

# The Atmosphere and atmospheric chemistry

## Importance of The Atmosphere:

The atmosphere is a protective blanket which nurtures life on the Earth and protects it from the hostile environment of outer space. The atmosphere is a source of carbon dioxide for plant photosynthesis and of oxygen for respiration. It provides nitrogen for nitrogen -fixing bacteria and ammonia-manufacturing plants to produce chemically bound nitrogen, which is an essential component of life molecules.

The atmosphere transports water from ocean to land, thus acting as the condenser in a vast solar powered still. Unfortunately, due to increase in industrial activity the atmosphere is used as dumping place for many pollutant materials, and this is causing damage to vegetation and materials, shortens human life, and alters the characteristics of the atmosphere itself.

Water vapor absorbs infrared radiation even more strongly than does carbon dioxide, thus greatly influencing the earth's heat balance. Clouds formed from water vapor reflect light from the sun and have a temperature-lowering effect. On the other hand, water vapor in the atmosphere acts as a kind of "blanket" at night, retaining heat from the earth's surface by absorption of infrared radiation.

## Physical Characteristics of The Atmosphere:

The components of our earth's atmosphere may be divided broadly as major and minor constituents. There are the 5 most abundant gases in the earth's atmosphere.

### **Major Constituents:**

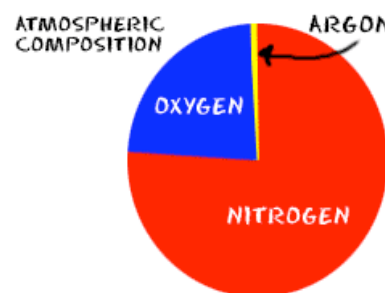
Nitrogen, 78.08% (by volume)

Oxygen, 20.95%

Water vapor, 0 – 3 or 4%

Argon, 0.934%

carbondioxide, 0.035%

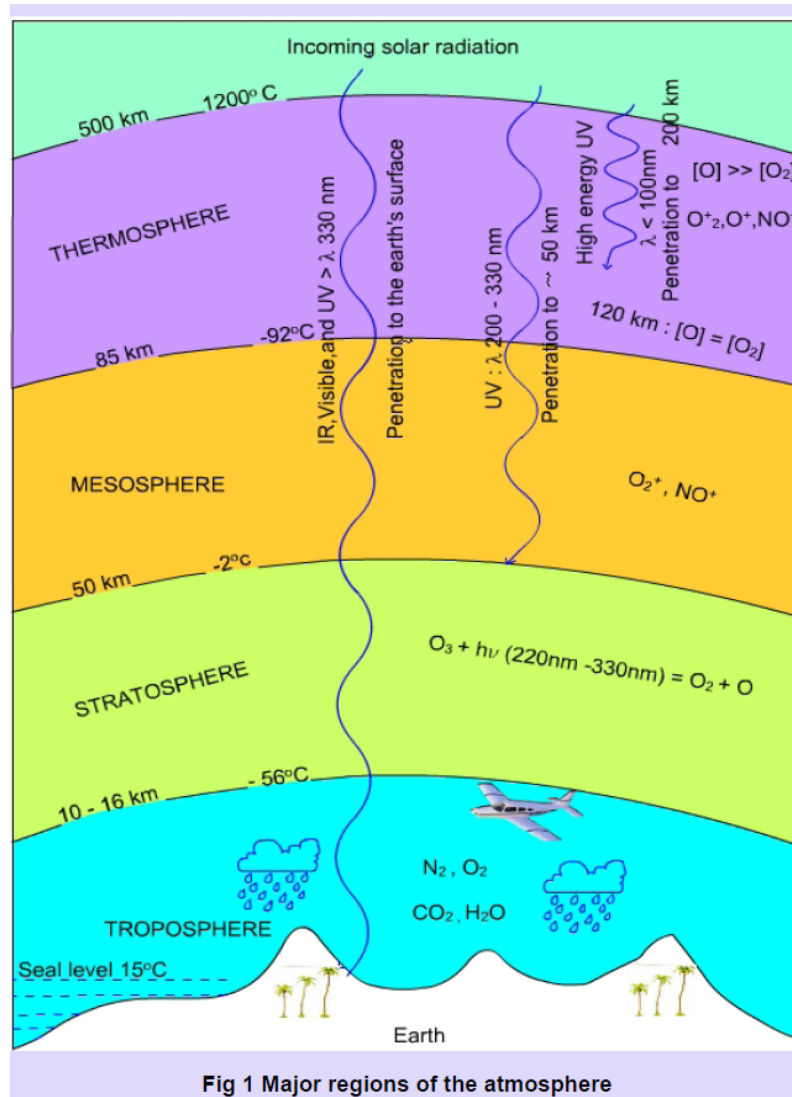


Water vapor and argon are the 3rd and 4th most abundant gases in the atmosphere. The concentration of water vapor can vary from near 0% to as high as 3% or 4%. Water vapor, a gas, is invisible. Clouds are visible because they are made up of small drops of liquid water or solid crystals of ice. Water is the only compound that exists naturally in solid, liquid, and gaseous phases in the atmosphere.

Oxygen is the second most abundant gas (by volume) in the atmosphere. Oxygen is the most abundant element (by mass) in the earth's crust, in ocean water, and in the human body.

The density of the atmosphere decrease sharply with increasing altitude. More than 99% of the total mass of the atmosphere is found within approximately 30 km of the earth's surface. The total masses of the global atmosphere is approximately  $5 \times 10^{15}$  metric tones which is roughly one millionth of the earth's total mass.

The characteristics of the atmosphere vary greatly, with altitude, time (season), location (latitude), and even solar activity. Temperature in the atmosphere may vary from as low as the  $-92^{\circ}\text{C}$  to over  $1200^{\circ}\text{C}$ . Atmospheric pressure drops from 1 atm. at sea level to  $3.0 \times 10^{-7}$  atm at 100 km above sea level.



## Major Regions Of The Atmosphere:

The atmosphere is broadly divided into four regions as shown in Fig.1 above and Table 1 below. It extends up to 500 km and the temperature may vary from as low as -92°C to over 1200°C.

**Table-1 Major regions of atmosphere and their characteristics**

Region	Altitude range Km	Temperature range °C	Significant chemical species
Troposphere	0 – 11	15 to -56	$N_2, O_2, CO_2, H_2O$
Stratosphere	11 – 50	-56 to -2	$O_3$
Mesosphere	50 -85	-2 to -92	$O_2^+, NO^+$
Thermosphere	85 -500	-92 to 1200	$O_2^+, O^+, NO^+$

**Troposphere:** The lowest layer of earth from sea level to an altitude of 10 to 16 km is called the troposphere. In this region the composition of the atmosphere is more or less uniform in the absence of air pollution mainly due to the constant circulation of air masses in this region.

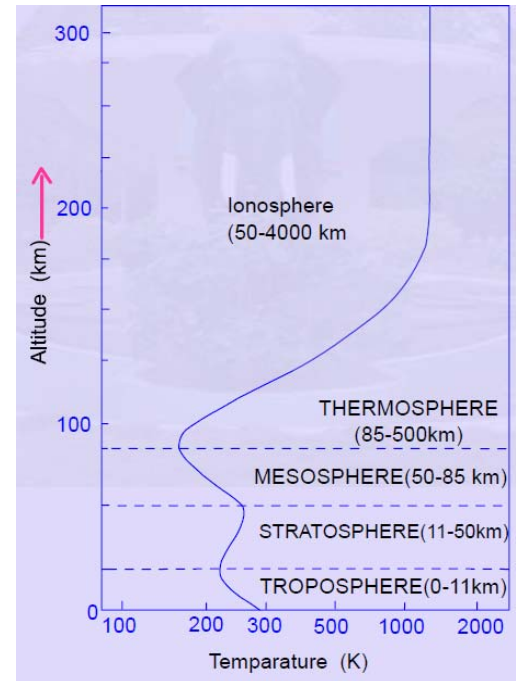
However air is far from uniform with respect to density and temperature in this region. Density decreases exponentially with increasing altitude. The water content also varies because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

The very cold layer at the top of troposphere is known as tropopause. Its low temperature and resulting condensation of water to ice particles prevents water from reaching altitudes at which it would photo dissociate through the action of intense UV light. If this happens, the hydrogen produced would escape the earth's atmosphere.

### **Stratosphere:**

The atmospheric layer directly above the troposphere is called the stratosphere. In this layer the temperature increases with increase in altitude, with a maximum of  $-2^{\circ}\text{C}$  at the upper limit of stratosphere.

