



Criteria Air Pollutants: Chemistry, Sources and Sinks

2

Abstract

Ambient air pollution is the foremost reason for global death and disease. An estimated premature death globally is related to ambient air pollution, mainly from emphysema, obstructive bronchiolitis, lung cancer, heart disease, stroke, and severe respiratory problems in children. The criteria air pollutants include particulate matter (PM), ozone (O₃), nitrogen dioxide (NO₂), sulphur dioxide (SO₂) and lead (Pb). The present chapter provides a summary of the types of criteria air pollutants, their National Ambient Air Quality Standards and their emission sources. This chapter also explains their level distribution and chemistry, and the sink in the earth's environment of these criteria pollutants is studied extensively. Description of global, regional emissions of criteria air pollutants, their contribution from different sectors, and efficiency of control strategies in developed and developing countries are also focused.

2.1 Introduction

Air pollution is one of the rapidly growing problems of today's world. The pollutant is emitted from different sources directly or indirectly to the ambient atmosphere. When one or several pollutants are present in the air in such a level for a long period of time, that can have some harmful effects on human, animal, plant and/or material properties which is called air pollution. It also affects the global economy, Earth Radiation Budget and climate change in the long-term perspective. Air pollution is now considered as the world's biggest threat to the environmental health and responsible for the seven million deaths over the world per year. It causes a number of deleterious effects and causes pulmonary illness, asthma and cardiovascular diseases after long-term exposure. Short-term exposure also creates problems like headache, mood alteration, dizziness, eye-irritation, nausea, coughing, etc. US Environmental Protection Agency (USEPA) has set up the National Ambient Air Quality Standards (NAAQS) for six pollutants, viz. particulate matter, carbon

monoxide, nitrogen dioxide, sulphur dioxide, ground-level ozone, and lead which is also known as “criteria air pollutants” or criteria pollutants. These criteria pollutants harm the environment and their components after their emission or after atmospheric transformation reactions such as oxidation/reduction. The atmospheric chemistry along with their source and sink information provides a clear picture about the criteria air pollutant in the atmosphere. A brief description of the origin (sources), chemical transformation and sinks of the criteria pollutants has been discussed in the present chapter. As far as emission concerns, criteria pollutants have varieties of origin including natural and anthropogenic sources. Natural sources include volcanic eruption, forest fire, lightning strikes and biological emissions. The anthropogenic sources include emissions from industries, vehicles, biomass burning, cooking activities and resuspension of soil/road dust. These pollutants either originate directly by primary emission sources or originate through their precursors via chemical transformation reactions into the atmosphere. The increasing burden of these in the atmosphere causes several harmful defects on the plants and animals including human being. There are complex relationships between the air pollutants’ atmospheric criteria pollutant levels, chemistry, sources and their sink. To identify the increasing atmospheric pollution levels, the ambient air quality standard is developed as a policy guideline that regulates the effect of human activity upon the environment so that pollutant emission into the air can be regulated. These standards are developed by several agencies such as US Environmental Protection Agency (USEPA), Central Pollution Control Board (CPCB) and many more across the world. Table 2.1 shows the National Ambient Air Quality Standards (NAAQS) reported by USEPA and CPCB for the six designated criteria air pollutants.

2.2 Air Pollution Sources and Their Emissions

There are two major categories among the air pollution sources, viz. anthropogenic and natural.

2.2.1 Anthropogenic Sources

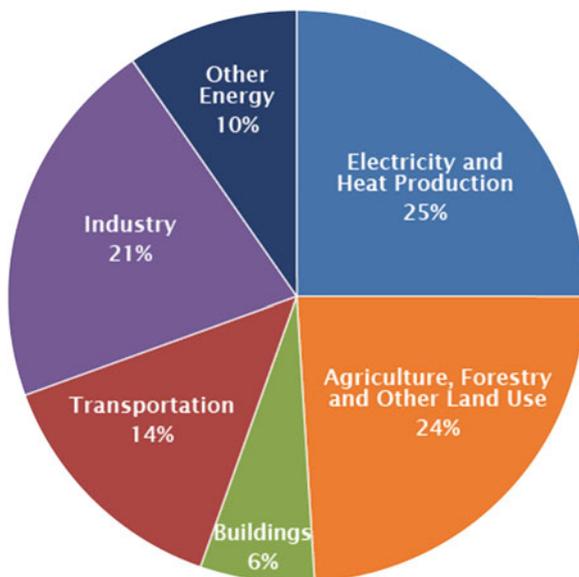
Anthropogenic sources are the results of various human activities such as fossil fuel combustion, industries emissions (cement factories, oil refineries, electroplating), emission from thermal power plants, emissions from agriculture activities (crop burning and ploughing), transportation emission (light motor vehicles and heavy-duty vehicles), mining, cooking, refuse burning, etc. The most widespread anthropogenic sources are identified and classified by using emission factors and further used to plan the air quality management programme (Bouhel et al. 1994). The clear picture of distribution of anthropogenic emissions from different sectors is shown in Fig. 2.1.

Table 2.1 National Ambient Air Quality Standards (NAAQS) for six criteria air pollutants

S. No.	Pollutant	NAAQS (USEPA)			NAAQS (CPCB)			Ecologically sensitive area
		Primary/secondary	Avg. time	NAAQS (USEPA)	Avg. time	Industrial, residential, rural and other areas	Ecologically sensitive area	
1.	Sulphur dioxide (SO ₂)	Primary	1 h	75 ppb	Annual	50 µg/m ³	20 µg/m ³	
		Secondary	3 h	0.5 ppb	24 h	80 µg/m ³	80 µg/m ³	
2.	Carbon monoxide (CO)	Primary	8 h	9 ppm	8 h	2 mg/m ³	2 mg/m ³	
		Secondary	1 h	35 ppm	1 h	4 mg/m ³	4 mg/m ³	
3.	Lead (Pb)	Primary and secondary	Rolling 3 months average	0.15 µg/m ³	Annual	0.50 µg/m ³	0.50 µg/m ³	
		Primary	1 h	100 ppb	24 h	1.0 µg/m ³	1.0 µg/m ³	
4.	Nitrogen dioxide (NO ₂)	Primary and secondary	Annual	53 ppb	Annual	40 µg/m ³	30 µg/m ³	
		Primary	8 h	0.070 ppm	24 h	80 µg/m ³	80 µg/m ³	
5.	Ozone (O ₃)	Primary and secondary	1 year	12.0 µg/m ³	8 h	100 µg/m ³	100 µg/m ³	
		Secondary	1 year	15.0 µg/m ³	1 h	180 µg/m ³	180 µg/m ³	
6.	Particulate matter (PM)	Primary and secondary	24 h	35 µg/m ³	Annual	40 µg/m ³	40 µg/m ³	
		Primary and secondary	24 h	150 µg/m ³	24 h	60 µg/m ³	60 µg/m ³	
	PM ₁₀	Primary and secondary	24 h	150 µg/m ³	Annual	60 µg/m ³	60 µg/m ³	
		Primary and secondary	24 h	100 µg/m ³	24 h	100 µg/m ³	100 µg/m ³	

USEPA United States Environmental Protection Agency, USA; CPCB Central Pollution Control Board, India

Fig. 2.1 Global distribution of anthropogenic emissions from different sectors in relation to air pollutants. (Source: IPCC 2014)



2.2.2 Natural Sources

Natural sources linked to the earth's processes, which release huge quantities of pollutants into the atmosphere within a very short period, include volcanic eruption, dust storms and forest fire. Few other natural sources/activities also released some amount of the pollutants but in significant amount such as grazing animals and lightning. Biogenic emissions are also a part of natural sources and emitted chemicals and gases through their biological activity, e.g. vegetation and microbial activity in soils (Zunckel et al. 2007). The global distribution of natural sources from different sectors is shown in Fig. 2.2.

Based on the nature of sources, anthropogenic and natural sources can be further classified as mentioned below.

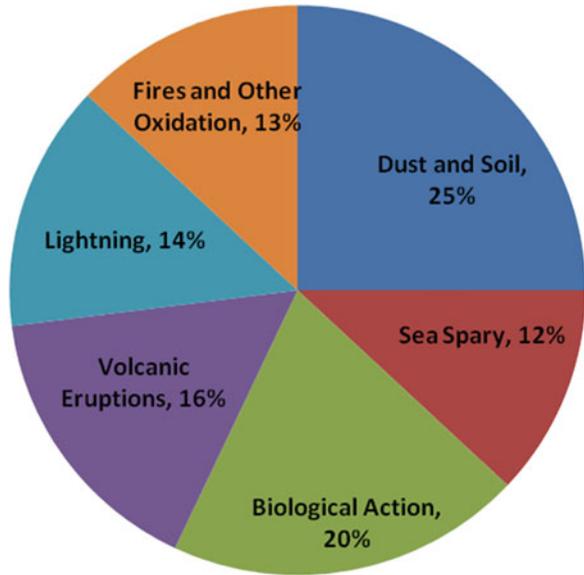
2.2.3 Stationary Sources

Stationary sources of air pollution are limited to a particular region while emitting pollution and typically connected with fixed structures like buildings and frequently release noxious wastes that remain moderately steady in due course of time, e.g. factories, refineries, boilers, power plants, etc. Stationary sources can have further subsections.

2.2.3.1 Point Source

Point source is a single, identifiable source of pollution with fixed geographical coordinates; they are usually high over the ground level with a small outlet diameter.

Fig. 2.2 Global distribution of natural emissions from different sectors in relation to air pollutants. (Source: IPCC 2014)



The term point source is frequently used for industrial smoke stacks and flare stacks. There are several point source processes, which released a significant amount of the criteria air pollutants into the atmosphere such as external combustion boilers (ECB), internal combustion engines (ICE), industrial processes, petroleum and solvent evaporation, etc.

2.2.3.2 Area Sources

Area sources are unlike point sources and have relatively larger horizontal dimensions. This is an area where several stationary sources are grouped together whose collective emissions can be significantly high as compared to the individual emissions. Thus, geographically they are considered as an area, and emissions are represented as a combined value. In this case, a residential area having several braziers continually emitting pollutants may be considered as area source. Mines and quarries are also considered as area sources.

2.2.3.3 Fugitive Sources

Fugitive sources are indefinable sources, which are difficult to identify. It may include seepage from the industries, oil spills, leak valves and pipes and pumps that release pollutants into the atmosphere. Such fugitive emissions only can be determined by using specific estimation techniques.

2.2.3.4 Volume Sources

Volume sources have comparatively huge horizontal and vertical dimensions. Examples include material sand piles, limestone piles and coal piles where wind may liberate particulate matter or dust.

