

SREENIVASA INSTITUTE OF TECHNOLOGY AND MANAGEMENT STUDIES, CHITTOOR
(AUTONOMOUS)

Approved by AICTE, New Delhi, Affiliated to JNTUA, Ananthapuramu.



LECTURE NOTES

Subject Name: AIR POLLUTION AND CONTROL (PE – I) &23CIV354A

Year / Branch: III BTECH-V SEM

Regulation: R23

Prepared By: K.SUMALATHA



III B.Tech– V Semester					
Course Code	AIR POLLUTION AND CONTROL (PE – I)	L	T	P	C
23CIV354A		3	0	0	3

Course Objectives:

The objectives of this course are to make the student to:

1. **Understand** the sources, classification, and effects of air pollution on humans and the environment.
2. **Analyze** meteorological factors influencing air pollution and dispersion modeling.
3. **Design** and evaluate control measures for particulate pollutants.
4. **Apply** techniques for controlling gaseous pollutants through chemical and physical processes.
5. **Assess** vehicular and indoor air pollution and propose control strategies.

UNIT– I

Air Pollution:

Definition - Sources & Classification of Air Pollutants - Effects of Air Pollution On Humans, Plants and Materials- Global Effects - Air Quality and NAAQS - National Clean Air Programmed- Sampling of Pollutants in Ambient Air - Stack Sampling.

UNIT– II

Meteorology and Air Pollution:

Factors Influencing Air Pollution, Wind Rose, Mixing Depths, Lapse Rates and Dispersion - Atmospheric Stability, Plume Rise and Dispersion, Prediction of Air Quality, Box Model - Gaussian Model - Dispersion Coefficient - Application of Tall Chimney for Pollutant Dispersion.

UNIT– III

Control of Particulate Pollutants:

Properties of Particulate Pollution - Particle Size Distribution - Control Mechanism - Dust Removal Equipment - Design and Operation of Settling Chambers, Cyclones, Wet Dust Scrubbers, Fabric Filters & ESP.

UNIT– IV

Control of Gaseous Pollutants:

Process and Equipment for The Removal By Chemical Methods - Design and Operation of Absorption and Adsorption Equipment - Combustion and Condensation Equipment.

UNIT– V

Automobile and Indoor Pollution:

Vehicular Pollution – Sources and Types of Emission – Effect of Operating Conditions- Alternate Fuels and Emissions-Emission Controls and Standards, Strategies to Control Automobile Pollution– Causes of Indoor Air Pollution-Changes in Indoor Air Quality- Control and Air Cleaning Systems-Indoor Air Quality

**COURSE OUTCOMES:**

After successful completion of this course, students will be able to:		POs related to COs
CO1	Explain the sources, classification, and global effects of air pollution.	PO1, PO2, PO3
CO2	Analyze meteorological parameters affecting air pollution dispersion.	PO1, PO2, PO3
CO3	Design control systems for particulate matter using appropriate removal techniques.	PO1, PO2, PO3, PO4
CO4	Apply suitable technologies for gaseous pollutant removal through adsorption, absorption, and combustion.	PO1, PO2
CO5	Evaluate vehicular and indoor air pollution sources and suggest mitigation strategies.	PO1, PO2, PO3, PO4

TEXT BOOKS:

1. Rao, M. N. and Rao H. V. N., Air Pollution, Tata McGraw-Hill, New Delhi, 2007
2. Khare M, Sharma P, Kota, S.H, Sumanth C, Air Pollution Science Engineering and Management Fundamentals, CRC Press, 2024.
3. Noel, D. N., Air Pollution Control Engineering, Tata McGraw Hill Publishers, 1999.

REFERENCEBOOKS:

1. Fundamentals of Air Pollution by Dr.B.S.N. Raju, Oxford&I.B.H
2. Air Pollution Control Engineering by Nevers,, Mc Graw- Hill, Inc., 2000.
3. Rao, C.S., Environmental Pollution Control Engineering, New Age International, New Delhi, 2006.
4. Mahajan S. P., Pollution Control in Process Industries, Tata Mc Graw-Hill Publishing Company, New Delhi, 1991.
5. Peavy H.S., Rowe D.R. and Tchobanoglous G., Environmental Engineering, Mc Graw Hill, New York, 1985.

Online Learning Resources:

<https://archive.nptel.ac.in/courses/105/107/105107213/>

CO-MAPPING

CO/PO	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12	PSO1	PSO2
CO-1	2	1	-	-	-	2	3	-	-	1	-	1	1	1
CO-2	2	2	-	2	2	3	3	-	-	-	-	1	2	2
CO-3	2	2	3	2	2	3	3	-	-	-	-	1	2	2
CO-4	2	1	2	2	3	3	3	-	-	-	-	1	2	2
CO-5	2	2	2	2	2	3	3	2	-	-	-	1	2	2

UNIT I

INTRODUCTION

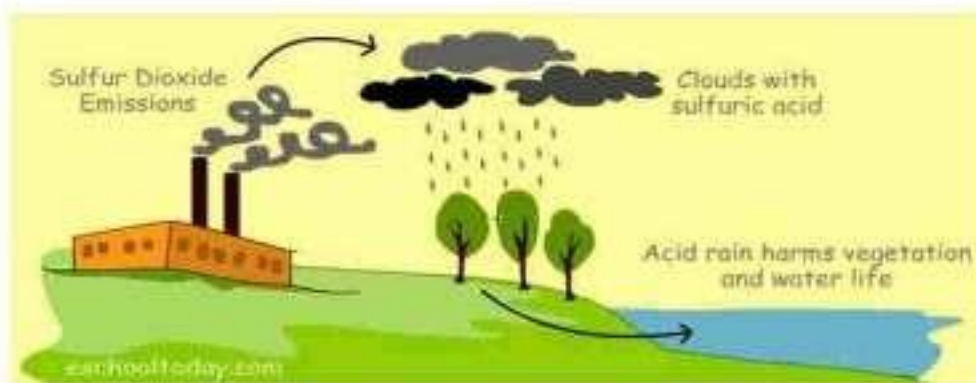
Long-term health effects can include chronic respiratory disease, lung cancer, heart disease, and even damage to the brain, nerves, liver, or kidneys. Continual exposure to air pollution affects the lungs of growing children and may aggravate or complicate medical conditions in the elderly.

Along with harming human health, air pollution can cause a variety of environmental effects: Acid rain is precipitation containing harmful amounts of nitric and sulfuric acids. These acids are formed primarily by nitrogen oxides and sulfur oxides released into the atmosphere when fossil fuels are burned.

The effects of air pollution?

1. Acidification:

Chemical reactions involving air pollutants can create acidic compounds which can cause harm to vegetation and buildings. Sometimes, when an air pollutant, such as sulfuric acid combines with the water droplets that make up clouds, the water droplets become acidic, forming acid rain. When acid rain falls over an area, it can kill trees and harm animals, fish, and other wildlife.



Acid rain destroys the leaves of plants. When acid rain infiltrates into soils, it changes the chemistry of the soil making it unfit for many living things that depend on the soil as a habitat or for nutrition. Acid rain also changes the chemistry of the lakes and streams that the rainwater flows into, harming fish and other aquatic life.

(iv) Other effects.

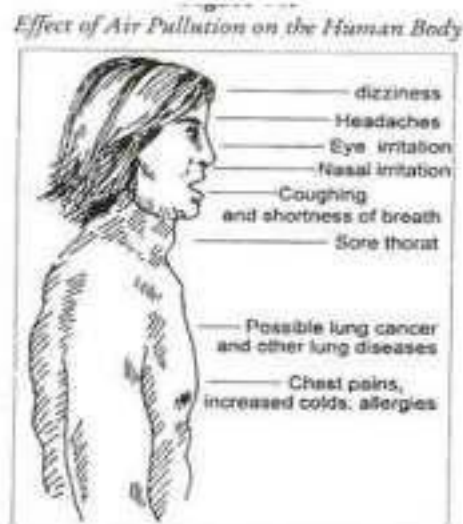
1. Effects on Human Health:

Some environmental poisons can cause acute illness and even death. Others may be harmful, but the disease may take years or even decades to appear. Air pollution mainly affects the respiratory system.

Bronchitis, emphysema, asthma and lung cancer are some of the chronic diseases caused due to exposure to polluted air. It is feared that lung cancer is caused mainly due to polluted air because carcinogens are found in it. Its mortality rate is higher in urban areas.

Figure shows the various effects of air pollution on the human body. Sulfur dioxide is the most serious and widespread air pollutant. Its lower concentration is a cause of spasms in the smooth muscle of bronchioles and its higher concentration induces increased mucus production.

Sulfur dioxide is also considered to cause cough, shortness of breath, spasm of the larynx and acute irritation to the membranes of the eyes. It also acts as an allergenic agent. When it reacts with some compounds, sulfuric acid is formed which may damage lungs.



Carbon monoxide often affects the oxygen carrying capacity of blood. Nitric oxide is reported to be a pulmonary irritant and its excess concentration may cause pulmonary haemorrhage.

Hydrogen sulfide is also toxic. Lead emitted from automobile exhausts is a cumulative poison and is dangerous particularly to children and may cause brain damage.

The particulate pollutants such as asbestos, silica, carbon, beryllium, lead, etc., are capable of exerting a noxious (fibrotic) local action in the interstitial areas of the lungs. Radioactive elements are also harmful to man and other living organisms. As described earlier, smog has a killer effect, which is also the result of air pollution. The death toll by smog varies from few persons to thousands.

In December 1952, about 4,000 persons died in London due to smog. Similar cases have been reported from London itself in 1956, 1957 and 1962 in which the death toll was between 700 and 1,000 persons. In other countries also smog deaths have been reported. In fact, the growing air pollution has now become a health hazard for man.

2. Effects on Animals and Plants:

The impact of air pollution on animals is more or less similar to that on man. Chronic poisoning results from the ingestion of forage contaminated with atmospheric pollutants. Among the metallic contaminants, arsenic, lead and molybdenum are important. Fluoride is another pollutant, which causes fluorosis among animals.

A number of livestock have been poisoned by fluorides and arsenic in North America. Bone lesions in animals due to excessive fluorides have also been reported.

Air pollution has caused widespread damage to trees, fruits, vegetables, flowers and in general, vegetation as a whole. The total annual cost of plant damage caused by air pollution in USA alone has been estimated to be in the range of 1 to 2 billion dollars. The most dramatic early instances of plant damage were seen in the total destruction of vegetation by sulfur dioxide in the areas surrounding smelters.

When the absorption of sulfur dioxide exceeds a particular level, the cells become inactive and are killed, resulting in tissue collapse and drying of leaves. Cotton, wheat, barley and apple are more sensitive to this pollutant.

Fluorides are responsible for various types of injuries to plants. The leaves of apple, apricot, fig, peach and prune are more susceptible to air borne fluorides. Fluorides seem to interfere with the photosynthesis and respiration of plants. Smog also causes injury to plants. Similar impact of ozone can be seen in the lesions to plants. Chlorine, ammonia, hydrogen sulfide, etc., are also harmful to vegetation.

3. Effects on Atmosphere:

Some of the effects of air pollution on atmospheric conditions, such as effect on ozone layer, greenhouse effect, etc., have already been discussed. There is an increase in the carbon dioxide concentration in the air due to increased combustion of fossil fuels. Carbon dioxide absorbs heat strongly and the radiative cooling effect of the earth is thus decreased.

The rising of temperatures and ozone holes are some of the problems which have attracted the attention of the scientists all over the world. These problems are not related to any region or a country but are the global problems and their impact on world climate may be hazardous to the whole world.

The local weather conditions are highly susceptible to air pollution. Its impact on temperature, humidity, rainfall and clouds is apparent. The 'smog dom' on large urban centres is the result of air pollution. Due to air pollution, visibility also reduces.

4. Other Effects:

Air pollution can also cause damage to property and materials. The smoke, grit, dust and oxides of sulphur have harmful effects on structures.

In 1972, when an oil refinery at Mathura was opened, its impact on Taj Mahal became a major issue. Sulfur dioxide is the most damaging of gaseous pollutants. Aluminum alloys, copper and copper alloys, iron and steel are corroded when exposed to contaminated air.

Hydrogen sulfide reacts with lead paints to form lead sulfide thereby producing a brown to black discolouration. The damage caused by air pollution to structures is not serious but from an aesthetic point of view, it is not desirable.

HEAT ISLANDS

An urban heat island (UHI) is an urban area or metropolitan area that is significantly warmer than its surrounding rural areas due to human activities.

An urban heat island (UHI) is an urban area or metropolitan area that is significantly warmer than its surrounding rural areas due to human activities.

Surfaces that were once permeable and moist become impermeable and dry. These changes cause urban regions to become warmer than their rural surroundings, forming an "island" of higher temperatures in the landscape. Heat islands occur on the surface and in the atmosphere.

How can we reduce the heat island effect?

1. Increase shade around your home. Planting trees and other vegetation lowers surface and air temperatures by providing shade and cooling through evapotranspiration. ...
2. Install green roofs. ...
3. Install cool roofs. ...
4. Use energy-efficient appliances and equipment. ...
5. Check on your friends, family, and neighbors.

The heat island effect occur?

Heat islands can occur year-round during the day or night. Urban-rural temperature differences are often largest during calm, clear evenings. This is because rural areas cool off faster at night than cities, which retain much of the heat stored in roads, buildings, and other structures.

warmer in the city than in rural areas?

It has been known for more than 100 years that cities are usually warmer than rural areas. This phenomenon is known as the urban heat island effect. As you can see in the graphic above, a significant portion of incoming solar energy is used to evaporate water from vegetation and soil in rural locations.

Ozone Holes

Ozone depletion occurs when chlorofluorocarbons (CFCs)—formerly found in aerosol spray cans and refrigerants—are released into the atmosphere. These gases, through several chemical reactions, cause the ozone molecules to break down, reducing ozone's ultraviolet (UV) radiation-absorbing capacity.

What is ozone, and why is it important?

Ozone is simply a molecule consisting of 3 oxygen atoms, which reacts strongly with other molecules. Ozone is created in the stratosphere when high energy uv radiation causes an O_2 molecule to split. The free oxygen atoms collide and react with other O_2 molecules to form O_3 .

Production is highest where the solar uv is the greatest eg near the tropics, but once created, the ozone is then circulated towards the poles by the atmosphere. The amount of ozone in the stratosphere can vary with location, season and even day to day climatic conditions.

The process of ozone creation is what makes the O_3 in the atmosphere very effective at shielding the Earth from harmful uv radiation, which can cause many biological problems, such as skin cancer. However, due to its high reactivity, the uv found in the troposphere at ground level can

also be dangerous as a toxic pollutant which is harmful to plants and lung tissue, and is a major cause of smog.

The discovery of the annual depletion of ozone above the Antarctic was first announced in a paper by Joe Farman, Brian Gardiner and Jonathan Shanklin which appeared in *Nature* in May 1985. Later, NASA scientists re-analyzed their satellite data and found that the whole of the Antarctic was affected.

All living cells, whether microbes, plants or animals, contain a complex molecule called DNA which carries the genetic code. This is the set of instructions which describes the structure and biochemistry of an organism. Unfortunately, DNA readily absorbs high-energy UV-B radiation and becomes damaged so that the instructions cannot be read properly. If the amount of UV-B entering the cell increases (as during the ozone hole), the risk of damage also increases and may result in malfunction or death of the organism. Some Antarctic organisms such as algae, lichens and mosses also contain a pigment called chlorophyll. This absorbs visible light as the energy source of photosynthesis for making organic compounds. Chlorophyll also absorbs UV-B light so that the system becomes bleached and non-functional. Even enzymes and other proteins are damaged by this high-energy radiation. Living organisms therefore have to protect themselves from UV-B. Humans can cover their skin with artificial sunscreens, but natural protection systems have also evolved. Many microbes, plants and other animals synthesize protective pigments. Our skin cells synthesize brown melanin to protect against sunburn (which is caused by UV-B radiation), and so do Antarctic lichens on rocks near the edge of the polar ice-cap. A variety of sunscreen pigments are produced by Antarctic organisms on land, in freshwater and in the sea. That is why exposed, snow-free rocks are often covered with bright orange and yellow lichens. Some lichens and microbes even live inside translucent rocks to shelter from high radiation levels and desiccating winds!

The Greenhouse Effect (producing global warming) and ozone depletion are two separate problems, however there are links between them. Warming at the earth's surface is caused by certain gases in the atmosphere which can trap energy from the sun. An increase in the amount of these gases produces an increase in the surface temperature. The largest increase is in carbon dioxide from burning coal, oil, gas and forests, but other gases such as methane (from cattle and rice fields) play a part. A link with ozone depletion is that CFCs are gases which also contribute to greenhouse warming.

A further link is that although the Greenhouse Effect warms the surface, it allows the higher atmosphere, where ozone is present, to cool. This means that more stratospheric clouds may form and so make the ozone hole worse.

Even if the problem of ozone depletion is solved, global warming will still remain. It will cause a rise in sea-level and change the regions where crops can be grown. The issue will be harder to tackle than ozone depletion, but is one which concerns everyone on our planet.

The only way to mend the ozone hole is to stop releasing CFCs and other ozone depleting gases into the atmosphere. The restrictions of the Montreal Protocol and its extensions are helping to do this.

Greenhouse Effect

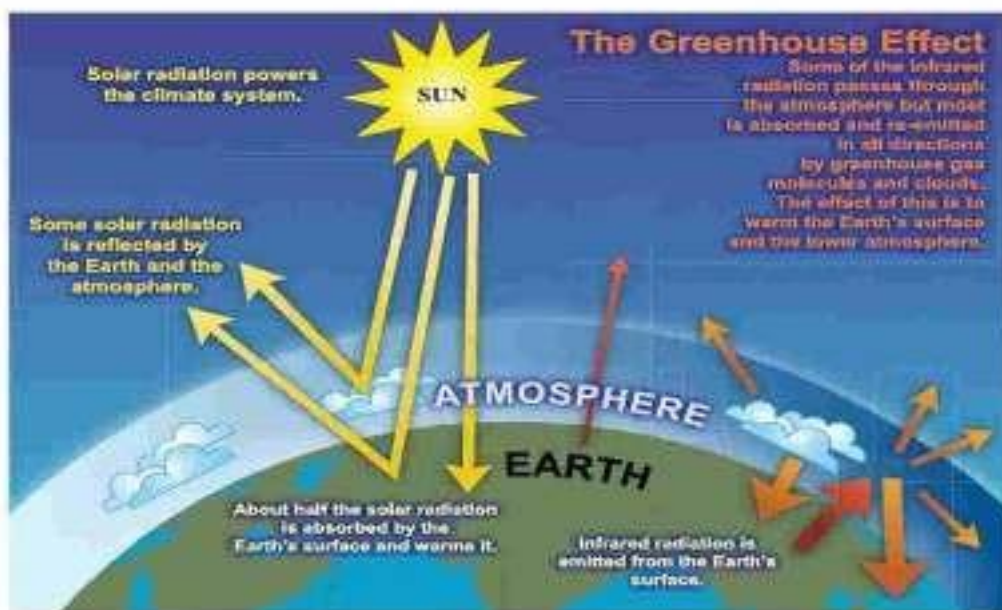
The Sun powers Earth's climate, radiating energy at very short wavelengths, predominately in the visible or near-visible (e.g., ultraviolet) part of the spectrum. Roughly one-third of the solar Energy that reaches the top of Earth's atmosphere is reflected directly back to space. The remaining two-thirds is absorbed by the surface and, to a lesser extent, by the atmosphere. To balance the absorbed incoming energy, the Earth must, on average, radiate the same amount of energy back to space. Because the Earth is much colder than the Sun, it radiates at much longer wavelengths, primarily in the infrared part of the spectrum (see Figure 1). Much of this thermal radiation emitted by the land and ocean is absorbed by the atmosphere, including clouds, and reradiated back to Earth. This is called the greenhouse effect. The glass walls in a greenhouse reduce airflow and increase the temperature of the air inside. Analogously, but through a different physical process, the Earth's greenhouse effect warms the surface of the planet.

Without the natural greenhouse effect, the average temperature at Earth's surface would be below the freezing point of water. Thus,

Earth's natural greenhouse effect makes life as we know it possible. However, human activities, primarily the burning of fossil fuels and clearing of forests, have greatly intensified the natural greenhouse effect, causing global warming. The two most abundant gases in the atmosphere, nitrogen (comprising 78% of the dry atmosphere) and oxygen (comprising 21%), exert almost no greenhouse effect. Instead, the greenhouse effect comes from molecules that are more complex and much less common. Water vapour is the most important greenhouse gas, and carbon dioxide (CO₂) is the second-most important one. Methane, nitrous oxide, ozone and several other gases present in the atmosphere in small amounts also contribute to the greenhouse effect. In the humid equatorial regions, where there is so much water vapour in the air that the greenhouse effect is very large, adding a small additional amount of CO₂ or water vapour has only a small direct impact on downward infrared radiation. However, in the cold, dry polar regions, the effect of a small increase in CO₂ or water vapour is much greater. The same is true for the cold, dry upper atmosphere where a small increase in water vapour has a greater influence on the greenhouse effect than the same change in water vapour would have near the surface. Several components of the climate system, notably the oceans and living things, affect atmospheric concentrations of greenhouse gases. A prime example of this is plants taking CO₂ out of the atmosphere and converting it (and water) into carbohydrates via photosynthesis. In the industrial era, human activities have added greenhouse gases to the atmosphere, primarily through the burning of fossil fuels and clearing of forests. Adding more of a greenhouse gas, such as CO₂, to the atmosphere intensifies the greenhouse effect, thus warming Earth's climate. The amount of warming depends on various feedback mechanisms. For example, as the atmosphere warms due to rising

levels of greenhouse gases, its concentration of water vapour increases, further intensifying the greenhouse effect. This in turn causes more warming, which causes an additional increase in

water vapour, in a self-reinforcing cycle. This water vapour feedback may be strong enough to approximately double the increase in the greenhouse effect due to the added CO₂ alone. Additional important feedback mechanisms involve clouds. Clouds are effective at absorbing infrared radiation and therefore exert a large greenhouse effect, thus warming the Earth. Clouds are also effective at reflecting away incoming solar radiation, thus cooling the Earth. A change in almost any aspect of clouds, such as their type, location, water content, cloud altitude, particle size and shape, or lifetimes, affects the degree to which clouds warm or cool the Earth. Some changes amplify warming while others diminish it. Much research is in progress to better understand how clouds change in response to climate warming, and how these changes affect climate through various feedback mechanisms.



Climate Change

The climate of the Earth is always changing. In the past it has altered as a result of natural causes. Nowadays, however, the term climate change is generally used when referring to changes in our climate which have been identified since the early part of the twentieth century. The changes we've seen over recent years and those which are predicted over the next 100 years are thought by many to be largely as a result of human behaviour rather than due to natural changes in the atmosphere.

The greenhouse effect is very important when we talk about climate change as it relates to the gases which keep the Earth warm. Although the greenhouse effect is a naturally occurring phenomenon, it is believed that the effect could be intensified by human activity and the emission of gases into the atmosphere. It is the extra greenhouse gases which humans have released which are thought to pose the strongest threat.

The Greenhouse Gases

Almost the Earth's entire atmosphere (99%) is made up of **nitrogen** (about 78%) and **oxygen** (about 21%). While both of these gases play important roles in the vast number of processes that support life on Earth, they play almost no direct role in regulating the climate. This is carried out by some of the trace gases in the remaining 1% of the atmosphere which occur in relatively small amounts:

Water vapour Carbon dioxide (produced by burning fossil fuel) Methane (a byproduct of agriculture) Nitrogen Oxides (from car exhausts) Ozone CFCs (chlorofluorocarbons from aerosol and refrigerators)

Although the proportion of the trace gases in the atmosphere appears relatively small, they can still have a big impact on climate change.

Extreme Weather

- Increasing temperatures means the World is likely to see less frosty days and cold spells, but we are expected to experience an increase in heat waves and hot spells
- Greater risk of drought in continental areas
- Increase in extreme precipitation events
- Hurricanes likely to be more intense in some parts of the World due to more rainfall and more intense winds
- An intensification of the Asian summer monsoon is expected
- There will be regional variation in temperature changes; increases will be higher over land and in the northern hemisphere
- However the temperature increase over the North Atlantic will be small

Sceptics

Some scientists disagree with the predictions for climate change, mainly because the climate had changed naturally before. In addition predicting changes to our climate is very complex and the use of computer models has raised some criticism.

On top of that, some experts believe **it is impossible to be certain about how our climate will change as it can be very unpredictable**. They also believe, the climate is supposed to change and it has done before. Many believe activities from humans cannot be to blame for changes in the climate. Some sceptics have criticised the reports of the IPCC as being based on unknown assumptions about the future and based on computer models which are not adequate for such a job.

Is It Too Late?

One of the main problems with carbon dioxide is the length of time it remains in the atmosphere as it can take around 100 years for it to disperse (even after some of it is absorbed by vegetation).

Therefore, even if we stopped CO₂ emissions immediately, the effects of what we've already done would still influence our weather for years to come.

However, carbon dioxide emissions are not going to stop and with that in mind, some change is certainly expected - the level of change depends on the amount of greenhouse gases we continue to use, which in turn is related to population growth, the use of new technologies and how much energy we use.

The European Commission has set a target adopted by all industrialised countries of cutting greenhouse gas emissions to an average of 30% below 1990 levels by 2020.

This is the magnitude of reduction which is required, the Commission believes, to have a 50/50 chance of limiting the global temperature increase to 2°C above pre-industrial levels.

By reducing the number of greenhouse gases even marginally, the rate of change should be less and therefore there will be less impact on our planet and our lives. A gradual change to our climate is easier to adapt as well - we should have more time to prepare our houses and other buildings for changes to the weather, wildlife should have more time to migrate, and the changes to our agricultural practices should be less sudden.

Most commentators say it isn't too late to address climate change and that we need to all work together to do our bit to reduce emissions and the damage we are currently doing to our local environment. We are already seeing change and will continue to do so, but if the scientific models are on the right lines, our climate will be a very different place in the next ten to twenty years to what it is now.

Global Warming Scientists say the temperature of the earth could rise by 3°C over the next 50 years. This may cause drought in some parts of the world, and floods in others, as ice at the North and South Poles begins to melt and sea level rise.

