

Air Pollution and Its Associated Impacts

on Atmosphere and Biota Health

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Abstract

Unregulated humans' activities have over-exploited the earth's natural resources, disturbed its terrestrial and aquatic ecosystems, and released vast amounts of pollutants into the environment. Air pollution is typically the presence of one or more contaminants in the atmosphere and in such quantity that is injurious to animals, plants, humans, and all other man-made and natural resources. World Health Organization (WHO) estimates that every 9 out of 10 people are exposed to high levels of air pollutants. World over air pollution is responsible for the death of about seven million people annually. A large proportion of this affected population (about 91%) resides in the developing economies in the South-East Asia and Western Pacific regions. The low- to middle-income groups are the ones who are most affected by air pollutants. Scientific studies have reported that a marginal increase of 10 μ g/m³ of ambient PM₁₀ levels in Asian cities could lead to a surge in the mortality rate by 0.6%, which is significantly higher than the trends estimated for Western cities. The atmospheric $CO₂$ concentrations have already crossed the 410 ppm mark, which has never been recorded in human history. Air pollution operates on variable time scales and at various levels, i.e., local, regional, and global; and also produce impacts such as greenhouse effect and global warming; stratospheric; ozone depletion; atmospheric deposition, and acid rain; suppression of rainfall; atmospheric visibility reduction, etc. The severity of the impacts also varies from one organism to another and from one ecosystem to another ecosystem. Impacts on biota health are generally measured

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in terms of their influence on the morphological, biochemical, and physiological status and the responses generated thereof. Plants exposed to air pollutants may exhibit (1) direct or visible effects, which are often linked with short-term exposures to high concentrations of air pollutants or (2) indirect or invisible from long-term exposure to pollutants. Several national and international regulatory frameworks have been established to control and manage air pollutants. Despite intergovernmental and local efforts, air pollution has continued to rise across the major urban centers of the world, especially in developing economies like India and China. Scientific understanding and timely policy interventions are crucial in combatting the problem of air pollution emissions from the developed and developing world and consequently reducing their impacts on the living and non-living world. In this chapter, we have attempted to deliberate upon the major atmospheric pollutants (sulfur dioxide, oxides of nitrogen, ground level ozone, suspended particulate matter, fluorides, and peroxyacyl nitrates), their impacts on the atmosphere (global warming, stratospheric ozone depletion, acid rain, etc.), and threats to the biota health.

Keywords

Air pollution \cdot Plants \cdot Human health \cdot Air quality \cdot Atmosphere

3.1 Introduction

Earth and its atmosphere have been incessantly evolving since its inception. The primitive Earth had a toxic atmosphere with no traces of molecular oxygen and was too hostile to support any organic life. Early photosynthetic organisms were stromatolites that looked much similar to modern-day cyanobacteria that emerged around 3.2–3.5 billion years ago (Blankenship [2010\)](#page-22-0). The gradual emergence and expansion of photosynthetic organisms over this Earth's surface paced the evolution of its atmosphere from an oxygen deficit to the present-day levels of around 21% (Allègre and Schneider [1994\)](#page-21-0). The present-day atmosphere is an outcome of the earth's evolutionary history of 4.5 billion years; living organisms have played a crucial role in shaping the Earth and its atmosphere (Knoll [2015](#page-25-0)). Historical records suggest that over the ages various lifeforms have dwelled in a unique synergy with the Earth's atmosphere until the large-scale human interventions made since the dawn of the industrial revolution. Intensified and unregulated human actions have not only looted the Earth of its natural resources but also resulted in widespread landuse changes, emission of pollutants, and large-scale disturbances in the terrestrial and aquatic ecosystems. The atmospheric $CO₂$ concentrations have already touched 410 parts per million (ppm) marks at Mauna Loa Observatory, Hawaii (NOAA) [\(https://www.co2.earth/\)](https://www.co2.earth/). Last time, the Earth's atmosphere possessed such high concentrations of $CO₂$ which was around three million years ago, when human had not even existed on this planet, and the average earth' surface temperature was as high as 2–3 °C relative to pre-industrial levels, while the average sea level (AMSL) was 15–25 m higher than at present (Lindsey [2020](#page-25-1); Sonwani and Saxena, [2022](#page-28-0)).

Typically, air pollution is defined as the presence of one or more contaminants (chemicals, particulate matter, or biological materials) in the atmosphere at such concentrations and for such duration, that it is injurious, or tends to be injurious, to natural flora and fauna including humans (Katulski et al. [2011](#page-24-0); Saxena and Sonwani, [2019a](#page-27-0); Saxena and Srivastava, [2020;](#page-27-1) Saxena et al. [2021a](#page-27-2)); results in deterioration of surface or groundwater quality, soil productivity; damages terrestrial or aquatic ecosystems, and or materials (Manisalidis et al. [2020](#page-25-2)). In the last few decades, the urban and industrial clusters in developing economies like India and China have emerged as the new epicenters of atmospheric pollution, firstly from unplanned and unregulated economic development and secondly due to poor implementation of the regulatory framework (Chung et al. [2011](#page-22-1)). Besides, in the rural regions, the burning of traditional biomass-based fuel for heating and cooking has remained the primary source of pollution in indoor environments. According to WHO, world over around 90% of people were exposed to high levels of atmospheric pollutants in 2016. The air pollution alone kills an alarming 7 million people annually, out of which a whopping 4.2 million premature deaths are caused by outdoor air pollutants (Sonwani et al. [2021a\)](#page-28-1). A large proportion of this burden, estimated to be around 91%, is shared by third world countries mainly in South-East Asia and Western Pacific regions (WHO [2020\)](#page-29-0). Chung et al. [\(2011](#page-22-1)) reported that a marginal increase of 10 μ g/m³ of ambient PM₁₀ levels in some Asian cities would increase the mortality rates by 0.6%, which is much higher relative to the Western cities. In financial terms, premature deaths due to air pollution cost about \$5 trillion in welfare losses worldwide (The World Bank [2016;](#page-28-2) Sonwani et al. [2021b\)](#page-28-3).

Air pollutants have been in existence for centuries. The first such complaint of air pollution from coal-burning was recorded in the thirteenth century in London (Katulski et al. [2011\)](#page-24-0). Two major types of air pollution episodes were identified in the twentieth century: (1) London smog or "Reducing smog" and (2) the photochemical smog also called a "Los Angeles Type Smog". The former is formed as a consequence of the combustion of coal under strong inversion conditions, while the latter is formed from photochemical interactions of hydrocarbons and oxides of nitrogen (emitted from sources like automobiles, incinerators, municipal dumps, etc.) in the presence of ultraviolet light from the sun (Jacobson and Jacobson [2002\)](#page-24-1). The worst pollution episode of London type smog occurred in 1952, which resulted in an estimated 4000 excess deaths than the normal (Brimblecombe [1987a,](#page-22-2) [b\)](#page-22-3). Asian region in recent decades has emerged as a new pollution epicenter of the twenty-first century. India alone accounts for 14 of the 20 worst polluted cities in the world in terms of atmospheric PM_{2.5} levels (IQAIR [2019](#page-24-2)). Recently, India has made a drastic shift in its policy toward regulating air pollution. India has committed to shifting its 40% of electricity generation to non-fossil fuels under the Paris agreement (2015). Besides, in 2019, India launched its first National Clean Air Programme (NCAP), which aims to reduce $20-30\%$ PM_{2.5} and PM₁₀ levels across 102 cities in India by 2024 relative to 2017 levels (Government of India [2019\)](#page-24-3). Lately, the Covid-19 shutdown in the country brought a short-term drop in air pollution levels. But as the lockdown restrictions have eased, the clear skies have disappeared again. The cities like New Delhi have already crept into the category of "severe" level of air

pollution. Burning of agricultural residue is one of the major reasons for air pollution in Northern India and several other regions of South Asia too. There is a sharp dip in the air quality in the National capital New Delhi during winter. The latest reports suggest that this year, the share of crop stubble burning to New Delhi's $PM_{2.5}$ load has gone beyond 36% (SAFAR-India [2020\)](#page-27-3). Huge economic losses are incurred by the airline companies due to dense foggy conditions prevailing over New Delhi in winter every year. In parts of Indonesia and Malaysia, burning of peatland and forests for land clearing for lucrative oil palm plantations also resulted in deterioration of air quality causing a choking smog which blankets not only parts of Indonesia but also spreads to Malaysia, Singapore, and southern Thailand.