2.2.4 Mobile Sources

Mobile sources are mostly associated with transportation and may be classified into on-road vehicles (motorcycles, passenger cars, trucks and commercial trucks and buses) and non-road vehicles and engines (aircraft, heavy equipment, boats, locomotives, marine vessels, farm machinery, recreation vehicles, etc.). Sometime, an unpaved road can also termed as mobile source because the allocation of emissions (primarily dust) is alike to that of a motor vehicle, i.e. the pollutants are emitted along a path. Briefly, criteria pollutants can be classified into the following.

2.3 Particulate Matter (PM)

Particulate matter (PM) refers to a suspension of solid, liquid or a combination of solid and liquid particles in the air (Hinds 1999). Particulate matters produced from both man-made and natural sources can be categorized into primary and secondary pollutants on the basis of their origin. Primary particulate matters are emitted directly from emission sources, and they are often associated with combustion sources. Secondary particulate matters are formed in the atmosphere by various photochemical reactions from primary pollutants like NO_x , SO_x and VOCs (Ito et al. 2005). The particulates emitted directly from their sources (construction sites, unpaved roads, fields, smokestacks or fires) are known as primary particulates like sulphur dioxides and nitrogen oxides that are emitted from power plants, industries and automobiles, while secondary particulates are formed by chemical reactions in the atmosphere. Sometimes outdoor particulate sources also contribute to indoor air pollution, apart from the outdoor PM sources: cooking, combustion activities such as use of unvented space heaters or kerosene heaters, candle burns, use of fireplaces and cigarette smoking. Indoor PM can also be of biological origin.

2.3.1 Particulate Matter in Atmosphere

Particulate matter of 10 micrometers or less in diameter is considered as PM_{10} . They are capable of penetrating deep into the lungs which causes severe respiratory problems. The fine particulates (aerodynamic diameters lesser than $2.5 \mu\text{m}$) are the most harmful among air pollutants. $\text{PM}_{2.5}$ particles can easily enter the alveoli and consequently be stuck to the lung parenchyma (Dockery 2009). $\text{PM}_{2.5}$ can cause various adverse health effects and cause cardiovascular problems, respiratory diseases and lung cancer (Hoek et al. 2013; Brook et al. 2010). The $\text{PM}_{2.5}$ is identified as a high-risk factor and placed on the ninth position out of all health risk factors in a study about the global burden of disease conducted in 1990–2010 (Lim et al. 2012). Figure 2.3 showed the annual PM_{10} distribution over the world considering periods from 2008 to 2015. It was mentioned that Eastern Mediterranean cities (Riyadh, Ma'ameer, Dora and Abu Dhabi) were observed with very high

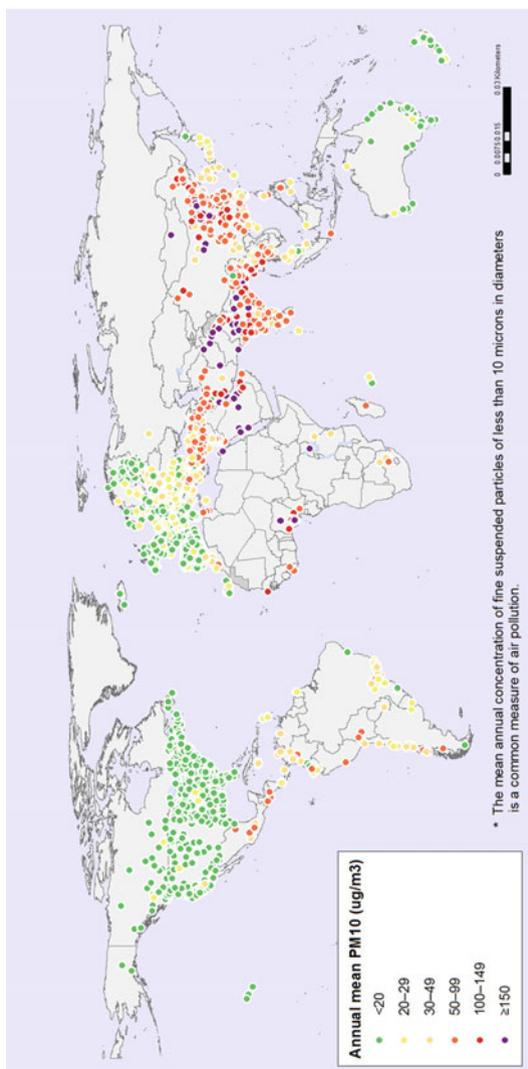


Fig. 2.3 Annual average 10 μm or less (PM_{10}) over the world for 2008–2015 (World Health Organisation 2016)

average concentration ($>200 \mu\text{g}/\text{m}^3$) over the world; the second highest level were observed in the cities of Southeast Asia (Delhi, Dhaka, Colombo and Karachi) with high annual average concentration ($150\text{--}200 \mu\text{g}/\text{m}^3$). The Western Pacific region was noticed with slightly low average levels but lies in the range of $100\text{--}149 \mu\text{g}/\text{m}^3$, whereas Africa region was found with relatively high concentration as compared to the levels of PM_{10} observed in America and Europe.

I) Urban Aerosols These are complex mixtures of primary pollutants (release directly from the sources such as motor vehicles, power plants, industries, forest fire, volcanic eruptions, etc.) and secondary pollutants (formed into the atmosphere through atmospheric transformation reactions such as gas-to-particle conversion mechanisms). Urban aerosol is rich in smaller particles ($<0.1 \mu\text{m}$) and usually found in the size range of $0.1\text{--}0.5 \mu\text{m}$ in diameter. Moreover, in urban areas, there are two major aerosol mass distribution modes including submicron size (accumulation mode) and the coarse particle mode. A significant variation of the aerosol size distribution was noticed, and high concentrations of fine particulate matter (less than $0.1 \mu\text{m}$ in diameter) are found near sources such as highways, but their levels dropped quickly with distance from the source, which explains the particle numbers as a function of their diameter in diverse conditions. There is approximately an order of magnitude more particles close to the freeway compared to the average urban concentration. Such type of distribution indicates towards the fine particles ($<0.1 \mu\text{m}$) in the urban area, where fine particles are found in their majority. In urban area atmospheric aerosol size distributions depend on their multimodal character. Thus, mass distribution is characterized by three modes (with a size range between 1.0 and $3 \mu\text{m}$). The particle size larger than the fine mode is considered as the coarse mode particle. Thus the three modes are present in the mass distribution and correspond to the nuclei mode (particles below $0.1 \mu\text{m}$) and accumulation mode ($0.1 < \text{Dp} < 1 \mu\text{m}$) (Whitby and Sverdrup 1980). Thus both accumulation mode and nuclei mode come under fine mode particle category. The boundaries between these sections are very precise. The classification of the particle distribution is based on their mass and volume distribution. Table 2.2 shows the global total emission estimate from different natural and man-made aerosol sources.

II) Rural Continental Aerosols With minor human disturbance, aerosols in the rural area are mainly of natural origin (Hobbs et al. 1985). The number distribution is characterized by two modes with a size range from 0.02 to $0.08 \mu\text{m}$ (Jaenicke 1993), while the mass distribution is dominated by the coarse mode centred at around $7 \mu\text{m}$. The mass distribution of continental aerosol, not affected by neighbouring sources, has a small accumulation mode and no nuclei mode. The PM_{10} concentration of rural area is approximately $20 \mu\text{g m}^{-3}$.

III) Marine Aerosols The marine sources of the aerosol play a significant role in atmospheric aerosol composition and contribute around $1000\text{--}10,000 \text{ Tg}$ per year. They usually have a large size fraction aerosol ($>2\text{--}20 \mu\text{m}$ diameter), thus cannot be transported at the remote distance. Sea salts are the major fractions of the marine

Table 2.2 Global sources of atmospheric aerosols (in megatonnes per year)

<i>Aerosol sources</i>	<i>Total emissions $D < 25 \mu\text{m}$</i>	<i>Emissions $D < 25 \mu\text{m}$</i>
<i>Manmade</i>		
<i>Primary:</i>		
Industrial dust	40–130	20–65
Soot	10–30	10–30
Biomass burning	50–190	50–190
Windblown dust	820	140
<i>Gas-particle conversion of:</i>		
SO ₂ : Smelters/power plants	120–180	120–180
NO _x : Autos/power plants	20–50	5–10
Anthropogenic VOCs	5–25	5–25
<i>Total manmade sources</i>	1065–1325	565–640
<i>Natural</i>		
<i>Primary:</i>		
Windblown dust	1000–3000	265
Forest, fires	3–150	2–75
Sea salt	1000–10000	20–100
Volcanoes	4–10000	0.4–100
Organics	26–50	—
<i>Gas-particle conversion of:</i>		
DMS, H ₂ S	60–110	60–110
Volcanic SO ₂	10–30	10–30
Biogenic NO _x	10–40	10–40
Biogenic VOCs	40–200	40–200
NH ₃ to NH ₄ ⁺ salts	80–270	80–270
<i>Total natural sources</i>	1363–3550	397–1390

Adapted by L. Barrie

aerosol and originate when the air bubbles burst at the ocean surface. Several small water droplets are produced during this process. An average 3 mm bubble throws out 100–200 film droplets into the atmosphere. After the droplets evaporation, it leaves sodium chloride around 85%, whereas sulphate of calcium and ammonium contributes around ~3.5% of the mass seawater. In the process of bubble blasting, it also ejects some of the organic chemicals and bacteria into the atmosphere near the ocean surface.

IV) Biogenic Aerosols These are the solid and liquid particles formed into the atmosphere after the chemical conversions of the substance released through plants. These substances include seeds, pollen, spores and fragments of animals and plants. These usually range between 1.0 and 250 μm in diameter. Bacteria, algae, protozoa, fungi and viruses are generally $<1 \mu\text{m}$ in diameter. In addition, oceans are important sources of biogenic aerosols. They are injected into the atmosphere by the bursting of air bubbles and by sea foam. Secondary biogenic aerosols are formed by gas-to-particle conversion of biogenic volatile organic compounds.

V) Volcanic Aerosols Volcanoes symbolize one of the most significant natural sources of pollutants to the atmosphere, both during and between eruptions. It releases gases and particulate matter into the atmosphere. After volcanic eruption, coarser particles are settled readily within the short period, while the fine particles are formed by the gas-to-particle conversion of reactions such as formation of sulphate aerosol from SO_2 . A blast from volcanoes at a higher altitude may play an important role at global level after their transboundary movement. Pollutants released from the volcanic eruptions also contribute in the stratospheric chemistry.

VI) Anthropogenic Aerosols Around 10–20% of aerosols are considered as anthropogenic, or human-made, which may come from a variety of the sources. Aerosol from the anthropogenic sources is less abundant as compared to the natural sources and can dominate the air downwind of urban and industrial areas. The major anthropogenic source of aerosols includes road dust, Aeolian wind, biomass burning, combustion-related sources and industrial processes. Anthropogenic emitted aerosol particle ($>5 \mu\text{m}$ diameter) dominate over aerosols, those formed in the atmosphere, by gas-to-particle conversion (secondary particles). In contrary to larger particles, smaller particles are produced mainly by gas-to-particle conversion released from the anthropogenic sources. Sulphate aerosols contribute around 35% of the fine aerosols in the atmosphere which are formed by oxidation of SO_2 emissions. Particle emissions universally dominated by fossil fuel combustion (primary coal) and biomass burning.

