

CHAPTER 1

Air Pollution: Sources and Effects

1.1 Introduction

Air pollution is a gas (or a liquid or solid dispersed through ordinary air) released into atmosphere in a large quantity to harm the health of people or other animals, kill plants or stop them growing properly, damage or disrupt some other aspect of the environment (such as making buildings crumble), or cause some other kind of nuisance (reduced visibility, perhaps, or an unpleasant odor).

As with water pollution and land contamination, it's the quantity (or concentration) of a chemical in the air that makes the difference between “harmless” and “pollution.” Carbon dioxide (CO₂), for example, is present in the air around you at a typical concentration of less than 0.05 percent and breathing it in usually does no harm (you breathe it out all day long); but air with an extremely high concentration of carbon dioxide (say, 5–10 percent) is toxic and could kill anybody in a matter of minutes. Forest fires, erupting volcanoes, and gases released from radioactive decay of rocks inside Earth are just three examples of natural air pollution that can have hugely disruptive effects on people and the planet.

1.1.1 Definition of air pollution

Air pollution may be described as “the imbalance in quality of air so as to cause adverse effects on the living organisms existing on earth”.

The World Health Organization (WHO) defines **air pollution** as “limited to situations in which the outer ambient atmosphere contains materials in concentrations which are harmful to man and his environment”.

Air pollution is broadly defined as “the presence in the atmosphere, of one or more contaminants such as fumes, dust, gases, mist, grit, odour, smoke, smog or vapours in considerable quantities and of duration which is injurious to human, animal or plant life or which unreasonably interferes with the comfortable enjoyment of life and property”.

Thus, **air pollution** is generally a disequilibrium condition of air caused by the introduction of foreign elements from natural and man-made sources into the air such that the air becomes injurious to biological communities.

1.1.2 Air pollution due to natural sources

Forest fires (which often start naturally) can produce huge swathes of smoke that drift for miles over neighboring cities, countries, or continents. Giant volcanic eruptions can spew so much dust into the atmosphere that they block out significant amounts of sunlight and cause the entire planet to cool down for a year or more. Radioactive rocks can release a gas called radon when they decay, which can build up in the basements of buildings with serious effects on people's health.

All these things are examples of serious air pollution that happen without any human activity; although we can adapt to natural air pollution, and try to reduce the disruption it causes, we can never stop it happening completely.

However, since Earth's atmosphere is very turbulent the natural air pollution will often disperse relatively quickly.

1.1.3 Air pollution due to anthropogenic activities

Today most of the natural resources are polluted due to increased pace of anthropogenic activities. The increase in population and transportation and industrial development has resulted in the release of all kinds of air pollutants into the environment. The natural capacity of the environment to tolerate and sustain development has dwindled in the face of the ever-increasing discharge of air pollutants.

The assessment of air quality and control of air pollution are difficult tasks facing an environmental manager. Both soil and water can be confined and gathered at one place while air cannot be gathered and confined in one place. Hence air quality assessment, air pollution prevention strategies and control technologies are of great importance in air quality management

1.1.4 Top-ten gases in anthropogenic air pollution

Any gas could qualify as pollutant if it reaches a high enough concentration to do harm. Theoretically, that means there are dozens of different pollution gases. In practice, about ten different substances cause most concern:

Sulfur dioxide: Coal, petroleum, and other fuels are often impure and contain sulfur as well as organic (carbon-based) compounds. When sulfur (spelled "sulphur" in some countries) burns with oxygen from the air, sulfur dioxide (SO₂) is produced. Coal-fired power plants are the world's biggest source of sulfur-dioxide air pollution, which contributes to smog, acid rain, and health problems that include lung disease.

Carbon monoxide: This highly dangerous gas forms when fuels have too little oxygen to burn completely. It spews out in car exhausts and it can also build up to dangerous levels inside a home if you have a poorly maintained gas boiler, stove, or fuel-burning appliance.

Carbon dioxide: This gas is central to everyday life and isn't normally considered a pollutant: we all produce it when we breathe out and plants such as crops and trees need

to "breathe" it in to grow. However, carbon dioxide is also a greenhouse gas released by engines and power plants. Since the beginning of the Industrial Revolution, it's been building up in Earth's atmosphere and contributing to the problem of global warming and climate change.

Nitrogen oxides: Nitrogen dioxide (NO₂) and nitrogen oxide (NO) are pollutants produced as an indirect result of combustion, when nitrogen and oxygen from the air react together. Nitrogen oxide pollution comes from vehicle engines and power plants, and plays an important role in the formation of acid rain, ozone and smog. Nitrogen oxides are also "indirect greenhouse gases" (they contribute to global warming by producing ozone, which is a greenhouse gas).

Volatile Organic Compounds (VOCs): These carbon-based (organic) chemicals evaporate easily at ordinary temperatures and pressures, so they readily become gases. That's precisely why they're used as solvents in many different household chemicals such as paints, waxes, and varnishes. Unfortunately, they're also a form of air pollution: they're believed to have long-term (chronic) effects on people's health and they also play a role in the formation of ozone and smog.

Particulates: These are the sooty deposits in air pollution that blacken buildings and cause breathing difficulties. Particulates of different sizes are often referred to by the letters PM followed by a number, so PM10 means soot particles of less than 10 microns (10 millionths of a meter or 10µm in diameter). In cities, most particulates come from traffic fumes.

Ozone: Also called trioxygen, this is a type of oxygen gas whose molecules are made from three oxygen atoms joined together (so it has the chemical formula O₃), instead of just the two atoms in conventional oxygen (O₂). In the stratosphere (upper atmosphere), a band of ozone ("the ozone layer") protects us by screening out harmful ultraviolet radiation (high-energy blue light) beaming down from the Sun. At ground level, it's a toxic pollutant that can damage health. It forms when sunlight strikes a cocktail of other pollution and is a key ingredient of smog (see box below).

Chlorofluorocarbons (CFCs): Once thought to be harmless, these gases were widely used in refrigerators and aerosol cans until it was discovered that they damaged Earth's ozone layer. We discuss this in more detail down below.

Unburned hydrocarbons: Petroleum and other fuels are made of organic compounds based on chains of carbon and hydrogen atoms. When they burn properly, they're completely converted into harmless carbon dioxide and water; when they burn incompletely, they can release carbon monoxide or float into the air in their unburned form, contributing to smog.

Lead and heavy metals: Lead and other toxic "heavy metals" can be spread into the air either as toxic compounds or as aerosols (when solids or liquids are dispersed through gases and carried through the air by them) in such things as exhaust fumes and the fly ash (contaminated waste dust) from incinerator smokestacks.

1.1.5 Composition of air

Air constitutes 80% of man's daily intake of materials by weight. We breathe 22,000 times a day on the average, inhaling 16 kg of air. The earth's atmosphere is an envelope of gases extending to a height of 200 km from the earth's surface. The atmosphere is a protective cover which sustains life and protects it from the unfriendly environment of outer space. The lower atmosphere, i.e., the troposphere contains about 70% of the mass of the atmosphere. It has mainly three categories of gaseous components: major, minor, and trace (Table 1.1). For major gases, like N₂ and O₂, the concentrations vary but to a very little extent with time, while for trace gases, the values tend to converge as the averaging time lengthens. Oceans as well as vegetation are the most important **sinks** for most atmospheric gases. A **sink** is a medium which is capable of retaining and interacting with along-lived pollutant, though not necessarily indefinitely.

Table 1.1 Average composition of clean dry air near sea level (ppm by volume)

Components	Average conc. (ppm)	Concentration in volume percent	Estimated residence time
Major			
Nitrogen, N ₂	78.09×10^4	78.09	Continuous
Oxygen, O ₂	20.94×10^4	20.94	Continuous
Minor			
Argon, Ar	93×10^2	0.93	Continuous
Carbon dioxide, CO ₂	32×10^2	0.0318	2 to 4 years
Trace			
Neon, Ne	18	0.0018	Continuous
Helium, He	5.2	0.00052	~ 2 million years
Methane, CH ₄	1.3	0.00013	4 to 7 years
Krypton, Kr	1.0	0.0001	Continuous
Hydrogen, H ₂	0.5	0.00005	Little is known about residence time
Carbon monoxide, CO	0.1	0.00001	0.5 year
Ozone, O ₃	0.02	0.000002	~ 60 days
Ammonia, NH ₃	0.01	0.000001	7 days
Nitrogen dioxide, NO ₂	0.001	0.0000001	5 days
Sulphur dioxide, SO ₂	0.0002	0.0000002	4 days
Hydrogen sulphide, H ₂ S	0.002	0.0000002	2 days
Xenon, Xe	0.081	-	Continuous

(Source: Engineering Tool Box (www.engineeringtoolbox.com))

1.1.6 Concentration units of air pollutants

The concentration of any pollutant can be expressed in a number of ways involving units of mass, or volume per unit mass or volume per volume of air. There are four ways in which the concentrations of pollutants can be expressed.

1. The ratio of the mass of pollutant m_p to the mass of pure air m_a plus the mass of the pollutant m_p in a given volume is called the **mass concentration ratio**, ω_p .

$$\omega_p = m_p / (m_a + m_p) \quad \dots(1.1)$$

2. The ratio y_p of the volume of pollutant v_p to the volume of pure air v_a is called the **volume concentration ratio**.

$$y_p = v_p / (v_a + v_p) \quad \dots(1.2)$$

3. The more common way of expression of the concentrations is **ppm** which is **volume concentration in parts per million**.

$$y_{ppm} = y_p \times 10^6 \quad \dots(1.3)$$

1 ppm of SO₂ = 1 part of the gas pollutant / 10⁶ parts of air

1 m³ of gas / 10⁶ m³ of air = 1 mL of gas / 1 litre air.

4. The fourth way is to express the concentration as the ratio of the mass of pollutant m_p to the volume of the pollutant v_p plus the volume of air v_a

$$\rho_p = m_p / (v_a + v_p) \quad \dots(1.4)$$

The concentration of the pollutant (gas or particle), p_p is generally given in micrograms per cubic meter or $\mu\text{g}/\text{m}^3$.

While all the above concentration ratios are interconvertible, the most important is the interconversion of y_{ppm} and p_p in $\mu\text{g}/\text{m}^3$ for gaseous pollutants.

Substituting Equations 1.2 and 1.3 in 1.4 we have

$$\rho_p = (m_p / v_p) y_{ppm} 10^{-6} \quad \dots(1.5)$$

Assuming that the perfect gas law holds for pollutants that are usually formed in the atmosphere, we can express the mass density of the pure component pollutant, m_p / v_p in units of $\mu\text{g}/\text{m}^3$ as,

$$\frac{m_p}{v_p} = \frac{PM_p (10^9)}{(8.314 \times 10^{-2}) T} \quad \dots(1.6)$$

where P is the total pressure in bars, M_p is the molecular weight of the pollutant, T is the absolute temperature in K, and 8.314×10^{-2} is the value of the universal gas constant expressed in units of $\text{m}^3 \text{ bar}/\text{kg mol} \text{ } ^\circ\text{K}$. At the standard temperature (25 °C) and pressure (1.0133 bars) the above equation reduces to

$$\frac{m_p}{v_p} = \frac{M_p (10^9)}{24.45} \quad \dots(1.7)$$

Substituting Equation 1.7 in Equation 1.5, we get the relation between ρ_p ($\mu\text{g}/\text{m}^3$) and y_{ppm}

$$\rho_p = \frac{M_p y_{ppm} (10^3)}{24.45} \quad \dots(1.8)$$

The constant in the denominator becomes 22.4 at 0 °C and 1 atmo pressure.

Thus

$$1 \text{ ppm} = \frac{(22.4 \times 10^{-3}) M_p \text{ g}}{10^6 \text{ m}^3} = \frac{M_p}{22.4} \times 1000 \mu\text{g} / \text{m}^3 \text{ at } 0^\circ\text{C} \quad \dots(1.9)$$

$$= \frac{M_p}{24.45} \times 1000 \mu\text{g} / \text{m}^3 \text{ at } 25^\circ\text{C} \quad \dots(1.10)$$

Any mass per unit volume measurement must take into account changing temperature as well as pressure while the mass per unit volume of an ideal gas is independent of temperature and pressure. 1 g mole of any gas at STP conditions occupies 22.4 litres (64 g of SO₂, or 30 g of NO or 46 g of NO₂ or 48 g of O₃, all of them occupy 22.4 litres at 0°C and 760 mm pressure while the volume occupied is 24.45 litres at 25°C and 760 mm pressure.).

In the volume scale the following relations hold good

$$\mu\text{g} / \text{m}^3 = \frac{n l 1^{-1} \times M_p \times 10^{-3} \times T_0 \times p}{V_0 \times T \times P_0} \quad \dots(1.11)$$

$$n l 1^{-1} = \frac{\mu\text{g} / \text{m}^3 \times V_0 \times 10^{-3} \times T \times P_0}{M_p \times T_0 \times P} \quad \dots(1.12)$$

where M_p is the gram molecular weight and V_0 is the molar volume of an ideal gas which is equivalent to $22.4 \times 10^{-3} \text{m}^3 \text{mole}^{-1}$ at standard temperature (T_0 in Kelvin) and pressure ($P_0 = 101.3 \text{ k Pa}$).

The important point is that mass per unit volume (i.e., $\mu\text{g}/\text{m}^3$) expressions do not allow an immediate comparison of one pollutant with another in terms of numbers of molecules. In contrast, an atmosphere containing $1 \mu l^{-1} \text{SO}_2$ contains the same number of pollutant molecules as one containing $1 \mu l^{-1} \text{O}_3$ or NO_2 because the molecular weight and the volume of gas containing 1 gram molecule have already been taken into account. Interconversions from ppm to $\mu\text{g}/\text{m}^3$ and vice versa at different temperatures for common air pollutants are given in Table 1.2 and Table 1.3.

Table 1.2 Amounts of different pollutants in $\mu\text{g m}^{-3}$ equivalent to 1 ppm or $1 \mu\text{l l}^{-1}$ (1000 nl l^{-1}) at different temperatures but standard atmospheric pressure

$T^{\circ}\text{C}$	SO_2	NO_2	NO	NH_3	O_3	CS_2	CO	H_2S	HF
-5	2914	2092	1365	774	2183	2001	1274	1550	910
0	2860	2054	1340	760	2143	1965	1250	1521	893
5	2809	2017	1316	747	2104	1929	1228	1494	877
10	2759	1981	1292	733	2067	1895	1206	1468	862
15	2711	1947	1270	721	2031	1862	1185	1442	847
20	2665	1914	1248	708	1997	1831	1165	1417	832
25	2620	1882	1227	696	1963	1800	1146	1394	818
30	2577	1850	1207	685	1931	1770	1127	1371	805
35	2535	1821	1187	674	1899	1742	1108	1348	792

Table 1.3 Amounts of different pollutants in ppb or nl l^{-1} equivalent to 1000 mg m^{-3} at different temperature but standard atmospheric pressure

$T^{\circ}\text{C}$	SO_2	NO_2	NO	NH_3	O_3	CS_2	CO	H_2S	HF
-5	343	478	733	1291	458	500	785	645	1099
0	349	487	746	1315	467	509	800	657	1120
5	356	496	760	1339	475	518	814	669	1140
10	362	505	774	1364	484	528	829	681	1161
15	368	514	787	1388	492	537	844	693	1181
20	375	523	801	1412	501	546	858	705	1202
25	382	531	815	1436	509	556	873	718	1222
30	388	540	828	1460	518	565	888	730	1243
35	394	549	842	1484	527	574	902	742	1263

Problem 1.1

The Central Pollution Control Board standards for NO_2 , SO_2 , and CO for sensitive, industrial and residential areas (exposure limits at atmospheric pressure and 25°C) are given in Table 1.4. Express their concentrations in ppm.

Table 1.4 CPCB standards ($\mu\text{g/m}^3$) at 1 atm pressure at 25°C

Parameter	Sensitive areas	Industrial areas	Residential areas
SO_2	30	120	80
NO_2	30	120	80
CO	0.75	1.5	1.0

Solution: One mole of an ideal gas at 1 atm and 25°C occupies a volume of 24.45 l ($24.45 \times 10^{-3} \text{ m}^3$).

SO₂ standards

The molecular weight of SO₂ = 32.06 + 2 × 16.0 = 64.60

In sensitive areas:

$$\text{ppm of SO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 30 \times 10^{-6} \text{ g} / \text{m}^3}{64.6 \text{ g/mol}} = 11.35 \times 10^{-9} \text{ or } 0.01135$$

In industrial areas:

$$\text{ppm of SO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 120 \times 10^{-6} \text{ g} / \text{m}^3}{64.6 \text{ g/mol}} = 0.045$$

In residential areas:

$$\text{ppm of SO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 180 \times 10^{-6} \text{ g} / \text{m}^3}{64.6 \text{ g/mol}} = 0.03$$

NO₂ standards

The molecular weight of NO₂ = 14 + 2 × 16 = 46.0

In sensitive areas:

$$\text{ppm of NO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 30 \times 10^{-6} \text{ g} / \text{m}^3}{46 \text{ g/mol}} = 0.0159 \times 10^{-6} = 0.016$$

In industrial areas:

$$\text{ppm of NO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 120 \times 10^{-6} \text{ g} / \text{m}^3}{46 \text{ g/mol}} = 0.0159 \times 10^{-6} = 0.016$$

In residential areas:

$$\text{ppm of NO}_2 = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 180 \times 10^{-6} \text{ g} / \text{m}^3}{46 \text{ g/mol}} = 0.0424$$

CO standards

The molecular weight of CO = 12 + 16 = 28.0

In sensitive areas:

$$\text{ppm of CO} = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 1000 \times 10^{-6} \text{ g} / \text{m}^3}{28 \text{ g/mol}} = 0.873$$

In industrial areas:

$$\text{ppm of CO} = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{mol} \times 1000 \times 10^{-6} \text{ g} / \text{m}^3}{28 \text{ g/mol}} = 0.873$$

In residential areas:

$$\text{ppm of CO} = \frac{24.45 \times 10^{-3} \text{ m}^3 / \text{ml} \times 2000 \times 10^{-6} \text{ g/m}^3}{28 \text{ g / mol}} = 17.500$$

Problem 1.2

A car emits CO as exhaust gas at 2% by volume. Calculate the concentration of CO in $\mu\text{g/m}^3$ at 0 °C and 25 °C at 1 atmospheric pressure.

Solution: 2% by volume of CO = 20 ml CO in 1 litre air = 20 ppm.

By Equations 1.9 and 1.10,

$$\text{At } 0 \text{ }^\circ\text{C, } 1 \text{ ppm of CO} = \frac{28}{22.4} \times 1000 \mu\text{g/m}^3 = 1250 \mu\text{g/m}^3$$

$$20 \text{ ppm of CO} = 1250 \times 20 = 25000 \mu\text{g/m}^3$$

$$\text{At } 25 \text{ }^\circ\text{C, } 1 \text{ ppm of CO} = \frac{28 \times 1000 \mu\text{g/m}^3}{24.45} = 1145.20 \mu\text{g/m}^3$$

$$20 \text{ ppm of CO} = 1145 \mu\text{g/m}^3 \times 20 = 22900 \mu\text{g/m}^3$$

Various units used for air pollutants are summarized in Table 1.5.

Table 1.5 Units of measurement in air pollution control

Parameter	Unit	Description
Emission		
Mass concentration c	mg/m ³ (at 0 °C 1013 mbar)	Pollutant mass per cubic metre exhaust gas in normal condition, usually dry
Volume concentration c _v	cm ³ /m ³ , also ppm v 1 cm ³ /m ³ = 1 ppm v	Pollutant volume per exhaust gas volume, parts per million
Emission mass flow	kg/h t/a	Emitted pollutant mass per unit of time
Emission factor	mg/kg kg/t	Emitted pollutant mass per mass of fired fuel or produced quantity
Emission factor	kg/TJ	Kilograms per terajoule; emitted pollutant mass per thermal power (in furnaces)
Emission factor	g/km	Emitted pollutant mass per kilometer driven (in motor vehicles)
Air quality concentrations		
Mass concentration c	mg/m ³ μg/m ³ 1000 μg = 1 mg	Pollutant mass per cubic metre of air
Volume concentration c _v (mixing ratio)	cm ³ /m ³ also ppm v ppb (μl/m ³)	Pollutant volume per air volume; Parts per million; Parts per billion

Table 1.5 Contd...

Parameter	Unit	Description
Air quality concentrations		
Pollutant concentration in rain water	mg/l µg/l	Pollutant mass per litre of rain water
Pollutant concentration (e.g., deposited particulate matter, but also wet precipitation and gases)	mg/g ² /day µg/g ² /day	Deposited pollutant mass per surface area and time
Pollutant dose	mg/m ² h	Concentration times time (c – t)
Dose of effect	µg/kg	Received (effective) pollutant mass per acceptor (recipient) mass

1.2 Classification of Air-pollutants, their Sources of Emission and Air Quality Standards

1.2.1 Classification

As clean air in the troposphere moves across the earth's surface, it collects the products of both natural events (dust storms and volcanic eruptions) and human activities (emissions from sources like transportation, fuel combustion, industrial operations, solid waste disposal and various other activities). These potential pollutants, called, **primary pollutants** which are emitted directly from the source, mix with the churning air in the troposphere. Some primary pollutants may react with one another or with the basic components of the atmosphere in chemical and photochemical reactions to form new pollutants which are called **secondary pollutants**. The reaction mechanisms and various steps involved in the process are influenced by many factors such as concentrations of reactants, the amount of moisture in the atmosphere, degree of photo-activation, meteorological forces, and local topography (Fig. 1.1). Long-lived pollutants travel far before they return to the earth as particles, droplets, or chemicals dissolved in precipitation.

Pollutants are also classified into the following categories: gaseous pollutants, particulate matter pollutants, aerosol pollutants, pesticides, metallic contaminants, carcinogenic pollutants, radioactive pollutants and biological contaminants. Gaseous pollutants include oxides of nitrogen, oxides of sulphur, CO and CO₂, hydrocarbons, etc.

Table 1.6(a) lists the major classes of pollutants found in ambient air, Carbon oxides (CO and CO₂), nitrogen oxides (mostly NO and NO₂ or NO_x), sulphur oxides (SO₂ and SO₃), volatile organic compounds (VOCs, mostly hydrocarbons), and suspended particles – all produced primarily by the combustion of fossil fuels.

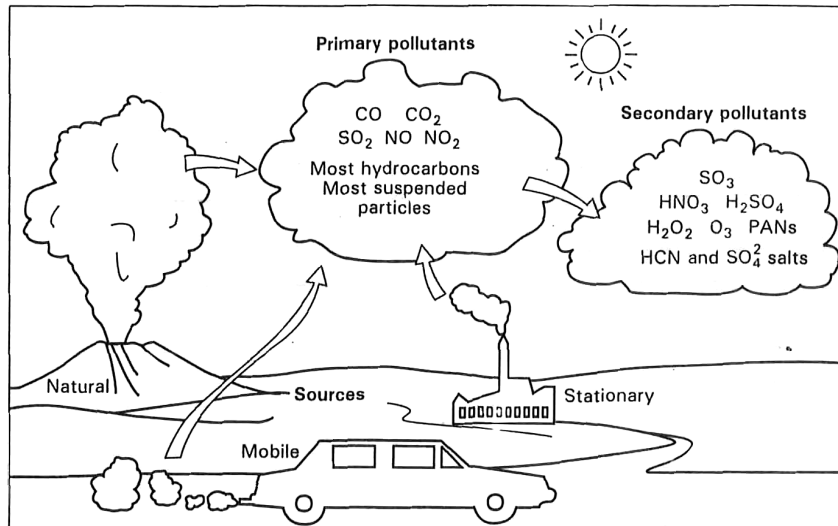


Fig. 1.1 Primary and secondary air pollutants

1.2.2 Emission sources of air pollutants

The various emission sources of air pollutants can be classified into natural and man-made sources as presented in Fig. 1.2.

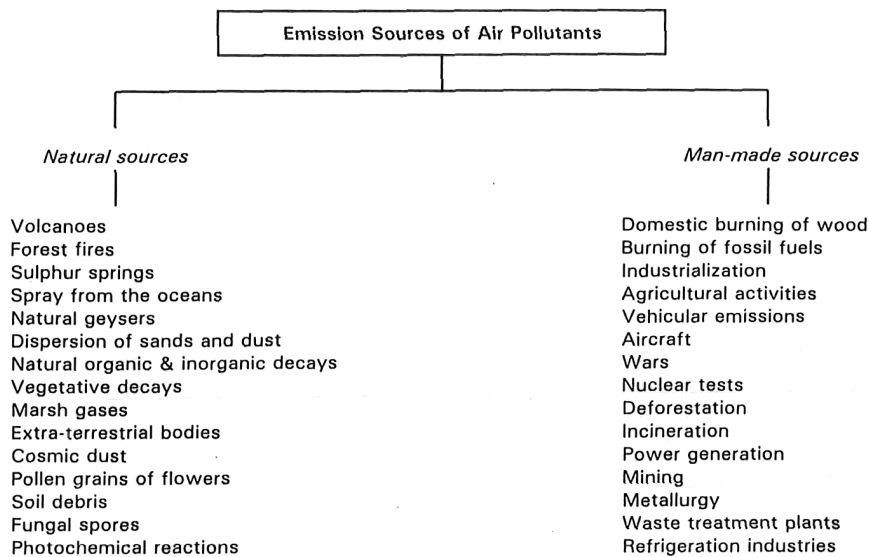


Fig. 1.2 Emission sources of air pollutants

Table 1.6 (a) Summary of sources, concentrations, and scavenging process of atmospheric trace gases

Contaminant	Major pollutant sources	Natural sources	Estimated emission pollutants	Annual Tg/yr* Natural	Atmospheric background concentrations	Estimated atmospheric residence time	Removal reactions and sinks	Remarks
SO ₂	Fossil fuel combustion	Volcanoes, reactions of biogenics emissions	212 ¹	20 ²	About 0.1 ppb ³	1-4 days	Oxidation to sulphate photo-chemical reactions or in liquid droplets	High reaction rates in summer due to photochemical processes
H ₂ S and organic sulphides ⁴	Chemical processes, sewage	Volcanoes, biogenic processes in soil and water	3	84 ⁵	H ₂ S: 0.05-0.1 ppb COS: 0.5 ppb ⁶	H ₂ S: 1-2 days COS: 1-2 yr ⁶	Oxidation to SO ₂ and SO ₄	Atmospheric data are incomplete COS residence time can be 20 yr ²
CO	Auto exhaust, general combustion	Forest fires, Photochemical reactions	700 ⁷	2100 ⁷	0.1-0.2 ppm (N. Hemisphere) 0.04-0.06 ppm (S. Hemisphere)	1-3 months	Photo-chemical reactions with	No long-term changes in the atmosphere have been detected
NO, NO ₂	Combustion	Biogenic processing in soil, lightning	75 ⁸ (as NO ₂)	180 ⁹ (as NO ₂)	About 0.1 ppb ¹⁰	2-5 days	Oxidation to nitrate	Natural processes mostly estimated; background concentrations are in doubt but may be as low as 0.01 ppb

Table 1.6(a) Contd...

Contaminant	Major pollutant sources	Natural sources	Estimated emission pollutants	Annual Tg/yr* Natural	Atmospheric background concentrations	Estimated atmospheric residence time	Removal reactions and sinks	Remarks
NH ₃	Waste treatment, combustion	Biogenic processes in soil	6 ¹¹	260 ⁹	About 10 ppm ⁹	1-7 days	Reaction with SO ₂ to form (NH ₄) ₂ SO ₄	Atmospheric measurements are sparse
N ₂ O	Small amounts from combustions	Biogenic processes in soil and water	3 ¹²	340 ¹³	330 ppb	20-100 yr	Photochemical in stratosphere	Some estimates place natural source at 100 Tg or less ¹²
CH ₄	Combustion, natural gas	Biogenic process in soil and water	160 ¹⁴	1050 ¹⁴	1.5 ppm	8 yr ¹⁵	Reaction with OH to form CO	Pollutant source includes 60 Tg yr ⁻¹
Isoprene and terpenes	None	Biogenic plant Emission	None	830 ⁷	0	1-2 h	Photochemical reactions with OH and	Not found ambient atmosphere away from source regions O ₂
Total non CH ₄ hydrocarbons	Combustion	Biogenic process in soil and vegetation	10 ¹⁷	2 × 10 ¹⁶	0-1 µg m ⁻³ for C ₂ S	Hours to a few days	Photochemical reactions with NO and O ₃	Concentration given for C ₂ S in rural atmosphere
CO ₂	Combustion	Biological processes	22,000 ¹⁶	10 ¹⁶	345 ppm (1981)	2-4 yr	Biogenic processes, photosynthesis absorption in oceans	Forest destruction and changes in earth's biomass may add 20-30 × 10 ³ Tg CO ₂ /yr atmosphere

Table 1.6(a) Contd...

Contaminant	Major pollutant sources	Natural sources	Estimated emission pollutants	Annual Tg/yr* Natural	Atmospheric background concentrations	Estimated atmospheric residence time	Removal reactions and sinks	Remarks
CH ₃ Cl	Combustion	Oceanic biological processes	2 ¹⁹	4-6 ^{16, 19}	660 ppt ^{19, 20}	1-2 yr ¹⁹	Stratospheric reactions	Photochemical reactions in stratosphere may impact on O ₃ layer
HCl, Cl ₂	Combustion, Cl manufacturing	Atmospheric reactions of NaCl, volcanoes	4 ²¹	100-200 ²³	About 0.5 ppb ²¹	About 1 wk	Precipitation	Volcanoes can release 10-20 Tg Cl yr ^{-1, 22}

Source: Elmer Robinson. (Pullman, Wash.: Washington State University)

Notes: *Tg/yr = 10¹² g/yr or 10⁶ metric ton/yr; 1-Based on 1978 global fuel usage and estimated sulphur contents. 2-Major reference is R. D. Cadle, 1980, Rev. Geophys. Space Phys. 18, 746-752. 3-P. J. Maroulis, A. L., Torres, A. B. Goldberg, and A. R. Bandy, 1980, J. Geophys. Res. 85, 7345-7349 4-Includes COS, CS₂, (CH₃)₂S₂, CH₄, and SH. 5-Adapted from D. F. Adams, S. O. Farwell, E. Robinson, and M. R. Pack, 1980, Biogenic sulphur emissions in the SURE region. Final report by Washington State University for Electric Power Research Institute, EPRI Report No. EA-1516, 6-A. L. Torres, P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, 1980, J. Geophys. Res. 85, 7357-7360. 7-P. R. Zimmerman, R. B. Chatfield, J. Fishman, P. J. Crutzen, and P. L. Hanst, 1978, Geophys. Res. Lett. 5, 679-682. 8-Based on 1978 global combustion estimates. 9-1. E. Galbally, Tellus 27, 67-70. 10-Approximate value combining values given in several references. 11-R. Soderfund, and B. H. Svensson, 1976. The global nitrogen cycle, in SCOPE Report 7, Swedish National Science Research Council, Stockholm. 12-1978 fuel usage figures apply to the following references: R. F. Weiss, and H. Craig, Geophys. Res. Lett. 3, 751-753; and D. Pierotti, and R. A. Rasmussen, 1976. Geophys. Res. Lett. 3, 263-267. 13-E. Robinson, and R. C. Robbins, Emissions, concentrations and fate of gaseous atmospheric pollutants, in Air Pollution Control, edited by W. Strauss, 1-93, Part 2 of New York: Wiley. 14-J. C. Sheppard, H. Westberg, J. F. Hooper, and K. Ganesan, 1982, J. Geophys. Res. 87, 1305-1312. 15-L. E. Heidt, J. P. Krasnec, R. A. Lueb, W. H. Pollock, B. E. Henry, and P. J. Crutzen, 1980, J. Geophys. Res. 85, 7329-7336. 16-R. E. Graedel. 1979. J. Geophys. Res. 84, 273-286. 17-Reference 13 tabulation updated to approximate 1978 emissions. 18-G.M. Woodwell, R. H. Whittaker, W. A. Reiners, G. E. Likens, C. C. Delwiche, and D. B. Botkin, 1978, Science 199, 141-146. 19-R. A. Rasmussen, L. E. Rasmussen, M. A. K. Khalil, and R. W. Dallye 1980, J. Geophys. Res. 85, 7350-7356. 20-E. Robinson, R. A. Rasmussen, J. Krasnec, D. Pierotti, and M. Jakubovic, 1977. Atm. Environ. 11, 213-215. 21-J. A. Ryan, and N. R. Mukherjee, 1975. Rev. Geophys. Space Phys. 13, 650-658. 22-R. D. Cadle, 1980. Rev. Geophys. 18, 746-752. 23-Based on estimated reaction of NaCl to form Cl₂.