It's normal for temperatures to sometimes be cooler for many hundreds of years, and then sometimes to be warmer. But this time, humans have caused the increase, with carbon from cars and factories.

Global warming is caused by the greenhouse effect. Normally, heat from the sun warms the earth and then escapes back into space. But carbon dioxide and other gases in the atmosphere trap the sun's heat, and this is slowly making the earth warmer.

The ozone layer is a layer of gas high above the surface of the earth that helps to protect it from the sun's ultraviolet radiation, which can damage our skins and cause cancer. Scientists have discovered holes in the ozone layer, caused by substances called chlorofluorocarbons. CFCs are used in refrigerators, aerosol cans and in the manufacture of some plastic products. Some companies now make aerosols that do not contain CFCs, and these are often marked "ozone-friendly".

Tropical rainforests are being burnt and cut down because people need more land for agriculture, more hard wood for furniture and firewood. Cutting down the rainforests is dangerous for many reasons.

We need the oxygen that comes from rainforests. The forests absorb carbon dioxide in the process called photosynthesis. Without trees carbon dioxide levels will increase.

Rainforests are the homes of many insects, plants, and animals that we need for medicine and other reasons. Many plants and animals will become extinct.

They can help catch water and give it back to the earth in the form of clouds, which bring us water. The roots of trees and plants in the rainforest keep water and soil in place. Without the rainforest, there are many problems like floods and mudslides.

Do you believe that some types of extreme weather may be caused by global warming? Extreme weather (downpours/ heavy rains, monsoons, tornadoes, hurricanes, droughts) is a part of nature but I think /don't think it is connected with environmental problems.

The greenhouse effect is the temperature rise that the earth experiences. This happens because of certain gases that get energy from the sun. Without the greenhouse effect, the earth would be too cold, not warm enough for people to live. The greenhouse effect begins with the sun and the energy it radiates to the earth. The earth and the atmosphere absorb some of this energy, but the rest is radiated back into space. Naturally occurring gases in the atmosphere trap some of this energy and reflect it back, warming the earth. Scientist believes that extra gases we release into the air intensify the greenhouse effect. Evidence that scientist have is the result of some of the warmest years in recorded history.

Global warming is the increase in the average temperature of the earth's surface. The increase in greenhouse gases, fossil fuel burning, and deforestation contributes to global warming. The average temperatures have climbed about 1.4° around the world since 1880. The rate of the warming is decreasing. The IPPC (International Panel on Climate Control) reports that 11 of the past 12 years are among the dozen warmest since 1850.

Global Warming-Contributing Factors

One of the biggest contributors to global warming is the methane from cow toots and feces. The methane from the cow comes from the methanotropic bacteria in its stomach. That bacteria helps the cows digest grass, their main diet. The methane is produced from carbon in the grass. Also, another contributor to global warming is combustion of fossil fuels in cars, factories, and electricity production. The release of carbon dioxide and other gases into the atmosphere has climbed. Methane and carbon dioxide have hit their highest levels in the last 400 years.

Global Warming: Local Effects

Human activity causing changes in the environment is known as global warming. Scientist reports that 1998 was the warmest year in measured history, with 2005 coming in second place.

Readings taken from the ice cores show that the greenhouse gases carbon dioxide and methane have reached their highest levels in the past 420,000 years. Arctic sea ice is melting, and has declined in the last 30 years. In the last century, the earth's temperature has raised about 1.2-1.4 degrees Fahrenheit. Researchers report that temperature will increase 10 degrees Fahrenheit by the end of the century. Hurricanes will become more frequent because of the warm weather. Rising sea levels can flood coastal areas. Severe droughts can become more common in dry areas, and species unable to adapt to the changing areas, would have to face extinction.

Prevention Strategy

To help, you can save energy around the house by unplugging appliances you are not using, and changing regular bulbs to fluorescent light bulbs. You can drive fewer hours in your car each day and instead walk to near places that you can. Also, believe it or not, taking a shower instead of a bath can help save more water! If you recycle cans, bottles, cardboard, and paper materials that will save a lot of room in landfills. If you carry water around with you, refill it in a metal canteen so that we don't have to use and make more plastic bottle. When you use the tap, be sure not to leave it running. When washing your clothes, it's better to hang them on an outside line to dry. This will save more energy using a dryer. To keep from running to the store all the time, you can grow fruits and vegetables, and go to the store for produce and other groceries. Another thing that can help stop global warming that we all love is flying the airplane. If you and your family took local trips, that could save a lot of oil, a popularly used nonrenewable source. If you plant trees that can majorly help the earth. Most trees now are getting cut down for paper so if we plant more it may come close to evening out.

Origins of Contaminants

Indoor contamination has different origins: the occupants themselves; inadequate materials or materials with technical defects used in the construction of the building; the work performed within; excessive or improper use of normal products (pesticides, disinfectants, products used for cleaning and polishing); combustion gases (from smoking, kitchens, cafeterias and laboratories); and cross-contamination coming from other poorly ventilated zones which then diffuses towards neighbouring areas and affects them. It should be borne in mind that substances emitted in indoor air have much less opportunity of being diluted than those emitted in outdoor air, given the difference in the volumes of air available. As regards biological contamination, its origin is most frequently due to the presence of stagnant water, materials impregnated with water, exhausts and so on, and to defective maintenance of humidifiers and refrigeration towers.

Finally, contamination coming from outside must also be considered. As regards human activity, three main sources may be mentioned: combustion in stationary sources (power stations); combustion in moving sources (vehicles); and industrial processes. The five main contaminants emitted by these sources are carbon monoxide, oxides of sulphur, oxides of nitrogen, volatile organic compounds (including hydrocarbons), polycyclic aromatic hydrocarbons and particles. Internal combustion in vehicles is the principal source of carbon monoxide and hydrocarbons and is an important source of oxides of nitrogen. Combustion in stationary sources is the main origin of oxides of sulphur. Industrial processes and stationary sources of combustion generate

more than half of the particles emitted into the air by human activity, and industrial processes can be a source of volatile organic compounds. There are also contaminants generated naturally that are propelled through the air, such as particles of volcanic dust, soil and sea salt, and spores and micro-organisms. The composition of outdoor air varies from place to place, depending both on the presence and the nature of the sources of contamination in the vicinity and on the direction of the prevailing wind. If there are no sources generating contaminants, the concentration of certain contaminants that will typically be found in "clean" outdoor air are as follows: carbon dioxide, 320 ppm; ozone, 0.02 ppm; carbon monoxide, 0.12 ppm; nitric oxide, 0.003 ppm; and nitrogen dioxide, 0.001 ppm. However, urban air always contains much higher concentrations of these contaminants.

Apart from the presence of the contaminants originating from outside, it sometimes happens that contaminated air from the building itself is expelled to the exterior and then returns inside again through the intakes of the air-conditioning system. Another possible way by which contaminants may enter from the exterior is by infiltration through the foundations of the building (e.g., radon, fuel vapours, sewer effluvia, fertilizers, insecticides and disinfectants). It has been shown that when the concentration of a contaminant in the outdoor air increases, its concentration in the air inside the building also increases, although more slowly (a corresponding relationship obtains when the concentration decreases); it is therefore said that buildings exert a shielding effect against external contaminants. However, the indoor environment is not, of course, an exact reflection of the conditions outside.

Contaminants present in indoor air are diluted in the outdoor air that enters the building and they accompany it when it leaves. When the concentration of a contaminant is less in the outdoor air than the indoor air, the interchange of indoor and outdoor air will result in a reduction in the concentration of the contaminant in the air inside the building. If a contaminant originates from outside and not inside, this interchange will result in a rise in its indoor concentration, as mentioned above.

Models for the balance of amounts of contaminants in indoor air are based on the calculation of their accumulation, in units of mass versus time, from the difference between the quantity that enters plus what is generated indoors, and what leaves with the air plus what is eliminated by other means. If appropriate values are available for each of the factors in the equation, the indoor concentration can be estimated for a wide range of conditions. Use of this technique makes possible the comparison of different alternatives for controlling an indoor contamination problem.

Buildings with low interchange rates with outdoor air are classified as sealed or energy-efficient. They are energy-efficient because less cold air enters in winter, reducing the energy required to heat the air to the ambient temperature, thus cutting the cost of heating. When the weather is hot, less energy is also used to cool the air. If the building does not have this property, it is ventilated through open doors and windows by a process of natural ventilation. Although they may be closed, differences of pressure, resulting both from the wind and from the thermal gradient existing between the interior and the exterior, force the air to enter through crevices and cracks, window and door joints, chimneys and other apertures, giving rise to what is called ventilation by infiltration.

The ventilation of a building is measured in renewals per hour. One renewal per hour means that a volume of air equal to the volume of the building enters from outside every hour; in the same way, an equal volume of indoor air is expelled to the exterior every hour. If there is no forced ventilation (with a ventilator) this value is difficult to determine, although it is considered to vary between 0.2 and 2.0 renewals per hour. If the other parameters are assumed to be unchanged, the concentration of contaminants generated indoors will be less in buildings with high renewal values, although a high renewal value is not a complete guarantee of indoor air quality. Except in areas with marked atmospheric pollution, buildings that are more open will have a lower concentration of contaminants in the indoor air than those constructed in a more closed manner. However, buildings that are more open are less energy-efficient. The conflict between energy efficiency and air quality is of great importance.

Much action undertaken to reduce energy costs affects indoor air quality to a greater or lesser extent. In addition to reducing the speed with which the air circulates within the building, efforts to increase the insulation and waterproofing of the building involve the installation of materials that may be sources of indoor contamination. Other action, such as supplementing old and frequently inefficient central heating systems with secondary sources that heat or consume the indoor air can also raise contaminant levels in indoor air.

Contaminants whose presence in indoor air is most frequently mentioned, apart from those coming from outside, include metals, asbestos and other fibrous materials, formaldehyde, ozone, pesticides and organic compounds in general, radon, house dust and biological aerosols. Together with these, a wide variety of types of micro-organisms can be found, such as fungi, bacteria, viruses and protozoa. Of these, the saprophytic fungi and bacteria are relatively well known, probably because a technology is available for measuring them in air. The same is not true of agents such as viruses, rickettsiae, chlamydias, protozoa and many pathogenic fungi and bacteria, for the demonstration and counting of which no methodology is as yet available. Among the infectious agents, special mention should be made of: *Legionella pneumophila*, *Mycobacterium avium*, viruses, *Coxiella burnetii* and *Histoplasma capsulatum*; and among the allergens: *Cladosporium*, *Penicillium* and *Cytophaga*.

Investigating Indoor Air Quality

Experience so far suggests that the traditional techniques used in industrial hygiene and heating, ventilation and air-conditioning do not always provide satisfactory results at present for solving the ever more common problems of indoor air quality, although basic knowledge of these techniques permits good approximations for dealing with or reducing problems rapidly and inexpensively. The solution to problems of indoor air quality often requires, in addition to one or more experts in heating, ventilation and air-conditioning and industrial hygiene, specialists in indoor air quality control, analytical chemistry, toxicology, environmental medicine, microbiology, and also epidemiology and psychology.

When a study is carried out on indoor air quality, the objectives set for it will profoundly affect its design and the activities directed at sampling and evaluation, since in some cases procedures giving a rapid response will be required, while in others overall values will be of interest. The duration of the programme will be dictated by the time required to obtain representative samples,

and will also depend on the season and on meteorological conditions. If the aim is to carry out an exposure-effect study, in addition to long-term and short-term samples for evaluating peaks, personal samples will be required for ascertaining the direct exposure of individuals.

For some contaminants, well-validated and widely used methods are available, but for the majority this is not the case. Techniques for measuring levels of many contaminants found indoors are normally derived from applications in industrial hygiene but, given that the concentrations of interest in indoor air are usually much lower than those occurring in industrial environments, these methods are frequently inappropriate. As for the measurement methods used in atmospheric contamination, they operate with margins of similar concentrations, but are available for relatively few contaminants and present difficulties in indoor use, such as would arise, for example, with a high-volume sampler for determining particulate matter, which on the one hand would be too noisy and on the other could modify the quality of the indoor air itself.

The determination of contaminants in indoor air is usually carried out by using different procedures: with continuous monitors, whole-time active samplers, whole-time passive samplers, direct sampling and personal samplers. Adequate procedures exist at present for measuring levels of formaldehyde, oxides of carbon and nitrogen, volatile organic compounds and radon, among others. Biological contaminants are measured using techniques of sedimentation on open culture plates or, more frequently nowadays, by using active systems that cause the air to impact on plates containing nutrient, which are subsequently cultured, the quantity of micro-organisms present being expressed in colony-forming units per cubic metre.

When a problem of indoor air quality is being investigated, it is usual to design beforehand a practical strategy consisting of an approximation in phases. This approximation begins with a first phase, the initial investigation, which can be carried out using industrial hygiene techniques. It must be structured so that the investigator does not need to be a specialist in the field of indoor air quality in order to carry out his work. A general inspection of the building is undertaken and its installations are checked, particularly as regards the regulation and adequate functioning of the heating, ventilation and air-conditioning system, according to the standards set at the time of its installation. It is important in this respect to consider whether the persons affected are able to modify the conditions of their surroundings. If the building does not have systems of forced ventilation, the degree of effectiveness of the existing natural ventilation must be studied. If after revision—and adjustment if necessary—the operational conditions of the ventilation systems are adequate for the standards, and if despite this the complaints continue, a technical investigation of a general kind will have to ensue to determine the degree and nature of the problem. This initial investigation should also allow an assessment to be made as to whether the problems can be considered solely from the functional point of view of the building, or whether the intervention of specialists in hygiene, psychology or other disciplines will be necessary.

If the problem is not identified and resolved in this first phase, other phases can follow involving more specialized investigations concentrating on potential problems identified in the first phase. The subsequent investigations may include a more detailed analysis of the heating, ventilation and air-conditioning system of the building, a more extensive evaluation of the presence of materials suspected of emitting gases and particles, a detailed chemical analysis of the ambient air in the building and medical or epidemiological assessments to detect signs of disease.

As regards the heating, ventilation and air-conditioning system, the refrigeration equipment should be checked in order to ensure that there is no microbial growth in them or accumulation of water in their drip trays, the ventilation units must be checked to see that they are functioning correctly, the air intake and return systems must be examined at various points to see that they are watertight, and the interior of a representative number of ducts must be checked to confirm the absence of micro-organisms. This last consideration is particularly important when humidifiers are used. These units require particularly careful programmes of maintenance, operation and inspection in order to prevent the growth of micro-organisms, which can propagate themselves throughout the air-conditioning system.

The options generally considered for improving indoor air quality in a building are the elimination of the source; its insulation or independent ventilation; separating the source from those who may be affected; general cleaning of the building; and increased checking and improvement of the heating, ventilation and air-conditioning system. This may require anything from modifications at particular points to a new design. The process is frequently of a repetitive nature, so that the study has to be started again several times, using more sophisticated techniques on each occasion.

Finally, it should be emphasized that, even with the most complete investigations of indoor air quality, it may be impossible to establish a clear relationship between the characteristics and composition of the indoor air and the health and comfort of the occupants of the building under study. Only the accumulation of experience on the one hand, and the rational design of ventilation, occupation and compartmentalization of buildings on the other, are possible guarantees from the outset of obtaining indoor air quality that is adequate for the majority of the occupants of a building.

NATURE AND SOURCES OF INDOOR CHEMICAL CONTAMINANTS

Characteristic Chemical Pollutants

Chemical contaminants of the indoor air can occur as gases and vapours (inorganic and organic) and particulates. Their presence in the indoor environment is the result of entry into the building from the outdoor environment or their generation within the building. The relative importance of these indoor and outdoor origins differs for different pollutants and may vary over time.

The major chemical pollutants commonly found in the indoor air are the following:

1. Carbon dioxide (CO₂), which is a metabolic product and often used as an indicator of the general level of air pollution related to the presence of humans indoors
2. Carbon monoxide (CO), nitrogen oxides (NO_x) and sulphur dioxide (SO₂), which are inorganic combustion gases formed predominantly during the combustion of fuels and ozone (O₃), which is a product of photochemical reactions in polluted atmospheres but may also be released by some indoor sources
3. Organic compounds that originate from a variety of indoor sources and outdoors. Hundreds of organic chemicals occur in indoor air although most are present at very low concentrations.

These can be grouped according to their boiling points and one widely used classification, shown in table 44.1, identifies four groups of organic compounds: (1) very volatile organic compounds (VVOC); (2) volatile (VOC); (3) semi-volatile (SVOC); and (4) organic compounds associated with particulate matter (POM). Particle-phase organics are dissolved in or adsorbed on particulate matter. They may occur in both the vapour and particle phase depending on their volatility. For example, polyaromatic hydrocarbons (PAHs) consisting of two fused benzene rings (e.g., naphthalene) are found principally in the vapour phase and those consisting of five rings (e.g., benz(a)pyrene) are found predominantly in the particle phase.

An important characteristic of indoor air contaminants is that their concentrations vary both spatially and temporally to a greater extent than is common outdoors. This is due to the large variety of sources, the intermittent operation of some of the sources and the various sinks present.

Concentrations of contaminants that arise principally from combustion sources are subject to very large temporal variation and are intermittent. Episodic releases of volatile organic compounds due to human activities such as painting also lead to large variations in emission with time. Other emissions, such as formaldehyde release from wood-based products may vary with temperature and humidity fluctuations in the building, but the emission is continuous. The emission of organic chemicals from other materials may be less dependent upon temperature and humidity conditions but their concentrations in indoor air will be greatly influenced by ventilation conditions.

Spatial variations within a room tend to be less pronounced than temporal variations. Within a building there may be large differences in the case of localized sources, for example, photocopiers in a central office, gas cookers in the restaurant kitchen and tobacco smoking restricted to a designated area.

Sources within the Building

Elevated levels of pollutants generated by combustion, particularly nitrogen dioxide and carbon monoxide in indoor spaces, usually result from unvented, improperly vented or poorly maintained combustion appliances and the smoking of tobacco products. Unvented kerosene and gas space heaters emit significant quantities of CO, CO₂, NO_x, SO₂, particulates and formaldehyde. Gas cooking stoves and ovens also release these products directly into the indoor air. Under normal operating conditions, vented gas-fired forced air heaters and water heaters should not release combustion products into the indoor air. However flue gas spillage and backdrafting can occur with faulty appliances when the room is depressurized by competing exhaust systems and under certain meteorological conditions.

Environmental tobacco smoke

Indoor air contamination from tobacco smoke results from sidestream and exhaled mainstream smoke usually referred to as environmental tobacco smoke (ETS). Several thousand different constituents have been identified in tobacco smoke and the total quantities of individual components vary depending upon the type of cigarette and the conditions of smoke generation.

The main chemicals associated with ETS are nicotine, nitrosamines, PAHs, CO, CO₂, NO_x, acrolein, formaldehyde and hydrogen cyanide.

Building materials and furnishings

The materials which have received greatest attention as sources of indoor air pollution have been wood-based boards containing urea formaldehyde (UF) resin and UF cavity wall insulation (UFFI). Emission of formaldehyde from these products results in elevated levels of formaldehyde in buildings and this has been associated with many complaints of poor indoor air quality in developed countries, particularly during the late 1970s and early 1980s. Table 44.2 gives examples of materials that release formaldehyde in buildings. These show that the highest emission rates may be associated with the wood-based products and UFFI which are products often used extensively in buildings. Particleboard is manufactured from fine (about 1 mm) wood particles which are mixed with UF resins (6 to 8 weight%) and pressed into wood panels. It is widely used for flooring, wall panelling, shelving and components of cabinets and furniture. The plies of hardwood are bonded with UF resin and are commonly used for decorative wall panelling and components of furniture. Medium-density fibreboard (MDF) contains finer wood particles than those used in particleboard and these are also bound with UF resin. MDF is most often used for furniture. The primary source of formaldehyde in all these products is the residual formaldehyde trapped in the resin as a result of its presence in excess needed for the reaction with urea during the manufacture of the resin. Release is therefore highest when the product is new, and declines at a rate dependent upon product thickness, initial emission strength, and presence of other formaldehyde sources, local climate and occupant behavior. The initial decline rate of emissions may be 50% over the first eight to nine months, followed by a much slower rate of decline. Secondary emission can occur due to hydrolysis of the UF resin and hence emission rates increase during periods of elevated temperature and humidity. Considerable efforts by manufacturers have led to the development of lower-emitting materials by use of lower ratios (i.e. closer to 1:1) of urea to formaldehyde for resin production and the use of formaldehyde scavengers. Regulation and consumer demand have resulted in widespread use of these products in some countries.

Formaldehyde emission rates from a variety of construction material furnishings and consumer products

	Range of formaldehyde emission rates (µg/m ² /day)
Medium-density fibreboard	17,600-55,000
Hardwood plywood panelling	1,500-34,000
Particleboard	2,000-25,000
Urea-formaldehyde foam insulation	1,200-19,200
Softwood plywood	240-720
Paper products	260-680

Fibreglass products	400-470
Clothing	35-570
Resilient flooring	<240
Carpeting	0-65
Upholstery fabric	0-7

Building materials and furnishings release a wide range of other VOCs which have been the subject of increasing concern during the 1980s and 1990s. The emission can be a complex mixture of individual compounds, though a few may be dominant. A study of 42 building materials identified 62 different chemical species. These VOCs were primarily aliphatic and aromatic hydrocarbons, their oxygen derivatives and terpenes. The compounds with the highest steady-state emission concentrations, in decreasing order, were toluene, m-xylene, terpene, n-butylacetate, n-butanol, n-hexane, p-xylene, ethoxyethylacetate, n-heptane and o-xylene. The complexity of emission has resulted in emissions and concentrations in air often being reported as the total volatile organic compound (TVOC) concentration or release. Table 44.3 gives examples of rates of TVOC emission for a range of building products. These show that significant differences in emissions exist between products, which means that if adequate data were available materials could be selected at the planning stage to minimize the VOC release in newly constructed buildings.

Total volatile organic compound (TVOC) concentrations and emission rates associated with various floor and wall coverings and coatings.

Type of material	Concentrations (mg/m ³)	Emission rate (mg/m ² hr)
Wallpaper		
Vinyl and paper	0.95	0.04
Vinyl and glass fibres	7.18	0.30
Printed paper	0.74	0.03
Wall covering		
Hessian	0.09	0.005
PVCa	2.43	0.10
Textile	39.60	1.60
Textile	1.98	0.08
Floor covering		
Linoleum	5.19	0.22
Synthetic fibres	1.62	0.12

Rubber	28.40	1.40
Soft plastic	3.84	0.59
Homogeneous PVC	54.80	2.30
Coatings		
Acrylic latex	2.00	0.43
Varnish, clear epoxy	5.45	1.30
Varnish, polyurethane, two-component	28.90	4.70
Varnish, acid-hardened	3.50	0.83

aPVC, polyvinyl chloride.

Wood preservatives have been shown to be a source of pentachlorophenol and lindane in the air and in dust within buildings. They are used primarily for timber protection for outdoor exposure and are also used in biocides applied for treatment of dry rot and insect control.

Consumer products and other indoor sources

The variety and number of consumer and household products change constantly, and their chemical emissions depend on use patterns. Products that may contribute to indoor VOC levels include aerosol products, personal hygiene products, solvents, adhesives and paints. Table 44.4 illustrates major chemical components in a range of consumer products.

Table 44.4 Components and emissions from consumer products and other sources of volatile organic compounds (VOC)

Source	Compound	Emission rate
Cleaning agents and pesticides	Chloroform	15 µg/m ² .h
	1,2-Dichloroethane	1.2 µg/m ² .h
	1,1,1-Trichloroethane	37 µg/m ² .h
	Carbon tetrachloride	71 µg/m ² .h
	m-Dichlorobenzene	0.6 µg/m ² .h
	p-Dichlorobenzene	0.4 µg/m ² .h

	n-Decane	0.2 µg/m ² .h
	n-Undecane	1.1 µg/m ² .h
Moth cake	p-Dichlorobenzene	14,000 µg/m ² .h
Dry-cleaned clothes	Tetrachloroethylene	0.5-1 mg/m ² .h
Liquid floor wax	TVOC (trimethylpentene and dodecane isomers)	96 g/m ² .h
Paste leather wax	TVOC (pinene and 2-methyl- 1-propanol)	3.3 g/m ² .h
Detergent	TVOC (limonene, pinene and myrcene)	240 mg/m ² .h
Human emissions	Acetone	50.7 mg/day
	Acetaldehyde	6.2 mg/day
	Acetic acid	19.9 mg/day
	Methyl alcohol	74.4 mg/day
Copy paper	Formaldehyde	0.4 µg/form
Steam humidifier	Diethylaminoethanol, cyclohexylamine	-
Wet copy machine	2,2,4-Trimethylheptane	-
Household solvents	Toluene, ethyl benzene	-
Paint removers	Dichloromethane, methanol	-
Paint removers	Dichloromethane, toluene, propane	-
Fabric protector	1,1,1-Trichloroethane, propane, petroleum distillates	-
Latex paint	2-Propanol, butanone, ethylbenzene, toluene	-
Room freshener	Nonane, decane, ethylheptane, limonene	-
Shower water	Chloroform, trichloroethylene	-

Other VOCs have been associated with other sources. Chloroform is introduced into the indoor air chiefly as a result of dispensing or heating tap water. Liquid process copiers release isodecanes into the air. Insecticides used to control cockroaches, termites, fleas, flies, ants and mites are widely used as sprays, fogging devices, powders, impregnated strips, bait and pet collars. Compounds include diazinon, paradichlorobenzene, pentachlorophenol, chlordane, malathion, naphthalene and aldrin.

Other sources include occupants (carbon dioxide and odours), office equipment (VOCs and ozone), mould growth (VOCs, ammonia, carbon dioxide), contaminated land (methane, VOCs) and electronic air cleaners and negative ion generators (ozone).

