Effects of Gaseous Pollutants on Medicinal Plants

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Abstract Plants are regarded as the crucial creatures in the formation of life on the planet Earth. Unfortunately, the climate of the Earth is rapidly deteriorating, primarily because of the increasing concentration of pollutant gases in the atmosphere, and the consequent rise of temperature and its after effects. Emissions from power plants and various factories (mostly a combination of oxides of carbon, nitrogen, and sulphur) and the release of greenhouse gases (carbon dioxide, methane, nitrous oxide, ozone, chlorofluorocarbons, etc.) are mainly responsible for this grave situation. The presence of these unwanted molecules in the atmosphere has a big impact on plants' growth and productivity. Since plants cannot move away from harmful conditions due to their sessile nature, they have to face the harsh environment and undergo various alterations in their form and function. Metabolic alterations, or more precisely, fluctuation in the concentration of secondary metabolites, are thought to be one of the plants' defense mechanisms against unfavorable environments. Secondary metabolites, although not required for a plant's usual functions, do form the immune system of plants. Climate change has the potential to alter the quality of natural products, as well as the flavor and medicinal value of various plant species. Rising temperatures, drought, salinity, and erratic rainfall, which are an outcome of all these gaseous emissions, have an obvious impact on plant growth and physiology. This chapter presents a brief discussion of these atmospheric impacts on the form and function of medicinal plants with a special focus on their secondary metabolism.

Keywords Climate change · Ecosystem · Gaseous pollutants · Medicinal plants · Secondary metabolites

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Abbreviations

CFC	Chlorofluorocarbons
TCM	Traditional Chinese Medicine
UV light	Ultraviolet light
WHO	World health organization

1 Introduction

Climate change is associated with changes in climate over a comparable length of time that is related to human activities and modifies the composition of the global atmosphere, either directly or indirectly. Over the last century, the global mean temperature of the earth's surface has risen by 0.74 °C. According to the fluctuation in surface temperature, the 1990s decade was the warmest in the past millennium, with 1998 being the warmest year. The temperature rise is ascribed to an alarming increase in atmospheric concentrations of a variety of toxic gases (largely oxides of carbon, nitrogen, and sulphur) emitted from households, various industries, and thermal power plants, and the so-called greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs), primarily as a result of increased industrialization (Fig.1). Carbon dioxide concentrations are expected to be 100% greater in 2100 than they were in the pre-industrial era. With global temperatures anticipated to climb by up to 6 °C by the end of the century in comparison to the pre-industrial levels, this agroclimatic indicator is unlikely to remain steady (Singh 2010). The presence of these toxic elements in