This temperature increase is due to the presence of ozone,  $\text{O}_3$ , which may reach a level of around 10 ppm by volume in the mid-range of the stratosphere. The heating effect is caused by the absorption of ultraviolet radiation energy by ozone. The ozone layer in the stratosphere thus acts as a protective shield for life on earth from the injurious effects of sun's ultraviolet rays and at the same time supplies heat source.



**Fig 2: Major regions of the atmosphere with temperature profile**

### **Mesosphere:**

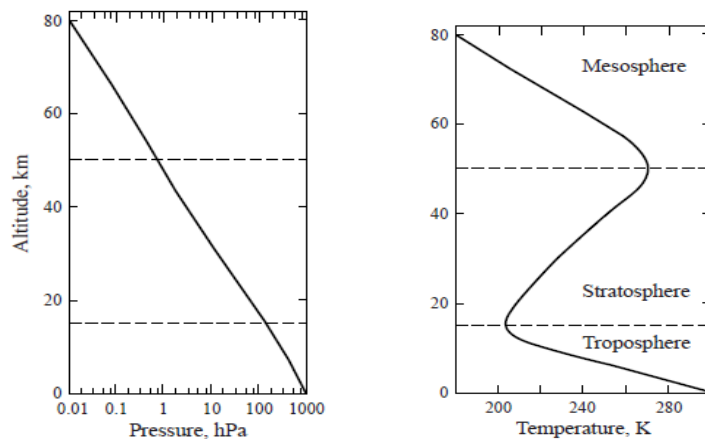
The mesosphere on the top of the stratosphere extends roughly to 85 km. In this region the temperature falls with increase in altitude, resulting in a temperature decrease to about  $-90^{\circ}\text{C}$ . This is due to the absence of high levels of radiation absorbing species, particularly ozone. The principal chemical species in this region are  $\text{O}_2^+$  and  $\text{NO}^+$ .

### **Thermosphere:**

The far outer reaches of the atmosphere above mesosphere is called thermosphere. In this region the temperature reaches to as high as  $1200^{\circ}\text{C}$ . Here the atmospheric gases, particularly oxygen and nitric oxide, split into atoms and also undergo ionisation by the absorption of very high energy radiation of  $<200\text{nm}$ .

## **VERTICAL PROFILES OF PRESSURE AND TEMPERATURE**

The figure below shows typical vertical profiles of pressure and temperature observed in the atmosphere. Pressure decreases exponentially with altitude. The fraction of total atmospheric weight located above altitude  $z$  is  $P(z)/P(0)$ . At 80 km altitude the atmospheric pressure is down to 0.01 hPa, meaning that 99.999% of the atmosphere is below that altitude. You see that the atmosphere is of relatively thin vertical extent. Astronomer Fred Hoyle once said, "Outer space is not far at all; it's only one hour away by car if your car could go straight up!"



**Figure : Mean pressure and temperature vs. altitude at 30°N, March**

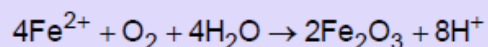
### Evolution of The Atmosphere:

Our present atmosphere is thought to have come from volcanic eruptions. Volcanoes emit a lot of water vapor and carbon dioxide. As the earth began to cool the water vapor condensed and began to create oceans. Carbon dioxide dissolved in the oceans and was slowly turned into rock. Smaller amounts of nitrogen (N<sub>2</sub>) are emitted by volcanoes. Nitrogen is relatively inert (unreactive) and remained in the air. Nitrogen concentration built up over time.

The oxygen is thought to have first come from photodissociation of water vapor and carbon dioxide by the ultraviolet light in sunlight. The O and OH react to form O<sub>2</sub> and H. Once molecular oxygen (O<sub>2</sub>) started to accumulate in the air it began to react with atomic oxygen (O) to form ozone (O<sub>3</sub>).

*For reactions, see class notes*

It is widely accepted that the present state of earth's atmosphere is quite different and the present changes were brought about by biological and accompanying chemical reactions. Approximately 3.5 billion years ago, when the first primitive life molecules were formed, the atmosphere was chemically reducing, coexisting primarily of methane, ammonia, water vapor and hydrogen. Cyanobacteria began to produce oxygen in ocean water, and the oxygen reacted with dissolved iron to form hematite or magnetite.



These two minerals precipitated out of the water to form a layer on the sea bed. Eventually the dissolved iron in the ocean was used up. Oxygen produced by cyanobacteria no longer reacted with iron and was free to diffuse from the ocean into the atmosphere. Once in the air, the oxygen could react with iron in sediments on the earth's surface. This produced red colored (rust colored) sedimentary rock. None of these so-called red beds are older than about 2 B years old.

Once formed, ozone began to absorb ultraviolet light and life forms were able to safely move from the oceans (which would absorb UV light in the absence of ozone) onto land. Eventually plants and photosynthesis would become the main source of atmospheric oxygen. Thus it appears that a real buildup up oxygen began around 2.3 B years ago.

## ENERGY FROM THE SUN TO EARTH'S SURFACE

The Sun's spectral output is composed of approximately 9% ultraviolet (and shorter) wavelengths, 41% visible light, and about 50% infrared radiation. Shorter wavelengths have higher energy content than longer wavelengths.

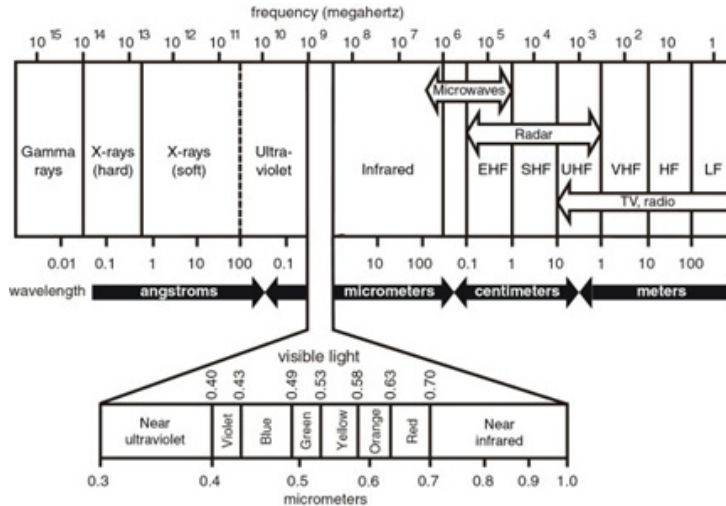
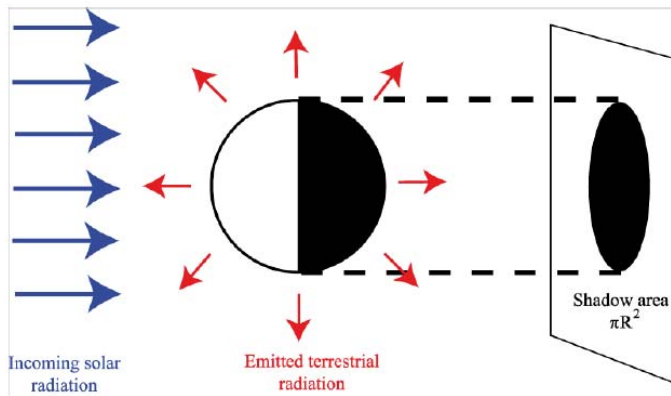


Figure 2.01  
The spectrum of electromagnetic radiation

## The Earth's energy budget /Earth's Radiation Balance

Nearly all the energy entering the climate system comes from the Sun in the form of electromagnetic radiation. At the top of the Earth's atmosphere, a surface at the mean Earth-Sun distance perpendicular to the rays receives about  $1368 \text{ W/m}^2$ . This is often called the solar constant  $S_0$ . A bit less than half of this energy comes in the form of radiation in the visible part of the electromagnetic spectrum, the remaining part being mainly in the near infrared, with a smaller contribution from the ultraviolet part of the spectrum.

On average, the total amount of incoming solar energy outside the Earth's atmosphere (Figis the solar constant times the cross-sectional surface (i.e., the surface that intercepts the solar rays, which corresponds to a surface  $\pi R^2$  where  $R$  is the Earth's radius of  $6371 \text{ km}$ ). For simplicity and because it is a reasonable approximation, we will neglect the thickness of the atmosphere compared to the Earth's radius in our computations of distances or surfaces. Some of this incoming flux is reflected straight back to space by the atmosphere, the clouds and the Earth's surface. The fraction of the radiation that is reflected is called the albedo of the Earth or planetary albedo ( $\alpha_p$ ). In present-day conditions, it has a value of about 0.3.