3.2 Air Pollutants: Types and Sources

The majority of the air pollutants in the atmosphere are short-lived and quickly removed by wet or dry deposition generally in the vicinity of their sources. Some of them are having longer residence times (half-life of a pollutant) in the atmosphere. Many of these pollutants undergo transformation or "aging" forming new secondary species and transported via local as well as long-transport pathways. More than 3000 air pollutants have been identified which are otherwise not present in the natural environments (Gheorghe and Ion [2011](#page-24-4)). The places from where these pollutants originate are called "Sources", and the places they disappear are called "Sinks". There are a wide variety of sinks such as forests and other vegetation, soil, material structures, water bodies, etc. The removal mechanism of a pollutant from the atmosphere into the sink is called "Scavenging", while the time of its stay in the atmosphere is called its half-life. The half-life of a pollutant is defined as the time it takes for the disappearance or scavenging of half of a pollutant emitted into the atmosphere from its source. Atmospheric conditions and topography to a greater extent influence the local as well as the regional concentrations of a pollutant (Watson et al. [1988](#page-29-1)). For example, urban zones located in the valleys where atmospheric inversions take place generally have high pollutants owing to lower atmospheric mixing heights. Such places are more likely to experience a high frequency of severe smog episodes. Several gases like CO_2 , CFCs, and N₂O have longer half-life times and tend to accumulate in the atmosphere over the years reaching concentrations high enough to substantially alter the natural composition of the air. The chlorofluorocarbons (CFCs) are chemically very inert and don't undergo any chemical degradation in the troposphere. In the stratosphere, high energetic ultraviolet (UV radiation) photolyze the CFC molecules, thereof releasing free chlorine atoms. Excess of free chlorine atoms disturbs the steady-state of ozone concentration in the stratosphere, triggering the destruction of stratospheric ozone, ultimately permitting harmful UV to penetrate the earth's surface (Vallero [2014;](#page-29-2) Saxena and Sonwani, [2019b](#page-27-4)).

Air pollutants can be distinguished by their chemical composition, persistence, transformation reactions, sources and sinks, and transportation mechanisms and effects on plants and animals including humans (Kampa and Castanas [2008\)](#page-24-5).

Pollutants emitted directly from their sources are categorized as the primary pollutants, whereas those formed by transformation reactions with atmospheric gases or by other pollutants are termed as secondary air pollutants (Bernstein et al. [2004\)](#page-22-4). The concentrations of a secondary atmospheric pollutant may decrease if a reduction in the emissions of precursors could be achieved (Gaba and Iordache [2011\)](#page-23-0). Air pollutants are also classified into (1) criteria pollutants and (2) hazardous air pollutants. Both the categories of pollutants are hazardous. Regulatory authorities conduct regular monitoring for the criteria pollutants to maintain the state of ambient air quality of a region (Katulski et al. [2011](#page-24-0)). The majority of the countries including India have devised their National Ambient Air Quality Standards (NAAQS) for air pollutants of utmost concern. Under the Clean Air Act (Environmental Protection Agency [2008](#page-23-1)), United States Environmental Protection has devised NAAQS for six pollutant criteria air pollutants namely: SO_2 , NO_2 , CO , tropospheric O_3 , suspended particulate matter, and lead (Saxena and Sonwani, [2019c\)](#page-27-5).

3.3 Air Pollution and Its Impacts on the Atmosphere

Air pollutants operate at local, regional, and global levels and produce different impacts on each level (Manisalidis et al. [2020](#page-25-2)). For example, the presence of tropospheric ozone is known to augment Earths' greenhouse effect, while ozone in the stratosphere produces overall cooling effects. Some of the impacts of air pollutants on the atmosphere are discussed as:

3.3.1 Greenhouse Effect and Global Warming

Earths' atmosphere is dynamic and continually in motion. The vertical and horizontal mass movements in the atmosphere are driven by differential vertical and horizontal heating of Earth by incoming solar radiations. The state of the atmosphere measured in terms of variations in temperature, precipitation, wind direction and speed, relative humidity, the extent of cloud cover, and solar flux measures in hours, days, or weeks defines its weather (Tinsley and Yu [2003\)](#page-29-3). These parameters, when observed within the geographical context and over longer durations (years, decades, centuries, thousands of years), define climate (Paruelo et al. [1998](#page-26-0)). In general, the climate is defined as the average weather conditions over a minimum period of 30 years. Air pollutants to a larger extent impact the global climate, likewise, the changing climate can impact air quality. The black carbon, a particulate product of incomplete combustion, is a strong radiative agent. This contributes to the warming of the Earth, while the particulate sulfates reflect the incoming solar radiation and exhibit a cooling effect on the Earth's atmosphere (Pöschl [2005](#page-26-1)).

The atmosphere allows the visible short-wave radiation from the sun to pass through it while inhibits the flow of long-wave infrared radiation back into space, a phenomenon which is known as the "Greenhouse Effect". The greenhouse effect helps the earth to maintain its average surface temperature at $\sim +15$ °C (Schneider

[1989\)](#page-27-6). Without the natural greenhouse effect, the average temperature on Earth is estimated to have been colder by approximately 30 \degree C, cold enough to sustain any of the present-day ecosystems. $CO₂$ and water vapors are the major gases that regulate the greenhouse effect on Earth. Other important greenhouse gases (GHGs) present in trace amounts in the atmosphere are CH_4 , N₂O, tropospheric O_3 , CFCs, PFCs, and SF6 (Lee [1973\)](#page-25-3). Accumulation of GHGs since the onset of the industrial revolution and change in earth's albedo from land-use activities have significantly raised the global average temperatures and consequently bringing in the anthropogenicinduced climate change (Ramanathan et al. [2001:](#page-26-2) Schmidt et al. [2006](#page-27-7)). As of 1750, the GHGs like $CO₂$, CH₄, and N₂O have shown a respective increase of 40%, 150%, and 20% as observed till 2011. United Nations Framework Convention on Climate Change (UNFCCC) refers to climate change to a change of climate that is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and that is in addition to natural climate variability observed over comparable periods. The alteration in the energy budget of the earth by atmospheric pollutants is measured in terms of radiative or climate forcing (Pachauri and Reisinger [2007\)](#page-26-3) defined as any variation forced on the energy balance of the Earth (Murphy et al. [2009\)](#page-26-4) and expressed in terms of watts per square meter (Wm^{-2}) . The causal substances responsible for radiative forcing are known as radiative forcing agents. Earth is warmed by positive forcing agents and cooled by negative forcing agents. Greenhouse gases are positive radiative forcing agents whose presence in the atmosphere reduces the earth's ability as a whole to re-radiate sunlight into space, as a consequence of which the earth absorbs more thermal energy and warms (Zhao et al. [2019](#page-29-4)). Climate change has posed danger for all countries, however, the nations with limited adaptive capability are at the greater risks of climate-induced extreme events. Many regions in India due to their fragility are highly vulnerable to climatic impacts. Several kinds of research have been carried in India to make future climatic projections as well as to assess the vulnerability of different regions of the country toward climate change and other associated risks. In their study on Karnataka, Kumar et al. ([2016a,](#page-25-4) [b\)](#page-25-5) have estimated that around 70% of the cultivated area of the State has been facing extreme to a high level of vulnerability from the climateassociated impacts. In another study from the Himalayan state of Arunachal Pradesh, Maiti et al. [\(2017](#page-25-6)) have highlighted that 7 out of 12 district studies show high social vulnerability toward changing climate. Sam et al. ([2020\)](#page-27-8) also emphasized that the formulation of local adaptive measures in India could potentially reduce the risk of climate-induced extreme events. Researchers have associated the probability and severity of heatwaves in India with global warming (van Oldenborgh et al. [2018\)](#page-29-5). Uprety and Saxena, [2021](#page-29-6) have predicted that the average temperatures in India would increase by 2.5–4.4 \degree C by end of the century w.r.t. to the current scenario, whereas the annual rainfall has been projected to show an average increase by 15–24%. Gupta and Jain [\(2018](#page-24-6)) have estimated that in the future the droughts in the Indian sub-continent would get more severe and frequent. Likewise, Chevuturi et al. [\(2018](#page-22-5)) have reported that the Leh region of India had shown a warming trend and reduced precipitation which could be associated with the reducing number of days with higher precipitation amounts over the region.

