Effects of Toxic Gases, Ozone, Carbon Dioxide, and Wastes on Plant Secondary Metabolism

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Abstract Various kinds of human activities along with environmental interactions or changes are occasioning the addition and accumulation of hazardous entities in the environment. The subsequent result of this is negative effects of these factors on living systems including plants. Factors such as heavy metals, toxic gases, ozone, and carbon dioxide have a major impact on plant growth and secondary metabolism of the plants. Secondary metabolites are the key players in plant adaptation to these environmental stresses and play a role in mitigating the negative effects of these stresses. Both primary and secondary metabolisms are altered under these stress environments, however, plants have evolved to endure these conditions through inducing several regulating mechanisms such as evapotranspiration of available water, controlled openings and closings of stomata as per the availability of water, over accumulation of various osmoprotectants and osmoregulators, induction of antioxidant machinery and fine tuning of transcriptional and post-transcriptional regulations of gene expressions. In most of the plants, the ultimate result of these

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defensive adaptations is regulated production of the secondary metabolites. In this chapter, we have discussed the effects of toxic gases, ozone, carbon dioxide as well as other wastes including the nanoparticles-wastes on plant secondary metabolites.

Keywords Toxic gases · Secondary metabolism · Secondary metabolites · Ozone · Carbon dioxide · Heavy metals · Nanoparticles · Wastes

Abbreviations

PSM	Plant Secondary Metabolites
CO_2	Carbon Dioxide
O_3	Ozone
SO_2	Sulfur Dioxide
H_2S	Hydrogen Sulfide
Cd	Cadmium
Cr	Chromium
Ni	Nickel
As	Arsenic
Ag	Silver
Au	Gold
NAA	Naphthalene acetic acid
NSC	Non-structural Carbohydrates

Introduction

Environmental stresses include drought, salinity, extreme temperatures, toxic gases, ozone, carbon dioxide, and other wastes released into environment because of climatic aberrations (Gosal et al. 2009; Wani et al. 2010; Wani and Gosal 2011; Wani and Hossain 2015). Plants being sessile organisms face several environmental perturbations during their life cycles (Kumar and Khare 2016). These environmental signals induce several changes in plants at physiological, biochemical and molecular levels (Sanghera et al. 2011; Wani et al. 2013, 2017; Khare et al. 2015). Both primary and secondary metabolisms get affected under change in environment or climate, however, plants have evolved to sustain under these conditions via inducing several counter-balancing mechanisms such as regulated use and evapotranspiration of available water, controlled openings and closings of stomata as per the availability of water, overaccumulation of various osmoprotectants and osmoregulators, induction of antioxidant machinery and fine tuning of transcriptional and post-transcriptional regulations of gene expressions (Kumar et al. 2010; Wani and Gosal 2010; Khare et al. 2015; Kumar and Khare 2015; Wani et al. 2016a, b; Wani and Kumar 2015; Shriram et al. 2016). In the past two centuries, air pollution problems have been aggravated due to population burst, rapid industrialization and other related anthropogenic activities to meet the global food and feed demands. There is a threatening increase in the atmospheric concentrations of various greenhouse gases namely carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) and toxic gas pollutants like sulfur dioxide (SO_2) nitrogen oxides (NO_x), besides secondary pollutants like ozone (O_3). There is a remarkable increase in the concentrations of greenhouse gases owing to various anthropogenic activities including industrialization in recent past.

Though there is considerable literature indicating the effects of these pollutants on plant growth, development and primary metabolism and metabolites. Though there is enough evidence indicating that plant primary metabolism and secondary metabolism are closely knitted (Fig. 1). Plant secondary metabolites are highly specialized products usually biosynthesized by the plants using their primary