In order to achieve a heat balance, the heat flux coming from the Sun must be compensated for by an equivalent heat loss. If this were not true, the Earth's temperature would rapidly rise or fall. As the radiations emitted by the Earth have a much longer wavelength than those received from the Sun, they are often termed longwave radiation while those from the Sun are called shortwave radiation. Treating the Earth as a black body, the total amount of energy that is emitted by a 1 m<sup>2</sup> surface ( $A\uparrow$ ) can be computed by Stefan-Boltzmann's law:

$$A\uparrow = \sigma T_e^4$$

where  $\sigma$  is the Stefan Boltzmann constant ( $\sigma = 5.67 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ ). This equation defines  $T_e$ , effective emission temperature of the Earth. The Earth emits energy in the directions, so the total amount of energy emitted by the Earth is  $A\uparrow$  times the surface of the Earth,  $4\pi R^2$ . To achieve equilibrium, we must thus have (Fig. 2.3):

Absorbed solar radiation = emitted terrestrial radiation

$$\pi R^2 (1 - \alpha_p) S_0 = 4\pi R^2 \sigma T_e^4$$

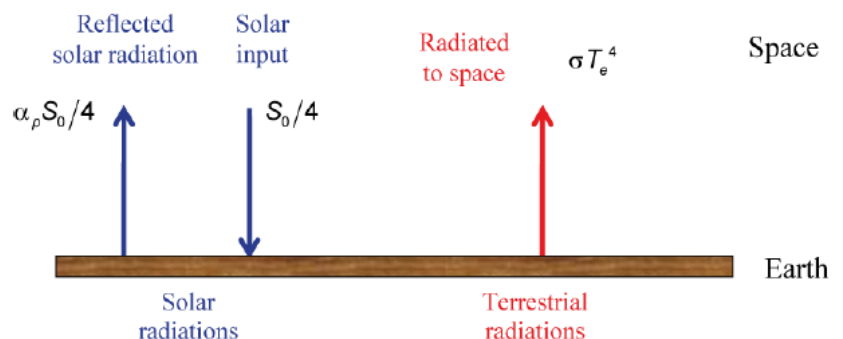
This leads to

$$\frac{1}{4} (1 - \alpha_p) S_0 = \sigma T_e^4$$

and finally to

$$T_e = \left( \frac{1}{4\sigma} (1 - \alpha_p) S_0 \right)^{1/4}$$

This corresponds to  $T_e = 255 \text{ K}$  ( $= -18^\circ\text{C}$ ). Note that we can interpret the above eqn as the mean balance between the emitted terrestrial radiation and the absorbed solar flux for 1 m<sup>2</sup> of the Earth's surface. As shown above, the factor 1/4 arises from the spherical geometry of the Earth, because only part of the Earth's surface receives solar radiation directly.



## The greenhouse effect

But the average surface temperature of the earth is maintained at relatively comfortable  $15^{\circ}\text{C}$  due to the atmospheric green house effect, in which water vapors and carbon dioxide, reabsorb much of the outgoing radiation and reradiate about half of it back to the surface. If this were not to be the case the surface temperature of the earth would have been averaged around  $-18^{\circ}\text{C}$ . Carbon dioxide though present at a much lower concentration than water vapour contributing in a major way in maintaining the heat balance. There is concern that an increase in the carbon dioxide level in the atmosphere would prevent sufficient energy loss from the earth's surface. This would cause a perceptible and damaging increase in the earth's temperature.

What if Earth did not have greenhouse gases?



Main greenhouse gases	$\text{CO}_2$ $\text{H}_2\text{O}$
Temperature without greenhouse gases	$-5^{\circ}\text{C}$ ( $23^{\circ}\text{F}$ )
Actual Average Temperature	$15^{\circ}\text{C}$ ( $59^{\circ}\text{F}$ )
Temperature change because of greenhouse gases	$20^{\circ}\text{C}$ ( $36^{\circ}\text{F}$ )

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The atmosphere is absorbing about 20% of the incoming solar radiation. As a consequence, the majority of the absorption takes place at Earth's surface. Some minor constituents of the atmosphere, especially water vapour, carbon dioxide and methane have the radiative properties. A significant fraction of the energy emitted by the Earth's surface is absorbed by the atmosphere and re-emitted, significantly increasing the temperature of the system. The alteration of the energy budget by some minor atmospheric constituents described above is called the greenhouse effect and those minor constituents the greenhouse gases. Examples include water vapour, carbon dioxide, methane, CFCs, ozone, nitrogen oxides.

Observations suggest that the global average land surface temperature has risen  $0.45\text{--}0.60^{\circ}\text{C}$  ( $0.8\text{--}1.0^{\circ}\text{F}$ ) in the last century. Greater increases in this trend ( $2\text{--}3^{\circ}\text{C}$ ) have been measured in the northern hemisphere due to a larger proportion of Earth's surface being land rather than water in this hemisphere (land temperatures increase much more quickly than water temperatures). The evidence comes from direct temperature observations and also from observations of sea-level rise and glacier recession. By 2100, it is likely that sea levels will be up by  $50 \pm 25\text{ cm}$ .

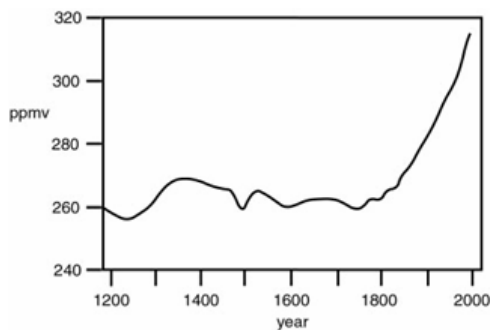


Figure : Longterm trend in global atmospheric  $\text{CO}_2$  concentrations

Rising temperatures and changes in soil moisture resulting from altered climate patterns are predicted to significantly affect the distribution and productivity of vegetation around the globe. The accurate prediction of exact changes in the distribution of major vegetation communities is very difficult due to the complexity of climate systems, lag times in vegetation's response to environmental dynamics, and physical barriers to the dispersal and migration of different plant types.



## **AIR POLLUTION :**

The six main inorganic pollutants are listed below (there are many more).

Inorganic pollutants : Nitrogen oxides, ozone, carbon monoxide, sulphur dioxide, particulate matter, lead (Pb).

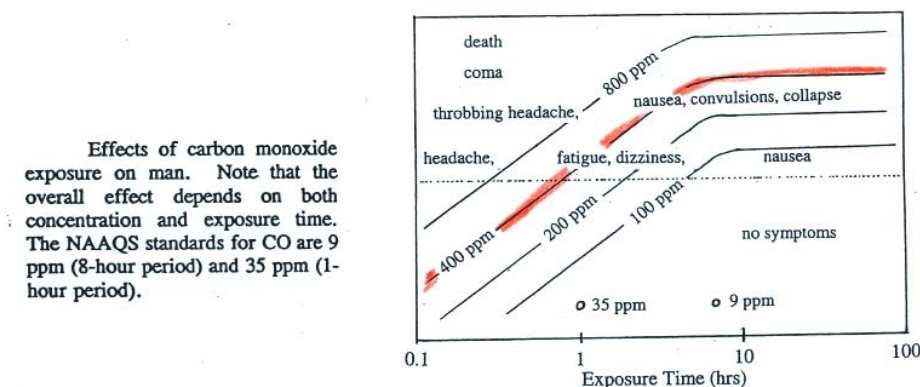
The concentration of lead in air has decreased significantly since lead was removed from gasoline.

### **Carbon monoxide :**

Carbon monoxide is insidious, you can't smell it or see it and it can kill you. Once inhaled, carbon monoxide molecules bond strongly to the hemoglobin molecules in blood and interfere with the transport of oxygen throughout your body. CO is emitted directly from an automobile tailpipe into the atmosphere for example. CO is produced by incomplete combustion of fossil fuel (insufficient oxygen). Complete combustion would produce carbon dioxide, CO<sub>2</sub>. Cars and trucks produce much of the CO in the atmosphere.

Vehicles must now be fitted with a catalytic converter that will change CO into CO<sub>2</sub> (and also NO into N<sub>2</sub> and O<sub>2</sub> and hydrocarbons into H<sub>2</sub>O and CO<sub>2</sub>). In large metropolitan areas, vehicles must also pass an emissions test every year and special formulations of gasoline (oxygenated fuels) are used during the winter months to try to reduce CO emissions.

So far we have been talking about carbon monoxide found in the atmosphere. Carbon monoxide is also a serious hazard indoors where it can build to much higher levels than would ever be found outdoors. You may have heard about an incident at the beginning of the school year in 2007 where carbon monoxide from a malfunctioning hot water heater sickened 23 Virginia Tech students in an apartment complex. The CO concentration is thought to have reached 500 ppm. You can get an idea of what kinds of health effects concentrations this high could cause from the figure below.