Worldwide, anthropogenic activities have produced an increase of 45% in the atmospheric concentrations of $CO₂$ from 280 ppm to present-day levels of 411 ppm (Shieber [2019](#page-28-4)). Such high concentrations of $CO₂$ have never been witnessed in human history; last time, the earth's atmosphere had these much high $CO₂$ concentrations which were around three million years ago, when the average earth' surface was as high as $2-3$ °C relative to pre-industrial levels, and average sea level was 15–25 m higher than at present. The cumulative impact of human activities on the global average temperature rise has been approximated to around 1.0 \degree C relative to the pre-industrial levels of 1750. At the present pace, the GHG emissions would result in warming up to $1.5 \degree$ C between 2030 and 2052 (IPCC) [2018\)](#page-24-7). United Nations Framework Convention on Climate Change (UNFCCC) has taken steps from time to time to develop a global consensus to check the GHGs emissions by various countries. Under UNFCCC's Paris agreement [\(2015](#page-29-7)), keen efforts have been made by the global community to restrengthen the commitment for the regulation of GHGs emissions, limit the global temperature rise in this century well below $2 \text{ }^{\circ}\text{C}$ above pre-industrial levels, and to pursue efforts to limit the temperature increase even further to 1.5 \degree C (UNFCCC [2015](#page-29-7)). IPCC which provides important scientific inputs for framing international policies toward climate change recently has also released a special report in 2018 to evaluate the global response concerning advancement made toward limiting the temperature rise in this century up to 1.5 °C above pre-industrial levels (IPCC [2018\)](#page-24-7).

3.3.2 Stratospheric Ozone Depletion

The stratospheric ozone layer or "Good" ozone is a region of the atmosphere between 10 and 50 km where 90% of the atmospheric ozone is contained. Stratospheric ozone (O_3) absorbs harmful ultraviolet (UV) radiations from the solar flux, which could otherwise harm life on the earth's surface. The total atmospheric O_3 mass is estimated to be around three billion metric tons, which constitutes only 0.00006% of the atmospheric mass of all gases combined. The highest O_3 concentrations nearly equal to \sim 15 ppm is found at roughly 32 km above the earth's surface. Total columnar ozone (TCO) is represented as a Dobson Unit (DU). One Dobson Unit is defined as the number of molecules of O_3 required to create a pure O_3 layer of 0.01 mm thickness at a temperature of 0° C and sea level (1 atm pressure) (Godish et al. [2014\)](#page-24-8). Natural O_3 formation and degradation begin by high-intensity, shortwave solar ultraviolet radiation $(<242 \text{ nm})$ in the stratosphere, as seen in the equations below:

$$
O_2 + hv \to O + O \tag{3.1}
$$

$$
O + O2 + M \rightarrow O3 + M
$$
 (3.2)

$$
O + O_3 \rightarrow 2O_2 \tag{3.3}
$$

$$
O_3 + hv \to O_2 + O(^{1}D)
$$
 (3.4)

where hu is a UV photon and M is a molecule that absorbs energy. These reactions are known as the Chapman Cycle. In the stratosphere, ozone production and degradation involve molecular-oxygen (O_2) , atomic oxygen (O) , and O_3 reactions (Rowland [2009\)](#page-27-9).

Ultraviolet radiations coming from the sun are classified into UV-A, UV-B, and UV-C radiations. Stratospheric ozone absorbs almost 99% of UV wavelengths below 320 nm. UV-C light (100–290 nm) has a relatively smaller wavelength and is extremely harmful to the living biota on the earth's surface. Most of it is absorbed by O_3 and O_2 molecules in the stratosphere. The UV-B (290–320 nm) are highly energetic UV radiations and harmful for living biota, roughly 95% of all UV-B is absorbed by the stratospheric ozone. UV-A (320–400 nm) has the longest wavelength and is the least harmful UV radiations (Rowland [2009\)](#page-27-9). Earth's surface receives a high influx of UV-A radiation and low to moderate influx of UV-B radiations depending upon the state of stratospheric $O₃$ (Cutchis [1974](#page-22-6)). Scientific deliberations on stratospheric O_3 depletion started in the late 1960s. In 1974, Sherwood Rowland and Mario Molinas suggested that chlorofluorocarbons (CFCs) in the stratosphere undergo photolytic break down releasing Cl atoms, which in turn chemically degrade the stratospheric O_3 . Later evidence suggested that O_3 layers could also be affected by the increased release of nitrous oxide (N_2O) from the denitrification of ammonium and nitrate fertilizer (Rowland [2009\)](#page-27-9). The stratospheric ozone hole was first discovered by a team of scientists, Farman, Gardiner, and Shanklin working in Antarctica; their findings were published in the "Nature" journal in 1985. The decline in the polar ozone was far more than the anticipated figures (Farman et al. [1985\)](#page-23-2). More information from satellite data suggested that the ozone depletion extended beyond the experimental sites, covering most of the Antarctic region. Technically, the ozone hole is defined as a geographical region having an ozone concentration of the air column lower than 220 DU (Newman et al. [2004\)](#page-26-5). In the 1980s, several deliberations between scientists and policymakers resulted in the framing of landmark international regulatory provisions aimed at phasing out and prohibiting the use of long-lived Cl and Br halocarbons (Godish et al. [2014\)](#page-24-8). Montreal Protocol of 1987, and subsequent amendments made therein, placed an international ban on the manufacture and distribution of CFCs, halons, and other ozone-depleting substances (ODS) with effect from 1989. It is expected that stratospheric O_3 would eventually recover to its pre-industrial levels, though it would take years for its complete recovery since CFCs and halons have a longer residence time in the atmosphere (Wilmouth et al. [2018](#page-29-8)).

In the lower troposphere, surface O_3 has a crucial role in increasing the oxidizing ability of the atmosphere but also has detrimental effects on plant and animal health including humans (Saxena et al. [2019](#page-27-10)). In India, surface ozone observations were carried out by various groups in different regions and their findings were highly useful to explain the regional air quality. South-East Asia is an anthropogenically active region and model simulations predicted major environmental consequences due to increased ozone values only in India, China, etc.

3.3.3 Atmospheric Deposition and Acid Rain

Atmospheric gases and particulates emitted from different sources are transported from air to water and soil through atmospheric deposition. This transfer process may be harmful or beneficial in terms of the impact of deposition on various sources. For instance, ozone deposition has detrimental effects on vegetation, while the deposition of nitrogenous compounds may be beneficial or detrimental. Nitrogen deposition can bring in additional nutrients for the plants, though the excessive deposition may cause eutrophication of water bodies (Smith et al. [1999\)](#page-28-5). The acidification of precipitation, also termed as "Acid Rain", is also an example of the detrimental effects of atmospheric deposition. During their atmospheric transport and deposition, gases and particles undergo different physical and chemical transformations. These transformations affect significantly the fate and behavior of different chemicals undergoing deposition (Pacyna [2008](#page-26-6)). Besides, atmospheric deposition has potential consequences of increasing glacier melting by the darkening of the surfaces of snow and ice; decreases the photosynthesis process on the surface of the leaves; acidification of water bodies; changes in the soil's properties, etc. (Menon et al. [2007](#page-26-7)).