Natural sources produce considerable pollutants but most of them are essential components of a balanced ecosystem. None of these natural pollutants normally accumulate to a level that is dangerous for life. However, many industrial activities (Table 1.6(b)) produce air pollutants in levels that exceed the normal natural assimilation processes. Air pollution problems are concentrated in and around urban areas because industries are concentrated in or around urban areas spewing poisonous gases, and particulates and increasing ambient temperature. Vehicular traffic is also dense in urban areas causing pockets of intense air pollution. All recorded air pollution episodes are around developed cities only. There is a qualitative difference between air pollution due to industries and air pollution due to vehicles, as can be seen by an analysis of the air polluted by them.

Table 1.6 (b) *Classification of anthropogenic or man-made air pollution sources*

Source type	Category	Important sources	Typical pollutants
Combustion	Stationary	Power plants, industrial boilers, diesel generators, municipal or industrial incineration	SO _x , NO _x , CO, smoke fly ash
	Refuse burning Mobile	Trace metal oxides Motor vehicles, aircraft	CO, HC, NO _x , SO _x , particulates
Roasting and heating processes	Non-ferrous metallurgical	Roasting, smelting and refining operations	Dust, smoke, metal fumes (Cu, Zn, and Pb), oxides of sulphur
	Ferrous metallurgical	Material handling, ore sintering and pelletising, coke ovens, blast furnaces, steel furnaces	Smoke, fumes, CO, odours, H ₂ S, organic vapour, fluorides
	Non-metallic minerals	Crushed stone, cement, glass, refractories, ceramic manufacture, coal cleaning	Mineral and organic particulates
Food and agriculture	Food processing	Drying, preserving, packaging	Vapour, odour, and dust
	crop spraying and dusting. Field burning	Pest and weed control Refuse burning	Organic phosphates, chlorinated HC, organic, lead Smoke, fly ash and soot
petroleum, chemicals, pulp and paper	Petroleum refining	Boilers, process heaters, catalyst regenerators, flares, storage tanks, compressor engines	So _x , HC, NO _x , particulate matter, CO, aldehyde, ammonia, odours
	Inorganic chemicals	Sulphuric acid plants, fertilizer manufacture, nitric acid and ammonia plants, phosphoric acid manufacture	So _x , HF, H ₂ S, NO _x , NH ₃ , particulate matter, H ₃ PO ₄ , etc.
	Organic chemicals	Plastics, paint and varnish manufacture, synthetic rubber, rayon, insecticides, soap and detergent manufacture, methanol, phenol, etc.	Particulate matter, odours, SO ₂ , CO, organic intermediates, solvent vapours
	Pulp and paper	Digester blow oxidation towers	Mercaptans, dimethyl sulphide, SO ₂

16 Air Pollution: Prevention and Control Technologies

Among the emission sources, some are stationary point sources while others are moving point sources. The pollution from industries is almost continuous. The vehicular pollution waxes and wanes according to the peak hour traffic during the day and night.

The common air pollutants, their sources and pathogenic effects are given in Table 1.7 while their typical effects on vegetation are shown in Fig. 1.3. Of the large number of primary pollutants emitted into the atmosphere, only a few are present in sufficiently high concentrations to be of immediate concern. The relative weighting factors and the tolerance limits of the major air pollutants are given in Table 1.8.

Table 1.7 Common air pollutants, their sources and pathological effects on man

Pollutant	Source	Pathological effects on man
Sulphur dioxide	Colourless gas produced by coal and oil combustion and certain industrial sources	Respiratory irritant, aggravates asthma and other lung and heart diseases, reduces lung function.
Nitrogen oxides	Brownish orange gas produced by motor vehicles and combustion at major industrial sources	Inhibits cilia action so that soot and dust penetrate far into the lungs.
Hydrogen sulphide	Refineries, chemical industries and bituminous fuels	Causes nausea, irritates eyes and throat.
Carbon monoxide	Burning of coal, gasoline, motor exhausts	Reduces oxygen carrying capacity of blood.
Hydrogen cyanide	Blast furnace, fumigation, chemical manufacturing, metal plating, etc.	Interferes with nerve cells, produces dry throat, indistinct vision, headache, etc.
Ammonia	Explosives, dye making fertilizer plants and lacquers	Inflames upper respiratory passages.
Phosgene or carbonyl chloride	Chemical and dye making	Induces coughing, irritation and fatal pulmonary edema.
Aldehydes	Thermal decomposition of oils, fats, or glycerols	Irritate nasal and respiratory tracts.
Arsines	Processes involving metal or acids containing arsenic, soldering	Damage red cells in blood, kidneys and cause jaundice.
Suspended particles (ash, soot, smoke, etc.)	Solid or liquid particles produced by combustion and other processes at major industrial sources (e.g. steel mills, power plants, chemical plants, incinerators and almost every manufacturing process)	Respiratory irritants, aggravate asthma and other lung and heart diseases (especially in combination with sulphur dioxide); many are known as carcinogens. Toxic gases and heavy metals absorb onto these particulates and are commonly carried deep into the lungs. Cause emphysema, eye irritation and possibly cancer.

Table 1.7 Contd...

Pollutant	Source	Pathological effects on man
Lead	Very small particles emitted from motor vehicles and smelters	Toxic to nervous and blood-forming systems, in high concentrations can cause brain and organ damage.
Ozone	A colourless gas formed from reactions between motor vehicle emissions and sunlight. It is the major component of smog.	Respiratory irritant, aggravates asthma and other lung and heart diseases, impairs lung functions, ozone is toxic to plants and corrodes materials.

Table 1.8 Major air pollutants, their weighting factors and tolerance limits

Pollutant	Relative toxicity (weighting factor)	Tolerance levels	
		ppm	µg/m ³
CO	1.00	32.0	40,000
hydrocarbons	2.08	-	19,300
SO _x	28.0	0.25	1430
NO _x	77.8	0.50	515
particulates	106.7	-	375

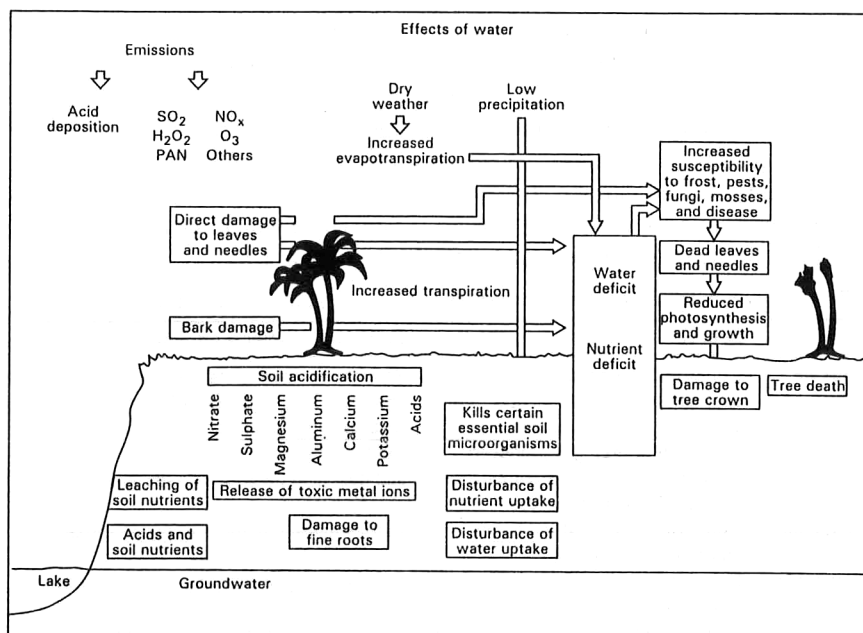


Fig. 1.3 Possible or suspected harmful effects of air pollutants on trees

1.2.3 Cycling of air pollutants

Air pollution emitted from various sources are removed from the atmosphere by different types of sinks. A typical cycle is shown in Fig. 1.4. Most pollutants have both natural and man-made sources: although the natural sources are often of sizeable magnitude at the global level, man-made sources predominate at local levels.

In the atmosphere, pollutants may move from a dry, gaseous phase into a liquid phase before falling to the earth's surface. If this is acidic in nature, it is popularly known as acid rain. Wet and dry deposition are the two main pathways by which atmospheric pollutants are returned to the surface of the earth. Other terms like rain-out and run off are also used (Fig. 1.5).

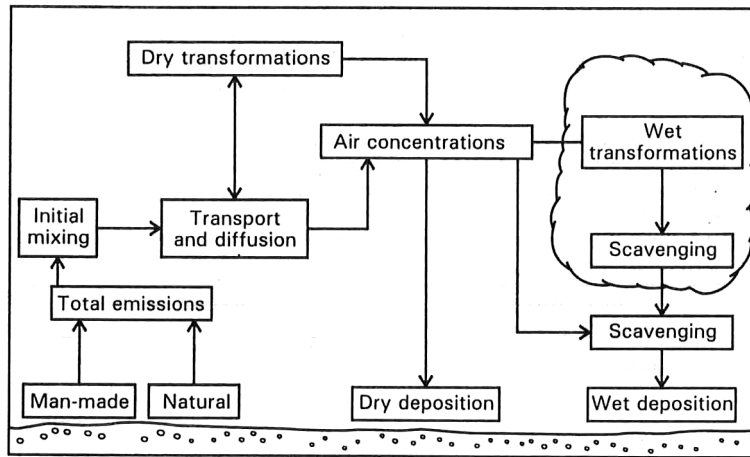


Fig. 1.4 Typical atmospheric cycle of a pollutant

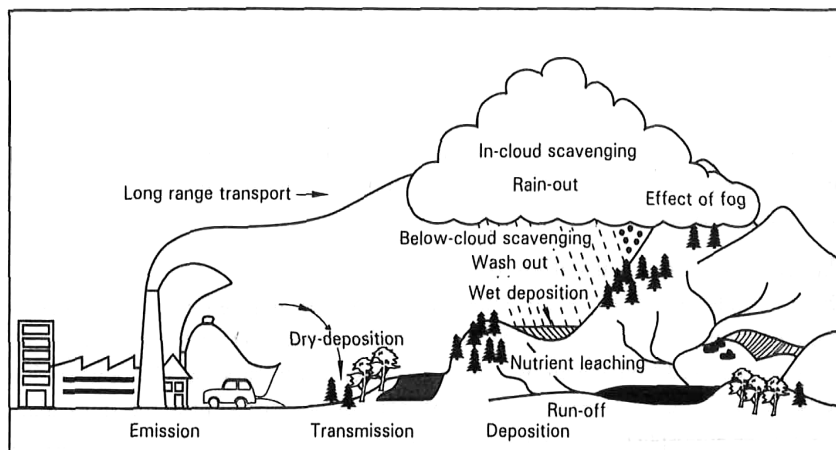


Fig. 1.5 Emissions and deposition of atmospheric pollutants

Dry deposition involves the transfer and removal of gases and particles at land and sea surfaces without the intervention of rain or snow. For gases removed at the surface, dry deposition is driven by a concentration gradient caused by surface depletion; for particles this mechanism operates in parallel with gravitational settling of the large particles. The efficiency of dry deposition is described by the deposition velocity, V_g , defined as

$$V_g \text{ (ms}^{-1}\text{)} = \frac{\text{Flux to surface (}\mu\text{g m}^{-2} \text{s}^{-1}\text{)}}{\text{Atmospheric concentration (}\mu\text{g m}^{-3}\text{)}} \quad \dots\dots(1.13)$$

Some typical values of deposition velocity are given in Table 1.9. For gases, such as sulphur dioxide, which have a fairly high V_g , dry deposition has little influence upon near surface concentrations, but may appreciably influence ambient levels at large downwind distances.

Table 1.9 *Some typical values of deposition velocity*

Pollutant	Surface	Deposition velocity (cm s ⁻¹)
SO ₂	Grass	1.0
SO ₂	Ocean	0.5
SO ₂	Soil	0.7
SO ₂	Forest	2.0
O ₃	Dry grass	0.5
O ₃	Wet grass	0.2
O ₃	Snow	0.1
HNO ₃	Grass	2.0
CO	Soil	0.05
Aerosol (< 2.5 mm)	Grass	0.15

1.3 Physico-Chemical Characteristics, Sources and Effects of Primary Air Pollutants

1.3.1 Particulate pollutants

1.3.1.1 Physico-chemical characteristics of particulate pollutants

Airborne small, solid particles and liquid droplets are commonly known as particulates. When present in air in excess, they pose a serious pollution threat. The life period of particulates varies from a few seconds to several months; it depends on the settling rate, size, and density of particles and turbulence.

Particulates can be inert or extremely reactive materials ranging in size from 100 μm down to 0.1 μm and less. The inert materials do not react readily with the environment nor do they exhibit any morphological changes as a result of combustion or any other process, whereas reactive materials could be further oxidized or may react chemically with the environment.

1.3.1.2 Classification of particulates

Dust: Particles of size 1-200 μm belong to this category and are formed by the natural disintegration of rocks and soil or by mechanical processes like grinding and spraying. They are removed from the air by gravity and other inertial processes by large settling velocities and also act as centres of catalysis for many of the chemical reactions taking place in the atmosphere.

Smoke: Particles of size 0.01-1 μm constitute smoke which can be either in the liquid or solid form and is formed by combustion or other chemical processes. Smoke may have different colours depending on the nature of materials burnt.

Fumes: Solid particles of size 0.1-1 μm which are normally released from chemical or metallurgical processes belong to this category.

Mists: Liquid droplets generally smaller than 10 μm which are formed by condensation in the atmosphere or released from industrial operations represent mist.

Fog: It is the mist in which the liquid is water and is sufficiently dense to obscure vision.

Aerosols: All airborne suspensions, either solid or liquid belong to this category and these are generally smaller than 1 μm .

Particles of size 1-10 μm have measurable settling velocities but are readily stirred by air movements, whereas particles of size 0.1-1 μm have small settling velocities. Particles below 0.1 μm , a sub microscopic size found in urban air, undergo random Brownian motion resulting from collision among individual molecules. The respective sizes of particulate matter and their sources of origin are given in Fig. 1.6.

Figure 1.7 gives the particle size distribution of a typical atmospheric particulate sample.

Urban air contains particulates, mainly of size 0.1-10 μm . The finest and the smallest particles are the ones which cause significant damage to health. Particulate matter larger than 10 μm which enters the respiratory system is filtered to a maximum extent by the horizontal lining of the nose. Particles of size 5-10 μm enter into the tracheal bronchial system, will be absorbed by mucus and sent back to the throat by small hair-like cilia and removed by spitting or swallowing. Particles smaller than 5 μm will be able to pass through many turns and bends into the upper respiratory system and finally enter the lungs and may be deposited there. Thus, particles of size 0.5-5 μm are sufficiently small to settle in the lungs by sedimentation; they may release slowly absorbed toxic gases causing serious health problems.

1.3.1.3 Chemical composition of particulate pollutants

As the chemical composition of particulate pollutants depends upon the origin of the particulates, it varies widely from place to place.

- (a) Calcium, aluminium, and silicon compounds will be present in particulates originating from soils and minerals.

(b) A number of organic compounds constitute smoke from coal, oil, wood, and solid waste.

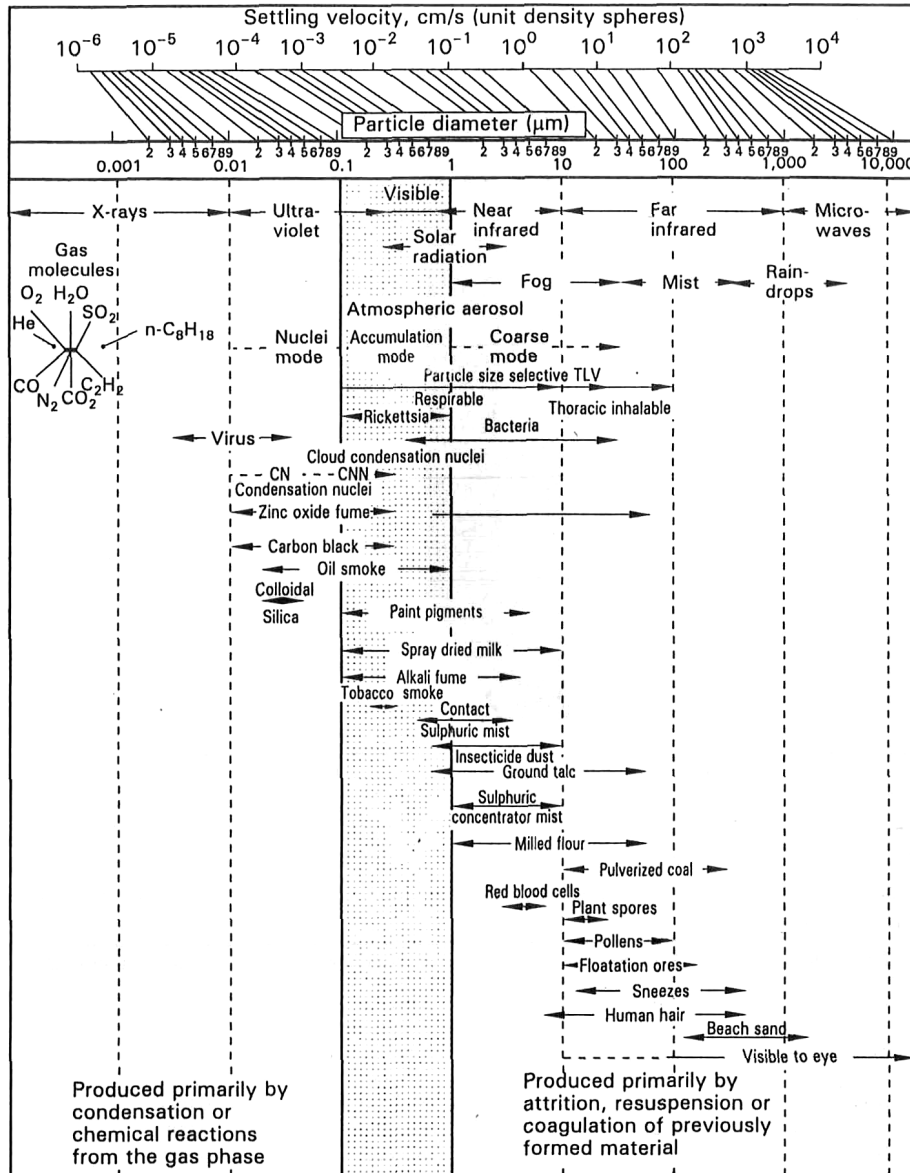


Fig. 1.6 Molecular and aerosol particle diameters, © P. C. Reist. Molecular diameters calculated from viscosity data. See Bird, Stewart, and Lightfoot, 1960, *Transport phenomena*, Wiley. (Adapted from Lapple, 1961, *Stanford Research Institute Journal*, 3rd quarter; and J. S. Eckert and R. F. Strigle, Jr., 1974 *JAPCA* 24: 961–965.)

- (c) Insecticide dust and certain fumes released from chemical plants also contain organic compounds. Hydrocarbons themselves can coalesce into aerosol droplets which may contain the highly harmful components of incomplete combustion known as Polycyclic Organic Matter (POM) which are derivative of benz- α -pyrene, a potential carcinogen.

Certain, toxic heavy metals like cadmium, lead, nickel and mercury are frequently observed in different types of particulates in a variety of combined forms such as oxides, hydroxides, sulphates and nitrates. The typical composition of particulates in a sample of the atmosphere in Hyderabad is given in Table 1.10.

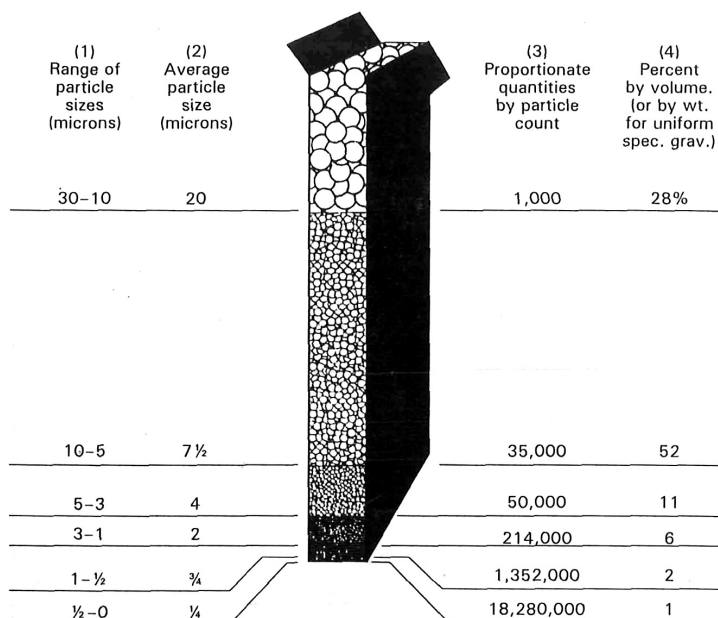


Fig. 1.7 Particle size distribution of a typical atmospheric particulate sample

(Source: The American Air Filter Co.)

Table 1.10 Composition of Suspended Particulate Matter (SPM) in a sample of the atmosphere in Hyderabad

Particulate	Composition ($\mu\text{g}/\text{m}^3$)	Particulate	Composition ($\mu\text{g}/\text{m}^3$)
Nitrate ions	2.8	Zinc	0.91
Ammonium ions	1.5	Antimony	0.02
Sulphate ions	9.3	Organic solvents	8.1
Lead	0.61	Arsenic	0.03
Iron	1.90	Molybdenum	0.006
Manganese	0.21	Beryllium	0.008

Table 1.10 Contd...

Particulate	Composition ($\mu\text{g}/\text{m}^3$)	Particulate	Composition ($\mu\text{g}/\text{m}^3$)
Nickel	0.17	Bismuth	0.007
Tin	0.02	Cobalt	0.001
Titanium	0.08	Sodium	1.20
Copper	0.06	Silicon	11.10
Chromium	0.02	Calcium	9.2
Vanadium	0.08		

Source: Y. Anjaneyulu, 1997. *Air pollution and its effects. Proceedings of international conference on air pollution and control technologies, ICIPACT-1997.*

1.3.1.4 Sources of emission of particulate pollutants

In arid regions like deserts, storms frequently stir up fine dust and sand reducing visibility and causing irritation of the respiratory tract. Autopsies carried out on dwellers of the Sahara Desert in North Africa, where sandstorms are frequent, showed that a significant number of particles was present in the lungs. The presence of sulphur dioxide in a dust laden atmosphere is dangerous to the respiratory tract, the lungs and, indirectly, the heart.

Table 1.11 Particulate emission rates

Emission source	Emission factor
Natural gas combustion	
Power plants	240 mg/m^3 of gas burned
Industrial boilers	290 mg/m^3 of gas burned
Domestic and commercial furnaces	310 mg/m^3 of gas burned
Distillate oil combustion	
Industrial and commercial furnaces	1.70 kg/m^3 of oil burned
Domestic furnaces	1 kg/m^3 of oil burned
Residual oil combustion	
Power plants	1.10 kg/m^3 of oil burned
Industrial and commercial furnaces	1 kg/m^3 oil burned
Coal combustion	
Cyclone furnaces Other pulverized coal furnaces Spreader stokers Other stokers	
Incineration	
Municipal, multiple chamber	8.00 kg/ton of refuse burned
Commercial, multiple chamber	1.40 kg/ton of refuse burned
Flue-fed incinerator	12.8 kg/ton of refuse burned
Domestic, gas fired	7.00 kg/ton of refuse burned
Open burning of refuse	7.20 kg/ton or refuse burned
Motor vehicles	
Petrol-powered engines	1.36 kg/m^3 of petrol burned

Table 1.11 *Contd...*

Emission source	Emission factor
Incineration	
Diesel-powered engines	12.5 kg/m ³ of fuel burned
Cement manufacturing	
Kraft pulp mills	17.2 kg/barrel of cement produced
Lime kilns	43 kg/ton of dried pulp produced
Recovery furnaces (with scrubbers)	70 kg/ton of dried pulp produced
Steel manufacturing	
Open-hearth furnace	10 kg/ton of steel produced
Electric arc furnace	7 kg/ton of metal charged
Sulphuric acid manufacturing	3 kg/ton of acid produced

Many industries emit fine particles with different emission rates (Table 1.11). Lead asbestos, manganese, beryllium, arsenic, copper, zinc are some of the many particulate pollutants that may be encountered. Since leaded petrol contains about 3 mL of tetraethyl lead per 3.785 litres, automobiles are a source of lead pollution. However, paint and industrial operations are the major sources of lead pollution. The Environmental Protection Agency (EPA) of USA determined that a lead level above 2 µg/m³ involves enough risk of adverse physiological effects to constitute endangerment to public health. In 1972, 27 cities of the United States had composite lead levels above the EPA limit [1].

Particulate emissions in USA have decreased substantially in the past few decades due to the Clean Air Regulation Act, 1970 (Fig. 1.8).

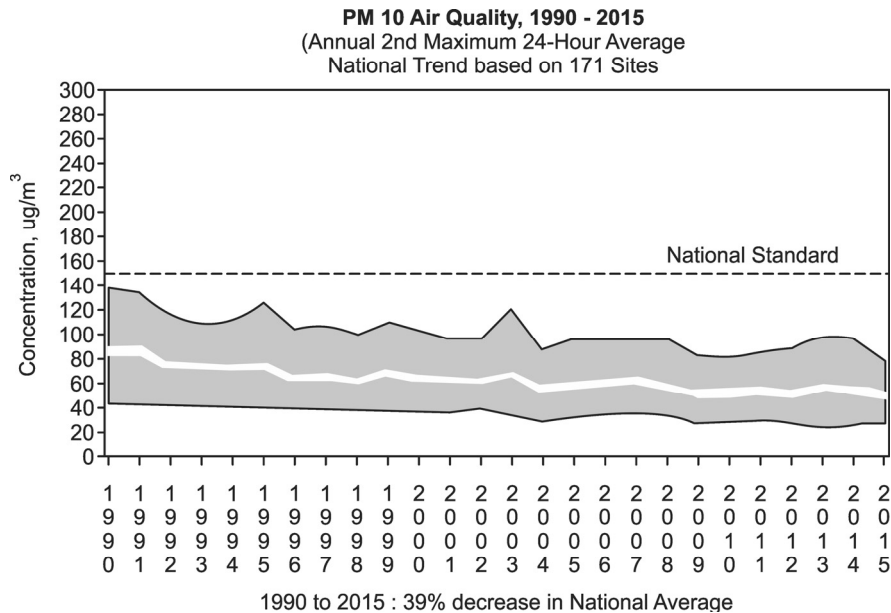


Fig. 1.8 Emission pattern of particulates in USA, 1990-2015
(Source: National ambient air pollutant emission estimates, USEPA1990-2015.)

1.3.1.5 National trends in PM 10 levels

Using a nation wide network of monitoring sites, US - EPA has developed ambient air quality trends for particle pollution, also called Particulate Matter (PM). PM10 describes inhalable particles, with diameters that are generally 10 micrometers and smaller. Under the Clean Air Act, EPA sets and reviews national air quality standards for PM. Air quality monitors measure concentrations of PM throughout the country. EPA, state, tribal and local agencies use that data to ensure that PM in the air is at levels that protect public health and the environment. Nationally, average PM10 concentrations have decreased over the years.

1.3.1.6 Effect of particulate pollutants on visibility

One of the main problems of particulate air pollution is the reduction in visibility caused by light scattering due to the particles. Scattering efficiency per unit mass of aerosol is critically dependent upon the size distribution of the aerosol, but aerosol mass loading is a good predictor of visibility impairment, as indicated in Fig. 1.9.

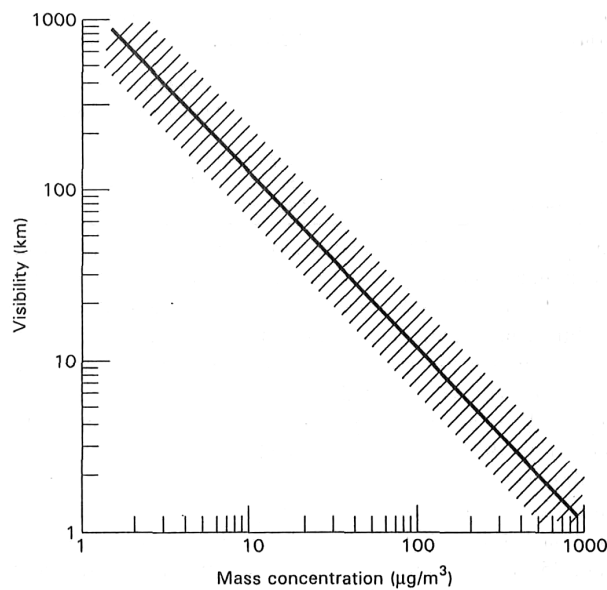


Fig. 1.9 Visibility of atmosphere as a function of SPM levels. Though this is approximate, most data fit within the shaded area

Problem 1.3

The most widely used equation for estimating visibility is the Koschmeider equation:

$$L_v = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{\text{Particle concentration } \mu\text{g}/\text{m}^3} \quad \dots(1.14)$$

where L_v is the visual range, the distance at which an average person can barely distinguish a dark object (such as a mountain or skyscraper) against the sky. This equation is an approximation, based on an average set of atmospheric particles.

- Use Equation 1.14 to estimate the visual range when the particulate concentrations equal to $2.00 \mu\text{g}/\text{m}^3$.
- If the particle concentration in the atmosphere is increased by $1 \mu\text{g}/\text{m}^3$, what is the percentage decrease in the visual range if the initial visual range is 20 km? If the initial visual range is 200 km, what is the percentage decrease?