2.3.2 Health Effects of PM_{10}

Detrimental effects of PM_{10} have been reported worldwide. Inhalation of PM causes risk of mortality. Long-term exposures to PM have been linked with decline in life span, due to cardiopulmonary mortality and lung cancer, among other diseases. Children with asthma are also more susceptible to ambient PM_{10} (Pope and Dockery 1992).

2.3.3 Chemistry of Particulate Matter

2.3.3.1 Chemical Composition of PM

The atmospheric aerosol has a very typical and made up of variety of chemical compounds. Every individual particle has its characteristic chemical composition which depends on their emission sources and their transformation in the atmosphere. These aerosols have variable levels of chemicals such as cations (sodium, potassium, calcium and ammonium) anions (sulphate, nitrate, fluoride and chloride), crustal elements, sea salt spray and organic materials including carbonaceous contents (elemental and organic carbon). The coarser fractions of the particulate matter mainly contain dust, crustal components, ions (nitrate, sodium, chloride) and biological particles such as pollen, spores, plant remains, etc., whereas fine particles

consist ammonium, sulphate, nitrate elemental and low molecular weight carbon components and some trace metals such as lead, nickel, copper, cadmium, etc.). In the atmospheric transformation processes, the sulphate aerosols are formed from the emissions from industries and volcanoes containing sulphur dioxide (SO_2) and dimethyl sulphide (DMS) released from biogenic sources such as marine planktons. Nitrate (NO_3^-) is formed after the oxidation of the atmospheric nitrogen dioxide (NO_2) predominantly formed after anthropogenic combustion activities such as biomass burning and vehicular emission. Apart from the above-mentioned ammonium salts are also other source for the atmospheric aerosols and formed after reactions with ammonia and several acids such as sulphuric (H_2SO_4) and nitric acids (HNO_3). Ammonium chloride (NH_4Cl) aerosol particle is formed after the atmospheric reactions between ammonia (NH_3) and hydrochloric acid (HCl), whereas the sea salt spray acts as major source for chloride ions. Usually, large fractions of the aerosol are contributed by carbonaceous content which is highly variable in the atmosphere and consists of organic carbon (OC) and elemental carbon (EC), whereas the ratio of both the fractions depends on the type of sources. The major sources of the carbonaceous aerosol are different in the urban and rural area. In most of the cases, the major sources of OC and EC in urban area are emissions from coal thermal power plants, vehicular emissions and other fossil fuel sources. In the rural area, it can be released majorly from biomass burning or crop burning. Aerosol particles in the atmosphere are also formed by secondary organic aerosol (SOA) formation after atmospheric oxidation of volatile organic compounds (VOC) emitted either from anthropogenic or biogenic sources.

2.3.3.2 Gas-Particle Conversion and Secondary Aerosol Formation

Nucleation is the process responsible for the formation of the smaller atmospheric aerosol particles through gas-to-particle conversion (Abraham 1974; Kaschiev 2000; Laaksonen et al. 1995; Anisimov 2003). In the process of gas-to-particle conversion, gases released into the air may be transformed into condensable molecular species, e.g. formation of sulphuric acid from SO_2 . The rate of the transformation of the condensable molecules to aerosol particles/droplets depends on the vapour concentration of the aerosol particles. In the case of sulphuric acid, water condensation also occurs to maintain equilibrium in condensed-phase activities. Apart from the above-mentioned concept, another theory is applied to sulphuric acid/water condensation where the sulphuric acid mass transfer acts as the limiting process (Pandis et al. 1994, 1995; Van Dingenen and Raes 1991).

The gas-particle partitioning is also found involved in the formation of secondary organic aerosol (SOA). The low volatile organic compounds undergo photooxidation reactions for the formation of SOA. Studies related to the SOA and its formations are the topic of great interest in today's research, and it may be due to their possible impacts on earth's radiative balance linked to the climate change (Pilinis et al. 1995), visibility degradation (Eldering et al. 1993; Eldering and Cass 1996) and health effects (EPA 1996). The formation of SOA from the volatile organic compounds (VOCs) is one of the most important oxidative mechanisms. Terpene family is contributing significantly in the formation of the SOA, which is

emitted from terrestrial vegetation (Altshuller 1983). Monoterpene and sesquiterpenes are the most important VOCs studied and reported in various studies as important contributors for the SOA formation (Claeys et al. 2004; Leaitch et al. 1999). Aromatics released from the anthropogenic sources are the other cause for the formation of SOA in the atmosphere (Jeffrie 1995). Thus the SOA contribute significantly to the particles specially $PM_{2.5}$, which is responsible for the adverse health impact such as lung and cardiovascular problems in human being.

2.3.4 Ambient PM and Their Atmospheric Processes

Transportation-related aerosol contributes at majority in the urban area atmosphere. These particles are mostly fine agglomerates of carbonaceous substances present in accumulation mode (Morawska et al. 2008). Particularly, PM has great contribution in the formation of secondary organic aerosol (SOA). Secondary particles are majorly made up of SO_4^{2-} , NO_3^- , NH_4^+ and SOA, whereas inorganic secondary aerosols originated through gas-phase precursors [e.g. sulphur dioxide (SO_2) and oxides of nitrogen (NO_x)] via oxidation reactions in the atmosphere (Seinfeld and Pandis 1998; Pinder et al. 2004). By the oxidation reaction, high molecular weight volatile organic compounds (VOCs) are converted into low volatile products which consequently condense onto the accessible aerosols (Seinfeld and Pandis 1998). Particulate heterogeneous reactions (inside clouds and fog) also contribute in the SOA formation (Jang and Kamens 2001; Jang et al. 2003). According to Robinson and co-workers, the gas-particle partitioning of semi-volatile organic compounds may produce gas-phase organic compounds in the atmosphere, which afterward participate in the SOA formation (Robinson et al. 2007). They also reported the elevated OC/EC ratio during night and early morning hours of foggy days in Indo-Gangetic Plain (IGP), which indicated towards the reported enhanced SOA production in aqueous phase (Kaul et al. 2011). OC/EC ratios further explain the identification within foggy and non-foggy days, episodic events to non-episodic events and primary aerosol to secondary aerosol (Chakraborty et al. 2016; Rastogi et al. 2016; Choudhary et al. 2018). Another study reported the elevated SOA during late afternoon and night in the winter especially during foggy days (Strader et al. 1999), whereas the high SOA level is observed during early morning in foggy period. Another study reported a daily average level of the SOA (obtained from EC/OC), varied between 1.2 and 7.4 μgCm^{-3} at Bakersfield, 1.2 and 6.8 μgCm^{-3} at Fresno, 0.3 and 1.3 μgCm^{-3} at Kern Wildlife Refuge and 1.0 and 1.7 μgCm^{-3} at the Chowchilla site. This observed that SOA corresponds to 8–34% of OC at Bakersfield and Fresno, 5–26% for Kern and around 20% for Chowchilla. This vision proposes that SOA is produced during wintertime, while majority of OC is the result of primary emissions (Chow et al. 1999).

2.3.4.1 Hygroscopicity and Ageing of PM

The hygroscopic nature of aerosols plays a significant role in the atmospheric processes, climate and health issues (Tang 1996; Hiller 1991; Gysel et al. 2002;

Ferron et al. 2005). Moreover, hygroscopicity has a significant role in the formation of the cloud condensation nuclei (CCN) which further alters the precipitation patterns and amount in a particular region (Reutter et al. 2009). The hygroscopic growth of the aerosols depends on the particles' diameter and relative humidity (Swietlicki et al. 2008; Massling et al. 2005). The ageing of the particulate matter was also studied in relation to the hygroscopicity and explained on the basis of changes in morphology formation of cluster aggregates. The ageing is also studied in relation with secondary organic aerosol formation in the atmosphere after several chemical transformations (Vu et al. 2015; Rönkkö et al. 2018). A major contribution of the secondary aerosol contents indicates towards the dominant role of ageing and long-range transport of fine mode aerosols. The long-range transport-driven dilution of the pollutants and aerosol ageing are both responsible for the decreased toxicological effects. Every particulate matter has a definite lifetime in the atmosphere, and before settling they travel few meters to thousands of kilometres through long-range transport under the influence of meteorological parameters such as wind directions and wind speed (Hämeri et al. 2001; Swietlicki et al. 2008).

2.4 Carbon Monoxide (CO)

Carbon monoxide (CO) is a colourless, odourless, flammable and tasteless gas. It is very toxic for several organisms including human being. CO does not have a direct role in regulation of global temperature but plays an important role in atmospheric processes. It affects the self-cleaning ability of the atmosphere from harmful gases. Carbon monoxide (CO) is the most widely dispersed and the most commonly occurring air pollutant. In the atmosphere, it is found in very low concentration areas (typical concentration of CO in troposphere is around 100 ppb), whereas in clean air, it may fall up to 50 ppb. The average lifetime of CO is several months in the atmosphere. The gas ultimately reacts with oxygen (O_2) to form carbon dioxide (CO_2).

2.4.1 Sources

Carbon monoxide are produced in the incomplete combustion of organic materials, such as gasoline, natural gas, oil, coal and wood. Carbon monoxide are released from a variety of natural (volcanoes and biomass burning) and anthropogenic sources (automobile and industrial fossil fuel combustion). The total annual global average CO emission is estimated to be as high as 2600 MT, out of which anthropogenic activities and natural processes contribute about 60% and 40%, respectively (USEPA 1991). The largest proportion of overall CO is released by the petrol-driven motor vehicle with internal combustion engines, which is increasing at an alarming rate since the past few decades (Cullis and Hirschler 1989). Power plants using coal, industrial processes and waste incinerators are the other common sources of CO in the atmosphere. Gas stoves, space heaters fuelled with oil/gas/kerosene and tobacco smoke are the major CO emission sources in indoor environment.

2.4.2 CO Level and Trend

The total estimated annual average CO emission from different sources is found to be around 200 million tons, adequate to elevate the atmospheric background level of CO by 0.03 ppm per year (Haagen-Smit and Wayne 1968). Figure 2.4 shows the significantly variable carbon monoxide (CO) concentration across the globe with seasonal changes. Agricultural burning activities affect the seasonal variations in CO in Central Africa which shift north and south of the equator according to the seasons. Biomass burning and internal combustion engines contribute a significant amount of CO in the Southern Hemisphere (Vallero 2014).