Atmospheric depositions on the terrestrial and aquatic ecosystems may happen through (1) dry deposition and (2) wet deposition. Primary and secondary particulates are removed by the gravitational force from the atmosphere over time without precipitation, this process is termed as "dry deposition" (Lovett and Kinsman [1990](#page-25-7)). Dry deposition primarily depends on the size, concentration, and reactivity of the particle deposited and the surface being affected (Lindberg et al. [1982\)](#page-25-8). Particles with a size of >0.8 mm are considered to be easy to settle whereas those with a diameter of <0.08 mm may remain suspended for a longer duration in the atmosphere and therefore transported over to longer distances (Ruijrok et al. [1995\)](#page-27-11). Dry deposition primarily delivers particulates of crustal origin predominantly rich in Ca^{2+} , Mg^{2+} , K^+ , and total phosphorous to the earth's surface. On the other hand, wet deposition is assisted by wet weather events (e.g., rain, snow, and hail) and dominantly deposits Na^+ , total nitrogen, NO_3^- , and fine particulates to the earth' surface (Morales-Baquero et al. [2013](#page-26-8)). In countries like India, where dry conditions prevail in a larger part of the year, dry deposition is an important process of removal of atmospheric pollutants (Sharma et al. [2008\)](#page-28-6). Wet deposition predominates in the higher precipitation regime zones (Balestrini et al. [2000\)](#page-21-1). Dry deposition is an important feature in the local removal of micropollutants in the industrialized regions too (Gambaro et al. [2009\)](#page-23-3). Studies have shown that dust load deposited from dry deposition has profound effects that impact on the lake, marine sediments, leaf surfaces, forest canopy, crop productivity, etc. (Gao et al. [2019\)](#page-23-4). The aerosol

deposition over snow or ice affects its reflective efficiency and increases the heat absorption and melting of Himalayan glaciers and polar ice (Hansen and Nazarenko [2004;](#page-24-9) Yasunari et al. [2013\)](#page-29-9). Wet deposition, on the contrary, is completely related to wet weather events (e.g., rain, snow, and hail). Wet deposition is responsible for the removal of the majority of aerosols from the atmosphere. Wet deposition can be classified as (1) in the cloud scavenging, where condensation occurs around one or more aerosols which are used as a core (nucleation) and (2) scavenging beneath the cloud, where the particles are impacted in the air column beneath the cloud. Both of these may occur individually or together, depending on the aerosol concentration in and below the cloud when precipitation is taking place (Roux et al. [2016\)](#page-27-12).

Acid rain refers to low pH precipitation events. Natural rain is slightly acidic, having a pH of 5.7 due to the formation of carbonic acid formed from the dissolution of atmospheric $CO₂$ following Henry's law governing the dissolution of gases. The acidity of rain is caused by the dissolution of atmospheric SO_2 and NO_2 , which undergo reactions with water molecules in the atmosphere to produce acidic compounds, i.e., H_2SO_4 and HNO_3 (Magaino [1997\)](#page-25-9). Acid rain is highly harmful to terrestrial plants, aquatic biota, crops, and materials. Such precipitation events are threats to the terrestrial and aquatic ecosystems, the local and regional geology is important in neutralizing the acidity. Soils and surface water having lower amounts of Ca and Mg carbonates exhibit lower buffering capacities and are most prone to damages from acid deposition. Acidity lowers the cation exchange capacity of the fertile soils, it also results in leaching away of an important nutrient, thus restricting their availability to the plants. On the other hand, the availability of toxic ions like Al^{3+} and Fe²⁺ increases in the soil solution (Aerts and Bobbink [1999](#page-21-2)). The acidic deposition has resulted in the chronic acidification of many lakes and streams in North America and the Scandinavian peninsular region (Godish et al. [2014](#page-24-8)). Beier et al. ([2017\)](#page-22-7) reported that the chronic acidification of the Adirondack region's (USA) forests, lakes, and streams affected the potential economic and cultural benefits they provide to society. Liu et al. ([2018\)](#page-25-10) observed that the Chinese fir sapling height growth rate (HGR) and basal diameter growth rate (DGR) decreased as acid rain pH decreased. In a similar study, Du et al. (2017) (2017) observed that acid rain-reduced leaf chlorophyll content on average by 6.7% per pH unit across the recorded plant species. Sosa-Echeverría et al. ([2019\)](#page-28-7) also emphasized that external emission sources play a decisive role in acid rain within Mexico City. In India, Roy et al. [\(2016](#page-27-13)) reported that 55 and 65% of the rainwater samples during monsoon seasons of 2013 and 2014 over Falta and Darjeeling, West Bengal (India) were acidic. In similar observations, Garg et al. ([2000\)](#page-23-6) reported that acidic rain events occurred throughout the year, with a frequency of 64% and 87% during monsoon and non-monsoon seasons, respectively, in Guwahati during June 2016–June 2017.

3.3.4 Suppression of Rainfall

Air pollutants produce diminishing effects on the intensity of rainfall. This could be a serious public issue especially for the water-scarce and densely populated regions of the world. Long-term precipitation data of 50 years collected from several mountain ranges in the western United States have suggested a gradual decrease in the rainfall by around 10–25% (Schiermeier [2007](#page-27-14)) during the observation period. Cloud is formed of tiny cloud droplets typically of a 10 μm radius. These droplets coalesce together to form precipitation-sized raindrops of radius $1000 \mu m (= 1 mm)$, thus the mass of typical raindrops is equivalent to one million cloud droplets.

The coagulation of tiny cloud droplets into raindrops is governed by their size, at least some of the cloud droplets in a cloud mass should have a size of radius $>15 \mu m$ for the effective formation of precipitation in that cloud (Rosenfeld [1999,](#page-26-9) [2000\)](#page-26-10). Hydrophilic aerosol particles are good cloud condensation nuclei (CCN). Water vapor easily condenses on the surface of such particles resulting in the formation of clouds under supersaturated conditions (Che et al. [2016](#page-22-8)). Whereas, the pollution aerosols act as small CCN, which produces a large number of smaller-sized cloud droplets. This leads to the suppression in the formation of precipitation-sized rain droplets within the cloud mass and prolongs the clouds' life, warm rain process, and ice precipitation (Rosenfeld [2000;](#page-26-10) Borys et al. [2003](#page-22-9); Rosenfeld et al. 2008). Besides, the sulfate aerosols are also known to suppress the precipitation from the clouds. Borys et al. [\(2003](#page-22-9)) have reported that an addition of 1 μ g m⁻³ of sulfate aerosols leads to the reduction of snowfall rate by 50% in the Colorado Rocky Mountains (USA). Thus, there is enough experimental evidence to suggest that anthropogenic aerosols can disturb the hydrological balance over a landmass by interfering with the cloud formation and precipitation.

3.3.5 Visibility Reduction

Visibility is considered as a primary air quality index. Visibility reduction results from the absorption and dispersal of sunlight by suspended particulate matter as well as from the atmospheric gases (Hyslop [2009\)](#page-24-10). Visibility is also limited by natural factors such as rain, snow, fog, aeolian dust, sea spray, hazes, etc. The first case of Arctic haze was reported in the 1950s. Industrial pollution of $SO₂$, elementary carbon (EC), HCs, metals, other gases, and particulate matter are the main cause of the Arctic haze. As the occurrence of Arctic haze was identified and researched over decades, observation of the Asian brown clouds was made in 1999 (Graff Zivin and Neidell [2013](#page-24-11)). The brown haze of about 3 km high covers the majority of the tropical Indian Ocean, South East, and East Asia. Studies have revealed high concentrations of sulfates, nitrates, organics, carbon (C), fly ash, and other pollutants as the major components of such haze (Chen et al. [2012](#page-22-10)).