Contribution from the external environment

Table shows typical indoor-outdoor ratios for the major types of pollutant that occur in indoor air and average concentrations measured in outdoor air of urban areas in the United Kingdom. Sulphur dioxide in the indoor air is normally of outdoor origin and results from both natural and anthropogenic sources. Combustion of fossil fuels containing sulphur and smelting of sulphide ores are major sources of sulphur dioxide in the troposphere. Background levels are very low (1 ppb) but in urban areas maximum hourly concentrations may be 0.1 to 0.5 ppm. Sulphur dioxide can enter a building in air used for ventilation and can infiltrate through small gaps in the building structure. This depends upon the air tightness of the building, meteorological conditions and internal temperatures. Once inside, the incoming air will mix and be diluted by the indoor air. Sulphur dioxide that comes into contact with building and furnishing materials is adsorbed and this can significantly reduce the indoor concentration with respect to the outdoors, particularly when outdoor sulphur dioxide levels are high.

Major types of chemical indoor air contaminant and their concentrations in the urban United Kingdom

Substance/group of substances	Ratio of concentrations indoors/outdoors	Typical urban concentrations
Sulphur dioxide	~0.5	10-20 ppb
Nitrogen dioxide	≤5-12 (indoor sources)	10-45 ppb
Ozone	0.1-0.3	15-60 ppb
Carbon dioxide	1-10	350 ppm
Carbon monoxide	≤5-11 (indoor source)	0.2-10 ppm
Formaldehyde	≤10	0.003 mg/m ³
Other organic compounds	1-50	5.2 µg/m ³
Toluene		6.3 µg/m ³ 5.6 µg/m ³

Benzene		
m-and p-xylenes		
Suspended particles	0.5-1 (excluding ETSa) 2-10 (including ETS)	50-150 µg/m ³

a ETS, environmental tobacco smoke.

Nitrogen oxides are a product of combustion, and major sources include automobile exhaust, fossil fuel-fired electric generating stations and home space heaters. Nitric oxide (NO) is relatively non-toxic but can be oxidized to nitrogen dioxide (NO₂), particularly during episodes of photochemical pollution. Background concentrations of nitrogen dioxide are about 1 ppb but may reach 0.5 ppm in urban areas. The outdoors is the major source of nitrogen dioxide in buildings without unvented fuel appliances. As with sulphur dioxide, adsorption by internal surfaces reduces the concentration indoors compared with that outdoors.

Ozone is produced in the troposphere by photochemical reactions in polluted atmospheres, and its generation is a function of intensity of sunlight and concentration of nitrogen oxides, reactive hydrocarbons and carbon monoxide. At remote sites, background ozone concentrations are 10 to 20 ppb and can exceed 120 ppb in urban areas in summer months. Indoor concentrations are significantly lower due to reaction with indoor surfaces and the lack of strong sources.

Carbon monoxide release as a result of anthropogenic activities is estimated to account for 30% of that present in the atmosphere of the northern hemisphere. Background levels are approximately 0.19 ppm and in urban areas a diurnal pattern of concentrations is related to use of the motor vehicle with peak hourly levels ranging from 3 ppm to 50 to 60 ppm. It is a relatively unreactive substance and so is not depleted by reaction or adsorption on indoor surfaces. Indoor sources such as unvented fuel appliances therefore add to the background level otherwise due to the outdoor air.

The indoor-outdoor relationship of organic compounds is compound-specific and may vary over time. For compounds with strong indoor sources such as formaldehyde, indoor concentrations are usually dominant. For formaldehyde outdoor concentrations are typically below 0.005 mg/m³ and indoor concentrations are ten times higher than outdoor values. Other compounds such as benzene have strong outdoor sources, petrol-driven vehicles being of particular importance. Indoor sources of benzene include ETS and these result in mean concentrations in buildings in the United Kingdom being 1.3 times higher than those outdoors. The indoor environment appears not to be a significant sink for this compound and it is therefore not protective against benzene from outdoors.

Typical Concentrations in Buildings

Carbon monoxide concentrations in indoor environments commonly range from 1 to 5 ppm. Table summarizes results reported in 25 studies. Concentrations are higher in the presence of environmental tobacco smoke, though it is exceptional for concentrations to exceed 15 ppm.

Summary of field measurements of nitrogen oxides (NO_x) and carbon monoxide (CO)

Site	NO _x values (ppb)	CO mean values (ppm)
Offices		
Smoking	42-51	1.0-2.8
Control	-	1.2-2.5
Other workplaces		
Smoking	NDa-82	1.4-4.2
Control	27	1.7-3.5
Transportation		
Smoking	150-330	1.6-3.3
Control	-	0-5.9
Restaurants and cafeterias		
Smoking	5-120	1.2-9.9
Control	4-115	0.5-7.1
Bars and taverns		
Smoking	195	3-17
Control	4-115	~1-9.2

aND = not detected.

UNIT II

BASIC ATMOSPHERIC PROPERTIES

The Earth's atmosphere is the gaseous envelope that surrounds our planet. While there is no exact upper limit for the extent of the atmosphere, we think of the exosphere as the region where our atmosphere merges into space, occurring at an altitude of approximately 500 km.

Our atmosphere is composed of different gases, the two most abundant of which are N₂ and O₂. N₂ accounts for 79% of the atmosphere and O₂ for 20%. The subscript "2"s indicate that the form of oxygen and nitrogen found commonly in the atmosphere are molecules of oxygen and nitrogen in which two atoms of N (and O) are bound together. We will study later that oxygen can exist in a triatomic form (O₃) called ozone which has the significant property of absorbing ultraviolet solar radiation.

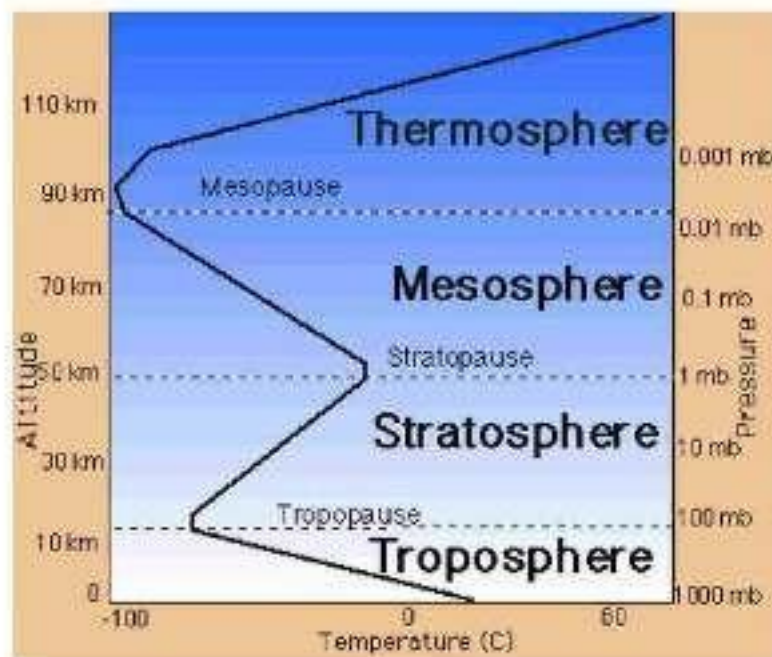
While oxygen and nitrogen are by far the most abundant molecules in our atmosphere, they are not the only important atmospheric constituents. Water vapor, whose abundance can vary from almost nothing in the driest of locales to about 4% of the atmosphere, is responsible for the formation of all clouds (when water vapor condenses into liquid droplets or freezes into ice crystals) and all the precipitation we receive on Earth. Additionally, water vapor is a greenhouse gas, and plays a key role in the heat budget of the Earth.

Another significant greenhouse gas is carbon dioxide CO₂. As you have likely read, CO₂ is emitted as a byproduct of many industrial processes, and its increasing abundance in the atmosphere is the source of much concern regarding future climate change via global warming. To understand weather and climate on the Earth, we must first understand the nature and properties of gases. To do that, we will focus and illustrate some of the most important concepts relating to the study of weather. Temperature

Temperature Everyone knows this word and could easily provide a definition for it. Most people would argue that temperature is 'how hot or cold we feel on a given day.' However, the definition of temperature is much more specific than this, and requires us to think about processes occurring on the molecular level. Temperature measures the random speed at which molecules move; a higher temperature means that molecules are moving more rapidly in their random motion, a lower temperature means they are moving more slowly.

Temperature Profile of the Earth

The temperature of the Earth varies as one moves upward from the surface of the Earth. Imagine you were a meteorologist rising in the Earth's atmosphere, taking temperature measurements as high as you could go (actually, you could not go as high as indicated here, but we can imagine doing so). If you plotted your results, you would get a graph like the one below:



This graph shows a great deal of interesting information. First, notice the axes. Altitude is shown on the left (in km), temperature is shown on the bottom (in degrees Centigrade), and the pressure of the atmosphere is shown on the right vertical axis, in a unit called millibars, abbreviated as mb. This shows that the pressure of the atmosphere decreases as you rise higher; meteorologists would say the pressure decreases with (increasing) height.

This graph shows that the vertical variation of the Earth's temperature is not quite so simple to describe. There are regions where the temperature increases with height, and regions where the temperature decreases with height. Notice also that the Earth's atmosphere is divided into different layers based upon whether the temperature is increasing or decreasing with height.

The lowest of these, the troposphere is where we live, and where essentially all of our weather occurs. If you took a full semester weather course, you would spend almost all of your time studying processes and events occurring in the troposphere. Notice that on average, temperature decreases with height in the troposphere at the rate of approximately $6.5^{\circ}\text{C}/\text{km}$, although this rate can vary from day to day and place to place, sometimes quite dramatically.

The region above the troposphere is the stratosphere, and in this region, temperatures actually increase with increasing height. What explains this behavior which is so different from our common experience in the troposphere? In the troposphere, sunlight is not absorbed by any gases to any appreciable degree, so the gases in the troposphere are not significantly warmed by the Sun. Rather, sunlight reaches the surface of the Earth, warms the Earth, and the Earth emits energy back into the atmosphere. The troposphere is thus not heated by the Sun directly, but by the Earth. So the farther one gets from the source of direct heating, in the case of the troposphere this is the Earth, the cooler it gets.

The stratosphere, though, is directly warmed by the Sun. The stratosphere has a higher concentration of ozone than the troposphere (and even though this concentration is one part of ozone per million), the stratosphere is sometimes called the ozone layer. Ozone, as noted above, is a very effective absorber of solar ultraviolet radiation. When stratospheric ozone absorbs this energy, the stratosphere warms, and of course, the ultraviolet energy does not reach the surface of the Earth since it has been absorbed in the stratosphere.

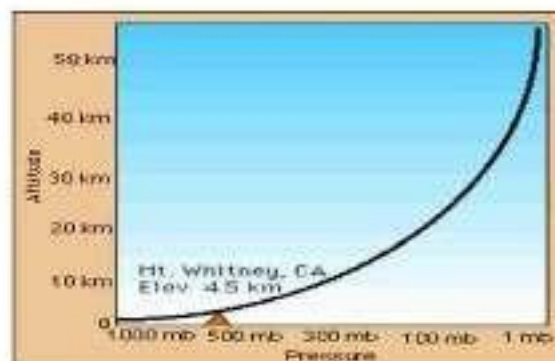
Many atmospheric scientists are concerned that the amount of ozone is being decreased because of the release in past decades of certain molecules called chlorofluorocarbons, molecules contained in aerosol sprays and refrigeration units. These molecules have been observed to rise into the stratosphere, where they react with ozone and convert it to O_2 , a much less efficient absorber of ultraviolet radiation.

The next layer up is the mesosphere. Air is very thin at this height, and almost no attention is given this region of the atmosphere, causing some scientists to dub it the "ignosphere."

The thermosphere is the region of the atmosphere where the most energetic solar energy is absorbed. Air is even thinner here than in the mesosphere, still, there are sufficient numbers of O and N atoms to absorb solar X-rays and gamma rays. If you look at the temperature scale, you might think it would feel very hot in the thermosphere. Actually, if you stuck your bare hand out in this region (and it managed not to explode because of the low external pressure), you would feel severe cold. Understanding this requires we use our definition of temperature: a measurement of the random speed of molecules and atoms. In the thermosphere, atoms move very rapidly as they absorb high energy solar radiation, however, the atmosphere is very thin at this altitude. So, while each atom has a lot of individual energy, there are so few atoms that the total energy, and hence temperature, of the region is low. Another way to think of this is to imagine sticking your hand out in the thermosphere; because there are so few atoms, your hand would radiate its energy to space before receiving any energy via collision with a fast moving molecule. This thought experiment nicely shows the difference between temperature and total energy content.

Pressure

One of the most important of all concepts needed to understand the nature of weather is that of pressure. Pressure is another word that is used commonly in everyday language (I can't take all this pressure); in science, pressure has a very specific meaning. We should think of pressure at a location as the weight of the column of air above that location. The diagram below shows how the pressure of the atmosphere decreases with height.



Be careful to observe that the horizontal axis on this graph shows pressures decreasing to the right.

The vertical profile of pressure is not surprising; if pressure is the weight of the column of air above you, there is simply less air above you as you go higher into the atmosphere.

Thus, when we hear on the news that there is a high pressure system somewhere that means that the column of air above that city is greater than the weight of columns of air in neighboring cities. The importance of this becomes more evident when we learn about one of the most important properties of fluids (both gases and liquids are fluids): whenever a force is exerted on a fluid, that force is transmitted equally in all directions in the fluid. A simple and everyday example of this is a toothpaste tube. We know that if we squeeze in the middle of a tooth paste tube, we can cause toothpaste to squirt out the end, even if the direction of our force was perpendicular to the long axis of the toothpaste. (Try moving a desk like this; if you push straight down on the desk, do you think you can make it move in a direction perpendicular to the force? Of course not, but this is exactly what happens with fluids—a force in any direction is transmitted equally in all other directions.) If you use a needle and puncture holes all over your tube and then squeeze, you will see toothpaste ooze out of every hole you have made (as long as the holes are large enough).

How does this apply to our study of weather? Suppose there are two cities at different pressures (one of course will have a higher pressure than the other). This means that the weight of the atmosphere is greater at one place than the other, and we would expect a greater downward force where the pressure is higher. We will experience this, but what is also true is that this greater force will act in all directions, including horizontally (parallel to the surface of the Earth). If we imagine a balloon of air (these are called parcels by meteorologists) situated somewhere between these two cities, this balloon will feel a force pushing it from both sides; however since the force coming from the side of the higher pressure will be greater, the balloon will feel a net force acting in the direction from high to low.

This simple thought experiment shows us that winds are caused by pressure differences; the speed of the wind depends on the nature of this pressure difference, the more drastic the pressure change, the faster the winds.

On news casts you are likely to hear pressure measured in the unit of 'inches of mercury'; this unit derives from the days of the first barometers. You can see a diagram of these early barometers and an explanation for how the height of mercury measure air pressure. The unit of pressure that will be used on all weather maps we will study is the millibar, abbreviated as mb. The average surface pressure on the Earth is 1013.25 mb. Interestingly, surface pressures on the Earth do not vary too much from this value; changes in surface pressure of just a few percent are enough to generate significant winds and pressure systems. For instance, the highest value of surface pressure ever recorded was 1084 mb (in Siberia), and the lowest surface pressure ever measured was 890 mb in the eye of a massive typhoon (Pacific hurricane). A low pressure system where the pressure is 20 or 30 mb less than surrounding regions would represent a major storm system indeed.

Relative Humidity

Humidity is a general measure for the amount of water vapor in the atmosphere; the more water vapor, the higher the humidity. There are a number of ways of defining humidity, but for purposes of our course we will focus on **relative humidity**. The word 'relative' means that we are making a comparison, or constructing a ratio. In this case, we are comparing how much water vapor is present in the atmosphere to how much water vapor it would take to **saturate** the atmosphere.

To understand the concept of saturation, consider this thought experiment. Suppose you have a large mug of very hot tea or coffee and you stir one teaspoon of sugar into the mug. The sugar will completely dissolve. Now add another teaspoon and if the mug is large enough the sugar will completely dissolve. You can continue this process until you get to the point that no more sugar will dissolve, and any new sugar that is added to the liquid results in an equal amount of sugar falling to the bottom of the mug as solid precipitate. At this point, we say the mug is saturated with sugar.

Suppose we try the experiment again with the same amount of liquid, only this time imagine the liquid has been left out for some time and has cooled down. Your experience should tell you that it will require much less sugar to saturate this cooler liquid.

Similarly, the atmosphere can become saturated with water vapor. At a particular temperature, there is a maximum amount of water vapor that can be dissolved in the atmosphere; attempting to add any more water vapor to the atmosphere will result in some water vapor returning to the liquid state. Just as in our thought example, the amount of water vapor it takes to saturate the atmosphere increases as the temperature of the atmosphere increases.

Relative humidity can then be expressed as:

$$\text{Relative Humidity} = [(\text{Actual Vapor in Air})/(\text{Saturation Vapor of the Air})] \times 100\%$$

This ratio is always expressed as a percentage. A higher value of RH means that the atmosphere is nearing saturation, a lower value means the atmosphere is far from saturation. A RH of 100% means that the amount of vapor in the atmosphere equals the amount of vapor required to saturate the atmosphere. (In almost all cases) when the RH reaches 100%, water droplets begin to condense from the vapor, and this initiates the process of cloud formation. (If the RH reaches 100% on or very near the ground, we will observe the formation of dew. Fogs occur when the air nearest the ground saturates and condenses; fogs are merely clouds on the ground.)

Let's look at the definition of RH again. The numerator--how much vapor is actually in the air at the moment of observation--can change as more or less water vapor is added to the atmosphere. This amount doesn't change too dramatically unless a frontal system moves through the area, changing the nature of the air in your location. The denominator--the amount of vapor required to saturate the atmosphere--does change much more readily. This occurs because the amount of vapor required to saturate the air depends on the temperature of the air, and the temperature of the air is in constant flux.

Given this information about RH, when during the day will we measure the highest values of RH? The lowest values of RH? Can you explain why dew formation occurs in the early morning hours and not in the late afternoon?

One of the important topics in the study of weather is the formation of clouds. As noted above, clouds form when a layer of air above the Earth's surface becomes saturated, in other words, when the RH of the atmosphere at some height reaches 100%. If we look to our equation defining RH again, we see that there are two general ways in which the RH can increase to reach 100%. The first is to increase the amount of water vapor in the atmosphere until the atmosphere becomes saturated, and the second is to lower the temperature of the air until the saturation vapor pressure decreases until the amount of vapor in the air can saturate the now cooler atmosphere. This second mechanism is the one that usually occurs in the atmosphere. You may have heard on weather broadcasts the term dew point. The dew point is the temperature to which you would have to cool the atmosphere to saturate the atmosphere without adding or subtracting any vapor.

The inclusion of these wastes, therefore, may require longer detention times and/or equipment with larger capacities, resulting in higher per unit treatment costs.

Industrial wastes often contain high levels of pollutants, such as heavy metals, grease, cyanide, and many organic compounds, which are incompatible with certain biological treatment technologies.

The efficiency of biological processes may be lowered with the presence of certain pollutants, thereby creating the potential for increased pass-through of pollutants and possible violation of the municipality's National Pollutant Discharge Elimination System (NPDES) permit for direct discharge.

Sufficient levels of some pollutants may even cause a complete breakdown.

To prevent such a breakdown, the treatment facility may have to substitute higher cost treatment alternatives or require additional treatment processes not otherwise necessary for treatment of the municipal wastes, and therefore, not subject to Federal subsidies.

.Meteorology and Air Pollution

The earth's atmosphere is about 100 miles deep. That thickness and volume sometimes are suggested to be enough to dilute all of the chemicals and particles thrown into it. However, 95% of this air mass is within 12 miles of the earth's surface. This 12-mile depth contains the air we breathe as well as the pollutants we emit.

This layer, called the troposphere, is where we have our weather and air pollution problems. Weather patterns determine how air contaminants are dispersed and move through the troposphere, and thus determine the concentration of a particular pollutant that is breathed or the amount deposited on vegetation.

An air pollution problem involves three parts:

1. The pollution source
2. The movement or dispersion of the pollutant
3. The recipient

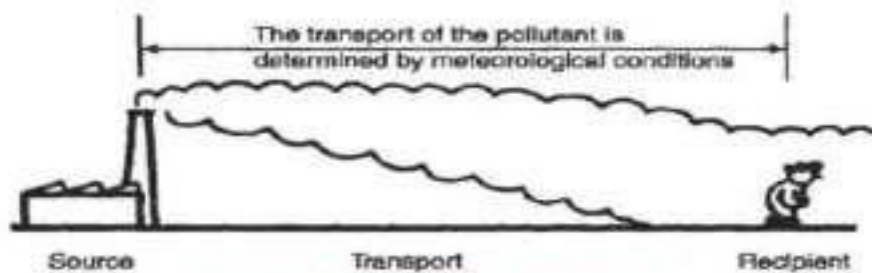


Figure 1. Meteorology of air pollutants.

This chapter concerns itself with the transport mechanism: how the pollutants travel through the atmosphere.

The environmental engineer should be conversant enough with some basic meteorology to be able to predict the dispersion of air pollutants.

BASIC METEOROLOGY

Pollutants circulate the same way the air in the troposphere circulates.

Air movement is caused by solar radiation and the irregular shape of the earth and its surface, which causes unequal absorption of heat by the earth's surface and atmosphere.

This differential heating and unequal absorption creates a dynamic system. The dynamic thermal system of the earth's atmosphere also yields differences in barometric pressure, associated with low-pressure systems with both hot and cold weather fronts.

Air movement around low-pressure fronts in the Northern Hemisphere is counterclockwise and vertical winds are upward, where condensation and precipitation take place.

High-pressure systems bring sunny and calm weather – stable atmospheric conditions – with winds (in the Northern Hemisphere) spiraling clockwise and downward.

Low- and high-pressure systems, commonly called cyclones and anticyclones, are illustrated in Fig. 2.

Anticyclones are weather patterns of high stability, in which dispersion of pollutants is poor, and are often precursors to air pollution episodes.

The high-pressure area indicates a region of stable air, where pollutants build up and do not disperse.

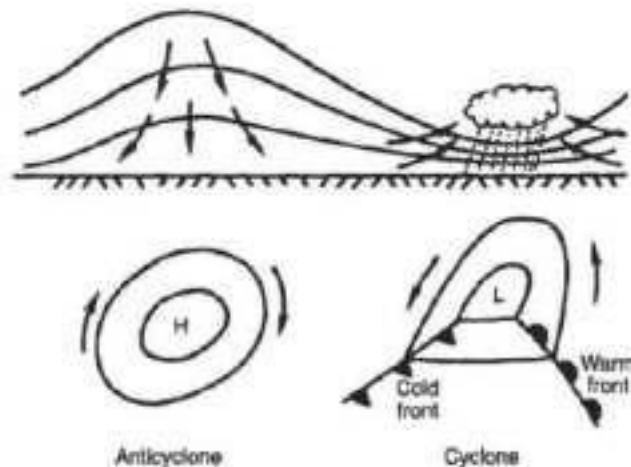


Figure 2. Anticyclone and cyclone.

Air quality management involves both control of air pollution sources and effective dispersion of pollutants in the atmosphere.

HORIZONTAL DISPERSION OF POLLUTANTS

The earth receives light energy at high frequency from the sun and converts this to heat energy at low frequency, which is then radiated back into space.

Heat is transferred from the earth's surface by radiation, conduction, and convection.

Radiation is direct transfer of energy and has little effect on the atmosphere.

Conduction is the transfer of heat by physical contact (the atmosphere is a poor conductor since the air molecules are relatively far apart).

Convection is transfer of heat by movement of warm air masses.

Solar radiation warms the earth and thus the air above it. This heating is most effective at the equator and least at the poles.

The warmer, less dense air rises at the equator and cools, becomes more dense, and sinks at the poles.

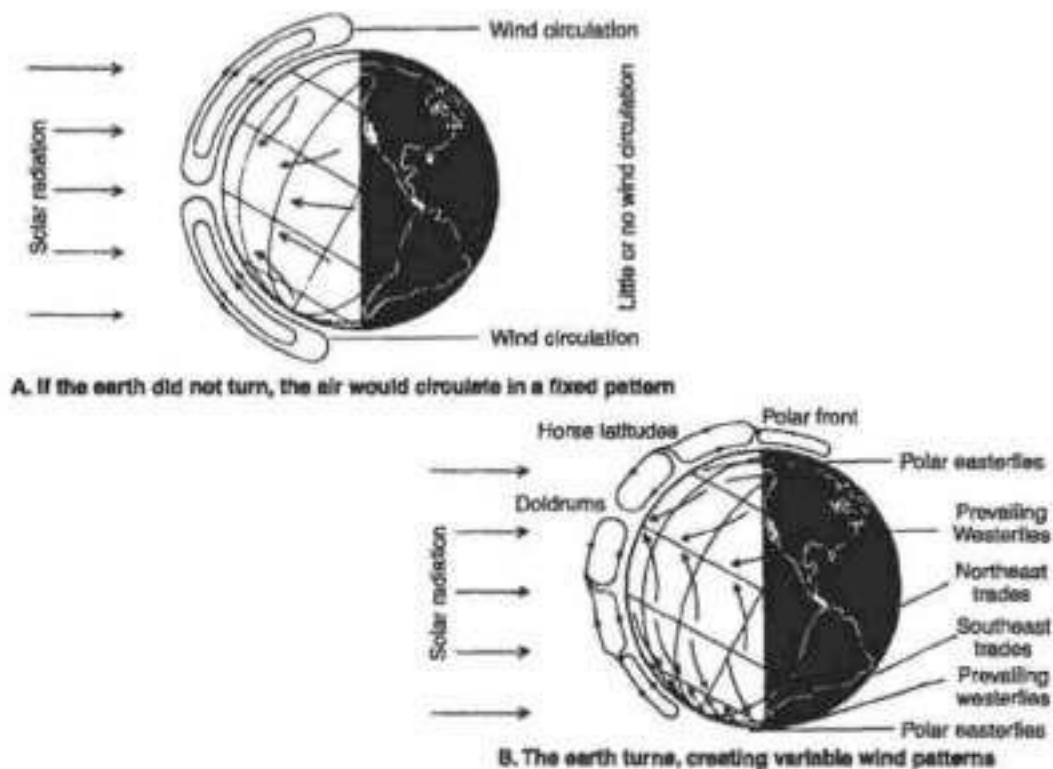


Figure 3. Global wind patterns.

If the earth did not rotate then the surface wind pattern would be from the poles to the equator.