### **Ozone :**

Tropospheric ozone is a key component of photochemical smog (also known as Los Angeles-type smog). Making ozone in the troposphere is also a more complex process as discussed in the class (see class notes for the reactions and graph).

A more complex series of reactions is responsible for the production of tropospheric ozone. The production of tropospheric ozone begins with nitric oxide (NO). NO is produced when nitrogen and oxygen in air are heated (in an automobile engine for example) and react. The NO can then react with oxygen to make nitrogen dioxide, a poisonous brown-colored gas. Sunlight can dissociate the nitrogen dioxide molecule producing atomic oxygen (O) and NO. O and O<sub>2</sub> react in a 4th step to make ozone (O<sub>3</sub>).

NO is produced early in the day (during the morning rush hour). The concentration of NO<sub>2</sub> peaks somewhat later. Peak ozone concentrations are usually found in the afternoon. Ozone concentrations are also usually higher in the summer



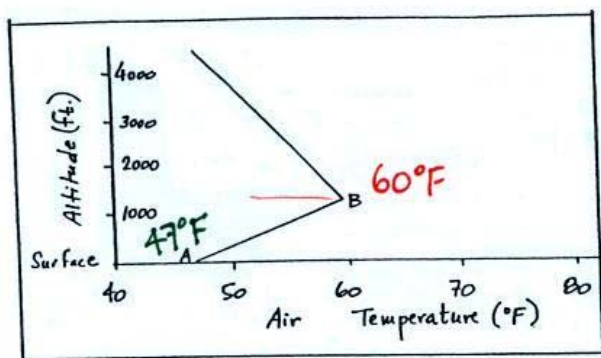
than in the winter. Ozone can react with a hydrocarbon of some kind which is also invisible to make a product gas. This product gas sometimes condenses to make a visible smog cloud or haze. The cloud is composed of very small droplets or solid particles.

### **Sulfur dioxide:**

Sulfur dioxide is produced by the combustion of sulfur-containing fuels such as coal. Combustion of fuel also produces carbon dioxide and carbon monoxide. People probably first became aware of sulfur dioxide because it has an unpleasant smell. Carbon dioxide and carbon monoxide are odorless. That is why sulfur dioxide was the first pollutant people became aware of. Volcanoes are a natural source of sulfur dioxide.

### **Inversion layers**

Surface temperature inversion layers form on long winter nights when the sky is clear and winds are calm. The ground cools quickly and becomes colder than the air above. Air in contact with the cold ground ends up colder than air above. In a temperature inversion layer, air temperature increases with increasing altitude. This produces a very stable layer of air at ground level. A very reasonable wintertime morning temperature profile in Tucson is shown below:



A typical wintertime, early morning, surface inversion layer. The inversion, a stable air layer, is where the air temperature is increasing with increasing altitude; between points A and B. The inversion will usually disappear later in the day as the ground is warmed by sunlight.

Temperature increases from 47° F at the ground (Point A) to about 60° F at 1000 feet altitude (Point B), that's the stable inversion layer. Temperature begins to decrease with increasing altitude above Point B. There is very little vertical mixing in a stable air layer.

### **The Great London smog:**

The Great London smog is still one of the two or three deadliest air pollution events in history. Because the atmosphere was stable, SO<sub>2</sub> emitted into air at ground level couldn't mix with cleaner air above, and the SO<sub>2</sub> concentration was able to build to dangerous levels. 4000 people died during this 4 or 5 day period and as many as 8000 additional people died in the following weeks and months.

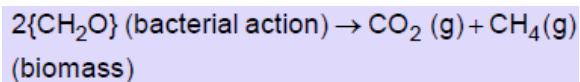
The sulfur dioxide didn't kill people directly. Rather the SO<sub>2</sub> aggravated an existing condition of some kind and hastened their death. The SO<sub>2</sub> probably also made people susceptible to bacterial infections such as pneumonia.

### **Organic Air Pollutants :**

A variety of organic compounds are emitted into the atmosphere by natural and human activities. They are so diverse that it is difficult to classify them neatly.

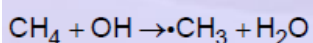
### Natural source of hydrocarbons:

Most of the organic compounds in the atmosphere (85%) originate from the natural source from vegetation. Among them the methane is of concern since it is the most important greenhouse gas after carbon dioxide. Methane is produced by the bacterial action, when dead organic matter is subjected to an oxygen-depleted highly reducing aqueous or terrestrial environment as per the following equation.



The present tropospheric concentration of methane is about 1.77 ppm and it is increasing at the rate of 0.5% every year. Methane undergoes photochemical dissociation in the stratosphere to give water vapour. But in the troposphere it undergoes photochemical reaction to give CO and O<sub>3</sub>.

The principal sink for methane decomposition is oxidation via hydroxyl radicals in the troposphere.



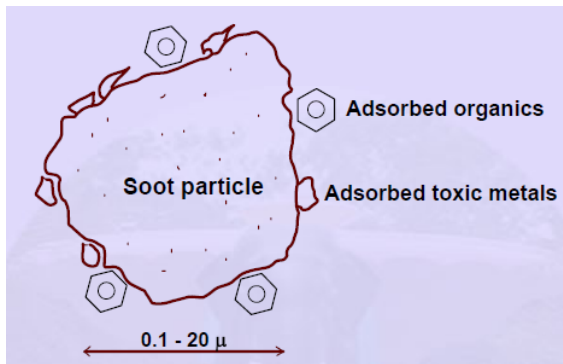
The other sinks for methane gas are the reaction with soil and loss to the stratosphere.

Ethylene, C<sub>2</sub>H<sub>4</sub>, is released to the atmosphere by a variety of plants. Most of the hydrocarbons emitted predominantly by trees are terpenes from conifer trees. These compounds contain olefinic bonds and hence are the most reactive compounds in the atmosphere.

The gaseous and volatile liquid hydrocarbons are of particular interest as air pollutants. Hydrocarbons can be saturated or unsaturated, branched or straight-chain, or can have a ring structure as in the case of aromatics or other cyclic compounds. Hydrocarbons predominate among the atmospheric pollutants because of their widespread use in fuels. They enter the atmosphere either directly from the fuel or as by-products of partial combustion of other hydrocarbons, which tend to be unsaturated and relatively reactive. Several alkenes including ethylene, propylene, butadiene and styrene are among the top 50 chemicals produced each year and are released to the atmosphere during their production and use similarly aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene and cumene are among the top 50 chemicals produced each year and these are also released into the atmosphere during their production and use.

The combustion processes of automobile engines produce significant amount of organic particulates. A significant amount of organic particulate matter is produced by automobile engines in combustion processes. The organic particulates of greatest concern are polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons (PAHs) commonly occur in urban atmospheres up to about 20 μg m<sup>-3</sup> level. Elevated levels of PAHs are observed in polluted urban atmospheres, in the vicinity of forest fires and burning of coal.

Soot is formed as a residue during the combustion of fuel in power plants and automobiles. It is due to the incomplete combustion of organic products. It is an impure form of elemental carbon (graphite). Soot particles are roughly spherical, whereas graphite has a layered structure. It is known that most PAH compounds are adsorbed on soot particles. Soot consists of many condensed aromatic rings containing 1-3% H, 5-10% O and trace metals such as Be, Cd, Cr, Mn, Ni and vanadium and also toxic organics such as benzo (a) pyrene. This is illustrated in the following figure.



**Figure : Soot particle from combustion of fossil fuels**

The hydrocarbons in air by themselves alone cause no harmful effects. They are of concern because the hydrocarbons undergo chemical reactions in the presence of sunlight and nitrogen oxides forming photochemical oxidants of which the predominant one is ozone.

## **ATMOSPHERIC DISPERSION OF POLLUTANTS**

Dispersion is the process by which contaminants move through the air and a plume spreads over a large area, thus reducing the concentration of the pollutants it contains.

## **AIR POLLUTION AND METEOROLOGY**

Obviously, air quality at a given site varies tremendously from day to day even though emissions may remain relatively constant. The determining factors have to do with the weather: how strong are the winds, in what direction are they blowing, what is the temperature profile, how much sunlight is available, and how long has it been since the last strong winds or precipitation were able to clear the air. Air quality is dependent on the dynamics of the atmosphere, the study of which is called *meteorology*.

### **Lapse rate**

The rate of decrease of temperature with altitude ( $-dT/dz$ ) is called the *lapse rate*.