Indo-Gangetic plains (IGP), in particular, are the hotspots of Asian brown haze or clouds. Large-scale agricultural, industrial, and other commercial activities in this

region generate a wide variety of atmospheric pollutants resulting in the formation of brown haze. The winter in North India is frequented by low visibility from fog formation. Indian capital city, New Delhi, and nearby regions, experience a high frequency of smog episodes during winter due to pollutants from the burning of crop stubble in the surrounding states of Punjab, Haryana, and Uttar Pradesh during the winter season (Kumar et al. [2016a,](#page-25-4) [b\)](#page-25-5) along with high relative humidity (RH), sufficient sunlight, and reduced vertical mixing (Chen et al. [2018](#page-22-11)). Smog episodes have been associated with serious health ailments, besides low visibility often disrupts railways, flights, and road transport services yearning economic losses. Visibility reduction is not only detrimental to ambient air quality (Gu et al. [2017](#page-24-12)) but can also diminish solar flux reaching the earth's surface. Volcanic emissions from the eruption of Mount Pinatubo, the Philippines in June 1991 released an estimated 20 million sulfur dioxide in the atmosphere. Sulfate aerosol emissions of this magnitude reduce the solar flux reaching the earth's surface lowering the tropospheric temperatures.

3.4 Impacts on Biota Health

Atmospheric pollution significantly affects human health, terrestrial and aquatic ecosystems, local and regional climate, and consequently society and economy (Correia et al. [2013;](#page-22-12) Fang et al. [2013](#page-23-7); Rao et al. [2017](#page-26-11)). The Geneva Convention held in 1979 on Long-range Transboundary Air Pollution emphasized the protection of humans and the natural ecosystem from the deleterious effects of atmospheric pollutants. The convention has endorsed the reduction of eight air pollutants: SO_x , NOx, persistent organic pollutants, non-methane volatile organic compounds, tropospheric ozone, heavy metals, particulate matters $(PM_{10}, PM_{2.5})$, and black carbon (De Marco et al. [2019\)](#page-23-8). The effects of air pollutants on lower and higher organisms are measured in terms of their influence on the morphological, biochemical, and physiological status and responses thereof. In plants, the penetrations of pollutants mainly occur via leaves (Fig. [3.1](#page-12-0)). Small penetration of pollutants may happen through the stems and trunk (Seyyednejad et al. [2011](#page-27-15)). Air pollution effects may be classified into (1) direct or visible and (2) indirect or invisible injury (Gheorghe and Ion [2011\)](#page-24-4). Visible injury is often linked with short-term exposures to high concentrations of air pollutants. The damaged portions of the leaf surface can offer easy entry for plant pathogens. Besides the visible injury in the form of discoloration, scabs, etc. can reduce the market values especially of the crops, for instance, visible injury can reduce the market value for tobacco, spinach, and horticultural crops. Invisible injury results from long-term exposure to pollutants. It impacts various physiological or biochemical processes in plants that can ultimately damage their growth and development, reduce nutritional quality, and yield (Liu and Ding [2008](#page-25-11)).

Fig. 3.1 Schematic representation of the environment of leaf surfaces. [adapted from Garrec [2020\]](#page-23-9)

3.4.1 Sulphur Dioxide $(SO₂)$

Sulfur dioxide $(SO₂)$ is a common atmospheric pollutant that affects plants, animals, men, and materials. SO_2 has a solubility of 228 g/L in the water at 0 °C. SO_2 is an important precursor for the formation of secondary atmospheric pollutants and acid rain. As of 2019, India contributes to the largest anthropogenic emissions of $SO₂$ in the world, which roughly equals to $>15\%$ of global emissions of SO₂ from anthro-pogenic sources (Kapil [2019](#page-24-13)). Under high humidity conditions, $SO₂$ is oxidized to SO_3 which forms sulfuric acid (H₂SO₄) when hydrated. SO_2 is taken up by the plants predominantly through the stomata. The uptake is dependent both on the stomatal conductance (Mudd [2012](#page-26-12)) as well as the prevailing environmental conditions such as the amount of light, temperature, relative humidity, wind speed, etc. Under the low light and water deficit condition, stomata remain closed and exhibit a lower degree of susceptibility to the $SO₂$ injury.

Nonvascular plants like lichens and bryophytes having low chlorophyll contents and no cuticle present are relatively more susceptible to $SO₂$ injury under high exposures. $SO₂$ has been the major culprit responsible for the dramatic decline in several bryophytes and lichens species in urban and industrialized regions of the world. Under high SO_2 polluted atmospheres, lichens become compact and sterile with a much smaller colony size. Among the plants, the most common type of acute injury due to SO_2 pollution is interveinal chlorosis. Some common species susceptible to SO_2 injury are oats (Avena sativa), cucumber (Cucumis sativus), and spinach (Spinacia oleracea), while celery (Apium graveolens), maize (Zea may), and citrus species (Mudd [1975](#page-26-13)) are known to exhibit resistance toward $SO₂$ injury. India is the largest emitter of sulfur dioxide in the world. Several studies have been conducted in India to evaluate its effects on plants and animals. Farooq et al. [\(1985](#page-23-10)) reported the depletion of starch and accumulation of free sugars in tissues in 2-month-old chilbil *Holoptelea integrifolia* exposed to $SO₂$ in experimental chambers. Similarly, Agrawal and Verma (1997) (1997) have also observed that $SO₂$ exposure leads to a reduction in total chlorophyll, ascorbic acid, starch, and protein contents in the 30-day-old two cultivars of wheat (Malviya 206 and Malviya 234). In another study, Verma and Agrawal ([1996\)](#page-29-10) observed that $SO₂$ fumigation to soybean (Glycine max) plants resulted in severe effects on photosynthetic pigments, ascorbic acid and protein contents, biomass, and productivity. A study by Dwivedi and Tripathi [\(2008](#page-23-11)) revealed a positive correlation between ambient air sulfur dioxide and sulfate contents in leaves of Ficus religiosa. The nonvascular plants show the acute direct impacts of $SO₂$ at much lower concentration relative to vascular plants, thus bryophytes and lichens often determine critical level set for ambient atmospheric $SO₂$ concentration in the natural environment. Experiments by Majernik and Mansfield (1970) (1970) revealed that exposure of SO₂ to fully hydrated 5-week-old broad bean (V. faba) leaves at 40% relative humidity and 18 °C, promoted stomatal opening, thereby promoting greater diffusion of sulfur dioxide into the leaves. Similar experiments by Unsworth et al. (1972) (1972) using ¹⁴C technique in the lichen species Cladonia alpestris, C. deformis, Stereocaulon paschle, and Umbilocaria muhlenbergii suggested that exposure to $SO₂$ at low pH resulted in a reduction of carbon fixation by lichen species. Similarly, studies have shown that exposure to $SO₂$ increased the rate of respiration in lichens and bryophytes.

3.4.2 Oxides of Nitrogen

Nitrogen in molecular form $(N₂)$ is the most abundant gas in the atmosphere. Lesser amounts of nitrogen exist as nitrous oxide (N_2O) , nitrogen dioxide NO_2 , nitric oxide (NO) , ammonia $(NH₃)$, and several other oxides of nitrogen. Nitrogen dioxide acute injury signs appears in plants when the latter is exposed to a threshold concentration of 2 ppm of $NO₂$ for a duration of 4-h. This rarely happens at its natural ambient background concentrations of $NO₂$. Natural sources of oxides of nitrogen include atmospheric lighting, the decay of organic matter, and forest fires. While human activities such as the burning of fossil fuels in factories, automotive, and other hightemperature processes are its primary sources, which often emits more than its natural sources. The usage of catalytic converters in the locomotive exhaust can prevent emissions of nitrogen oxides to a larger extent (Forcetto and Daemme [2017\)](#page-23-12). Many oxides of nitrogen are important precursors resulting in the formation of secondary pollutants including smog, acid rain, ground-level ozone, and formation of particulates (Brown et al. [2006](#page-22-13); Yung et al. [2007;](#page-29-12) Ghazali et al. [2010\)](#page-24-14).