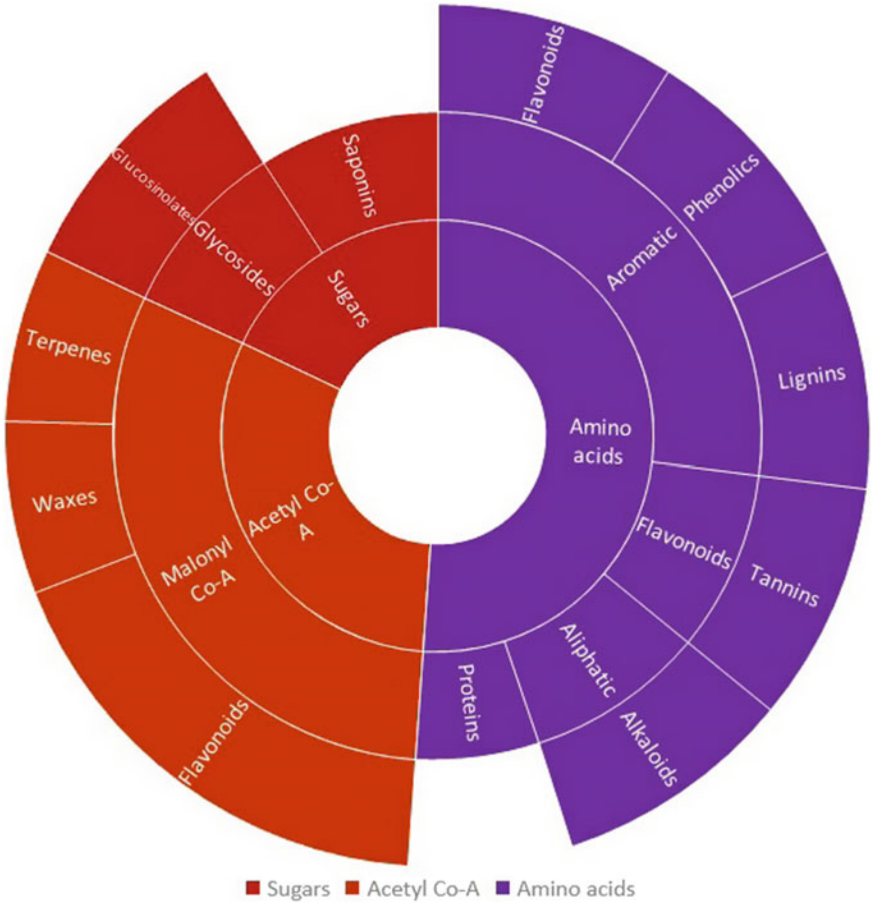

Fig. 1 Generalized biosynthetic relation in plant primary and secondary metabolites

metabolites as substrates. However, there is lack of substantial data and in-depth understanding about the impacts of toxic gases, greenhouse gases and ozone on plant secondary metabolism as a whole and on the production of plant secondary metabolites (PSMs). Nevertheless, there is a recent upsurge on the significance of altered plant secondary metabolism and enhanced production of PSMs under the influence of these gases as well as other wastes including the nanoparticles-wastes released into the environment. We are presenting herein the review of these issues through this chapter.

Effects of CO_2 on Plant Secondary Metabolites

Greenhouse gases together constitute as a major environmental challenge for medicinal plants. Among those, CO_2 is one of the major causes with a tremendous rise since industrialization took place. About half of the anthropogenic CO_2 emission between 1750 and 2011 has occurred in the last 40 years (IPCC 2014) and yet we are not certain about the potential effects of this abrupt change on medicinal plants. Since medicinal plants are potent sources for PSMs, they possess significant plasticity to adapt with the changing environments. Though, this metabolic plasticity conferred due to PSMs may affect other secondary metabolites which are usually the basis for their medicinal activity (Mishra 2016). For example; when *Digitalis lanata* known for its use in heart failures (Rahimtoola 2004) was treated with elevated CO_2, there was a 3.5-fold increase in digoxin, a cardenolide glycoside. In the same experiment where digoxin showed enhancement, other three glycosides viz. digitoxin, digitoxigenin and digoxin-mono-digitoxoside showed a decline in their concentration (Stuhlfauth et al. 1987; Stuhlfauth and Fock 1990). In addition, time also plays a crucial role in deciding the metabolic flux in relation to PSMs. For instance, in a typical time related experiment on *Hymenocallis littoralis* whose bulbs are known for their antineoplastic and antiviral properties, the elevated CO_2 resulted in increase in 3 types of alkaloids (pancratistatin, 7-deoxynarciclasine and 7-deoxy-trans dihydronarciclasin) in the first year and decrease in their concentration for the subsequent year (Idso et al. 2000). Similarly, in *Ginkgo biloba* a traditional Chinese medicinal plant used in Alzheimer's disease, vascular or mixed dementia (Weinmann et al. 2010) elevated CO_2 and O_3 together resulted in altered terpenoid content, 15% increase in quercetin aglycon and 10% decrease in keampferol aglycon, 15% in isorhamnetin and bilobalide to some extent (Huang et al. 2010). In a typical study on *Papaver setigerum*, elevated CO_2 levels from 300–600 μmol mol^{-1} corresponding roughly to the concentrations that prevailed during middle of the twentieth century, the present concentration, and near and long-term projections for the current century (Ziska et al. 2008) resulted in enhancement of four alkaloids viz. morphine, codeine, papaverine and noscapine. Further, it is also predicted that increase in CO_2 may result in high plant carbon: nutrient ratios producing excess of non-structural carbohydrates (NSCs). These

