Chemical Stress on Plants

7

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Abstract

Chemical stress in plants due to micronutrient deficiency or toxicity, heavy metal and air pollutant can affect the crop growth and development and hampers its productivity and restricts the crop from reaching its full yield potential. Micronutrients play important role in several enzymatic reactions in the plants. However, intensive agriculture, imbalanced fertilizer application and negligence of micronutrient application to the soil have led worldwide micronutrient deficiencies in the agricultural soil. Deficiency or excess of these elements cause several plant disorder or stress. Therefore, understanding of role of micronutrients in plants and stress due to their deficiency and toxicity is necessary for better crop production. Heavy metals are non-degradable and accumulate in our soil, water and crops and finally reach us. Remediation of these heavy metal is necessary with emphasis on reduction, reuse and recycle of these metals and at the same time bioremediation including phytoremediation should be devised which is environmental friendly to tackle the increasing menace in environment. Air pollutants and emerging contaminants are new stress which are impacting crop production and their detail understanding is further required with location-specific remediation measures.

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Keywords

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7.1 Introduction

Chemical stress in plants refers to stress arising from micronutrient deficiency or toxicity, heavy metal stress and to it newly added categories of air pollutant and emerging contaminants stress. With an increase in urbanization, vehicular emission and irrigation with wastewater, quality of soil, water and air is deteriorating and plants are most affected due to it. In the time of meeting food demands of our population, mitigating the stress is one of the concern and challenge we need to understand and focus. In this chapter, we will discuss how different types of chemical stress impact crop growth and development and what efforts can be put to tackle it to minimize the yield loss through it.

7.2 Micronutrient Stress in Plants

Plants require 17 essential nutrients for completion of their life cycle. These nutrients are carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), chlorine (Cl) and nickel (Ni). All these nutrients are known as essential plant nutrients. According to law of essentiality, in the absence of any of these nutrients plant cannot complete their life cycle, these elements are directly involved in the metabolism of the plant and deficiency of an element can be corrected only by supplying the element in question (Arnon 1954). N, P, K, Ca, Mg, and S are known as major or macronutrients, because they are required in large quantities (1 to 150 g per kg of plant dry matter) by the plants. Fe, Zn, Mn, Cu, B, Mo, Cl and Ni are required by plants in very small quantity (0.1 to 100 mg per kg of plant dry matter) and therefore known as minor or micronutrients (Marschner 1997).

All these essential nutrients are required by plants in balanced proportions. Deficiency or excess of these elements in the soil causes several plant disorder or stress. The plant stress caused by deficiency or toxicity of nutrients is known as nutritional stress. Plants generally expressed these stress in the form of visible symptoms like chlorosis and stunted growth. Stress might extend to the entire plant with loss of yield if relief of stress is not employed. Nutrient stress is a primary constraint to plant growth over the majority of the earth's land surface. Sub-optimal availability of primary nutrients like N and P is nearly universal which is generally elevated by the application of synthetic fertilizers. However, intensive agriculture, imbalanced fertilizer application and negligence of micronutrient application to the soil have led worldwide micronutrient deficiencies in the agricultural soil

(Sillanpaa 1990; White and Zasoski 1999; Shukla et al. 2014). Analysis of 190 soil samples from 15 countries revealed that 49% of these soils were low in zinc and 31% low in boron (Sillanpaa 1990). Recent Indian studies reported extensive deficiency of micronutrients in farms due to regular withdrawal of these nutrients through crop uptake (Shukla et al. 2014). At present, about 49% of soils in India are potentially deficient in Zn, 33% in B, 12% in Fe, 5% in Mn, 3% in Cu and 11% in Mo (Gupta 2005; Singh 2008).

All essential elements are associated with some metabolic activities in the plants (Arnon 1954). Major elements are main building block elements, while micronutrients play important role in enzymatic activities in several physiological processes. Metallic micronutrients (Zn, Cu, Fe, Mn, Ni and Mo) are effective as components or as activators or inhibitors of enzymes in the plant metabolic process. Ni is involved in N metabolism as metal component of the enzyme urease; Mo is important for N metabolism as metal component of the nitrogenase (N_2 fixation) and nitrate reductase enzymes. B is crucial for cell wall and membrane integrity, whereas chlorine plays a role in osmoregulation and stomata movement. The deficiency or toxicity of micronutrients affects associated physiological activity and thus disrupts the normal process leading to plant disorders or stress. Generally, micronutrient deficiencies exert secondary influences on the growth of plants by changes in growth pattern, chemical composition, antioxidant defence capacity of plants and decrease in the resistance of plants to biotic and abiotic environmental stresses (Hajiboland 2011). Therefore, deficiency or toxicity of micronutrients can impede these vital physiological processes leading to plant stress and poor yield. The micronutrient-related plant stress has been described below.