Exposure of $NO₂$ in plants beyond tolerable threshold levels triggers complex physiological responses and changes in antioxidant enzyme activity. The use of tolerant species which could catabolize the atmospheric $NO₂$ is considered a viable ecological method to reduce its air concentrations. A recent experiment conducted by Sheng and Zhu ([2019\)](#page-28-8) revealed that $NO₂$ exposure in garden plants (6 µL/L NO₂ in glass chambers and subsequently transferred to a natural environment for a 30-day recovery) affected the leaf chlorophyll content and induced biochemical defense responses. Mansfield et al. (1982) (1982) also suggested that $SO₂$ interferes with the induction of the nitrite reductase, an enzyme responsible for the reduction of $NO₂$ to NH_3 , which possibly the main mechanism by which $NO₂$ toxicity is regulated by the plant cells. Besides, atmospheric nitrogen deposition results in soil degradation thus indirectly affecting the soil biota. Acidic deposition of oxidized and reduced nitrogenous compounds is characterized by loss of buffer capacity of the soils and reduces their cation exchange capacity (CEC). Lowering of the CEC of the soils leads to the increased loss of the Ca^{2+} and Mg^{2+} and other micronutrients to the soil solution, and increased availability of harmful metals like Al^{3+} and Fe^{2+} (Aerts and Bobbink [1999\)](#page-21-2). Besides, the lower pH triggers the inhibition of nitrification, resulting in an increase of ammonium to nitrate ratios. Because of their high sensitivity to atmospheric $NO₂$, lichens can be used as potential cost-effective bioindicators of $NO₂$ pollution in the air (Conti [2008](#page-22-14)).

Lichen distribution, colony size, and concentration of elemental nitrogen in thalli have been used for biomonitoring nitrogen distribution and deposition patterns (Johansson et al. [2012](#page-24-15)) in many parts of the world. Owing to their unique biology, and lack of a cuticle layer to regulate the atmospheric absorption and the leaching of nutrients, lichens dynamically concentrate such nutrients in proportion to their atmospheric abundances. Increased nitrogen deposition favors the growth and abundances of eutrophic nitrogen-loving lichen species over oligotrophic species, growing in nutrient-deficient environments (Root et al. [2015\)](#page-26-14). Bignal et al. [\(2007](#page-22-15)) reported the ecological impacts of nitrogen oxides from vehicular sources on vegetation at two experimental sites in England. Their findings suggested that $NO₂$ emissions from vehicular emissions exerted a strong influence on vegetation within the first 50–100 m from the road. In India, Pandey and Agrawal ([1994\)](#page-26-15) reported that exposure of SO_2 and NO_2 (0.1 ppm $SO_2 + 0.2$ ppm NO_2 for 4 h daily for 50 days) to 45-day-old Tomato plants (Lycopersicon esculentum) produced reduced root growth and low root:shoot ratio.

3.4.3 Ground Level Ozone

Ground level or tropospheric ozone is a secondary air pollutant unlike good ozone in the stratosphere. It is produced in the troposphere by a series of complex photochemical reactions from its precursor gases, i.e., NO_x and VOCs (Brown et al. [2006;](#page-22-13) Ghazali et al. 2010). The emissions of precursors of $O₃$ have decreased or remained constant in the last few decades especially in developed countries. But in the developing countries China and India, due to rapid industrial development and

Fig. 3.2 Effects of ozone on vegetation: from plant cells to ecosystems. [Source: \odot J.P. Garrec]

urbanization, emissions of such gases have been continuously increasing (IPCC [2007;](#page-24-16) Ohara et al. [2007\)](#page-26-16). Other than precursors, meteorological parameters like solar irradiations and temperature influence atmospheric ozone concentration.

Ozone is highly phytotoxic, its adverse effects on plants were first identified in the 1950s (Ashmore [2005](#page-21-4)), which can affect many plant species growing in the wild as well as the cultivated ones (Runeckles et al. [1992](#page-27-16); Saxena et al. [2021b\)](#page-27-17). Common symptoms of ozone injury include a decrease of photosynthetic pigments, visible leaf injury, and decline of photosynthetic activity in plants exposed to higher doses of atmospheric ozone (Krupa and Manning [1988;](#page-25-14) Soldatini et al. [1998](#page-28-9); Guidi et al. [1998;](#page-24-17) Saitanis and Karandinos [2001](#page-27-18)). The acute visible injury in plants (Fig. [3.2](#page-15-0)) could decrease the economic value of species such as horticulture crops whose market value highly depends on their visible appearance (Fumagalli et al. [2001\)](#page-23-13). For instance, in North Athens, an ozone episode of 1998 caused such severe reddening and necrosis on Chicorium endivum and Lactuca sativa devalued the market price of that local crops (Velissariou [1999\)](#page-29-13). Many examples of ozone injury to the crops have been reported from India (Bambawale [1986](#page-22-16)), Taiwan (Sheu and Liu [2003](#page-28-10)). Proietti et al. [\(2016](#page-26-17)) reported a decrease in Gross Primary Production (GPP) ranging from 0.4 to 30%, in European forest from ozone exposure during 2000–2010. Heck and Dunning ([1967\)](#page-24-18) have also observed that plants are grown under shorter photoperiods and lower light intensities are more sensitive to ozone stress relative to those grown under longer photoperiods and lower light intensities or shorter photoperiods and higher light intensities. Further work by Hoshika et al.

[\(2013](#page-24-19)) suggests that ozone exposure and water stress together delayed the time of the closing signal in snap bean. Gas chamber experiments by Alonso et al. ([2001\)](#page-21-5) also suggested that cumulative effects of ozone and drought decreased antioxidant enzyme activities in Pinus halepensis exposed to 40 nL L⁻¹ concentrations of ozone. Studies have revealed that ozone exposure resulted in reduced chlorophyll contents of leaves, many workers have used plant's chlorophyll content as a reliable indicator of ozone injury (Agrawal et al. [1993](#page-21-6); Welfare et al. [1996;](#page-29-14) Della Torre et al. [1998\)](#page-23-14). In India, Sarkar and Agrawal ([2012\)](#page-27-19) observed that the growth parameters such as pollen viability and grain yield were reduced under elevated O_3 stress exposure to two high-yielding rice cultivars (Oryza sativa L. cvs Malviya dhan 36 and *Shivani*). Bhatia et al. [\(2011](#page-22-17)) reported that ozone exposure to rice (Oryza sativa L.) has been associated with a decrease in methane and nitrous oxide (GHGs) emissions. In similar observations, Singh et al. ([2018\)](#page-28-11) reported that elevated ozone exposure of 30 ppb above ambient levels to 14 widely grown Indian cultivars exposed to 30 ppb elevated O_3 resulted in foliar injury and severely affected grain yield. Mina et al. ([2010\)](#page-26-18) have also observed the effects of O_3 exposure on different growth stages of Potato (Solanum tuberosum).

3.4.4 Suspended Particulate Matter

Suspended particulate matter includes the solid and liquid particles suspended into the air. These particulates vary in their shape, size, and composition and originate from diverse natural and anthropogenic sources (El Morabet [2019\)](#page-23-15). Based on their size which is measured in terms of their aerodynamic diameter (dp), suspended particulate matters are classified into three commonly used size categories as (1) coarse particulates (dp = 2.5–10 µm), (2) fine particulates (dp \leq 2.5 µm), and (3) ultrafine particulates (dp ≤ 0.1 µm) (Seinfeld and Pandis [2016\)](#page-27-20). The aerodynamic diameter of a particle is defined as the diameter of a unit density spherical particle, having the same settling velocity as that of the particle under consideration. Coarser particulates are generally of crustal in origin, i.e., derived from aeolian action on dry soil, road dust sediments, combustion particles, municipal and solid waste debris, etc. Whereas, the fine and ultrafine particulates are originated directly from the combustion processes, the nucleation of the small particulates, and/or gas to particle conversion mechanisms.