NSCs may be then are accessible for incorporation in C-based secondary metabolites (Heyworth et al. 1998). Pertaining to this prediction, a test carried out on *Hypericum perforatum* showed that elevated CO_2 resulted in enhancement of hypericin, pseudohypericin and hyperforin belonging to the class of phenolics (Zobayed and Saxena 2004). After observing the potential effects of secondary metabolites from Broccoli on cancer and cardiovascular diseases (Mahn and Reyes 2012), it was essential to evaluate effect of CO_2 on this plant. For this, widely exploited Broccoli (*Brassica oleracea*) var. italica Plenck was subjected to elevated CO_2, and this experiment showed increase in methylsulfinylalkyl glucosinolates glucoraphanin and glucoiberin derived from Glucosinolates (Schonhof et al. 2007). In a similar experiment on *Catharanthus roseus*, widely known for its anti-cancerous, anti-viral and diuretic properties (Ezuruike and Prieto 2014) when treated with elevated CO_2 showed increase in almost all of the PSMs viz. alkaloids, flavonoids, phenolic and tannins (Saravanan and Karthi 2014). In *Zingiber officinale*, elevated CO_2 resulted in increase in Flavonoid and Phenolic content (Ghasemzadeh et al. 2010). It was observed that with elevated CO_2, *Quercus ilicifolia* showed increase in tannins and phenolic content (Stiling and Cornelissen 2007). Ibrahim and Jaafar (2012) subjected *Eleais guineensis* (Oil Palm) to elevated CO_2 levels (400–1200 μmol mol^{-1}). In this study, the authors observed increase in flavonoids and phenolic contents attributed it to increase in primary metabolite phenylalanine a metabolic precursor for most of the secondary metabolites. Further on identical lines, Ibrahim et al. (2014) working on *Labisia pumila* showed that there was an increase in flavonoids and phenolics in response to increased artificial atmospheric CO_2 levels. These findings were more inclined towards increase in levels of secondary metabolites as a response to elevated CO_2 as compared to present atmospheric CO_2 concentration. But in a study carried out on *Pseudotsuga manziesii*, it was seen that the level of terpenes specifically monoterpenes decreased significantly (Snow et al. 2003).

Similar studies performed in vitro will play a crucial role in assessing the effect of CO_2 in in vivo conditions. A typical in vitro study has focused on *Panax ginseng* suspension culture of roots, a plant that frequently featured in prescriptions of traditional Chinese, Japanese and Korean medicine for cancer, immunomodulation and other stress related ailments (Wang et al. 2007; Chang et al. 2003). Elevated CO_2 levels in this suspension culture showed increase in phenolic and flavonoid contents (Ali et al. 2005). Thus, such findings are very essential to correlate the effects of CO_2 on in vivo studies with that of in vitro.

By reviewing the overall trend in such findings, it is very essential to focus on entire secondary metabolome of medicinal plants, beside evaluating the effects with respect to time duration, seasonal variation, temperature, nutrient availability etc. since other parameters either singly or in combination are going to play a significant role in altering the metabolic plasticity of medicinal plants. Looking at the paramount productive threshold of such metabolic alterations, appropriate conservatory practices are needed before these plants lose their bioactive components in the long run.