Solution:

- Visibility range when particulate concentration is $2.00 \mu\text{g}/\text{m}^3$:

$$L_v = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{2 \mu\text{g}/\text{m}^3} = 600 \text{ km}$$

- When the initial visibility range is 20 km:

$$20 \text{ km} = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{x \mu\text{g}/\text{m}^3}$$

$$x = 60 \mu\text{g}/\text{m}^3$$

If the concentration of SPM is increased by $1 \mu\text{g}/\text{m}^3$,

$$L_v = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{60 + 1 \mu\text{g}/\text{m}^3} = 19.67 \text{ km}$$

So the percentage decrease in the visibility range is 1.65.

When the initial visual range is 200 km:

$$L_v = 200 \text{ km} = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{x \mu\text{g}/\text{m}^3}$$

$$x = 6 \mu\text{g}/\text{m}^3$$

When the SPM concentration is increased by $1 \mu\text{g}/\text{m}^3$,

$$L_v = \frac{1200 \text{ km } \mu\text{g}/\text{m}^3}{6 + 1 \mu\text{g}/\text{m}^3} = 171.4 \text{ km}$$

So the decrease in the visibility range is 14.3%.

1.3.1.7 Effects of particulate pollutants on plants

Plants are adversely affected by gaseous pollutants and deposition of particulates on soil. The deposition of toxic metals on soil makes the soil unsuitable for plant growth. Several particulate pollutants fall on the soil by acid rain; this tends to lower the pH of the soil making it more acidic and infertile. Deposited particulates on leaves restrict the absorption of CO_2 , thereby reducing the rate of photosynthesis. Dust mixed with mist or light rain forms a thick crust on the upper surfaces of leaves; this blocks the sunlight

necessary for carbon assimilation. Some plants are very sensitive to the traces of toxic metals, which inhibit the action of the plant enzyme system. Arsenic is a cumulative, potent, protoplasmic poison which inhibits the SH-group in enzymes. This is present in almost all types of soils in minute quantities and affects plant growth.

1.3.1.8 Effects of particulate pollutants on human health

The effects of particulate pollutants are largely dependent on the particle size. Air borne particles, i.e., dust, soot, fumes, and mists are potentially dangerous to human health. The nasal system prevents coarser particulates bigger than 5 microns from entering the respiratory system. Soluble aerosols will be absorbed into the blood from the alveoli while the insoluble aerosols are carried to the lymphatic stream and get deposited in pulmonary lymphatic depot points or in the lymph glands, where they create toxicity in the respiratory system. Lead interferes with the development and maturation of red blood cells. It is reported that a smoker can easily develop symptoms of asthma which is also due to a concentration of lead greater than in non-smokers.

1.3.1.9 Effects of particulate pollutants on materials

Particulates affect a variety of materials in various ways. They cause damage to buildings, paints, furniture, etc. Painted surfaces are very susceptible to damage in wet conditions.

1.3.2 Sulphur oxides

Sulphur dioxide is one of the major air pollutants discharged by various pollutant sources. Further, it reacts photo chemically or catalytically with other pollutants or normal atmospheric constituents to form sulphur trioxide, sulphuric acid and salts of sulphuric acid.

It is estimated that sulphur dioxide remains in the air for an average of two to four days; during this time it may be transported a distance of 1,000 km before it is deposited on the ground. Thus, the harmful effects of SO₂ and its deposition as sulphuric acid may be felt far away from the source; the pollution problem becomes an international one affecting countries which may not have pollutant sources discharging sulphur dioxide.

SO₂ is an unpleasant and highly irritating gas, when it is present in concentrations greater than 1 ppm and adversely affects men, animals, plants and materials. It is perhaps the most damaging among the various gaseous air pollutants. Along with SO₂, SO₃, is discharged, at about 1-5 percent of the SO₂ concentration, and it combines rapidly with moisture in the atmosphere to form sulphuric acid which has a low dew point. Both these oxides are rapidly removed from the atmosphere by rain or settle out as aerosol due to which their concentration is less compared to their emissions from human activities.

1.3.2.1 Sources of emission of sulphur oxides

The global sulphur fluxes per year into the atmosphere by anthropogenic and natural sources are shown in Fig. 1.10 while their distribution in different forms between various global compartments is shown in Fig. 1.11.

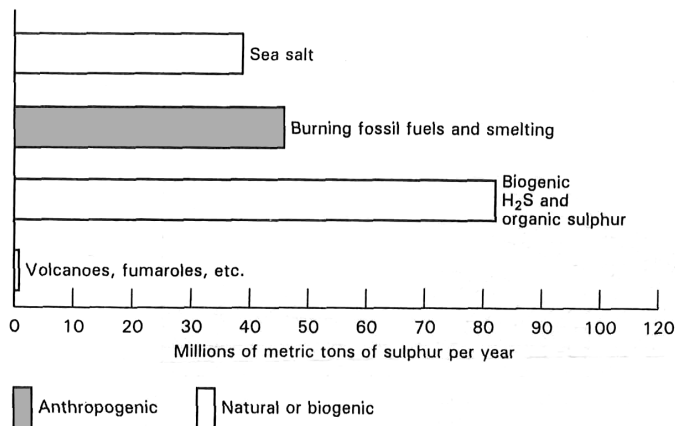


Fig. 1.10 Sulphur fluxes into the atmosphere
(Source: R.J. Charlson, 1968. *J. Air Pollut. Contr. Assoc.* 18, 652.)

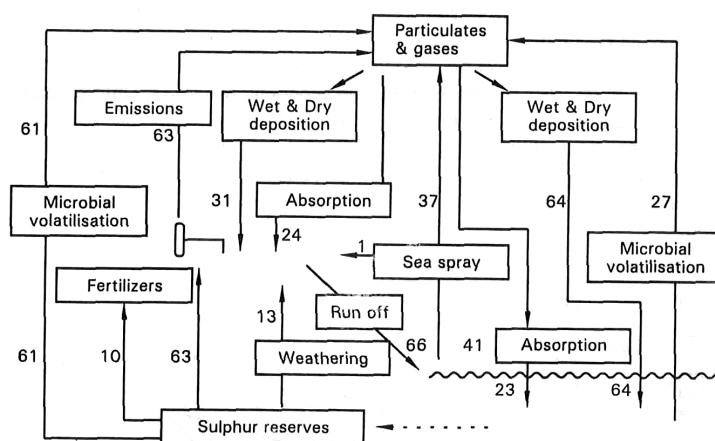


Fig. 1.11 Distribution of sulphur between various environmental phases
(expressed in gigamoles of sulphur per annum)
(Source: Economic commission for Europe (OECD). *Airborne sulphur pollution. Air pollution study no. 1 U.N.* 1984. New York.)

Global emission of SO₂ from natural sources due to microbial activity, volcanoes, sulphur springs, volatilization from various surfaces including vegetation, sea spray, and weathering processes (OECD, 1984) amount to 128 Mt of sulphur (S) per annum (a⁻¹). These are only 50% greater than those caused by human activities (currently 70 Mt a⁻¹), although they are more widely distributed over the surface of the planet and provide natural background levels of SO₂ of about 0.1 ppm. However, biogenic emissions of reduced S-containing compounds from vegetation, wetlands, and oceans are larger.

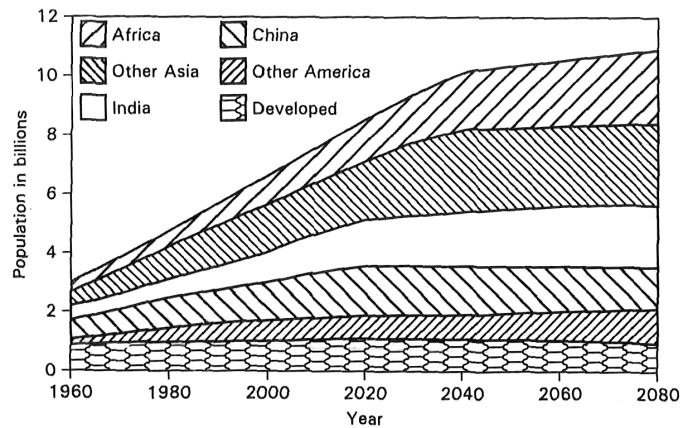


Fig. 1.12(a) Projections of population increase (in billions) in different parts of the world (data from the UN population division)

More than 90% of the anthropogenic emissions of SO₂ are over Europe, North America, India and the Far East. Emissions of SO₂ were highest (77 Mt S a⁻¹) during the late 1970s but have fallen over the last two decades as a result of emission controls, changes in the patterns of fuel consumption, and economic recession. Unfortunately, forecasts of increased coal consumption beyond year 2000 (Fig. 1.12) predict that global anthropogenic emissions of SO₂ will probably rise again by 30% over the present day rates to 85 Mt S a⁻¹. Typical urban levels in developed countries currently range from 0.1 to 0.5 ppm but concentrations in excess of these levels are still common despite legislation

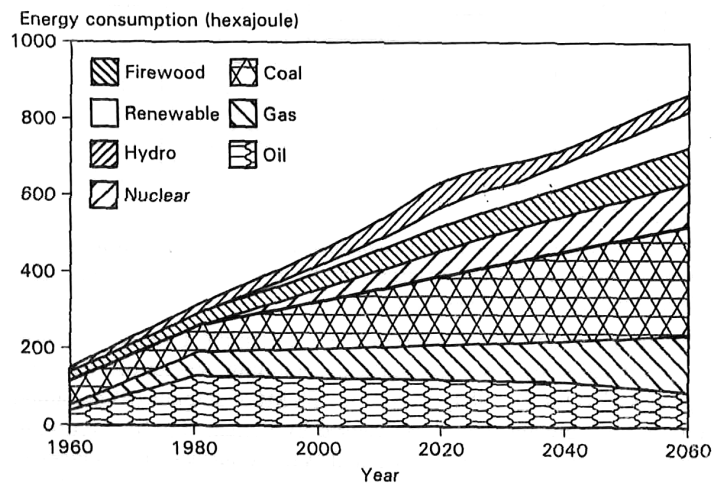


Fig. 1.12(b) Projected worldwide energy consumption for different types of fuels (Source: Proceedings of the World Energy Conference, Cannes, 1986.)

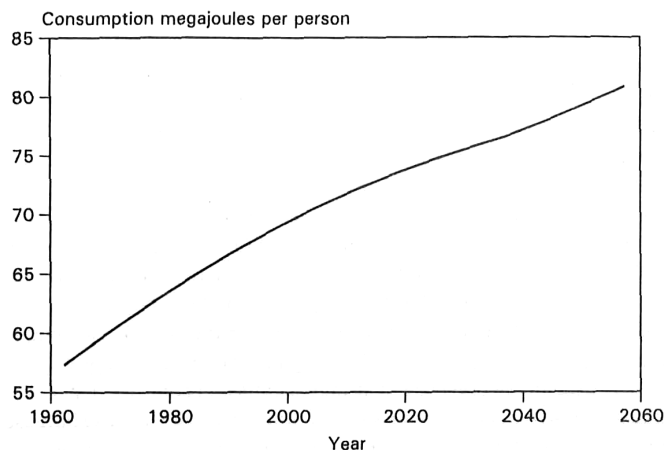


Fig.1.12(c) Future likely trend of global energy consumption per capita derived from data in Figs. 1.12(a) and 1.12(b)

In USA it is observed that fossil fuel concentration in stationary sources contribute more than 80% of SO_2 emission from anthropogenic sources. Out of these anthropogenic emissions nearly 85% are mainly from thermal power plants while only 2% come from highway vehicles. Petroleum refining, copper smelters and cement manufacturing are only the significant on combustion sources. As a result of use of fuels with lower sulphur content, flue gas scrubbing, and more extensive controls on sulphuric acid plants and smelters in USA, SO_2 emissions are fairly stabilized at the 1984 levels (Fig. 1.13(a) and Fig. 1.13(b)) with a 25% overall reduction in total SO_2 emission.

SO_2 emissions can be reduced by using fuels with the lowest possible S content: considerable advances have been made in the removal of S from fuels (including pulverized coal) before combustion. Consequently, the balance between the higher costs of such fuels and those associated with the installation of additional pollution controls is now becoming important.

Fluidized-bed combustion involves the burning of small particles of solid or liquid fuel at 500-700 °C. These are held in a state of suspension by upwardly directed jets of air injected under pressure. Steam and water pipes immersed in the 'bed' then transfer the heat to turbines very efficiently. The potential amount of SO_2 emitted by combustion varies according to the S content of the fuel. However, limestone or dolomite particles can be added to a fluidized bed to reduce SO_2 emissions by up to 90% because the S is trapped in the form of sulphates of calcium or magnesium within the ash. This technique therefore adds to the amount of 'involuntary' S that may be recovered and allows coal of higher S content to be used in the presence of stringent emission controls. The lower temperature of combustion also reduces the emissions of nitrogen oxides and CO because of the air saturating conditions. Of all the combustion technologies likely to be used for future power generation, coal still appears to have many advantages (Table 1.12).

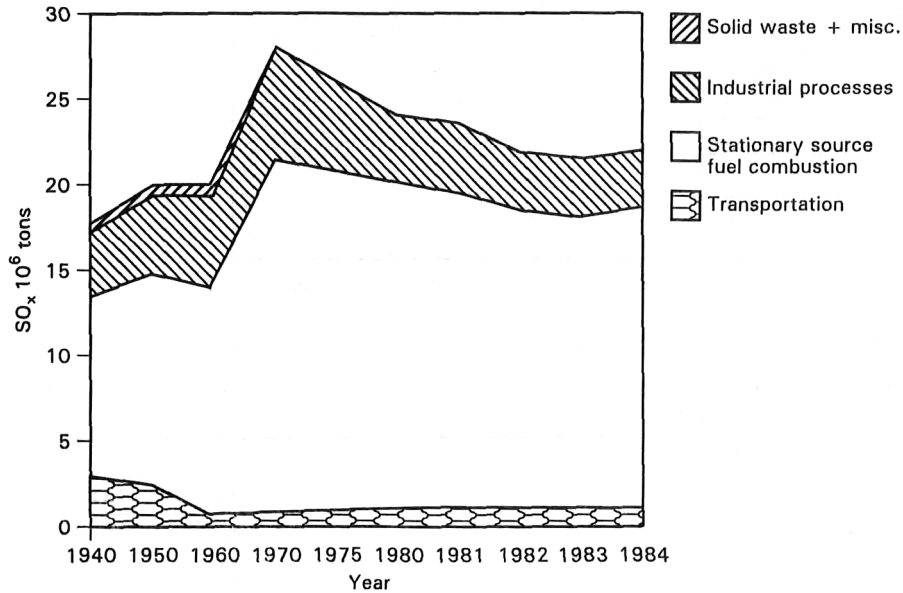


Fig. 1.13(a) Trends in sulphur oxide emissions in USA, 1940-1984 (USEPA, 1940-1984)

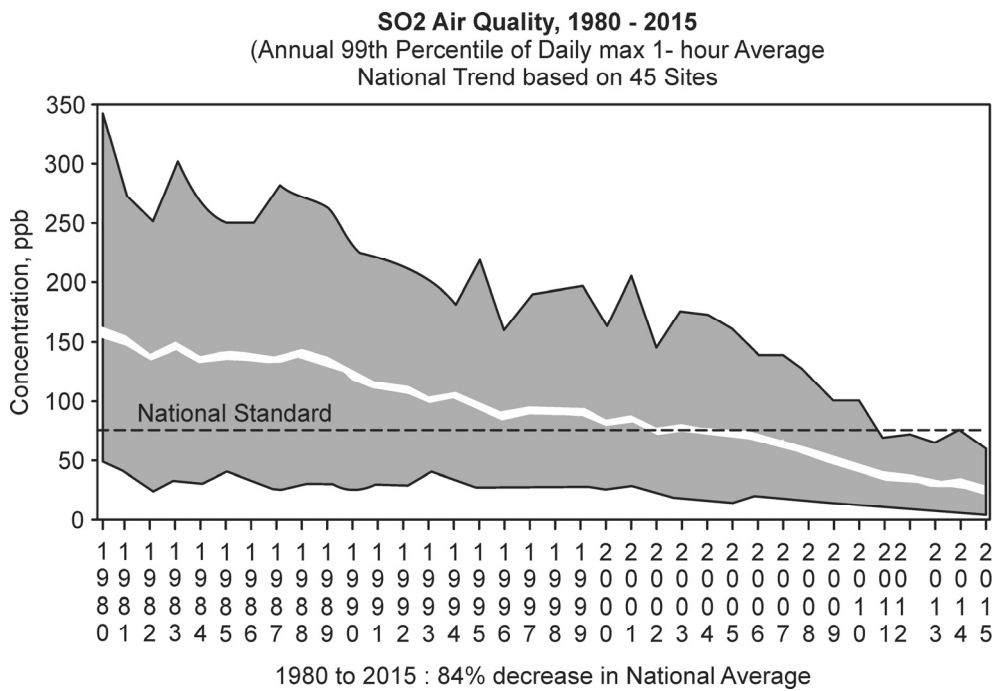


Fig. 1.13(b) Trends in sulphur dioxide emissions in USA, 1980-2015

Table 1.12 Efficiencies and emission problems (without flue-gas desulphurization) of power generation by different combustion processes

Type of power plant	Maximum thermal efficiency	Emission		
		CO	SO ₂	NO ₂ + NO
Oil-fired	35-37%	Trace	High	V. high
Natural gas-fired	35-37%	Trace	Low	V. high
Conventional coal-fired	35-40%	Low	High	V. high
Gas turbine	18-28%	High	V. high	V. high
Fluidized bed	40-50%	Trace	low	Low

1.3.2.2 National trends in sulfur dioxide levels

Using a nation wide network of monitoring sites, US-EPA has developed ambient air quality trends for sulfur dioxide (SO₂). Trends starting in 1980, 1990, and 2000 are shown here. Under the Clean Air Act, EPA sets and reviews national air quality standards for SO₂. Air quality monitors measure concentrations of SO₂ throughout the country. EPA, state, tribal and local agencies use that data to ensure that SO₂ in the air is at levels that protect public health and the environment. Nationally, average SO₂ concentrations have decreased substantially over the years.

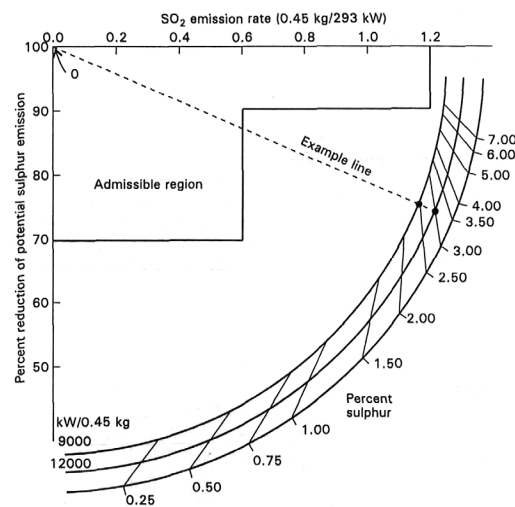


Fig. 1.14 Graphical representation of new source performance standards for SO₂ emissions from coal-fired power plants

(Source: J. Mol burg, 1980. A graphical representation of the NSPS for sulphur dioxide. *Journal of air pollution control association*. 30(1): 172.)

Most anthropogenic SO₂ emissions are mainly through tall stacks injecting the gases into the troposphere to heights at which the temperatures of the surrounding air and the rapidly cooling stack gases match. A discrete plume is then often carried away at that

level. The behavior of this plume is dependent upon the prevailing weather conditions and the contents may be dry-deposited close by or carried many hundreds of kilometers away from the source. However, when the plume encounters wet conditions, considerable amounts of gaseous SO₂ (and nitrogen oxides) are removed by wet deposition.

For coal-fired, steam-electric power plants the emission standard for SO₂ is complex and is best illustrated in Fig. 1.14 where a region of allowable SO₂ emissions is identified. The sulphur content (% sulphur) of the fuel and the fuel's energy content (kW/kg) are parameters used to determine a point on one of the indicated arcs. A line drawn from the origin to the sulphur/heat point crosses the "admissible region" boundary at one point, corresponding to the allowable SO₂ emission rate.

Problem 1.4

Estimate the emission rate of SO₂ in a 5000 megawatt (MW) coal-fired power plant which is 60% efficient. The coal to be burned contains 2.5% sulphur and coal has a heat content of 9495 kW/0.45 kg. What is the permissible emission rate of SO₂ and if a control system has to be installed, what percent reduction in SO₂ emission should it achieve?

Solution: Since the power plant is working with 60% efficiency, and it delivers 5000 MW of electricity (5.0×10^6 kW), the input heat rate is

$$Q_{in} = \frac{Q_{out}}{\eta} = \frac{5.0 \times 10^6 \text{ kW}}{0.60} = 8.3 \times 10^6 \text{ kW}$$

Converting it in terms of kW/day we have

$$Q_{in} = 8.3 \times 10^6 \text{ kW} \times \frac{24 \text{ h}}{\text{day}} = 1.992 \times 10^8 \text{ kW/day}$$

From Fig. 1.14 at 2.5% sulphur and 9495 kW/0.45 kg of coal, the maximum allowable emission rate is 0.45 kg/293 kW and controls must achieve an SO₂ reduction of about 87%. Totally daily emissions would be:

$$\begin{aligned} \text{SO}_2 \text{ emission rate} &= \frac{1.992 \times 10^8 \text{ kW}}{\text{day}} \times \frac{0.45 \text{ kg}}{293 \text{ kW}} = \frac{0.8964 \times 10^8}{293} \\ &= 3.06 \times 10^5 \text{ kg/day} = 306000 \text{ kg/day} \end{aligned}$$

This is also a significant amount.

1.3.3 Removal mechanisms of sulphur oxides

The transformation from SO₂ gas to sulphate particles (SO₄) is gradual, taking a matter of days. During that time, sulphur may be deposited back onto the land or into water, either in the form of SO₂ or sulphate. In either form, sulphur can be deposited by precipitation (wet deposition), or by slow, continuous removal processes that occur without

precipitation (dry deposition). Figure 1.15 suggests the effects of time and distance on the conversion and deposition of sulphur.

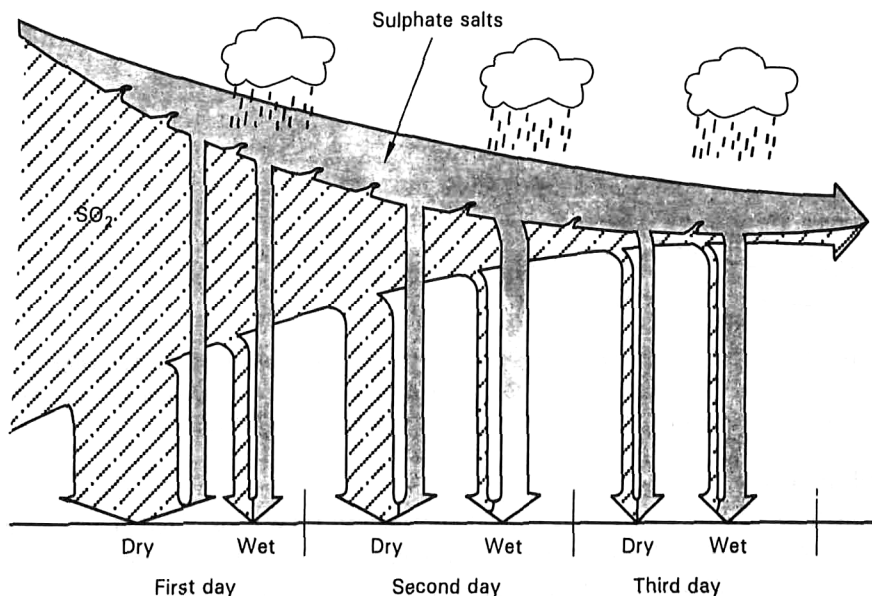
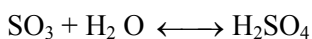
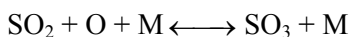
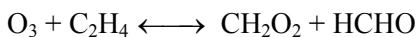


Fig. 1.15 The effects of time and distance on conversion and deposition of sulphur pollutants
(Source: Office of Technology Assessment (OTA) 1984. *Acid rain and transported air pollutants. Implications of public policy. Washington DC.*)

SO₂ in the discharged plumes may react with atomic oxygen formed within the stratosphere to form SO₃, and finally sulphuric acid as shown below.

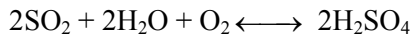


However, a second mechanism based upon one reaction which relies upon the extensive presence of free radical hydrocarbons, may also contribute to a smaller extent to the removal of SO₃.



A third photochemical reaction may produce an energized form of SO₂ which then combines with O₂ to form SO₄. However, as this chemical compound has never been positively identified in the atmosphere, this light-driven acidification process is highly unlikely.

M^1 is a third entity, such as a surface or another gas molecule, which is capable of carrying away excess energy associated with the formation of the new bond.



This process has been shown to be catalysed by metal salts such as iron and manganese, commonly found in flyash. Flyash particles serve as nucleation sites for droplet formation and the sulphuric acid droplet may in turn react with metal salts (such as NaCl from sea salt particles), metal oxides such as MgO, Fe₂O₃, ZnO, and Mn₂O₃, or ammonia to produce corresponding sulphates.

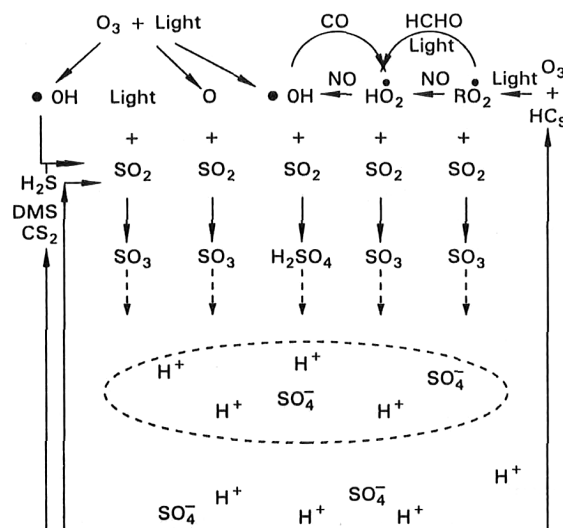
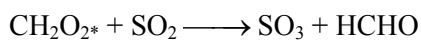
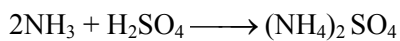
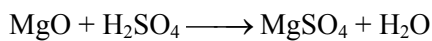
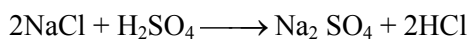


Fig. 1.16 Some inter relationships between the wet and dry mechanisms of SO₂ removal

(Source: Dis Con and Penkett, AERE, U. K. Harwell and D. Reidel. Publ. Co., The Netherlands.)

As shown in Fig. 1.16 the reaction of SO₂ with highly reactive hydroxyl (•OH) free radicals formed from O₃ or monoatomic oxygen are responsible for sulphuric acid formation in the atmosphere. The predominance of this mechanism of acidification involving OH radicals indicates that warm, bright summer days, which favour O₃, and monoatomic oxygen formation (and hence OH radicals) promote dry-phase acidification, while wet-phase reactions are predominant in winter.

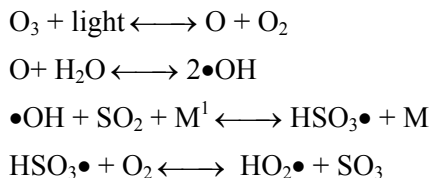


Figure 1.16 shows a number of interrelationships between the wet and dry mechanisms of SO₂ removal.

1.3.3.1 Effects of sulphur oxides on plants

Cell and leaf anatomy: Since the leaf is the primary indicator of air pollution effects on plants, the functions of the leaf are given below. Atypical plant cell has three main components (Fig. 1.17): the cell wall, the protoplast, and the inclusions. Much like the human skin, the cell wall is thin in young plants and gradually thickens with age. Protoplast is the term used to describe the protoplasm of one cell. It consists primarily of water, but it also includes protein, fat, and carbohydrates. The nucleus is the dense bit of protoplasm that controls the operation of the cell. The protoplasm located outside the nucleus is called cytoplasm. Within the cytoplasm are three types of tiny bodies or plastids: chloroplasts, leucoplasts and chromoplasts. Chloroplasts contain the chlorophyll that manufactures the plant's food through photosynthesis. Leucoplasts convert starch into starch grains. Chromoplasts are responsible for the red, yellow and orange colour of the fruit and flowers.

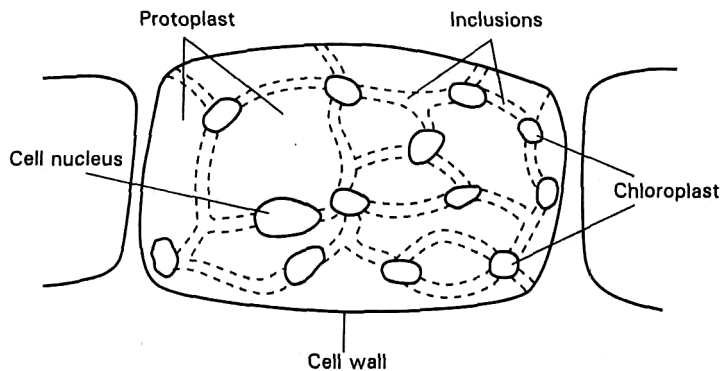


Fig. 1.17 Typical plant cell

(Source: I. Hindawi, 1970. *Air pollution injury to vegetation*. U.S. Dept. of Health, Education and Welfare, National Air Pollution Control Administration, Washington DC. US Govt. Printing Office.)

A cross-section through a typical mature leaf reveals (Fig. 1.18) three primary tissue systems: the epidermis, the mesophyll, and the vascular bundle. Chloroplasts are usually not present in epidermal cells. The opening in the underside of the leaf is called the stoma. (The plural of stoma is stomata.) The mesophyll, which includes both the palisade

parenchyma and the spongy bundles carries water, minerals and food throughout the leaf and to and from the main stem of the plant. The guard cells regulate the passage of gases and water vapour in and out of the leaf. When it is hot, sunny and windy, the processes of photosynthesis and respiration are increased. The guard cells open and allow for increased transpiration of water and minerals from the roots.