There are different inventory-related studies reported for the carbon monoxide such as MACCity inventory (based on Representative Concentration Pathway) which found a drop in CO release from the USA and Europe during the period of 2000–2010 due to rising pollution control (Granier et al. 2011; Riahi et al. 2007). Some other studies (working on REAS and EDGAR4.2 inventories) showed the increasing emission from China (Kurokawa et al. 2013; EC-JRC/PBL 2011). Several authors also confirm an increase of CO emissions in China with 18% and 6% in the period of 2001 to 2006 and 2005 to 2009, respectively (Zhao et al. 2012). Surface levels of CO show descending trends over the USA influenced by the drop in emission (EPA 2011), consistent with the space-based trends.

2.4.3 Chemistry and Sink of CO

The formation of atmospheric CO is governed by the interrelationship among anthropogenic emissions, atmospheric chemistry and climate. Levy (1971) found that carbon monoxide (CO) is oxidized by hydroxyl free radicals (OH) to form hydroperoxyl radicals (HO₂) in the troposphere.



It also estimated that under the environment enriched with oxides of nitrogen reactions following X and Y produce ozone (Crutzen and Zimmermann 1991). On contrary in the absence of proper concentration NO_x, hydroperoxyl radicals kill ozone. Moreover, reaction chain is a CO sink and generates carbon dioxide. According to DeMore and co-workers, the first and fast reaction (X) is independent of temperature (DeMore et al. 1994); it directs to a global mean CO life of 2 months in the atmosphere and is the important OH radical sink in the troposphere (Crutzen and Zimmermann 1991; Sze 1977). CO together with CH₄ is an important index of tropospheric oxidizing capacity, symbolized particularly by the levels of ozone and hydroxyl free radicals. Based on observation and model estimation, several authors reported that CO levels have also increased very much from preindustrial levels, affecting atmospheric chemistry (Khalil and Rasmussen 1990; Crutzen and

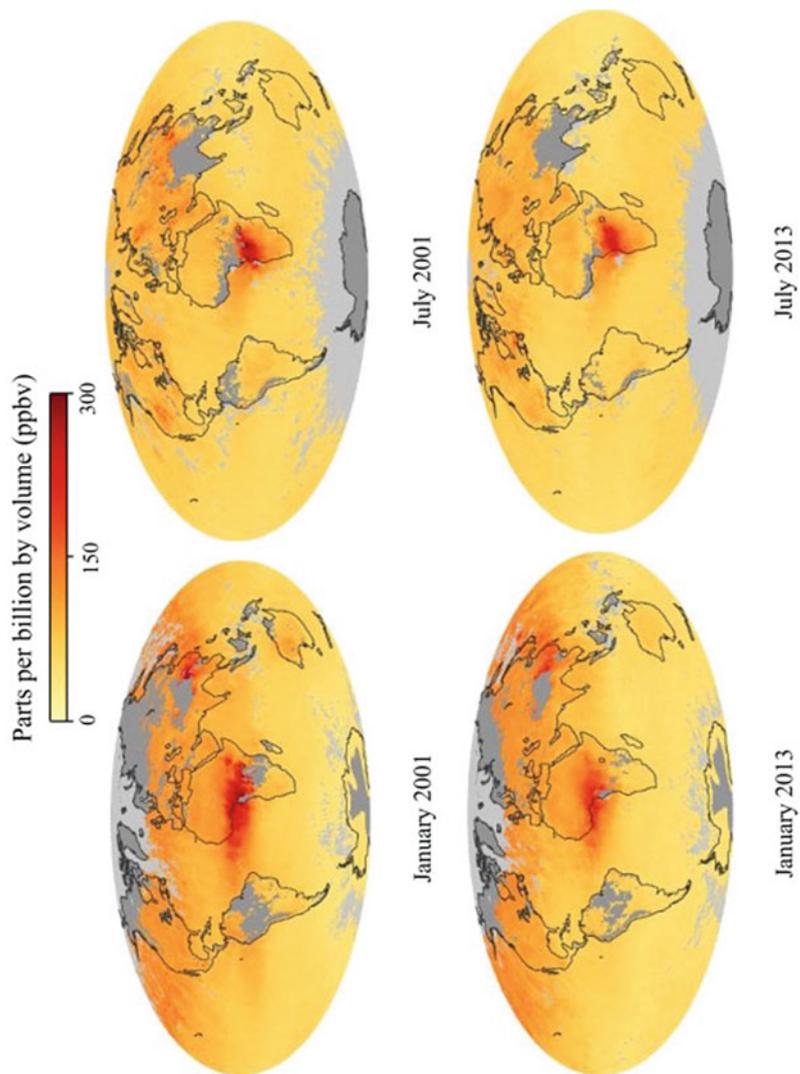
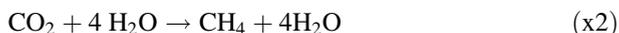


Fig. 2.4 Global distribution of carbon monoxide. (Source: Vallero, in *Fundamentals of Air Pollution* (Fifth Edition), 2014)

Zimmermann 1991; Thompson and Cicerone 1986). Moreover some authors observed the increasing levels of CO and CH₄ at slow rate in early 1990 (Khalil and Rasmussen 1995; Novelli et al. 1994). Apart from the above-mentioned chemical transformations, changes in the temperature and H₂O can also change the distribution and concentration of CO and CH₄ in the atmosphere (Wang and Prinn 1998; Klonecki and Levy 1997). Most of the accumulated CO from the lower atmosphere which usually move by atmospheric mixing of the possible sink in the upper atmosphere were oxidized to CO₂ under the influence of ultraviolet, visible and near-infrared solar radiation (Fleagle and Businger 1963). Lower molecular weight of the CO as compared to the air causes a migration of the lighter weight CO into the stratosphere. Soil is another driving force responsible for the removal of atmospheric CO through the earth's surface where CO is oxidized and converted into methane in the presence of soil moisture and microorganisms (*Methanobacterium formicum* and *Methanosarcina barkeri*). This has been confirmed by Schnellen (1947) who established that pure cultures of *Ms. barkeri* and *Mb. formicum* change CO into methane, CH₄; in the deficiency of H₂, CO reacts with H₂O, according to Stephenson (1949), in two phases:



the CO₂ and N₂ subsequently reacting



In the presence of H₂, these bacteria convert CO into methane and water:



A quite substantial amount of methane produces from CO in the presence of pure H₂O, according to the equation:



Haemoglobin (Hb) also acts as important sink for the atmospheric CO. An average healthy person is exposed to a small amount of CO which present in the air he/she inhales. When CO reaches the lung surface through the bronchi and alveoli, it gets discharged into the blood. After attaining equilibrium with the blood, each ppm of CO in air inactivates 1/6 of 1% of the body's haemoglobin.

2.5 Lead (Pb)

Lead is a bluish-white, soft, shiny, highly malleable, ductile metal. Lead is a metal having very poor conductivity. It is a non-corrosive but tarnishes upon exposure to air. Lead has been recognized and included in the EPA National Priorities List (NPL) (HazDat 2006). There are so many sources of lead in air. One of the major

contributors has been from leaded gasoline. Before EPA regulations, millions of tons of lead are added into the atmosphere through use of lead in gasoline. Even after restriction a high level of this lead is still present into the soil and dust. Other sources include lead paints and industrial emissions, which released a significant quantity into the ambient atmosphere. These industrial sources included smelters, manufacturing operations, incinerators, refineries, power plants, recycling facilities, etc.

Leaded gasoline is the major source for lead. It is released into the ambient atmosphere after the combustion of leaded gasoline in the form of small particulates. These particulates remain suspended in the atmosphere for a definite time period and fallout into the soil and dust and thus it creates poison generations unless covered or removed. Due to the dispersive nature of gasoline, the lead may be easily emitted from a motor vehicle and may enter into the human body and may cause several health-related problems in the population especially children and elderly people in the urban area. Lead poisoning may happen at workplace and at home, it totally depends on the activities that happen in a respective environment that people get affected by lead exposure. The most common sources at occupational/home are radiator repair shop or lead factory, industry related to lead battery recycling, furniture refinishing or making stained glass and demolition or painting, etc.

2.5.1 Sources

Lead is an omnipresent criteria air pollutant in the environment. On the universal scale, a large amount of pollutant is emitted into the atmosphere from the motor vehicle using alkyl lead-added gasoline. The source apportionment through mass balance confirmed the decrement of the atmospheric lead concentration along with the reduction in the alkyl lead level in petrol from the 1980s. The concentration of Pb in the air depends on the levels of Pb released in nearby areas through emission, height of emission outlet area, the topography and other features including meteorological conditions. Other sources/processes such as manufacturer of lead compounds and goods and refuse incineration also released lead emissions. Several other industrial actions such as coal combustion, iron and steel manufacturing and copper smelting also considered as additional sources into the atmosphere. The natural sources such as sediments, rock and minerals typically have lower levels of lead.

2.5.2 Levels and Distribution of Lead

Figure 2.5 shows major lead pollution sources and their contribution in different emission sectors.

It is observed that a total annual average lead released into the atmosphere through different sources is 0.33×10^9 kg (Nriagu and Pacyna 1988). The reported lead concentration through natural sources in the atmosphere was 0.6 ng/m^3 during

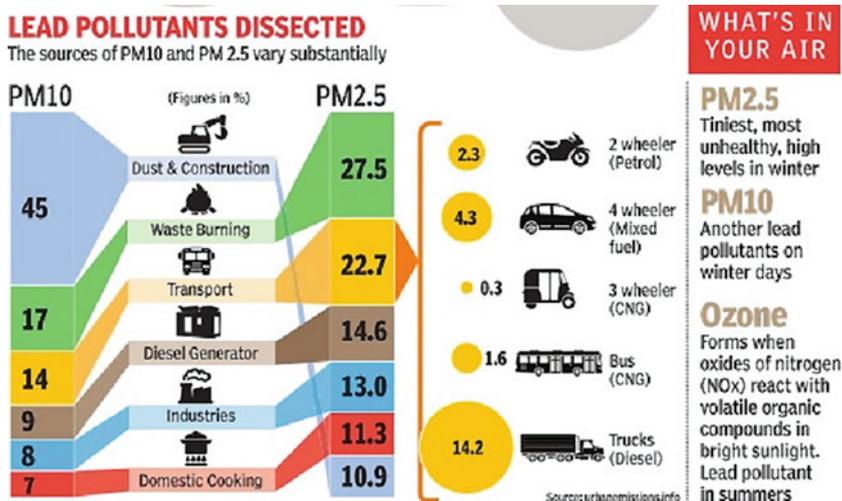


Fig. 2.5 Contribution of the lead sources from different sectors

preindustrial time (Patterson 1965). Several site-specific studies found lead levels in the range of 0.005–0.44 $\mu\text{g}/\text{m}^3$ in different cities of France and the USA during 1984–1985 with the highest concentration at Paris (Delumyea and Kalivretenos 1987). On using lead-free petrol, a drastic decrease in lead concentration in air is observed in industrial and urban areas having high traffic density from the past several years. It was from 0.17 and 0.19 $\mu\text{g}/\text{m}^3$ to 1.30 and 1.37 $\mu\text{g}/\text{m}^3$, respectively (Ministerium Für Umwelt 1989). Most of the lead in the air is generally found associated with the fine mode of the particulate matter especially below 1 μm . Most of the lead in the atmosphere (>90%) are released from the emission generated from the combustion of leaded petrol emission with inorganic particles such as PbBrCl, whereas the rest of the 10% lead are dominated by organic lead (predominantly lead alkyls). In contrast to the above-mentioned, predominance of the coarser particles came into the existence in the vicinity of smelters, which may be deposited at few hundred meters. Lead either deposited onto land/ocean by dry or wet deposition processes. The deposition of the lead-containing particles depends on several factors such as rainfall, wind speed, wind directions and the emission height. The fallout of lead-based compounds is released from the industrial emission and depends their distance from sources. Moreover some of the authors found lead deposition at a long distances and has been confirmed by determination of glacier ice and snow deposited at distant location, like Greenland, until about 1960 (Murozumi et al. 1969). Nevertheless, successive analysis showed a descending trend in the same glacial strata (Boutron et al. 1991).