Effects of Ozone on Plant Secondary Metabolites

Ozone is widely known for its bioprotective activity against ultra violet radiations. However, its surface concentration i.e., ground level O_3 is increasing due to the rise in O_3 precursor emission in many pollution prone areas. Ground-level ozone pollution is already decreasing global crop yields (from 2.2–5.5% for maize to 3.9–15% and 8.5–14% for wheat and soybean, respectively), to differing extents depending on genotype and environmental conditions. These ill effects are also seen on medicinal plants. However, due to very limited focus on O_3 related effects on medicinal plants and their PSMs content it has become mandatory to evaluate its potential consequences.

In a study done on *Melissa officinalis*, a traditional medicinal plant used for treatment in dementia, anxiety and central nervous system (CNS) related disorders with elevated ozone concentrations showed that the total anthocyanins increased to a substantial extent along with phenolics and tannins (Pellegrini et al. 2011; Shakeri et al. 2016). A group of scientists from Brazil conducted an experiment to check effect of chronic ozone exposure on *Capsicum baccatum*. It was found that pericarp of ozone exposed plants showed 50% decrease in capsaicin and dihydrocapsaicin also the seeds showed significant reduction in capsaicin but no change in dihydrocapsaicin as compared to the control plants. Additionally, total carotenoid and phenolic content in the pericarp increased by 52.8 and 17% respectively (Bortolin et al. 2016). A similar study on Ecophysiological and antioxidant traits of *Salvia officinalis* under ozone stress (120 ± 13 ppb for 90 consecutive days) showed an increase in phenolic content; notably in Gallic acid (2-fold increase), Catechinic acid (increase was observed once in the total fumigation period of 90 days), Caffeic acid (8-fold increase) and Rosmarinic acid (122% increase on 60th day of treatment) (Pellegrini et al. 2015). Another experiment on *Betula pendula* with elevated O_3 displayed an increase in hyperoside a flavonoid, with decreased papyriferic acid a triterpenoid and dehydrosalidroside hyperoside, betuloside belonging to phenolics (Lavola et al. 1994). In a similar O_3 elevation experiment on *Pinus taeda* L, unveiled an increasing in condensed tannins without any rise in total concentration of phenols indicating that the O_3 related increase in foliar tannins was due to change in allocation within the phenolic group rather than to increase in total phenolics (Jordan et al. 1991). Albeit O_3 related effects are known on edible crops, similar effects are yet to be diagnosed on medicinal plants on a wide scale and plan proper conservatory policies/practices.

Effect of ozone as an indicator of secondary metabolites alterations in *in vitro* conditions has also studied in recent past. A study on *Pueraria thomsnii* suspension cultures showed an increase in puerarin production by cells treated with ozone, the increase was prominent 20 h after the treatment (Sun et al. 2012). The highest puerarin production was seen about 35 h after ozone treatment, which was 2.6-fold of the control. This outcome indicates that exposure to ozone might be a potential tool to improve puerarin production of *P. thomsnii* cells. Along with puerarin, O_3 exposure also indicated an increase in levels of ABA which was much higher than that of the control cells. The highest ABA production was observed at about 15 h after ozone treatment, which was about 11 times that of the control (Sun et al. 2012).

On identical lines, a study was carried out about ozone exposure on *Hypericum perforatum* cell suspension culture by Xu et al. (2011). In this experiment 6-day old cell culture were exposed to 30–180 nL L^{-1} ozone for 0–6 h. It was observed that cell suspension (5-day old) treated with 90 nL L^{-1} ozone dose showed maximum hypericin production (harvested on 21st day). Also, hypericin produced was maximum when cells were exposed 15th day of the suspension culture and harvested on 21st day. The ozone exposure time was optimized to be 3 h for highest hypericin production keeping the above parameters unchanged (Xu et al. 2011). Various secondary metabolites with altered production under the influence of higher CO_2 and O_3 levels are given in Fig. 2.