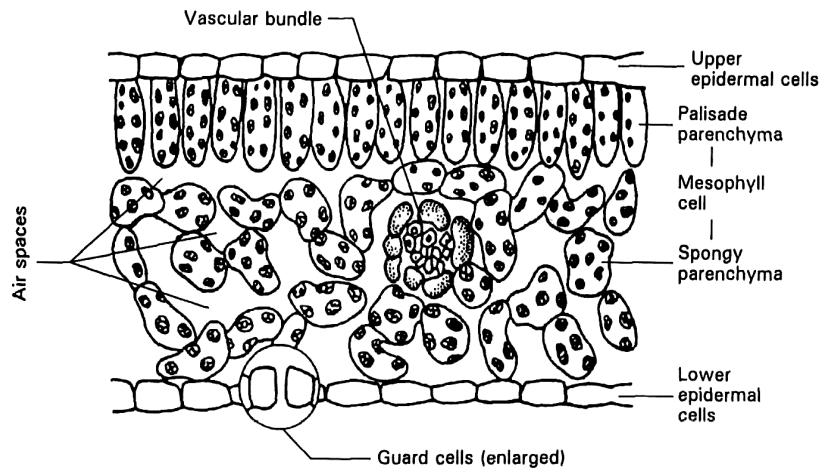


Fig. 1.18 Cross-section of intact leaf

(Source: I. Hindawi, 1970. *Air pollution injury to vegetation*. U.S. Dept. of Health, Education and Welfare, National Air Pollution Control Administration, Washington DC. US Govt. Printing Office.)

The layer of still air above the leaf will be the first barrier encountered by a gaseous pollutant before reaching a leaf. The imaginary still air on both sides of the plant imposes a 'boundary layer resistance' to the entry of atmospheric pollutants (Fig. 1.19). Their movement across such a layer is achieved by diffusion of gas molecules in response to differences in concentration. The boundary layer resistance also varies with wind speed and leaf properties such as size, shape, and orientation. As wind speed increases, resistance to the inward movement of pollutant molecules falls and uptake increases; in this way, increased wind speed can facilitate the uptake of pollutants. Moreover, the boundary layer is generally thinner at the edges of a leaf than at the centre, which accounts for increased pollutant damage often seen at margins of leaves, especially on grasses and cereals.

A greater proportion of a leaf surface is occupied by epidermal cells than stomatal pores; the waxy cuticle covering them offers a greater penetration barrier to most pollutant gases. SO_2 deposited on wet leaf and stem surfaces may also dissociate and react with cuticular waxes, a certain amount of SO_2 may then enter leaves by penetrating the damaged cuticle even though most atmospheric SO_2 still enters through the stomata. When the cuticle remains damp for long periods, especially at night or in the winter, the

deposition rate of SO_2 onto a leaf surface increases despite the fact that the stomata are closed. This causes additional damage for evergreens which retain their leaves and needles over winter.

For stomata to open, guard cells of the stomata have to be turgid which causes the gap between them to widen. In most plants, this occurs during the day as normal exchanges of water and CO_2 take place. As a result, uptake of atmospheric gases like SO_2 into plants takes place during the day. In very dull conditions, the stomatal opening is reduced and therefore, the rates of SO_2 uptake are also reduced. At night, however, when the stomata are closed, the rates of removal of SO_2 (or O_3) by plants approach those of other inert surfaces. Consequently those changes in stomatal aperture which provide a plant with mechanisms to control the movement of CO_2 into leaves and H_2O outwards, also influence pollutant gas uptake. Stomatal behaviour, frequency and distribution are therefore important factors which affect the amount of pollutant entering a plant.

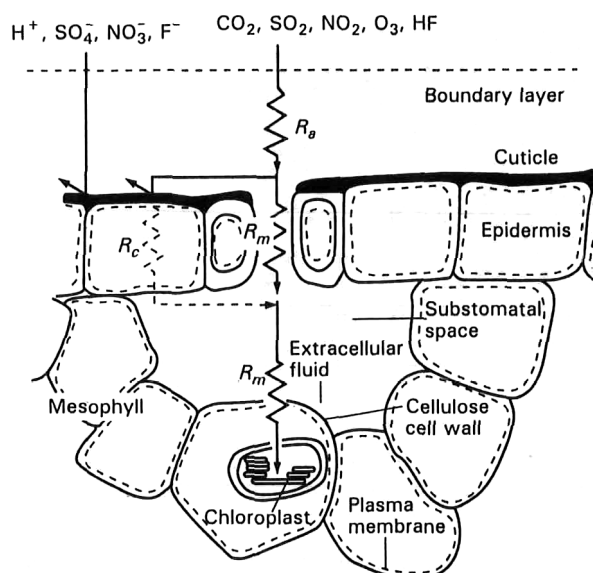


Fig. 1.19 Likely access routes for SO_2 into a leaf

(Source: Alan Wellburn, 1998. *Airpollution and climate change-the biological impact*. Longman, U.K.)

SO_2 is nearly 30 times as soluble as CO_2 in aqueous fluid. This means that SO_2 uptake takes place mainly on the lower inner surfaces of the stomatal guard cells, where most (77-90%) of the transpired H_2O is lost, rather than from the mesophyll extracellular fluid which contributes only 10-23% of H_2O loss but 85% of CO_2 uptake. This is largely because removal mechanisms of CO_2 are associated with photosynthetic carbon fixation. Uptake of SO_2 close to the stomata also means that the immediate effects of SO_2 are focused in this area. Indeed, SO_2 injuries both to the plasma membranes of guard cells

and to the transport cells loading the vascular elements of leaves (companion cells in angiosperms, Strasburger cells in gymnosperms) are especially important. This means that increased levels of acidity and other ions (e.g., sulphite and sulphate) occur at these damaged locations and together they can have a detrimental effect upon the ability of a plant to move and use H₂O and photosynthetic products.

Inhibition of photosynthesis due to decrease in pH or increase in acidity is frequently recognized as one of the immediate effects of SO₂ pollution on plants.

Thus, the increase in acidity due to SO₂ pollution is likely to be significant. For example, direct effects of SO₂ have been demonstrated upon the enzyme of CO₂ fixation, ribulose-1,5 bi-phosphate carboxylase/oxygenase, which requires a pH change in the stroma from pH 7.5 to pH 9.0 to become active. It has been calculated that a reduction of chloroplast stroma by 0.5 of a pH unit will cause a 50% decrease in net photosynthesis. So even a small change could significantly affect the growth of polluted plants over a long period. The injurious levels of SO₂ for different types of trees are given in Table 1.13.

Table 1.13 *Injurious levels of SO₂ for different types of trees*

Tree	Concentration of SO ₂ (ppm)	Time to produce injury (hours)
Apple	0.48	6
Pear	0.48	6
Mango	0.50	7
Mountain ash	0.54	3
Ponderosa pine	0.50	8

1.3.3.2 Effects of sulphur oxides on human health

Irritant properties: Sulphur dioxide and its derivatives produce strong irritation in the eyes and also within the nasal passageways. It causes intense irritation, even at 2.5 ppm levels, to the eyes and the respiratory tract. It is absorbed by the nasal system, leading to swelling and stimulated mucus secretion. Sulphur dioxide damages lung tissue and promotes respiratory diseases. Raised levels of SO₂ in the atmosphere may also cause lung cancer. Higher concentrations of SO₂ induce desquamation or peeling off of the surface epithelium in the mucosa. Cilia which protect the respiratory tract are also affected by SO₂. SO₃ on a molar basis produces more than four times the irritant response of SO₂ because it combines immediately with water to form sulphuric acid. Sulphates in particulates can also cause similar irritation and the intensity of the effect is dependent upon the concentration of gaseous SO₂. SO₂ also induces an involuntary coughing reflex. The eye irritation combined with the choking cough immediately draws the attention of those affected by the hazards of the surrounding atmosphere, although there is a wide variation in response susceptibility between individuals. The taste threshold limit is 0.3 ppm, and SO₂ produces an unpleasant smell at 0.5 ppm. SO₂ can also be detected by smell by some individuals better than others, but at very high concentrations (>3 ppm) this sense of smell is quickly paralysed in all.

The threshold concentration of SO₂ producing injury to plants, man and animals is presented in Table 1.14. Table 1.15 shows the human response to different levels of SO₂ for different periods.

Table 1.14 *The threshold concentrations of SO₂ producing injury*

Category	Short term exposure (one hour/day)	Long term exposure (one hour/day)
Plants	0.5-2.0	0.01-0.05
Man	0.5-3.0	0.02-0.10
Animals	1.0-4.0	0.05-0.20

Table 1.15 *Human response to different levels of SO₂ for different periods*

Concentration ($\mu\text{l l}^{-1}$)	Period	Effect
0.03-0.05	Continuous	Condition of bronchitic patients worsened
0.3-1	20 seconds	Brain activity changes
0.5-1.4	1 minute	Odour perceived
0.3-1.5	15 minutes	Increased eye sensitivity
1-5	30 minutes	Increased lung air way resistance, sense of smell lost
1.6-5	>6 hours	Constriction of nasal and lung passageways
5-20	>6 hours	Lung damage reversible if exposure ceases
20 upwards	>6 hours	Water logging of lung passageways and tissues, eventually leading to paralysis and/or death.

The primary effect of most air pollutants on human health seems to be the injury of delicate tissues, by causing damage to the cellular membranes. This often sets in motion an inflammatory response—a complex series of interactions between damaged cells, surrounding tissues, and the immune system. One of the first symptoms of inflammation is leakage of fluid (plasma) from blood vessels. Exposure of respiratory tissues to severe irritants can result in so much edema (fluid accumulation) in the lungs that one effectively drowns. Bronchitis is a persistent inflammation of bronchi and alveoli (large and small airways in the lung) that causes a cough, copious production of sputum (mucus and dead cells) and involuntary muscle spasms that constrict airways. Acute bronchitis can obstruct airways so severely that death results. Smoking is undoubtedly the largest cause of chronic bronchitis in most countries. Persistent smog and acid aerosols can also cause this disease.

Severe bronchitis can lead to emphysema, an irreversible obstructive lung disease in which airways become permanently constricted and alveoli are damaged or even destroyed. Stagnant air trapped in blocked airways swells the tiny air sacs in the lung (alveoli), blocking blood circulation. As cells die from lack of oxygen and nutrients, the walls of the alveoli break down, creating large empty spaces incapable of gas exchange (Fig. 1.20). Thickened walls of the bronchioles lose elasticity and breathing becomes more difficult. Victims of emphysema make a characteristic whistling sound when they breathe. Often they need supplementary oxygen to make up for reduced respiratory capacity.

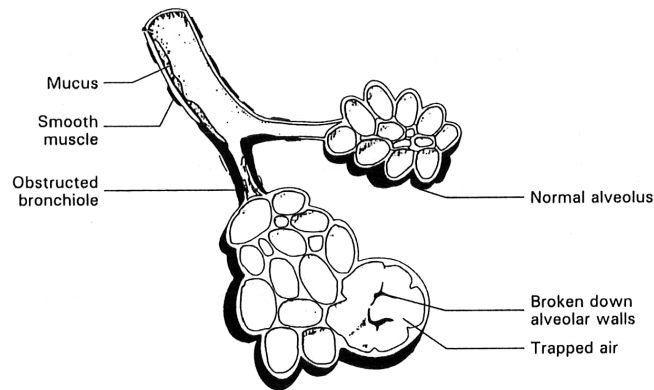


Fig. 1.20 *Emphysema results from chronic irritation and obstruction of airways and alveoli. In extreme cases, alveolar walls break down and enlarged air sacs full of trapped stagnant air fill the lungs*

Figure 1.21 shows the major air passageways into the lungs which terminate in the alveoli (fluid-lined air sacs) across which O_2 and CO_2 exchanges take place with the bloodstream. The mode of entry of SO_2 into this system, however, differs from those associated with nitrogen oxides, O_3 and photochemical oxidants because more than 95% of inhaled SO_2 is absorbed in the airways above the larynx (voice box) and less than 1% gets down into the lung alveoli when an individual is resting. Exercise increases the exposure of lung alveoli to SO_2 but at the same time, the upper airways are constricted and the mucus lining dries up. This bronchoconstriction and dryness may induce chronic bronchitis in some individuals, especially those predisposed to asanma. The same group often also show a sensitivity to sodium sulphite used commercially as sterilizing agent or as a preservative.

During severe short term exposures to SO_2 , sulphate and sulphite anions formed on the cell surfaces of the nasal linings penetrate the surface mucosal cells and bind to granules within mast cells beneath. This causes local release of histamine which then acts as a local modulator to cause constriction of the airways and initiates local inflammation. Ciliary cells lining parts of the airways often release extra mucus to carry away some of the harmful anions as the nose is blown or one coughs. Similarly, tears running from the eyes provide relief from the local irritation.

Cardiovascular stress from lack of oxygen in the blood is a common complication of all obstructive lung diseases. About twice as many people die of heart failure associated with smoking as die of lung cancer. Irritants in the air are so widespread that about half of all lungs examined at autopsy in the United States have some degree of alveolar deterioration.

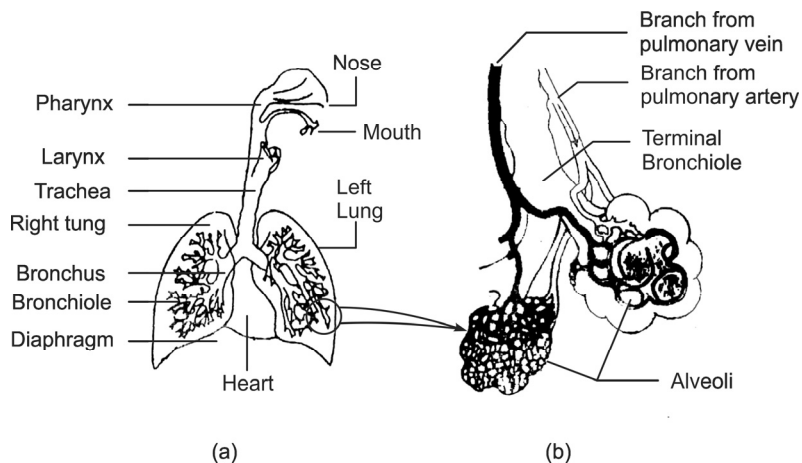


Fig. 1.21 Cut away diagrams of the mammalian respiratory system at different scales of resolution

Figure 1.22 summarizes the effect of various concentrations of SO₂ and exposure time on human health while Fig. 1.23 gives daily mortality as a function of SO₂ concentration observed in London.

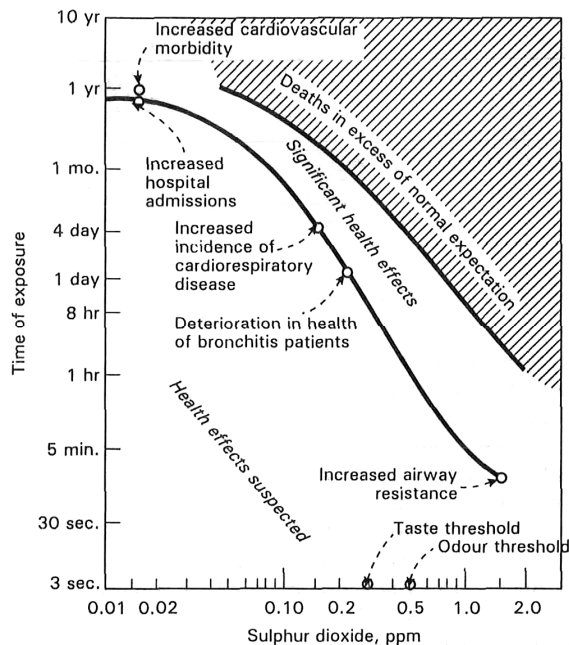


Fig. 1.22 Hazards to health from SO₂ pollution

(Source: A. M. Squires, *Chemical Engineering*, Vol. 74, No., 23, Nov. 6, 1967)

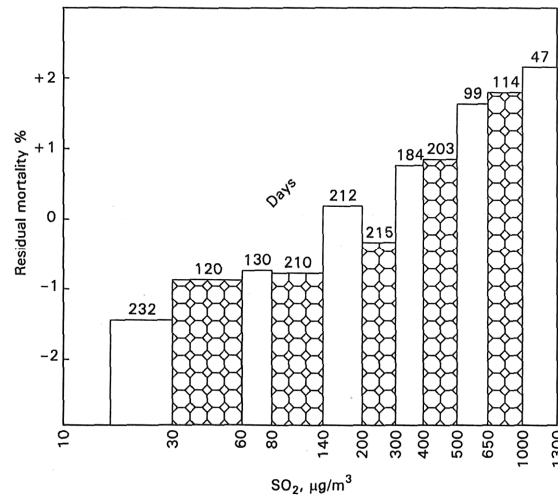


Fig. 1.23 Daily mortality as a function of SO₂ concentration

(Source: Helen Dwight Reid Educational Foundation, Heldref Publications, 1319 Eighteenth St., N. W. Washington, D.C. 20036-1802.) [2]

During accidental non-fatal exposure, victims experience inflammation of the eyes, nausea, vomiting, abdominal pain, a sore throat, bronchitis, and often pneumonia. Normally, the lungs are (and have to be) highly sterile, but this weakening of natural antibacterial mechanisms points the way to emergency treatment of SO₂-exposure cases. Prompt use of oxygen and bronchodilators along with heavy doses of antibiotics prevents permanent damage and may save life.

The possibilities of chronic poisoning by SO₂ over longer periods at low levels are greater for the general population than accidental acute cases. A number of theories confirm the high correlation between chronic chest disease and levels of SO₂ in urban air and indicate that chronic exposure to SO₂ along with particulate matter plays a significant role in the cause and development of chronic respiratory disease.

Thus, sulphur dioxide is found to be more harmful in a dusty atmosphere. This effect may be explained as follows: The respiratory tract is lined with hair-like cilia, which by their regular sweeping action force out foreign substances entering the respiratory tract through the mouth. However, SO₂ and H₂SO₄ molecules paralyse the cilia, rendering them ineffective in rejecting particulates, which thus penetrate deeper into the lungs. By themselves these molecules are too small to remain in the lungs, but some SO₂ molecules are also absorbed on larger particles, which penetrate into the lungs and settle there, bringing concentrated amounts of the irritant SO₂ into prolonged contact with the fine lung tissues.

The British Committee on air pollution estimated that a total of 4,000 more deaths than usual were caused by killer pollutants in the 1952 air pollution episode. The relationship between death rate and smoke and SO₂ concentrations observed is illustrated

in Fig. 1.24. During this air pollution episode over a period of two months, there were 8,000 more deaths than usual. Symptoms of the illness were cough with little sputum, sore throat, nasal discharge, and sudden vomiting. Further, those with a previous history of chest trouble (such as chronic bronchitis, bronchiectasis, asthma, or one of the forms of pulmonary fibrosis) were among the most severely ill. The combined action of sulphuroxides and particulate matter was the suspected cause of irritation and disaster. During the episode, the concentration of sulphur oxides reached 0.7ppm, and at one location, the level was 1.3 ppm for a short period of time. Such heavy concentrations came from industry and home heating by coal and coke, which contain, on the average, 1.5% sulphur. It was estimated that 190 million tons of coal was used in England in 1948, and this sent into the atmosphere 4.7 million tons of deadly SO₂. In the winter of 1956, another episode took place which caused 1,000 additional deaths.

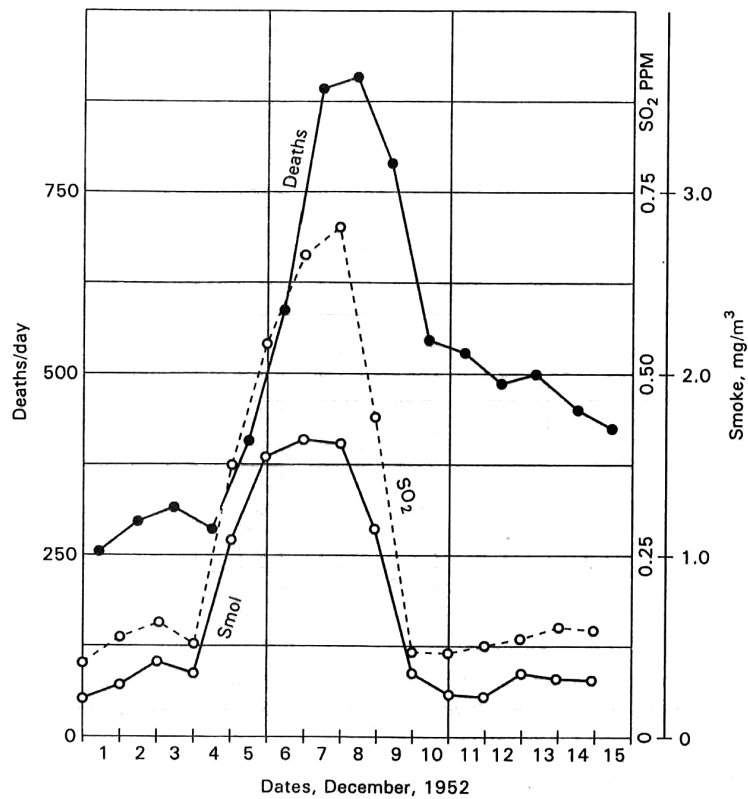


Fig. 1.24 Daily air pollution and deaths in London, 1952

(Source: American Industrial Hygiene Association Air Pollution Manual, 1960.)

Each year air pollutants cause a lot of damage to various materials. Expensive cleaning methods are required to remove soot and grit deposited on buildings, cars and clothes. Air pollutants break down exterior paint on cars and houses, and they deteriorate

roofing materials. Irreplaceable marble statues, historic buildings, and stained-glass windows throughout the world have been pitted and discoloured by air pollutants. Damage to buildings in the United States from acid depositions alone was estimated at \$5 billion per year. The various harmful effects of SO_x on materials are summarized in Table 1.16. The relationship between the corrosion of mild steel and mean SO₂ concentrations for various exposure times observed in Chicago are summarized in Fig. 1.25.

Table 1.16 Harmful effects of air pollutants on materials

Material	Effects	Principal air pollutants
Stone and concrete	Surface erosion, discoloration, soiling	Sulphur dioxide, sulphuric acid, nitric acid, particulate matter
Metals	Corrosion, tarnishing, loss of strength	Sulphur dioxide, sulphuric acid, nitric acid and particulate matter
Ceramics and glass	Surface erosion	Hydrogen fluoride, particulate matter
Paints	Surface erosion, discoloration, soiling	Sulphur dioxide, hydrogen sulphide, ozone, particulate matter
Paper	Embrittlement, discoloration	Sulphur dioxide
Rubber	Cracking, loss of strength	Ozone
Leather	Surface deterioration, loss of strength	Sulphur dioxide
Textile	Deterioration, fading, soiling	Sulphur dioxide, nitrogen dioxide, ozone, particulate matter

1.3.3.3 Effects of sulphur oxides on materials

SO₂ is injurious not only to man and plants, but it also attacks rapidly marble, limestone, roofing slate, electrical contacts, paper, textiles, and buildings. It can even dissolve nylon. Paper absorbs sulphur dioxide which will be oxidized to H₂SO₄ causing the paper to become brittle and fragile. Air with SO₂ accelerates the corrosion rates of metals such as Fe, steel, Zn, Cu.

1.3.3.3.1 Factors that influence deterioration of materials

Moisture, temperature, sunlight, and position of the exposed material are among the more important factors that influence its rate of deterioration.

Moisture, in the form of humidity, is essential for most of the mechanisms of deterioration to occur. Metal corrosion does not appear to occur even at relatively high SO₂ pollution levels until the relative humidity exceeds 60 percent. On the other hand humidities above 70 to 90 percent will promote corrosion without air pollutants. Rain reduces the effects of pollutant-induced corrosion by dilution and washing away of the pollutant.

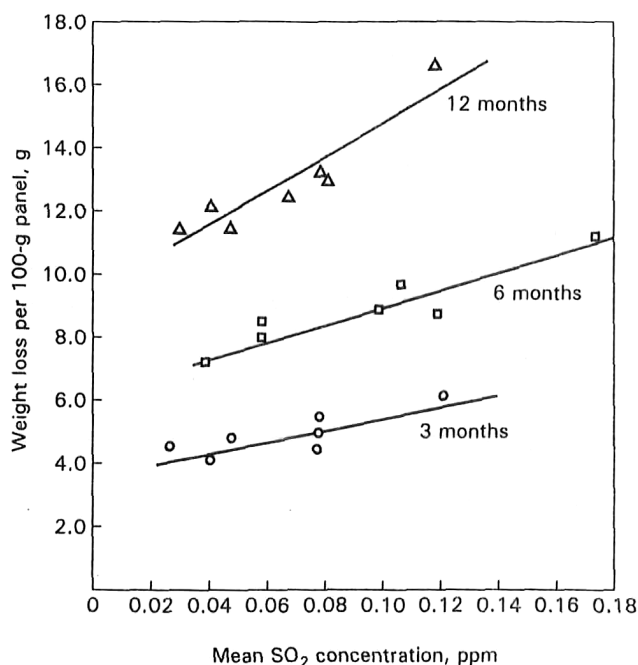


Fig. 1.25 Relationship between corrosion of mild steel and corresponding mean sulphur dioxide concentrations for various exposure times at seven sites in Chicago (September, 1963-64)

(Source: Air and Waste Management Association Publication.) [3]

Solubilization and oxidation/reduction reactions typify direct chemical attack. Frequently, water must be present as a medium for these reactions to take place. Sulphur dioxide and SO₃ in the presence of water react with limestone (CaCO₃) to form calcium sulphate (CaSO₄) and gypsum (CaSO₄ 2H₂O). Both CaSO₄ and CaSO₄ 2H₂O are more soluble in water than CaCO₃, and both are leached away when it rains. The tarnishing of silver by H₂S is a classic example of an oxidation/reduction reaction.

Indirect chemical attack occurs when pollutants are absorbed and then react with some component of the absorbent to form a destructive compound. The compound may be destructive because it forms an oxidant, reductant, or solvent. Further, a compound can be destructive by removing an active bond in some lattice structure. Leather becomes brittle after it absorbs SO₂, which reacts to form sulphuric acid because of the presence of minute quantities of iron. The iron acts as a catalyst for the formation of the acid. A similar result has been noted for paper.

Oxidation/reduction reactions cause local chemical and physical differences on metal surfaces. These differences, in turn, result in the formation of microscopic anodes and cathodes. Electrochemical corrosion results from the potential that develops in these microscopic batteries.

Higher air temperatures generally result in higher reaction rates. However, when low air temperatures are accompanied by cooling of surfaces to the point where moisture condenses, then the rates may be accelerated.

1.3.4 Nitrogen oxides

Natural stratospheric oxides of nitrogen are produced by the action of cosmic rays in the upper atmosphere. Emissions of oxides of nitrogen from man-made sources vary in different areas. Nitrogen oxides are 10 to 100 times greater in the urban atmosphere as compared to rural areas.

Oxides of nitrogen which include N_2O , NO , NO_2 , N_2O_3 , and N_2O_5 are usually represented by the symbol NO_x . The two major pollutants among them are nitric oxide, NO , and nitrogen dioxide, NO_2 .

As N_2 circulates, between plants and animals and microbes in the soil, wide differences exist between different reduced and oxidized components. The electronic configuration about an N atom may vary widely; this permits a number of different oxidation-reduction states of N to exist (Fig. 1.26). This, in turn, gives rise to a wide range of N-based compounds and together these features dominate the biological nitrogen cycle (Fig. 1.27).

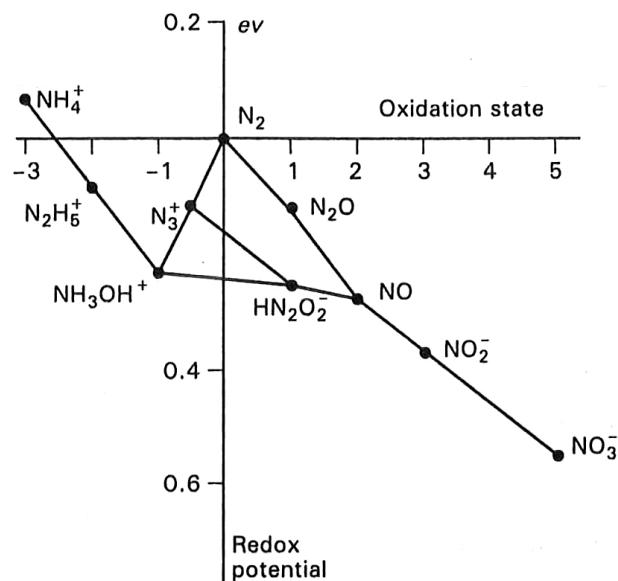


Fig. 1.26 Oxidation states of nitrogen at pH 7.0 in relation to redox potentials

(Source: *Air Pollution Climatic Change*, Alan Well burn, Longman, 1998.)

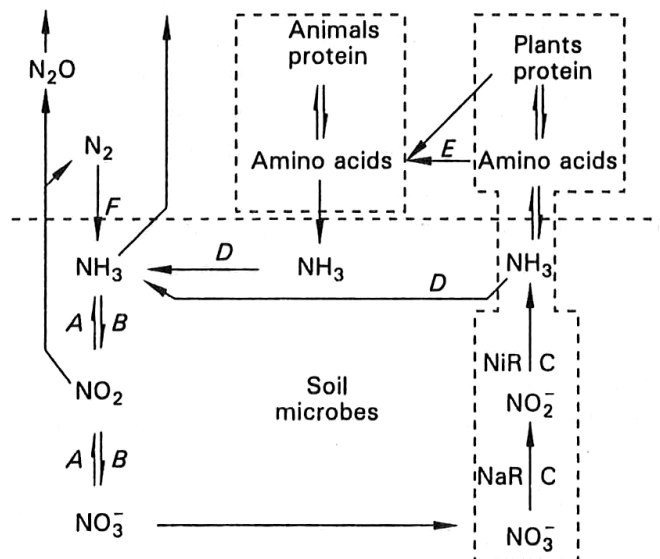


Fig. 1.27 The nitrogen cycle as it relates to plants, animals, the soil and the atmosphere. The various processes are as follows: A = denitrification or dissimilatory nitrogen metabolism which releases N_2O ; B = microbial nitrification; C = assimilatory nitrogen metabolism; NaR = nitrate reductase; NiR = nitrite reductase; D = decay after death or putrefaction; E = digestion; and F = nitrogen fixation

(Source: Air Pollution Climatic Change, Alan Wellbum, Longman, 1998.)

Any excess artificial fertilizer remaining after application, which has not drained away, is usually removed by denitrification. Increasing global use of artificial fertilizers therefore contributes to higher NO_x levels. Table 1.17 shows the global transfer rates of nitrogen by various processes.

Table 1.17 Global transfer rates of nitrogen by various processes

Process	10^{12} g N per year
Denitrification/nitrification	160
Natural nitrogen fixation	150
Fires and combustion	70
Industrial fixation	40
Ionic exchange by rain, etc.	80
Run off to oceans	35

1.3.4.1 Sources of emission of nitrogen oxides

Major man-made activities like combustion of coal, oil, natural gas and gasoline produce up to 50 ppm of oxides of nitrogen. Atmospheric nuclear explosions can be another potential serious source of man-made stratospheric oxides of nitrogen. There are two ways of formation of oxides of nitrogen during the combustion of fossil fuels. Thermal NO_x are created when nitrogen and oxygen in the combustion air are heated to a high enough temperature (above about 1000 K) to oxidize the nitrogen. Fuel NO_x result from the oxidation of nitrogen compounds that are chemically bound in the fuel molecules themselves. Different fuels have different amounts of nitrogen in them, with natural gas having almost none and some coal having as much as 3% by weight. Both thermal NO_x and fuel NO_x can be significant contributors to the total NO_x emissions, but fuel NO_x often is the dominant source.