7.2.1 Micronutrients and Their Role

Zinc is active in many enzymatic reactions and is necessary for chlorophyll synthesis and carbohydrate formation. Because zinc is not readily translocated within the plant, deficiency symptoms first appear on younger leaves. Copper is essential for plant growth and activation of many enzymes. Copper deficiency interferes with protein synthesis and causes a build-up of soluble nitrogen compounds. Iron is a constituent of many organic compounds in plants. It is essential for synthesizing chlorophyll, which gives plants their green colour. Boron primarily regulates the carbohydrate metabolism in plants. It is essential for protein synthesis, seed and cell wall formation, germination of pollen grains and growth of pollen tubes. Boron is also associated with sugar translocation. Boron requirements vary greatly from crop to crop. Rates required for responsive crops such as alfalfa, celery, sugar beets and table beets can cause serious damage to small grains, beans, peas and cucumbers. Molybdenum functions largely in the enzyme systems of nitrogen fixation and nitrate reduction. Plants that cannot fix adequate N or incorporate nitrate into their metabolic system because of inadequate molybdenum may become nitrogen deficient. The micronutrient-wise details of major function and deficiency and toxicity stress have been described below.

7.2.1.1 Zinc (Zn)

Zinc deficiency is the widespread micronutrient deficiency problem; almost all crops and calcareous, sandy soils, peat soils, and soils with high phosphorus and silicon are expected to be deficient (Hafeez et al. 2013). Zn is the only metal that is present in enzymes of all six enzyme classes including oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases. Carbonic anhydrase, dehydrogenase; Cu-Zn superoxide dismutase (CuZnSOD); alkaline phosphatase; phospholipase; carboxypeptidase and RNA polymerase are major enzymes associated with Zn (Broadley et al. 2007; Hafeez et al. 2013). Therefore Zn plays very important role in carbohydrate metabolism, maintenance of the integrity of cellular membranes, protein synthesis, regulation of auxin synthesis, pollen formation and tolerance of environmental stresses like effects of short periods of heat and salt stress.

Zinc deficiency results in the development of visible abnormalities in plants such as stunted growth, chlorosis and smaller leaves (little leaf), spikelet sterility, decreasing number of tillers, shortening of internodes (rosetting), drastic decrease in leaf size (little leaf), death of shoot apices (dieback), increasing crop maturity period and inferior quality of harvested products (Hafeez et al. 2013). Zn has intermediate mobility in the plant and therefore symptoms initially come on middle leaves. Zn deficiency can also adversely affect the quality of harvested products, and plants' susceptibility to injury by high light intensity or temperature and infection by fungal diseases. Zn-deficient leaves display interveinal chlorosis, especially midway between the margin and midrib, producing a striping effect; some mottling may also occur (McCauley 2009). Crop-specific symptoms include smaller leaf size in alfalfa, grey or bronze banding in cereal leaves. In Zn-deficient plants, the rate of protein synthesis and the protein concentration are strongly reduced, whereas amino acids accumulate. Low protein and high amino acid concentration in Zn-deficient plants are not only the result of reduced transcription and translation but also of enhanced rates of RNA degradation due to high RNAase activity under Zn deficiency. Zinc toxicity is observed very rarely in crop plants and occurs mainly in soils contaminated by mining and smelting activities or treated with sewage sludge. At very high Zn supply, Zn toxicity can readily be induced in non-tolerant plants with inhibition of root. Quite often, Zn toxicity leads to chlorosis in young leaves. This may be an induced deficiency of other micronutrients for example, Mg or Fe because of the similar ion radius.