2.5.3 Exposure, Chemistry and Sink of Lead

Most of the lead in the atmosphere are present along with the fine particulate matter and easily undergo into the human respiratory system through inhalation and may be easily retained and absorbed into the body.

The particle size distribution and ventilation rate are the factors affecting absorption of particles through the respiratory system. The absorbed portion of lead is circulated in several important components such as blood, soft tissues, bones and teeth. An adult human contains most of the lead (95%) in their bones, while it may found up to 70% in children (Barry 1981). About 99% of the lead in the circulatory system is bound to red blood cells. The level of lead in the body increases over time/age, more frequently in males especially in their bones (Barry and Mossman 1970).

Some of the studies also confirmed the mobilization of lead during pregnancy (Gulson et al. 2016; Wells et al. 2011). Some reports also indicate that children, mostly infants, have a larger level of lead (USEPA 1994). Another recent study also found an inverse connection between blood lead concentration and IQ score (Lanphear et al. 2005). The chronic exposure of lead in human leads to the development of cancer, elevated blood pressure and neurodegradation. Blood, urine, bone, tooth and hair are identified as major biomarkers related to lead exposure. There can be several pathways for the lead metabolism at cellular levels, but at molecular levels, the replacement of Zinc (Zn) with lead (Pb) in zinc proteins with functional consequences is one of the major paths. Despite the fact that scientist detected the hazards of the lead exposure from several decades, vagueness remains as to the threshold for adverse effects on our health and the low concentrations of exposure during our life as a risk factor for chronic disease (Maret 2017).

Lead is basically removed by the several processes such as rainfall, sedimentation and snowfall from the atmosphere. Thus the soil and sediments are the ultimate sinks for lead, whereas an average healthy man is exposed by a mean of about 300 mug of lead/day in his food with a range of 100–400 mug (Haar 1975). Lead is transported continuously among different matrices such as air, water and soil through natural and physicochemical processes such as weathering, runoff, wet and dry deposition and stream/river flow; nevertheless, soil and sediments are identified as important sinks for lead.

2.6 Nitrogen Dioxide (NO₂)

Nitrogen dioxide is a reddish-brown gas with an unpleasant and annoying odour. This is a primary gas released into the atmosphere after burning of fuel. NO₂ is a strong oxidizing agent that plays an important role in atmospheric transformation reactions and converted into gaseous nitric acid, toxic organic nitrates and tropospheric ozone (major component of smog). Due to its contribution in the formation of photochemical smog, it is identified as one of the important air pollutants having significant impacts on human health. The elevated concentration of NO₂ causes health-related problems such as problems related to short-term exposure

(cardiovascular and respiratory) and long-term exposure (cancer and mental development in children). Apart from the above-mentioned, nitrogen dioxide also reacts with different atmospheric pollutants and produces high levels of ozone (which also have adverse impacts on human and plants).

2.6.1 Sources of NO₂

Atmospheric oxidation of ammonia, microbial activities in soil and lightning are the most important natural processes resulting to the formation of the NO₂ (Lamarque et al. 1996; Lee et al. 1997). The anthropogenic sources are of more significance than natural sources in terms of the NO₂ and O₃ air pollution, as they are more concentrated in the more populated areas. The high-temperature fuel combustion in vehicles and in industrial and utility boilers is the main man-made source of NO₂ emissions. The emissions from power plants, motor vehicle and off-road equipment are the other major sources for nitrogen dioxide in the atmosphere. Petrol and metal refining, manufacturing and food processing industries also released a significant amount of NO₂ into the atmosphere. The oxides of nitrogen are emitted in the form of NO, but it readily converts into the NO₂ due to the oxidation processes in the atmosphere. In the presence of O₃, the reaction happens at a very high rate. In most of the cases, formation of NO₂ is under the influence of ground-level O₃.

2.6.2 Levels and Distribution of NO₂

In the ambient atmosphere, oxides of nitrogen exist in the form of nitric oxide (NO) and nitrogen dioxide (NO₂). Both act as the pollutants in the lower atmosphere, whereas nitrous oxide (N₂O) acts as a greenhouse gas. It can be emitted in the form of NO, a colourless, tasteless gas. NO₂ is a gas with pungent, irritating odour with strong oxidizing properties. In the atmosphere, it is readily converted to the nitric acid and ammonium salts. In dry atmospheric condition, the nitrogen oxide is converted to the nitrate aerosols. These chemicals are removed from the atmosphere through wet and dry deposition process. Around 10% and 90% of the total NO_x was contributed by natural and anthropogenic sources, respectively (Godish 1991). The natural sources include lightning, volcanic eruption and photochemical destruction of the nitrogenous compounds in the upper atmosphere. Fossil fuel burning, thermal power plants and vehicular emission are the major activities contributing NO₂ in the atmosphere and contribute about 50% of the total anthropogenic emission. Other source includes incinerators, mining activities, welding process, etc. Global annual emissions of the nitrogen oxides are found to be 50 million metric tons (World Resources Institute 1994). The USA produces around 20 million metric tons (MMT) of NO_x, and it is 40% of the NO_x produced by mobile sources, whereas about 11–12 MMT of NO_x is produced from stationary sources, out of which around 30% is the result of fuel combustion and 70% is from electric utility furnaces (Cooper and Alley 1986).

Table 2.3 Sector-wise global NO_x emission and projections in Mg

Sector	2010	2015	2020	2025	2030	2035
Petroleum refining plants	1544	1404	1404	1404	1404	1404
Commercial and institutional plants	878	699	667	647	625	602
Residential plants	6617	5519	4726	4751	4796	4859
Plant related to agroforestry and aquaculture	705	747	892	1056	1220	1292
Combustion-based industrial plants	5941	4843	4150	3965	3782	3647
Public power sector	16,146	9341	9424	9439	10,701	11,500
District heating plants	2766	2713	2180	2356	2203	2790
Oil/gas extraction	6490	5454	6007	8039	9555	9452
Total	41,087	30,719	29,450	31,659	34,287	35,546

Data Source: Nielsen et al. (2013)

The global annual average of NO₂ in urban areas is observed in the range of 20–90 µg/m³. Hourly averages near busy roads usually exceed 1000 µg/m³ (World Bank 1998). The picture of NO_x emissions would be more clear if the projection issues can be brought into focus; therefore, Table 2.3 shows clearly the NO_x projections in different years. The ambient concentration of the NO₂ depends on several factors such as day timing, season and meteorological parameters. The high value of the NO₂ is observed usually in the typically, urban concentration peak in the morning and afternoon rush hours due to the high volume of traffic on road. The winter season was observed with a higher level of NO₂ as compared to other seasons across the world, and it is due to the traffic conjunction in foggy days and increased use of heating fuels and low mixing height. Since, the change of NO₂ from NO depends on its concentration in the atmosphere and solar intensity. The levels of NO₂ are usually found higher during warm and sunny days. NO_x levels drop speedily as distance increases from its source. Levels of NO_x in rural areas are very close to its background concentrations in the absence of any major source (USEPA 1990). Nevertheless, oxides of nitrogen may participate in the long-range transport, and thus they participate in the acid rain formation/deposition and elevated ozone in the upper atmosphere even in the absence of nearby emission sources. The indoor levels of the NO_x found relatively high as compared to the outdoor level of NO_x, thus one of the major causes of concern for indoor environment and human health. Sources of indoor NO_x include cigarette smoke, cooking appliances and space heaters. The level of NO₂ may exceed up to 200 µg/m³ over a period of several days. The real-time NO₂ concentration may reach up to 500–1900 µg/m³ during cooking and 1000–2000 µg/m³ where a gas-fired water heater is also in use. The smoke of single cigarette may have 150,000–225,000 µg/m³ of NO and some quantity of NO₂ (Canada, Federal-Provincial Advisory Committee on Air Quality 1987).

The findings reflected that tropospheric NO₂ column concentration has raised in China (11 ± 2.6%/yerr), South Asia (1.76 ± 1.1%/year), Middle East (2.3 ± 1%/year) and South Africa (2.4 ± 2.2%/year). Tropospheric NO₂ column concentration

confirms some drop in the Eastern USA ($-2 \pm 1.5\%/year$) and Europe ($0.9 \pm 2.1\%/year$). It was drawn that even though tropospheric NO_2 column concentration drops in the main developed countries in the past few years, the current tropospheric NO_2 column concentration in these countries is still considerably more than those found in newly and rapidly developing countries (excluding China). Tropospheric NO_2 column concentration is observed with some drop in South America and Central Africa, characterized by main biomass burning area in the Southern Hemisphere. Ghude et al. (2013) reported the situation for India and observed a growth rate of $3.8\% \pm 2.2\% year^{-1}$ between 2003 and 2011 for man-made sources, which is significantly linked to the escalation in oil and coal utilization in India. Hilboll et al. (2013) observed tropospheric NO_2 column concentration to be drastically rising over China, the Middle East and India, with values over East-Central China tripling from 1996 to 2011. An important concentration of NO_2 drops during the period, which is observed in the USA, Western Europe and Japan. In terms of city-wise emissions, Dhaka, Bangladesh ($+27.2 \pm 3.9\% year^{-1}$), and Baghdad, Iraq ($+20.7 \pm 1.9\% year^{-1}$), were at a higher level, while Los Angeles, USA, ($-6.00 \pm 0.72\% year^{-1}$) was at the lower position. Megacities (population > 10 million) in China, India and the Middle East have indexed increasing NO_2 columns of +5 to 10% $year^{-1}$. Lamsal et al. (2011) observed a rise in man-made NO_x release over land by 9.2% globally and by 18.8% from East Asia throughout 2006–2009. The emission from North America observed to drop by 5.7% in the similar period. Delmas et al. (1997) found fossil fuel burning ($\sim 50\%$) and biomass burning ($\sim 20\%$) as dominant sources of NO_x globally. Natural sources (lightning and microbial activity in soils) are observed by contributing less than 30% of total emissions. Huntrieser et al. (2002) observed that a higher NO_x is originated by lightning (mean 3 TgN $year^{-1}$) as compared to the NO_x released by aircraft (0.6 TgN $year^{-1}$) for Europe as well as on a global scale. Figure 2.6 shows a world map of nitrogen dioxide tropospheric column density.