The global fluxes of reactive nitrogen gases into the atmosphere per year are shown in Fig. 1.28.

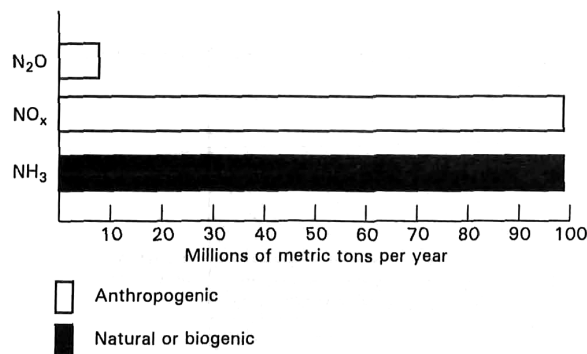


Fig. 1.28 Fluxes of reactive nitrogen gases into the atmosphere

(Source: American Industrial Hygiene Association Air Pollution Manual, 1960.)

Anthropogenic impacts upon the global exchange of N are considerable but the bulk of the global N cycling remains microbial.

1.3.4.2 US -National trends in nitrogen dioxide levels

Using a nationwide network of monitoring sites, US EPA has developed ambient air quality trends for nitrogen dioxide (NO_2). Under the Clean Air Act, EPA sets and reviews national air quality standards for NO_2 . Air quality monitors measure concentrations of NO_2 throughout the country. EPA, state, tribal and local agencies use that data to ensure that NO_2 in the air is at levels that protect public health and the environment. Nationally, average NO_2 concentrations have decreased substantially over the years. Figure 1.29 shows the trends in nitrogen oxide emissions from 1980-2015.

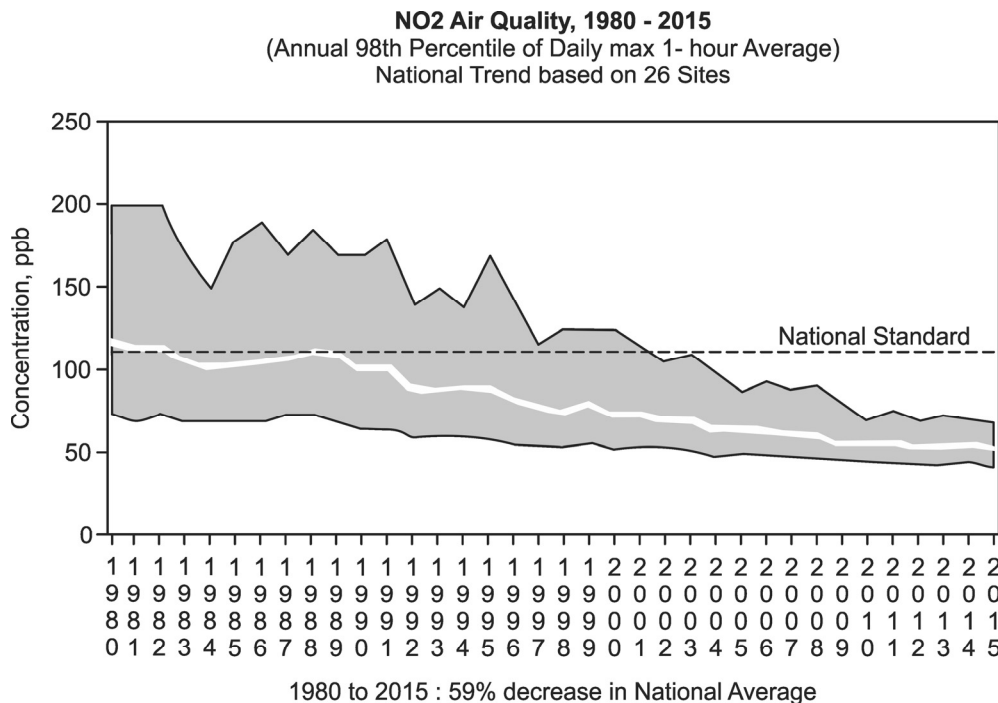
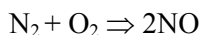


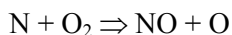
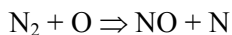
Fig. 1.29 Trends in nitrogen oxide emissions in USA, 1980-2015

1.3.4.3 Nitric oxide

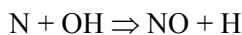
Nitric oxide is colourless, but it is photo chemically converted to NO₂, which is one of the major NO_x. NO is mainly formed by the combination of atmospheric N₂ and O₂ at high temperatures with a lesser contribution from N-containing components of fuels.



The above reaction is often quoted as the major process, but actually it takes place in separate reactions (see below) involving highly reactive atoms created within a flame – the second being much faster than the first.



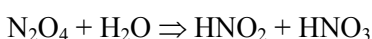
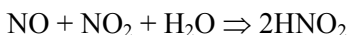
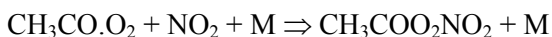
In the fuel-rich regions of a flame, highly reactive hydroxyl (OH*) radicals form NO but HCN, NH₃, or amines have also been identified as precursors of NO.



Odd as it may first appear, the amount of NO produced decreases as the N content of the fuel rises. By contrast, removal of S from fuels increases the amount of NO produced. Therefore, burning of heavy oil, which usually has a low N content, leads to NO emissions as great as those from power plants using coal with much higher N content.

1.3.4.4 Nitrous acid

Nitrous acid forms rapidly in the gas phase by reactions between NO, NO₂ and H₂O but decomposes to NO and nitric acid in aqueous solution by a series of inter conversions.

**1.3.4.5 Nitrous oxide**

The most abundant nitrogen oxide in the atmosphere is N₂O. This is mainly released by denitrification which is an undesirable agricultural process carried out by certain soil microbes using nitrate instead of O₂ to respire. Soil conditions where O₂ levels are low favour denitrification. Consequently, stagnant, waterlogged or compacted soils are major sources of N₂O, and one of the main purposes of ploughing and draining is to discourage this anaerobic process.

Global production of N₂O by denitrification each year amounts to about 5% of the total global pool of atmospheric N₂O but, because N₂O is a relatively unreactive molecule, it has a long residence time of 20 years or more in the atmosphere. Any subsequent atmospheric increase in N₂O levels due to enhanced denitrification will therefore develop slowly but persist for a long time.

The composition of nitrogen oxides in the atmosphere is therefore very complex. A multitude of different reactions are influenced to a greater or lesser extent by temperature, light flux, and different levels of dilution because all these molecules, atoms or radicals have to collide to react. The chances of this are reduced as pressure falls with increasing altitude but, as molecules rise upwards, some of the intervening collisions with unreactive molecules are reduced and radiation levels increase. Consequently, half-lives of reacting species vary with altitude and some intermediates, which exist for very short periods at ground level, persist for longer in the stratosphere. On the other hand, those species which are relatively inert at ground level have a chance to be slowly transported upwards into the stratosphere where they subsequently react. N₂O is a good example of this possibility.

1.3.4.6 Removal mechanisms of nitrogen oxides

Apart from photolytic breakdown (Fig. 1.30), a number of reactions of alternative phenomena like dry and wet deposition (Fig. 1.31) may remove NO_x.

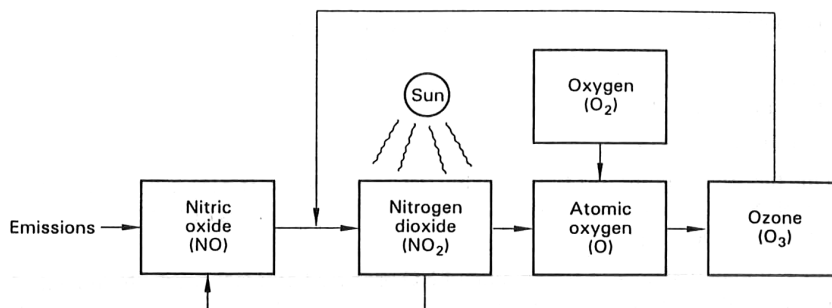


Fig. 1.30 Simplified atmospheric nitrogen photolytic cycle

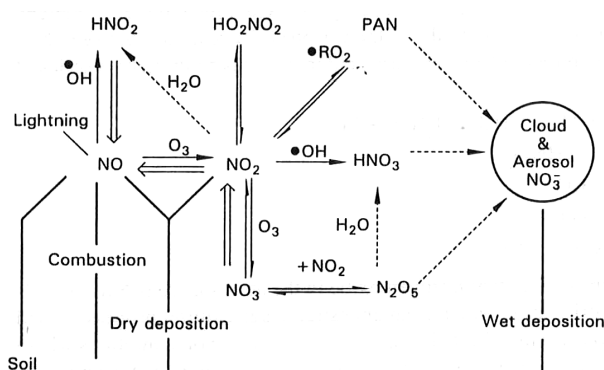


Fig. 1.31 Atmospheric interconversions of oxides of nitrogen

(Source: Dis Con and Penkett, AERE, Harewell, UK, and D. Reidel Publ. Co. Dordrecht, The Netherlands.)

1.3.4.7 Dry deposition

All oxides of nitrogen are removed from the atmosphere by absorption at ground level by land or ocean surfaces. The velocity of deposition of each atmospheric gas differs widely and depends upon the nature of the uptake surfaces. Rates for chemical species like nitric acid are very high because they are so reactive, while the deposition velocity of NO_2 is lower than that of SO_2 or O_3 but much higher than that of NO or N_2O . Estimates of global wet and dry deposition rates of both nitrate and nitric acid amount to about 25 million tons per annum, while dry deposition of NO_2 accounts for an additional third of this amount.

Measurements of deposition rates are complicated because the gases may interact in many different ways. For example, undissolved nitric acid forms ammonium nitrate aerosol – a salt which has a high a dissociation constant so that significant equilibrium levels of both NH_3 and nitric acid are present. The relative deposition rates of different nitrogen-containing compounds are as follows:



1.3.4.8 Effects of nitrogen oxides on plants

Plant growth may be inhibited by continuous exposure to 0.5 ppm of NO_x . Levels of NO_x in excess of 2.5 ppm for periods of four hours or more are required to produce necrosis (surface spotting due to plasmolysis or loss of protoplasm).

Higher concentrations of NO_x affect the leaves of plants, retard the photosynthetic activity and cause chlorosis. NO_2 is highly injurious to plants. Vegetative growth is suppressed when plants are exposed to 0.3-0.5 ppm of NO_2 for 10 to 15 days. Exposure to 10 ppm of NO_2 checks the metabolic activities in plant tissues, e.g. bean and tomato plants, on fumigation showed decreased activity of CO_2 absorption and photosynthetic rate.

Generally, the movement of nitrogen oxides into leaves is subject to similar diffusive resistances as found for SO_2 but the stomata are not the only path of entry for nitrogen oxides. Cuticular resistance against NO_x entry is lower than that for SO_2 or O_3 . This means that, even when stomata are closed, some oxides of nitrogen possibly enter the leaf through the epidermal layers even though this is a small fraction of the whole.

Inside a leaf, the exposed surface area of the moist cell wall below is considerably larger than the external surface area of a leaf and this provides a large surface area for the absorption of nitrogen oxides. The solubility of nitrogen oxides in the extra cellular fluid is therefore an important factor in determining their rate of uptake. Both gaseous NO_2 and NO are only slightly soluble in H_2O , but NO_2 vastly increases its apparent solubility by reacting with H_2O to produce nitric acid. Gaseous NO , however, does undergo a comparatively slow reaction with H_2O to form both nitric acid and nitrous acid. Normally, nitrous acid is oxidized in solution to nitric acid by O_3 , H_2O_2 and other oxidizing agents, but it may be converted back to NO when reducing agents like ferrous iron are present.

1.3.4.9 Effects of nitrogen oxides on human health

NO is biochemically inert and not extremely toxic. The health effects vary with the degree of exposure. NO_2 has irritating effects on the mucous membrane. An exposure to 50 to 100 ppm of NO_2 for 30 to 50 minutes for a period of 5 to 8 weeks causes inflammation of lung tissues. NO_2 poisoning results in Silo filler's disease when the NO_2 is produced by the fermentation of ensilage containing nitrates. The threshold limit value for NO_2 is 5 ppm (Table 1.18). Breathing it for 30 min to 1 h could affect lung tissues, while breathing it for 30 minutes to 1 h at 100 ppm-150 ppm could produce serious pulmonary edema, or swelling of lung tissues. A few breaths at 200 ppm-700 ppm may cause fatal pulmonary edema.

Table 1.18 *Likely effects of nitrogen dioxide upon humans*

Pollutant range, ppm	Symptoms
0-0.21	No effects
0.11-0.21	Slight odour detected
0.22-1.1	Some metabolic effects associated with either toxicity, adaptation or repair of lung tissues (e.g. inhibited metabolism of prostaglandin E ₂)
1.1-2	Significant changes to respiratory rate and lung volume. Enhanced susceptibility to infection and evidence of tissue repair
2.1-5.3	Deterioration of lung tissue not balanced by repair mechanisms
Above 5.3	Gross distortion of lung tissues and emphysema, possible death if prolonged

The WHO has recommended a value of 0.23 ppm of NO₂, not to be exceeded for a period of 1 h. Over a period of 24 h, this should be reduced below 0.08 ppm to safeguard human health.

The lack of immediate warning symptoms from oxides of nitrogen means that exposure symptoms such as coughing, headaches and chest tightness develop a day later. If particularly severe, they are followed by either sudden circulatory collapse or congestion and water accumulation in the lungs a short while after this. Treatment with rest, oxygen, steroids and antibiotics is often recommended. However, once initial recovery is made, affected individuals are always likely to have a subsequent history of chronic chest complaints.

Damage is not just confined to the lungs. NO causes the of red blood cells (RBC) to form a type of methaemoglobin. In addition, excess blood nitrate may reduce blood pressure. The destruction of RBCs will be enhanced, inducing liver and kidney defects as increased efforts are made by the body to eliminate the products of blood break down through the bile duct or urine. The deterioration of the liver and kidneys then often gives rise to jaundice and other related conditions. Unfortunately, in workers who do not experience sudden massive doses but have steady inhalations over a period of time, the chronic illness they later suffer is often unrecognized and not directly linked with their occupation.

Penetration and retention of NO₂ depends on many factors. In tissue fluids, for example, reactivity of NO₂, its dilution in inspired air, the length of exposure, and the depth and frequency of breathing are all important. As NO₂ is soluble, it readily enters tissue fluids much as it enters the extracellular fluid of plants. By the same measure, NO has the potential to enter with rather more difficulty as a mixture of nitrate, nitrite and undissociated nitrous acid. Consequently, the airways passing through the nasal regions, the terminal bronchioles of the lungs, and finally, the alveoli all have their surfaces exposed to the products of nitrogen oxides in solution.

During light breathing, about 40% of the oxides of nitrogen are taken up in the nose and throat regions but, as when the body is exercised and deeper breathing takes place through the mouth, this balance shifts towards the lung tissues which then become the most important uptake surfaces. At low concentrations of NO_2 , the most sensitive areas are the junctions between the bronchioles and the alveolar regions. With higher concentrations, the injury extends to the larger airways and into deeper tissues.

Other changes due to exposure to oxides of nitrogen include accumulation of tissue fluid and cellular debris or mucus. There is also a clumping of certain white blood cells which normally accumulate as one of the first lines of defence against infection. Animal lungs have a remarkable ability to rid themselves of inhaled microbes, some of which are pathogenic, and this is essential to keep the alveoli sterile. Low concentrations of NO_2 , however, disturb these natural defences of the lungs and cause them to become more susceptible to bacterial attack.

1.3.4.10 Risk from NO_2 indoors

The levels of indoor NO_2 range from 20 to 250 ppb with at least as much NO. These levels of NO_2 are around one-eighth of the industrial Threshold Limit Value (TLV) but are experienced for a duration longer than an industrial working day by those who do not venture out frequently – young children, pregnant mothers, and the old are at a greater risk medically.

Smoking adds to indoor pollution. Cigarette smoke contains oxides of nitrogen, especially NO, as well as a multitude of other potential irritants.

The levels of NO_2 in the home during the winter can be considerable, especially in kitchens and living rooms. Table 1.19 shows the concentrations of NO_2 detected in different rooms of domestic homes.

Table 1.19 Range of NO_2 concentrations detected in different rooms of domestic homes

Concentration, ppb	Bedrooms (%)	Kitchens (%)	Living rooms (%)
0-21	48	11	40
22-42	33.5	29	49
43-63	13.5	19	18
64-84	2.5	13	5
85-105	2	10	2
106-126	0	7	1
127-147	0.5	3	1
148-168	0	1	1
> 168	0	5	0

1.3.4.11 Effects of nitrogen oxides on materials

NO_x affects a number of materials like cotton, rayon, acetate and viscose rayon. It was found that NO_x levels reaches 1 to 2 ppm, during the combustion of natural gas which is used to heat dryers. Higher concentrations of particulate nitrates in airborne dust accumulate adjacent to cracked areas of metals like nickel and brass.

1.3.5 Carbon monoxide

Carbon monoxide is the most abundant gaseous pollutant emitted through anthropogenic sources into the troposphere – 0.075 Gt per annum which is a very high rate when compared to other gaseous pollutants and this rate is still rising.

Carbon monoxide is a colourless, odourless, tasteless gas which is present in small concentrations (0.1 ppm) in the natural atmosphere and has a residence time of about six months. CO is produced markedly when carbonaceous fuels are burned under less than ideal conditions. Incomplete combustion, yielding CO instead of CO₂, results when any of the following four variables are not kept sufficiently high:

1. oxygen supply
2. flame temperature
3. gas residence time at high temperature, and
4. combustion chamber turbulence.

1.3.5.1 Sources of emission of carbon monoxide

Carbon monoxide in urban areas is produced mainly by automobiles, burning coal, oil, etc. (Table 1.20). About 70% of CO emission is from the transportation sector, with almost all of that coming from motor vehicles, Personal exposure to CO is very much determined by the proximity of heavy motor vehicular traffic.

Table 1.20 *Main sources of CO emission*

Contributor	CO emission (%)
Automobiles	
Transportation	64
Motor vehicles	59.5
Aircraft	2.5
Railroads	0.1
Industrial processes	
Iron, steel, paper and petroleum industries, etc.	9.6
Miscellaneous sources	
Forest fires	6.9
Agricultural burning (forest debris, crop residues, brush and weeds, etc.)	8.3

Carbon monoxide pollution is of basic concern in most large cities of the world, where traffic is usually congested and heavy. In New York City alone, automobile traffic produces 3.76×10^6 kg of CO daily; and in Los Angeles, the estimate is 9 million kg per day. A car emits about 11.69 mg of CO/km at 25 kmph and about 96 mg of CO/km at 10 kmph. The trends in CO emissions of USA between 1980 and 2015 are shown in Fig. 1.32.

Biogenic processes, by contrast, produce a tenth of the CO produced by human activities. Half of this comes from the oceans and the other half from a variety of natural processes such as volcanoes, electrical storms, and 'marsh gas' from rotting vegetation, etc.

1.3.5.2 US-National trends in CO levels

Using a nationwide network of monitoring sites, EPA has developed ambient air quality trends for carbon monoxide (CO). Under the Clean Air Act, EPA sets and reviews national air quality standards for CO. Air quality monitors measure concentrations of CO throughout the country. EPA, state, tribal and local agencies use that data to ensure that CO remains at levels that protect public health and the environment. Nationally, average CO concentrations have decreased substantially over the years.

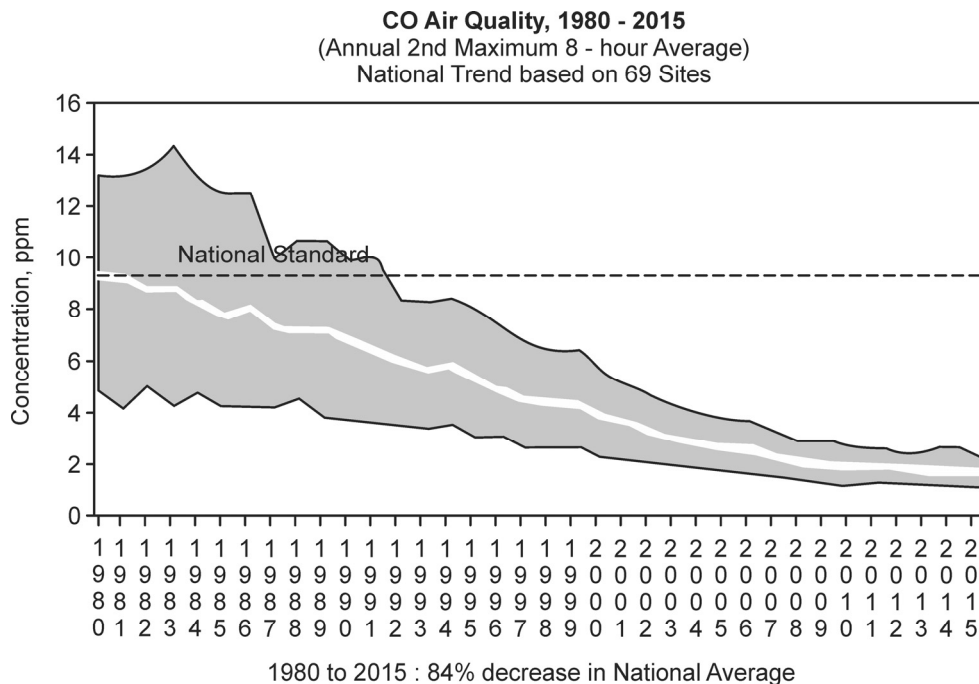
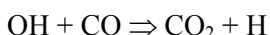


Fig. 1.32 Trends in carbon monoxide emission in USA. 1980-2015
(Source: National ambient air pollutant emission estimates. USEPA.)

1.3.5.3 Removal mechanisms of carbon monoxide

Over land areas and away from major sources, atmospheric levels of CO are relatively constant which means that natural sinks exist for the removal of excess CO. Various removal mechanisms include oxidation of CO to CO₂ in the troposphere by OH radicals, oxidation in the stratosphere, or absorption by soil microbes or plants.

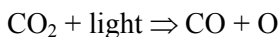
CO is produced by incomplete combustion and adds to global warming because it is rapidly oxidized to CO₂ as in the reaction below.



Removal of CO, therefore, depends on the presence of sufficient OH radicals which, in turn, requires atomic O and H₂O. Consequently, sunny but wet atmospheric conditions are most favourable for OH production and CO removal. Overcast and cold but dry winter days are far from ideal. Any CO that rises above the troposphere into the stratosphere is oxidized to CO₂ by atomic O or O₃.

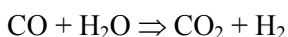


But this is counter balanced by photolysis of CO₂ back to CO.

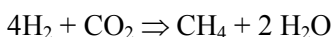
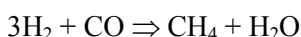


The oceans are a major sink for CO₂ but not for CO. A function of partial pressure, the solubility of CO in sea water is much less than that of CO₂ or SO₂. However, the surface waters of oceans contain many times the theoretical CO concentrations that would be expected from gaseous uptake from the atmosphere. In other words, marine biological activity contributes substantial quantities of CO to surface waters and transfers more CO into the atmosphere.

Soils have a variety of soil microbes which oxidize CO to CO₂ or reduce it to CH₄. For example, an anaerobic CH₄ producer like *Methanobacterium for micum* generates H₂:



This H₂ then reduces CO or CO₂.



Generally, different soils remove CO at different rates but cultivated soils are much less efficient in doing this than natural soils high in organic matter. Agricultural processes, therefore, select against those microbes most efficient at CO removal. Consequently, the health of non-cultivated soils is vital, not just for protection against acid deposition, but also to reduce CO levels.

Some global estimates of the total potential capacity for soil microbial uptake of CO have been put as high as 14 Gt per annum, well in excess of what is discharged by human activities. By contrast, other calculations have estimated global rates of removal to be 0.45 Gt per annum, much lower than the annual rate of production. Various assumptions account for these discrepancies. Soil microbial uptake has been established as the major

global mechanism for CO removal, but this is a slow temperature-dependent process which explains the rhythmical seasonal changes in levels of global atmospheric CO. As northern forest soils warm in summer they supplement the steady uptake of CO by tropical forest soils. Furthermore, as more tropical and temperate areas are brought into cultivation, the cyclical seasonal changes in global CO concentrations become more pronounced. Should northern forest soils also suffer damage by other types of pollution then overall levels of CO and, thereby, CO₂ will rise and enhance global warming.

1.3.5.4 CO Plant uptake

Oxidation of CO to CO₂ by certain crops has been detected using ¹⁴CO. However, if respiration is artificially inhibited with dinitrophenol, then this process is much reduced. The implication of this is that the major oxidation of CO by plants is linked to the cytochrome oxidase activity of mitochondria. Some trees, however, do not take up CO at all while green algae have their nitrogen metabolism inhibited by CO. Some seaweeds are even capable of emitting CO. Consequently, any judgment on the relative significance of vegetation to remove CO is difficult to make. Current estimates indicate global uptake of CO by vegetation to be 25% of that of soils.

1.3.5.5 Effects of carbon monoxide

CO is a colourless, odourless gas which is lethal to humans within a few minutes at concentrations exceeding 1,000 ppm (Table 1.21). All the gaseous pollutants of carbon mainly cause severe damage to the respiratory system. But CO affects the human body in a unique manner. It affects human health by forming carboxyhaemoglobin, which restricts transport of oxygen from lungs to cells.

Table 1.21 *Effects of CO on humans and the accompanying carboxyhaemoglobin blood concentrations*

Exposure ^a ($\mu\text{l l}^{-1}$)	Effects and symptoms	COHb/Hb ^b (%)
0-10	No discomfort or effect	0-2
10-50	Some tiredness, impaired vigilance and reduction in manual dexterity	2-10
50-100	Slight headache, tiredness and irritability	10-20
100-200	Mild headache	20-30
200-400	Severe headache, visual impairment, nausea, general weakness and vomiting	30-40
400-600	As above, but with greater possibility of collapse	40-50
600-800	Fainting, increased pulse rate and convulsions	50-60
800-1600	Coma, weak pulse and possibility of death	60-70
1600 +	Death within a short period	70+

(Source: American Industrial Hygiene Association Air Pollution Manual, 1960.)

- (a) After 2 h exposure. (b) Likely percentage of carboxyhaemoglobin (COHb) to total haemoglobin (Hb) content of blood sometime afterwards in a resting individual but which may be achieved three times faster during heavy work.

1.3.5.5.1 Blood biochemistry and pollution

Haemoglobin, the red pigment of RBCs, consists of the protein globin and a *tetrapyrrole* ring system called haem which contains ferrous iron. If this iron is oxidized to the ferric form, the haemoglobin turns into methaemoglobin which is unable to bind O₂. Oxidation of haemoglobin to methaemoglobin occurs naturally as RBCs age and is accelerated by the additional presence of H₂O₂. Normally, free radical scavenging ensures that this does not occur prematurely but free radical generation by other pollutants such as O₃ or PAN promotes early formation of methaemoglobin. Ultimately, these older RBCs high in methaemoglobin are broken up by certain white blood cells while they pass through the spleen.

During normal respiration, O₂ combines with haemoglobin to form oxyhaemoglobin, an association-dissociation reaction which is dependent upon the partial pressure of O₂, the temperature and pH. Changes of blood acidity are largely due to alteration in blood levels of dissolved CO₂ and the equilibrium between the different forms of CO₂.



The enzyme carbonic anhydrase brings about a faster interconversion between dissolved CO₂ and carbonic acid while H⁺ ions from the dissociation of carbonic acid cause the dissociation of oxyhaemoglobin.

Lactate, which is produced by contracting muscles working at low O₂ levels, also produces acidity which then causes more O₂ to be released from oxyhaemoglobin to alleviate the local shortage. The final factor that encourages the release of O₂ from haemoglobin is 2, 3-diphospho-glycerate. This substance combines reversibly with haemoglobin to change its structure in favour of O₂ release. Consequently, 2, 3 diphospho-glycerate is released by tissues which are especially short of O₂ to ensure that O₂ is delivered to those cells most in need.

About 7% of CO₂ produced by body tissues is dissolved in the blood plasma and carried to the lungs as a dissolved gas. The bulk is transported as bicarbonate and the remainder reacts with haemoglobin to form carbaminohaemoglobin. At the high partial pressures of CO₂ in the tissue capillaries, the formation of this complex is encouraged, but in the lungs where partial pressures of CO₂ are low it splits apart again.

CO combines with haemoglobin with an affinity which is between 200 and 300 times greater than the affinity of haemoglobin for O₂. The resultant carboxyhaemoglobin is extremely stable. CO at very low concentrations in the blood will combine with over half of the haemoglobin and immediately reduce the O₂-carrying capacity by a similar proportion. Only high O₂ partial pressures such as those achieved when treating CO poisoning cases with pure O₂ can reverse the combination of haemoglobin with CO. Other O₂-releasing mechanisms may also be affected adversely by CO. For example, levels of 2, 3-diphospho-glycerate in plasma circulating through O₂-deficient tissues are lower in the presence of CO.

With the bloodstream carrying less oxygen, brain functions are affected and the heart rate increases in an attempt to offset the oxygen deficit.

The amount of carboxyhaemoglobin in the blood is normally expressed as a percentage of the saturation level, % CO Hb. Three factors: the CO concentration, the length of time exposed, and the breathing rate control the extent of CO Hb formation in blood.

They are related by the following equation

$$\% \text{ COHb} = 0.005 [\text{CO}]^{0.85} (\alpha t)^{0.63} \quad \dots(1.15)$$

where % COHb = carboxyhaemoglobin as a percentage of saturation

[CO] = carbon monoxide concentration in ppm

α = a physical activity level coefficient

t = exposure time in minutes.

For low activity, $\alpha = 1$, while for heavy work, a factor of 3 is sometimes used. Equation 1.15 breaks down for large values of time, corresponding to the bloodstream reaching saturation.

Problem 1.5

CPCB standard for CO: Calculate the % COHb expected to form for a 1 h exposure to 40 ppm (the CPCB standard) for low activities, and for heavy work.

Solution: From Equation 1.15, for low activities with $\alpha = 1$

$$\% \text{ COHb} = 0.005 \times (40)^{0.85} \times (60)^{0.63} = 1.52$$

Assuming $\alpha = 3$ for heavy activity

$$\% \text{ CO Hb} = 0.005 \times (40)^{0.85} \times (3 \times 60)^{0.63} = 4.56$$

At small percentages of COHb, certain physiological effects can be observed whose severity increases with increasing concentration. Heart patients will be the worst sufferers since to offset the reduction in oxygen, the heart has to work under more stress.

The brain functions to perceive and react will also be greatly affected by the reduction of oxygen in the bloodstream. Impairment in time-interval discrimination was observed at 2.5% COHb while at 5%, psychomotor response times were affected. Patients with heart disease experienced increased physiological stress. Many people will experience dizziness and headache at 10% COHb while concentrations above 50% can be lethal.