7.2.1.2 Iron (Fe)

Iron (Fe) plays a crucial role in chlorophyll synthesis and functioning of redox systems in the chloroplasts. It is constituent of several proteins and enzymes, namely cytochromes, ferredoxin, nitrate reductase, leghaemoglobin, nitrogenase, catalase, peroxidases, isoenzymes of superoxide dismutase (FeSOD), aconitase, xanthine oxidase, lipoxygenases and ascorbate peroxidase (Broadley et al. 2007). The deficiency of Fe causes decline in activities of these enzymes in the plant tissues leading to reduction in photosynthetic process. Fe deficiency reduces chlorophyll synthesis that leads to interveinal chlorosis with a sharp distinction between veins and chlorotic areas in young leaves. As the deficiency develops, the entire leaf will become whitish-yellow and progress to necrosis. Slow rate of plant growth also occurs. Among various factors responsible, reduction in formation of common precursor of chlorophyll and heme synthesis i.e. aminolevulinic acid (ALA), and the rate of ALA formation is controlled by Fe (Pushnik and Miller 1989). Other changes that occur in plants under iron deficiency stress include accumulation of phenolics and riboflavin in roots, reduction in lignin and suberin content in the roots, increase in phosphoenolpyruvate carboxylase (PEPC) activity in the roots and enhanced production of organic acids, particularly citric and malic acid.

7.2.1.3 Copper (Cu)

Copper is a redox-active transition element which plays significant roles in photosynthesis, respiration, C and N metabolism, and protection against oxidative stress (Pilon et al. 2006; Broadley et al. 2007). In higher plants, the most abundant copper protein is plastocyanin, which is involved in the photosynthetic electron transport in PS-I in the thylakoid lumen of chloroplasts. Another major copper protein, Cu/Zn SOD is involved in the scavenging of reactive oxygen species. Other major forms include Cu-binding chaperones and numerous enzymes, particularly single and multi-Cu-containing oxidase enzymes (cytochrome c oxidase, diamine oxidases, ascorbate oxidase, polyphenol oxidases). Due to the role of Cu in PS-I, Cu-deficient plants have low rates of photosynthesis and reduced carbohydrate synthesis, at least during the vegetative stage. The low carbohydrate concentrations in Cu-deficient plants can explain the impaired pollen formation and fertilization, and are the main reason for reduced nodulation and N_2 fixation in Cu-deficient legumes (Cartwright and Hallsworth 1970). Cu-deficient plants display chlorosis in younger leaves, stunted growth, delayed maturity (excessively late tillering in grain crops), lodging, and, in some cases, melanosis (brown discoloration). Stunted growth, distortion of young leaves, chlorosis/necrosis starting at the apical meristem extending down the leaf margins, and bleaching of young leaves (‘white tip’ or ‘reclamation disease’ of cereals grown in organic soils), and/or ‘summer dieback’ in trees are typical visible symptoms of Cu deficiency. In cereals, grain production and fill is often poor, and under severe deficiency, grain heads may not even form. Impaired lignification of cell walls is a typical anatomical change induced by Cu deficiency in higher plants. Copper deficiency affects grain, seed and fruit formation more strongly than vegetative growth. The main reason for the decrease in the formation of generative organs is the non-viability of pollen from Cu-deficient plants.

7.2.1.4 Manganese (Mn)

Mn is a constituent in protein of photosystem II, Mn-containing superoxide dismutase (MnSOD) and oxalate oxidase. Manganese acts as cofactor, activating about 35 different enzymes. Most of these enzymes catalyse oxidation-reduction, decarboxylation and hydrolytic reactions (Broadley et al. 2007; Schmidt et al. 2016). Manganese has a primary role in the tricarboxylic acid cycle (TCA) in oxidative and non-oxidative decarboxylation reactions. Photosynthesis in general and photosynthetic O_2 evolution in PS-II in particular are the processes that are most strongly depressed by Mn deficiency. Manganese deficiency has the most severe effect on the concentration of non-structural carbohydrates that leads to depression in root growth of Mn-deficient plants. In Mn-deficient leaves, the concentration of thylakoid-membrane constituents such as glycolipids and polyunsaturated fatty acids may be decreased by up to 50% and it can be attributed to the role of Mn in biosynthesis of fatty acids, carotenoids and related compounds. A decrease in lignin concentration is particularly evident in roots and is an important factor responsible for the lower resistance of Mn-deficient plants to root-infecting pathogens. Mn deficiency impairs cell elongation more strongly than cell division. Chloroplasts are the most sensitive of all the cell organelles to Mn deficiency. As a result, a common symptom of Mn deficiency is interveinal chlorosis in young leaves. However, unlike Fe, there is no sharp distinction between veins and interveinal areas, but rather a more diffuse chlorotic effect. Two well-known Mn deficiencies in arable crops are grey speck in oats and marsh spot in peas. White streak in wheat and interveinal brown spot in barley are also symptoms of Mn deficiency (Jacobsen and Jasper 1991). In dicotyledonous plants, intercostal chlorosis of the younger leaves is the most distinct symptom of Mn deficiency, whereas in cereals, greenish grey spots on the older leaves (‘grey speck’) are the major symptoms. In legumes, Mn-deficiency symptoms on the cotyledons are known as ‘marsh spot’ in peas or ‘split seed’ disorder in lupins; the latter disorder includes discoloration, splitting and deformity of seeds.

