g to  $\mu\text{g}$

For  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  concentration measurement the radiometric method is also used. It stands on beta-ray absorption in a sample captured on filtering material. The difference between the beta-ray absorption of the exposed and non-exposed filtering material, which is proportional to the mass of the captured suspended particle matter, gives the information on its concentration.

The suspended particulate matter continual monitoring is also carried out using the tapered element oscillating microbalance (TEOM). It measures the mass of the sample captured on a replaceable filter according to the oscillating tapered element frequency variation. The air sample passes through a filter where the dust particles are captured and runs through a hollow tapered element to a vacuum pump with an electronic flow control.

### **Carbon monoxide Measurement**

CO concentration is measured by the method of *NDIR Gas-Filter Correlation (GFC) Spectroscopy* or *Gas Chromatography-Flame Ionization*.

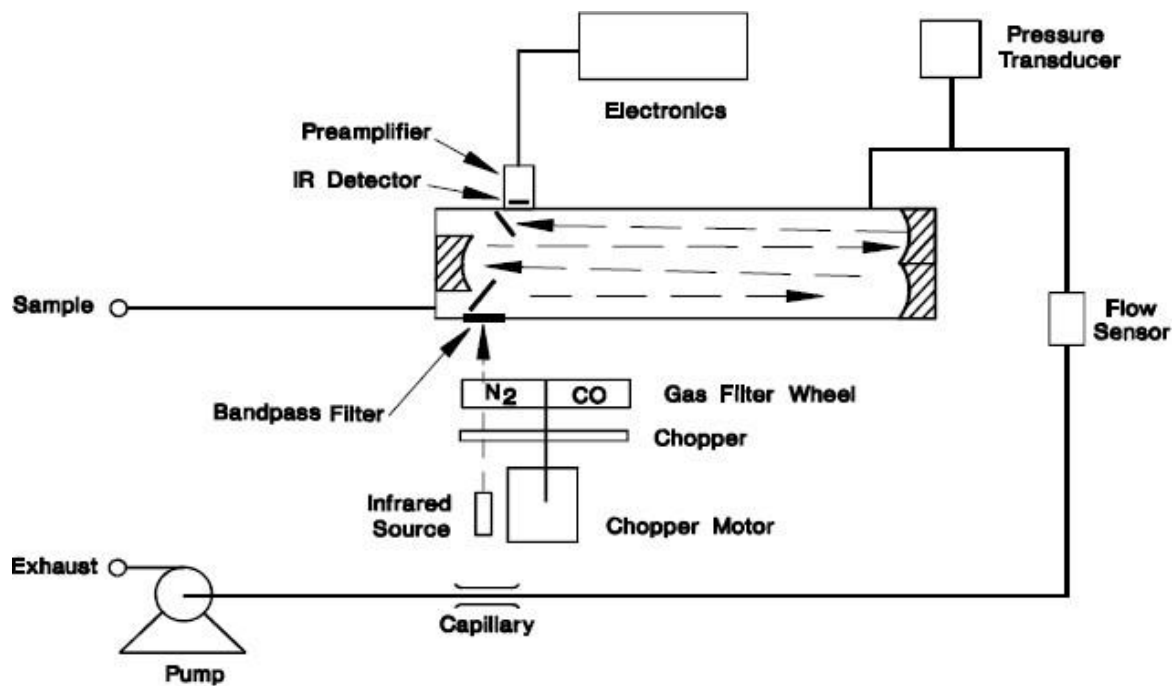
### **Gas-Filter Correlation (GFC) Spectroscopy**

Carbon monoxide has a characteristic infrared absorption near  $4.6 \mu\text{m}$ . The absorption of infrared radiation by the CO molecule therefore can be used to measure CO concentration in the presence of other gases. The NDIR method is based on this principle. Nondispersive infrared systems have several advantages. They are not sensitive to flow rate, they require no wet chemicals, they are reasonably independent of ambient air temperature changes, they are sensitive over wide concentration ranges, and they have short response times. Further, NDIR systems may be operated by nontechnical personnel.

Because infrared absorption is a non-linear measurement technique, it is necessary to transform the basic analyzer signal into a linear output. The sample is drawn into through the Sample bulkhead,

as shown in Figure. The sample flows through the optical bench. Radiation from an infrared source is chopped and then passed through a gas filter alternating between CO and N<sub>2</sub>. The radiation then passes through a narrow bandpass interference filter and enters the optical bench where absorption by the sample gas occurs. The infrared radiation then exits the optical bench and falls on an infrared detector.