In urban areas CO levels vary from 5 to 50 ppm; it is estimated that in congested highways drivers may be exposed to CO concentrations upto 100 ppm. Cigarette smoke contains more than 400 ppm CO. Smokers frequently have COHb levels between 5 to 10%. Further cigarette smoke in bars and restaurants often raises indoor CO levels to 20-30 ppm, which is close to the 1 h ambient standard [4].

It can be seen from Fig. 1.33 which depicts the relative accumulation of COHb with different exposure times of CO that within 3–4 h COHb reaches 50% of its saturation value. CO will be removed from the bloodstream when clean air is breathed and about half of the CO from the blood will be removed in the breathing process within 3–4 h. So the physiological effects caused by CO exposure will be temporary.

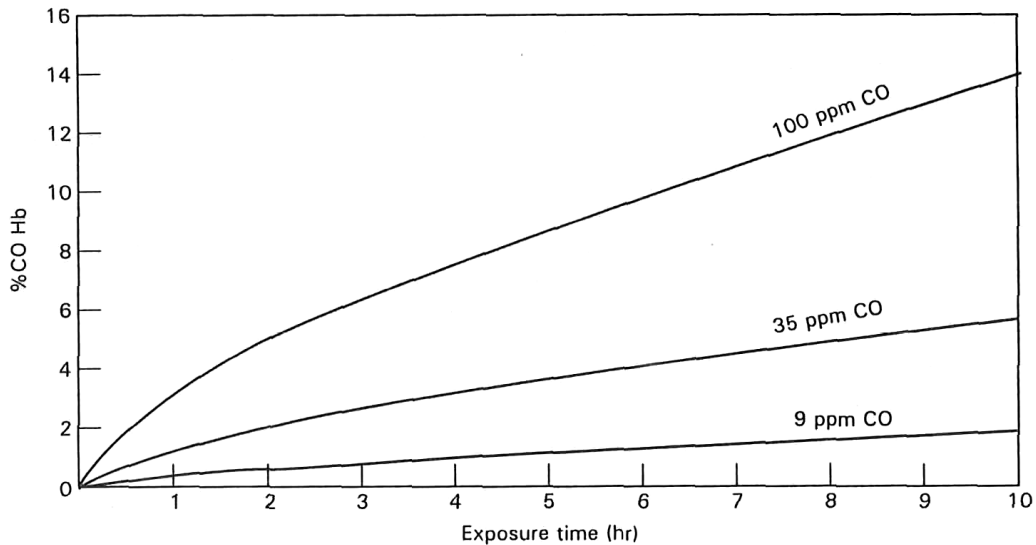


Fig. 1.33 Percent CO Hb plotted for different exposure times with varying concentrations of CO

Exposure of humans to CO may cause a variety of clinical effects (Table 1.21). Generally the onset of responses is hastened by heat, humidity and exertion. At work, it is the younger rather than the older workers who are more susceptible to CO, but alcoholism, obesity, old age, heart conditions, and lung diseases all exacerbate the problem. However, some physiological compensation or conditioning occurs with repeated exposures in steelworkers and smokers.

As COHb levels or duration of exposure increase, health effects become more serious

COHb level, percent	Demonstrated effects
Less than 1.0	No apparent effect
1.0 to 2.0	Some evidence of effect on behavioural performance
2.0 to 5.0	Central nervous system effects impairment of time interval discrimination, visual acuity, brightness discrimination and certain other psychomotor functions
Greater than 5.0	Cardiac and pulmonary functional changes
10.0 to 80.0	Headaches, fatigue, drowsiness, coma, respiratory failure, death

There are clinical differences between O₂ deprivation and CO poisoning. In the former, respiratory symptoms precede nervous symptoms, but in the latter this order is reversed. This has led to the suggestion that the driving out of O₂ from RBCs is not the only physiological effect of CO.

The progressive symptoms listed in Table 1.21 approach without warning because CO is non-irritating and odourless. Only the presence of other contaminants such as hydrocarbons, mercaptans, ammonia or traces of other materials gives an advance warning of any hazard within fumes. It was a long time before CO poisoning became universally accepted as a specific disease in the industrial and urban environments because many of the early symptoms caused by CO are also associated with repetitive work or stressful situations. It is now recognized that misjudgments due to enhanced blood CO levels lead to more accidents at work, on the road, and in the home.

Unfortunately, the affinity of CO for human fetal haemoglobin is higher than that for normal haemoglobin. This means that unborn babies in the womb are especially sensitive to CO poisoning. Undoubtedly, the single most important factor which exposes an unborn child to greater than average CO concentrations is smoking by the mother. The relationship between maternal smoking and low birth weight is undeniable. Most of the number of developmental and clinical defects in the newborn ascribed to deprivation of O₂ are mostly neurological. However, as with adults, it is still not possible to distinguish in these babies the direct effects of CO caused by O₂ deprivation from those caused by other factors in tobacco smoke.

Related to CO poisoning is the disease Shinshu myocardiosis. This occurs in those exposed to high levels of CO over long periods and is typified by defective heart valves as well as by angina pectoris and arteriosclerosis. It was first detected in 1955 in the village of Kinasa, Japan where, during cold winters, it had been the custom for silk production to continue in tightly sealed, heated rooms. As a result, many of the workers experienced severe circulatory problems due to CO poisoning.

The effects of carboxyhaemoglobin levels and duration of exposure on human health are shown in Fig. 1.34. Carbon monoxide concentrations of 50-100 ppm are commonly encountered in the atmosphere of crowded cities, especially at heavy traffic rush hours. For example, in parts of New York city, the 8 AM and 4 PM concentrations of CO are respectively 86 and 76 ppm. In tunnels, CO concentrations may exceed 100 ppm. Such concentrations adversely affect people's ability to drive and can cause accidents.

The WHO recommends that levels of CO be reduced so that the level of carboxyhaemoglobin in the blood of the general population does not exceed 3%. This means that exposures should not exceed 50 ppm over 30 minutes, 25 ppm over 1 h, and 10 ppm over 8-24 h.

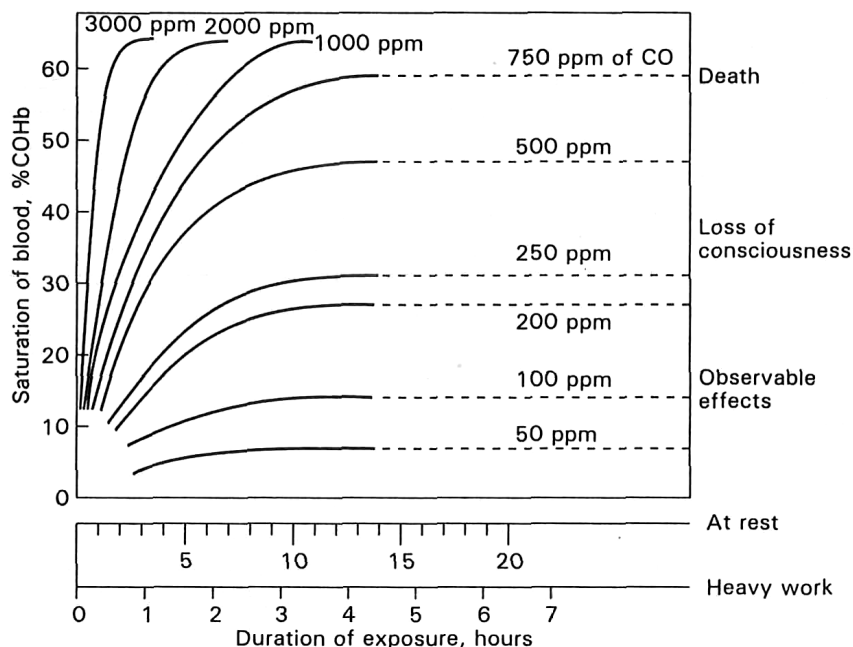
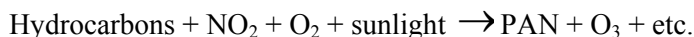


Fig. 1.34 COHb levels in the blood depend upon the amount of CO in the atmosphere, duration of exposure, and type of physical activity

1.3.6 Hydrocarbons

As their name indicates, the components of hydrocarbons are hydrogen and carbon; hydrocarbons constitute the major chemicals in petrol and other petroleum products. They are a nuisance and a health hazard, mainly because of their photochemical reactions. In the presence of sunlight, nitrogen dioxide reacts with hydrocarbons to give a series of extremely complex reactions; chief among the products of these reactions are peroxyacetyl nitrate (PAN) and ozone:



Historically, the hydrocarbons have been regarded as important to human health only through their role in the formation of photochemical oxidants. With the exception of the aromatics, hydrocarbons have been considered toxicologically inert. In the 1980s, the USEPA began a major effort to identify and regulate toxic organic compounds that fall into the hydrocarbon category. Many of the polynuclear aromatic hydrocarbons (PAHs) have been recognized as carcinogens for many years. Other air toxics, including pesticides, polychlorinated biphenyls (PCBs), and dioxins, have also been identified.

1.3.6.1 Sources of emission of hydrocarbons

The various sources and their contribution to the emission of global hydrocarbons are given in Table 1.22. Natural sources, particularly trees emit huge quantities of hydrocarbons into the air. Plants, mostly emitting terpenes belong to the families *Coniferae* and *Mystaceae* and the genus *Uterus*. Automobile exhausts emit the maximum amount of hydrocarbons into the atmosphere. Some industrial sources, especially refineries, emit hydrocarbons, but the major source of this type of pollution is automotive emissions. The emissions from incomplete combustion in car engines, along with evaporative emissions from fuel tanks, carburettors, and crank cases, amount to approximately 12 million tons per year. Human activities contribute nearly 20% of the hydrocarbons emitted to the atmosphere every year; animals contribute about 80-85million tones of methane to the atmosphere every year.

Table 1.22 Global emissions of hydrocarbons

Source	Emission (%)
Petroleum	55.05
Gasoline	38.5
Refining	7.2
Oil	0.4
Evaporation of solvents in storage	8.8
Coal	3.3
Wood (fuel and forest fire)	2.2
Industrial uses	0.8
Organic solvent evaporation	11.3
Incinerators and refuse burning	28.3
Power generation	0.2

Among the various hydrocarbons involved in air pollution, 565 have been clearly identified by gas chromatography. The emission trends of the volatile organics in a typical highly industrialized country like USA with a massive transportation network is shown in Fig. 1.35. It indicates declining trends after the implementation of the clean air regulations of 1990 in USA. From different source categories.

1.3.6.2 Effects of hydrocarbons on plants

Exposure to hydrocarbons and photochemical oxidants is injurious to plants and causes chlorosis. Ozone enhances plant injury creating light flecks or stipples on the upper leaf surface inhibiting photosynthetic activity of leaves. Ethylene even at 1 ppm concentration shows adverse effects on vegetation. Acetylene and propylene at 50-500 ppm show extreme toxicity towards plants, damaging growth of vegetation.

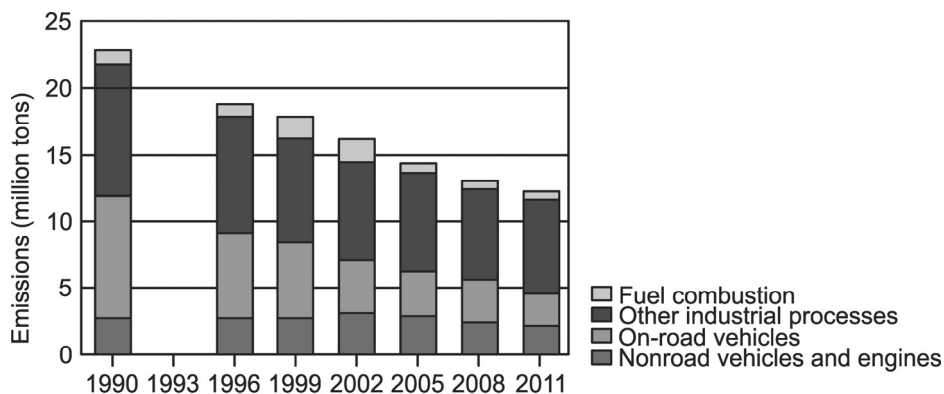


Fig. 1.35 Trends in volatile organic compound emissions in USA, 1990-2011 by Source Category (USEPA)

1.3.6.3 Effects of hydrocarbons on human health

Hydrocarbons at high concentrations (500-1000 ppm) have carcinogenic effects on lungs. They mainly cause swelling when they enter the lungs. Aromatic hydrocarbons like benzene, toluene etc., are more dangerous than acyclic and alicyclic hydrocarbons. The inhalation of their vapours irritates the mucous membrane.

Secondary pollutants (PAN) produced by hydrocarbons and NO_x result in the formation of photochemical smog which causes irritation of eyes, nose, throat and respiratory distress. Excess of hydrocarbons increases mucous secretion as a result of which the respiratory tracts are blocked causing coughs. Continuous cough causes pressure in the trachea of the lungs due to which the lining membrane of alveoli bursts.

1.3.6.4 Carcinogens

Carcinogens such as polycyclic hydrocarbons are present in the exhaust emissions of internal combustion engines, diesel or petrol. The two major carcinogens are benzopyrene, which is a strong cancer-inducing agent, and benzanthracene, which is a weak one. They are essentially non-volatile organic compounds associated with solids or polymeric substances in the air. Benzopyrene is present in trace amounts into bacco, charcoal, boiled stacks and gasoline exhausts, etc.

These compounds are not very stable, and they are destroyed at varying rates by other air pollutants and by sunlight. However, as a result of industrialization and urbanization, these substances are discharged into the atmosphere in significant quantities, causing a steady increase in the frequency of human lung cancer in the world. The concentrations of carcinogens in the New York air which has a large transport network are given in Table 1.23.

Table 1.23 Concentrations of carcinogens in New York air

Location	Benzopyrene Annual Avg.	$\mu\text{g}/1000 \text{ m}^3$ Max.	Benanthracene Annual Avg.	$\mu\text{g}/1000$ m^3 Max.
Herald square	3.9	9.4	5.6	16.0
Scarsdale, Westchester Country (suburb)	0.3	0.6	0.6	1.2

Source: *Air pollutants and their effects on human health animal and plants.*

Esber. I. Shaheen Tech. of Air. Poll. Control, Pennwell Books, 1992 .

1.3.6.5 Effects of hydrocarbons on materials

Hydrocarbon pollutants damage long chains of carbon atoms causing loss of tensile strength of polymers. Ozone forms new carbon chain links between parallel carbon chains so that the material becomes less elastic and more brittle.

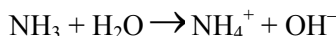
1.3.7 Ammonia

Ammonia (NH_3), which is a pungent gas, is used as a raw material in large quantities by industries for the synthesis of ammonium nitrate, plastics, explosives, dyes and drugs. It is also used as a refrigerant.

1.3.7.1 Sources of emission of ammonia

Emission of NH_3 into the atmosphere from the biological degradation of proteins on soil surfaces occurs on a very large scale. This is known as 'NH₃ volatilisation' and compared to this, the industrial contribution is negligible. Atmospheric concentrations of NH_3 in temperate rural regions range from 5 to 10 ppm but are much higher near the equator. In urban regions, higher levels of NH_3 upto 280 ppm are recorded and it may be found in increasing levels close to industrial and intensive agricultural sources. In some developed countries, atmospheric levels of NH_3 are still rising with the accelerated use of artificial fertilizers and higher stocking rates of farm animals.

NH_3 readily forms cations or complexes of varying stability which affects the rate of volatilisation. Most important is the affinity of NH_3 for H_2O that results in ammonium ions – this is strongly enhanced by increased alkalinity. This means that there is an increased likelihood of NH_3 volatilisation at high pH.



The variation of CO_2 levels or changes in temperature will have a marked influence on the NH_3 – NH_4^+ relationship as both ionization of H_2O and the dissociation of NH_3 are temperature dependent. Furthermore, the exchange of NH_3 between solution and the air above varies markedly with temperature.

In soils, NH_3 may be either adsorbed onto clay or organic particles and react with carbonyl and other acidic groups to form exchangeable salts, or it may combine with

other organic components to form non-exchangeable products. In view of this, different soils have different rates of NH_3 volatilisation and these, in turn, are affected by their water contents, as OH^- ions are removed in the process of conversion of NH_4^+ to NH_3 (the reaction $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$ in reverse). As NH_3 is volatilised from the soil surface to the atmosphere, the soil solution becomes acidified at rates which depend on the soil buffer capacity. In view of this, volatilisation of NH_3 is more likely from soils where the acidity produced can be neutralized by high levels of carbonate or other forms of alkalinity. This explains why larger emissions of NH_3 occur from natural calcareous soils or after liming.

The anions present in applied fertilizers also affect the rate of NH_3 volatilisation from soils. Urea is frequently used as an alternative fertilizer because the enzyme urease, which is widely distributed in plants, microbes and soils, catalyses the hydrolysis of urea to bicarbonate and NH_4^+ . As urease activity tends to be greater in soils with large organic contents and rather less in calcareous soils, the usual increase of NH_3 volatilisation from alkaline soils and decrease from acid soils is reversed when urea is used as a fertilizer.

NH_3 volatilisation also takes place at a higher rate from stored animal manures in stockyards or from sewage works. The factors involved are similar to those of applied slurries on fields. Periodic addition of fresh material to the tops of piles of manure or the agitation of sewage ponds, therefore, greatly accelerates rate of NH_3 volatilisation. Most NH_3 in the atmosphere arises from the direct hydrolysis of the urea in animal urine, other contributions being of less importance.

In Europe, as much as 10% of useful N is lost directly by NH_3 volatilisation and, in warmer climates, this can rise to as much as 30%. The amounts of N released into the atmosphere globally by NH_3 volatilisation are very large – between 115 and 245 million tons of nitrogen oxide. The background atmospheric levels of NH_3 over Belgium, Denmark, and the Netherlands, which are intensive arable and livestock-raising countries, are often around 25 ppm with peaks up to 75 ppm. The estimates of total N released into the atmosphere from these countries are especially high.

The large releases of NH_3 to the atmosphere over the last three decades are due to

- (a) increased animal stocking levels,
- (b) increased human population,
- (c) increased use of artificial fertilizers, in the form of either NH_4^+ nitrate or urea, and
- (d) decreased sinks for NH_3 or NH_4^+ uptake.

The first three go hand in hand. As material standards improve, humans move from plant-oriented to animal-based diets. This means more food has to be grown to feed animals and this can only be done by using more artificial fertilizers.

Much could be done to reduce N losses associated with the application of N fertilizers due to NH_3 volatilisation and run-off of excess nitrate into groundwater. Direct injection of anhydrous NH_3 or urea at the right depth into soil has not yet been extensively

exploited. Even substituting urea for NH_4^+ in irrigation waters will reduce losses due to NH_3 volatilisation to below 2% in poorer regions where N is unduly expensive, and losses by this route tend to be greater because of higher temperatures.

1.3.7.2 Removal mechanisms of ammonia

Once in the atmosphere, NH_3 neutralizes sulphuric or nitric acids and, by decreasing acidity, promotes the oxidation of SO_2 to sulphate by O_3 . Normally, atmospheric NH_3 has an average lifetime of 0.5 h before conversion to NH_4^+ . At wind speeds of 10 m s^{-1} , therefore, a molecule of NH_3 travels about 18 km before it turns into NH_4^+ .

Measurement of rates of NH_3 deposition are complicated because some intensively farmed lands give off more NH_3 than they receive. On the other hand, fluxes towards damp acidic ecosystems are considerable and cannot be accounted for by stomatal uptake alone as they form perfect sinks for NH_3 . For example, the uptake rate of wet heathland in the Netherlands may be as high as $100 \text{ kg N ha}^{-1} \text{ a}^{-1}$.

In most areas where atmospheric levels of NH_3 are high, elevated concentrations of SO_2 also occur. This leads to a phenomenon known as code position where fluxes are linked together. One explanation for this is that when NH_3 turns into NH_4^+ , then oxidation of SO_2 into sulphate is enhanced. Removal of SO_2 from the atmosphere as ammonium sulphate at the surface then ensures that the high rates of code position of SO_2 and NH_3 are maintained. Similar processes occur in aerosol particles which form clouds. The hygroscopic nature of NH_4^+ and sulphate causes these particles to attract more water vapour so that they increase in size and eventually fall as rain, etc. Indeed, wet deposition of NH_4^+ as ammonium sulphate in rainfall is the major removal pathway of NH_3 from the atmosphere.

1.3.7.3 Effects of ammonia on plants

Most plants are affected visibly by atmospheric NH_3 when there has been an industrial spillage and high local concentrations are achieved. Generally, no visible or invisible effects are detected on even the most sensitive species at levels of 70 ppb NH_3 or below. However, there are some claims that deposition of NH_3 and NH_4^+ on certain plants that prefer low levels of N induces leaching of potassium and magnesium which, over the long term, leads to mineral deficiencies.

At higher levels of NH_3 , little effect on photosynthesis is detected but long-term exposures visibly injure sensitive conifers such as yew, spruces, and cypresses. However, this injury is usually associated with reduced frost hardiness and increased susceptibility to fungal attack. Vegetable and horticultural crops are generally more resistant. Cauliflower and Brussels sprouts, however, may show characteristic black spots at levels of 0.7 ppm NH_3 for 10 days as well as reduced frost hardiness.

The ecosystems most sensitive to nitrogen-based atmospheric compounds are those which contain species of plants which are specially adapted to low levels of N and nutrients (Table 1.24). There is increased competition from faster-growing plant species which were previously restricted in these ecosystems because of the low availability of N.

Ultimately, this process leads to the disappearance of the original plant species characteristic of such ecosystems – a loss of irreplaceable genetic resources.

Table 1.24 *Ecosystems thought to be especially sensitive to excessive inputs of nitrogen*

Type	Details	
Wetlands	1.	Ombrotrophic mires i.e. bog-like areas only supplied with nutrients from rainfall, e.g. raised bogs
	2.	Mires in granitic areas or otherwise nitrogen-limited
Lakes	1.	Clear water lakes partially covered with certain species, e.g. water lobelia, quillwort, shore weed
	2.	Nutrient-lacking lakes with a high number of pond weeds
Others	1.	Heathlands with a high amount of lichen cover with limited mineral availability
	2.	Meadows with limited mineral availability used for extensive grazing and haymaking to which artificial fertilizers have never been added
	3.	High-altitude coniferous forests

Fears of too much N also reaching natural forest stands by similar processes have also been raised. Indeed, one possible explanation of recent forest decline suggests that too much N from the atmosphere encourages pathogens.

Vegetational changes due to excessive N input also exert changes upon animal populations. Fish are starved of O₂ because of competition with rapidly growing plants. Similarly, vigorous attacks of bark beetles occur in N-enriched forests.

1.3.7.4 Effects of ammonia on human health

Atmospheric NH₃ is not normally a hazard to health. Occasionally, industrial spillage releases large amounts of NH₃ which immediately reacts with the moist linings of the throat or the surface of the cornea to form ammonium hydroxide which then causes chemical burns. At much lower levels, the buffering of these layers is normally sufficient to absorb any NH₃ and very little penetrates into the lungs. Irritation of the eyes and throat occurs at levels of 350-700 ppm NH₃—well above ambient atmospheric levels. However, physiological changes have been detected at much lower levels. For example, at 16 ppm NH₃, levels of NH₄⁺ and urea in the bloodstream are increased. The TLVs vary from country to country. Most are around 25 ppm NH₃ for an 8 h day.

1.3.8 Organic lead

1.3.8.1 Sources of emission of organic lead

Lead is discharged into the atmosphere in the organic form as tetraethyl lead ((CH₃CH₂)₄Pb) or trimethyl lead ((CH₃)₃Pb) in unburnt or partially combusted fuel vapours. The amounts involved in developed countries were huge. In the late 1960s, for

1.3.8.3 Effects of lead on human health

Human intake of lead is mainly through food, especially from vegetables grown near busy roads. Plants take up very little lead from the soil because it is usually insoluble and tightly bound to soil particles. Most lead in plants enters through the stomata inorganic form. Once inside, some persists in organic form and the remainder is converted to inorganic lead. In certain circumstances, lead levels in lettuces, for example, approach 1 mg g⁻¹ which means that food intakes amounting to 300 mg of lead day⁻¹ may be achieved. Of this, less than one-tenth (15-30 mg day⁻¹) is taken into the bloodstream from the digestive system.

A much higher proportion of lead (30-50%) is likely to directly enter the bloodstream by breathing for people living or working near busy roads, where airborne lead levels might range from 1 to 5 ppb. People who breathe 20 m³ of air per day are likely to absorb 6-50 mg lead day⁻¹ from their lungs into the blood stream--as much again as they might take up from their diet. Consequently, the current TLV for total airborne lead set at 0.15 ppb is frequently exceeded and the direct uptake of airborne lead often matches the dietary intake, although more usually it is 20-30% of the diet in the bulk of the population not living immediately near busy roads.

In contrast to the other major pollutants, lead is a cumulative poison. Another difference is that it is ingested through food and water, in addition to being inhaled. Of the portion ingested through food, approximately 5-10% is absorbed by the body. About 20-50% of the inspired portion is absorbed. The unabsorbed portions are excreted in the faeces and urine. Lead is measured in the urine and blood for diagnostic evidence of lead poisoning. An early manifestation of acute lead poisoning is a mild anaemia. Fatigue, irritability, mild headache, and pallor is distinguishable from other causes of anaemia occur when the blood level of lead increases to 60-120 mg/100 g of whole blood. Blood levels in excess of 80 mg/100 g result in constipation and abdominal cramps. When an acute exposure results in blood levels of lead greater than 120 mg/100 g, acute brain damage (encephalopathy) may result. Such acute exposure results in convulsions, coma, cardiorespiratory arrest and death. Acute exposure may occur over a period of one to three weeks. Chronic exposure to lead may result in brain damage characterised by seizures, mental incompetence, and highly active, aggressive behavior. Weakness of extensor muscles of the hands and feet and eventual paralysis may also result. Atmospheric lead occurs as a particulate. The particle size range is 0.16-0.43 μ m.

Symptoms due to organic lead differ from those of inorganic lead. Most effects of tetraethyl and trimethyl lead are upon the nervous system. They first show as sleeplessness and general irritability but, following heavy exposures, they progress to emotional instability and hallucinations accompanied by impaired vision and hearing. More often, at low persistent levels, they cause headaches, general fatigue and sometimes depression.

Inorganic lead poisoning also starts with fatigue and irritability but it is often accompanied by anaemia and abdominal pain. The anaemia is mainly due to the fact that

one of the early enzymes of haem synthesis, d-amino-aevulinate dehydratase, is specifically inhibited by inorganic lead while RBCs show increased fragility and have shortened life spans. Chronic low level exposure of adults to inorganic lead may increase blood pressure and in children, disturb the metabolism of vitamin D which affects the growth of their long bones. Kidney disturbances are also associated with inorganic lead but the general slowing of nerve impulses occurs with both inorganic and organic forms of lead.

1.3.9 Hydrogen sulphide

The offensive smell of hydrogen sulphide (H₂S), well known as the odour of rotten eggs renders it a highly disturbing and objectionable pollutant.

1.3.9.1 Sources of emission of hydrogen sulphide

Hydrogen sulphide is emitted into the atmosphere by the degradation of industrial wastes in stagnant waters, swamps, and other areas where bacterial action reduces sulphur compounds to hydrogen sulphide, which is highly insoluble in water. It is estimated that decaying organic matter in the world emits 70 million tons of H₂S. Industrially, this gas comes from sewage treatment plants and the petroleum industry. The global emissions of sulphur by various activities are summarised in Table 1.25.

Table 1.25 Total global emissions of sulphur^a from both anthropogenic and natural sources

Component	10 ¹² mol y ⁻¹	Percent
Anthropogenic ^b	2.40	73.9
Biomass burning ^c	0.07	2.1
Biogenic Marine ^d	0.48	14.8
Terrestrial ^e	0.01	0.3
Volcanic ^f	0.29	8.9

a--excludes sea-salt sulphate transfer, b-mainly SO₂ and carbonyl sulphide (OCS), c-not human-induced (the 95% that is initiated by humans is included in the component above), d-oceanic emissions are mainly CH₃SCH₃ (88%), the remainder being H₂S (<10%), and OCS plus CS₂ (<2%), e—emissions from land are mainly (>60%) from tropical regions (20°N-20°S) and consist primarily of OCS (47%), CH₃SCH₃ (27%) and H₂S (20%). f—mainly SO₂ and sulphates (>98%). (Source: Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J. and Stoiber, R. E. Sulphur emissions to the atmosphere from natural sources, *Journal of Atm. Chemistry*, 14, 1992, 315-337.)

The standard levels of various countries are presented in Table 1.26.

Decay of organic matter in sewers and breakdown of animal and plant wastes by microbial activity are other major sources of H₂S and organic sulphides. Tanneries, glue and fur-dressing factories, abattoirs, waste treatment plants, and sugar-beet processing all produce significant quantities of H₂S which accounts for the fact that these are some of

the industries least wanted in the neighbourhood. Tanning is very prone to accidental discharges because the first stage of hair removal uses a paste of sodium sulphide and the following chrome tanning process uses sulphuric acid. If care is not taken to prevent the two effluents from mixing, H₂S is liberated. The manufacture of paper, rayon and S dyes, and the vulcanising of rubber, are other industrial processes where H₂S may be generated. Special safety precautions are required in all these industries to protect workers. In areas around pulp mills, levels of H₂S may be as high as 11.5 ppm; even higher levels have been recorded inside them. However, in urban areas, levels of H₂S are normally lower than 5.4 ppb.

Table 1.26 Standards for H₂S

Country	State or town	Type of regulation	Max, ground level 30 min concentration, µg/m ³	
U.S.A	California	Adverse level Standard		150
	New York State			150
Germany		Standard		150
			(30 min in) 8 h up to 300)	
U.S.S.R		Standard	8 (20 min)	8
Czechoslovakia		Standard	15	5

The human threshold of odour detection for H₂S is between 0.15 and 1.5 ppb but these limits are lower for mercaptans. To a certain extent, sensitivity depends on the individual but the rotten egg smell is clearly apparent to almost everyone at about three times these levels. H₂S is almost always accompanied by other malodorous substances such as methyl mercaptan, carbon disulphide, dimethyl monosulphide, and dimethyldisulphide. The 'quality' of the odour is changed accordingly – presumably from 'bad' to 'worse'.

Microorganisms of the soil, sewage treatment plants, as well as the plankton of the oceans, produce considerable quantities of CH₃SCH₃, CH₃SSCH₃, and CH₃SH. Estimates suggest that biogenic emissions of CH₃SCH₃, exceed those of H₂S and that a large proportion of these come from the oceans.

1.3.9.2 Effects of hydrogen sulphide on human health

Normally, the smell of H₂S is sufficient to warn humans of the presence of this gas at levels below 20 ppb and to cause them to retreat or to take remedial action. However, paralysis of the sense of smell occurs at higher levels. So victims may be unaware of the dangers (Table 1.27). High concentrations of H₂S are actually as toxic as hydrogen cyanide, HCN. In fact, both have the same TLV of 100 ppm and have similar effects. Respiratory failure occurs within seconds due to paralysis of the nervous control of breathing.