To determine whether an atmosphere is stable or unstable, we need to compare its *atmospheric lapse rate* (*ambient lapse rate*)  $-dT_{\text{ATM}}/dz$  to the *adiabatic lapse rate*  $-dT_A/dz$ . Note that stability is a *local* property of the atmosphere defined by the local value of the atmospheric lapse rate; an atmosphere may be stable at some altitudes and unstable at others. Also note that stability refers to both upward and downward motions; if an atmosphere is unstable with respect to rising motions it is equivalently unstable with respect to sinking motions. Instability thus causes rapid vertical mixing rather than unidirectional transport.

### **Adiabatic Lapse rate**

If a parcel of air in the earth's atmosphere rises through the atmosphere, it experiences decreasing pressure and thus expands. This expansion lowers the temperature of the air parcel, and therefore the air cools as it rises. The rate at which *dry air* cools as it rises is called the dry adiabatic lapse rate and is independent of the ambient air temperature.

The term "adiabatic" means that there is no heat exchange between the rising parcel of air under consideration and the surrounding air. The *dry* adiabatic lapse rate may be calculated from basic physical principles. Adiabatic lapse rate (commonly denoted by  $\Gamma$ )

$$\Gamma = -\frac{dT}{dz} = -1.00^{\circ}\text{C}/100\text{m} \quad (-9.8^{\circ}\text{C}/\text{Km}) \quad dT/dz|_{\text{dry-adiabatic}} = -9.8^{\circ}\text{C}/\text{km},$$

where  $T$  = temperature and  $z$  = altitude.

$\Gamma$  is a constant, independent of atmospheric conditions. We can diagnose whether an atmosphere is stable or unstable with respect to vertical motions simply by comparing its lapse rate to  $\Gamma = 9.8^{\circ}\text{C km}^{-1}$ :

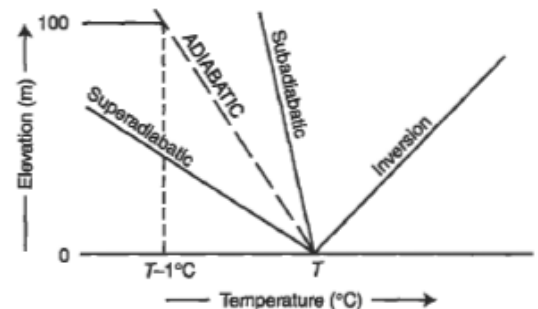
### Ambient Lapse rate

The actual measured rate at which air cools as it rises is called the ambient lapse rate. The relationships between the ambient lapse rate and the *dry* adiabatic lapse rate essentially determine the stability of the air and the speed with which pollutants will disperse. These relationships are shown in the Fig below. There are three stability categories.

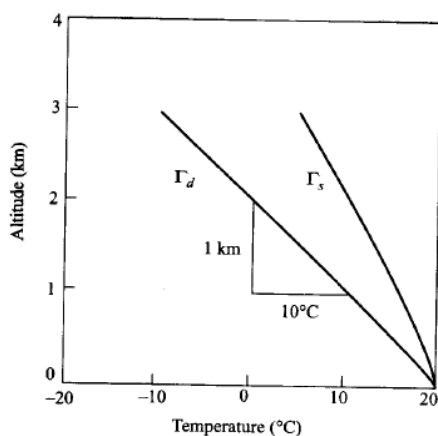
$$\begin{aligned} -\frac{dT_{ATM}}{dz} &> \Gamma && \text{unstable} \\ -\frac{dT_{ATM}}{dz} &= \Gamma && \text{neutral} \\ -\frac{dT_{ATM}}{dz} &< \Gamma && \text{stable} \end{aligned}$$

When the ambient lapse rate is exactly the same as the dry adiabatic lapse rate, the atmosphere has neutral stability. Superadiabatic conditions prevail when the air temperature drops more than  $9.8^{\circ}\text{C}/\text{Km}$  ( $1.00^{\circ}\text{C}/100\text{m}$ ). Subadiabatic conditions prevail when the air temperature drops at a rate less than  $9.8^{\circ}\text{C}/\text{Km}$ .

A special case of subadiabatic conditions is the temperature inversion. Particularly stable conditions are encountered when the temperature increases with altitude ( $dT_{ATM}/dz > 0$ ), such a situation is called a *temperature inversion*.



**Figure. Ambient lapse rates and the dry adiabatic lapse rate.**

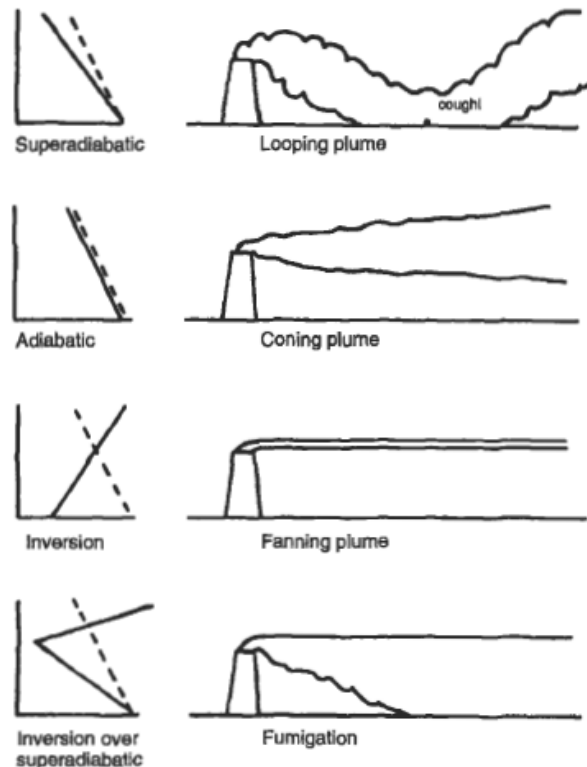


**The dry adiabatic lapse rate**

$\Gamma_d$  is a constant  $10^{\circ}\text{C}/\text{km}$ , but the saturated adiabatic lapse rate  $\Gamma_s$  varies with temperature. In the troposphere,  $\Gamma_s$  is approximately  $6^{\circ}\text{C}/\text{km}$ .

Plume : a long cloud of smoke or vapour which spreads from its point of origin.

Atmospheric stability may often be recognized by the shapes of plumes emitted from smokestacks as seen in the following Figs. Neutral stability conditions usually result in coning plumes, while unstable (superadiabatic) conditions result in a highly dispersive looping plume. Under stable (subadiabatic) conditions, the *fanning* plume tends to spread out in a single flat layer. One potentially serious condition is called *fumigation*, in which pollutants are caught under an inversion and are mixed owing to strong lapse rate. A looping plume also produces high ground-level concentrations as the plume touches the ground.



**Figure - Plume shapes and atmospheric stability**

Consider a parcel of air at some given altitude. It has the same temperature and pressure as the air surrounding it. Our test for atmospheric stability will be based on the following mental experiment. If we imagine raising the parcel of air slightly, it will experience less atmospheric pressure, so it will expand. Because it will have done work on its environment (by expanding), the internal energy in the parcel will be reduced so its temperature will drop. Assuming that the parcel is raised fast enough to be able to ignore any heat transfer between the surrounding air and the parcel, the cooling will follow the adiabatic lapse rate. After raising the parcel, note its temperature, and compare it with the temperature of the surrounding air. If the parcel, at this higher elevation, is now colder than its surroundings, it will be denser than the surrounding air and will want to sink back down again. That is, whatever it was that caused the parcel to start to move upward will immediately be opposed by conditions that make the parcel want to go back down again. The atmosphere is said to be stable. If, however, raising the parcel causes its temperature to be greater than the surrounding air, it will be less dense than the surrounding air and it will experience buoyancy forces that will encourage it to keep moving upward. The original motion upward will be reinforced and the parcel will continue to climb. This is an unstable atmosphere.

If an ambient temperature profile for air that cools more

rapidly with altitude than the dry adiabatic lapse rate. In this case the ambient air temperature is said to be superadiabatic. Imagine a 20 °C parcel of air at 1 km to be just like the air surrounding it. If that parcel is raised to 2 km, it will cool adiabatically to 10 °C. The 10 °C parcel of air at 2 km is now warmer than the surrounding air (0 °C in the figure), so it is less dense and more buoyant and wants to keep rising ("warm air rises"). In other words, shoving the parcel of air up some in a superadiabatic atmosphere creates forces that want to keep it moving upward. Conversely, a parcel of air at 1 km that is nudged downward becomes colder than the surrounding air and so it keeps sinking. It does not matter whether the parcel of air is nudged up or down; in either case, it keeps on going so the atmosphere is said to be unstable.