The CO gas filter acts to produce a reference beam that cannot be further attenuated by CO in the sample cell. The N<sub>2</sub> side of the filter wheel is transparent to the infrared radiation and therefore produces a measure beam that can be absorbed by CO in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude related to the concentration of CO in the sample cell. Other gases do not cause modulation of the detector signal, since they absorb the reference and measure beams equally. Thus, the GFC system responds specifically to CO concentrations.



**Schematic of GFC Monitor**

### **Measurement of BTEX**

BTEX are measured using gas chromatograph with a built-in pre-concentration system. Hydrocarbons are pre-concentrated on adsorbent material, desorbed thermally and separated on an column, to reach optimal separation from interfering hydrocarbons. BTEX Analyzer employs a high-sensitivity photoionization detector (PID) as the sensing element. This detector is specific to volatile organic compounds. The Benzene, Toluene, Ethylbenzene, and Xylene's in the gas sample are physically separated using proprietary GC columns. A dual column configuration with timed backflush to vent is used to strip off moisture and heavier hydrocarbons. A pre-cut column is used in series with the analytical column. At sample injection a fixed volume of sample is carried to the pre-cut column. Backflush is timed so that only the BTEX and other similar components are eluted to the analytical column. Contaminants on the pre-cut column are backflushed to vent. Benzene, Toluene, Ethylbenzene, and Xylene's are separated from potentially interfering components on the analytical column and elute to the detector for analysis.

### **OZONE MEASUREMENT**

#### **Ozone Measurement in India**

- The first Columnar 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.
- 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 in 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 is collaborating at both the national and international levels through international intercomparison 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.

### **Techniques for Measuring Atmospheric Ozone**

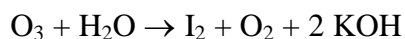
IMD's National Ozone Centre at New Delhi is designated as Secondary Regional Ozone Centre for Regional Association II (Asia) of the World Meteorological Organisation. The centre maintains and controls a network of ozone monitoring stations including Maitri (Antarctica). The following parameters of ozone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

1. Surface Ozone Measurement using Electrochemical Concentration Cell (ECC)
2. Surface Ozone Measurement using UV Photometer
3. Columnar Ozone using Dobson/ Brewer Spectrophotometer
4. Vertical Distribution of Ozone using Electrochemical Ozonesonde

#### **1. Surface Ozone Measurement using 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 the redox reaction:  $2 \text{KI} +$



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:



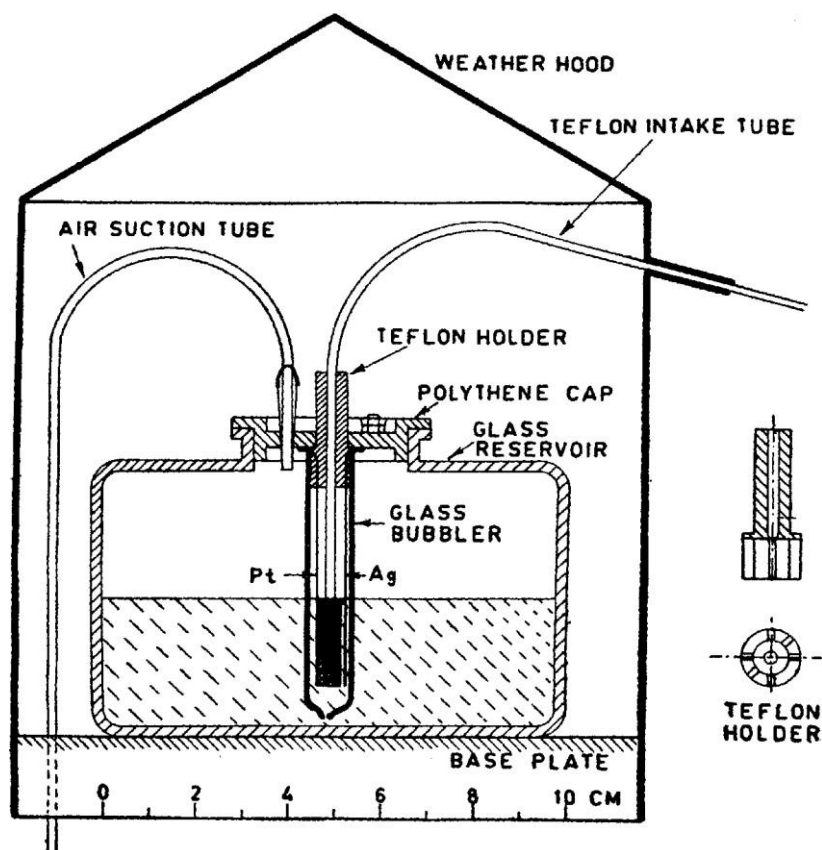
By measuring the electron flow (i.e., the cell current) and the rate at which ozone enters the cell per unit time, ozone concentrations can be calculated. The surface ozone sensor is shown below. The ozone recording system consists of a modified bubbler sensor, a suitable miniature pump, a network for supplying a polarising potential to the bubbler and a recorder capable of full scale deflection for a current of 2  $\mu$  A. The recorder is calibrated by a micro ampere current source. From the record, the ozone current in  $\mu$ A is determined and the partial pressure P of ozone is calculated from the formula:

$$P(\mu \text{ mb}) = 4.31 \times 10^{-3} i T t$$

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%.



**Surface Ozone Sensor**

The surface ozone measurement system is successfully operating from the following stations using Electrochemical Concentration Cell:

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

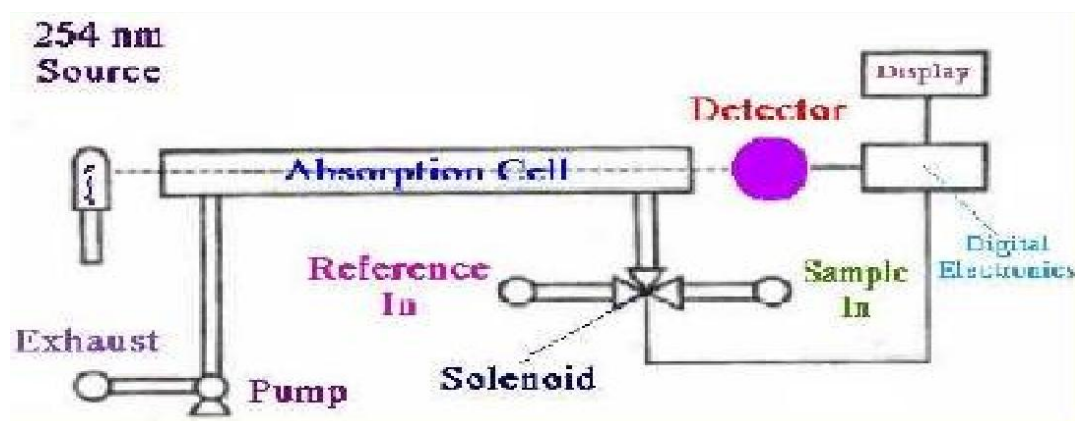
## 2. Surface Ozone measurement by UV Photometer

The measurement of the ozone is determined by UV absorption analysis. The 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. IMD has installed ozone analyzer (Model Serinus 10 of Ecotech, Australia make) at nine locations (**Delhi, Pune, Kodaikanal, Trivandrum,**

**Nagpur, Ranichauri, Guwahati, Visakhapatnam, Port Blair).** The ozone analyzer follows these principles and measurement techniques:

- Ozone shows strong absorption of UV light at 254nm
- 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.
- The strength of the UV signal being detected is proportional to the amount of UV light being absorbed by Ozone.