7.2.1.5 Nickel (Ni)

Nickel is involved in the function of at least nine proteins including methyl-coenzyme M reductase, superoxide dismutase, Ni-dependent glyoxylase, acireductone dioxygenase, NiFe-hydrogenase, carbon monoxide dehydrogenase, acetyl-CoA decarbonylase synthase and methylene urease, of which urease and the Ni-urease accessory protein (Eu3) have roles in plants (Ragsdale 1998; Chen et al. 2009; Broadley et al. 2007). Nickel is required by plants for proper seed germination. Additionally, it is necessary for the functioning of urease which converts urea to ammonium. Ni is beneficial for N metabolism in legumes and other plants in which ureides are important in metabolism. Though Ni deficiency symptoms are not well documented, some of symptoms include chlorosis and interveinal chlorosis in young leaves that progresses to plant tissue necrosis. Other symptoms include poor seed germination and decreases in crop yield. Plants without Ni supply have low urease activity in the leaves, and foliar application of urea leads to an accumulation of urea and severe necrosis of the leaf tips.

7.2.1.6 Molybdenum (Mo)

Mo requirement of plants is lower than other nutrients. In higher plants, only few enzymes (nitrate reductase, xanthine dehydrogenase, aldehyde oxidase and sulphite reductase) have been found to contain Mo as a cofactor (Broadley et al. 2007). In addition, Mo is a cofactor of nitrogenase in N_2-fixing bacteria. The functions of Mo are therefore closely related to N metabolism in the plants. Molybdenum is needed for enzyme activity in the plant and for nitrogen fixation in legumes, therefore Mo deficiency symptoms often resemble N deficiency symptoms (stunted growth and chlorosis) in legumes. Other symptoms of Mo deficiency include pale leaves that may be scorched, cupped, or rolled. Leaves may also appear thick or brittle, and will eventually wither, leaving only the midrib. In dicotyledonous species, a strong reduction in size and irregularities in leaf blade formation (whiptail) are the most typical visual symptom. When there is severe deficiency, marginal chlorosis and necrosis on mature leaves with a high nitrate concentration also occur. Molybdenum deficiency is widespread in legumes and certain other plant species (e.g. cauliflower and maize) grown in acid mineral soils.

7.2.1.7 Boron (B)

Like other metallic micronutrients such as Zn, Cu, Fe, Mn and Mo which are effective in functioning of enzymes as components or as activators, similar function for boron has not been established. Boron is unique among all the trace elements. Very small quantities are necessary for normal crop production, but slightly higher concentrations cause injury, e.g. germination inhibition, root growth inhibition, shoot chlorosis and necrosis. Primary functions of B in plants are related to cell wall formation and reproductive tissue. Leguminous crops have relatively large boron demand, therefore boron deficiency has been reported to be most pronounced on leguminous crops such as lucerne, red clover and alfalfa and cruciferous crops such as cabbage, cauliflower, rutabagas, turnips and radish. Other effect of boron deficiency includes inhibition of apical growth, necrosis of terminal buds, reduction in leaf expansion, breaking of tissues due to brittleness and fragility, abortion of flower initials and shedding of fruits and cell wall abnormalities (Gupta 1979; Brown et al. 2002; Broadley et al. 2007). In addition to chlorosis, leaves may develop dark brown, irregular lesions and finally leaf necrosis in severe cases. Under boron deficiency, disturbances in cell wall growth may have led to brittle leaves and stems, distorted thicken and curl leaf tips. Boron deficiency in cauliflower, turnip, radish, cauliflower and other root crops commonly causes brown heart. Deficiency in cauliflower shows up as a darkening of the head and is associated with hollow and darkened stems.