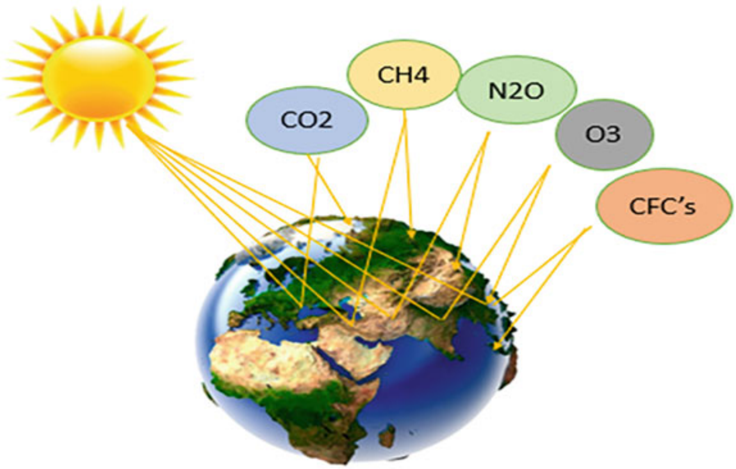

Fig. 1 Diagram showing gaseous pollutants

the air, soil, and water gives rise to some secondary stress factors like increased temperature, rising sea level, drought, salinity, and excess of heavy metals, among others. All these pollutants and the consequent environmental conditions are active in the growing plants individually or collectively at the same time (Aref et al. 2013a, b; Hussein et al. 2017; Iqbal and Ghouse 1982; Iqbal et al. 2000b; Qureshi et al. 2006; Husen 2022a; Husen et al. 2014, 2016, 2017, 2018, 2019; Getnet et al. 2015; Embiale et al. 2016). The physiological status of plants is determined solely by the local climatic factors; for example, photosynthesis is influenced by temperature, carbon dioxide, water, and nutritional ingredients. Planting a crop in an ecologically unsuitable location increases production costs and, as a result, diminishes the likelihood of economic success. Environmental conditions of the habitat determine the size of plants, the duration of phenological stages, and the time and volume of harvest at a specific location (Iqbal and Khudsar 2000; Kumar et al. 2020). Plant growth and development are influenced by a variety of environmental conditions and soil characteristics (Iqbal and Ghouse 1985; Hamdo et al. 2010; Husen 2022a). Climate change is responsible for the variations in environmental conditions across the globe, which have a big impact on chemical constituents, especially the secondary metabolites in plants (Iqbal et al. 2011). Significant biological and pharmacological functions are attributed to these plant components.

Climate change has a wide range of negative consequences for various sectors, including human health, water, air, soil, microbial populations, plants, and their medicinal components (Ahmad et al. 2011). Climate change is caused by several variables, including a growing global population, fast industrialization, and the widespread use of chemical fertilizers and pesticides in agricultural fields. Rising temperatures, drought, and changes in rainfall patterns are all examples of changing climatic conditions. All these characteristics have an impact on how humans, plants, and microbial population function. Anthropogenic activities have played a significant role in causing global climate change. Excessive emissions of gases like CO_2, SO_2, NO_2, and O_3 have resulted in global warming and consequently climatic shift (Mishra 2016). Plants, unlike humans, cannot move away from harmful conditions due to their sessile nature; they have to resort to additional mechanisms to ensure their protection and survival (Iqbal et al. 1996; Anjum et al. 2012b; Husen 2021a, b, c, d). Metabolic alterations, or more precisely, fluctuation in the nature and content of secondary metabolites, are thought to be one of the plant's defense strategies against the unfavorable environments (Pichersky and Gang 2000; Ober 2005). Secondary metabolites are molecules that aren't required for a plant's usual functions, but together with alkaloids, terpenes, and cyanogenic glycosides, they form a plant's immune system (Wink 2003; Hartmann 2007). Climate change has the potential to alter the quality of natural products, as well as the flavor and medicinal value of particular plants (Gore 2006). Secondary metabolite production is increased in stressed situations; nevertheless, secondary metabolite production is influenced by several elements such as plant competition, intensity and duration of light, soil characteristics, and degree of humidity, among others (Das 2012). In comparison to other living organisms, medicinal and aromatic plants are less resistant to climate change. Because climate change has a profound impact on plant life cycles and distributions, many medicinal plants have become indigenous to specific geographic locations. Global warming is supposed to cause a widespread plant extinction around the world. It is estimated that due to further increases in greenhouse gas emissions, more than half of the plants would be damaged by 2080 (Das and Mukherjee 2018). The reaction of plants to climate change varies depending on the plant species and developmental stage. Various plants have different species-specific thresholds, and their reactions, such as root elongation, root growth angle disruption, and yield loss, differ with species (Malhi et al. 2021).

This chapter discusses the impact of gaseous pollutants and the climate change on medicinal plants and their products, particularly on secondary metabolites (SMs). Special attention has been paid to the natural behavior, physiology and metabolism under harsh environmental conditions.

2 Medicinal Plants and their Importance

Plants play a vital role in the medicinal and healthcare regimes of people living in remote locations as in mountainous or desert regions, who often have a strong faith in the efficacy of herbal medicines, and generally lack access to contemporary healthcare facilities (Anis et al. 2000; Beigh et al. 2002, 2003a, b). Ayurvedic, Unani, and other traditional medicinal systems, as well as plant-based pharmaceutical enterprises, amply utilize the medicinal plants (Kumar et al. 2017; Parveen et al. 2020a, b, 2022; Husen 2021f, 2022b).