2.6.3 Chemistry of NO_2 in the Atmosphere

Atmospheric photochemical reactions are particularly related to meteorological parameters such as temperature, pressure, wind speed and solar radiation. It also depends on the absolute concentration and the relative ratios of NO_x (NO , NO_2) and volatile organic carbons (VOCs) (Nevers 2000). The magnitude of ozone concentration variation is high in clear days as compared to cloudy days. Several studies found the relative higher concentration of ozone in weekends as compared to weekdays due to the relative low concentration of the ozone precursors (NO_x and VOCs) at weekends (Cleveland et al. 1974; Sakamoto et al. 2005 and Qin et al. 2004).

In the urban areas, NO is released from different emission sources and decreases the ground-level ozone concentration in absence of solar radiation, while in the rural areas, ozone concentration shows the comparatively less diurnal variability due to absence of NO_x emission sources (Frey et al. 2013). Sillman (1999), Kley et al. (1999) and Jenkin and Clemitshaw (2000) have reported complete information of the

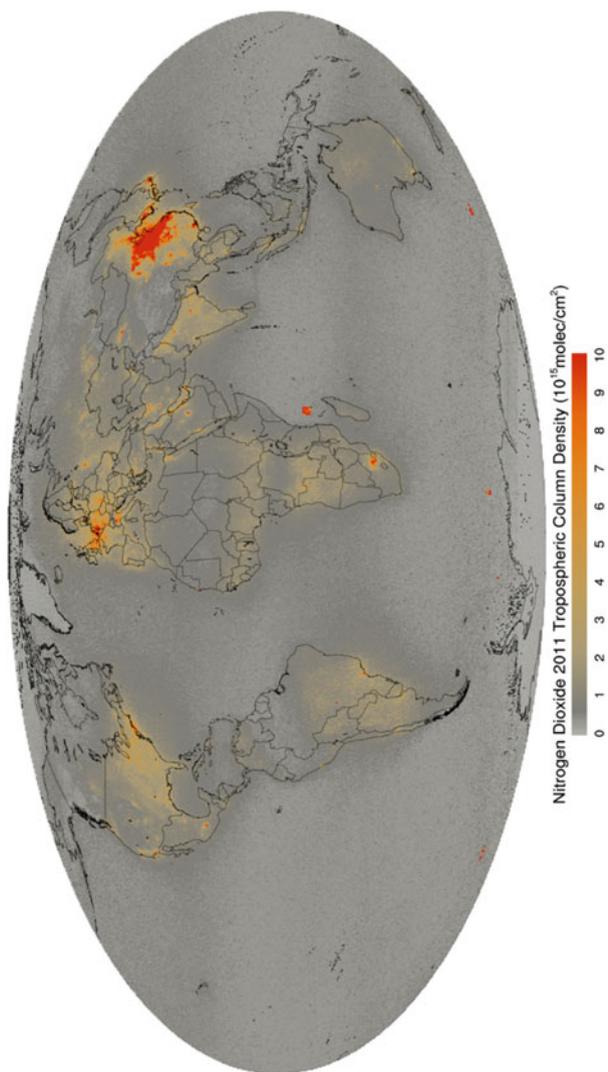
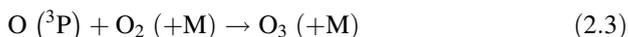
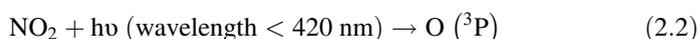


Fig. 2.6 World map of nitrogen dioxide tropospheric column density (10^{15} molecules/cm²) based on ozone monitoring instrument (OMI) onboard NASA's Aura satellite during 2011. (Source: https://en.wikipedia.org/wiki/Nitrogen_dioxide)

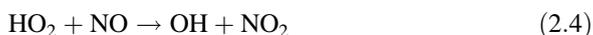
ground-level ozone formation. The general mechanisms for catalytic O₃ formation from the oxidation of VOCs and NO_x by sunlight are well characterized. NO_x are emitted into the atmosphere in the form of NO (nitric oxide) after the burning of fossil fuels. NO is transformed quickly (reaction (2.1)) during daytime to NO₂ (nitrogen dioxide) via reaction with O₃ already present at the surface.



Due to photolysis reactions (reaction (2.2)), nitrogen dioxide is again transformed to NO. In general, this particular reaction produces no net flux in reactions as a photo-stationary state is reached where concentrations of NO and NO₂ becomes related to O₃:



Though other daytime reactions (Jenkin and Clemitshaw 2000) change NO_x, those are the consequences of the photooxidation of carbon monoxide (CO) and VOCs. The transitional compounds formed through those processes generate highly reactive free radicals, including the hydroperoxyl radical (HO₂) and organo-peroxy radicals (RO₂). These radicals also convert NO to NO₂ (reactions (2.4) and (2.5)) but, in so doing, do not consume O₃. Hence, the photolysis of NO₂ (reaction (2.2)) followed by reaction (2.3) results in a net source of ozone.



In particular conditions, formation of secondary aerosols during night-time conversion from NO_x (including nitric acid, HNO₃) at a particular geographic location, related transport and deposition was observed by Takemoto et al. (2001). Krupa (1997) reported an everyday pattern of urban O₃ concentration and its precursors in the atmosphere, which emphasize the prevalence of daytime O₃ production. The concentrations of nitric oxide and VOCs in the morning are high due to the presence of high volume of traffic on roads. These exhausts clean some of the O₃ present (reaction (2.1)) and responsible for the production of NO₂. A time later in the day, NO concentration reaches its height when NO is oxidized to NO₂ without completely consuming O₃. The above-mentioned reaction is balanced due to the presence of high quantity of hydrocarbons, mainly aldehydes in the atmosphere which lead to high NO₂: NO ratio and a peak in O₃ concentrations in mid- to late afternoon. Afterward throughout the day, NO₂ exchange decreases (lower sunlight), and new exhaust of NO depletes the accessible O₃.

Apart from the above-mentioned, a significant chemistry also plays an important contribution in atmospheric chemistry in the absence of sunlight during night. Thus the night-time levels of OH are (approximately) zero. As an alternative, the nitrate radical, NO₃, is formed during night by the reaction of NO₂ with ozone. Moreover, NO₃ radicals react with NO₂ to set up a chemical equilibrium with N₂O₅



Reaction R6 occurs over the daytime. Nevertheless, NO₃ is rapidly photolysed by sunlight, and as a result NO₃ and its equilibrium associate N₂O₅ are both greatly dormant during the daytime.



Figure 2.7 gives an impression of night-time chemistry. It is important to note that night-time chemistry could not be in isolation from daytime chemistry: reaction R6 needs ozone to oxidize NO₂ to NO₃, and ozone is a result of daytime photochemistry. The chemistry of the two most significant night-time variety, NO₃ and N₂O₅, is explained below.

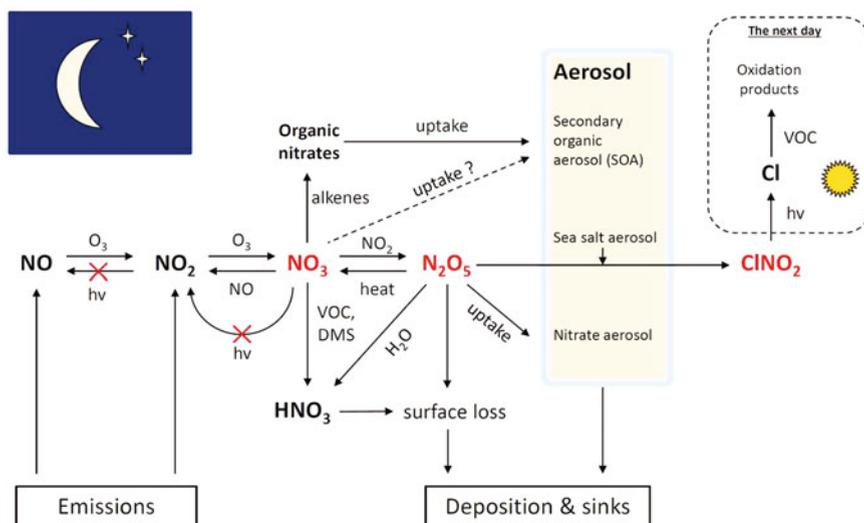


Fig. 2.7 Night-time chemistry in troposphere. The species coloured in red are generated only at night. DMS, dimethyl sulphide; $h\nu$ represents a photon of light. (Source: ECG Environmental Briefs, ECGEB No. 3)

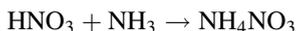
2.6.4 Sink of NO₂

Wet and dry depositions are the two important processes for the atmospheric scavenging of the NO₂ from lower atmosphere. Globally 24 (+ 9) million tonnes of average annual nitrogen removal is determined as -NO₃ and HNO₃ through dry and wet deposition, while a total of seven million tonnes of atmospheric N is scavenged by dry deposition of NO₂ per year (Ehhalt and Drummond 1982). Crutzen expected that the worldwide sink for NO_x ranges within 25 and 85 million tonnes of nitrogen per year (Crutzen 1983). Biological processes such as plant metabolism are also involved in the NO_x exchange at the earth's surfaces by plants. There are several factors affecting the exchange of NO_x between plant canopy and atmosphere, and these factors include stomata gas exchange, light intensity, wind speed, canopy height, pollutant level in atmosphere and their solubility in aqueous medium (Johansson 1989; Fraquhar et al. 1983). The efficiency of these metabolic processes for NO₂ assimilation is also studied (Rogers et al. 1979). NO₂ is taken up by plants very fast than NO due to its high solubility of NO₂ as compared to NO₂ (Fraquhar et al. 1983; Johansson 1987). NO is also absorbed by the microbial activities, but the rate of absorption is relatively less as compared to NO₂ absorption (Johansson and Galbally 1984). Both NO and NO₂ are somewhat soluble in aqueous media, and the rate of their sink in surface waters is very small in absence of reactions in the water (Lee and Schwartz 1981).

The nitrogen dioxide is removed from the atmosphere as nitric acids and nitrates through dust fall and rainfall. In these series of complex reactions involving OH radicals, NO₂ combines with water vapour to form nitric acid. The overall reactions as follows:



Most of this nitric acid are formed in the aqueous phase aerosols. Some of the nitric acid reacts with ammonia and metallic particles in the atmosphere to form nitrates of ammonium.



Such type of particles is deposited after dissolution of nitrates in rain and snow. Thus the combine fallout contributes to acid deposition.