The toxicological problems associated with H₂S, like those of HCN, are caused by an inhibition of electron flow through cytochrome oxidase to O₂ in the mitochondria during

respiration. The skin of victims of acute intoxication caused by H₂S is usually grey-green in colour as are the internal organs. Most of the metabolic consequences of sub lethal exposure to H₂S stem from this partial inhibition of cytochrome oxidase in mitochondria. This also increases the number and volume of RBCs. However, the main clinical effect is irritation of the lung passages and eyes which leaves the victim with pneumonia and conjunctivitis a few days after the exposure (Table 1.27).

Table 1.27 *Effects of hydrogen sulphide on humans*

Exposure range	Effects and symptoms
0-0.2 ppb	No discomfort
0.2-1.2 ppb	Odour detected
1.2-5.4 ppb	Consciousness of 'bad egg' smell
5.4 nl l ⁻¹ –10 ppm	Some discomfort and headache
10-20 ppm	Eye irritation threshold
20-50 ppm	Severe eye irritation and impairment
50-100 ppm	Characteristic eye damage called 'gas eye'
100-320 ppm	Loss of sense of smell, nausea and increased lung irritation
320-530 ppm	Lung damage and water accumulation
530-1000 ppm	Shortage of breath, stimulation of respiratory centre, convulsions, and chance of respiratory arrest
1000 ppm and above	Immediate collapse and respiratory failure, followed by death

Recovery from acute poisoning is usually without aftereffects but some cases show persistent clinical symptoms which result from the initial O₂ deprivation. TLVs for maximum exposure to H₂S set at 10 ppm H₂S for 8 h daily exposures would appear to be too high because these levels are also known to cause eye irritation.

Chronic problems due to exposure to H₂S are conjunctivitis, headaches, dizziness, diarrhoea, and loss of weight. Early French medical writers used the phrase *plomb desfosses* to describe the colic and diarrhoea of Paris sewer men probably from such a cause, which resembled that normally associated with lead poisoning.

1.3.10 Fluorides

Hydrogen fluoride, HF, is a highly corrosive and irritant gas. A typical fluoride concentration in the atmosphere is 0.05 mg/m³. Because of its extreme toxicity, HF is a problem wherever processes involving fluorides take place, such as in the production of phosphate fertilizers, smelting of certain iron ores, and manufacturing of aluminium.

1.3.10.1 Sources of emission of fluorides

Fluorine is a gas so reactive that it does not occur naturally in elemental form. However, many fluoride-containing minerals such as fluorspar, cryolite, and certain apatites are used by industry. Some industries also produce HF either as a by-product or to form various useful fluoro-derivatives (Table 1.28).

Table 1.28 *Industrial and commercial processes involving fluorine compounds which may release fluoride and HF*

Emission Process	Processes using large amounts of fluorine-derivatives
Aluminium smelting	Clouding of electric bulbs
Steel production	Cut glass finishing
Phosphate fertilizers	Aviation fuel production
Enamel and pottery manufacture	Insecticides and rodenticides
Brick making	Separation of uranium isotopes
Missile propulsion	Synthesis of plastics
Beryllium, zirconium, tantalum and niobium purification	Aerosol, refrigerant and lubricant manufacture
Cleaning of castings	Wood preservation
Welding	Cement reinforcing
Sandstone and marble cleaning	Furniture cane bleaching
Cryolite, fluorspar and apatite mining	Water supplementation

Industrial emissions are superimposed upon significant natural background sources. Consequently, levels in both air and water supplies vary widely. The majority of rural and urban air monitoring sites record very low levels of atmospheric fluoride measured as total dissolved fluoride. Near phosphate fertilizer plants, aluminium smelters, or volcanoes, however, levels may rise above 200 ppm. Water supplies around these areas may also show elevated levels, well above the 1 ppm recommended as an optimum to provide an 'acceptable' incidence of dental caries and at the same time allow for the correct bone growth of children.

1.3.10.2 Effects of fluorides on plants

Fluoride deposition on plants not only causes them damage but may result in a second untoward effect. Grazing animals may accumulate an excess of fluoride, which mottles their teeth and ultimately causes them to fall out.

Problems associated with fluoride in plants are well known in relationship to fluorosis in farm animals. Animals grazing on pasture very close to brick works, smelters and phosphate fertilizer factories, or fed forage gathered from such areas, may show fluorosis, a condition also occasionally found in humans. The major recommendation has been to ensure that the yearly average fluoride content of herbage does not exceed $40 \text{ mg l}^{-1}\text{y}^{-1}$.

Application of lime to crops and herbage has long been known to be a practical means of reducing the effects of fluoride injury. Originally, it was thought that the lime caused the immobilization of the fluoride on the surfaces of the leaves as insoluble calcium fluoride. However, calcium chloride spraying has an alleviating effect similar to that of lime and recent studies have shown that the remedy actually relies upon additional

calcium entering the leaves to interact with the fluoride inside and redress any calcium imbalances in the regulatory processes.

1.3.10.3 Accumulation by plants

Crop loss in the USA due to fluoride is ranked fourth in importance after O₃, SO₂ and nitrogen-based air pollutants. However, on a weight for weight basis, fluoride is the most phytotoxic of all atmospheric pollutants. Injuries to the most susceptible plants occur at concentrations between 10 and 1000 times lower than those of other air pollutants. Rates of uptake of fluoride into leaves are also faster than those of any other pollutant and go on to cause problems to animals feeding upon these plants.

Both gaseous and particulate fluorides are deposited on plant surfaces and some penetrate directly if the leaf is old or weathered. Nevertheless, the main access into a plant is through the stomata. An important feature of fluoride uptake and transport in plants is that it is later carried in the transpiration stream towards the leaf tips or margins where it accumulates and phytotoxic effects usually develop. Plant species show wide ranges of susceptibilities to fluoride but environment factors, such as light, temperature, humidity, water stress, etc., all influence plant response. Young conifers, gladioli, peaches and vines are especially sensitive while tea and cotton are very resistant.

There are several mechanisms, which reduce fluoride levels in plants. These include shedding of individual leaves or surface waxes, leaching by rain, or volatilisation. Fluoride levels are often lowest during summer months because of more favourable meteorological conditions for better dispersal of fluoride pollution and greater turnover of leaves in grass swards during summer.

There are many reports of changes in photosynthesis, respiration or metabolism of amino acids, proteins, fatty acids, lipids, and carbohydrates in plants due to fluoride. Certain enzymes are modulated by the presence or absence of fluoride but these do not explain the wide range of metabolic changes known to occur. These are due to interactions between fluoride and calcium or magnesium. Calcium and fluoride together, for example, stimulate phosphate uptake which means that calcium adsorption sites on cell membranes are involved in response to fluoride, Cytoplasmic calcium is a ubiquitous regulator of cell metabolism and many, but not all, of its effects are mediated by a calcium-binding protein calmodulin, which in turn stimulates a variety of enzymes. Moreover, calcium ions are known to affect the transport selectivity of membranes with respect to other substances. Because of this, fluoride exerts an effect on various regulatory activities (see Table 1.29) and this probably explains why it is so phytotoxic at such low concentrations.

Table 1.29 *Physiological effects of fluoride on plants*

Process	Disturbance	Likely cation interaction
Respiration & carbohydrate Metabolism	Glycolysis inhibited	Mg ²⁺
	Pentose phosphate pathway enhanced	Mg ²⁺
	Unusual mitochondrial swelling	Mg ²⁺
	Oxidative phosphorylation reduced	Mg ²⁺
Photosynthesis	Unusual chloroplast structure	Mg ²⁺
	inhibited pigment synthesis	Mg ²⁺
	Increased PEPC activity	Mg ²⁺
	Reduced electron flow	Ca ²⁺
Amino acid & protein metabolism	Increased in free amino acids and asparagine	Ca ²⁺ /Mg ²⁺
	Decrease in ribosome sizes	Ca ²⁺ /Mg ²⁺
Nucleic acid metabolism	Changes in transcription and translation	Ca ²⁺ /Mg ²⁺
Fatty acid and lipid metabolism	Increased esterase activities	Ca ²⁺ /Mg ²⁺
	Decreased unsaturated/saturated ratios	Ca ²⁺ /Mg ²⁺
Other metabolic changes	Increase in peroxidase activities	Ca ²⁺ /Mg ²⁺
	Decrease in acid phosphatase activity	Ca ²⁺ /Mg ²⁺
Transport and translocation	Altered plasma membrane ATPases	Ca ²⁺
Fruit development	Poor fertilization and seed germination	Ca ²⁺
	Reduced pollen tube growth	Ca ²⁺
	Reduced seed number and fruit size	Ca ²⁺

Fluoride also forms magnesium-fluorophosphate complexes and, consequently, many enzyme pathways are adversely affected by fluoride. Most reactions involving ATP, for example, require additional magnesium complex to function correctly. If these natural complexes are also disturbed by the presence of additional fluoride then key reactions are inhibited.

Normally, soils contain 20-500 mg g⁻¹ fluoride but, because it has limited solubility in soil water, uptake by roots is relatively low, and there is little relationship between soil fluoride and total plant fluoride content. Consequently, atmospheric sources of fluoride are more important than fluoride in groundwater in determining the amount of fluoride in or on a crop.

1.3.10.4 Effects of fluorides on human health

Food and drinks are the most important sources of human fluoride intake. Normally, these contain below 1 mg l⁻¹ of fluoride. Tea, fish and other sea-foods are heavily laden exceptions. Other vegetables and cereals grown in areas subjected to high fluoride emissions may also be enriched in fluoride. The various physiological effects of fluoride on humans are shown in Table 1.30.

Table 1.30 *Physiological effects of fluoride on humans*

Process	Disturbance
Carbohydrate metabolism	Glycogen levels depleted, glycogen turnover depressed, phosphorylase activity reduced.
Lipid metabolism	Activation of acetate inhibited liver lipases, activated certain esterases inhibited.
Mineral metabolism	Interference in iron uptake; sulphite and phosphate counteract the inhibiting effect of Ca^{2+} upon intestinal absorption.
Hormonal balances	Effect on parathyroid function*.

*Calcium levels are influenced by the parathyroid hormone produced by the parathyroid and a hormonal derivative of vitamin D (called 1,2,5-dihydroxyl-cholecalciferol) found in the liver and kidneys – both raise blood serum levels of calcium. Release of calcitonin from the thyroid, however, causes enhanced calcification of the bone tissues which then reduces blood calcium levels again.

1.3.11 Radon

1.3.11.1 Sources of emission of radon

Radon, which occurs naturally, is the heaviest known gas. It is colourless, odourless, almost inert, soluble in water (especially at low temperatures), and radioactive. Radon gas comes from a decay process of underground uranium ore. It is by far the most important source of ionizing radiation to affect humans. In most developed countries, radon accounts for 40-50% of the total ionizing radiation received by the population.

There are 27 isotopes of radon ($^{200-226}\text{Rn}$) but only three have half lives longer than an hour (^{210}Rn , 2.4 h; ^{211}Rn , 14.6 h and ^{222}Rn , 3.82 days). Of these, ^{222}Rn is the most important and arises from the decay of ^{238}U (Fig. 1.37)²²². Rn also decays into a series of radionuclides known as radon daughters or progeny. Principal among these are ^{214}Pb (half-life, 26.8 minutes), ^{210}pb (22.3 years), ^{210}Bi (5 days) and ^{210}Pb (138.4 days). The final product is ^{206}Pb which is non-radioactive. Most of the decays involved (Fig. 1.37) release α particles but some (e.g. ^{210}Pb or ^{210}Bi) emit β radiation.

Radon occurs naturally, although it may also build up in homes that were built on land with radioactive fill. Radon is a dangerous source of radiation and it has been estimated that radon gas is responsible for about 20,000 deaths per year from lung cancer in USA. The Environmental Protection Agency estimates that 8 million homes have critical levels of radon.

Sources of radon such as ^{238}U and ^{227}Ra are concentrated in certain acidic igneous rocks with a low melting point such as granite. It is, however, the distribution and accessibility of ^{238}U in such rocks that affect the emanation of radon. The number of faults and fissures in rocks affect the transport of radon from the solid rock into the intervening gas or liquid phases, and from there upwards – different overlying strata having different diffusion characteristics.

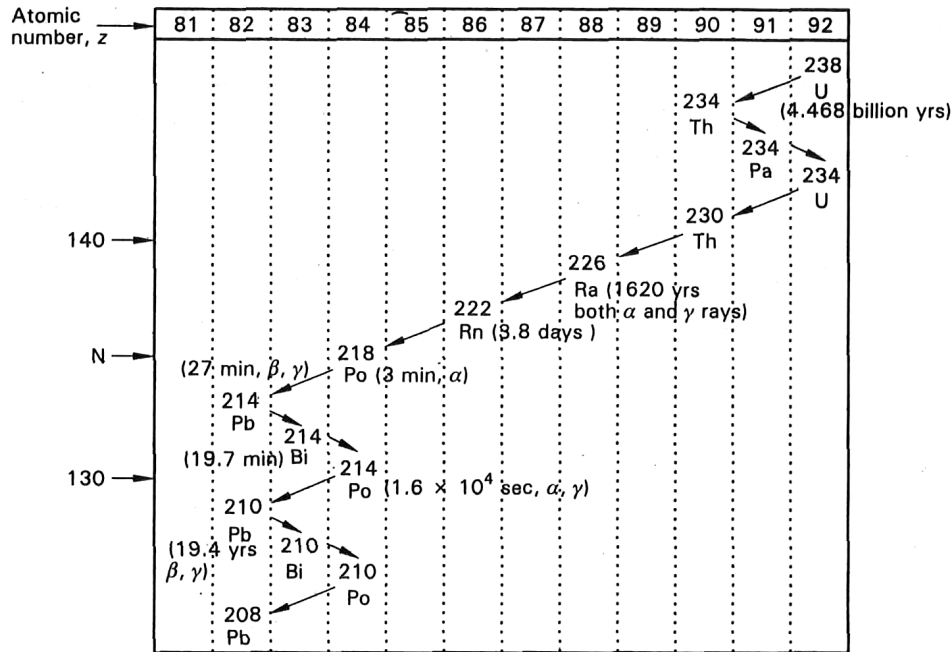


Fig. 1.37 The major decay transitions of ^{238}U to radon and then into radon daughters, α particles are released when decays move to the left and lose two protons. β particles are formed when movement is to the right and the number of protons increases by one

Radon emerges into the atmosphere by a variety of routes, including from the ground below and around the water supplies, and from natural gas or building materials; being denser than other gases, it tends to concentrate at low points. Consequently, lower storeys of buildings in radon-prone areas have higher levels of radon than upper floors. Further, most buildings have a slightly lower internal atmospheric pressure which forces radon inwards rather than outwards. This means that newer buildings which have fewer draughts are worse than older ones.

1.3.11.2 Effects of radon on human health

After seeping through the earth, the gas clings to particulate matter and is breathed by humans, causing damage in the lungs and eventually lung cancer.

The major hazard to humans of radon comes from breathing in radon daughters rather than radon itself. As a gas, almost as much radon comes out during expiration as went in during inhalation. Very little decays come out during expiration as went in during inhalation. Very little decays inside but being soluble, some does enter the bloodstream by diffusion. By contrast, non-gaseous radon daughters either adhere to dust particles or form clusters around water in aerosols. Both forms are inhaled but the radon daughters are deposited along the airways where they remain and decay. Consequently, the major

deposition of radon daughter contaminated particles occurs in the pharynx and at the junction of the bronchi.

Their relatively short half lives (apart from ^{210}Pb) mean that most of the radiation dose is by the linings of air ways which then causes pulmonary fibrosis and cancer. The risk of lung cancer due to exposure of radon for people of different areas is shown in Fig. 1.38.

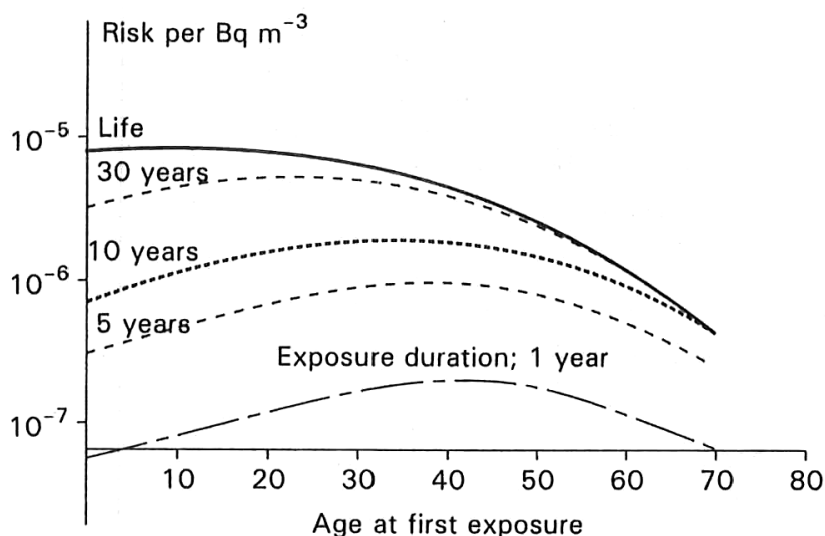


Fig. 1.38 Lifetime risks of lung cancer due to exposure of radon
(National Council on Radiation Protection and Measurement, 1984)

A strong trend towards conserving energy at home has caused people to plug any leaks in order to prevent cold air from coming into their homes, and to keep warm air inside. By doing so, fresh air in these homes is limited, and those who were unknowingly exposed to the danger of radon contributed to the high concentration of radon gas by sealing it in their homes. An amount of 4 picocuries per litre of air, which is 4-trillionths of a curie, is suggested as a safety standard for home owners. One simple way of dissipating the gas would be to open doors and windows when feasible and bring in some air circulation; or by simply using a fan to dissipate this gas and get in some fresh air. It may be much more complicated, especially when some homes are built on landfills contaminated with radioactive waste. In some regions of the world, well waters contain radon gas.

Treatment, once the problem is recognized, is relatively simple. The ground below and around can be sealed off from the rest of the building but leaks may still occur. A much better solution is to create a small porous sump area at the base of a radon-prone building and then continuously pump out any gas that seeps into the building.

1.4 Secondary Air Pollutants-Photochemical Reactions – Ozone –PAN-Photochemical Smog

Secondary air pollutants are chemical products that are formed from the reactions of various primary air pollutants with one another; some of the important secondary pollutants are products of photochemical reactions.

When oxides of nitrogen, various hydrocarbons, and sunlight come together, they can initiate a complex set of reactions that produce a number of secondary pollutants known as photochemical oxidants.

1.4.1 Ozone and photochemical smog

Ozone is a major component of photochemical smog – the brownish haze that covers many urban areas during the hot, sunny days of summer. Ozone is produced by chemical

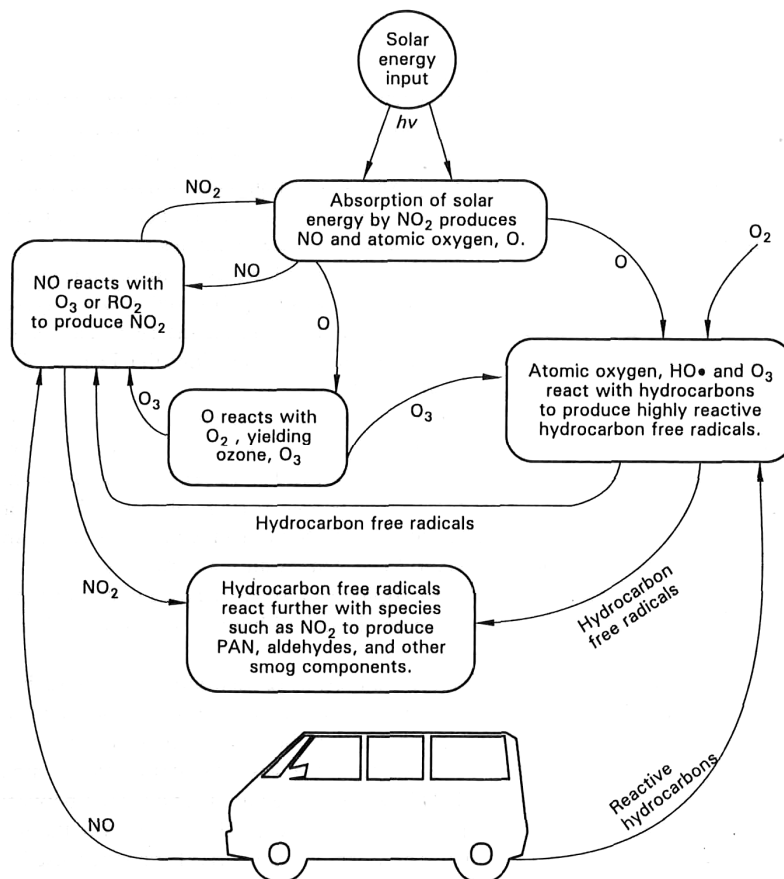


Fig. 1.39 Generalized scheme for the formation of photochemical smog

reactions between hydrocarbons and nitrogen oxides in the presence of sunlight – so the products of these reactions are called photochemical smog. The greater the intensity of sunlight and the warmer the day, the larger the amount of ozone produced. Since hydrocarbons and oxides of nitrogen are mainly generated by automobiles, the ozone levels gradually rise in the morning and peak between noon and 4 pm. On cloudy days, ozone production is reduced; after sunset, it stops altogether.

Photochemical smog has in addition to ozone, peroxyacetyl nitrates which are excellent oxidizing agents that readily react with many other compounds, including those found in living things, causing destructive changes. The general scheme for the formation of photochemical smog is shown in Fig. 1.39.

1.4.2 Conditions for photochemical smog

The conditions for the formation of photochemical smog are air stagnation, abundant sunlight, and high concentrations of hydrocarbons and nitrogen oxides in the atmosphere. Smog arises from photochemical reactions in the lower atmosphere by the interaction of hydrocarbons and nitrogen oxides released by exhausts of automobiles and some stationary sources. This interaction results in a series of complex reactions producing secondary pollutants such as ozone, aldehydes, ketones, and peroxyacetyl nitrates.

Photochemical smog is mainly an urban air pollution problem as the main contributing pollutants are from automobile emission sources. It was first observed in Los Angeles and has been found to be a severe problem in many cities. During the 1970s and 1980s it proved to be a daunting challenge to health officials in many cities like Denver, Salt Lake city, Milwaukee, Chicago, New York and Boston.

Photochemical smog is now a worldwide problem, especially in cities of lower latitudes which have high rates of population growth and rapid industrialisation. Currently, those most affected are Mexico city and Baghdad. Levels of O_3 in these and similar places are often over 100 ppb for considerable periods of time. Moreover, tropospheric O_3 is no longer just confined to summer. Significant wintertime levels are now being experienced in cities like Madrid and Athens during periods when stable, high pressure, sunny conditions occur. Tropospheric O_3 produced over populous areas spreads out in the manner of low-level clouds. In India Mumbai, and New Delhi are good candidates for photochemical smog.

Due to their climate and their geographic features, large metropolitan areas such as Log Angeles, Lake City, Phoenix, and Denver are troubled more with photochemical smog than the East Coast metropolitan areas. Most of these cities are located within a range of mountains. The prevailing winds are from the west. As cool air flows into a valley, it pushes the warm air upward. This warm air becomes sandwiched between two layers of cold air and acts like a lid on the valley, a condition known as a thermal inversion. The air is trapped in the valley. The warm air cannot rise further because it is covered by a layer of cooler air pushing down on it. It cannot move out of the area because of the ring of mountains. Without normal air circulation, smog accumulates.

Harmful chemicals continue to increase in concentration until a major weather change causes the warm air to move up and over the mountains.

Photochemical smog episodes have a distinctive daily rhythm. In the absence of wind around dawn, when urban activities are low, levels of CO, NO, and HCs increase as morning traffic builds up. Amounts of NO₂ then rise to a maximum about 1½ h after the peak of NO when the sun is reasonably high. The later appearance of aldehydes and then O₃ follow the disappearance of NO so that concentrations of O₃ are highest shortly after noon, just after the aldehyde peak has passed. This then allows other free radical chain reactions to form PANs and other irritants. As a rough approximation, one molecule of PAN is produced for every fifty O₃ molecules. In the late afternoon, returning traffic then generates more NO and NO₂ which immediately scavenges most of the O₃ and reactive aldehydes. This means that levels of nitrogen oxides do not follow their distinctive biphasic daily patterns normally found in windy and often variable, cloud covered conditions. Figure 1.40 presents the typical levels of the smog constituents at various times of the day observed in Los Angeles

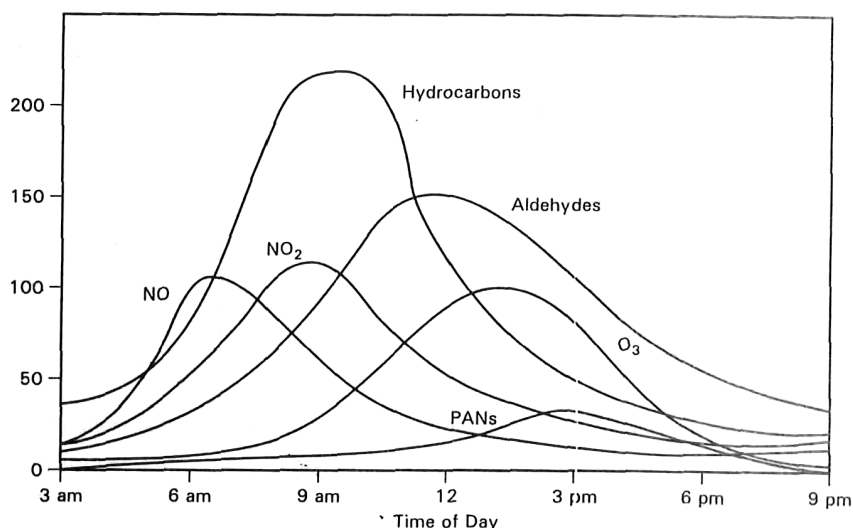


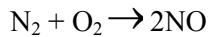
Fig. 1.40 Development and decay of components in a typical smog over a large conurbation during a bright, warm working day with no wind. Typical values observed in Los Angeles on July 9, 1965

The typical smog episode occurs in hot, sunny weather under low humidity conditions. The characteristic symptoms of the smog are the brown haze in the atmosphere, reduced visibility, eye irritation, respiratory distress and plant damage. The control of photochemical smog may require substantial reduction in NO_x produced in urban areas. At the same time it is also necessary to control the release of hydrocarbons from numerous mobile and stationary sources.

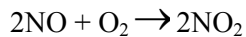
1.4.3 Sequence of photochemical reactions in photochemical smog

The NO – NO₂– NO₃ photochemical reaction sequence:

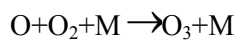
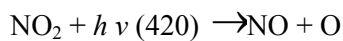
In the process of combustion NO will be formed.



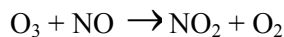
The nitric oxide thus emitted can oxidize to NO₂.



If sunlight is available, NO₂ can photolyse, and the freed atomic oxygen can then help to form ozone, as per the following pair of reactions:



where $h\nu$ represents a photon ($\lambda < 0.38 \mu\text{m}$) and M represents a molecule (usually O₂ and N₂ since they are most abundant in air) whose presence is necessary to absorb excess energy from the reaction. Without M, the ozone would have too much energy to be stable, and it would dissociate back to O and O₂:



Since this reaction is very rapid the concentration of O₃ will be low until the NO value decreases to a low value in the atmosphere. This set of reactions creates a cycle that is represented in Fig. 1.41.

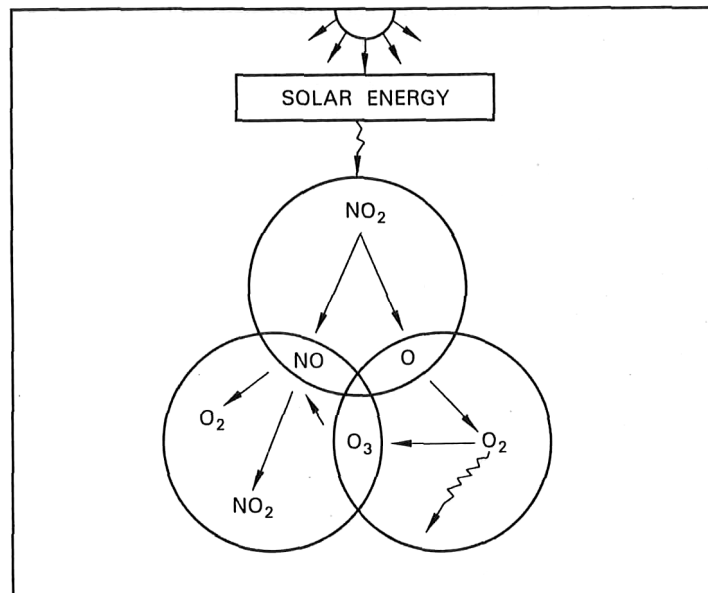


Fig. 1.41 The cycle of chemical reactions initiated by the photochemical dissociation of NO₂

If these were the only reactions involved, when they reach steady state, the rates of production and destruction of each of these important products of photochemical smog—NO, NO₂, and O₃—will be equal, and there would be no net change in their concentrations over time. Due to the rapid rate of reaction the NO concentration will not rise after smog sets in the day even though there are fresh emissions in the afternoon. However on many smoggy days, ozone levels are found to be much higher than those expected from the above reactions. This was found to be due to some other set of reactions involving hydrocarbons.

In the presence of certain hydrocarbons, the equilibrium set within the cycle of chemical reactions shown in Fig. 1.41, is destroyed and ozone begins to accumulate in the air.

For purely inorganic systems, kinetic calculations and experimental measurements cannot explain the rapid transformation of NO to NO₂ that occurs in an atmosphere under going photochemical smog formation and predict that the concentration of NO₂ should remain very low. However, in the presence of reactive hydrocarbons, NO₂ accumulates very rapidly by a reaction process beginning with its photodissociation, it may be concluded therefore, that the organic compounds form species which react with NO directly rather than with NO₂.

A number of chain reactions have been shown to result in the general type of species behaviour shown in Fig. 1.42.

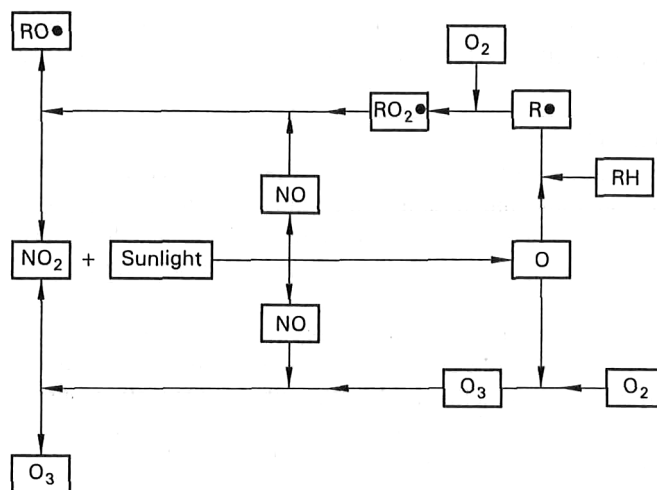
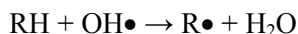
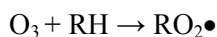
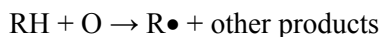
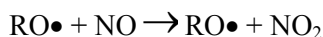
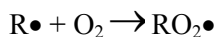


Fig. 1.42 Interaction of hydrocarbons with the atmospheric nitrogen oxide photolytic cycle

The greatest global problem with unsaturated hydrocarbons is their ability to promote the formation of photochemical smog in the presence of nitrogen oxides; strong sunlight and stable meteorological conditions.