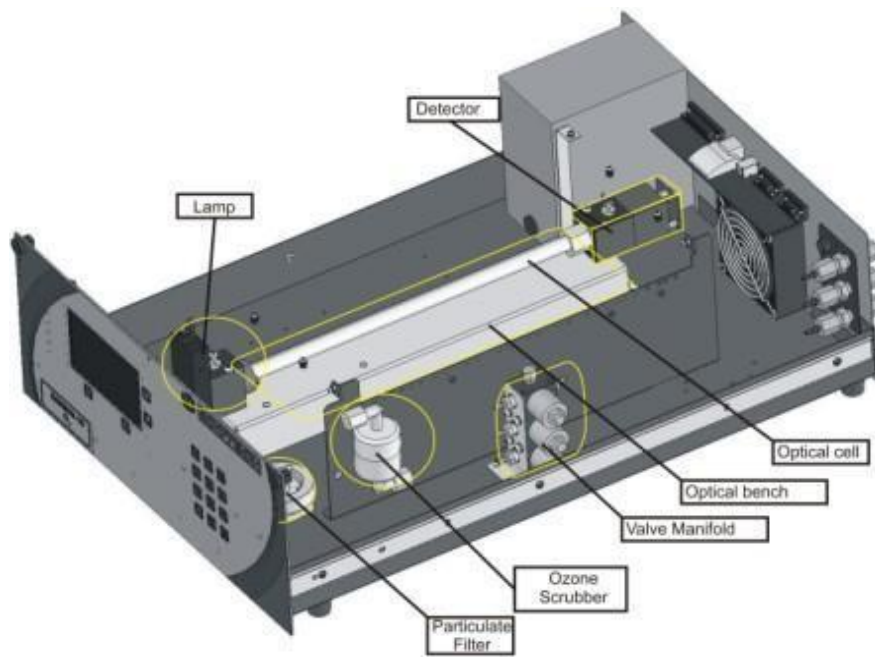
The Ozone analyzer uses the Beer-Lambert relationship to calculate the ozone concentration.  $O_3$  is not the only gas that absorbs UV (254nm),  $SO_2$  and aromatic compounds also absorb radiation at this wavelength. To eliminate these interferences a second cycle is performed where sample air is passed 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 Ozone analyzer uses non-dispersive ultraviolet (UV) absorption technology to measure ozone to a sensitivity of less than 0.5ppb in the range of 0-20ppm. The Ozone analyzer measures Ozone with the following components and techniques:

- Mercury vapour lamp
- Photodiode detector
- Ozone scrubber

The Ozone ( $O_3$ ) 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**

### 3. Measurement of Vertical Distribution of Ozone

(IMD Ozonesonde)

The observations of vertical distribution of ozone are being made at Delhi, Pune and Trivandrum once every fortnight using the Indian Electrochemical Ozonesonde. The ozonesonde was designed at Instruments Division of the IMD, Pune. All parts of the sonde are manufactured and assembled by the India Meteorological Department. Indian ozone sonde is a hybrid of a Brewer-Milford type ozone sensor made of Plexiglass and a non- reactive Teflon pump. It consists of the electrolytic reaction cell, a miniature air pump operated by a small motor, a DC amplifier for the ozone current, a modulator coupled to a VHF transmitter, a motor driven programmer with switches on the various elements in sequence and batteries. All the components are embedded in a polystyrene flight box for physical and thermal protection during transport, preparation, launch, flight and recovery. A schematic diagram of the sonde is shown in the figure below. Typical flow rate of the gas sampling is about  $200\text{cm}^3/\text{min}$ . The anode is a silver wire (length  $\approx 5\text{cm}$ ,  $\phi \approx 0.5\text{ mm}$ ) and the cathode a cylindrical Pt-gauze ( $3\text{ cm}^2$ ) in a neutrally buffered aqueous KI-solution (0.25%).

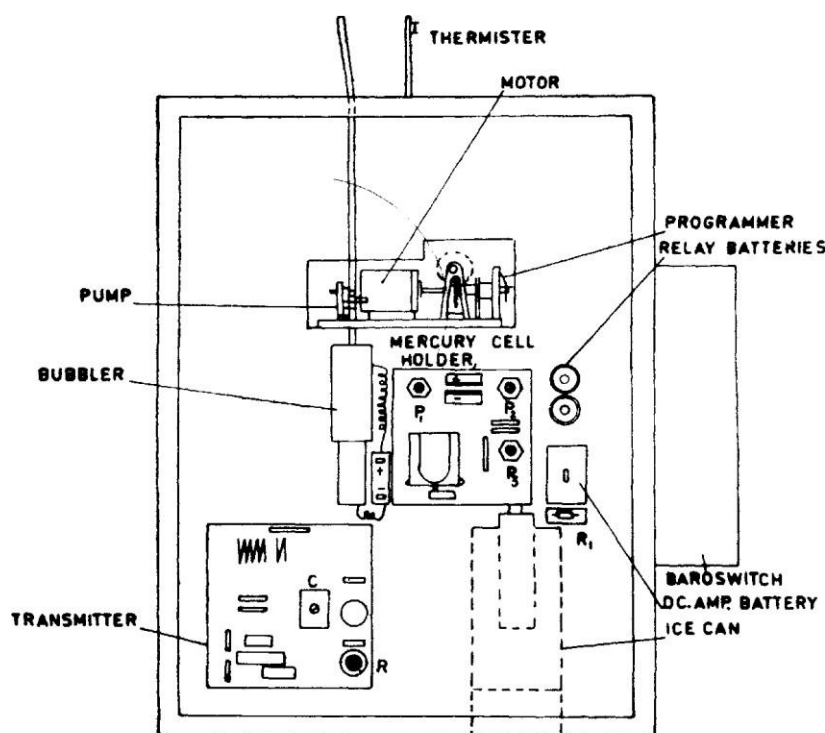


FIG. X - OZONESONDE  
(FRONT VIEW)

IMD Ozonesonde Schematic Diagram

Radiosonde measurements of ozone are made worldwide, although at fewer stations and typically only once per day or less often. The most common radiosonde ozone sensor is the electrochemical type.