2.7 Sulphur Dioxide (SO₂)

Sulphur is emitted into the atmosphere in various states of oxidation. Despite its ubiquity in all spheres of the globe, the most recognizable form of sulphur in the atmosphere is SO₂ as it is a precursor for sulphate aerosol – a key component of PM. Sulphur dioxide is a colourless gas with nasty and sharp smell. About 99% of the sulphur dioxide in the atmosphere is released from anthropogenic sources.

2.7.1 Sources

The atmospheric sources of SO₂ are natural as well as anthropogenic, but over the years, the anthropogenic component has increased overwhelmingly. The primary source of SO₂ is combustion of coal and oil (which contain 1–2% sulphur by weight) with smaller contributions from other industrial activities such as metal smelting and manufacture of H₂SO₄ and industrial activity with material processing containing sulphur, e.g. the generation of electricity from coal, oil or gas that contains sulphur. Some mineral/ore processing industries also released sulphur dioxide into the atmosphere after mineral/ore processing containing sulphur. In the mineral processing, several types of gases and elements are released such as sulphur and sulphur dioxide. SO₂ is the important result, produced after fossil fuels combustion. Motor vehicles are also important sources of sulphur dioxide in the atmosphere. SO₂ can be oxidized to sulphur trioxide, which can be further transformed into sulphuric acid mist in the presence of water vapour. SO₂ is a precursor to sulphates, which are one of the main components of respirable particles in the atmosphere. It simply reacts with other compounds to form toxic substances, like sulphurous acid (H₂SO₃) and sulphate particles.

2.7.2 Emissions of Oxides of Sulphur

The bottom-up mass balance approach is taken into consideration for the estimation of the global SO₂ emission from 1850 to 2005, and the country level record data is generated through coal burning, petroleum processing, oil leakage from shipping, natural gas manufacturing steps, biomass combustion, pulp and paper processing, metal smelting and crop residue burning (CRB). The global emission found at highest in the 1970s and reduced until 2000, but further increase is observed with increasing emissions from China, international shipping and developing countries (Smith et al. 2011). It ascribed the decreasing tendency to alteration in fossil fuel use, rise in the quantity of sulphur release from oil and non-ferrous metals and control on coal-fired power plants. Several other emission estimates of quantification are comparatively mentioned in Smith et al. (2004). It was also found that North America and Europe are accountable for around 50% of the total global SO₂ emission in 1990, whereas up to 50% or less represents the emissions from Asia in 2010 (Klimont et al. 2013). The directions to control emission from the power plants decrease the total emissions.

Emissions and levels of pollutants in the Eastern USA largely affected the annual concentration of SO₂ in the USA. At the end of the industrial revolution, Western Europe was identified as the highest global SO₂ emitter in the world (Smith et al. 2011), whereas it was observed somewhat higher as compared to the USA and Canada. The highest SO₂ concentration in Western Europe was observed during the 1970s, and after that there was a decline. The concentration of the SO₂ emission in 2005 was found comparable to the 1890–1900 levels. The SO₂ emission in USSR decreased after the collapse of USSR, whereas it was rapidly increasing in the 1940.

The Chinese SO₂ releases increased in the year 1940s and 2005, whereas a sharp increase in the emission is observed in the 1980s in India. Thus, overall SO₂ emission in different countries was found in the order of China, USA, Europe, South and East Asia (Smith et al. 2011). Figure 2.8 indicates a world map describing region-/country-wise SO₂ release during 2010. The high growth in the energy-related sectors the coal combustion activities also raised leads to rise in the SO₂ emission up to 73% in China (Gao et al. 2009). Other study indicated that around 53% of the total emission rose in years 2000–2006 due to its emission from power plants in China (Lu et al. 2010). After the policy implementation to curb air pollution emission (released from power plants), the emission growth rate becomes slower in the 2005, and decreasing emission was observed after 2006. The transport of the SO₂ from the Asian continent to the SW area of Japan was also studied even though SO₂ has short lifetime. Several air pollution reduction techniques are used to reduce the SO₂ emissions from the power plants after 1990 and reported by the US Energy Information Administration (US EIA). These techniques include scrubbers, flue gas desulfurization (FGD) and use of coal having low sulphur content. Coal production was more in 2007 where an important amount of SO₂ reduced (US EIA 2012). A long-term analysis (1989–2010) determination of SO₂ concentrations was carried out in South Korea from 1989 to 2010 (Ray and Kim (2014). The investigators found that lower SO₂ levels are observed from 2000 to 2010, which was 3–5 times higher than the values reported in the period of 1989 to 1999.

2.7.3 Levels and Trend of SO₂

The global SO₂ emissions were of the order of 115 Gg-SO₂ during 2005 with China contributing 32 Gg-SO₂ (~28%, Smith et al. 2011). Due to its profound impacts on human health and aquatic and terrestrial ecosystems including acid rain, SO₂ has been regulated in power plants and transport sectors in various developed countries employing desulfurization and end-of-pipe abatement techniques. However, over the Asian region, anthropogenic SO₂ emissions are not well-controlled and projected to increase under current regulations (Wang et al. 2013). SO₂ can be toxic at high levels causing reduced respiration, inflammation of the airways and lung damage (ATSDR 1998). Plants exposed to high levels of SO₂ incur acute foliar injury, where it can be oxidized to sulphite, which is very toxic and can interfere with photosynthesis and energy metabolism. The SO₂ emissions over India were estimated at 8.8 Tg for 2010 with sector-wise contribution of 66% and 32% from power plant industries and fuel-wise contribution of 76 and 19% from coal and oil, respectively, to the national SO₂ emissions (Lu et al. 2010). High SO₂ levels have been detected in ambient air of megacities like Beijing (60 ppbv in winter, Lin et al. 2011) and Kolkata (6.4 ppbv in winter, Mallik and Lal 2014). For India, the National Ambient Air Quality Standards require annual average SO₂ to be less than 30, 23 and 5.7 ppbv for industrial, residential and sensitive areas, respectively. Several precursors of SO₂ in lower oxidized state (reduced sulphur compounds, RSCs), including dimethyl

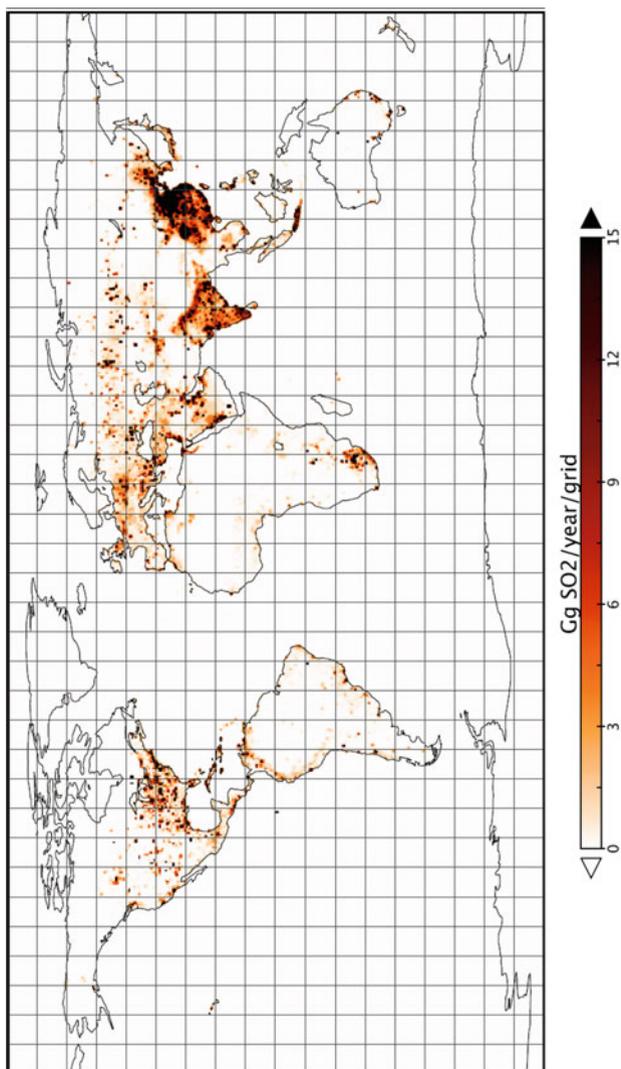
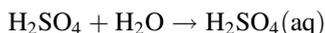


Fig. 2.8 Anthropogenic emissions of sulphur dioxide in 2010, gridded by 0.5x0.5 degree. (Source: Klimont et al. 2013)

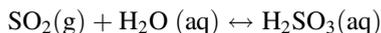
sulphide (DMS), hydrogen sulphide (H_2S), carbon disulphide (CS_2) and carbonyl sulphide (COS), contribute significantly to the global sulphur budget. Once released into the atmosphere, these are oxidized to produce SO_2 . Landfills are a major source of anthropogenic RSCs. Due to its comparatively long lifetime, COS is able to penetrate into the stratosphere where its photolysis and subsequent oxidation contributes to the stratospheric sulphate layer. Being the major precursors of sulphate aerosols which exert a negative radiative forcing on the atmosphere, sulphur gases indirectly play a crucial role in the earth's radiative balance and are of great interest to geoengineering (climate engineering) experts.

2.7.4 Chemistry of SO_2

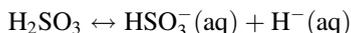
Sulphur dioxide in the atmosphere reacts with oxygen and generates sulphur trioxide (SO_3), which then reacts with water vapours to form sulphuric acid. The hydroxyl radicals and few reactions in sequence participated in the mechanism and mentioned as follows:



This freshly generated sulphuric acid in the atmosphere concentrated near the base of cloud, where the pH levels near about or below 3 have been recorded. In the presence of significant amount of the water in air, some of the atmospheric SO_2 get dissolved into it. In this case, most of the oxidation of SO_2 to H_2SO_4 occurs in the liquid phase rather than the gas phase. After the dissolution of the SO_2 in water, it easily converted to sulphurous acid (H_2SO_3).



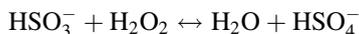
The levels of the H_2SO_3 is analysed by the equilibrium constant for this reaction. H_2SO_3 has a large enough K_a (1.7×10^{-2}) that in the atmospheric aerosols it consequent ionized to HSO_3^- bisulphite ion:



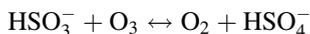
Due to the equilibrium between gaseous SO_2 and dissolved H_2SO_4 (aq), that $[\text{H}_2\text{SO}_3(\text{aq})]$ corresponds to only H_2SO_3 that does not ionized to bisulphite, and it remains at constant 1.0×10^{-7} M.

The dissolved SO_2 is oxidized by minute quantity of hydrogen peroxide (H_2O_2) and ozone (O_3) that are also present in aerosol droplets to sulphate ions (SO_4^{2-}). In the further step, the ozone and hydrogen peroxide are the products of the

photodissociation reactions in the photo chemical smog. The reactions can be written as follows:



This is the acid-catalysed reaction but the reaction with ozone is unaffected from acid.