Medicinal plants are particularly important because of their secondary metabolites of pharmacological qualities, which are widely used in the pharmaceutical, cosmetic, and nutritional industries (Beigh et al. 2002; Hassan et al. 2012). According to the World Health Organization, about 80% of the world's population and 65% of Indians utilize natural and traditional methods of healing and curing with medicinal herbs (Bannerman 1980; Prashantkumar and Vidyasagar 2008). In Indian society, there are people, known as 'Vaidyas' and 'Hakeems', who have a deep understanding of medicinal plants and their applications for healing. They utilize the native herbal plants as a source of raw materials to create medications for disease therapy (Chopra and Khoshoo 1986). Herbal medication is now gaining ground in India as an alternative to modern Allopathy for treating chronic disorders. Plants produce a variety of secondary metabolites with unique properties that help improving the human immune system and treating various ailments (Husen and Iqbal 2022). In terms of toxicity or side effects, plant extracts have more positive points than negative ones (Van Huyssteen 2007). Even those living in developed countries are now opting for herbal medicine because of their low cost and negligible side effects. Terpenoids, phenols, steroids, flavonoids, tannins, and aromatic compounds are only a few of the chemicals derived from plants. Secondary metabolites are employed by plants for immunity against pathogens and herbivores; over 12,000 secondary metabolites have been isolated, with many more in the process of identification. Different components of plants are consumed more frequently than their derived oil during eating. By now, just a small number of medicinal plants, about half a million plants, have been identified; therefore, medical plant research has a bright future.

3 Secondary Metabolites under Changed Climate

Isolated plant metabolites, such as phenols, terpenes, and alkaloids, have been used in a variety of ways, including alterations to the core skeleton of products and medications. The isoprenoid, polyketide, and shikimate pathways are the primary pathways for the synthesis of secondary metabolites in plants (Verpoorte and Memelink 2002). Secondary metabolites have been proven in numerous studies to lessen the risk of a variety of major diseases and syndromes, including diabetes, TB, ulcers, asthma, cancer, Alzheimer's disease, and cardiovascular disease (Basu and Imrhan 2007; Holst and Williamson 2008; Crozier et al. 2009; Fang et al. 2011; Akula and Ravishankar 2011; Miller and Snyder 2012). According to studies, within 10 years (2005–2015), around 60 plant extracts and 110 purified compounds were obtained from 112 medicinal plants, and they showed efficacy in the treatment of multidrug-resistant pathogenic disorders (Gupta et al. 2019). Anthropogenic activities of the modern world have played a major role in polluting the atmosphere with a variety of toxic gases and particulate matters, although some natural events taking place occasionally also cause environmental degradation (Yunus and Iqbal 1996; Iqbal et al. 2000b). The pollutants so produced are responsible for increase in the atmospheric temperature, thus affecting the climatic condition. The gaseous as well as particulate pollutants not only remain suspended in the air but also settle down on the earth surface, thus rendering the air, soil and water toxic and unhealthy for life activities (Ansari et al. 2012; Iqbal et al. 2000a). These atmospheric changes result in conditions like drought, salinity, flooding, and extreme low or high temperature swings (Gupta et al. 2019). Plant growth and development are bound to be influenced by abiotic variables, as each plant species requires specific environmental conditions to thrive (Table 1).

Under harsh environmental conditions, plants tend to alter their set patterns of metabolic and functional activities in order to adapt to the changed environment (Anjum et al. 2012a; Iqbal and Khudsar 2000; Iqbal et al. 2005). This results in alteration of their physiological, structural and developmental traits (Aquil et al. 2003; Dhir et al. 1999; Singh et al. 2000). Finally, both the primary and secondary growth patterns get affected and exhibit a drastically modified picture (Hussein et al. 2017; Iqbal and Ghouse 1982; Iqbal et al. 2000b, 2010c; Verma et al. 2006), to the extent that even the schedule and duration of the formation of secondary vascular tissues (wood and bark) and also their composition (i.e. relative proportion of the component cell types, like axial parenchyma, fibres, tracheids/vessel elements, sieve-tube elements, ray cells, etc.) may undergo alteration (Gupta and Iqbal 2005; Iqbal et al. 2000a, 2010a, b; Mahmooduzzafar et al. 2010).