However, the rotation of the earth continually presents new surfaces to be warmed, so that a horizontal air pressure gradient exists as well as the vertical pressure gradient.

The resulting motion of the air creates a pattern of winds around the globe, as shown by Fig. 3.

Seasonal and local temperature, pressure and cloud conditions, and local topography complicate the picture.

Land masses heat and cool faster than water so that shoreline winds blow out to sea at night and inland during the day.

Seasonal and local temperature, pressure and cloud conditions, and local topography complicate the picture.

Land masses heat and cool faster than water so that shoreline winds blow out to sea at night and inland during the day.

Valley winds result from cooling of air high on mountain slopes.

In cities, brick and concrete buildings absorb heat during the day and radiate it at night, creating a heat island (Fig. 4), which sets up a self-contained circulation called a haze hood from which pollutants cannot escape.

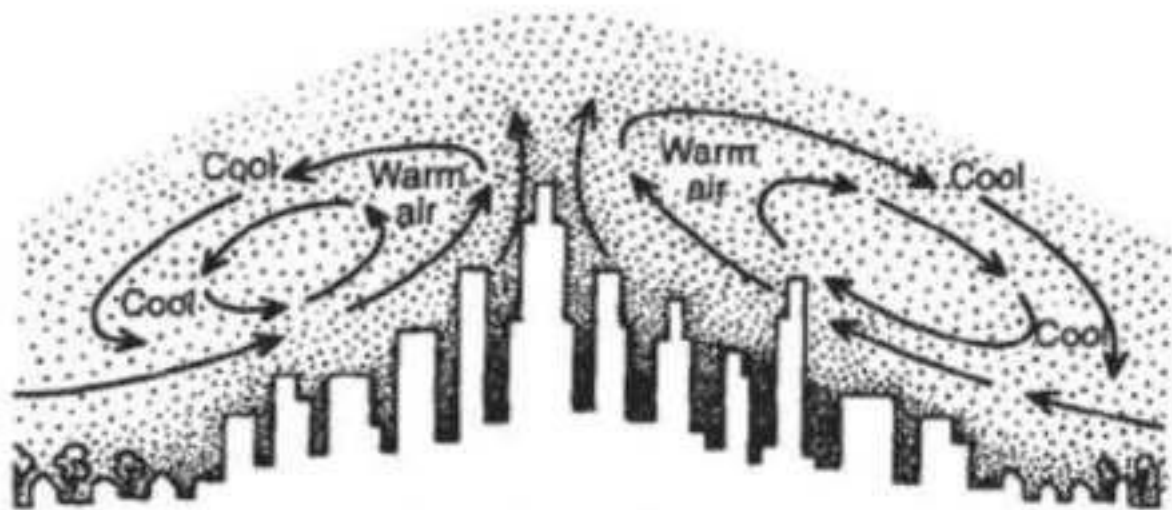


Figure 4. Heat island formed over a city.

Horizontal wind motion is measured as wind velocity. Wind velocity data are plotted as a wind rose, a graphic picture of wind velocities and the direction from which the wind came. The wind rose in Fig. 5 shows that the prevailing winds were from the southwest.

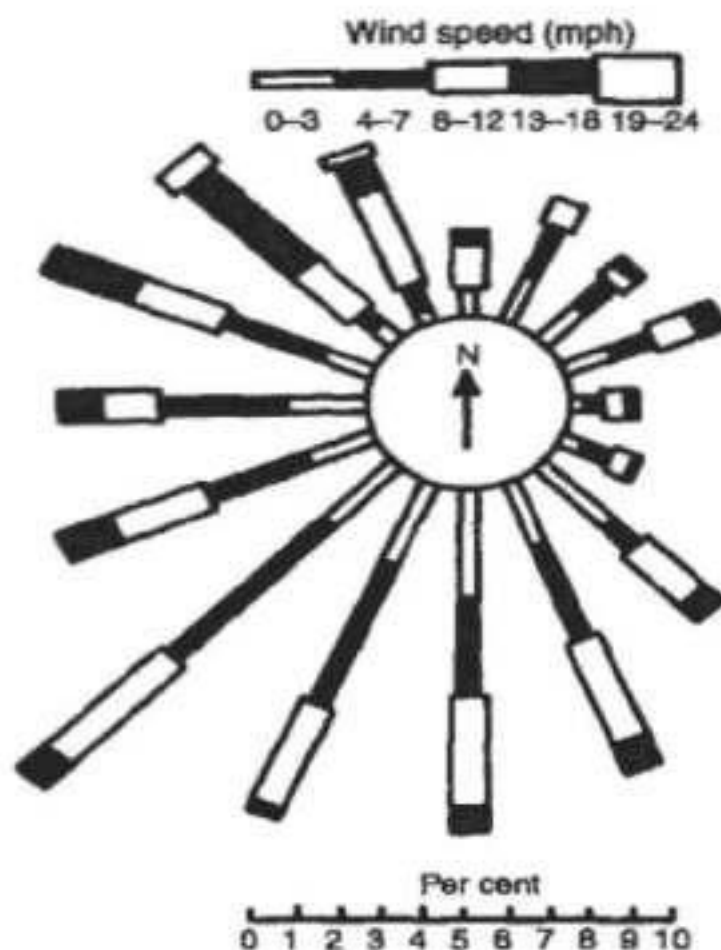


Figure 5. Typical wind rose.

The three features of a wind rose are:

1. The orientation of each segment, which shows the direction from which the wind came.
2. The width of each segment, which is proportional to the wind speed.
3. The length of each segment, which is proportional to the percent of time that wind at that particular speed was coming from that particular direction.

Air pollution enforcement engineers sometimes use a pollution rose, a variation of a wind rose in which winds are plotted only on days when the air contamination level exceeds a given amount.

Figure 6 shows pollution roses at three points plotted only for days when the SO_2 level exceeded $250 \mu\text{g}/\text{m}^3$.

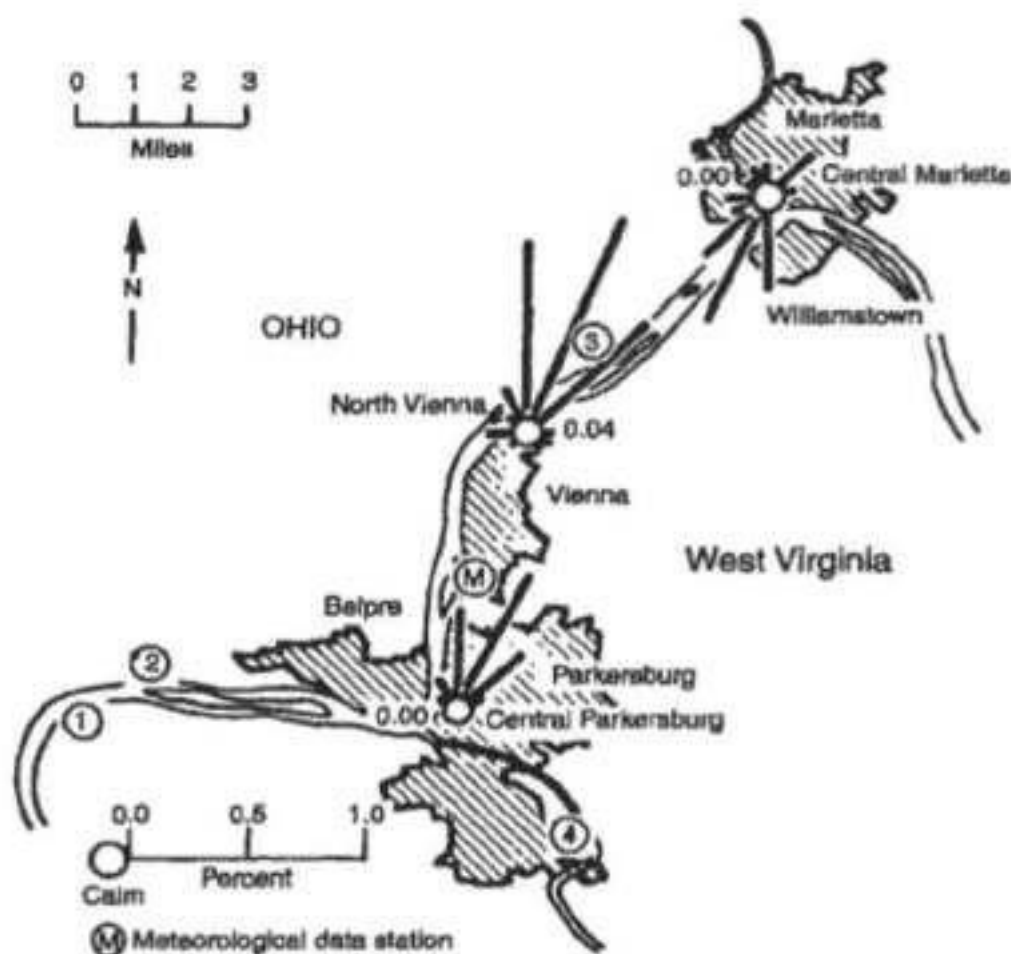


Figure 6. Pollution roses for SO₂ concentrations greater than 250 pg/m³. The four chemical plants are the suspected sources, but the roses clearly point to Plant 3, identifying it as the primary culprit.

Note that because the roses indicate the directions from which the wind is coming the apparent primary pollution source is plant 3.

Wind is probably the most important meteorological factor in the movement and dispersion of air pollutants, or, in simple terms, pollutants move predominantly downwind.

UNIT III CONTROL OF PARTICULATES

Vertical dispersion of Pollutants

As 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.

$$dT/dz|_{\text{dry-adiabatic}} = -9.8^{\circ}\text{C/km},$$

where T = temperature and z = altitude.

The actual measured rate at which air cools as it rises is called the ambient or prevailing 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 Fig. 7.

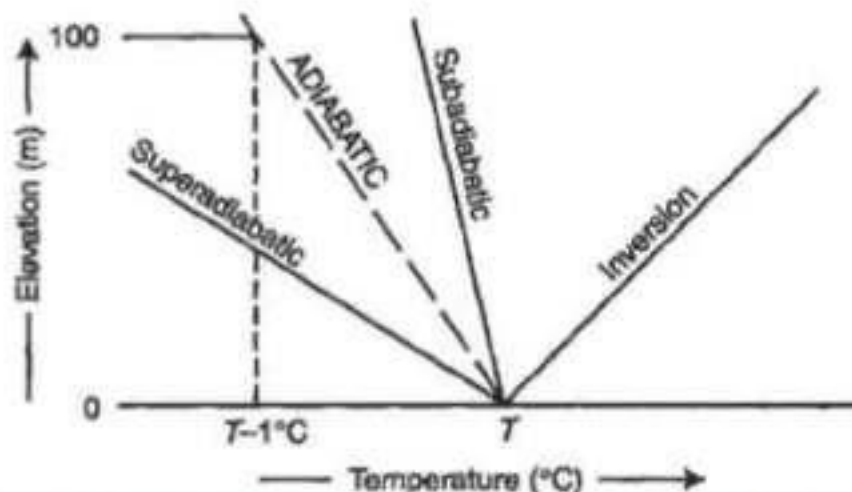


Figure 7. Ambient lapse rates and the dry adiabatic lapse rate.

When the ambient lapse rate is exactly the same as the dry adiabatic lapse rate, the atmosphere has neutral stability.

Super adiabatic conditions prevail when the air temperature drops more than $9.8^{\circ}\text{C}/\text{Km}$ ($10^{\circ}\text{C}/100\text{m}$).

Sub adiabatic conditions prevail when the air temperature drops at a rate less than $9.8^{\circ}\text{C}/\text{Km}$.

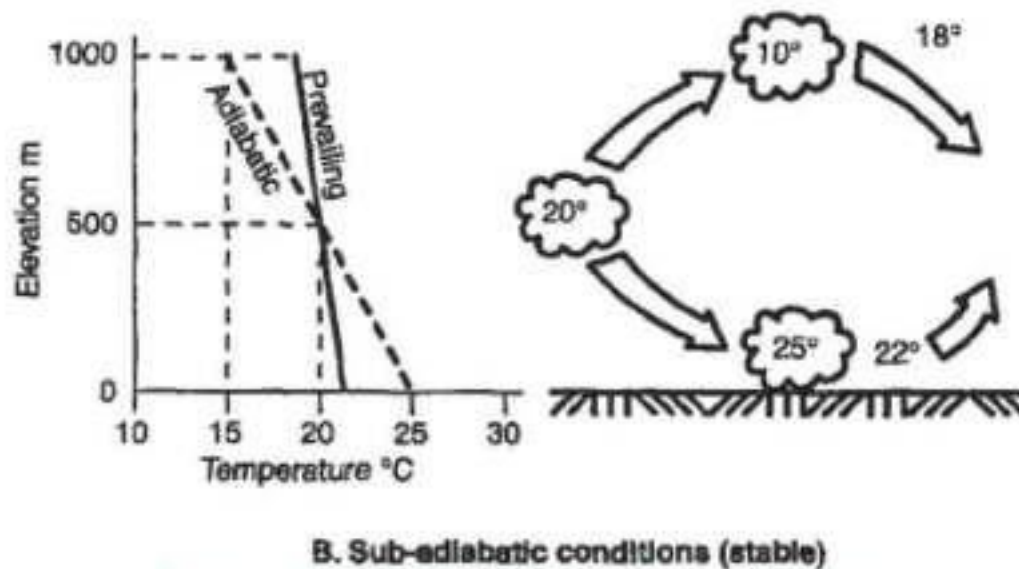
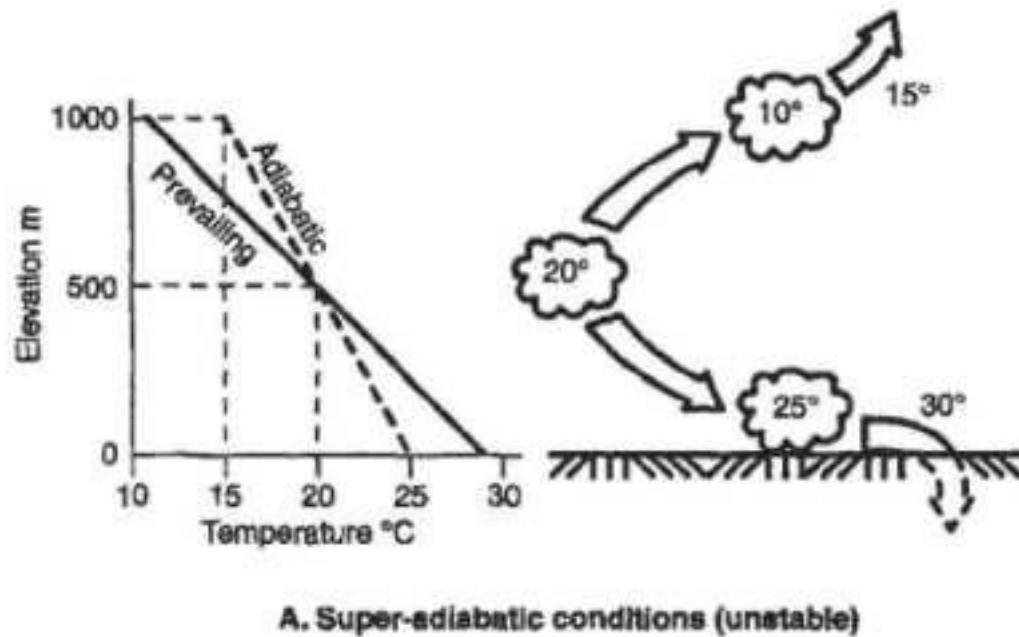


Figure 8. Stability and vertical air movement.

A special case of sub adiabatic conditions is the temperature inversion, when the air temperature actually increases with altitude and a layer of warm air exists over a layer of cold air.

Super adiabatic atmospheric conditions are unstable and favor dispersion; sub adiabatic conditions are stable and result in poor dispersion; inversions are extremely stable and trap pollutants, inhibiting dispersion.

These conditions may be illustrated by the following example, illustrated in Fig. 8:

The air temperature at an elevation of 500 m is 20°C, and the atmosphere is superadiabatic, the ground level temperature is 30°C and the temperature at an elevation of 1 km is 10°C.

The (super adiabatic) ambient lapse rate is -20°C/km.

If a parcel of air at 500 m moves up adiabatically to 1 km, what will be its temperature? According to the dry adiabatic lapse rate of - 9.8oC/Km the air parcel would cool by 4.9 oC to about 15°C.

However, the temperature at 1 km is not 15°C but 10°C. Our air parcel is 5°C warmer than the surrounding air and will continue to rise.

In short, under sub adiabatic conditions, a rising parcel of air keeps right on going up. Similarly, if our parcel were displaced downward to, say, 250m, its temperature would increase by 2.5 oC to 22.5 oC.

The ambient temperature at 250 m, however, is 25 oC, so that our parcel of air is now cooler than the surrounding air and keeps on sinking.

There is no tendency to stabilize; conditions favor instability.

Now let us suppose that the ground level temperature is 22 oC, and the temperature at an elevation of 1 km is 15°C.

The (sub adiabatic) ambient lapse rate is now -7 oC/Km.

If our parcel of air at 500 m moves up adiabatically to 1 km, its temperature would again drop by 4.9 oC to about 15°C, the same as the temperature of the surrounding air at 1 km.

Our air parcel would cease rising, since it would be at the same density as the surrounding air.

If the parcel were to sink to 250 m, its temperature would again be 22.5 oC, and the ambient temperature would be a little more than 20°C.

The air parcel is slightly warmer than the surrounding air and tends to rise back to where it was. In other words, its vertical motion is damped, and it tends to become stabilized; subadiabatic conditions favor stability and limit vertical mixing.

Figure 9 is an actual temperature sounding for Los Angeles. Note the beginning of an inversion at about 1000 ft that puts an effective cap on the city and holds in the air pollution.

This type of inversion is called a subsidence inversion, caused by a large mass of warm air subsiding over a city.

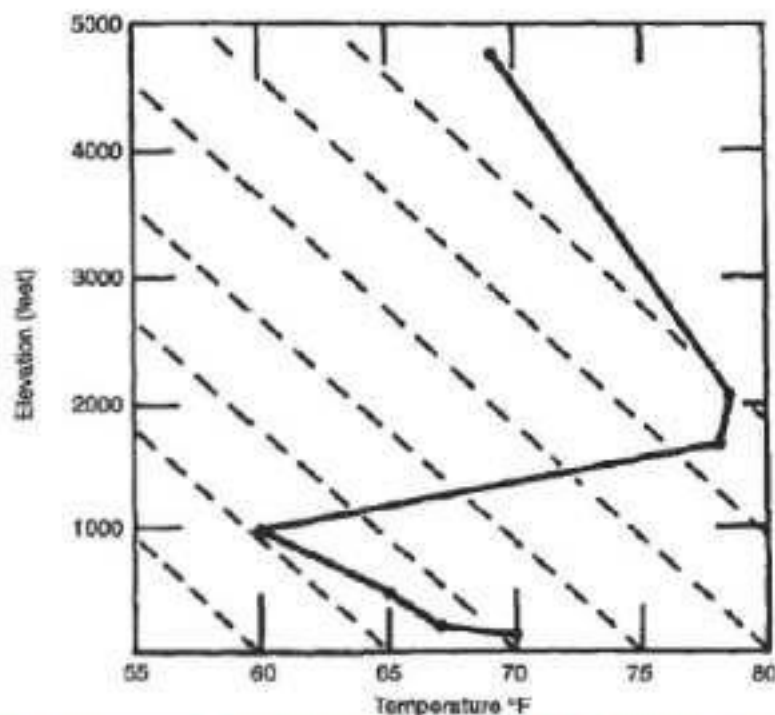


Figure 9. Temperature sounding for Los Angeles, 4 PM, October 1962. The dotted lines show the dry adiabatic lapse rate.

A more common type is the radiation inversion, caused by radiation of heat from the earth at night. As heat is radiated, the earth and the air closest to it cool, and this cold air is trapped under the warm air above it (Fig. 10).

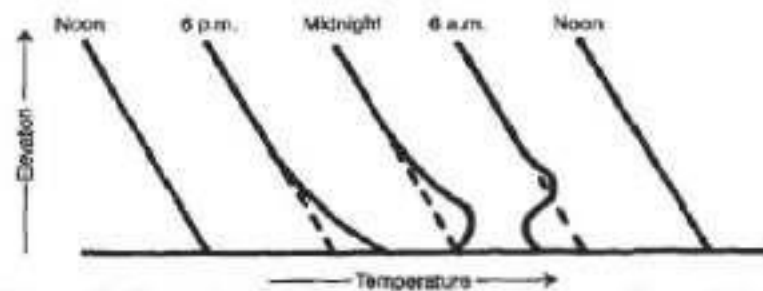


Figure 10. Typical ambient lapse rates during a sunny day and clear night.

Pollution emitted during the night is caught under the "inversion lid." Atmospheric stability may often be recognized by the shapes of plumes emitted from smokestacks as seen in Figs. 11 and 12.

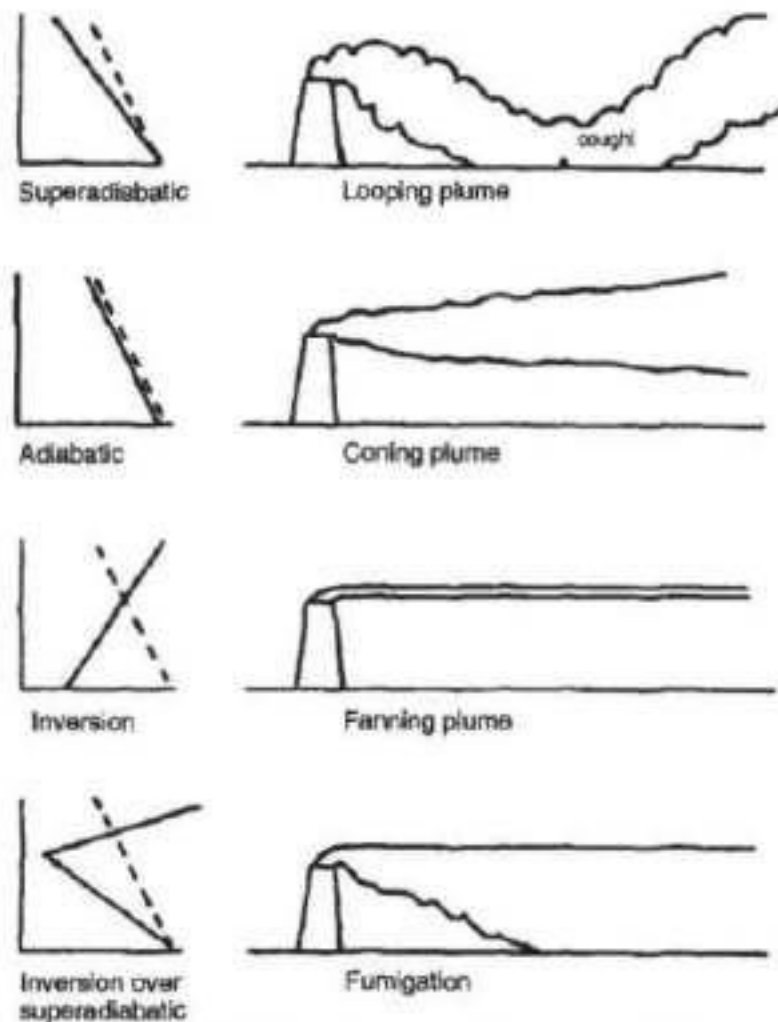


Figure 11. Plume shapes and atmospheric stability.

Neutral stability conditions usually result in coning plumes, while unstable conditions result in a highly dispersive looping plume.

Under stable conditions, the funning 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.



Figure 12. Iron oxide dust looping plume from a steel mill

A looping plume also produces high ground-level concentrations as the plume touches the ground.

Assuming adiabatic conditions in a plume allows estimation of how far it will rise or sink, and what type of plume it will be during any given atmospheric temperature condition, as illustrated by Example 1.

EXAMPLE 1.

A stack 100 m tall emits a plume whose temperature is 20°C . The temperature at the ground is 19°C . The ambient lapse rate is $-4.5^{\circ}\text{C}/\text{km}$ up to an altitude of 200 m. Above this the ambient lapse rate is $+20^{\circ}\text{C}/\text{km}$. Assuming perfectly adiabatic conditions, how high will the plume rise and what type of plume will it be?

Figure 13 shows the various lapse rates and temperatures.

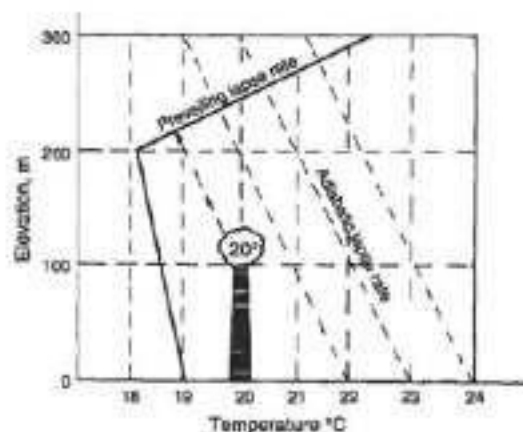


Figure 13. Atmospheric conditions in Example 1.

The plume is assumed to cool at the dry adiabatic lapse rate 10°C km . The ambient lapse rate below 200 m is subadiabatic, the surrounding air is cooler than the plume, so it rises, and cools as it rises.

At 225 m, the plume has cooled to 18.7°C , but the ambient air is at this temperature also, and the plume ceases to rise.

Below 225 m, the plume would have been slightly coning. It would not have penetrated 225 m.

Effect of Water in the Atmosphere

The dry adiabatic lapse rate is characteristic of dry air. Water in the air will condense or evaporate, and in doing so will release or absorb heat, respectively, making calculations of the lapse rate and atmospheric stability complicated.

In general, as a parcel of air rises, the water vapor in that parcel will condense and heat will be released.

The rising air will therefore cool more slowly as it rises; the wet adiabatic lapse rate will in general be less negative than the dry adiabatic lapse rate.

The wet adiabatic lapse rate has been observed to vary between -6.5 and -3.5°C /Km .

Water in the atmosphere affects air quality in other ways as well.