Many studies have revealed that in the urban environments the PM_{10} and $PM_{2.5}$ atmospheric concentrations are closely linked to vehicular emissions and other combustion processes (Prajapati and Tripathi [2007](#page-26-19); Kumar and Yadav [2016;](#page-25-15) Kumar et al. [2016a](#page-25-4), [b\)](#page-25-5). World over, countries including India have established the legal framework to regulate the ambient concentration of suspended particulates especially PM_{2.5} (dp \leq 2.5 µm) and PM₁₀ (dp \leq 10 µm). Ultrafine particles can penetrate the systemic circulation and exhibit high levels of toxicity relative to coarse and fine mode particles. Moreover, the larger surface area of the fine particles increases their potential to adsorb high content of hazardous substances including heavy metals (Bernstein et al. [2004](#page-22-4)). Deposition of particulates on the leaf surface may obstruct the amount of sunlight, result in the plant by increasing leaf surface temperature (Rahul and Jain [2014](#page-26-20)), and, the effect on plant physiology and biochemistry (Rai [2016](#page-26-21)). Particulates with diameter lesser than the stomatal aperture can directly enter the sub-stomatal cavity, may result in stomata clogging (Vijaywargiya and Pandey [2003\)](#page-29-15), which in turn could decrease the rate of carbon dioxide exchange (Darley [1966\)](#page-22-18), carbon assimilation, transpiration (Singh and Rao [1982\)](#page-28-12), and therefore net photosynthesis (Singh and Sthapak [1999\)](#page-28-13). Studies have reported an increase in the number of epidermal cells and stomata, necrotic lesions, and death of epidermal cells in plant species exposed to particulate pollution (Jafri et al. [1979;](#page-24-20) Borka [1981;](#page-22-19) Shanmughavel [1997](#page-27-21); Pal et al. [2000](#page-26-22)).

Plant leaves provide a large surface area for impingement, absorption, and accumulation of air pollutants. Vegetation cover can be used as an important means for filtering out suspended particulates in the air, especially in the high traffic density locations and industrial zones (Freer-Smith et al. [1997](#page-23-16)) for enhancement of urban air quality (Beckett et al. [1998;](#page-22-20) Freer-Smith et al. [2005\)](#page-23-17). The capacity to filter atmospheric pollutant may vary from one species to other (Liu and Ding [2008](#page-25-11)). Sett [\(2017](#page-27-22)) suggested that cuticular and epidermal traits of the leaves in response to the dust pollution could be used as the bioindicator of the pollution levels.

3.4.5 Fluorides

Fluoride compounds have severe impacts on the animals and terrestrial and aquatic ecosystems (Weinstein and Davison [2004](#page-29-16); Divan et al. [2008;](#page-23-18) Walna et al. [2013\)](#page-29-17). Natural sources of fluoride emissions into the atmosphere are rock weathering, volcanic eruptions, or the marine environment (Barnard and Nordstrom [1982\)](#page-22-21), while the principal anthropogenic sources are fertilizer production and application, household detergents, aluminum smelters, cement industries, ceramic and pottery works and glass manufacture (Cape et al. [2003](#page-22-22)). Common examples of fluoride pollutants are SiF₆, HF, CF₄, and F₂ in the gaseous phase and CaF₂, NH₃F, Ca₃AlF₆, AlF_6 , NaF, and Na₂SiF₆ in the particulate phase. Hydrogen fluoride (HF), is the most hazardous fluoride pollutant. Fluorine emitted from anthropogenic sources in the gaseous phase is hydrolyzed under moist conditions to form HF. Hydrogen fluoride undergoes a rapid chemical reaction with silicates to form volatile SiF_6 . HF also reacts with many materials forming nonvolatile, stable fluoride compounds (Kirk and Lester [1986\)](#page-25-16). The distribution and deposition of its compounds are primarily governed by the magnitude of their emissions from the source, chemical reactivity of the fluoride compounds (Hara et al. [1998](#page-24-21)), size of the particulates, and meteorological conditions (Gasic et al. [2010;](#page-23-19) Scheringer [2009\)](#page-27-23).

Damage to plants from fluoride compounds can happen at concentrations about 1000 times lower than those causing any visible effects on human health (Manins et al. [2001\)](#page-25-17). Atmospheric HF can result in visible injury in plants at concentrations as low as 0.3 μm^{-3} (Cape et al. [2003\)](#page-22-22). Fluoride contamination affects photosynthesis and other physiological processes in plants. It enters into the transpiration stream of plants through stomata or roots (Feng et al. [2003\)](#page-23-20) and accumulates in leaf margins.

Symptoms of fluorine damage includes tip necrosis in confers that spreads to the base, while in broadleaf plants include marginal and tip necrosis that spread inward (Krupa [2001;](#page-25-18) Sharma and Kaur [2018\)](#page-28-14). The vegetation contaminated by fluoride deposition if eaten by domestic animals may produce serious effects since these animals are typically vulnerable to fluoride (Shupe [1969\)](#page-28-15). Studies have shown that roughly 96% of the ingested fluoride accumulates as mineral crystals in the teeth and bones in the bodies of animals (Zipkin [1972](#page-29-18)). Irrigation from fluoride contaminated water has been linked to a gradual decrease in the germination pattern of Oryza sativa L. Mondal [\(2017](#page-26-23)). In India, groundwater contamination of fluoride is a major environmental issue. Many studies have been conducted in India to document the effects of fluoride on plants (Mondal [2017](#page-26-23); Sharma and Kaur [2018](#page-28-14); Khound and Bharali [2018;](#page-24-22) Usham et al. [2018](#page-29-19)).

3.4.6 Peroxyacyl Nitrates

Peroxyacetic nitric anhydride $(CH_3COO_2NO_2)$, also known as peroxyacetyl nitrate, is a powerful respiratory and eye irritant. Peroxyacetyl nitrate (PAN) is an important reservoir species of NO_x in the atmosphere, consequently leads to the formation of ozone and hydroxyl radicals in the lower troposphere (Singh and Hanst [1981\)](#page-28-16). PAN has a longer residence time in the atmosphere and can be further transported and distributed to remote locations away from their source of origin (Mudd [1975;](#page-26-13) Teklemariam and Sparks [2004;](#page-28-17) Fischer et al. [2014\)](#page-23-21). The presence of non-methane volatile organic compounds (NMVOCs) and NOx is a prerequisite for the formation of PAN, both these precursors can be made available from natural as well as anthropogenic sources (Roberts [2007](#page-26-24); Fischer et al. [2014\)](#page-23-21). The burning of fossil fuels is the major source of NOx production, with additional inputs from biomass burning, natural lighting, and soils.

In plants like bean leaves (*Phaseolis vulgaris L.*), PAN could induce the oxidization of sulfhydryl groups on enzymes required for the photophosphorylation, thus producing inhibitory effects on the cyclic photophosphorylation of chloroplasts (Koukol et al. [1967\)](#page-25-19). Plants are susceptible to PAN pollution and show visible injury at much lower concentrations. Studies by Temple and Taylor ([1983\)](#page-28-18) have shown that PAN exposure of 14 nmol mol⁻¹ to petunia and tomato plants for 4-h duration initiated acute injury symptoms (Taylor [1969](#page-28-19)). In the susceptible plant species like lettuce and beet, the foliar injury was initiated at a threshold concentration of 15 nmol mol⁻¹ and for 4-h exposure, while severe injury resulted from 25–-30 nmol mol $^{-1}$ concentration of PAN for 4-h exposure.

Besides major air pollutants, there are many minor pollutants such as hydrogen sulfide (H_2S) , carbon monoxide (CO) , vapors of metals like mercury, arsenic, cadmium, etc.; heavy metals bound in particulates; bromine $(Br₂)$ and iodine $(I₂)$; soot dust; chlorides of sodium, potassium and calcium, sodium sulfate dust; pesticides, insecticides, and herbicides which were known to significantly affect the biota health.