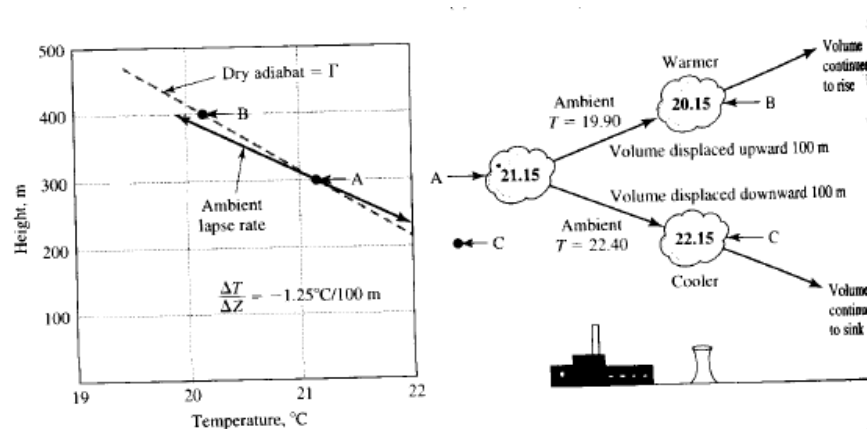


Fig : Unstable atmosphere

the ambient temperature profile is drawn for the subadiabatic case in which the ambient temperature cools less rapidly than the adiabatic lapse rate. If we once again imagine a parcel of air at 1 km and 20 °C that is for one reason or another nudged upward, it will find itself colder than the surrounding air. At its new elevation, it experiences the same pressure as the air around it, but it is colder, so it will be denser and will sink back down. Conversely, a parcel starting at 1 km and 20 °C that starts moving downward will get warmer and less dense than its surroundings, so buoyancy forces will push it back up again. In other words, anything that starts a parcel of air moving up or down will cause the parcel to experience forces that will want it to return to its original altitude. The subadiabatic atmospheric profile is therefore stable.

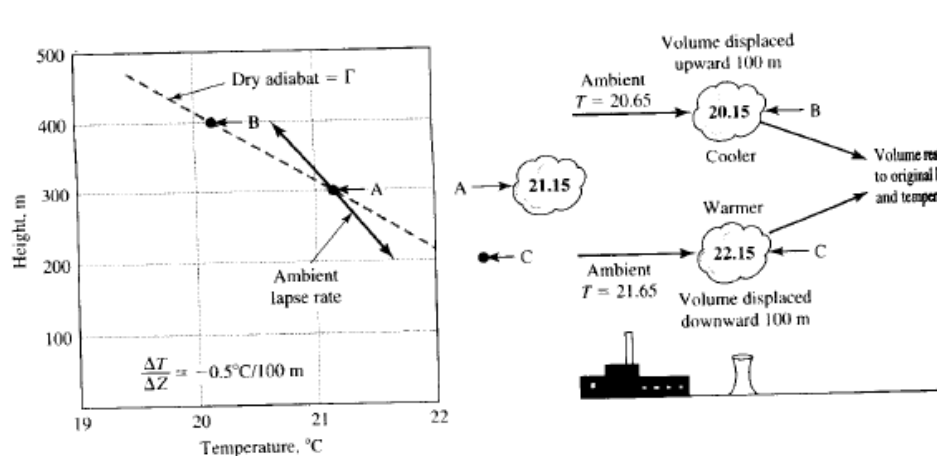


Fig : Stable atmosphere

If the ambient lapse rate is equal to the adiabatic lapse rate, moving the parcel upward or downward results in its temperature changing by the same amount as its surroundings. In any new position, it experiences no forces that either make it continue its motion or make it want to return to its original elevation. The parcel likes where it was, and it likes its new position too. Such an atmosphere is said to be neutrally stable.

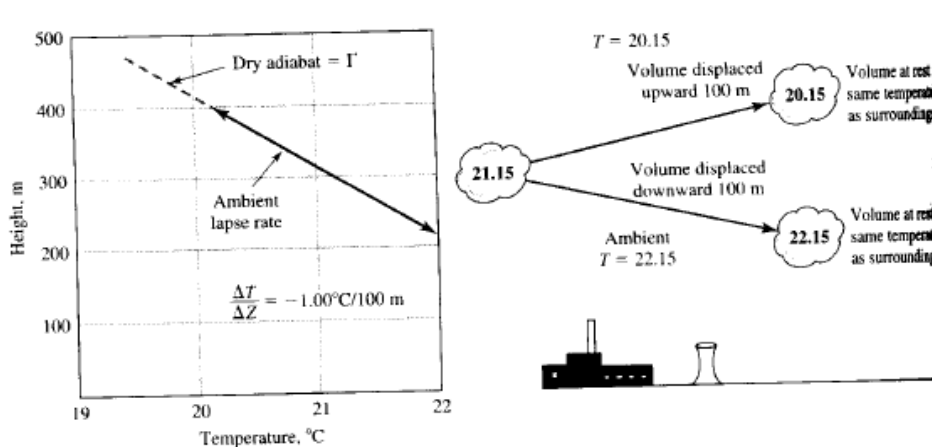


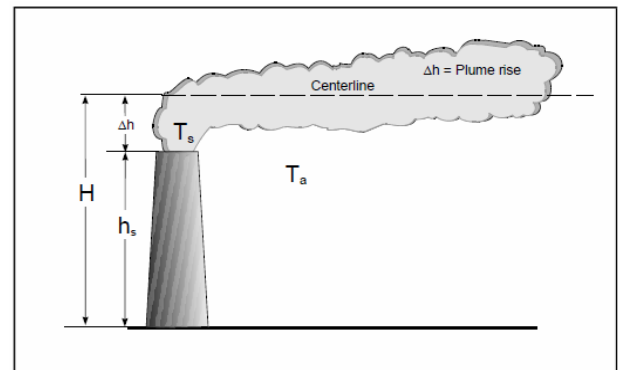
Fig : Neutral stability

An extreme case of a subadiabatic lapse rate is one in which ambient temperatures increase with altitude. Such temperature inversions yield a very stable air mass, and pollution tends to stay trapped there. In Chapter 9, it will be noted that the heating caused by absorption of incoming solar energy by oxygen and ozone in the upper atmosphere creates a stratospheric temperature inversion. That inversion causes the stratosphere to be extremely stable, often trapping pollutants for many years.

## ATMOSPHERIC DISPERSION : Gaussian model

Pollutants enter the atmosphere in a number of different ways. For example, wind blows dust into the air. When plant material decays, methane is released. Automobiles, trucks and buses emit pollutants from engine exhausts and during refueling. Electric power plants along with home furnaces give off pollutants as they try to satisfy mankind's need for energy.

One method of pollution release has received more attention than any other pollution released from stationary point sources, i.e., stacks. Stacks come in sizes – from small vent on a building's roof to a tall stack. Their function is to release pollutants high enough above the earth's surface so that emitted pollutants can sufficiently disperse in the atmosphere before reaching ground level. All else being equal, taller stacks disperse pollutants better than shorter stacks because the plume has to travel through a greater depth of the atmosphere before it reaches ground level. As the plume travels it spreads and disperses.



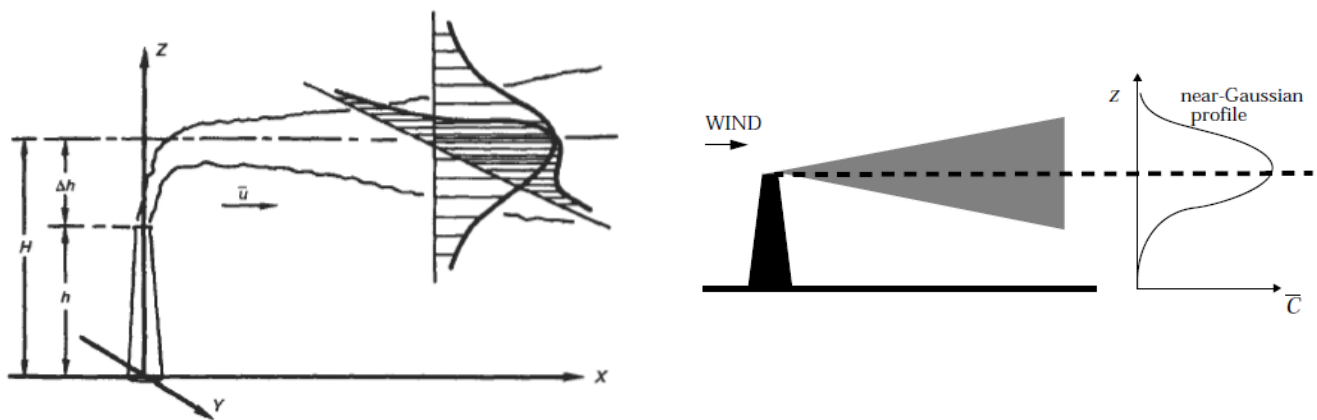


The plume spreads both horizontally and vertically. If it is a gaseous plume, the motion of the molecules follows the laws of gaseous diffusion.