Fogs are formed when moist air cools and the moisture condenses.

Aerosols provide the condensation nuclei, so that fogs tend to occur more frequently in urban areas.

Serious air pollution episodes are almost always accompanied by fog (remember that the roots of the word "smog" are "smoke" and "fog").

The tiny water droplets in fog participate in the conversion of SO_3 to H_2SO_4 .

Fog sits in valleys and stabilizes inversions by preventing the sun from warming the valley floor, thus often prolonging air pollution episodes.

ATMOSPHERIC DISPERSION

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.

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.

The principles on which the model is based are:

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

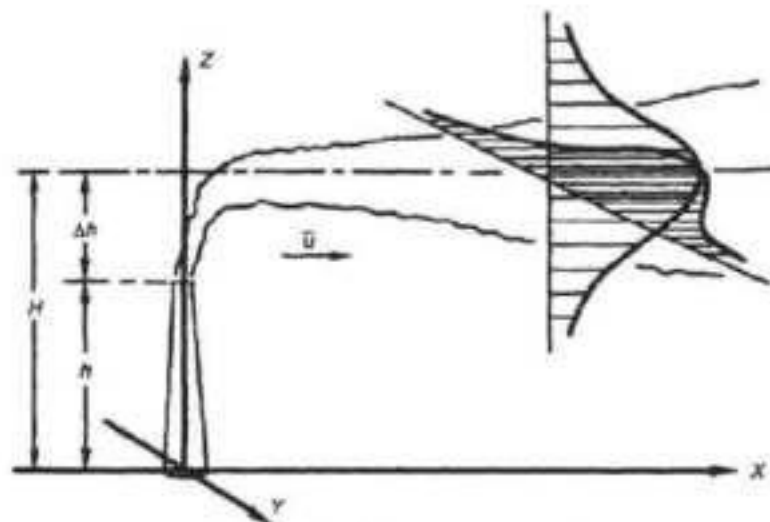


Figure 14. Gaussian dispersion model.

Figure 14 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. 14.

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 $Z=H$

and the downwind concentration emanating from this elevated source may be written

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

where

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

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

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

σ_y = the standard deviation of the plume in the y direction (m), and

σ_z = the standard deviation of the plume in the z direction (m).

The units of concentration are grams per cubic meter (g/m^3). Since pollution concentrations are usually measured at ground level, that is, for $z = 0$, the Eq. usually 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 Eq. 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 σ_y , and σ_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. Table 1 shows the relationship between stability class, wind speed, and sunshine conditions.

Table 1. Atmospheric Stability under Various 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

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 super adiabatic conditions; Class D with neutral conditions; and Classes E and F with sub adiabatic conditions. A seventh, Class G, indicates conditions of extremely severe temperature inversion, but in considering frequency of occurrence is usually combined with Class F.

Urban and suburban populated areas rarely achieve stability greater than Class D, because of the heat island effect; stability classes E and F are found in rural and unpopulated areas.

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,

Wind is often measured in weather stations at an elevation of 10 m above ground level.

Effective Stack Height

The effective stack height is the height above ground at which the plume begins to travel downwind the effective release point of the pollutant and the origin of its dispersion.

A number of empirical models exist for calculating the plume rise h – the height above the stack to which the plume rises before dispersing downwind.

Three equations that give a reasonably accurate estimate of plume rise have been developed by Carson and Moses (1969) for different stability conditions.

For super adiabatic conditions

$$\Delta h = 3.47 \frac{V_s d}{u} + 5.15 \frac{Q_h^{0.5}}{u};$$

for neutral stability

$$\Delta h = 0.35 \frac{V_s d}{u} + 2.64 \frac{Q_h^{0.5}}{u}$$

and for sub adiabatic conditions

$$\Delta h = -1.04 \frac{V_s d}{u} + 2.24 \frac{Q_h^{0.5}}{u}$$

where

V_s = stack gas exit speed (in m/s) ,

d = stack diameter (in m), and

Q_h = heat emission rate from the stack (in kJ/s).

As before, length is in meters and time is in seconds, and the heat emission rate is measured in kilojoules per second.

EXAMPLE 4

A power plant has a stack with a diameter of 2 m and emits gases with a stack exit velocity of 15 m/s and a heat emission rate of 4,800 kJ/s. The wind speed is 5 m/s. Stability is neutral. Estimate the plume rise. If the stack has a geometric height of 40 m, what is the effective stack height?

$$\Delta h = 0.35 \frac{(15)(2)}{5} + 2.64 \frac{\sqrt{4800}}{5} = 38.7 \text{ m}$$

$$H = h_g + h$$

$$H = 40 \text{ m} + 38.7 \text{ m} = 78.7 \text{ m.}$$

The accuracy of plume rise and dispersion analysis is not very good.

Un calibrated models predict ambient concentrations to within an order of magnitude at best.

To ensure reasonable validity and reliability, the model should be calibrated with measured ground level concentrations.

The model discussed applies only to a continuous, steady point source of emission.

Discrete discontinuous emissions or puffs, larger areas that act as sources, like parking lots, and line sources, like highways, are modeled using variants of the Gaussian approach, but the actual representation used in each case is quite different.

CLEANSING THE ATMOSPHERE

Processes by which the atmosphere cleans itself do exist, and include the effect of gravity, contact with the earth's surface, and removal by precipitation.

Gravity

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 μm 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 μm 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,

ρ = particle density, and

μ = viscosity of air.

The settling velocity modifies the Gaussian dispersion equation, to give the analogous 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 0.5 in the first term arises because falling particles are not reflected at the ground surface.

The rate, ω , 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 ω = the deposition rate (in $\text{g/s}\cdot\text{m}^2$).

EXAMPLE 5

Using the data of Example 3, and assuming that the emission consists of particles 10 μm in diameter and having a density of 1 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 g/m-s at 25°C.

The settling velocity is

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

From example 3

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

The deposition rate is then

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

Surface Sink Absorption

Many atmospheric gases are absorbed by the features of the earth's surface, including stone, soil, vegetation, bodies of water, and other materials. Soluble gases like SO₂ dissolve readily in surface waters, and such dissolution can result in measurable acidification.

Precipitation

Precipitation removes contaminants from the air by two methods.

Rain out is an "in cloud" process in which very small pollutant particles become nuclei for the formation of rain droplets that grow and eventually fall as precipitation.

Washout is a "below cloud" process in which rain falls through the pollutant particles and molecules, which are entrained by the impinging rain droplets or which actually dissolve in the rainwater.

The relative importance of these removal mechanisms was illustrated by a study of SO₂ emissions in Great Britain, where the surface sink accounted for 60% of the SO₂, 15% was

removed by precipitation, and 25% blew away from Great Britain, heading northwest toward Norway and Sweden.

Polluted air results from both emissions into the air and meteorological conditions that control the dispersion of those emissions.

Pollutants are moved predominantly by wind, so that very light wind results in poor dispersion. Other conditions conducive to poor dispersion are:

- Little lateral wind movement across the prevailing wind direction,
- Stable meteorological conditions, resulting in limited vertical air movement,
- Large differences between day and night air temperatures, and the trapping of cold air in valleys, resulting in stable conditions,
- Fog, which promotes the formation of secondary pollutants and hinders the sun from warming the ground and breaking inversions,
And High-pressure areas resulting in downward vertical air movement and absence of rain for washing the atmosphere.

Air pollution episodes can now be predicted, to some extent, on the basis of meteorological data. The EPA and many state and local air pollution control agencies are implementing early warning systems, and acting to curtail emissions and provide emergency services in the event of a predicted episode.

UNIT IV

CONTROL OF GASEOUS EMISSIONS

The molecules at a surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. This preferential accumulation of substrate molecules at the surface is called adsorption which is purely surface phenomenon.

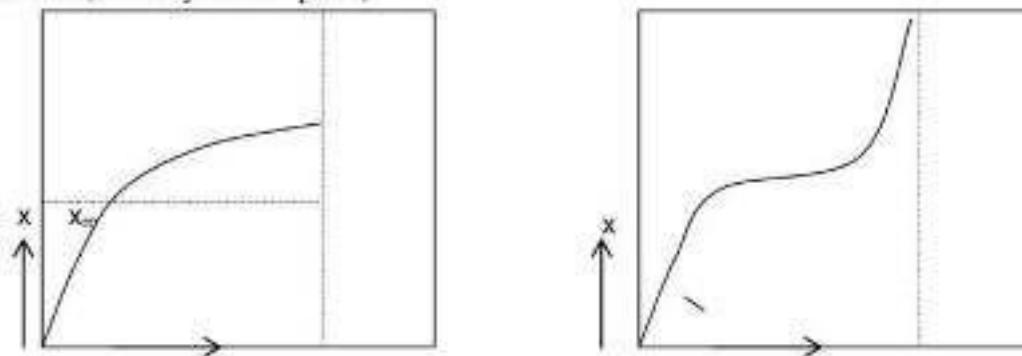
The surface active material is referred to as the adsorbent and the molecules which are accumulated on the adsorbent called adsorbate molecules. The strength by which adsorbate molecules are attached with the adsorbents determines the nature of adsorption. Normally, release of energy in the range of 8 to 25 kJ/mole due to adsorption is termed as physisorption whereas a much larger energy comparable to chemical bonding energy leads to chemisorption. There are always some exceptions to these values. The prescribed value of energy differentiating physisorption and chemisorption are based on general experience.

When an adsorbed molecule receives energy equal to or greater than the energy of adsorption, it will leave the surface. This phenomenon is the reverse of adsorption and is called as desorption. When the number of molecules striking the surface and staying there is equal to the number of molecules that are leaving (evaporating) the surface is called to be in equilibrium.

All the atoms or molecules adsorbed on the surface do not have identical environment as distribution of free energy on the surface is not always smooth because of the difference in the energy of the molecular orbitals of the adsorbent and also due to other internal interactions.

Adsorption Isotherms

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. Two types of typical adsorption isotherms are shown in the following Figures A & B. Figure A shows adsorption with monolayer formation at saturation point, Figure B shows a situation when several layers of adsorbate molecules are formed on the surface of the adsorbent (multilayer adsorption).



X_m is the amount of the substrate required to make a monolayer where as P_o is the saturation equilibrium concentration of the substrate.

Arrangement of adsorbed molecules on the surface of the adsorbent could normally be monolayer in nature. Normally, chemisorption leads to monolayer adsorption whereas multilayer arrangement of substrate molecules is observed due to physisorption only. Multilayer formation is also possible due to chemisorption followed by physisorption

Gibb's Adsorption Isotherm:

This isotherm normally considers the case when adsorbents are liquid and adsorbate are soluble or partially soluble in it e.g., surfactants / water or organic liquid / water system.

Considering a system having a plane interface between them the Gibb's free energy of a system containing two components could be written as follows:

$$G = n_1 \mu_1 + n_2 \mu_2$$

Where n_1 and n_2 are the number of moles and μ_1 and μ_2 are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on the surface of another, an additional term of surface energy has to be introduced, and hence, equation (36-2-1) modifies to

$$G = n_1 \mu_1 + n_2 \mu_2 + \gamma \sigma$$

where γ is the surface energy per unit area and σ is the surface area. It is now clear that equation (36-2-1) is for bulk while equation (36-2-2) will be applicable for the surface of the adsorbent liquid. The complete differential of (36-2-2) may be written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma$$

We find that the total free energy G of the whole system depends on independent variables, namely, T, P, n_1, n_2 and σ , thus,

$$G = f(T, P, n_1, n_2, \sigma)$$

and complete differential of G will be,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \sigma} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \sigma} dP + \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \sigma} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, \sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma} \right)_{T, P, n_1, n_2} d\sigma$$

$$\text{or } dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$$

At constant temperature and pressure, above equation reduces to ,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$$

Comparing equation (36-2-3) and (36.2.5), we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0$$

A corresponding equation for the bulk of the system may be,

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$$

Where n_1^0 and n_2^0 are the number of moles of adsorbent liquid and solute in the bulk. From the equation (36-2-6) and (36-2-7), we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma}$$

Here, the term $\frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma}$ represents the corresponding excess moles of solute per unit area on the surface of the adsorbent and now be represented by Γ_2

$$\therefore -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute $\mu_2 = \mu_2^0 + RT \ln a_2$

$$\text{or } d\mu_2 = RT d \ln a_2$$

When solution is very dilute activity a_2 of solute could be replaced by its concentration.

$$\therefore \Gamma_2 = -\frac{c_2}{RT} \left(\frac{d\gamma}{dc_2} \right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = - \frac{e}{RT} \left(\frac{\partial \gamma}{\partial c} \right)_T$$

In the above equation γ is essentially surface energy per unit area, which may easily be replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends to accumulate at the interface its surface excess is positive, and so $\frac{d\gamma}{dc}$ is negative. This means surface tension decreases when a solute accumulates at the surface.

Example: the surface tension of the dilute solution of phenol in water at 27 °C were the following:

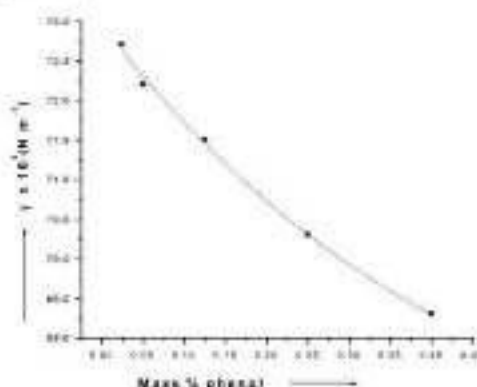
Mass % phenol	0.024	0.05	0.125	0.25	0.40
$\gamma \times 10^3 / (\text{Nm}^{-1})$	72.7	72.2	71.3	70.3	69.3

Calculate surface excess concentration (Γ) at a concentration of 0.15 mass of phenol. Comment on the significance of the observed value of Γ .

Solution : A plot of γ vs mole of phenol gives a curvature with negative slope for 0.15 mol of phenol slope is $-\frac{1.7}{0.1875}$, putting values in equation,

$$\Gamma = - \frac{C}{RT} \left(\frac{\partial \gamma}{\partial c} \right)_T$$

$$\begin{aligned} \text{We get, } \Gamma &= - \frac{0.15}{8.31 \times 300 \text{ K}} \left(- \frac{1.7}{0.1875} \right) \\ &= 5.45 \times 10^{-4} \text{ mol m}^{-2} \end{aligned}$$



The positive value of Γ signifies that phenol is surface active and accumulates at the interface.

Freundlich Adsorption Isotherm

It is an empirical relation between the amount of an adsorbate adsorbed per unit weight ($x/m, \text{mg g}^{-1}$) of adsorbent and the adsorbate equilibrium concentration ($C_e, \text{moles L}^{-1}$) in the fluid as follows:

$$x/m = K C_e^n$$

Where, K and n are Freundlich coefficients

x = weight of adsorbate adsorbed on m unit weight of adsorbent

C_e = equilibrium concentration of adsorbate

From equation , we get

$$\log(x/m) = \log K + n \log C_e$$

The coefficients K and n can be determined from the intercept and slope of a plot of $\log(x/m)$ versus $\log C_e$.

From the appearance of the type I isotherm (Figure A) it is seen that for low values of concentration the amount adsorbed (x/m) is nearly proportional to C_e , whereas for large values it is nearly constant (or proportional to C_e^0). So it is reasonable that for intermediate values of C_e , x/m should be proportional to some power of C_e lying between 0 and 1. This is the motivation behind the empirical Freundlich adsorption isotherm.

Freundlich adsorption isotherm may be verified by performing a simple experiment for the adsorption of oxalic acid on charcoal. Supposing m gram of charcoal is added in 50 mL C_i M solution of oxalic acid. After adsorption is established equilibrium concentration of oxalic acid was determined as C_f . Hence, amount of oxalic acid adsorbed per unit weight of charcoal,

$$x/m \text{ (mg g}^{-1}\text{)} = (C_i - C_f) \times 63 \times 50$$

In a series of such experiment with different initial concentration of oxalic acid, values of x/m (mg g^{-1}) is determined. A plot of $\log x/m$ versus C_f is made and Freundlich coefficients K and n are determined.

Langmuir Adsorption Isotherm

In the Langmuir model the adsorbent surface is considered to possess a number of active interaction sites for adsorption. Langmuir derived a relation between adsorbed material and its equilibrium concentration. His assumptions are:

1. There are fixed adsorption sites on the surface of the adsorbent. At a given T&P some fraction of these sites are occupied by adsorbate molecules. Let this fraction be θ .
2. Each site on the surface of the adsorbent can hold one adsorbate molecule.
3. The heat of adsorption is the same for each site and is independent of θ .
4. There is no interaction between molecules on different sites.

Considering the processes of adsorption and desorption of the molecules on the surface, the Langmuir adsorption isotherm may be obtained as follows:

Rate of adsorption of molecules on the surface of the adsorbent = $k_a C_e (1 - \theta)$

Rate of desorption = $k_d \theta$

At equilibrium

$$k_a \theta = k_d C_e (1 - \theta)$$

$$\theta = \frac{k_a C_e}{k_a + k_d C_e} = \frac{K_L C_e}{1 + K_L C_e}, \text{ where } K_L = \frac{k_a}{k_d} \text{ is the adsorption coefficient}$$

$$\text{Since, } \theta = \frac{x}{x_m}$$

$$\therefore \frac{x}{x_m} = \frac{K_L C_e}{1 + K_L C_e}$$

where x and x_m are the amount of the adsorbent adsorbed at equilibrium concentration C_e and maximum amount of adsorbate for the formation of monolayer, respectively.

rearranging equation we get

$$\frac{C_e}{x} = \frac{1}{K_L x_m} + \frac{C_e}{x_m}$$

If we plot $\frac{C_e}{x}$ vs C_e , we will get a straight line. Slope of which will be $\frac{1}{x_m}$ and intercept as

$$\frac{1}{K_L x_m}$$

Therefore, from values of intercept and slope of the plot values of x_m and K_L could be calculated. In the case for the adsorption of gaseous substrate C_e, x , and x_m will be replaced by p, V , and V_m , respectively.

For chemisorption Langmuir's equation works very well but fails for the cases where multilayer formation takes place.

Example: the volume of CH_4 (corrected to STP) adsorbed per gram of charcoal at 240 K various pressures of CH_4 is:

$P/(\text{Torr})$	38	55	78	104	133	173	218
$V/(\text{cm}^3 \cdot \text{g}^{-1})$	14.14	17.52	21.38	24.72	28.00	31.35	34.50

Verify that the data obey Langmuir adsorption isotherm. Also determine Langmuir constant K_L and the volume corresponding to complete surface coverage. Calculate the fraction of charcoal surface which is covered by CH_4 molecules at $P=150$ torr.

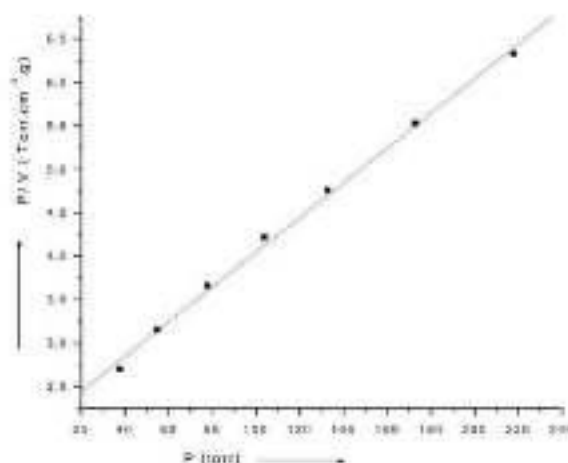
Plot of p/v vs p as shown below is linear which shows that the data verify the Langmuir monolayer adsorption isotherm.

$$\frac{p}{V} = \frac{p}{V_{\infty}} + \frac{1}{K_L V_{\infty}}$$

Slope of the curve $= 0.02 \text{ cm}^3 \cdot \text{g}^{-1}$

$$\therefore V_{\infty} = \frac{1}{\text{slope}} = \frac{1}{0.02 \text{ cm}^3 \cdot \text{g}^{-1}} = 50.0 \text{ cm}^3 \cdot \text{g}^{-1}$$

$$\text{intercept} = 2.05 \text{ torr cm}^3 \cdot \text{g}^{-1} = \frac{1}{K_L V_{\infty}}$$



$$\therefore K_L = \frac{1}{V_{\infty} \times \text{intercept}} \quad K_L = \frac{1}{(50.0 \text{ cm}^3 \cdot \text{g}^{-1})(2.05 \text{ torr} \cdot \text{cm}^3 \cdot \text{g}^{-1})}$$

$$= 9.75 \times 10^{-3} \text{ torr}^{-1}$$

Fraction of the surface covered (θ)

at $P=150$ torr,

$$\theta = \frac{K_L p}{1 + K_L p}$$

$$= \frac{(9.75 \times 10^{-3} \text{ torr}^{-1})(150 \text{ torr})}{1 + (9.75 \times 10^{-3} \text{ torr}^{-1})(150 \text{ torr})}$$

$$\theta = 0.593 \Rightarrow 59.3\% \text{ of the surface is covered by } \text{CH}_4 \text{ molecules.}$$

Langmuir adsorption isotherm for several non-dissociatively adsorbed species:

If two species A and B are adsorbed on the surface. Then applying Langmuir hypothesis for species A, we have,

$$v_{a(A)} = k_{a(A)} p_A (1 - \theta_A - \theta_B)$$

$$v_{d(A)} = k_{d(A)} (\theta)_A$$

$$\therefore k_{a(A)} \theta_A = k_{d(A)} p_A (1 - \theta_A - \theta_B)$$

$$\theta_A = \left(\frac{k_{a(A)}}{k_{d(A)}} \right) p_A (1 - \theta_A - \theta_B)$$

$$\theta_A = K_A p_A (1 - \theta_A - \theta_B) \left(\because K_A = \frac{k_{a(A)}}{k_{d(A)}} \right)$$

Similarly for species B,

$$\theta_B = K_B p_B (1 - \theta_A - \theta_B)$$

$$\text{OR, } \theta_B = K_B p_B - K_B p_B \theta_A - K_B p_B \theta_B$$

$$\theta_B (1 + K_B p_B) = K_B p_B - K_B p_B \theta_A$$

$$\theta_B = \frac{K_B p_B - K_B p_B \theta_A}{1 + K_B p_B}$$

Now, putting the value θ_B from (36-2-20) into equation (36-2-18), we get

$$\therefore \theta_A = K_A p_A \left(1 - \theta_A - \frac{K_B p_B - K_B p_B \theta_A}{1 + K_B p_B} \right)$$

$$\theta_A = K_A p_A - K_A p_A \theta_A = \frac{K_A p_A - K_A p_A \theta_A}{1 + K_A p_A}$$

$$\theta_A = \frac{K_A p_A - K_A p_A \theta_A}{1 + K_A p_A}$$

$$\therefore \theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}$$

Similarly, we can obtain

$$\therefore \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

In general, Langmuir adsorption isotherm for species A under conditions of several non-dissociatively adsorbed species could be derived as,

$$\frac{x_A}{x_{A+B}} = \frac{K_{(A)} p_A}{1 + \sum_i K_i p_i}$$

where sum runs over all species.

Multilayer Adsorption

Important assumption of Langmuir theory is the formation of monolayer. Because of monolayer formation a saturation in adsorption would reach at higher equilibrium concentration of the adsorbate. This type of adsorption occurs due to short range chemical forces which do not allow penetration through the primary adsorbed molecules. Multilayer formation has been observed when molecules are adsorbed through weak forces (long range forces normally under physical adsorption) due to cohesive forces exerted by the molecules of the adsorbate.

At high pressure multilayer adsorption takes place. The theory of multimolecular (multilayer) adsorption was developed by Stephen Brunauer, Paul Emmet and Edward Teller and is called BET isotherm. This isotherm derived by them successfully accounts for all types of adsorption.

BET Isotherm

It assumes that the surface possess uniform, localised sites and that adsorption on one site does not affect adsorption on neighbouring sites just as in Langmuir theory. Also, molecules can be adsorbed in second, third,... and n^{th} layers with the surface available for layer equal to the coverage of the next lower layer.

The rate constants for adsorption and desorption of the primary layer are k_a and k_d and those of the subsequent layers are all k'_a and k'_d . The number of sites corresponding to zero, monolayer, bilayer, ... coverage at any stage are N_0 , N_1 , N_2 , etc. and N_i in general. The condition for equilibrium of the initial layer is the equality of the rates of its formation and desorption,

$$k_a p N_0 = k_d N_1$$

The condition for equilibrium of the next layer is

$$k'_a p N_1 = k'_d N_2 \text{ and in general } k'_a p N_{i-1} = k'_d N_i, \quad i = 2, 3, \dots$$

This condition may be expressed in terms of N_0 as follows:

$$N_i = \left(\frac{k'_a}{k'_d} \right) p N_{i-1}$$

$$= \left(\frac{k'_a}{k'_d} \right)^2 p^2 N_{i-2} = \left(\frac{k'_a}{k'_d} \right)^{i-1} p^{i-1} N_1 = \left(\frac{k'_a}{k'_d} \right)^{i-1} \left(\frac{k'_a}{k_d} \right) p^i N_0$$

$$N_i = \left(\frac{k'_a}{k'_d} \right)^{i-1} \left(\frac{k'_a}{k_d} \right) p^i N_0$$

Writing $\frac{k_d'}{k_d} = x$ and $\frac{k_d}{k_d} = cx$, then

$$N_i = x^{i-1} \exp^{-x} N_0$$

$$N_i = c(x)^i N_0$$

Now, we calculate the total volume, V , of adsorbed material. V is proportional to the total number of particles adsorbed, and so

$$V = N_1 + 2N_2 + 3N_3 + \dots = \sum_{i=1}^{\infty} iN_i$$

Because each layer contributes number of particles according to its thickness, i.e., a monolayer one particle, a bilayer site two particles etc.