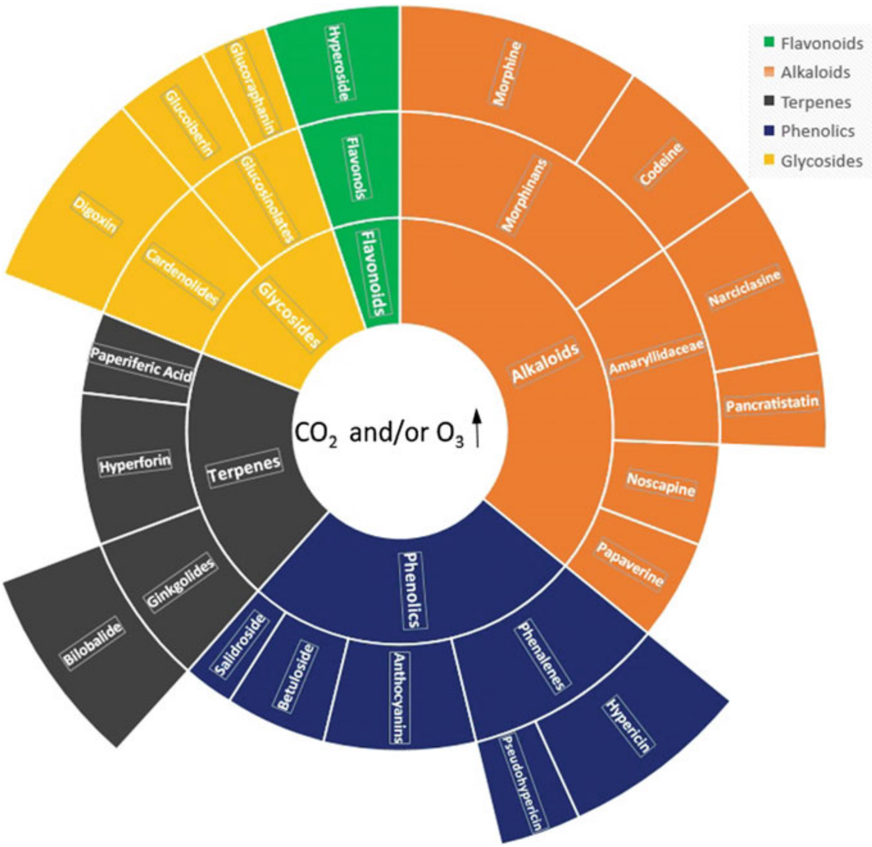

Fig. 2 Secondary metabolites altered in selected medicinal plants (covered in the text portion) in response to elevated Carbon dioxide (CO_2) and Ozone (O_3) levels

Effects of Toxic Gases on Plant Secondary Metabolites

Sulfur dioxide is one of the major air pollutants having ability to get enter in the plant system via roots as well as via stomatal opening by means of photosynthesis and respiration. Depending on the type of the plant and different environmental factors, differential responses of the plants against SO_2 exposure have been observed. Some responses include damage to the photosystem (Swanepoel et al. 2007), changes in the stomatal density and perturbations in efficiency of carbon fixation (Chung et al. 2011; Haworth et al. 2012; Silva et al. 2015). The atmospheric SO_2 along with H_2S also acts as sulfur source which can be up-taken through stomata of the plants apart from the sulfate uptake from the roots. Owing to the importance of the sulfur in many important pathways, this stomatal uptake influences the metabolic profile of the plant. Glucosinolates are sulfur containing secondary metabolites which plays significant role in sulfur storage which helps in re-distribution of sulfur during sulfur deprived condition (Falk et al. 2007). Two members from genus *Brassica* have been exposed to the 0.25 $\mu l\ l^{-1}$ of SO_2 for seven days to investigate the deviations in the glucosinolate content (Aghajanzadeh et al. 2015). The glucosinolate content showed negligible change in the shoot under sulfur deprived as well as sufficient conditions. But under sulfur deprivation environment, when foliarly absorbed sulfur was the only source of sulfur, glucosinolate content in root; notably some fraction of indolic glucosinolates showed reduction. Sulfur plays crucial role in the grapes and wine industry which is applied in several chemical forms. So, the overall plant profile including secondary metabolism alters notably. The SO_2 induced re-programming is observed in grape berry transcriptome allied with biotic defense responses as well as oxidative signaling. The SO_2 induced fumigation showed altered anthocyanin synthesis although the minor abundance of flavon-3-ol transcript after fumigation with SO_2 indicates no rapid degradation of anthocyanin (Giraud et al. 2012).