However, the reaction chains involved are long and complicated because one reaction involving a free radical generates another. This in turn, reacts to form a third, etc. Moreover, there are many starting points which finally rejuvenate $\text{OH}\bullet$ readily through chain reactions with a wide variety of hydrocarbons released into the atmosphere. Aldehydes and ketones also produce free radicals in strong light such as $\text{RO}_2\bullet$ radicals while O_3 itself may attack unsaturated HCs to produce similar free radicals including reactive aldehydes.



These reactions show how hydrocarbons help in the conversion of NO to NO_2 and the break up of O_2 .

The mechanism of ozone build-up in the presence of reactive hydrocarbons is shown in Fig. 1.42. The ozone build-up is possible only when the ozone, formed by the reaction of oxygen atom (O) with O_2 , does not get consumed again to restore NO_2 after reacting with NO as indicated in the figure.

The sequence of the reactions mentioned above is a chain reaction in which the products of one reaction are consumed in the next. Consequently, we may find that a large number of reactive free radicals are formed and accumulate in the air.

1.4.4 Role of hydrocarbons in photochemical smog

The evaporation of solvents and the incomplete combustion of fuels release a wide range of hydrocarbons into the atmosphere. The analysis of ambient air samples at various times has shown the presence of over 600 different atmospheric hydrocarbons (HCs) when smog has set in. These include acetylene, benzene, butanes, ethane, hexanes, pentanes, propane and toluene – all of which are characteristic of anthropogenic emissions.

1.4.5 Formation of free radicals in air

Free radicals are highly reactive chemical species that are formed by the photo dissociation of several inorganic and organic compounds. The main compounds forming free radicals of importance in air pollution are hydroxyl radicals, aldehydes, ketones, peroxyacetyl nitrates, hydrogen peroxide, organic peroxides and nitrous and nitric acids.

The hydroxyl radical plays a central role, via the peroxy radicals with which it is intimately related, in the production of ozone and hydrogen peroxide. It also contributes to the formation of sulphuric and nitric acids, in the atmosphere. Thus atmospheric

processes leading to ozone formation will also tend to favour production of other secondary pollutants, including the strong acids, HNO_3 and H_2SO_4 .

1.4.6 Hydroxyl and hydroperoxyl radicals in the atmosphere

The hydroxyl radical $\text{HO}\cdot$ is the single most important reactive intermediate species in atmospheric chemical processes. It is formed by several mechanisms (Fig. 1.43). At higher altitudes it is produced by photolysis of water.

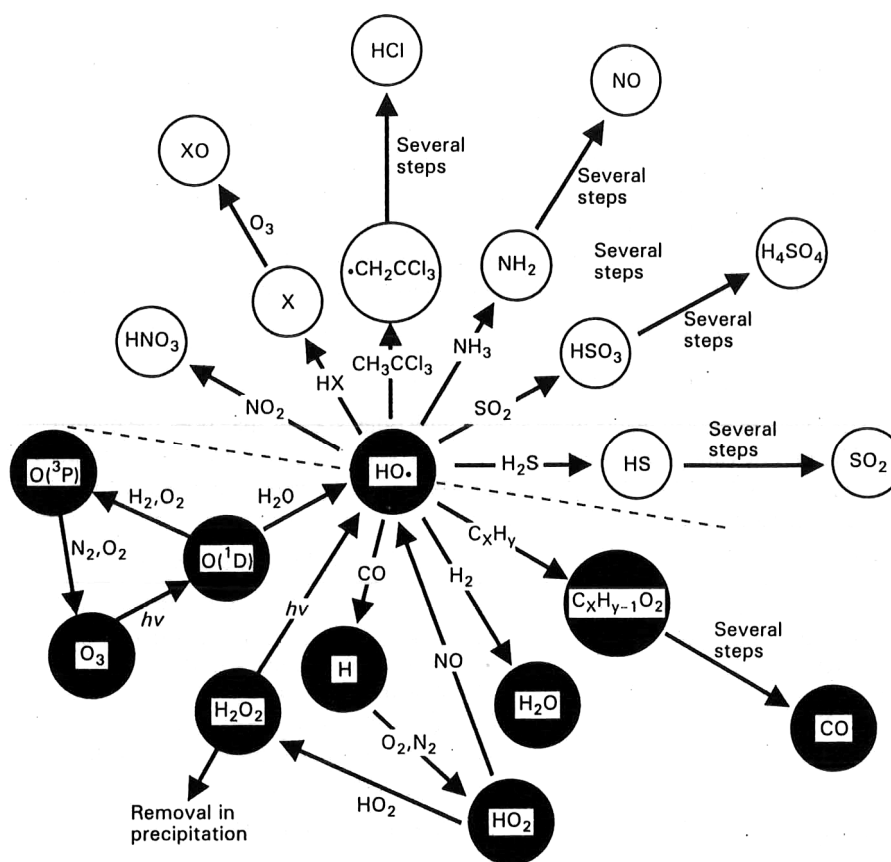
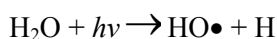
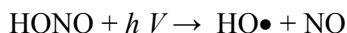
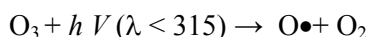


Fig. 1.43 Control of trace gas concentrations by $\text{HO}\cdot$ radical in the troposphere

In the presence of organic matter, the hydroxyl radical is produced in abundant quantities as an intermediate in the formation of photochemical smog. To a certain extent in the atmosphere, and for laboratory experimentation, $\text{HO}\cdot$ is made by the photolysis of nitrous acid vapour.



In the relatively unpolluted troposphere, hydroxyl radical is produced as the result of the photolysis of ozone.

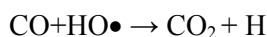
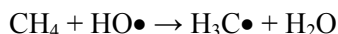


The above is followed by the reaction of a fraction of the excited oxygen atoms with water molecules.

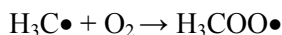


The involvement of the hydroxyl radical in chemical transformations of a number of trace species in the atmosphere is summarized in Fig. 1.43 and some of the pathways illustrated are discussed below. Among the important atmospheric trace species that react with the hydroxyl radical are carbon monoxide, sulphur dioxide, hydrogen sulphide, lethane, and nitric oxide.

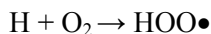
Hydroxyl radical is most frequently removed from the troposphere by reaction with methane or carbon monoxide.



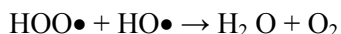
The highly reactive methyl radical, $\text{H}_3\text{C}\bullet$ reacts with O_2 to form the methylperoxy radical $\text{H}_3\text{COO}\bullet$.



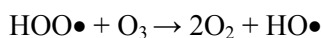
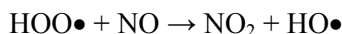
The hydrogen atom produced in the reaction, $\text{CO} + \text{HO}\bullet \rightarrow \text{CO}_2 + \text{H}$, reacts with O_2 to produce the hydroperoxyl radical.



The hydroperoxyl radical can undergo chain termination reactions such as:



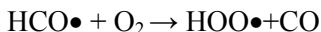
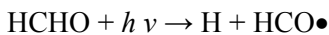
or, reactions that regenerate the hydroxyl radical.



It is estimated that the global concentration of hydroxyl radicals, averaged diurnally and seasonally, ranges from 2×10^5 to 1×10^6 radicals per cm^3 in the troposphere. The concentration of $\text{OH}\bullet$ radical is found to be higher in tropical regions due to their higher humidity and sunlight. Similarly the southern hemisphere has 20% higher levels of $\text{HO}\bullet$ than the northern hemisphere.

The hydroperoxyl radical $\text{HOO}\bullet$ is an intermediate in some important chemical reactions. In addition to its production by the reactions discussed above, in polluted atmospheres, hydroperoxyl radical is made by the following two reactions, starting with

the photolytic dissociation of formaldehyde to produce a reactive formyl radical,



The hydroperoxyl radical reacts more slowly with other species than does the hydroxyl radical. The kinetics and mechanisms of hydroperoxyl radical reactions are difficult to study because it is hard to retain these radicals free of hydroxyl radicals, which are summarized in Table 1.31.

Table 1.31 Generalized chemical kinetic mechanism in photochemical box model

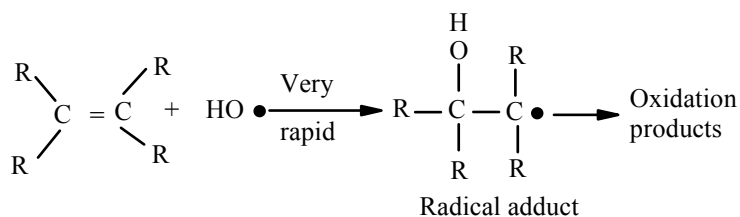
1. $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$	19. $\text{OLEF} + \text{O} \rightarrow \text{RO}_2 + \text{ALD} + \text{HO}_2$
2. $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$	20. $\text{OLEF} + \text{O}_3 \rightarrow \text{RO}_2 + \text{ALD} + \text{HO}_2$
3. $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	21. $\text{OLEF} + \text{HO} \rightarrow \text{RO}_2 + \text{ALD}$
4. $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	22. $\text{PARAF} + \text{HO} \rightarrow \text{RO}_2$
5. $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$	23. $\text{ALD} \xrightarrow{h\nu} 0.5\text{RO}_2 + 1.5\text{HO}_2 + 1.0\text{CO}$
6. $\text{NO}_3 + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO}_2$	24. ALD atmospheric layer deposition
7. $\text{HONO} \xrightarrow{h\nu} \text{HO} + \text{NO}$	25. $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$
8. $\text{HO} + \text{NO} \xrightarrow{\text{O}_3} \text{HO}_2 + \text{CO}_2$	26. $\text{RO} + \text{O}_2 \rightarrow \text{ALD} + \text{HO}_2$
9. $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2$	27. $\text{RIO}_2 + \text{NO}_2 \rightarrow \text{PAN}$
10. $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	28. $\text{RO} + \text{NO}_2 \rightarrow \text{RONO}_2$
11. $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HOONO}_2$	29. $\text{RO}_2 + \text{O}_3 \rightarrow \text{RO} + 2\text{O}_2$
12. $\text{HOONO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	30. $\text{RIO}_2 + \text{NO} \xrightarrow{\text{O}_3} \text{RO}_2 + \text{NO}_2$
13. $\text{HO} + \text{HONO} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	31. $\text{PAN} \rightarrow \text{RIO}_2 + \text{NO}_2$
14. $\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M}$	32. $\text{AROM} + \text{HO} \xrightarrow{\text{O}_3} \text{RO}_2 + \text{R}_2\text{O}_2 + 2\text{ALD} + \text{CO}$
15. $\text{HO} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}$	33. $\text{R}_2\text{O}_2 + \text{NO} \rightarrow \text{R}_2\text{O} + \text{NO}_2$
16. $\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$	34. $\text{R}_2\text{O} + \text{O}_2 \rightarrow \text{ALD} + \text{HO}_2 + 2\text{CO}$
17. $\text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	35. $\text{R}_2\text{O}_2 + \text{O}_3 \rightarrow \text{R}_2\text{O} + 2\text{O}_2$
18. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	36. $\text{RIO}_2 + \text{O}_3 \rightarrow \text{RO}_2 + 2\text{O}_2$

Source: K. L. Demerjian and K. L. Schere, 1979, *Proceedings, Ozone/Oxidants: Interactions with Total Environment II* (Pittsburgh: Air Pollution Association).

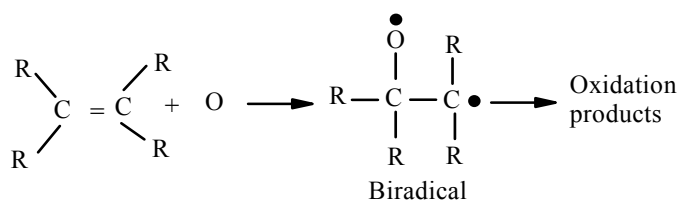
Note: M stands for any available atom or molecular which by collision with the reaction product carries off the excess energy of the reaction and prevents the reaction product from flying a part as soon as it is formed.

Olefins (OLEF) with large number of double bonds also react photochemically to form free radicals (Table 1.31). On reacting with oxygen some free radicals form peroxy compounds from which new peroxides or free radicals are produced (PARAF) that can cause polymerization of olefins.

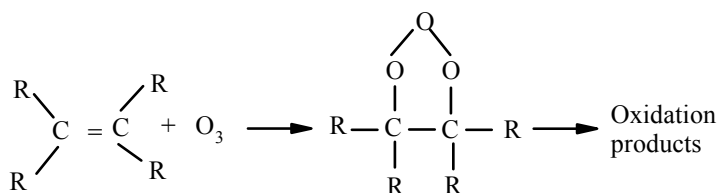
Olefins are much more reactive, undergoing reactions with the hydroxyl radical,



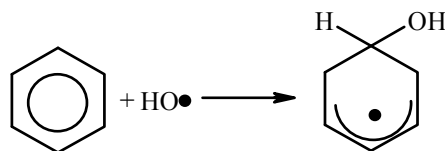
(where R may be one of a number of hydrocarbon moieties or an H atom) with oxygen atoms, or

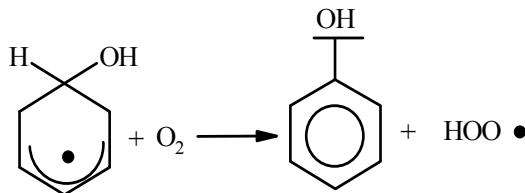


with ozone,



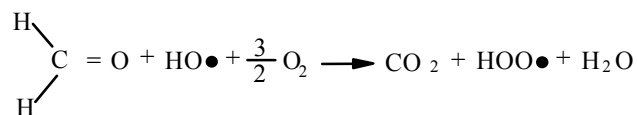
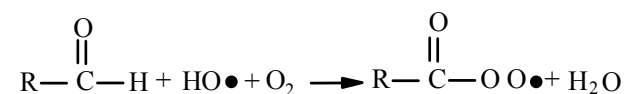
Aromatic hydrocarbons, Ar-H, may also react with O and HO•. Addition reactions of aromatics with HO• are favoured. The product of the reaction of benzene with HO• is phenol, as shown by the following reactions sequence:



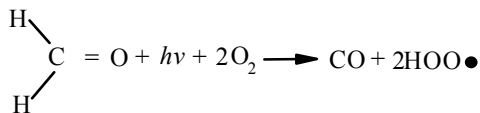
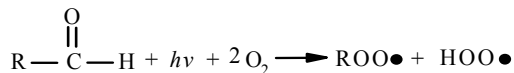


In the case of alkyl benzenes, such as toluene, the hydroxyl radical attack may occur on the alkyl group, leading to reaction sequences such as those of alkanes.

Aldehydes react with $\text{HO}\bullet$



Undergo photochemical reactions:



The hydroxyl radical which reacts with some hydrocarbons at rates that are almost diffusion-controlled, is the predominant reactant in the early stages of smog formation.

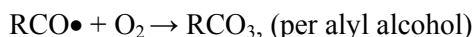
Significant contributions are made by the hydroperoxyl radical ($\text{HOO}\bullet$) and O_3 after smog formation is well under way.

One of the most important reaction sequences in the smog formation process begins with the abstraction by $\text{HO}\bullet$ of a hydrogen atom from a hydrocarbon and leads to the, oxidation of NO to NO_2 as follows:

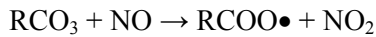


This radical participates in a number of reactions leading to the formation of more reactive molecules like proxy alyl radical aldehydes and ketones which react with NO and hydrocarbons.

The alyl radical, $\text{RCO}\bullet$ reacts with O_2 to produce a peroxy radical, $\text{RCOO}\bullet$:



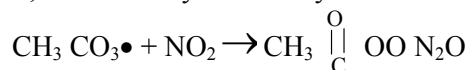
This strongly oxidizing species very effectively oxidizes NO to NO_2 :



This explains the once puzzling rapid conversion of NO to NO₂ in an atmosphere in which the latter is undergoing photo dissociation. The alkoxy radical product, RO• is not as stable as ROO•. In cases where the oxygen atom is attached to a carbon atom that is also bonded to H, a carbonyl compound is likely to be formed.

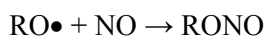
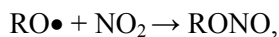
Many free radicals like these that are generated in strong sunlight are responsible for the eye irritation of those exposed to photochemical smog.

Peroxyacetyl nitrate (PAN), one of the important constituent products is formed through a number of routes, most notably acetaldehyde oxidation as shown below.



Where R is the methyl group, the product is peroxyacetyl nitrate. Although it is thermally unstable, peroxyacetyl nitrate does not undergo photolysis rapidly, reacts only slowly with the HO• radical, and has a low water solubility. Therefore, the major pathway by which it is lost from the atmosphere is thermal decomposition, the opposite of the above reaction.

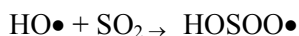
Alkyl nitrates and alkyl nitrites may be formed by the reaction of alkoxy radicals (RO•) with nitrogen dioxide and nitric oxide respectively:



Addition reactions with NO₂ such as these are important in terminating the reaction chains involved in smog formation. Since NO₂ is involved both in the chain initiation step and the chain terminating step, moderate reductions in NO_x emissions alone may not curtail smog formation and in some circumstances may even increase it.

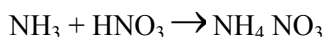
1.4.7 Inorganic products from smog

Some of the important inorganic products from smog are sulphates and nitrates which are responsible for acidic precipitation, corrosion, reduced visibility, and adverse health effects. The oxidation of SO₂ to sulphate species takes place more rapidly (5-10% per hour) under smoggy conditions than in a clean atmosphere. A number of oxidants such as O₃, NO₃, and N₂O₅ as well as reactive radical species, particularly HO•, HOO•, O, RO• and ROO•, which are likely to be present in smog conditions oxidize SO₂ to sulphates.



The presence of HO• (typically at a level of 3×10^6 radicals/cm³ but appreciably higher in a smoggy atmosphere) makes this a likely route. The addition of SO₂ to RO• or ROO• can yield organic sulphur compounds also.

Inorganic nitrates or nitric acid are also formed in smog reactions, particularly those involving N₂O₅ with water and NO₂ with hydroxyl radical. Nitric acid freed by these reactions reacts with ammonia in the atmosphere to form ammonium nitrate.



Both nitric acid and nitrites are some of the damaging constituents of smog products which not only affect plant and animals but also corrode materials.

1.4.8 Adverse effects of photochemical smog

The major constituents of smog, with the exception of carbon dioxide, are powerful poisons. Many aspects of their toxic effects, both individually and in combination with one another, are not completely known. The danger, however, to people with susceptibility to respiratory and cardiac difficulties is widely recognised. Those with incipient or advanced bronchial asthma, chronic bronchitis, and pulmonary emphysema are apt to be hard hit. The various components of smog may affect people with different susceptibilities in different ways.

1.4.9 Short - and long-term effects

Photochemical smog causes irritation of the eyes, nose, throat, and chest. Eye irritation is not caused by O₃ but by PANs and trace free radical HCs. O₃ is a powerful oxidant that may injure the bronchiolar and alveolar walls of the lungs. Surface epithelial cells of the airways are damaged by O₃ and afterwards, these are replaced by thick cuboidal cells with few or small cilia (cell hairs). Apart from loss of cilia, additional changes to the epithelial (surface lining) cells include cytoplasmic vacuolation (formation of internal cellular spaces) and condensation of abnormal mitochondria.

Respiratory irritation and difficulty in breathing have been common, and the correlation of the oxidizing power of smog with its irritating action is having implications beyond the simple annoyance factor. The air passageways of the lungs do more than carry the air and waste gases to and from the air sacs. The passageways are lined with mucus-secreting epithelium and serve to condition the air before it reaches the alveoli. The air is changed in three important ways; it is warmed to body temperature, it is saturated with moisture, and it is filtered free from most of the dust particles and other foreign substances. The cells that form the epithelial lining are ciliated, that is, they have hair-like protoplasmic appendages that project into the passageways and, by continuous, coordinated, rhythmic action, work the mucus and entrapped foreign material upward to the throat where it is either swallowed or expelled. Both the mucous secreting ability and the ciliary action of the epithelium have been sensitive to adversities, and excessive

exposure to foreign material such as smoke, dust, and toxic substances impair their functioning, causing an increase in susceptibility to various respiratory disorders.

The other constituent of photochemical smog that might be expected to affect health is NO_2 .

Effects of O_3 are also made worse by exercise. It is now recommended that athletic activities should cease when levels of O_3 are high and that groups at risk (e.g. children who spend proportionately more time outdoors than any other group in the population) be moved indoors.

Epidemiological studies of enhanced respiratory infections and reduced lung functions in populations exposed to photochemical smogs are hampered by the fact that such surveys are dealing with complex and changing mixtures of O_3 , nitrogen oxides, PANs, and other components of smog. Shorter-term dose response studies have indicated that, although nitrogen oxides and O_3 cause similar adverse effects on lungs, more than five times the level of NO_2 is required to elicit effects similar to that caused by a given level of O_3 .

1.4.10 Effects on plants

Before the biological importance of air pollution was fully realized, it was found that plants grown in bad smog areas suffered injury from what often appeared to be obscure causes. It is now apparent that many plants have been more sensitive than humans to the acute effect of smog and in fact, can be used as indicators of the harmful level of air contaminants.

Two ingredients of photochemical smog have been recognized as being particularly injurious; ozone and PAN (peroxyacetyl nitrate). With PAN, injury has been appearing on some plants as a characteristic silverying on the bottoms of the leaves. Ozone, on the other hand, kills cells on the tops of the leaves and appears as flecking or stippling of the upper surfaces.

Still conditions during photochemical smog episodes provide some protection to vegetation because undisturbed boundary layers of still air around the leaves offer additional resistance to the diffusion of O_3 . Later, as winds move tropospheric O_3 around, damage to vegetation may be experienced many kilometres away as these leaf boundary layers are stripped away.

Access of O_3 into the leaf takes place through the stomata although waxy leaf surfaces may be partially degraded by O_3 . Most plants have open stomata during the day. Consequently, O_3 damage is initiated in the Light but cacti, etc., which only open their stomata at night to conserve water loss, have their period of maximum sensitivity to O_3 during periods of darkness.

Responses to O₃ are determined by a wide variety of environmental or genetic factors. Moist surfaces within the leaves allow O₃ to dissolve and diffuse down a concentration gradient similar to that of CO₂. Solubilities, rates of decomposition, and the pH values of the various media all influence the amount of O₃ that is taken up. O₃ is approximately one-third as soluble as CO₂ but 100-fold less soluble than SO₂.

Injury to plants from photochemical air pollution was reported in the mid-1940s when losses occurred to spinach and other sensitive plants in California. Since then, crop damage has taken place in many parts of the world. It is now impossible to raise orchids in metropolitan areas. Vegetable and citrus growing have been hit hard by injury and reduced yields.

Ornamental plants have not escaped the onslaught of air pollution, City parks have been becoming increasingly limited in the plants that can be successfully grown, and park superintendents find that they must be more restrictive in selecting types of plants that can tolerate smog. Home gardeners are usually puzzled by the failure of their favourite specimens to flourish. Injury is common to petunia, snapdragon, chrysanthemum, larkspur, carnation, orchid, pansy, rose and zinnia.

The principal effects of PAN have been the silverying, bronzing, and glazing of the lower leaf surface. Petunias are affected at very low concentrations (0.005 ppm for 8 h). Pinto beans are affected at 1.0 ppm for 30 minutes.

Not as much has been known about the effects of NO₂, but long-time exposure to 0.5 ppm has been said to damage tomato plants.

1.4.11 Effects on materials

Deterioration of materials by photochemical smog has been thought to be primarily the result of the ozone content of smog. Thus the most specific effect of smog on materials has been the cracking of rubber. In fact an early, specific analytical method for the determination of atmospheric ozone was the depth of cracks on stretched rubber bands. An important economic effect of smog in Los Angeles in the 1940s happened to be the deterioration of the side walls of automobile tires. Addition of an anti-ozonant has alleviated the problem. A variety of other rubber products (hoses, gaskets, wire insulation) are also still affected. Another important effect believed to be caused by ozone is the fading of dyes.

Natural polymers like rubber, cotton, cellulose, or leather, as well as paints, elastomers, plastics, nylon and fabric dyes, are all degraded by O₃. Only when the double bonds in their structures are protected by adjacent groups can attack be resisted. The electronegative chlorine atom adjacent to the double bond in neoprene is a good example of this type of protection. Similar protective mechanisms have been built into recent polymers but sacrificial autoxidants can also be incorporated. The annual global cost of

this type of damage to materials is huge and constitutes just over 30% of that caused by all forms of atmospheric pollution to non-living materials.

Problems

1. The maximum one-hour carbon monoxide levels in Calcutta reach 35 ppm. Calculate the equivalent concentration in terms of mass fraction (w_p) and in milligrams per cubic meter at 25 °C and 1 atm.
2. The mean concentration of sulphur dioxide in Mumbai is 47 mg/m³. What is the equivalent concentration in parts per million at 25 °C and 1 atm?
3. The exhaust gas from a motor vehicle shows a carbon monoxide concentration of 2% by volume. What is the concentration of CO in mg/m³ at 0 °C and 1 atm?
4. A 1000 MW power plant of 25% thermal efficiency is proposed. The plant burns 3% sulphur coal with a heating value of 6000 kcal/kg and emits 64,000 m³/min of flue gas. What is the concentration of SO₂ in the flue gas in ppm? Assume that the density of SO₂ is 1920 g/m³.
5. A captive power plant of 1 MW with 40% thermal efficiency is to be designed which will use residual oil with 1% sulphur content. The emission factors for burning 1 m³ of oil are: particulates = 1 kg, NO₂ = 10 kg and SO₂ = 16 S kg where S is the percent sulphur content of oil. What are the rates of emission of particulates, NO₂ and SO₂ to the atmosphere if no control devices are provided? The heating value of the oil is 8000 kcal/kg, and its density may be taken as 950 kg/m³.
6. Consider a new 38% efficient, 600 MW power plant burning 5.79 kW/kg coal containing 1 % sulphur. What would be the maximum allowable SO₂ emission rate (kg/day) and how efficient must the scrubber be?
7. In the above power plant, how many kg per day of sulphur would be released from the fuel? If the scrubber were 90% efficient, how many kg per day of sulphur and SO₂ would be released?
8. A new coal fired power plant has been built using a sulphur emission control system that is 70% efficient. What maximum percent sulphur content can the fuel have if 9.66 kW/kg coal is burned? If 5.79 kW/kg coal is burned, what maximum sulphur content can the fuel have?

1.4.12 US-National trends in ozone levels

Using a nationwide network of monitoring sites, US-EPA has developed ambient air quality trends for ozone. Trends are shown here for the 8-hour ozone standards. Under the Clean Air Act, EPA sets and reviews national air quality standards for ozone. Air quality monitors measure concentrations of ozone throughout the country. EPA, state, tribal and local agencies use that data to ensure that ozone is at levels that protect public health and

the environment. Nationally, average ozone levels declined in the 1980's, leveled off in the 1990's, and showed a notable decline after 2002 (Figure 1.44).

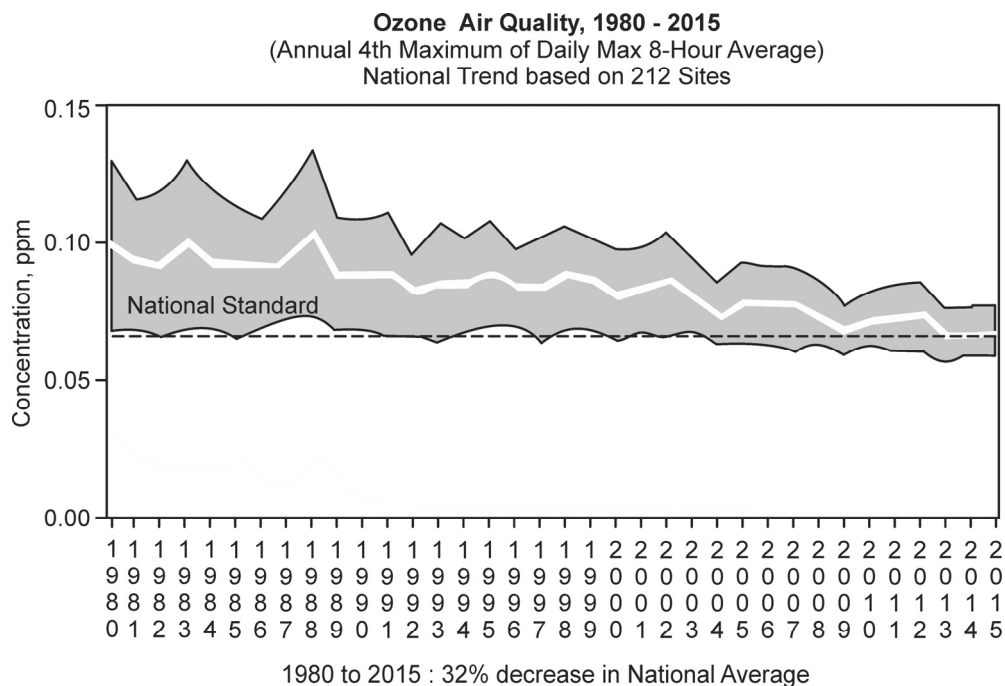


Fig. 1.44 Trends on Ozone Levels from 1980-2015

Questions

Short Answer Questions

1. List out the emission sources of Air Pollutants.
2. How does the food and agricultural sector contribute to air pollution sources? Name a few pollutants.
3. How are air pollutants classified based on their source of pollution?
4. Outline the atmospheric cycle of a pollutants.
5. Classify different types of particulates based on the particle size.
6. Brief how human health is affected by particulate pollutants.
7. Show the formation mechanism of sulfur oxides in the atmosphere.
8. Write a short note on emission sources of hydrocarbons.

9. Brief about Carcinogenic air pollutants and their significance.
10. Explain about radon emission and its sources.

Essay Questions

1. Explain in detail about the gases produced by Anthropogenic activities
2. Explicate the different Pathological effects caused due to pollutant gases.
3. Describe the removal mechanisms employed for nitrogen oxides.
4. What is Blood biochemistry and pollution? Explain in detail.
5. List out the Physiological effects of fluoride on plants in detail.
6. Schematize the formation of Photochemical smog.
7. Analyze the sequence of photochemical reactions in photochemical smog.
8. Explain in detail about Hydroxyl and hydroperoxyl radicals in the atmosphere.
9. Analyze the inorganic products produced in smog. Give the chemical reactions.

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