Currently, increase in normal temperature is a common and predictable feature all over the globe (Bhatla and Tripathi 2014). Temperature increases up to 5 °C have

Table 1 Impact of elevated carbon dioxide and ozone on secondary metabolites of some well-known medicinal plant species

Sr. No	Plant name	Disease treated	Pollutant	Alterations caused	References
1	*Ginkgo biloba* L.	Alzheimer disease	Elevated CO_2	Altered terpenoid content, 15% increase in quercetin aglycon and a 10% decrease in kaempferol aglycon, 15% in isorhamnetin and bilobalide to some extent	Gupta et al. (2019)
2	*Quercus ilicifolia* Wangenh.	Gynecological problems	Elevated CO_2	Increase in tannins and phenolic content	Stiling and Cornelissen (2007); Ibrahim and Jaafar (2012)
3	*Melissa officinalis* L.	Dementia, Anxiety and Central nervous system (CNS) related disorder	Elevated ozone	Increased in total anthocyanins to a substantial extent along with phenolics and tannins	Pellegrini et al. (2011); Shakeri et al. (2016)
4	*Capsicum Baccatum* L.	Asthma and digestive Problems	Elevated ozone	50% decrease in capsaicin and dihydrocapsaicin, seeds showed significantly reduction in capsaicin but no change in dihydrocapsaicin	Bortolin et al. (2016)
5	*Papaver setigerum* DC.	Eye and lung inflammation	Elevated CO_2	Enhancement of four alkaloids viz. morphine, codeine, papaverine and noscapine	Ziska et al. (2008)
6	*Hymenocallis Littoralis* (Jacq.) Salisb.	Neoplastic diseases and viral infections	Elevated CO_2	Increase in three types of alkaloids (pancratistatin, 7-deoxynarciclasine and 7-deoxy-trans dihydronarciclasin)	Idso et al. (2000)
7	*Salvia officinalis* L.	Gastritis, diarrhea, bloating, and heartburn	Ozone stress	An increase in phenolic content, notably in Gallic acid, Catechinic acid, Caffeic acid and Rosmarinic acid	Pellegrini et al. (2011)

been observed recently, and this can have a drastic impact on many plant species with reference to their survival, growth and yield (Cleland et al. 2012; Noor et al. 2019). Temperature spikes affect plant metabolic and growth performances due to changes in metabolic pathways that control signaling, functioning and defense programs within the plant. Consequent upon these conditions, production of primary metabolites, such as amino acids, carbohydrates, and Krebs cycle intermediate products, and also of various nitrogenous as well as non-nitrogenous secondary metabolites, gets affected. In general, an increased production of secondary metabolite protects plants from biotic stress, thus providing a connecting link between the biotic and abiotic stresses (Arbona et al. 2013). Some genotypic adjustments or changes could aid in the damage mitigation or plant adaptation to changing environmental conditions (Springate and Kover 2014). By way of an early activation of metabolic reactions, plants can overcome chemical imbalances, which is a must for their survival. Plants capable to modify their morphology and physiology in response to environmental changes can survive well under harsh environments (Millar et al. 2007; Noor et al. 2019).