If there were complete monolayer coverage the volume adsorbed would be V_{mono} , with

$$V_{\text{mono}} = N_0 + N_1 + N_2 + \dots = \sum_{i=0}^{\infty} N_i$$

Because each site contributes only one particle to the total it follows then

$$\begin{aligned} V &= \sum_{i=1}^{\infty} iN_i = \sum_{i=1}^{\infty} ic(x)^i N_0 \\ &= cN_0 \sum_{i=1}^{\infty} i(x)^i \end{aligned}$$

$$= cN_0 xp \sum_{i=1}^{\infty} i (xp)^{i-1}$$

$$= cN_0 xp \frac{1}{(1-xp)^2}$$

$$V = cN_0 xp (1-xp)^{-2}$$

From equation (36-2-29),

$$V_{\text{total}} = \sum_{i=0}^{\infty} N_i = N_0 + N_1 + N_2 + \dots$$

$$= N_0 + \sum_{i=1}^{\infty} N_i$$

$$= N_0 + \sum_{i=1}^{\infty} c(xp)^i N_0$$

$$= N_0 + \frac{cN_0 xp}{1-xp}$$

$$= N_0 + cN_0 xp (1 + xp + (xp)^2 + \dots)$$

$$\because (1-xp)^{-1} = 1 + xp + (xp)^2 + \dots$$

From equation (36-2-30) and (36-2-31), we have

$$\frac{V}{V_{\text{total}}} = \frac{cN_0 xp (1-xp)^{-2}}{N_0 + cN_0 xp (1-xp)^{-1}}$$

$$= \frac{cxp}{1 + (c-2)xp + (1-c)(xp)^2}$$

$$= \frac{c(p/p^*)}{1 + (c-2)p/p^* + (1-c)p^2/p^{*2}}$$

$$= \frac{cz}{1 + (c-2)z + (1-c)z^2}$$

$$x = \left(\frac{K'_d}{k'_d} \right) = \frac{1}{p^*}$$

p^* = equilibrium pressure, (ads) $\rightleftharpoons$ vapour

putting $z = p/p^*$

$$\frac{V}{V_{\text{mono}}} = \frac{cz}{1 + cz - 2z + z^2 - cz^2} = \frac{cz}{(1-z)\{1 - (1-c)z\}}$$

$$= \frac{c \cdot p/p^*}{(1 - p/p^*)\{1 - (1-c)p/p^*\}}$$

$$= \frac{c \cdot p/p^*}{(1 - p/p^*)[1 + (c-1)p/p^*]}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{\text{mono}} \cdot c}{1(1-c)z}$$

$$\frac{V}{(z/(1-z))} = \frac{V_{\text{mono}} \cdot c}{1(1-c)z}$$

$$\frac{z}{(1-z)} \cdot \frac{1}{V} = \frac{1}{cV_{\text{mono}}} + \frac{(c-1)z}{cV_{\text{mono}}}$$

$\frac{(c-1)}{cV_{\text{mono}}}$ can therefore be obtained from the slope of a plot of $\frac{z}{(1-z)V}$ against z , and cV_{mono} can

be found from the intercept at $z=0$, the result being combined to give c and V_{mono} from the corresponding value of V_{mono} at 273 K and 1 atm, number of molecules present in V_{mono} could be

calculated. By knowing the contact area of a molecule, surface area of the adsorbent per unit mass could be determined.

Determination of Heat of adsorption

The temperature dependence of K can be used to determine the isomeric enthalpy of adsorption (ΔH^θ or ΔH^θ , the enthalpy of adsorption at a fixed surface coverage).

From Langmuir adsorption isotherm fraction of covered surface, $\theta = \frac{Kp}{1 + Kp}$

or $Kp = \frac{\theta}{1 - \theta}$, where θ is constant

$\ln K + \ln p = \text{constant}$ so, from the equation $\left(\frac{d \ln K}{dT} \right)_\theta = \frac{\Delta H^\theta}{RT^2}$

$$\therefore \left(\frac{\partial \ln P}{\partial T} \right)_\theta = - \left(\frac{d \ln K}{dT} \right)_\theta = - \frac{\Delta H^\theta}{RT^2}$$

using $\frac{d \left(\frac{1}{T} \right)}{dT} = - \frac{1}{T^2}$, this rearranges to,

$$\left(\frac{\partial \ln P}{\partial T} \right)_\theta = + \frac{\Delta H^\theta}{R} \times \left(\frac{d \left(\frac{1}{T} \right)}{dT} \right)$$

$$\left(\frac{\partial \ln P}{\partial T} \right)_\theta \left(\frac{dT}{d \left(\frac{1}{T} \right)} \right)_\theta = \frac{\Delta H^\theta}{R}$$

$$\left(\frac{d \ln P}{d \left(\frac{1}{T} \right)} \right)_\theta = \frac{\Delta H^\theta}{R}$$

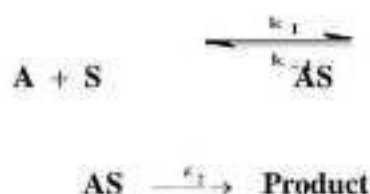
Thus, a plot of $\ln P$ against $1/T$ should be a straight line with slope $-\frac{\Delta H^\ddagger}{R}$. Therefore $\Delta H^\ddagger$ could be determined from the slope.

Reaction on surfaces

In case a solid immersed in a solution, the reactants in the solution must diffuse to the interface, get adsorbed there and participate in a given reaction mechanism on the solid surface, the product on the surface must then desorb and diffuse into the solution.

Unimolecular reactions on surfaces

Consider the surface catalysis of isomerisation or dissociation of a substance A on surface S as follows, substance S gets adsorbed on the surface forming AS and then dissociates to product,



Reaction velocity, $v = k_2 C_{AS}$

Where, C_{AS} = concentration $\left(\frac{\text{moles}}{\text{cm}^2} \right)$ of A on the surface

If, C_s = total of surface sites/cm² and represents the surface sites covered by A, then

$$C_{AS} = C_s \theta$$

or, reaction velocity,

$$v = k_2 C_s \theta$$

Again, if let C_a = concentration of A either in gas or solution

Since C_s is constant, it can be incorporated into rate constant

$$v = k_2' \theta$$

Applying steady state approximation to AS,

$$\frac{dC_{AS}}{dt} = 0 = k_1 C_a (1 - \theta) - k_{-1} \theta - k_2 \theta$$

where C_a represents the concentration of A either in gas or solution,

$$\theta = \frac{k_1 C_a}{k_1 C_a + k_{-1} + k_2}$$

$$\therefore v = \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1} + k_2}$$

$$\frac{1}{v} = \frac{1}{k_2} + \frac{k_{-1} + k_2}{k_1 k_2 C_a}$$

A plot of $\frac{1}{v}$ vs $\frac{1}{C_a}$ yields $\frac{1}{k_2}$ as the intercept and $\frac{k_{-1} + k_2}{k_1 k_2}$ as the slope.

Usually it is more convenient to use limiting cases as follows:

Case I

k_2 , the rate of decomposition is very large compared with the rate of adsorption and desorption. In this case, $k_2 \gg (k_1 C_a + k_{-1})$ and hence equation (36.4.4) reduces to,

$$\therefore v = k_1 C_a$$

Physically, the assumption that k_2 is large implies that an adsorbed molecule decomposes immediately after coming in contact with the surface. This situation is found for the decomposition of HI on Pt and N_2O on gold.

Case II

k_2 is very small (negligible) in comparison to $(k_1 C_a + k_{-1})$ and hence equation (36.4.4) reduces to

$$\begin{aligned} \therefore v &= \frac{k_1 k_2 C_a}{k_1 C_a + k_{-1}} \\ &= \frac{k_2 K C_a}{K C_a + 1}, \quad K = \frac{k_1}{k_{-1}} \end{aligned}$$

at low concentration of the species A, $KC_a \ll 1$

$$\therefore v = k_2 K C_a$$

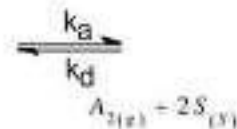
Whereas at high concentration $KC_a \gg 1$ or $\theta \approx 1$

$$\therefore v = k_2$$

Sub-Case of I

A diatomic molecule A_2 dissociates upon adsorption to the surface.

This reaction can be written as



Because two surface sites are involved in the adsorption and desorption process, the rates of adsorption, v_a , and desorption v_d , are

$$v_a = k_a p_{A_2} (1 - \theta)^2 C_s$$

$$v_d = k_d \theta^2 C_s$$

Where, C_s = total surface sites/ cm^2 , θ = fraction of the surface covered and p represents the pressure of the molecules A_2 .

At equilibrium, these rates are equal, and so

$$k_a p_{A_2} (1 - \theta)^2 = k_d \theta^2$$

$$K p_{A_2} (1 - \theta)^2 = \theta^2$$

$$\theta = \frac{K^{1/2} p_{A_2}^{1/2}}{1 + K^{1/2} p_{A_2}^{1/2}}$$

$$\frac{1}{\theta} = 1 + \frac{1}{K^{1/2} p_{A_2}^{1/2}}$$

A plot of $\frac{1}{\theta}$ vs $\frac{1}{p_{A_2}^{1/2}}$ will yield a straight line with slope $\frac{1}{K^{1/2}}$ and intercept 1.

Bimolecular reactions on surfaces:

A bimolecular reaction between two molecules A and B on a surface may occur through different alternative steps out of which following two are important

(i) Langmuir – Hinshelwood mechanism:

The two reacting molecules A and B react after being adsorbed on neighbouring sites on the surface of the catalyst. This mechanism is called as Langmuir - Hinshelwood mechanism. Reaction rate v , for such reaction may be written as follows:

$$v = k\theta_A\theta_B$$

Putting the values of θ_A and θ_B from equations we get

$$v = \frac{kK_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

Above equation could be subjected to two special cases as follows:

1. If the pressures of A and B species, p_A and p_B are both sufficiently low so that $K_A p_A$ and $K_B p_B$ may be neglected in comparison with unity, the rate equation becomes,

$$v = kK_A K_B [A][B]$$

This would mean reaction to be second order. This a frequently observed behaviour in Langmuir –Hinshelwood mechanism.

2. If a reactant A is very weakly adsorbed, $k_A p_A$ in the denominator of equation may be neglected, and the rate equation become,

$$v = \frac{kK_A K_B p_A p_B}{(1 + K_B p_B)^2}$$

Reaction of hydrogen with ethylene on copper follows a nearly similar rate law as follows:

$$v = \frac{K [H_2][C_2H_4]}{(1 + K [C_2H_4])^2}$$

If reactant B is adsorbed very strongly such that $K_B p_B \gg 1$, equation becomes

$$v = \frac{k K_A p_A}{K_B p_B}$$

The rate is now inversely proportional to P_B . Such behavior is observed in reaction between carbon monoxide and oxygen on quartz and on platinum. In these cases rate is inversely proportional to the pressure of carbon monoxide, which must be strongly adsorbed

(ii) Langmuir - Rideal mechanism:

If reaction is due to collision of a gaseous molecules A with an adsorbed B molecules, the mechanism is known as Langmuir – Rideal mechanism and the rate law in this case will be,

$$v = k \theta_A p_A$$

$$\text{OR, } v = \frac{k K_A p_A p_B}{1 + K_A p_A + K_B p_B}$$

The reaction of ethylene and H_2 on copper surface presents nearly similar situation of Langmuir – rideal mechanism. C_2H_4 gets adsorbed much strongly on the surface. Rate equation for the reaction of C_2H_4 and H_2 on copper surface follows as below:

$$v = \frac{k [H_2][C_2H_4]}{(1 + c [C_2H_4])^2}$$

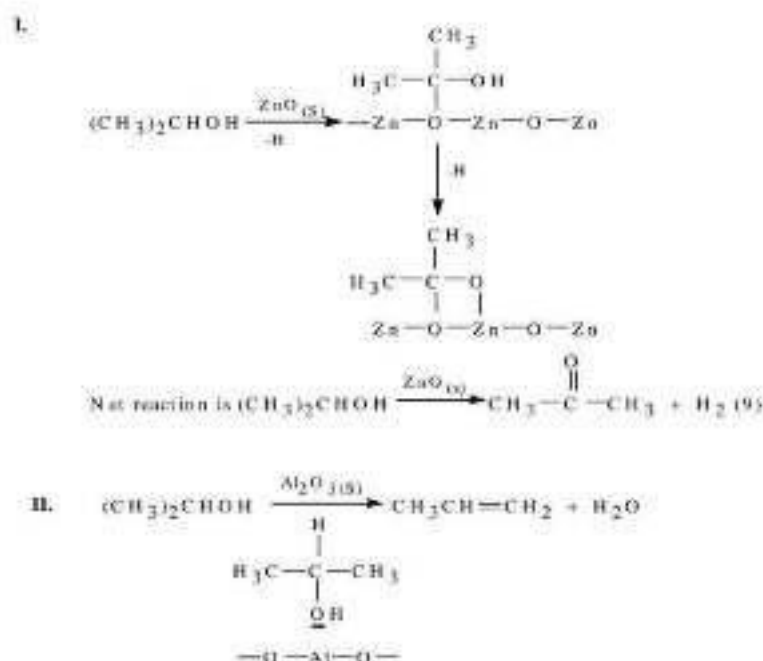
Surface Catalysis

Many industrial chemical reactions are carried out in the presence of solid catalyst e.g., Fe-catalyzed synthesis of NH_3 from N_2 and H_2 , SiO_2/Al_2O_3 catalyzed cracking of high molecular weight hydrocarbons to gasoline. Reactions involving catalysts of a phase different from reactants are known as heterogeneous catalyst. Besides other usual applications, heterogeneous catalysis is extremely important and will be discussed in details.

Heterogeneous catalysis, like its homogeneous counterpart, changes the rate of a reaction by providing an alternate reaction mechanism. Solid catalysts lower activation energies by much greater extent than homogeneous catalysts. For the reaction $2\text{HI} \longrightarrow \text{I}_2 + \text{H}_2$ without catalyst, the activation energy is 44 kcal/mol, 25 kcal/mol when catalyzed by Au, and is only 14 kcal/mol when catalyzed by Pt. Uncatalyzed reaction $2\text{H}_2\text{O}_{(\text{aq})} \longrightarrow 2\text{H}_2 + \text{O}_2$ has activation energy 17 kcal/mol, 12 kcal/mol when catalyzed by colloidal Pt and only 2 kcal/mol when catalyzed by enzyme catalase.

Similarly, decomposition of N_2O in gas phase without a catalyst has activation energy 250 kJ/mol, and with catalyst with Au and Pt is about 125 kJ/mol.

The substances most often studied and used as heterogeneous catalyst are transition metals, alloys and semiconducting oxides and sulfides. The effectiveness of a catalyst can be measured by the amount of product formed per unit time per unit surface area of the catalyst. Activity of a catalyst depends on the nature of active sites present on the surface e.g., point defects, lattice distortion or % d-character of the metallic bond within the solid metal. Catalysts with different surface property may lead to the formation of different product from the same starting reactant. For example, isopropanol undergoes dehydrogenation on a surface of ZnO while dehydration occurs on Al_2O_3 . ZnO is n-type semiconductor whereas Al_2O_3 is an ionic insulator and acts as a Lewis acid. The probable mechanism may be given as follows:



In surface catalyzed reactions activation energy is normally lowered due to adsorption of reacting molecules on the surface of the catalysts. After adsorption surface molecules are not allowed to perform translational motion but are able to perform vibrational motion.

Applications of Adsorption

The process of adsorption is very important as it has many applications in domestic as well as in industrial processes, to name some of them are follows:

1. **In heterogeneous catalysis:** Surface active material are widely used as catalyst mostly due to adsorption processes. If the surface active materials (adsorbents) have different phase with that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and substrate are in same phase is called homogeneous catalysis.
2. **In removal of colouring material:** Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.
3. **In ion exchange resins:** Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.
4. **In adsorption indicators:** Several dyes like eosin and fluorescein are used as indicators in the titrations of Cl^- , Br^- etc. against Ag^+ (Fajan's method).
5. **In gas masks:** Activated charcoal is used to remove toxic gases in gas masks.
6. **In dyeing of cloth:** Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes, alums work as efficient mordants in dyeing cloths.
7. **In de humidizers:** Many substances when they adsorb water change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue. Silica is colourless but after adsorbing water becomes blue.

UNIT V

AIR QUALITY MANAGEMENT

Air pollutants are added in the atmosphere from variety of sources that change the composition of air and affect the biotic environment. The concentration of air pollutants depend not only on the quantities that are emitted from air pollution sources but also on the ability of the atmosphere to either absorb or disperse these emission. The pollution concentrations vary spatially and temporarily causing the air pollution pattern to change with different locations and time due to changes in meteorological and topographical condition. The sources of air pollutants include vehicles, industries, domestic and natural sources. The presence of air pollutants in the ambient air adversely affects the health of the population. In order to prevent and control air pollution, the Air (Prevention and Control of Pollution) Act was enacted in 1981. The responsibility has been further emphasized under Environment (Protection) Act, 1986. It is necessary to assess the present and anticipated air pollution through air quality survey/monitoring programs. Therefore, Central Pollution Control Board had started National Ambient Air Quality Monitoring (NAAQM) Network during 1984 - 85 at national level and gradually the number of stations has increased over the years. The programme was later renamed as National Air Quality Monitoring Programme (NAMP). The ambient air quality monitoring network involves measurement of a number of air pollutants at different locations in the country. Air quality monitoring requires proper selection of pollutants, selection of locations, frequency and duration of sampling, sampling techniques, infrastructural facilities, man power and operation and maintenance. The areas selected for monitoring are based on high traffic density, industrial growth, human population and its distribution, emission source, public complaints, the land use pattern etc. Generally, the basis of a network design are the pollution source and the pollutants present. The criteria pollutants measured are Suspended Particulate Matter (SPM), Respirable Suspended Particulate Matter (RSPM), Sulphur dioxide (SO₂), Oxides of Nitrogen (NO_x), and Carbon Monoxide (CO) etc.

The quality of the air that we breathe affects our health and quality of life. It can also have major impacts on the ecosystem. Measuring and understanding air pollution provides a sound scientific basis for its management and control. Historically, air pollution problem has typically been high levels of smoke and sulphur dioxide arising from the combustion of sulphur-containing fossil fuels such as coal for domestic and industrial purpose. However, now the major threat to clean urban air is posed by vehicular emission. A variety of pollutants are emitted by petrol and diesel-engine motor vehicles. These include carbon monoxide (CO), oxides of nitrogen (NO_x), volatile organic compounds (VOCs) and particulates (PM₁₀ and PM_{2.5}). The sources of particulate matter levels are vehicles, engine gensets, small scale industries, biomass incineration, boilers and emission from power plants, re-suspension of traffic dust, commercial and domestic use of fuels, etc. Fine particles contain microscopic

solids or liquid droplets that are very small and they can penetrate deep into the lung and cause serious health problems. Generally, coarse particles are directly emitted and fine particles can be formed in the atmosphere. Photochemical reactions resulting from the action of sunlight on nitrogen dioxide (NO₂) and VOCs from vehicles leads to the formation of ozone. Ozone is a secondary long-range pollutant, which affects areas far from the original emission site. The report presents results of ambient air quality monitoring carried out during the year 2008 at various monitoring stations under NAMP. Four criteria pollutants namely sulphur dioxide, nitrogen dioxide, respirable suspended particulate matter and suspended particulate matter have

been monitored regularly at various monitoring locations. The air quality is described in terms of low, moderate, high and critical levels based on an exceedance factor. The pollutants that are exceeding the standards in many cities are suspended particulate matter and respirable suspended particulate matter. Results of additional pollutants such as benzene and carbonmonoxide monitored in Delhi and ammonia in six cities have also been presented. The next few chapters present details of the National Air Quality Monitoring Programme and major findings during the year 2008. Also detailed are the initiatives taken for air pollution control.

Air Pollutants

a) Sulphur dioxide (SO₂)

SO₂ is formed when fuel containing sulfur is burned. Sulfur is prevalent in raw materials such as crude oil, coal, and ore that contain common metals like aluminum, copper, zinc, lead etc. SO₂ reacts with other gases in the atmosphere to form sulphates that can cause harm to human health. Effects of SO₂ include respiratory illness, visibility impairment, acid rain and aesthetic damage. Sulfur oxides are emitted in significant quantities from thermal power plants, smelting process of sulfide ores to produce copper, lead and zinc and also from petroleum refining processes. The diesel driven vehicles are specific source of sulfur dioxide generated during combustion process. Sulfate particles, can be transported over long distances and deposited far from the sources. SO₂ can result in respiratory illness, particularly in children and the elderly, and it can also aggravate existing heart and lung diseases.

b) Oxides of Nitrogen (NO_x)

Oxides of nitrogen are a generic term for a group of highly reactive gases that contain nitrogen and oxygen in varying amounts. Nitrogen dioxide (NO₂) along with particulates is seen as a reddish brown layer over urban areas. Nitrogen oxides are formed when fuel is burned at high temperature. Sources of nitrogen oxides includes vehicles, industrial processes that burn fuel. Oxides of nitrogen react with Volatile Organic Compounds (VOCs) to form ground level ozone. They also react to form nitrates, acid aerosols. They also contribute to nutrient overload that deteriorates water quality. Nitrogen dioxide irritates the nose and throat, and it appears to increase susceptibility to respiratory infections.

c) Particulate Matter (RSPM10 & PM_{2.5})

Particulate matter is a mixture of many subclasses of pollutants that contain many different chemical species. The particle size is often described by aerodynamic diameter. Aerodynamic diameter depends on particle density and is defined as the diameter of a particle with the same settling velocity as spherical particle with unit density i.e. 1 g/cm³ (USEPA, 1996). PM₁₀ are the particles with upper size limited by a 50% cut at 10 µm aerodynamic diameter (USEPA, 1996). PM₁₀ can be formed by physical processes of crushing, grinding and abrasion of surfaces. Mining and agricultural activities are some of the sources of large size particles. PM_{2.5} are the particles with upper size limited by a 50% cut at 2.5 µm aerodynamic diameter (USEPA, 1996). Particulate matter is called primary if it is in the same form chemical form in which it is emitted into the atmosphere. The primary particulate matter includes wind blown dust such as road dust, fly ash, soot etc. Particulate matter is called secondary if it is formed by chemical reactions in the atmosphere. Secondary particulate matter include sulphates, nitrates etc.

The size of particles is directly linked to their potential for causing health problems. Small particles less than 2.5 micrometers in diameter pose the greatest problems, because they can get deep into your lungs, and some may even get into your blood stream. Numerous scientific

studies have linked particle pollution exposure to a variety of problems, including increased respiratory symptoms, such as irritation of the airways, coughing, or difficulty breathing, decreased lung function; aggravated asthma; development of chronic bronchitis; irregular heartbeat; nonfatal heart attacks; and premature death in people with heart or lung disease (USEPA, 2008). People with heart or lung diseases, children and older adults are the most likely to be affected by particle pollution exposure (USEPA, 2008). Environmental effects of particulate matter include visibility reduction, aesthetic damage etc.

Composition of Particulate Matter

Atmospheric particles include combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; and soil-like particles from resuspended dust. The major constituents of RSPM are organic and elemental carbon, metals/elements like silicon, magnesium, iron, ions like sulphates, nitrates, ammonium etc. Understanding composition of particulate matter is most important to gain insight into the health effects caused and sources to be controlled. Composition of particulate matter varies from place to place and season depending upon sources present.

(i) Elemental Carbon

Elemental carbon (EC), also called "black carbon" or "graphitic carbon", has a chemical structure similar to impure graphite. Atmospheric elemental carbon is from primary anthropogenic sources and is not formed by reactions involving gaseous hydrocarbon precursors in the atmosphere. EC plays an important role in atmospheric chemistry because of its adsorptive and catalytic properties, which can capture other pollutants to react on its surface.

(ii) Organic Carbon

Organic carbon (OC), a mixture of hydrocarbons and oxygenates, is formed by a variety of processes, including combustion and secondary organic aerosol (SOA) formation. Organic carbon may be emitted as primary particles directly from sources, but secondary organics can also be formed in the atmosphere from the low vapor pressure products of atmospheric chemical reactions. OC is a complex mixture of different organic compounds, containing polycyclic aromatic hydrocarbons and other components.

(iii) Elements/Metals

Calcium, aluminum, silicon, magnesium, and iron are some of the crustal material found predominately in the coarse particles. Most of the elements are emitted from coal, oil combustion, vehicles, and industrial processes. Other sources include crustal material from road dust, tyre wear, construction activities etc.

(iv) Ions

The common ions found in particulate matter are sodium, sulphates, nitrates, calcium, chloride, potassium. Potassium and nitrate may be found in both the small size and coarse particles. Potassium comes from soil in coarse particles and in small size particles it comes from wood burning. Nitrate is formed by reaction of gas phase nitric acid with gas-phase ammonia forming particulate ammonium nitrate.

d) Carbon Monoxide (CO)

Carbon monoxide is a colorless, odorless and poisonous gas. It is formed by incomplete combustion of carbon containing fuels. Major source of CO are vehicles. Incomplete combustion is most likely to occur at low air-to-fuel ratios in the engine. These conditions are common during vehicle starting when air supply is restricted and are not tuned properly, and at altitude, where thin air effectively reduces the amount of oxygen available for combustion. CO enters the bloodstream through lungs and forms carboxyhemoglobin which inhibits blood's oxygen carrying capacity to organs and tissues. Persons with heart disease are especially sensitive to carbon monoxide poisoning and may experience chest pain if they breathe the gas while exercising. Infants, elderly persons, and individuals with respiratory diseases are also particularly sensitive.

e) Ozone

Ozone is a secondary pollutant formed in the atmosphere by reaction between oxides of nitrogen and volatile organic compounds (VOCs) in the presence of sunlight. Vehicles, industrial emissions, gasoline vapours, chemical solvents emit oxides of nitrogen and VOCs that form ozone. Peak O₃ levels occur typically during the warmer times of the year.

f) Ammonia

Ammonia is found in small quantities in the atmosphere, and is produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia occurs naturally and is produced by human activity. Ammonia and ammonium salts are also found in small quantities in rainwater. It is an important source of nitrogen which is needed by plants and animals. Ammonia gas can be dissolved in water and is called liquid ammonia or aqueous ammonia. Once exposed to open air, liquid ammonia quickly turns into a gas. Exposure to ammonia may occur by breathing or consuming food or water containing ammonia. No health effects have been found in humans exposed to typical environmental concentrations of ammonia. Exposure to high levels of ammonia in air may be irritating to skin, eyes, throat, and lungs and cause coughing and burns. Lung damage and death may occur after exposure to very high concentrations of ammonia.

g) Hazardous Air Pollutants

Hazardous air pollutants are also known as toxic air pollutants which may cause health effects such as reproductive effects, cancer etc. Toxic air pollutants include benzene, perchlorethylene, methylene chloride, dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds. Sources of benzene are gasoline and perchlorethylene, is emitted from some dry cleaning facilities. Methylene chloride is used as a solvent and paint stripper by a number of industries. As per USEPA, 2007 (Source: <http://www.epa.gov/ttn/atw/allabout.html>) people exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of experiencing serious health effects and these health effects can include damage to the immune system, as well as neurological, reproductive (e.g., reduced fertility), developmental, respiratory, cancer and other health problems. Also as per USEPA, 2007, in addition to exposure from breathing air toxics, some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain.