3.5 Impacts of Air Pollutants on Human Health

Humans are exposed to air pollutants directly via inhalation, ingestions, and through dermal contact or indirectly from ingestion of contaminated water, soil, or through the food chain. According to WHO, world over around 90% of the people were exposed to high levels of atmospheric pollutants in 2016. The air pollution alone kills an alarming 7 million people annually, out of which a whopping 4.2 million premature deaths are caused by outdoor air pollutants. A large proportion of this burden, estimated to be around 91%, is shared by third world countries mainly in South-East Asia and Western Pacific regions (WHO [2020](#page-29-0)). Short-term exposure to air pollutants exposure to humans may induce symptoms ranging from acute to severe breathing problems, wheezing, eyes burning, skin irritation, higher rates of hospitalization, whereas, the long-term exposure is closely associated with more complicated health issues leading to cardiovascular diseases, chronic asthma, effects on the nervous system, reduced activity of the immune system, cardiovascular mortality, carcinogenicity, etc. (Manisalidis et al. [2020\)](#page-25-2). Traffic-related air pollution (TRAP) is the predominant source of air pollution in urban areas throughout the world. In rural regions, especially those in the developing countries, indoor domestic emissions from coal and biomass burning are the major pollution source (Laumbach and Kipen [2012\)](#page-25-20). The occurrence of sporadic events like the Bhopal gas tragedy in 1984 in the Indian state of Madhya Pradesh that claimed around 2000 from the release of methyl isocyanate (MIC) from pesticide plant is another serious concern of air pollution exposure to humans, especially in the occupational environments. Many urban regions of India and China in recent decades have emerged as the new hotspots of the world, where a large proportion of the world's population lives and is exposed to the dangers of air pollution.

The majority of the air pollution-related health issues include respiratory and allergic diseases such as asthma, chronic obstructive pulmonary disease (COPD), pneumonia, skin irritation, and tuberculosis (Laumbach and Kipen [2012\)](#page-25-20). Nations across the world including India have devised their National Ambient Air Quality Standards (NAAQS) to regulate the ambient concentrations for air pollutants of utmost concern. USEPA has identified six pollutant criteria air pollutants, i.e., $SO₂$, NO₂, CO, tropospheric O₃, suspended particulate matter, and lead for regular monitoring to maintain the ambient air quality of different regions. $NO₂$ is a respiratory irritant, as it penetrates deep in the lung. Its inhalation may induce respiratory diseases, coughing, wheezing, dyspnea, bronchospasm, and even pulmonary edema at higher ambient concentrations. It may affect the T-lymphocytes in the body as their concentrations exceed 2.0 ppm. Likewise, the $SO₂$ is a sensory irritant and penetrates deep into the lung converted into bisulfite and interacting with sensory receptors, causing bronchoconstriction. Its inhalation, particularly in the industrialized and high traffic density locations, induces respiratory irritation, bronchitis, mucus production, and bronchospasm, (Manisalidis et al. [2020](#page-25-2)). Air pollutants act as unspecific irritants and immunomodulators; studies by revealed that high pollution levels especially NO_x and $PM₁₀$ are positively correlated with increased risk of asthma among asthmatics in Taiwan. Chronic exposure to such pollutants could further enhance the risk of lung cancer-sensitive individuals. In India, Singh et al. [\(2000\)](#page-28-20) have observed severe respiratory symptoms and reduced forced expiratory volume among the Traffic Police personals of Jaipur City, Rajasthan due to high exposure of air pollutants. Ambient concentrations of $PM_{2.5}$ and PM_{10} are reported to exhibit adverse health effects on humans such as heart disease, stroke, blood pressure, and cardiovascular diseases (Brook et al. [2010](#page-22-23); Lee et al. [2014\)](#page-25-21). Bourdrel et al. ([2017\)](#page-22-24) in their review work on cardiovascular effects of air pollution found that a 10 μ g/m³ increase in long-term exposure to PM_{2.5} was associated with an 11% increase in cardiovascular mortality. Exposure to carbon monoxide affects the oxygen-carrying capacity of the blood resulting in impaired concentration, slow reflexes, confusion, and in extreme cases deaths. In India, Suresh and Das, [2003](#page-28-21) reported that the levels of various antioxidants in the RBC lysate such as catalase, superoxide dismutase, and glutathione peroxidase were found to be low in a traffic policeman in the city of Hyderabad.

Besides, exposure to air pollutants in particular heavy metals and dioxins adversely affects the central nervous system, and is closely associated with cognitive dysfunction, Alzheimer's disease and Parkinson's disease, structural brain effects, and white matter injury (Genc et al. [2012](#page-24-23); Babadjouni et al. [2017](#page-21-7)). Dioxins are known to decrease nerve conduction velocity and impair the mental development of children (Thömke et al. [1999;](#page-29-20) Walkowiak et al. [2001](#page-29-21)). Exposure of As, Pb, and Hg has been linked to symptoms such as memory disturbances, anger, fatigue, sleep disorders, blurred vision, slurred speech, and hand tremors (Ewan and Pamphlett [1996;](#page-23-22) Ratnaike [2003](#page-26-25)). Maternal exposure to air pollutants affects the developing fetus (Schell et al. [2006\)](#page-27-24). Maternal exposure to lead increases the risks of spontaneous abortion and reduced fetal growth, congenital malformations (Bellinger [2005\)](#page-22-25). Dioxins can be transferred to the developing fetus from the mother via the placenta, they act as endocrine disruptors and affect the growth and development of the central nervous system of the fetus (Wang et al. [2004](#page-29-22)). Oxygen supply to the fetus is maintained from the mother's blood. Breathing polluted air during pregnancy can result in premature birth, low birth weight impaired lung development, increased later respiratory morbidity, early alterations in immune development, and can increase the baby's risk of contracting illnesses (Proietti et al. [2013](#page-26-26); Korten et al. [2017;](#page-25-22) La Marca and Gava [2018\)](#page-25-23). Besides, the prenatal exposure of PAHs affects the child's behavior and neurodevelopment, a decrease of IQ, increase of attentiondeficit hyperactivity disorder, a decrease of brain-derived neurotrophic factor, and reduction of left hemisphere white matter (Sram et al. [2017](#page-28-22)). Furthermore, epidemiological evidence suggests that periods of elevated air pollution affect the semen quality and damage sperm DNA (Dejmek et al. [2000](#page-23-23); Rubes et al. [2005\)](#page-27-25).

Besides the above-mentioned health implications, many of the air pollutants are known to be potential carcinogens that can either initiate and/or promote carcinogenesis by a diverse number of mechanisms such as DNA adducts and DNA protein cross-links formation, epigenetic alterations, regenerative cell proliferation, oxidative stress, inhibition of DNA repair, and altered cell cycle regulation. Common air carcinogens are formaldehyde, benzene, PAHs, ETS (environmental tobacco smoke), etc.

3.6 Conclusions

Effects of air pollution on plant and animal biota and natural and man-made materials are manifested directly as well as indirectly. The severity of the impacts of pollutants is variable and differs from one ecosystem to another and one organism to another. Emissions of such pollutants also strongly interfere with the atmospheric processes at local, regional, or global scales. Common atmospheric impacts of air pollutants are greenhouse effect and global warming; stratospheric; ozone depletion; atmospheric deposition, and acid rain; suppression of rainfall; atmospheric visibility reduction, etc. Developing economies are at higher risks of their owing to higher abatement costs associated with it. Even a marginal increase of 10 μ g/m³ of ambient PM_{10} levels in Asian cities could lead to a surge in the mortality rate by 0.6%, which is significantly higher than the trends estimated for Western cities. Plants are highly susceptible to direct damages caused by contacting the air pollutants and indirectly from the changing state of the atmosphere, e.g., global warming, acid rain, stratospheric ozone depletion, etc. At the intergovernmental level several efforts have been made to regulate the air pollutants, e.g., the Geneva Convention on Long-range transboundary air pollution (1979) to regulate SO_x , NO_x , persistent organic pollutants, non-methane volatile organic compounds, tropospheric ozone, heavy metals, particulate matters, and black carbon; Montreal protocol to regulate ozonedepleting substances; the Paris agreement for control of GHGs, etc. Despite these efforts, control of air pollutants is still a far-off dream for policymakers, especially in developing economies like India and China, which are now the new pollution epicenters of the world. Therefore, timely policy interventions based on scientific facts must be made to regulate the air pollutants world over and minimize their impacts on living biota and atmospheric processes.

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