With respect to the various approaches to supply sulfur to the plants, there is keen interest in understanding the effect of one more sulfur containing gas; hydrogen sulfide (H_2S). The high dosage of H_2S is proved to be responsible for defoliation, leaf lesions, decreased growth rate, and tissue death in some plants (Montesinos-Pereira et al. 2016). But contrastingly, H_2S have also been reported to act as fundamental molecule produced by plants which works to control plant functioning (Zhang et al. 2010). This is also a signaling molecule which is proved to promote the antioxidant activities in many plants against abiotic stresses. The application of H_2S alleviated the antioxidant potential and quality in some plants as well (Montesinos-Pereira et al. 2016). The Bronco cabbage (*Brassica oleracea*) was applied with the incrementing levels of sodium hydrosulfide (as H_2S donor) to check the physiological and antioxidative changes. It was reported that the lower levels of treatment showed increased contents of carotenoids, anthocyanins, flavonols, total phenolics and sinigrin (Montesinos-Pereira et al. 2016). Hydrogen sulfide has been also reported to mediate nicotine biosynthesis in *Nicotiana tabacum* when the growth of plants is induced under high temperature (Chen et al. 2016).

Effects of Heavy Metal Wastes on Plant Secondary Metabolites

Toxic heavy metals such as cadmium (Cd), chromium (Cr), Nickel (Ni), Arsenic (Ar) etc. have been severely incorporated in the environment via variable sources including industrial effluent, fertilizers, pesticides and metal smelters. In soil they are present as free metal ions, metal complexes in soluble form, exchangeable metal ions, and insoluble or precipitated oxides, carbonates, hydroxides or they may also form a part of structural silicates (Rai et al. 2004). Plants exposed to heavy metal contaminated environment tend to change the secondary metabolite profile. This interaction may lead to either suppression or stimulation of the secondary bioactive compounds. The heavy metal exposure is a cause of induction of oxidative stress triggering formation of highly active signaling molecules which further helps in production of secondary metabolites which affects the medicinal potency of the plant (Nasim and Dhir 2010).

Chromium (Cr) is a carcinogenic heavy metal which is released in the environment via carpet, textile, leather tanning or electroplating industry. *Ocimum tenuiflorum* L. from the family Lamiaceae was cultivated in Hoagland solution (5%) containing variable concentrations of Cr(IV) (0, 10, 20, 50, 100 μM) to analyze the Euginol content, a major component of *Ocimum* oil. Significant increment in eugenol content up to 100 μM in comparison to control was observed. Approximately 25% increase was observed in eugenol content when plants were exposed to 20 μM chromium for 72 h. Effect of chromium on two therapeutically important secondary metabolites phyllanthin and hypophyllanthin from *Phyllanthus amarus* was studied by Rai and Mehrotra (2008). Increment in production of both the secondary metabolites was observed under increasing concentrations (20, 50, 100 μM) without much increase in the accumulation of chromium in leaves. Cadmium (Cd) is another non-essential, toxic heavy metal which is widespread in the environment. The constant increase in the cadmium levels is observed in the soil throughout the world. The phyllanthin and hypophyllanthin levels were analyzed in *Phyllanthus amarus* under various concentrations of cadmium. The quantity of both the secondary metabolites showed increment up to 50 ppm of cadmium treatment which reduced further at 100 ppm of cadmium (Rai et al. 2005). In another experiment, cadmium treatment was proved to improve the biosynthesis of artemisinic acid, arteannuin B and artemisinin in medicinal plant *Artemisia annua* L. (Zhou et al. 2016). Nickel (Ni) is a heavy metal which is present in industrially contaminated as well as pristine soils. A medicinal plant, St. John's wort (*Hypericum perforatum* L.) was screened for the effect of nickel on its secondary metabolite profile by Murch et al. (2002). The plants showed 15–20 fold reduction in amount of pseudohypericin and hypericin, whereas ability of plants to synthesize or amass hyperforin was completely vanished. Another heavy metal Arsenic (As) which enters the environment via weathering, biological activities as well as volcanic eruptions is also a component of pesticides/chemical fertilizers and

Table 1 Effects of ozone and carbon dioxide on plant secondary metabolite production