3.1 Impact of CO_2 on Secondary Metabolites

Since the industrial revolution, CO_2 levels have risen substantially, posing a serious threat to human life and plant physiology. Since 1750, CO_2 emissions have increased considerably as a result of anthropogenic activity (Gupta et al. 2019). Although CO_2 basically favours photosynthesis and hence the phenomenon of plant growth (Ruhil et al. 2015), yet its excessive concentrations become toxic for plants. Medicinal plants have the ability to adapt to changing environmental circumstances. Secondary metabolites provide elasticity to their metabolic pathways, but this may have an impact on metabolite production, which is the foundation of their therapeutic efficacy (Mishra 2016). Secondary metabolite concentrations in plants are regulated not only by CO_2 concentration, but also by the exposure period. *Digitalis lanata* is used to treat heart failure and contains medicinal qualities (Rahimtoola 2004). When exposed to high levels of CO_2, however, digoxin (a cardenolide glycoside) concentrations increased by 3.5-fold, whereas other glycoside concentrations, such as digoxin-monodigitoxoside, digitoxin, and digitoxigenin, declined dramatically (Table 1). According to Weinmann et al. (2010), *Ginkgo biloba* is used to treat Alzheimer's disease, vascular dementia, and mixed dementia. When *G. biloba* is exposed to high levels of CO_2 and O_3 together, the terpenoid content changes, with a 15% increase in quercetin aglycon but a 10%, 15%, and to some extent, a drop in kaempferol aglycon, isorhamnetin, and bilobalide concentrations, respectively. Ghasemzadeh et al. (2010a, b) reported an increase in the concentrations of phenolic and flavonoid in *Zingiber officinale* due to increases in CO_2 levels. (Stiling and Cornelissen 2007) observed elevation in the concentrations of phenols and tannins in *Quercus ilicifolia* related to increases in CO_2 levels. Similar studies with *Elaeis guineensis* (oil palm) revealed an increase in phenols and flavonoids, and also in the primary metabolite phenylalanine, which is a precursor of various secondary metabolites (Ibrahim and Jaafar 2012; Rehman et al. 2021).

3.2 Impact of Ozone on Secondary Metabolites

Ozone layer in the stratosphere absorbs damaging ultraviolet light with wavelengths in the UV-B band between 280 and 320 nm, which can injure plants and animals (Montzka et al. 2018). Although ozone is prevalent in the stratosphere, it is considered a pollutant when present in the lower atmosphere (troposphere). It should, therefore, have harmful effects on plants also. Because the effects of O_3 on medicinal plants are little studied, it is important to extend future research in this direction (Table 1). *Melissa officinalis* is utilized to treat central nervous system issues, dementia, and anxiety. However, when exposed to high levels of O_3, its levels of phenols, tannins, and anthocyanins were slightly enhanced (Pellegrini et al. 2011; Shakeri et al. 2016). When a suspension culture of *Pueraria thomsonii* was exposed to O_3, it showed no elevation in the production of puerarin after 20 hours of exposure (Sun et al. 2012). However, a maximum of 2.6-fold increase in puerarin could be obtained after 35 hours (Gupta et al. 2019).

3.3 Plant Response to SO_2 and NO_x

Plants have long been used to pattern the degree of ambient air pollution because they are the first recipients of contaminants and act as their scavengers (Kaler et al. 2017). Pollutants emitted from various sources are normally the oxides of carbon, nitrogen and sulphur in gaseous form. They accumulate or impose themselves on the plant's leaf surface in particular and enter the leaf through stomata. Thus, they penetrate into the intercellular spaces of mesophyll cells and progressively diffuse into the cell sap. Air pollution has a negative impact on the health of plants; plant cells become inactive when pollutants are present in large concentrations (Iqbal et al. 1996; Munsif et al. 2021). Pollutants such as SO_2, NO_2, and H_2S cause a greater depletion of soluble sugars in the leaves of plants grown in polluted locations. Changes in the biochemical parameters of plant tissues are normally proportional to the load of contaminants inside the plant. Plant symptoms produced by air pollution may be chronic or acute, depending on the nature and extent of injury or damage (Dhanam et al. 2014). A chronic injury can kill a whole tissue or ruin the entire area of a leaf or needle. Acute damage occurs when a plant is overly sensitive to a particular pollutant or is exposed to high levels of pollution for a brief period of time. SO_2 is oxidized inside the leaf to sulphur trioxide (SO_3), which then reacts with water to generate sulfuric acid (H_2SO_4). As a result, acid production in the plant's body disrupts metabolic activities and reduces the plant's output (Sharma et al. 2017). Similarly, NO_2 interacts with the cell walls to create nitrous acid (HNO_2) and nitric acid (HNO_3), which lower the cellular pH, inhibit metabolism, and cause toxicity and growth suppression. Discolored spots or light brown hue, as well as bleached or necrotic spots in interveinal sections of leaves, are the morphological signs induced by NO_2 (Das and Mukherjee 2018; Adak and Kour 2021).