The most commonly used model for the dispersion of gaseous air pollutants is the Gaussian model developed by Pasquill, in which gases dispersed in the atmosphere are assumed to exhibit ideal gas behavior. Rigorous derivation of the model is beyond the scope of this text, but the principles on which the model is based are:

- The predominant force in pollution transport is the wind; pollutants move
- The greatest concentration of pollutant molecules is along the plume center line.
- Molecules diffuse spontaneously from regions of higher concentration to regions
- The pollutant is emitted continuously, and the emission and dispersion process is steady state.

The following Figure shows the fundamental features of the Gaussian dispersion model, with the geometric arrangement of source, wind, and plume. We can construct a Cartesian coordinate system with the emission source at the origin and the wind direction along the x axis. Lateral and vertical dispersions are along the y and z axes, respectively. As the plume moves downwind, it spreads both laterally and vertically away from the plume centerline as the gas molecules move from higher to lower concentrations. Cross sections of the pollutant concentration along both the y and the z axes thus have the shape of Gaussian curves, as shown in Fig.



Since stack gases are generally emitted at temperatures higher than ambient, the buoyant plume will rise some distance before beginning to travel downwind. The sum of this vertical travel distance and the geometric stack height is  $H$ , the *effective* stack height. The source of the pollutant plume is, in effect, a source elevated above the ground at elevation and the downwind concentration emanating from this elevated source may be written

$$C(x, y, z) = \frac{Q}{2 \pi \sigma_y \sigma_z u} e^{-\frac{1}{2} \left( \frac{y}{\sigma_y} \right)^2} \left\{ e^{-\frac{1}{2} \left( \frac{z-H}{\sigma_z} \right)^2} + e^{-\frac{1}{2} \left( \frac{z+H}{\sigma_z} \right)^2} \right\}$$

where

$C(x, y, z)$  is the concentration at some point in space with coordinates  $x, y, z$ , and

$Q$  = the emission rate of the pollution source (in g/s),

$u$  = the average wind speed in (m/s),

$\sigma_y$  = the standard deviation of the plume in the  $y$  direction (m), and

$\sigma_z$  = the standard deviation of the plume in the  $z$  direction (m).

$x$  = distance in horizontal direction

$z$  = distance in vertical direction

The units of concentration are grams per cubic meter ( $\text{g/m}^3$ ). Since pollution concentrations are usually measured at ground level, that is, for  $z = 0$ ,

the above equation reduces to

$$C(x, y, 0) = \frac{Q}{\pi u \sigma_y \sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left(\exp\left(-\frac{(H)^2}{2\sigma_z^2}\right)\right)$$

This equation takes into account the reflection of gaseous pollutants from the surface of the ground.

We are usually interested in the greatest value of the ground level concentration in any direction, and this is the concentration along the plume centerline; that is, for  $y = 0$ . In this case the above equation reduces to

$$C(x, 0, 0) = \frac{Q}{\pi u \sigma_y \sigma_z} \exp\left(\frac{-H^2}{2\sigma_z^2}\right)$$

Finally, for a *source of emission* at ground level,  $H = 0$ , and the ground level concentration of pollutant downwind along the plume centerline is given by

$$C(x, 0, 0) = \frac{Q}{\pi u \sigma_y \sigma_z}.$$

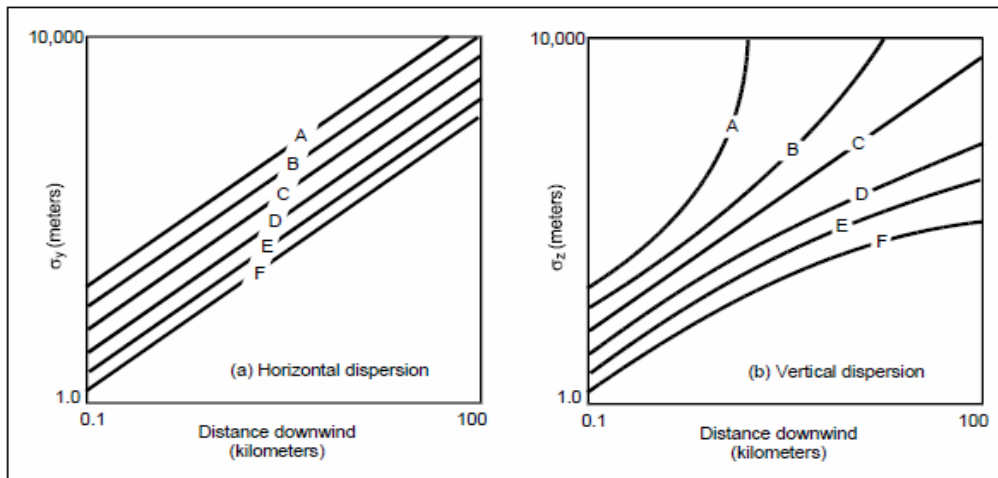
For a release above ground level the maximum downwind ground level concentration occurs along the plume centerline when the following condition is satisfied:

$$\sigma_z = \frac{H}{\sqrt{2}}.$$

The standard deviations  $\sigma_y$  and  $\sigma_z$  are measures of the plume spread in the crosswind (lateral) and vertical directions, respectively. They depend on atmospheric stability and on distance from the source. Atmospheric stability is classified in categories A through F, called stability classes. The following Table shows the relationship between stability class, wind speed and sunshine conditions

Wind speed at 10 m (m/s)	Day Incoming solar radiation			Night Thin overcast	
	Strong	Moderate	Slight	1/2 low cloud	3/8 cloud
<2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	E
>6	C	D	D	D	D

The above Table shows the relationship between stability class, wind speed, and sunshine conditions. Class A is the least stable; Class F is the most stable. In terms of ambient lapse rates, Classes A, B, and C are associated with superadiabatic conditions; Class D with neutral conditions; and Classes E and F with subadiabatic conditions. A seventh, Class G, indicates conditions of extremely severe “temperature inversion”, but in considering frequency of occurrence is usually combined with Class F.



### Horizontal and vertical dispersion coefficients

**Q. An oil pipeline leak results in emission of 100g/h of  $H_2S$ . On a very sunny summer day, with a wind speed of 3.0 m/s, what will be the concentration of  $H_2S$ ? Given  $\sigma_y = 210m$  and  $\sigma_z = 160m$**

**Ans :**

$$Q = 100 \text{ g/h} = 0.0278 \text{ g/s.}$$

$$C(1500, 0, 0) = \frac{0.0278 \text{ g/s}}{\pi(3.0 \text{ m/s})(210 \text{ m})(160 \text{ m})} = 8.77 \times 10^{-8} \text{ g/m}^3 = 0.088 \mu\text{g/m}^3.$$

## Variation of Wind Speed With Elevation

The model used so far assumes that the wind is uniform and unidirectional, and that its velocity can be estimated accurately. These assumptions are not realistic: wind direction shifts and wind speed varies with time as well as with elevation. The variation of wind speed with elevation can be approximated by a parabolic wind velocity profile. That is, the wind speed  $u$  at an elevation  $h$  may be calculated from the measured wind speed  $u_0$  at a given elevation  $h_0$  using the relationship

$$u = u_0 \left( \frac{h}{h_0} \right)^n$$

The exponent  $n$ , called the stability parameter, is an empirically determined function of the atmospheric stability, and is given in the following Table . Wind is often measured in weather stations at an elevation of  $h_0$  (10 m) above ground level.

**Table : Relationship between the Stability Parameter and Atmospheric Stability**

Stability condition	$n$
Large lapse rate (Classes A, B, C)	0.20
Zero or small lapse rate (Class D)	0.25
Moderate inversion (Class E)	0.33
Strong inversion (Classes F and G)	0.50

---

### Windspeed at the Stack

Suppose an anemometer at a height of 10 m above ground measures the windspeed at 2.5 m/s. Estimate the windspeed at an elevation of 300 m in rough terrain if the atmosphere is slightly unstable.