7.2.1.8 Chloride (Cl)

Cl is the most abundant inorganic anion in plant cells. Chloride acts as a counter anion to stabilize the membrane potential and is involved in turgor and pH regulation of plant cell. Cl is required in the splitting of water at the oxidizing site of PS II, i.e. for O_2 evolution. In most plants, the principal effects of Cl deficiency are wilting and a reduction in leaf surface area and thereby plant dry weight. Even in water culture when plants are exposed to full sunlight, wilting of leaf especially at leaf margins are typical Cl deficiency symptoms. With severe deficiency, curling of the youngest leaves followed by shrivelling and necrosis may occur. Plants with insufficient Cl concentrations show chlorotic and necrotic spotting along leaves with abrupt boundaries between dead and live tissue. Wilting of leaves at margins and highly branched root systems are also typical Cl-deficient symptoms, found mainly in cereal crops. Cl deficiencies are highly cultivar specific and can be easily mistaken for leaf diseases. Chlorine toxicity occurs worldwide and is a general stress factor limiting plant growth particularly in arid and semiarid region.

7.2.2 Strategies to Reduce Micronutrient Stress

Micronutrient stress mainly occurs due to deficiency or toxicity of micronutrients in soil. Therefore, soil test followed by supply of micronutrient to the plant is main step in reducing micronutrient deficiency stress while proper management of soil and water is required to elevate toxic effect. Micronutrients especially B are very sensitive to plant, because the range of micronutrient deficiency and toxicity level in plant is generally narrow and further varied with crop and cultivar. Therefore, a suspected micronutrient deficiency should be confirmed by soil and plant analyses before micronutrient fertilizer is applied to avoid toxic effect.

7.2.2.1 Soil Deficient in Micronutrients

Zinc deficiency is widespread among plants grown in highly weathered soils and in calcareous soils. In the latter case, Zn deficiency is often associated with Fe deficiency (lime chlorosis). The low availability of Zn in calcareous soils of high pH is mainly due to the adsorption of Zn to clay or $CaCO_3$. Zinc toxicity is observed very rarely in crop plants and occurs mainly in soils contaminated by mining and smelting activities and treated with sewage sludge. Iron deficiency is a worldwide problem in crop production on calcareous soils (lime-induced chlorosis). On the other hand, Fe toxicity (bronzing) is a serious problem in crop production on waterlogged acidic soils; it is the second-most severe yield-limiting factor in wetland rice. Iron deficiency can be also induced by high levels of manganese. Manganese deficiency is abundant in plants growing in soils derived from parent material inherently low in Mn, and in highly leached tropical soils. It is also common in soils of high pH containing free carbonates, particularly when combined with high organic matter content. High iron levels can also cause manganese deficiency. Copper deficiency is often observed in plants growing on Cu deficient soils (e.g. ferrallitic and ferruginous coarse textured soils, or calcareous soils derived from chalk) and on soils high in organic matter where Cu is complexed with organic substances. High N availability can also lead to Cu deficiency. Toxic levels of Cu can occur under natural conditions or due to anthropogenic inputs. Anthropogenic inputs include those from the long-term use of Cu-containing fungicide (e.g. in vineyards), industrial and urban activities (air pollution, urban waste and sewage sludge), and the application of pig and poultry slurries. A high Cu supply usually inhibits root growth before shoot growth. Boron deficiency may occur under a wide range of soil conditions. Alkaline soils have reduced uptake of boron due to high pH. Leached soils may be boron deficient because of low boron reserves. The soil types most frequently deficient in boron are sandy soils, organic soils and some fine-textured lake bed soils. Boron deficiency frequently develops during drought periods when soil moisture is inadequate for maximum growth. Mo deficiency is widespread in acid mineral soils with large concentrations of reactive Fe oxidihydrate that led to adsorption of MoO_4. Furthermore, adsorption of molybdate increases with decreasing soil pH.