Sulphur gases are substantial air pollutants that can be created naturally by volcanic activity, but large concentrations owe to anthropogenic emissions from fossil fuel combustion (Sun et al. 2018). Plant metabolism can be significantly altered by air pollutants such as SO_2, H_2S, NO_2, or O_3, which affect a variety of molecules such as sugars, polyamines, phenylpropanoids, and several specialized phytochemicals (Khaling et al. 2015; Papazian et al. 2016). The majority of air pollutants, such as CO, SO_2, NO_2, and O_3, interact with plants near the leaf surface, where they can diffuse through stomatal pores and enter intracellular regions (Castagna and Ranieri 2009; Räsänen et al. 2017). Once absorbed, these hazardous chemicals disrupt stomatal functioning, leaf transpiration, gas exchange, and CO_2 fixation (Nighat et al. 2000; Rai et al. 2011). Chlorophyll content and photosynthetic rate are the main target and the major sufferers, and their disruption affects the entire form and function of the plant (Dhir et al. 2001; Wali et al. 2004, 2007). The reduced CO_2 availability and photosynthetic efficiency have a significant impact on plant central carbon metabolism. Oxidative stress caused by the production of reactive oxygen species (ROS) in tissues then compels the plant to develop appropriate responses to the pollutants load through activation of enzymatic and/or non-enzymatic antioxidant system and the production of specific secondary metabolites (Ainsworth et al. 2012; Yendrek et al. 2015; Aref et al. 2016).

3.4 Role of Methane and CFC's

Methane (CH_4), one of the most significant greenhouse gases, was previously thought to be a physiologically inert gas. However, the discovery that CH_4 has a variety of biological activities in animals, including anti-inflammatory, antioxidant, and anti-apoptosis activities, has cast doubt on this viewpoint. Meanwhile, it has been identified as a potential gaseous signaling molecule in plants, however the biosynthetic and metabolic pathways, as well as the mechanisms of CH_4 signaling, are yet unknown. Plants have traditionally been thought of as conduits for CH_4 transport and emission from the soil to the atmosphere (Li et al. 2020). Agricultural soils are the major source of methane and nitrous oxide gases and a sink of carbon dioxide. About 30% and 11% of the global agricultural output of methane and nitrous oxide, respectively, come from rice fields. Alterations in the conventional crop management regimes may likely cause reductions in the emission of these gases from the rice field. Organic soil amendments reportedly increase CH_4 emission from rice fields and improve the flag leaf photosynthesis of the rice crop over the control (NPK application alone). The combined application of NPK and Azolla compost caused a 15.66% higher CH_4 emission with 27.43% more yield over the control and increased the capacity of soil carbon storage, with a high carbon efficiency ratio (Bharali et al. 2018; Gupta et al. 2021). FCs (chlorofluorocarbons) are normally harmless and non-flammable compounds made up of carbon, chlorine and fluorine atoms. However, they are known to destroy the ozone layer, and this is likely to allow greater amounts of the sun's radiation reach the earth and affect the plants. It is, therefore, apprehended that the plants may consequently experience abnormal and reduced growth due to possible protein denaturation and DNA damage (Gupta 2018).

4 Conclusion

Plants have a wide range of species and produce a large number of secondary metabolites, many of which are physiologically active and extremely beneficial to humans, being utilized mainly for therapeutic purposes. Medicinal plants have been used to develop new allopathic medicines for the past few decades. Changing climatic circumstances and abiotic stress factors have an impact on plants' natural behavior and physiology, which has an impact on essential secondary metabolites. Gaseous pollutants (such as SO_2 and NO_2) and greenhouse gases (like CO_2, ozone, methane, and CFCs) have direct toxic effects on plants and also change climatic conditions, affecting water, pH level, and salinity, which again have a bearing on metabolite production in plants. Some environmental factors, such as temperature and elevated CO_2, basically enhance the secondary metabolism in plants, whereas extreme temperatures (too hot or too cold), drought, and high salinity negatively affect the metabolites, growth, and productivity of plants.

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