I.II Air (Prevention and Control of Pollution) Act 1981

Government of India enacted the Air (Prevention and Control of Pollution) Act 1981 to arrest the deterioration in the air quality. The act prescribes various functions for the Central Pollution Control Board (CPCB) at the control level and State Pollution Control Boards at the state level. The main functions of the Central Pollution Control Board are as follows:

- To advise the Central Government on any matter concerning the improvement of the quality of the air and the prevention, control and abatement of air pollution.
- To plan and cause to be executed a nation-wide programme for the prevention, control and abatement of air pollution.
- To provide technical assistance and guidance to the State Pollution Control Board.
- To carry out and sponsor investigations and research related to prevention, control and abatement of air pollution.
- To collect, compile and publish technical and statistical data related to air pollution; and
- To lay down standards for the quality of air. The main functions of the State Pollution Control Boards are as follows:
 - To plan a comprehensive programme for prevention, control and abatement of air pollution and to secure the execution thereof.
 - To advise the State Government on any matter concerning prevention, control and abatement of air pollution.
 - To collect and disseminate information related to air pollution.
 - To collaborate with Central Pollution Control Board in programme related to prevention, control and abatement of air pollution; and
 - To inspect air pollution control areas, assess quality of air and to take steps for prevention, control and abatement of air pollution in such areas.

I.III National Ambient Air Quality Standards (NAAQS)

The ambient air quality objectives/standards are pre-requisite for developing programme for effective management of ambient air quality and to reduce the damaging effects of air pollution. The objectives of air quality standards are:

- To indicate the levels of air quality necessary with an adequate margin of safety to protect the public health, vegetation and property;
- To assist in establishing priorities for abatement and control of pollutant level;
- To provide uniform yardstick for assessing air quality at national level; and
- To indicate the need and extent of monitoring programme.

Air Quality Monitoring and AQI Considerations

The air quality monitoring network in India can be classified as (i) online and (ii) manual. The pollutant parameters, frequency of measurement and monitoring methodologies for two networks are very different. The AQI system for these networks could be at variance, especially for reporting and completeness in terms of parameters. (i) Online Monitoring network: These are automated air quality monitoring stations which record continuous hourly, monthly or annually averaged data. In India, ~ 40 automatic monitoring stations are operated (e.g. Figure 3.2: continuous stations in Delhi), where parameters like PM₁₀, PM_{2.5}, NO₂, SO₂, CO, O₃, etc. are monitored continuously. Data from these stations are available almost in real-time. Thus such networks are most suitable for computation of AQI sub-indices, as information on AQI can be

generated in real time. For AQI to be more useful and effective, there is a need to set up more online monitoring stations for continuous and easy availability of air quality data for computation of AQI for more Indian cities.

Manual:

The manual stations involve mostly intermittent air quality data collection, thus such stations are not suitable for AQI calculation particularly for its quick dissemination. In India, air quality is being monitored manually at 573 locations under National Air Monitoring Programme (NAMP). In most of these manually operated stations, only three criteria pollutants viz. PM₁₀, sulphur dioxide (SO₂) and nitrogen dioxide (NO₂) are measured, at some stations PM_{2.5} and Pb are also measured. The monitoring frequency is twice a week. Such manual networks are not suitable for computing AQI, as availability of monitored data could have a lag of 1-3 days and sometimes not available at all. However, some efforts are required to use the information in some productive manner. Historical AQIs on weekly basis can be calculated and used for data interpretation and ranking of cities or towns for further prioritization of actions on air pollution control.

Computation and Basis of Sub-index Breakpoints Segmented linear functions are used for relating actual air pollution concentration (X_i) (of each pollutant) to a normalized number referred to as sub-index (I_i). While AQI system is not complex in understanding, to arrive at breakpoints which will relate to AQI description is of paramount significance. Consequences of inappropriate adoption of breakpoints could be far reaching; it may lead to incorrect information to general public (on health effects) and decisions taken for pollution control may be incorrect. The basis for linear functions (for this study) to relate air quality levels to AQI requires careful consideration. Services of practicing doctors and experts in this field (see Appendix 1) have proved very useful. In this study, in addition to dose response relationship, the breakpoints adopted by other countries/agencies (USEPA 2014; U.K. 2013; Malaysia 2013; GVAQI 2013; Ontario 2013) have been examined for using these in INDAQI. It is important that an AQI system should build on AQS and pollutant dose-response relationships to describe air quality in simple terms which clearly relates to health impacts. The first step for arriving at breakpoints for each pollutant is to consider attainment of INAQs (Table 3.1). The index category is classified as 'good' for concentration range up to half of INAQs (for example, for SO₂ AQI=0-50 for concentration range of 0-40 µg/m³) and as 'satisfactory' up to attainment of INAQs (i.e. SO₂ range 41-80 µg/m³ linearly maps to AQI=51-100). To arrive at breakpoints for other categories (for each pollutant), we require a thorough research/review of dose response relationships, which is described here.

3.3.1 Carbon Mono-oxide (CO) Carbon monoxide (CO) is an important criteria pollutant which is ubiquitous in urban environment. CO production mostly occurs from sources having incomplete combustion. Due to its toxicity and appreciable mass in atmosphere, it should be considered as an important pollutant in AQI scheme. CO rapidly diffuses across alveolar, capillary and placental membranes. Approximately 80-90% of absorbed CO binds with Hb to form Carboxyhaemoglobin (COHb), which is a specific biomarker of exposure in blood. The affinity of Hb for CO is 200-250 times than that of oxygen. In patients with hemolytic anemia, the CO production rate was 2-8 times higher and blood COHb concentration was 2-3 times higher than in normal person (WHO 2000). The initial symptoms of CO poisoning may include headache, dizziness, drowsiness, and nausea. These initial symptoms may advance to vomiting, loss of consciousness, and collapse if prolonged or high exposures are encountered and may lead

to Coma or death if high exposures continue. A US study estimated that 6 per cent of the congestive heart failures and hospitalizations in the cities were related to an increase in CO concentration in ambient atmosphere (WHO 2000). Reduction in the ability of blood to transport oxygen leads to tissue hypoxia. The body compensates for this stress by increasing cardiac output and the blood flow to specific areas, such as the heart and brain. As the level of COHb in the blood increases, the person suffers from effects which become progressively more serious. CO has both 1 hr and 8 hr standard. Figure 3.3 shows air pollution level and percent of COHb. The symptoms associated with various percent blood saturation levels of COHb

Nitrogen Dioxide (NO₂)

The major source of NO₂ is combustion processes. An appreciable quantity of NO₂ is present in rural and urban environments. Further, NO₂ is showing alarmingly high increasing trend in Indian cities due to increase in number of vehicles. On inhalation, 70–90% of NO₂ can be absorbed in the respiratory tract of humans, and physical exercise increases the total percentage absorbed (Miller et al., 1982). NO₂ exposure can cause decrement in lung function (i.e. increased airway resistance), increased airway responsiveness to broncho-constrictions in healthy subjects at concentration exceeding 1 ppm (WHO 2000). Below 1 ppm level, there are evidences of change in lung volume, flow volume, characteristics of lung or airway resistance in healthy persons. It has been established that continuous exposure with as little as 0.1 ppm NO₂ over a period of one to three years, increases incidence of bronchitis, emphysema and have adverse effect on lung performance (WHO 2000). Exposure to excessive NO₂, affects the defence mechanism leaving the host susceptible to respiratory illness. Chronic exposure of NO₂ may lead to chronic lung disease and variety of structural/morphological changes in lung epithelium conducting airways and air-gas exchange region. Exposure to high levels (>1.0 ppm) of NO₂ causes Eustachian of bronchiolar and alveolar epithelium, inflammation of epithelium and definite emphysema (WHO 2000). Normal healthy people exposed at rest or with light exercise for less than 2 hours to concentrations of more than 4700 µg/m³ (2.5 ppm) experience pronounced decrements in pulmonary function; generally, such people are not affected at less than 1880 µg/m³ (1 ppm). One study showed that the lung function of people with chronic obstructive pulmonary disease is slightly affected by a 3.75-hour exposure to 560 µg/m³ (0.3 ppm). A wide range of findings in asthmatics has been reported; one study observed no effects from a 75-minute exposure to 7520 µg/m³ (4 ppm), whereas others showed decreases in FEV₁ (forced expiration volume in one second) after 10 minutes of exercise during exposure to 560 µg/m³ (0.3 ppm). The lowest concentration causing effects on pulmonary function was reported from two laboratories that exposed mild asthmatics for 30–110 minutes to 560 µg/m³ (0.3 ppm) during intermittent exercise (WHO 2000). WHO (2003) has reported some but not all studies show increased responsiveness to bronchoconstrictors at nitrogen dioxide levels as low as 376–560 µg/m³ (0.2–0.3 ppm); in other studies, higher levels had no such effect. Studies of asthmatics exposed to 380–560 µg/m³ indicate a change of about 5% in pulmonary function and an increase in airway responsiveness to bronchoconstrictors. Asthmatics are more susceptible to the acute effects of nitrogen dioxide as they have higher baseline airway responsiveness. For acute exposures, only very high concentrations (1990 µg/m³; > 1000 ppb) affect healthy people. Asthmatics and patients with chronic obstructive pulmonary disease are clearly more susceptible to acute changes in lung function, airway responsiveness and respiratory symptoms. Given the small changes in lung function (< 5% drop in FEV₁ between air and nitrogen dioxide exposure) and changes in airway responsiveness reported in several studies, 375–565 µg/m³ (0.20 to 0.30

ppm) is a clear lowest-observed effect level. A 50% margin of safety is proposed because of the reported statistically significant increase in response to a bronchoconstrictor (increased airway responsiveness) with exposure to 190 $\mu\text{g}/\text{m}^3$ and a metaanalysis suggesting changes in airway responsiveness below 365 $\mu\text{g}/\text{m}^3$ (WHO 2000). After giving due consideration to INAQS for NO_2 , two categories good (Sub-Index: 0-50) and satisfactory (51-100), the breakpoint concentrations are fixed as 40 $\mu\text{g}/\text{m}^3$ and 80 $\mu\text{g}/\text{m}^3$. Various studies reported that the small change in lung function (< 5% drop in FEV1 between air and nitrogen dioxide exposure) and changes in airway responsiveness gives 375–565 $\mu\text{g}/\text{m}^3$ (0.20 to 0.30 ppm), as the lowest-observed-effect level. Therefore, breakpoints of 280 $\mu\text{g}/\text{m}^3$ for poor, 400 $\mu\text{g}/\text{m}^3$ for very poor and 400+ $\mu\text{g}/\text{m}^3$ for severe category are adopted. For moderately-polluted category an intermediate value of 180 $\mu\text{g}/\text{m}^3$ (between 80 and 280 $\mu\text{g}/\text{m}^3$) has been adopted. It may be noted that minor tweaking has been done with breakpoints so that these also corroborate with international breakpoints adopted by other countries. The details of proposed break points for IND-AQI and breakpoints of USEPA, China and EU

Particulate Matter (PM):

PM10 and PM2.5 PM levels in Indian cities are about 4-5 times higher than in the US cities (WRI, 1996). These high PM levels may have severe impact on public health. The sixteen-year long survey by Dockery et al. (1994) has revealed that there is a strong correlation between ambient PM concentrations and increase in mortality and hospitalizations due to respiratory diseases. Several epidemiological studies (Pope, 1989; Schwartz, 1996) have linked PM10 (aerodynamic diameter $\leq 10 \mu\text{m}$) and PM2.5 with significant health problems, including: premature mortality, chronic respiratory disease, emergency visits and hospital admissions, aggravated asthma, acute respiratory symptoms, and decrease in lung function. PM2.5 is of specific concern because it contains a high proportion of various toxic metals and acids, and aerodynamically it can penetrate deeper into the respiratory tract. A HEI study, (Wichmann et al., 2000) reported that the concentration of both ultrafine.

Clean Air Implementation Plans

Air quality management aims at the preservation of environmental quality by prescribing the tolerated degree of pollution, leaving it to the local authorities and polluters to devise and implement actions to ensure that this degree of pollution will not be exceeded. An example of legislation within this approach is the adoption of ambient air quality standards based, very often, on air quality guidelines (WHO 1987) for different pollutants; these are accepted maximum levels of pollutants (or indicators) in the target area (e.g., at ground level at a specified point in a community) and can be either primary or secondary standards. Primary standards (WHO 1980) are the maximum levels consistent with an adequate safety margin and with the preservation of public health, and must be complied with within a specific time limit; secondary standards are those judged to be necessary for protection against known or anticipated adverse effects other than health hazards (mainly on vegetation) and must be complied "within a reasonable time". Air quality standards are short-, medium- or long-term values valid for 24 hours per day, 7 days per week, and for monthly, seasonal or annual exposure of all living subjects (including sensitive subgroups such as children, the elderly and the sick) as well as non-living objects; this is in contrast to maximum permissible levels for occupational exposure, which are for a partial

weekly exposure (e.g., 8 hours per day, 5 days per week) of adult and supposedly healthy workers.

Typical measures in air quality management are control measures at the source, for example, enforcement of the use of catalytic converters in vehicles or of emission standards in incinerators, land-use planning and shut-down of factories or reduction of traffic during unfavourable weather conditions. The best air quality management stresses that the air pollutant emissions should be kept to a minimum; this is basically defined through emission standards for single sources of air pollution and could be achieved for industrial sources, for example, through closed systems and high-efficiency collectors. An emission standard is a limit on the amount or concentration of a pollutant emitted from a source. This type of legislation requires a decision, for each industry, on the best means of controlling its emissions (i.e., fixing emission standards).

The basic aim of air pollution management is to derive a clean air implementation plan (or air pollution abatement plan) (Schwela and Köth-Jahr 1994) which consists of the following elements:

- + description of area with respect to topography, meteorology and socio economy
- + Emissions inventory
- + Comparison with emission standards
- + Air pollutant concentrations inventory
- + Simulated air pollutant concentrations
- + Comparison with air quality standards
- + Inventory of effects on public health and the environment
- + Causal analysis
- + control measures
- + cost of control measures
- + cost of public health and environmental effects
- + Cost-benefit analysis (costs of control vs. costs of efforts)
- + Transportation and land-use planning
- + Enforcement plan; resource commitment
- + Projections for the future on population, traffic, industries and fuel consumption

- Strategies for follow-up.

Some of these issues will be described below.

Emissions Inventory; Comparison with Emission Standards

The emissions inventory is a most complete listing of sources in a given area and of their individual emissions, estimated as accurately as possible from all emitting point, line and area (diffuse) sources. When these emissions are compared with emission standards set for a particular source, first hints on possible control measures are given if emission standards are not complied with. The emissions inventory also serves to assess a priority list of important sources according to the amount of pollutants emitted, and indicates the relative influence of different sources—for example, traffic as compared to industrial or residential sources. The emissions inventory also allows an estimate of air pollutant concentrations for those pollutants for which ambient concentration measurements are difficult or too expensive to perform.

Air Pollutant Concentrations Inventory; Comparison with Air Quality Standards

The air pollutant concentrations inventory summarizes the results of the monitoring of ambient air pollutants in terms of annual means, percentiles and trends of these quantities. Compounds measured for such an inventory include the following:

- Sulphur dioxide
- Nitrogen oxides
- suspended particulate matter
- Carbon monoxide
- Ozone
- Heavy metals (Pb, Cd, Ni, Cu, Fe, As, Be)
- polycyclic aromatic hydrocarbons: benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzoghi)perylene, coronen
- volatile organic compounds: *n*-hexane, benzene, 3-methyl-hexane, *n*-heptane, toluene, octane, ethyl-benzene xylene (*o*-,*m*-,*p*-), *n*-nonane, isopropylbenzene, propylbenzene, *n*-2-/3-/4-ethyltoluene, 1,2,4-/1,3,5-trimethylbenzene, trichloromethane, 1,1,1 trichloroethane, tetrachloromethane, tri-/tetrachloroethene.

Comparison of air pollutant concentrations with air quality standards or guidelines, if they exist, indicates problem areas for which a causal analysis has to be performed in order to find out which sources are responsible for the non-compliance. Dispersion modelling has to be used in performing this causal analysis (see “Air pollution: Modelling of air pollutant dispersion”).

Devices and procedures used in today's ambient air pollution monitoring are described in "Air quality monitoring".

Simulated Air Pollutant Concentrations; Comparison with Air Quality Standards

Starting from the emissions inventory, with its thousands of compounds which cannot all be monitored in the ambient air for economy reasons, use of dispersion modelling can help to estimate the concentrations of more "exotic" compounds. Using appropriate meteorology parameters in a suitable dispersion model, annual averages and percentiles can be estimated and compared to air quality standards or guidelines, if they exist.

Inventory of Effects on Public Health and the Environment; Causal Analysis

Another important source of information is the effects inventory (Ministerium für Umwelt 1993), which consists of results of epidemiological studies in the given area and of effects of air pollution observed in biological and material receptors such as, for example, plants, animals and construction metals and building stones. Observed effects attributed to air pollution have to be causally analysed with respect to the component responsible for a particular effect—for example, increased prevalence of chronic bronchitis in a polluted area. If the compound or compounds have been fixed in a causal analysis (compound-causal analysis), a second analysis has to be performed to find out the responsible sources (source-causal analysis).

Control Measures; Cost of Control Measures

Control measures for industrial facilities include adequate, well-designed, well-installed, efficiently operated and maintained air cleaning devices, also called separators or collectors. A separator or collector can be defined as an "apparatus for separating any one or more of the following from a gaseous medium in which they are suspended or mixed: solid particles (filter and dust separators), liquid particles (filter and droplet separator) and gases (gas purifier)". The basic types of air pollution control equipment (discussed further in "Air pollution control") are the following:

- For particulate matter: inertial separators (e.g., cyclones); fabric filters (baghouses); electrostatic precipitators; wet collectors (scrubbers)
- For gaseous pollutants: wet collectors (scrubbers); adsorption units (e.g., adsorption beds); afterburners, which can be direct-fired (thermal incineration) or catalytic (catalytic combustion).

Wet collectors (scrubbers) can be used to collect, at the same time, gaseous pollutants and particulate matter. Also, certain types of combustion devices can burn combustible gases and vapours as well as certain combustible aerosols. Depending on the type of effluent, one or a combination of more than one collector can be used.

The control of odours that are chemically identifiable relies on the control of the chemical agent(s) from which they emanate (e.g., by absorption, by incineration). However, when an odour is not defined chemically or the producing agent is found at extremely low levels, other

techniques may be used, such as masking (by a stronger, more agreeable and harmless agent) or counteraction (by an additive which counteracts or partially neutralizes the offensive odour).

It should be kept in mind that adequate operation and maintenance are indispensable to ensure the expected efficiency from a collector. This should be ensured at the planning stage, both from the know-how and financial points of view. Energy requirements must not be overlooked. Whenever selecting an air cleaning device, not only the initial cost but also operational and maintenance costs should be considered. Whenever dealing with high-toxicity pollutants, high efficiency should be ensured, as well as special procedures for maintenance and disposal of waste materials.

The fundamental control measures in industrial facilities are the following:

Substitution of materials. Examples: substitution of less toxic solvents for highly toxic ones used in certain industrial processes; use of fuels with lower sulphur content (e.g., washed coal), therefore giving rise to less sulphur compounds and so on.

Modification or change of the industrial process or equipment. Examples: in the steel industry, a change from raw ore to pelleted sintered ore (to reduce the dust released during ore handling); use of closed systems instead of open ones; change of fuel heating systems to steam, hot water or electrical systems; use of catalysers at the exhaust air outlets (combustion processes) and so on.

Modifications in processes, as well as in plant layout, may also facilitate and/or improve the conditions for dispersion and collection of pollutants. For example, a different plant layout may facilitate the installation of a local exhaust system; the performance of a process at a lower rate may allow the use of a certain collector (with volume limitations but otherwise adequate). Process modifications that concentrate different effluent sources are closely related to the volume of effluent handled, and the efficiency of some air-cleaning equipment increases with the concentration of pollutants in the effluent. Both the substitution of materials and the modification of processes may have technical and/or economic limitations, and these should be considered.

Adequate housekeeping and storage. Examples: strict sanitation in food and animal product processing; avoidance of open storage of chemicals (e.g., sulphur piles) or dusty materials (e.g., sand), or, failing this, spraying of the piles of loose particulate with water (if possible) or application of surface coatings (e.g., wetting agents, plastic) to piles of materials likely to give off pollutants.

Adequate disposal of wastes. Examples: avoidance of simply piling up chemical wastes (such as scraps from polymerization reactors), as well as of dumping pollutant materials (solid or liquid) in water streams. The latter practice not only causes water pollution but can also create a secondary source of air pollution, as in the case of liquid wastes from sulphite process pulp mills, which release offensive odorous gaseous pollutants.

Maintenance. Example: well maintained and well-tuned internal combustion engines produce less carbon monoxide and hydrocarbons.

Work practices. Example: taking into account meteorological conditions, particularly winds, when spraying pesticides.

By analogy with adequate practices at the workplace, good practices at the community level can contribute to air pollution control - for example, changes in the use of motor vehicles (more collective transportation, small cars and so on) and control of heating facilities (better insulation of buildings in order to require less heating, better fuels and so on).

Control measures in vehicle emissions are adequate and efficient mandatory inspection and maintenance programmes which are enforced for the existing car fleet, programmes of enforcement of the use of catalytic converters in new cars, aggressive substitution of solar/battery-powered cars for fuel-powered ones, regulation of road traffic, and transportation and land use planning concepts.

Motor vehicle emissions are controlled by controlling emissions per vehicle mile travelled (VMT) and by controlling VMT itself (Walsh 1992). Emissions per VMT can be reduced by controlling vehicle performance - hardware, maintenance - for both new and in-use cars. Fuel composition of leaded gasoline may be controlled by reducing lead or sulphur content, which also has a beneficial effect on decreasing HC emissions from vehicles. Lowering the levels of sulphur in diesel fuel as a means to lower diesel particulate emission has the additional beneficial effect of increasing the potential for catalytic control of diesel particulate and organic HC emissions.

Another important management tool for reducing vehicle evaporative and refuelling emissions is the control of gasoline volatility. Control of fuel volatility can greatly lower vehicle evaporative HC emissions. Use of oxygenated additives in gasoline lowers HC and CO exhaust as long as fuel volatility is not increased.

Reduction of VMT is an additional means of controlling vehicle emissions by control strategies such as

- use of more efficient transportation modes
- increasing the average number of passengers per car
- spreading congested peak traffic loads
- reducing travel demand.

While such approaches promote fuel conservation, they are not yet accepted by the general population, and governments have not seriously tried to implement them.

All these technological and political solutions to the motor vehicle problem except substitution of electrical cars are increasingly offset by growth in the vehicle population. The vehicle problem can be solved only if the growth problem is addressed in an appropriate way.

Cost of Public Health and Environmental Effects; Cost-Benefit Analysis

The estimation of the costs of public health and environmental effects is the most difficult part of a clean air implementation plan, as it is very difficult to estimate the value of lifetime reduction of disabling illnesses, hospital admission rates and hours of work lost. However, this estimation and a comparison with the cost of control measures is absolutely necessary in order to balance the costs of control measures versus the costs of no such measure undertaken, in terms of public health and environmental effects.

Transportation and Land-Use Planning

The pollution problem is intimately connected to land-use and transportation, including issues such as community planning, road design, traffic control and mass transportation; to concerns of demography, topography and economy; and to social concerns (Venzia 1977). In general, the rapidly growing urban aggregations have severe pollution problems due to poor land-use and transportation practices. Transportation planning for air pollution control includes transportation controls, transportation policies, mass transit and highway congestion costs. Transportation controls have an important impact on the general public in terms of equity, repressiveness and social and economic disruption - in particular, direct transportation controls such as motor vehicle constraints, gasoline limitations and motor vehicle emission reductions. Emission reductions due to direct controls can be reliably estimated and verified. Indirect transportation controls such as reduction of vehicle miles travelled by improvement of mass transit systems, traffic flow improvement regulations, regulations on parking lots, road and gasoline taxes, car-use permissions and incentives for voluntary approaches are mostly based on past trial-and-error experience, and include many uncertainties when trying to develop a viable transportation plan.

National action plans incurring indirect transportation controls can affect transportation and land-use planning with regard to highways, parking lots and shopping centres. Long-term planning for the transportation system and the area influenced by it will prevent significant deterioration of air quality and provide for compliance with air quality standards. Mass transit is consistently considered as a potential solution for urban air pollution problems. Selection of a mass transit system to serve an area and different modal splits between highway use and bus or rail service will ultimately alter land-use patterns. There is an optimum split that will minimize air pollution; however, this may not be acceptable when non-environmental factors are considered.

The automobile has been called the greatest generator of economic externalities ever known. Some of these, such as jobs and mobility, are positive, but the negative ones, such as air pollution, accidents resulting in death and injury, property damage, noise, loss of time, and aggravation, lead to the conclusion that transportation is not a decreasing cost industry in urbanized areas. Highway congestion costs are another externality; lost time and congestion costs, however, are difficult to determine. A true evaluation of competing transportation modes, such as mass transportation, cannot be obtained if travel costs for work trips do not include congestion costs.

Land-use planning for air pollution control includes zoning codes and performance standards, land-use controls, housing and land development, and land-use planning policies. Land-use

zoning was the initial attempt to accomplish protection of the people, their property and their economic opportunity. However, the ubiquitous nature of air pollutants required more than physical separation of industries and residential areas to protect the individual. For this reason, performance standards based initially on aesthetics or qualitative decisions were introduced into some zoning codes in an attempt to quantify criteria for identifying potential problems.