The ozonesonde consists of an electrochemical ozone sensor connected to an interface unit and a modified radiosonde. Consequently, humidity, pressure, temperature, and geopotential height can be measured simultaneously with ozone sampling. Upper-air winds are also measured. This lightweight, balloon-borne instrument is capable of

measuring the vertical distribution of atmospheric ozone up to 3 hPa. The uncertainty of the ozone measurement is of order 5–10% of the local values. The electrochemical concentration cell (ECC) ozone sensor detects ozone on the basis of an iodine–iodide oxidation-reduction or redox electrode reaction in neutral buffered solution. The sensor consists of an electrochemical concentration cell that contains two platinum electrodes immersed in separate potassium iodide solutions of different concentrations, which are separate anode and cathode chambers. The chambers are linked with an ion bridge. As air containing ozone flows into the cathode solution, a chemical reaction occurs and the platinum electrodes carry electrons between the cells of the sensor. An electrical current is generated in proportion to the rate at which ozone enters the cell. The ozone concentration is determined from the electric current measurement using an equation that considers the airflow rate, air pressure, and pump temperature. The interface can also be used with other sensor types, such as the Brewer–Mast sensor. The Brewer–Mast sensor uses similar ozone detection reaction, but instead of a reference chamber, the driving potential for the measurement circuit is an electrical circuit. The ECC-type sensor is more accurate and is more widely used.

### **Total Ozone Measurement**

Total ozone observations are made with the Dobson spectrophotometer by measuring the relative intensities of selected pairs of ultraviolet wavelengths, called the A, B, C, C', and D wavelength pairs, emanating from the sun, moon or zenith sky. The A wavelength pair, for example, consists of the 3055 Å wavelength that is highly absorbed by ozone, and the more intense 3254 Å wavelength that is relatively unaffected by ozone. Outside the earth's atmosphere the relative intensity of these two wavelengths remains essentially fixed. In passing through the atmosphere to the instrument, however, both wavelengths lose intensity because of scattering of the light by air molecules and dust particles; additionally, the 3055 Å wavelength is strongly attenuated while passing through the ozone layer whereas the attenuation of the 3254 Å wavelength is relatively weak. The relative intensity of the A wavelengths as seen by the instrument, therefore, varies with the amount of ozone present in the atmosphere since as the ozone amount increases the observed intensity of the 3055 Å wavelength decreases, whereas the intensity of the 3254 Å wavelength remains practically unaltered. Thus, by measuring the relative intensities of suitably selected pair wavelengths with the Dobson instrument, it is possible to determine how much ozone is present in a vertical column of air extending from ground level to the top of the atmosphere in the neighborhood of the instrument. The result is expressed in terms of a thickness of a layer of pure ozone at standard temperature and pressure

### **Principle of Operation of the Dobson Spectrophotometer**

The principle of operation of the Dobson spectrophotometer is best explained with reference

to Figure 1. Light enters the instrument through a window in the top of the instrument and, after reflection in a right-angled prism, falls on slit S1 of a spectroscope. This spectroscope consists of a quartz lens which renders the light parallel, a prism which breaks up the lights into its spectral colours, and a mirror which reflects the light back through the prism and lens to form a spectrum in the focal plane of the instrument. The required wavelengths are isolated by means of slits S2, S3, and S4 located at the instrument's focal plane.

Two shutter rods are mounted in the base of the spectrophotometer. The left-hand S4 shutter rod is used only when spectrophotometer tests are conducted, and should be pushed all the way into the instrument when ozone observations are made. The right-hand wavelength selector rod blocks out light passing either through slit S2 or S4. When this rod is set to position labels SHORT, only slits S2 and S3 are open so that observations can be made on A, B, C, or D wavelength pairs. With the wavelength selector rod in the LONG position, only slits S3 and S4 are open and observations can be made on the C' wavelengths. If C' pair measurements are not made, then these rods should be locked in place to avoid an accidental movement of the right hand rod. Selection of the wavelengths