Component	Treatment	Medicinal Plant	Affected secondary metabolites	References
O_3	Elevated O_3	*Capsicum baccatum*	Capsaicin↓, Dihydrocapsaicin↓, Carotenids↑, Phenolics↑	Bortolin et al. (2016)
O_3	Elevated O_3	*Salvia officinalis*	Gallic acid↑, Catechinic acid↑, Caffeic acid↑, Rosmarinic acid↑	Pellegrini et al. (2015)
CO_2	Elevated CO_2 and Light intensity	*Labisia pumila*	Flavonoids↑, Phenolics↑	Ibrahim et al. (2014)
CO_2	Elevated CO_2	*Catharanthus roseus*	Phenolics↑, Flavonoids↑, Tannins↑, Alkaloids↑	Saravanan and Karthi (2014), Singh and Agarwal (2015)
O_3	Elevated O_3	*Melissa officinalis*	Phenolics↑, Anthocyanins↑, Tannins↑	Tonelli et al. (2015), Pellegrini et al. (2011)
O_3	Elevated O_3	*Pueraria thomsnii*	Puerarin↑, ABA↑	Sun et al. (2011)
O_3	Elevated O_3	*Hypericum perforatum*	Hypericin↑	Xu et al. (2011)
CO_2	Elevated CO_2	*Zingiber officinale*	Flavonoids↑, Phenolics↑	Ghasemzadeh et al. (2010, 2011)
O_3 and CO_2	Elevated O_3 and CO_2	*Ginkgo biloba*	Tannins↓, Quercetinaglycon↑, Keampferolaglycon↓, Isorhamnetin↓, Bilobalide↓	Huang et al. (2010), He et al. (2009)
CO_2	Elevated CO_2	*Papaver setigerum*	Morphine↑, Codeine↑, Papaverine↑ and Noscapine↑	Ziska et al. (2008)
CO_2	Elevated CO_2	*Quercus ilicifolia*	Tannins↑, Phenolics↑	Stiling and Cornelissen (2007)
CO_2	Elevated CO_2	*Brassica oleracea* var. italica Plenck	Methylsulfinylalkyl glucosinolates glucoraphanin↑, Glucoiberin↑	Schonhof et al. (2007)
CO_2	Elevated CO_2	*Hypericum perforatum L.*	Hypericin↑, Pseudohypericin↑, Hyperforin↑	Mosaleeyanon et al. (2005), Zobayed and Saxena (2004)
CO_2	Elevated CO_2	*Panax ginseng* C. A. Mayer	Phenolics↑, Flavonoids↑	Ali et al. (2005)

(continued)

Table 1 (continued)

Component	Treatment	Medicinal Plant	Affected secondary metabolites	References
CO_2	Elevated CO_2	*Pseudotsuga manziesii*	Monoterpenes↓	Snow et al. (2003)
CO_2	Elevated CO_2	*Hymenocallis littoralis* (Bulbs)	Pancratistatin↑, 7-deoxynarciclasine↑, 7-deoxy-trans dihydronarciclasin↑	Idso et al. (2000)
O_3	Elevated O_3	*Betula pendula*	Dehydrosalidroside hyperoside↓, Betuloside↓, Platyfylloside↓, Salidroside↓, papyriferic acid↑, hyperoside↑	Saleem et al. (2001), Lavola et al. (1994)
O_3	Elevated O_3	*Loblolly pine*	Tannins↑	Jordan et al. (1991)
CO_2	Elevated CO_2	*Digitalis lanata*	Digoxin↑, Cardenolide↑	Stuhlfauth and Fock (1990), Stuhlfauth et al. (1987)

residues from mining (Cao et al. 2009). A traditional Chinese medicinal plant *Sculellaria baicalensis* Georgi was screened accumulation and uptake of arsenic. The experiment concluded that the concentration of five flavone compounds were nor expressively by lower arsenic concentration. But the higher concentration of arsenic showed inhibition of baicalin and wogoninside formation whereas generation of baicalein, wogonin and oroxylin A was accelerated (Cao et al. 2009). Chamomile plant (*Matricaria chamomilla*) was grown in nutrient solution containing copper (Cu) (3, 60, 120 μM) for ten days (Kováčik et al. 2008). In methanolic extracts total eleven secondary active compounds were examined (protocatechuic, *p*-hydroxybenzoic, vanillic, chlorogenic, salicylic acid, gentisic, syringic, caffeic, sinapic and *o*-/*p*-coumaric acid). The detected compounds showed increment at 60 μM copper treatment whereas concentrations of the same were either lower or showed no change compared to the control at 120 μM (Kováčik et al. 2008) (Table 1).