The limitations of the assimilative capacity of the environment must be identified for long-term land-use planning. Then, land-use controls can be developed that will prorate the capacity equitably among desired local activities. Land-use controls include permit systems for review of new stationary sources, zoning regulation between industrial and residential areas, restriction by easement or purchase of land, receptor location control, emission-density zoning and emission allocation regulations.

Housing policies aimed at making home ownership available to many who could otherwise not afford it (such as tax incentives and mortgage policies) stimulate urban sprawl and indirectly discourage higher-density residential development. These policies have now proven to be environmentally disastrous, as no consideration was given to the simultaneous development of efficient transportation systems to serve the needs of the multitude of new communities being developed. The lesson learnt from this development is that programmes impacting on the environment should be coordinated, and comprehensive planning undertaken at the level where the problem occurs and on a scale large enough to include the entire system.

Land-use planning must be examined at national, provincial or state, regional and local levels to adequately ensure long-term protection of the environment. Governmental programmes usually start with power plant siting, mineral extraction sites, coastal zoning and desert, mountain or other recreational development. As the multiplicity of local governments in a given region cannot adequately deal with regional environmental problems, regional governments or agencies should coordinate land development and density patterns by supervising the spatial arrangement and location of new construction and use, and transportation facilities. Land-use and transportation planning must be interrelated with enforcement of regulations to maintain the desired air quality. Ideally, air pollution control should be planned for by the same regional agency that does land-use planning because of the overlapping externalities associated with both issues.

Enforcement Plan, Resource Commitment

The clean air implementation plan should always contain an enforcement plan which indicates how the control measures can be enforced. This implies also a resource commitment which, according to a polluter pays principle, will state what the polluter has to implement and how the government will help the polluter in fulfilling the commitment.

Projections for the Future

In the sense of a precautionary plan, the clean air implementation plan should also include estimates of the trends in population, traffic, industries and fuel consumption in order to assess

responses to future problems. This will avoid future stresses by enforcing measures well in advance of imagined problems.

Strategies for Follow-up

A strategy for follow-up of air quality management consists of plans and policies on how to implement future clean air implementation plans.

Role of Environmental Impact Assessment

Environmental impact assessment (EIA) is the process of providing a detailed statement by the responsible agency on the environmental impact of a proposed action significantly affecting the quality of the human environment (Lee 1993). EIA is an instrument of prevention aiming at consideration of the human environment at an early stage of the development of a programme or project.

EIA is particularly important for countries which develop projects in the framework of economic reorientation and restructuring. EIA has become legislation in many developed countries and is now increasingly applied in developing countries and economies in transition.

EIA is integrative in the sense of comprehensive environmental planning and management considering the interactions between different environmental media. On the other hand, EIA integrates the estimation of environmental consequences into the planning process and thereby becomes an instrument of sustainable development. EIA also combines technical and participative properties as it collects, analyses and applies scientific and technical data with consideration of quality control and quality assurance, and stresses the importance of consultations prior to licensing procedures between environmental agencies and the public which could be affected by particular projects. A clean air implementation plan can be considered as a part of the EIA procedure with reference to the air.

AIR QUALITY MONITORING

Air quality monitoring means the systematic measurement of ambient air pollutants in order to be able to assess the exposure of vulnerable receptors (e.g., people, animals, plants and art works) on the basis of standards and guidelines derived from observed effects, and/or to establish the source of the air pollution (causal analysis).

Ambient air pollutant concentrations are influenced by the spatial or time variance of emissions of hazardous substances and the dynamics of their dispersion in the air. As a consequence, marked daily and annual variations of concentrations occur. It is practically impossible to determine in a unified way all these different variations of air quality (in statistical language, the population of air quality states). Thus, ambient air pollutant concentrations measurements always have the character of random spatial or time samples.

Measurement Planning

The first step in measurement planning is to formulate the purpose of the measurement as precisely as possible. Important questions and fields of operation for air quality monitoring include:

Area measurement:

- + representative determination of exposure in one area (general air monitoring)
- + representative measurement of pre-existing pollution in the area of a planned facility (permit, TA Luft (Technical instruction, air))
- + smog warning (winter smog, high ozone concentrations)
- + measurements in hot spots of air pollution to estimate maximum exposure of receptors (EU-NO₂ guideline, measurements in street canyons, in accordance with the German Federal Immission Control Act)
- + checking the results of pollution abatement measures and trends over time
- + screening measurements
- + scientific investigations - for example, the transport of air pollution, chemical conversions, calibrating dispersion calculations.

Facility measurement:

- + measurements in response to complaints
- + ascertaining sources of emissions, causal analysis
- + measurements in cases of fires and accidental releases
- + checking success of reduction measures
- + monitoring factory fugitive emissions.

The goal of measurement planning is to use adequate measurement and assessment procedures to answer specific questions with sufficient certainty and at minimum possible expense.

An example of the parameters that should be used for measurement planning is presented in table in relation to an assessment of air pollution in the area of a planned industrial facility. Recognizing that formal requirements vary by jurisdiction, it should be noted that specific reference here is made to German licensing procedures for industrial facilities.

Parameters for measurement planning in measuring ambient air pollution concentrations (with example of application)

Parameter	Example of application: Licensing procedure for industrial facilities in Germany
Statement of the question	Measurement of prior pollution in the licensing procedure; representative random probe measurement
Area of measurement	Circle around location with radius 30 times actual chimney height (simplified)
Assessment standards (place and time dependent): characteristic values to be obtained from measurement data	Threshold limits IW1 (arithmetic mean) and IW2 (98th percentile) of TA Luft (Technical instruction, air); calculation of I1 (arithmetic mean) and I2 (98th percentile) from measurements taken for 1 km ² (assessment surface) to be compared with IW1 and IW2
Ordering, choice and density of measurement sites	Regular scan of 1km ² , resulting in "random" choice of measurement sites
Measurement time period	1 year, at least 6 months
Measurement height	1.5 to 4 metres above ground
Measurement frequency	52 (104) measurements per assessment area for gaseous pollutants, depending on the height of the pollution
Duration of each measurement	1/2 hour for gaseous pollutants, 24 hours for suspended dust, 1 month for dust precipitation
Measurement time	Random choice
Measured object	Air pollution emitted from the planned facility
Measurement procedure	National standard measurement procedure (VDI guidelines)
Necessary certainty of measurement results	High
Quality control, requirements, calibration, maintenance	VDI guidelines
Recording of measurement data, validation, archiving, assessment	Calculation of quantity of data I1V and I2V for every assessment area

Costs	Depend on measurement area and objectives
-------	---

The example in shows the case of a measurement network that is supposed to monitor the air quality in a specific area as representatively as possible, to compare with designated air quality limits. The idea behind this approach is that a random choice of measurement sites is made in order to cover equally locations in an area with varying air quality (e.g., living areas, streets, industrial zones, parks, city centres, suburbs). This approach may be very costly in large areas due to the number of measurement sites necessary.

Another conception for a measurement network therefore starts with measurement sites that are representatively selected. If measurements of differing air quality are conducted in the most important locations, and the length of time that the protected objects remain in these "microenvironments" is known, then the exposure can be determined. This approach can be extended to other microenvironments (e.g., interior rooms, cars) in order to estimate the total exposure. Diffusion modelling or screening measurements can help in choosing the right measurement sites.

A third approach is to measure at the points of presumed highest exposure (e.g., for NO₂ and benzene in street canyons). If assessment standards are met at this site, there is sufficient probability that this will also be the case for all other sites. This approach, by focusing on critical points, requires relatively few measurement sites, but these must be chosen with particular care. This particular method risks overestimating real exposure.

The parameters of measurement time period, assessment of the measurement data and measurement frequency are essentially given in the definition of the assessment standards (limits) and the desired level of certainty of the results. Threshold limits and the peripheral conditions to be considered in measurement planning are related. By using continuous measurement procedures, a resolution that is temporally almost seamless can be achieved. But this is necessary only in monitoring peak values and/or for smog warnings; for monitoring annual mean values, for example, discontinuous measurements are adequate.

The following section is dedicated to describing the capabilities of measurement procedures and quality control as a further parameter important to measurement planning.

Quality Assurance

Measurements of ambient air pollutant concentrations can be costly to conduct, and results can affect significant decisions with serious economic or ecological implications. Therefore, quality assurance measures are an integral part of the measurement process. Two areas should be distinguished here.

Procedure-oriented measures

Every complete measurement procedure consists of several steps: sampling, sample preparation and clean-up; separation, detection (final analytical step); and data collection and assessment. In

some cases, especially with continuous measurement of inorganic gases, some steps of the procedure can be left out (e.g., separation). Comprehensive adherence to procedures should be strived for in conducting measurements. Procedures that are standardized and thus comprehensively documented should be followed, in the form of DIN/ISO standards, CEN standards or VDI guidelines.

User-oriented measures

Using standardized and proven equipment and procedures for ambient air pollutant concentration measurement cannot alone ensure acceptable quality if the user does not employ adequate methods of quality control. The standards series DIN/EN/ISO 9000 (Quality Management and Quality Assurance Standards), EN 45000 (which defines the requirements for testing laboratories) and ISO Guide 25 (General Requirements for the Competence of Calibration and Testing Laboratories) are important for user-oriented measures to ensure quality.

Important aspects of user quality control measures include:

- acceptance and practice of the content of the measures in the sense of good laboratory practice (GLP)
- correct maintenance of measurement equipment, qualified measures to eliminate disruptions and ensure repairs
- carrying out calibrations and regular checking to ensure proper functioning
- carrying out interlaboratory testing.

Measurement Procedures

Measurement procedures for inorganic gases

A wealth of measurement procedures exists for the broad range of inorganic gases. We will differentiate between manual and automatic methods.

Manual procedures

In the case of manual measurement procedures for inorganic gases, the substance to be measured is normally adsorbed during the sampling in a solution or solid material. In most cases a photometric determination is made after an appropriate colour reaction. Several manual measurement procedures have special significance as reference procedures. Because of the relatively high personnel cost, these manual procedures are conducted only rarely for field

Material	Procedure	Execution	Comments
SO ₂	TCM procedure	Absorption in tetrachloromercurate solution (wash bottle); reaction with formaldehyde and pararosaniline to red-violet sulphonic acid; photometric determination	EU-reference measurement procedure; DL = 0.2 µg SO ₂ ; s = 0.03 mg/m ³ at 0.5 mg/m ³
SO ₂	Silica gel procedure	Removal of interfering substances by concentrated H ₃ PO ₄ ; adsorption on silica gel; thermal desorption in H ₂ -stream and reduction to H ₂ S; reaction to molybdenum-blue; photometric determination	DL = 0.3 µg SO ₂ ; s = 0.03 mg/m ³ at 0.5 mg/m ³
NO ₂	Saltzman procedure	Absorption in reaction solution while forming a red azo dye (wash bottle); photometric determination	Calibration with sodium nitrite; DL = 3 µg/m ³
O ₃	Potassium iodide procedure	Formation of iodine from aqueous potassium iodide solution (wash bottle); photometric determination	DL = 20 µg/m ³ ; rel. s = ± 3.5% at 390 µg/m ³
F ⁻	Silver bead procedure; variant 1	Sampling with dust preseparator; enrichment of F ⁻ on sodium carbonate-coated silver beads; elution and measurement with ion-sensitive lanthanum fluoride-electrode chain	Inclusion of an undetermined portion of particulate fluoride immissions
F ⁻	Silver bead procedure; variant 2	Sampling with heated membrane filter; enrichment of F ⁻ on sodium carbonate-coated silver beads; determination by electrochemical (variant 1) or photometric (alizarin-complexone) procedure	Danger of lower findings due to partial sorption of gaseous fluoride immissions on membrane filter; DL = 0.5 µg/m ³
Cl ⁻	Mercury rhodanide procedure	Absorption in 0.1 N sodium hydroxide solution (wash bottle); reaction with mercury rhodanide and Fe(III) ions to iron thiocyanato complex; photometric determination	DL = 9 µg/m ³
Cl ₂	Methyl-orange procedure	Bleaching reaction with methyl-orange solution (wash	DL = 0.015 mg/m ³

		bottle); photometric determination	
NH ₃	Indophenol procedure	Absorption in dilute H ₂ SO ₄ (Impinger/wash bottle); conversion with phenol and hypochlorite to indophenol dye; photometric determination	DL = 3 µg/m ³ (impinger); partial inclusion of compounds and amines
NH ₃	Nessler procedure	Absorption in dilute H ₂ SO ₄ (Impinger/wash bottle); distillation and reaction with Nessler's reagent, photometric determination	DL = 2.5 µg/m ³ (impinger); partial inclusion of NH ₄ ⁺ - compounds and amines
H ₂ S	Molybdenum-blue procedure	Absorption as silver sulphide on glass beads treated with silver sulphate and potassium hydrogen sulphate (sorption tube); released as hydrogen sulphide and conversion to molybdenum blue; photometric determination	DL = 0.4 µg/m ³
H ₂ S	Methylene blue procedure	Absorption in cadmium hydroxide suspension while forming CdS; conversion to methylene blue; photometric determination	DL = 0.3 µg/m ³

Table 55.3 Manual measurement procedures for inorganic gases

DL = detection limit; s = standard deviation; rel. s = relative s.

A special sampling variant, used primarily in connection with manual measurement procedures, is the diffusion separation tube (denuder). The denuder technique is aimed at separating the gas and particle phases by using their different diffusion rates. Thus, it is often used on difficult separation problems (e.g., ammonia and ammonium compounds; nitrogen oxides, nitric acid and nitrates; sulphur oxides, sulphuric acid and sulphates or hydrogen halides/halides). In the classic denuder technique, the test air is sucked through a glass tube with a special coating, depending on the material(s) to be collected. The denuder technique has been further developed in many variations and also partially automated. It has greatly expanded the possibilities of differentiated sampling, but, depending on the variant, it can be very laborious, and proper utilization requires a great deal of experience.

Automated procedures

There are numerous different continuous measuring monitors on the market for sulphur dioxide, nitrogen oxides, carbon monoxide and ozone. For the most part they are used particularly in measurement networks. The most important features of the individual methods are collected

Table 55.4 Automated measurement procedures for inorganic gases

Material	Measuring principle	Comments
SO ₂	Conductometry reaction of SO ₂ with H ₂ O ₂ in dilute H ₂ SO ₄ ; measurement of increased conductivity	Exclusion of interferences with selective filter (KHSO ₄ /AgNO ₃)
SO ₂	UV fluorescence; excitation of SO ₂ molecules with UV radiation (190–230 nm); measurement of fluorescence radiation	Interferences, e.g., by hydrocarbons, must be eliminated with appropriate filter systems
NO/NO ₂	Chemiluminescence; reaction of NO with O ₃ to NO ₂ ; detection of chemiluminescence radiation with photomultiplier	NO ₂ only indirectly measurable; use of converters for reduction of NO ₂ to NO; measurement of NO and NO _x (=NO+NO ₂) in separate channels
CO	Non-dispersive infrared absorption; measurement of IR absorption with specific detector against reference cell	Reference: (a) cell with N ₂ ; (b) ambient air after removal of CO; (c) optical removal of CO absorption (gas filter correlation)
O ₃	UV absorption; low-pressure Hg lamp as radiation source (253.7 nm); registration of UV absorption in accordance with Lambert-Beer's law; detector: vacuum photodiode, photosensitive valve	Reference: ambient air after removal of ozone (e.g., Cu/MnO ₂)
O ₃	Chemiluminescence; reaction of O ₃ with ethene to formaldehyde; detection of chemiluminescence radiation with photomultiplier	Good selectivity; ethylene necessary as reagent gas

It should be emphasized here that all automatic measurement procedures based on chemical-physical principles must be calibrated using (manual) reference procedures. Since automatic equipment in measurement networks often runs for extended periods of time (e.g., several weeks) without direct human supervision, it is indispensable that their correct functioning is regularly and automatically checked. This generally is done using zero and test gases that can be produced by several methods (preparation of ambient air; pressurized gas cylinders; permeation; diffusion; static and dynamic dilution).

Measurement procedures for dust-forming air pollutants and its composition

Among particulate air pollutants, dustfall and suspended particulate matter (SPM) are differentiated. Dustfall consists of larger particles, which sink to the ground because of their size and thickness. SPM includes the particle fraction that is dispersed in the atmosphere in a quasi-stable and quasi-homogenous manner and therefore remains suspended for a certain time.

Measurement of suspended particulate matter and metallic compounds in SPM

As is the case with measurements of gaseous air pollutants, continuous and discontinuous measurement procedures for SPM can be differentiated. As a rule, SPM is first separated on glass fibre or membrane filters. It follows a gravimetric or radiometric determination. Depending on the sampling, a distinction can be made between a procedure to measure the total SPM without fractionation according to the size of the particles and a fractionation procedure to measure the fine dust.

The advantages and disadvantages of fractionated suspended dust measurements are disputed internationally. In Germany, for example, all threshold limits and assessment standards are based on total suspended particulates. This means that, for the most part, only total SPM measurements are performed. In the United States, on the contrary, the so-called PM-10 procedure (particulate matter $\leq 10\mu\text{m}$) is very common. In this procedure, only particles with an aerodynamic diameter up to 10 μm are included (50 per cent inclusion portion), which are inhalable and can enter the lungs. The plan is to introduce the PM-10 procedure into the European Union as a reference procedure. The cost for fractionated SPM measurements is considerably higher than for measuring total suspended dust, because the measuring devices must be fitted with special, expensively constructed sampling heads that require costly maintenance. Table contains details on the most important SPM measurement procedures.

Table Measurement procedures for suspended particulate matter (SPM)

Procedure	Measuring principle	Comments
Small filter device	Non-fractionated sampling; air flow rate 2.7–2.8 m ³ /h; filter diameter 50 mm; gravimetric analysis	Easy handling; control clock; device operable with PM-10 preseparator
LIB device	Non-fractionated sampling; air flow rate 15–16 m ³ /h; filter diameter 120 mm; gravimetric analysis	Separation of large dust quantities; advantageous for analysis of dust components; control clock
High-Volume-Sampler	Inclusion of particles up to approx. 30 μm diameter; air flow rate approx. 100 m ³ /h; filter diameter 257 mm; gravimetric analysis	Separation of large dust quantities, advantageous for analysis of dust components; relatively high noise level

FH 62 I	Continuous, radiometric dust measuring device; non-fractionating sampling; air flow rate 1 or 3 m ³ /h; registration of dust mass separated on a filter band by measuring attenuation of β -radiation (krypton 85) in passage through exposed filter (ionization chamber)	Gravimetric calibration by dusting of single filters; device also operable with PM-10 preseparator
BETA dust meter F 703	Continuous, radiometric dust measuring device; non-fractionated sampling; air flow rate 3 m ³ /h; registration of dust mass separated on a filter band by measuring attenuation of β -radiation (carbon 14) in passage through exposed filter (Geiger Müller counter tube)	Gravimetric calibration by dusting of single filters; device also operable with PM-10 preseparator
TEOM 1400	Continuous dust measuring device; non-fractionated sampling; air flow rate 1 m ³ /h; dust collected on a filter, which is part of a self-resonating, vibrating system, in side stream (3 l/min); registration of the frequency lowering by increased dust load on the filter	Relationship between frequency lowering and dust mass must be established through calibration

Recently, automatic filter changers have also been developed that hold a larger number of filters and supply them to the sampler, one after another, at timed intervals. The exposed filters are stored in a magazine. The detection limits for filter procedures lie between 5 and 10 $\mu\text{g}/\text{m}^3$ of dust, as a rule.

Finally, the black smoke procedure for SPM measurements has to be mentioned. Coming from Britain, it has been incorporated into EU guidelines for SO₂ and suspended dust. In this procedure, the blackening of the coated filter is measured with a reflex photometer after the sampling. The black smoke values that are thus photometrically obtained are converted into gravimetric units ($\mu\text{g}/\text{m}^3$) with the help of a calibration curve. Since this calibration function depends to a high degree on the composition of the dust, especially its soot content, the conversion into gravimetric units is problematic.

Today, metal compounds are often routinely determined in suspended dust immission samples. In general, the collection of the suspended dust on filters is followed by a chemical dissolution of the separated dusts, since the most common final analytical steps presuppose converting the metallic and metalloid compounds in an aqueous solution. In practice, the most important methods by far are atom absorption spectroscopy (AAS) and spectroscopy with plasma excitation (ICP-OES). Other procedures for determining metallic compounds in suspended dust are x-ray fluorescence analysis, polarography and neutron activation analysis. Although metallic compounds have been measured for more than a decade now as a component of SPM in outside air at certain measurement sites, important unanswered questions remain. Thus the conventional sampling by separating the suspended dust on filters assumes that the separation of the heavy metal compounds on the filter is complete. However, earlier indications have been found in the literature questioning this. The results are very heterogeneous.

A further problem lies in the fact that different compound forms, or single compounds of the respective elements, cannot be distinguished in the analysis of metallic compounds in suspended dust using the conventional measurement procedures. While in many cases adequate total determinations can be made, a more thorough differentiation would be desirable with certain especially carcinogenic metals (As, Cd, Cr, Ni, Co, Be). There are often big differences in the carcinogenic effects of elements and their individual compounds (e.g., chromium compounds in oxidation levels III and VI - only those in level VI are carcinogenic). In such cases a specific measurement of the individual compounds (species analysis) would be desirable. Despite the significance of this problem, only first attempts at species analysis are being made in measurement technique.

Measurement of dustfall and metallic compounds in dustfall

Two fundamentally different methods are used to collect dustfall:

- sampling in collecting vessels
- sampling on adhesive surfaces.

A popular procedure for measuring dustfall (deposited dust) is the so-called Bergerhoff procedure. In this procedure the entire atmospheric precipitation (dry and wet depositions) is collected over 30 ± 2 days in vessels about 1.5 to 2.0 metres above the ground (bulk deposition). Then the collecting vessels are taken to the lab and prepared (filtered, water evaporated, dried, weighed). The result is calculated on the basis of the surface area of the collecting vessel and exposure time in grams per square meter and day ($\text{g/m}^2\text{d}$). The relative detection limit is $0.035 \text{ g/m}^2\text{d}$.

Additional procedures for collecting dustfall include the Liesegang-Löbner device and methods which collect the deposited dust on adhesive foils.

All measurement results for dustfall are relative values that depend on the apparatus used, as the dust separation is influenced by the flow conditions at the device and other parameters. The

differences in the measurement values obtained with the different procedures can reach 50 per cent.

Also important is the composition of the deposited dust, such as the content of lead, cadmium and other metallic compounds. The analytical procedures used for this are basically the same as those used for suspended dust.

Measuring special materials in dust form

Special materials in dust form include asbestos and soot. Collecting fibres as air pollutants is important since asbestos has been classified as a confirmed carcinogenic material. Fibres with a diameter of $D \leq 3\mu\text{m}$ and a length of $L \geq 5\mu\text{m}$, where $L:D \geq 3$, are considered carcinogenic. Measurement procedures for fibrous materials consist of counting, under the microscope, fibres that have been separated on filters. Only electron microscopic procedures can be considered for outside air measurements. The fibres are separated on gold-coated porous filters. Prior to assessment in an electron scan microscope, the sample is freed of organic substances through plasma incineration right on the filter. The fibres are counted on part of the filter surface, randomly chosen and classified by geometry and type of fibre. With the help of energy dispersive x-ray analysis (EDXA), asbestos fibres, calcium sulphate fibres and other inorganic fibres can be differentiated on the basis of elemental composition. The entire procedure is extremely expensive and requires the greatest care to achieve reliable results.

Soot in the form of particles emitted by diesel motors has become relevant since diesel soot was also classified as carcinogenic. Because of its changing and complex composition and because of the fact that various constituents are also emitted from other sources, there is no measurement procedure specific to diesel soot. Nevertheless, in order to say something concrete about the concentrations in ambient air, soot is conventionally defined as elemental carbon, as a part of total carbon. It is measured after sampling and an extraction step and/or thermal desorption. Determination of the carbon content ensues through burning in an oxygen stream and coulometric titration or non-dispersive IR detection of the carbon dioxide formed in the process.

The so-called aethalometer and the photoelectric aerosol sensor are also used for measuring soot, in principle.

Measuring Wet Depositions

Together with dry deposition, wet deposition in rain, snow, fog and dew constitute the most important means by which harmful materials enter the ground, water or plant surfaces from the air.

In order to clearly distinguish the wet deposition in rain and snow (fog and dew present special problems) from the measurement of total deposition (bulk deposition, see section "Measurement of dustfall and metallic compounds" above) and dry deposition, rain catchers, whose collection opening is covered when there is no rain (wet-only sampler), are used for sampling. With rain sensors, which mostly work on the principle of conductivity changes, the cover is opened when it starts to rain and closed again when the rain stops.

The samples are transferred through a funnel (open area approx. 500 cm² and more) into a darkened and if possible insulated collection container (of glass or polyethylene for inorganic components only).

In general, analysing the collected water for inorganic components can be done without sample preparation. The water should be centrifuged or filtered if it is visibly cloudy. The conductivity, pH value and important anions (NO_3^- , SO_4^{2-} , Cl^-) and cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+ and so on) are routinely measured. Unstable trace compounds and intermediate states like H_2O_2 or HSO_3^- are also measured for research purposes.

For analysis, procedures are used that are generally available for aqueous solutions such as conductometry for conductivity, electrodes for pH values, atom adsorption spectroscopy for cations (see section "Measuring special materials in dust form", above) and, increasingly, ion exchange chromatography with conductivity detection for anions.

Organic compounds are extracted from rain water with, for example, dichloromethane, or blown out with argon and adsorbed with Tenax tubes (only highly volatile materials). The materials are then subjected to a gas chromatographic analysis (see "Measurement procedures for organic air pollutants", below).

Dry deposition correlates directly with ambient air concentrations. The concentration differences of airborne harmful materials in rain, however, are relatively small, so that for measuring wet deposition, wide-mesh measuring networks are adequate. Examples include the European EMEP measurement network, in which the entry of sulphate and nitrate ions, certain cations and precipitation pH values are collected in approximately 90 stations. There are also extensive measurement networks in North America.