**Solution** we find that the wind profile exponent for a slightly unstable atmosphere (stability class C) is 0.20. Rearranging (8.43) gives

$$u_H = u_a \left( \frac{H}{z_a} \right)^p = 2.5 \cdot \left( \frac{300}{10} \right)^{0.2} = 4.9 \text{ m/s}$$

■

## PLUME RISE MODEL

In most cases, pollutants injected into ambient air possess a higher temperature than the surrounding air. Most industrial pollutants, moreover, are emitted from smokestacks or chimneys and therefore possess an initial vertical momentum. Both factors (thermal buoyancy and vertical momentum) contribute to increasing the average height of the plume above that of the smokestack. This process terminates when the plume's initial buoyancy is lost by mixing with ambient air.

The physical consequence of the above phenomenon is generally quantified by a single parameter, the plume rise  $\Delta h$ , defined as the vertical displacement of the plume in this initial dispersion phase. Several studies have provided semiempirical formulae for evaluating  $\Delta h$  (e.g., Briggs, 1975):

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### For stable and near neutral conditions :

The final plume height  $H$  is the sum of the stack height  $H_s$  and the combined momentum and buoyancy plume rise  $\Delta H$  ie.,  $H = H_s + \Delta H$ . Briggs proposed the following equations to describe the buoyant rise of a warm plume

$$\Delta H = 2.6 (F_b / u_s)^{1/3}$$

The method defines buoyancy flux parameter  $F_b$  (or simply  $F$ ) by

$$F = \frac{g (T_s - T_A) v r^2}{T_s}$$

$g$  = acceleration due to gravity ( $\text{m/s}^2$ )

$T_s$  and  $T_A$  = Temperatures of the emitted gas and the environment respectively, at the point of emission

$v$  = exit velocity of plume ( $\text{m/s}$ )

$D$  = Diameter of the stack at the top ( $\text{m}$ )

$\bar{u}$  = mean wind speed through the atmosphere layer of depth frequently taken to correspond to  $u$  at the height  $H_s$  of the stack

$S$  = a stability parameter ( $1/s^2$ ) defined by

$$S = \frac{g}{T_A} \left[ \frac{\Delta T_A}{\Delta z} + 0.01^\circ\text{C/m} \right], \text{ where, } \frac{\Delta T_A}{\Delta z} = \text{temperature lapse rate}$$

### For unstable and neutral conditions :

Where the plume theoretically would never stop rising as a result of ambient air entrainment

$$\Delta h(x) = 1.6 F_b^{1/3} u^{-1} x^{2/3} \quad \text{or} \quad \Delta h = \frac{1.6 F^{1/3} x_f^{2/3}}{u_h}$$

$x_f$  = distance downwind to point of final plume rise, m

$$\begin{aligned} \text{Use } x_f &= 120F^{0.4} \quad \text{if } F \geq 55 \text{ m}^4/\text{s}^3 \\ x_f &= 50F^{5/8} \quad \text{if } F < 55 \text{ m}^4/\text{s}^3 \end{aligned}$$

A large power plant has a 250-m stack with inside radius 2 m. The exit velocity of the stack gases is estimated at 15 m/s, at a temperature of 140 °C (413 K). Ambient temperature is 25 °C (298 K) and winds at stack height are estimated to be 5 m/s. Estimate the effective height of the stack if (a) the atmosphere is stable with temperature increasing at the rate of 2 °C/km, (b) the atmosphere is slightly unstable, Class C.

**Solution** First, find the bouyancy parameter  $F$

$$\begin{aligned} F &= gr^2v_s \left( 1 - \frac{T_a}{T_s} \right) \\ &= 9.8 \text{ m/s}^2 \times (2 \text{ m})^2 \times 15 \text{ m/s} \times \left( 1 - \frac{298}{413} \right) = 164 \text{ m}^4/\text{s}^3 \end{aligned}$$

a. With the atmosphere stable, we need to use

$$\begin{aligned} S &= \frac{g}{T_a} \left( \frac{\Delta T_a}{\Delta z} + 0.01^\circ\text{C/m} \right) \\ &= \frac{9.8 \text{ m/s}^2}{298 \text{ K}} (0.002 + 0.01) \text{K/m} = 0.0004/\text{s}^2 \\ \Delta h &= 2.6 \left( \frac{F}{u_h S} \right)^{1/3} \\ &= 2.6 \left( \frac{164 \text{ m}^4/\text{s}^3}{5 \text{ m/s} \times 0.0004/\text{s}^2} \right)^{1/3} = 113 \text{ m} \end{aligned}$$

So the effective stack height is  $H = h + \Delta h = 250 + 113 = 363 \text{ m}$ .

b. With an unstable atmosphere, Class C,

Since  $F > 55 \text{ m}^4/\text{s}^3$ , the distance down wind to the point of final plume rise that should be used is

$$\begin{aligned} x_f &= 120F^{0.4} = 120 \times (164)^{0.4} = 923 \text{ m} \\ \Delta h &= \frac{1.6F^{1/3} \times x_f^{2/3}}{u_h} = \frac{1.6(164)^{1/3}(923)^{2/3}}{5} = 166 \text{ m} \end{aligned}$$

and the effective stack height is  $H = 250 + 166 = 413 \text{ m}$ .

Particles in the air, if they are larger than about a millimeter in diameter, are observed to settle out under the influence of gravity; the carbon particles from elevated diesel truck exhaust are a very good example of such settling. However, most particles of air pollutants are small enough that their settling velocity is a function of atmospheric turbulence, viscosity, and friction, as well as of gravitational acceleration, and settling can be exceedingly slow. Particles smaller than 20  $\mu\text{m}$  in diameter will seldom settle out by gravity alone. Gases are removed by gravitational settling only if they are adsorbed onto particles or if they condense into particulate matter. Sulfur trioxide, for example, condenses with water and other airborne particulates to form sulfate particles.

Particles small enough to stay in the air for appreciable periods of time are dispersed in the air, but in a slightly different way than gaseous pollutants are dispersed. The dispersion equation must be modified by considering the settling velocity of these small particles. For particles between 1 and 100  $\mu\text{m}$  in diameter, the settling velocity follows Stokes' law

$$V_t = gd^2 \frac{\rho}{18\mu}$$

where

$V_t$  = settling or terminal velocity,

$g$  = acceleration due to gravity,

$d$  = particle diameter,

$\rho$  = particle density, and

$\mu$  = viscosity of air.

The settling velocity modifies the Gaussian dispersion equation,

$$C(x, y, 0) = \frac{Q}{2\pi u \sigma_y \sigma_z} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \exp\left(-\frac{(H - (V_t x/u))^2}{2\sigma_z^2}\right)$$

for dispersion of small particles.

The factor of  $\frac{1}{2}$  in the first term arises because falling particles are not reflected at the ground surface.

The rate,  $\omega$ , at which particulate matter is being deposited on the ground, is related to the ambient concentration as shown in

$$\omega = V_t C(x, y, 0) = \frac{Q}{2\pi u \sigma_y \sigma_z} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \exp\left(-\frac{(H - (V_t x/u))^2}{2\sigma_z^2}\right)$$

where  $\omega$  = the deposition rate (in  $\text{g/s-m}^2$ ).

If assuming that the emission consists of particles  $10\text{ }\mu\text{m}$  in diameter and having a density of  $1\text{ g/cm}^3$ , calculate (1) the ambient ground level concentration at 200 m downwind along the plume centerline, and (2) the deposition rate at that point. The viscosity of the air is  $0.0185\text{ g/m-s}$  at  $25^\circ\text{C}$ .  
the settling velocity is

$$V_t = (9.8\text{ m/s}^2)(10^{-5}\text{ m})^2 \frac{(1\text{ g/cm}^3)}{(10^{-6}\text{ m}^3/\text{cm}^3)(18)(0.0185\text{ g/m-s})} = 0.0029\text{ m/s},$$

or  $0.29\text{ cm/s}$ .

$$Q = 18\text{ g/s}$$

$$\begin{aligned} C(0.2, 0, 0) &= \frac{18\text{ g/s}}{2\pi(5\text{ m/s})(35\text{ m})(19\text{ m})} \\ &\times \exp \left\{ -\frac{1}{2} \left[ \frac{60\text{ m} - \left( \frac{(0.0029\text{ m/s})(200\text{ m})}{5\text{ m/s}} \right)}{19\text{ m}} \right]^2 \right\} \\ &= 6.03 \times 10^{-6}\text{ g/m}^3 \end{aligned}$$

or  $6.03\text{ }\mu\text{g/m}^3$ . The deposition rate is then

$$\begin{aligned} \omega &= (0.0029\text{ m/s})(6.03 \times 10^{-6}\text{ g/m}^3\text{-s}) \\ &= 1.75 \times 10^{-8}\text{ g/m}^2\text{-s} \end{aligned}$$

or  $17.5\text{ ng/m}^2\text{-s}$ .