A, B, C, C', or D when making ozone measurements is accomplished by rotating Q1 and Q2 levers to positions specified in a Table of Settings of Q provided with the instrument. Thick, flat quartz plates mounted immediately in front of the first and last slits (S1 and S5) are fixed to the Q levers. Depending on the direction in which the quartz plates are rotated, the light beam passing through them is refracted upwards or downwards, thereby providing for wavelength selection. Changes in the refractive index of the spectrophotometer quartz prisms due to changes in the temperature of the instrument are allowed for by making slight adjustments to the settings of Q1. An optical wedge, consisting of two quartz flats coated with chromel, is mounted in the instrument in front of slit S3. The position of the wedge is controlled by turning a graduated dial located on top of the instrument. With the dial set at  $0^\circ$  the thin portion of the optical wedge is positioned in front of slit S3 so that light passes through the optical wedge and slit S3 with practically no loss of intensity. With the dial set at  $300^\circ$ , however, the S3 light beam is almost completely absorbed by the thick portion of the optical wedge. It follows that there exists a "balance" setting of the dial somewhere between  $0^\circ$  and  $300^\circ$  where the intensity of the light beam passing through the optical wedge and slit S3 will have been reduced to the level of the intensity of the S2 wavelength beam (or S4 wavelength beam if observations on C' wavelengths are made). Now, for any given position of the dial the intensity of the light passing through the optical wedge is reduced in a definite ratio which is determined during the original calibration of the spectrophotometer. In order to measure the relative intensity of the two wavelengths on which observations are made, then, it is necessary only to be able to detect the balance position of the dial. Indication of the balance position of the dial is effected in the following manner. Assume that the dial is initially set off-balance so that the two light beams leaving slit S3 and slit S2 (or slit S4) are of unequal intensity. The light beams then pass through a rotating sector wheel, driven by a motor, which chops them and allows them to proceed alternately into a second monochromometer and, finally, to fall on the photomultiplier located behind slit S5. (The purpose of the second monochromometer is to eliminate scattered light, and to direct the slit images to the photomultiplier tube such that the images fall on the same part of the cathode.) Since the two light beams falling alternately on the photomultiplier are of unequal intensity, they give rise to a pulsating electron current flowing out of the photomultiplier. This current is amplified by an alternating current amplifier, rectified by a commutator, and causes a deflection on an indicating direct current microammeter. The rectification causes a positive reading on the microammeter if intensity is different in one sense (for example:  $I_{S2} > I_{S3}$ ) and a negative reading if the intensity difference is of the other sense. If now the dial is turned to the balance position, the two light beams falling alternately on the photomultiplier become of equal intensity. They then give rise to a steady, direct current which cannot be amplified by an alternating current amplifier. Since there is no pulsating current to amplify and rectify, the microammeter reads zero. Thus, a null reading on the

microammeter is an indication of the balance position of the dial. The relative intensities of the two wavelengths on which observations are made may then be obtained from the balance position dial reading and calibration tables supplied with the instrument.