Oxides of sulphur become adsorbed onto the particle surfaces and may be carried out to the larger distances from their sources before their deposition (dry/wet deposition). Like nitric acid and nitrate formed from NO_x, sulphuric acid, sulphate and particulate all contribute to acid deposition.

2.7.5 Sink of SO₂

There are three most important pathways for the removal of the SO₂ from the atmosphere: (1) oxidation (gas-phase homogeneous photochemical reaction with other minor components in cloud droplets), (2) wet deposition of SO₂ (in-cloud scavenging or below-cloud scavenging) and (3) direct deposition of SO₂, at the land. It has been observed that in the polluted area, the direct deposition of the SO₂ may play a major role for the atmospheric removal of SO₂ (Garland and Branson 1976). The observation of the SO₂ dry deposition have been done at different land use pattern and topography in the last few decades, including grassland, desert area, bare soil, croplands and forest (Brook et al. 1999). Scavenging through aerosol and its deposition to the ocean's plane are the important sinks for SO₂. No studies reported a comparative significance of these elimination methods, due in large part to the lack of an autonomous technique for determining SO₂ deposition to the surface (Faloona et al. 2009). The ocean deposition flux is measured by a Pacific Atmospheric Sulfur Experiment (PASE), which has two main advantages over field experiments in the assessment of marine sulphur budget: (1) the dimethyl sulphide (DMS) ocean flux is calculated, by suppressing the major source of sulphur in the atmosphere, and (2) the SO₂ deposition to the ocean surface is also directly calculated limiting major sinks.

2.8 Tropospheric Ozone (O₃)

Ozone is found both in the troposphere and in the stratosphere. Tropospheric ozone contributed about 10% of the total ozone present in the atmosphere. It is also called as the bad ozone due to its very significant role in the formation of photochemical air pollution and oxidizing nature in the atmosphere (Krupa and Manning 1988). It is one of the important greenhouse gases present in the atmosphere. The permissible limits of the tropospheric ozone are already mentioned in Table 2.1. Ozone

concentrations in the lower atmosphere typically range from less than 10 ppb (remote tropical oceans) to 100 ppb (upper troposphere) and usually surpass 100 ppb downwind of polluted metropolitan cities (IPCC 2001). The stratospheric ozone layer is the naturally occurring jacket of O_3 molecules, while most of the tropospheric ozone is formed via man-made sources (Aneja et al. 2001). Stratospheric O_3 is helpful in protecting the biosphere, but the tropospheric O_3 is harmful to the plants (Aneja et al. 1991). Ozone is heavier than air; it is brought down from the stratosphere by vertical winds produced during electrical storms (Kasibhatla 1993). However, the tropospheric O_3 is produced when sunlight reacts with nitrogen oxides, and hydrocarbons are emitted by the combustion of coal or petroleum fuels (Finlayson-Pitts and Pitts 1997). When oxidant levels in the air are high, more than 90% of the air is ozone. These levels are usually at their highest point in the afternoon and are relatively low at night (Atkinson 2000). The formation of the tropospheric ozone is a non-linear process and form from the various precursors such as volatile organic carbon (VOCs), oxides of nitrogen (NO_x) and carbon monoxide (CO). The formation of the ozone can also be affected by the regional pollutants (NO_x and VOCs) transported from a distant location through long-range transport under the influence of the regional weather patterns. The ambient level of O_3 is highest during summer, calm, spring and sunny days where primary pollutants are already present in the atmosphere. It was reported that the O_3 levels can be higher in the rural area as compared to the urban. It was also observed that the O_3 at high altitude can be comparatively stable all over the day and night (Seinfeld and Pandis 1998).

The tropospheric O_3 is of global concern due to its importance in greenhouse effect. OH radical (oxidizing agent) is one of the important precursors of the tropospheric ozone. Several models have been developed for the understanding about the factors controlling the tropospheric ozone concentration which further help for better understanding of emission control studies for ozone (NRC 1991). But these models are basically limited to the study performing for the identification of the ozone levels and its precursors such as HO_x , NO_x and hydrocarbons. Wet deposition can have an important but indirect role in the atmospheric scavenging of the tropospheric ozone, which was found involved in the scavenging of nitric acid and hydrogen peroxide which are pools for NO_x and HO_x . It was also mentioned earlier that a simple below-cloud scavenging of nitric acid and hydrogen peroxide parameterization can explain the wet deposition in the ozone model (Giorgi and Chameides 1985). It is also mentioned that the precipitation form, cirrus, may be a significant sink for the nitric acid in the upper atmosphere (Lawrence and Crutzen 1998).

2.8.1 Chemistry of Tropospheric Ozone

Figure 2.9 is an explanation of gas-phase O_3 chemistry in the troposphere highlighting the pairing within the cycles of O_3 , HO_x and NO_x . Ozone is transported from stratosphere to troposphere via stratosphere-troposphere exchange (S-T exchange). It is removed by dry deposition onto the surfaces. A fraction is consumed

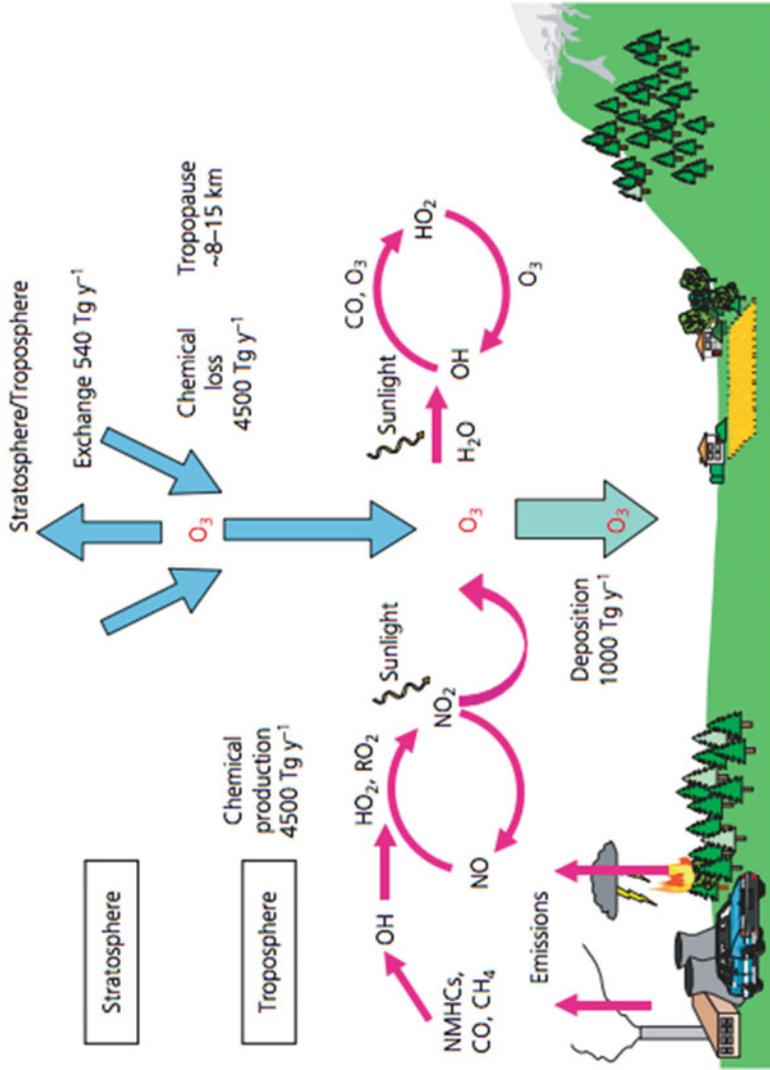
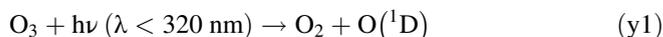


Fig. 2.9 A schematic diagram of the sources and sinks of O₃ in the troposphere. (Source: IPCC Fourth Assessment Report Working Group I Report “The Physical Science Basis”)

in chemical reaction within the troposphere. For budgeting purpose, one has to calculate the chemical production and loss of O_3 with all precautions in order to reduce uncertainty especially in the troposphere (Wang et al. 1998; Hauglustaine et al. 1998)

2.8.2 Sinks of the Tropospheric Ozone

First processes involved in the sink of the tropospheric ozone are the photochemical reaction (y1), where O_3 molecules break by sunlight. In the presence of an environment rich in NO, the reaction (y2) controls the ozone destruction.



On contrary, in NO-deficient atmosphere, the oxidation of CO_2 can lead to ozone loss. After the y3 and y4 reactions, the produced HO_2 reacts with ozone as an alternative to reaction y5:



Further, ozone can be destroyed by the direct reaction with OH radical:



After the chemical dissociation, O_3 is eliminated from the atmosphere through dry deposition, which is highly effective during unstable atmospheric conditions. Since ozone is considered as a phototoxic agent, it has the most damaging impact on plant metabolism as compared to other pollutants in the troposphere.

2.9 Conclusions

Till now, several studies have been involved in the determination and identification of the source, atmospheric chemistry and sink of the criteria pollutants. The criteria air pollutants are the pollutants responsible for several deleterious health effects after their exposure to the human being. Of the many pollutants, particulate matter, sulphur dioxide, nitrogen dioxide, carbon monoxide, lead and tropospheric ozone are ubiquitous and widely monitored for ambient levels, sector-wise contributions,

regional emission inventories and global trends over the past decades. These criteria pollutants also have air quality standards associated with them to enable their monitoring and regulation. Fossil fuel combustion is a major anthropogenic source of NO_x , and over 60% of the global energy demand is met by coal and oil followed by natural gas, renewable and nuclear energy. The concentration of O_3 , CO , NO_x and hydrocarbons greatly influences the radical balance and the self-cleaning capacity of our atmosphere. A very high concentration of sulphur dioxide was observed in the 1970s after the industrial revolution and was found decreasing in the late twentieth century. Nevertheless, China and other developing countries were observed with a high level of increasing SO_2 in recent time. The daytime and night-time chemistry of the pollutants is widely discussed by several authors in different atmospheric conditions. The initial initiatives to curb air pollution were taken in the transport sector by switching fuel, changing emission norms and the involvement of the new pollution control technologies especially for the control of PM in the developed nations in the world. The reduced lead level in petrol also changes the lead concentration in the ambient atmosphere. The technological modifications in power plants are one of the leading causes for the significant decline in the total PM pollution. The well-established link between human emissions/activity and climate and its repercussions is a matter of serious concern. The impact of human activities on the earth system has been so profound that scientists are pressing for a declaration of “Anthropocene” as an epoch. The damages cannot be undone completely and people, societies and governments must seriously start making concerted efforts to limit and abate polluting the atmosphere as each of us is a stakeholder in the present and future of the earth’s atmosphere and climate.

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