Nanoparticle Wastes and Plant Secondary Metabolites

The synthesis of numerous types of nanoparticles has gained unprecedented attention in recent years, due to their vast array of applications (Mapara et al. 2015). Nanoparticles are the tiny entities ranging from the size 1 to 100 nm, formed with metal or metal oxides as a base. The waste materials out from industries, medical products and agriculture are emerging as sources for increasing the nano-waste amount in the environment. As plants are immobile with two foremost sinks of the environment, water and soil; they cannot escape the severe effects and successive metabolism changes due to nano-pollution (Marslin et al. 2017). The induction of reactive oxygen species in plants due to the interaction with nanoparticles alters the secondary metabolism. Increment in important secondary metabolite artemisinin was observed in the hairy root cultures of *Artemisia annua* treated with 900 mg L^{-1} of silver (Ag) nanoparticles for 20 days. The increase in amount ($\sim$3.9 folds) can be correlated with signalling molecule production (hydrogen peroxide), lipid peroxidation levels and catalase activity (Zhang et al. 2013). Silver nanoparticles also showed positive growth in anthocyanin and flavonoid synthesis in *Arabidopsis* as the expression level for the genes responsible for their synthesis showed up-regulation (Garcia-Sanchez et al. 2015). Improvement in content of a steroidal saponin, diosgenin in fenugreek (*Trigonella foenum-graecum*) was observed under the influence of silver nanoparticles (2 µg kg^{-1}) (Jasim et al. 2017). In barley plant, treatment with cadmium oxide nanoparticles was proved to be responsible for increment in ferulic acid and isovitexin. The concentration of cadmium oxide nanoparticles in air was approximately 2×10^5 particles cm^{-3}. On the similar line, callus tissue of *Prunella vulgaris*, a plant with important antiviral properties was cultivated in medium fortified with naphthalene acetic acid (NAA) along with gold (Au) and/or silver (Ag) nanoparticles (Fazal et al. 2016). Authors recorded maximum accumulation of phenolics and flavonoids along with the enhanced callus induction (Fazal et al. 2016). A generalized scheme is presented in Fig. 3 to

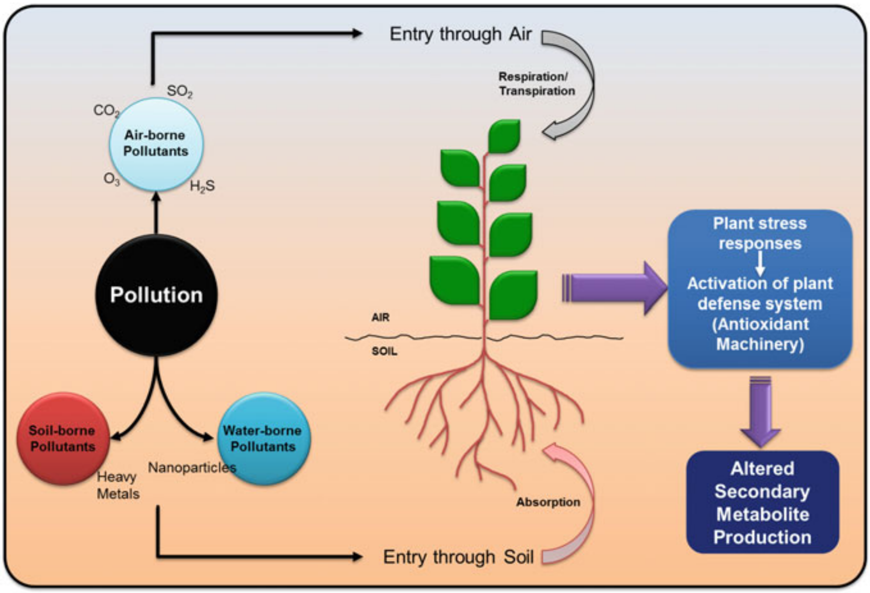

Fig. 3 Toxic gases (SO_2, H_2S), Ozone (O_3), Carbon dioxide (CO_2) and waste (Heavy metal waste, Nano-waste) mediated alteration in plant secondary metabolism

summarize the effects of toxic gases, O_3, CO_2 and wastes (heavy metal wastes and nano-wastes) on plant secondary metabolism.

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