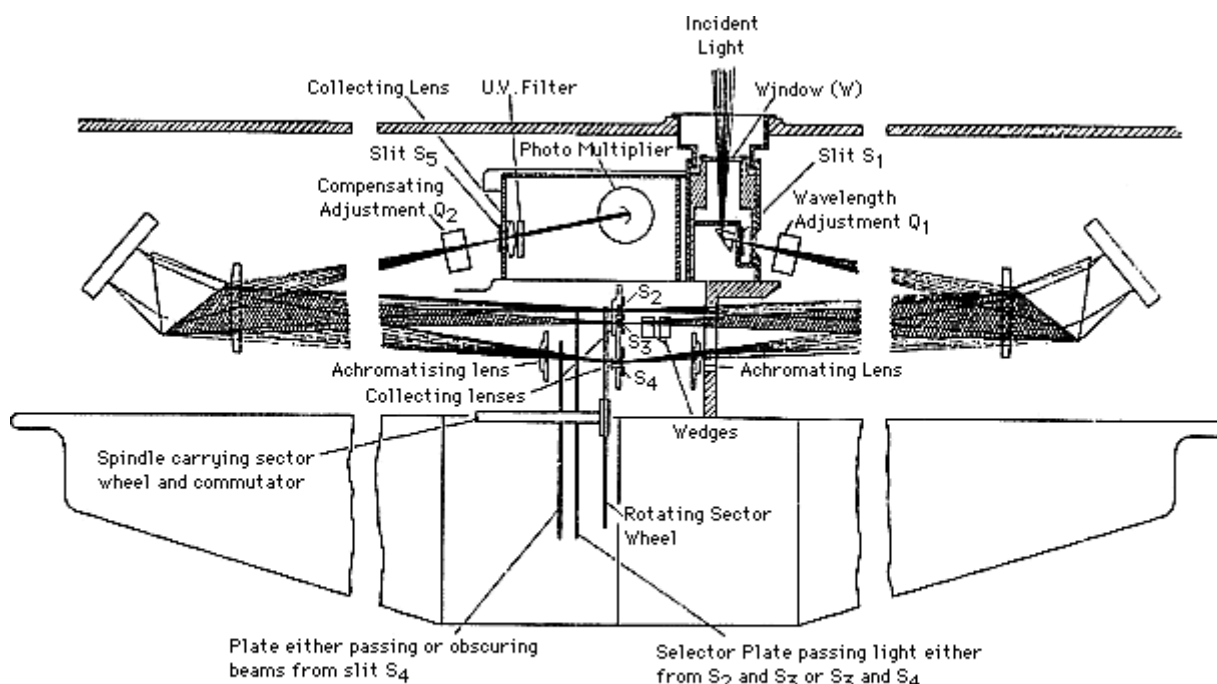


Figure 1. Optical system of the Dobson spectrophotometer.

### pH Measurement

The pH of a precipitation sample is related to the free activity as the negative logarithm of the hydrogen ion concentration by the equation:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

where  $\text{H}^+$  activity or concentration of free hydrogen ions in  $\square\text{eq/l}$ . The pH of a precipitation sample is determined electrometrically, using a standard pH meter with a glass electrode. The glass electrode potential varies as the activity of  $\text{H}^+$  in solution. Although the meter actually measures electrical potential, it is generally calibrated to give data as pH. The temperature effect on electrometric pH measurements can be controlled by using instrument that has temperature compensation. A temperature of  $25^\circ\text{C}$  is recommended for pH measurement. The pH meters installed at all the GAW stations have Automatic Temperature Compensation probe which give pH value at  $25^\circ\text{C}$ . The pH of precipitation water varies between 3.50 to 8.00 pH units.

### MEASUREMENT OF CONDUCTIVITY OF RAINWATER

Conductivity meter and Conductivity Cell is used to measure the conductivity of the solution. Potassium Chloride (KCl) solution of known concentration and conductivity is used for calibration.

Operation of conductivity meter is very simple and does not require any special training.

Manufacturer's directions for operation of the instrument used should be followed. The cell has to be rinsed thoroughly with deionised water between each measuring sample and excess water should be shaken off. The conductivity cell must be clean. The measured value should be expressed in 0.1

$\mu\text{S}/\text{cm}$ . The conductivity meters supplied at GAW stations have Automatic Temperature Compensation probe which give conductivity value at 25°C.

### **Nephelometer**

Nephelometers, as a whole, are highly versatile instruments that quantify particle light scattering. Integrating nephelometers quantify particle light scattering integrated over all directions. For visibility applications, scattering extinction serves as a surrogate for total light extinction which is related to visibility.

Other applications of the integrating nephelometer include:

- 1) Measurements of Rayleigh scattering coefficients,
- 2) Determination of aerosol size distributions and refractive indices,
- 3) Detection of sulfuric acid - ammonium sulfate aerosol; and
- 4) Estimation of particle mass concentrations.

Nephelometer sampling procedures depend on the intended uses of the data. To determine visibility reduction, total light scattering is desired, including light scattering caused by 1) liquid water associated with soluble particles and 2) molecules in clean air. Mass concentration measurements from nephelometers are typically overestimated once relative humidity is above 80%. This is due to the fact that small particles grow to sizes that scatter light more efficiently as they acquire liquid water at approximately 80% relative humidity. To compensate for this, the air stream can be heated to remove liquid water when an indicator of particle mass is desired. Some systems are able to control both temperature and humidity to characterize the hygroscopic properties of suspended particles. Such heating mechanisms, however, can increase the volatilization of ammonium nitrate and volatile organic compounds from particles. Although light scattering is often highly correlated with mass concentrations, this relationship depends on several variables and may be different from location to location and for different seasons of the year. Particle scattering measured by integrating nephelometers includes systematic errors owing to: 1) non-monochromatic light sources; 2) limits of the integration angle; and 3) and non-Lambertian light sources. Further modification of the nephelometer response can also be achieved by adding a size-selective inlet to the nephelometer air intake.

### **Sunskyradiometer**

Sky radiometer measures the direct solar radiation and diffuse radiation at various scattering angles from the Sun at different wavelengths in narrow band. The measured sky spectral radiances can be used to obtain the different optical and size properties of the aerosols in the total atmospheric column. The principle is based on the dependence of the light scattering phase function on aerosol

particle size and wavelength. Thus, the detected sky spectral radiant intensities at different measured angles from the Sun combined with direct solar radiance can be used to extract the volume size distribution numerically.

Skyradiometer Model POM-02 of Prede Co. Ltd, Japan make is used in **IMD-Skynet**. Sky radiometers make measurements in eleven narrow wavebands in the ultraviolet, visible and infrared parts of the solar spectrum (315, 340, 380, 400, 500, 675, 870, 1020, 1627, 2200 nm). The radiometer has a narrow field of view and is mounted on a sun tracker to make measurements of the direct solar radiation. It can also make scans across the sky at user-defined angles away from the sun. The instrument provides highly accurate angular and spectral scans with scan accuracy of  $\pm 1^\circ$  with a maximum scan rate of 30 degrees/sec. Calibration methodology and data reduction procedures for this instrument are presented in Nakajima et al. (1996). This instrument measures both direct and diffuse solar irradiance in two geometries; almucantar and principal plane. The observing scheme is to take measurements in the almucantar geometry (measurements in the same elevation as the

sun, but varying azimuthal angle) every ten minutes, while taking direct solar measurements every minute.

## Major Parameters Retrieved from Skyradiometer Data

### Aerosol Optical Thickness

Aerosol optical thickness, AOT, (also called aerosol optical depth, AOD) is a measure of extinction of solar radiation due to the interaction of radiation with aerosols, primarily due to the processes of scattering and absorption between the point of observation and the top of the atmosphere. Aerosol optical thickness is dimensionless. It is a measure of the integrated columnar aerosol load and the most important parameter for evaluating direct radiative forcing.

### Angström exponent (Alfa)

Angström exponent (Alpha,  $\alpha$ ) is the name of the exponent in the formula used to describe the dependency of the aerosol optical thickness, or aerosol extinction coefficient on wavelength.

Depending on particle size distribution, the spectral dependence of the aerosol optical thickness is given approximately by

$$\frac{\tau_{\lambda}}{\tau_{\lambda_0}} = \left( \frac{\lambda}{\lambda_0} \right)^{-\alpha}$$

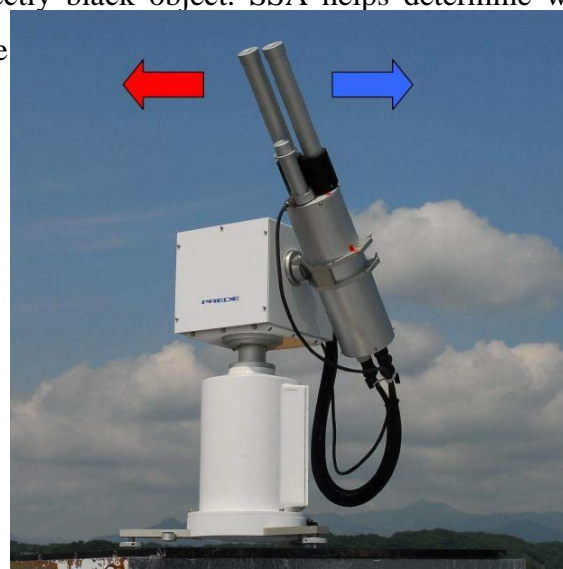
where  $\tau_{\lambda}$  is the optical thickness at wavelength  $\lambda$ , and  $\tau_{\lambda_0}$  is the optical thickness at the reference wavelength  $\lambda_0$ . Ångström exponent values generally range from greater than 2.0 for particles near combustion sources to values close to zero for coarse-mode-dominated desert dust aerosols.

### Single Scattering Albedo (SSA)

In the atmosphere: aerosol particles can scatter and absorb solar and infrared radiation. Single scattering albedo is a measure of the reflectivity of a particle and is a key optical characteristic in assessing the radiative effects of aerosols. Single scattering albedo is defined as the ratio of scattering efficiency to total extinction efficiency (a sum of scattering and absorption). Values of single scattering albedo range from 1.0 for non-absorbing particles (perfectly white object) to below 0.5 for strongly absorbing particles and zero for a perfectly black object. SSA helps determine whether



climate



POM-02 Zenith Measurement

Azimuth Scanning