7.2.3 Methods Used for Supply of Micronutrients to the Plants

The selection of nutrient source, rate, method and time of application are important factors to be considered during micronutrient application. The main sources of micronutrients are their salts and chelates. The amount of nutrient contents varied with type of source. The most commonly and widely used sources of micronutrients have been given in Table 7.1. The micronutrient deficiency stress is corrected generally by three types of micronutrient applications viz. soil application, foliar application and seed treatment. Soil and foliar applications are the most prevalent methods, but cost involved and difficulty in obtaining high quality micronutrient fertilizers are major concerns with these in developing countries. Micronutrient seed treatments which include seed priming and seed coating are becoming an attractive and easy alternative (Farooq et al. 2012). Soil application of micronutrients, especially inorganic salts, has not found much effective due to immediate reaction like adsorption, fixation and chemical precipitation of micronutrient cations with the mineral portion of soil. However, application of chelated micronutrient in soil has been reported with good absorption and crop response (Malhotra and Srivastava 2015). Soil application of a micronutrient like Zn from $ZnSO_4$ gets fixed in the surface soil, while the chelated-Zn remains soluble and becomes evenly distributed throughout the soil, as evident from 46-times higher uptake of Zn by a perennial fruit crop like

Table 7.1 Common fertilizer sources of micronutrient

Micronutrient	Sources	Micronutrient content (%)
Boron	Borax	11
	Boric acid	17
	Solubor	17–21
	Sodium pentaborate	18
	Sodium tetraborate	14–20
Copper sources	Cupric chloride	47
	Copper sulphate	25
	Copper chelates	8–13
Iron sources	Iron sulphate	20
	Iron chelates	5–12
Manganese sources	Manganese sulphate	27
	Manganese chelates	5–12
Molybdenum	Ammonium molybdate	54
	Sodium molybdate	39
Zinc	Zinc oxide	80
	Zinc sulphate monohydrate	36
	Zinc chelate	14

citrus from Zn-EDTA as compared to ZnSO4 on sandy soils. In non-citrus crops like wheat, banana, pear, apple, grapevine, etc., similar results have also been reported. Interestingly, some recommendations have advocated soil application of micronutrients as one of the means to realize good yield of a crop, e.g. combination of $ZnSO_4$ (300 g/tree), $FeSO_4$ (300 g/tree), 600 N, 200 P, 100 K (g/tree) in citrus has enhanced crop yield (Malhotra and Srivastava 2015).

Nutrients can be absorbed through plant leaves. In some situations, foliar-applied micronutrients are more readily available to the plant than soil-applied micronutrients. Foliar application of micronutrients in a wide range of crops has been reported effective with respect to growth, yield, quality and shelf life (Malhotra and Srivastava 2015). Foliar application of boric acid at 100 ppm resulted in maximum number of primary branches (18.30), yield per plant (2.07 kg) and fruit yield (30.50 t/ha) in tomatoes at Dharwad, India (Patil et al. 2008). Followed by mixture of micronutrients (Bo, Zn, Mn and Fe at 100 ppm and Mo at 50 ppm) fruit yield of 27.98 t/ha is recorded, which was significantly different from control as well as other treatments. The maximum benefit ratio of 1.80 was obtained with application of boron followed by mixture of micronutrients (1.74) compared to control (1.40). The foliar application of boron and Zn has been reported to increase yield and quality of onion in West Bengal, India. Among various levels (0, 0.1, 0.2 and 0.5%) of B application, 0.5% boron significantly increased the yield (30.74 t ha) and quality (total soluble solids, and pyruvic acid) of onion. Application of 0.5% Zn also exhibited the yield (33.34 t ha) and quality attributes of onion (Manna et al. 2014).

Amelioration of micronutrient is becoming a costly affair due to very low use efficiency of micronutrient. Of late, micronutrient seed treatment including seed priming and seed coating has offered an attractive and easy alternative. Micronutrient-enriched seed successfully addressed Zn and Mo deficiencies in some vegetable crops and increased yields beyond those achieved through soil fertilization due to difference in root health activating early seedling emergence. Therefore, seed treatment is becoming a promising technique to enhance use efficiency of micronutrient. Under all India coordinated research project on micronutrient, seed treatments of crops with several formations [Teprosyn F-2498 (600 g ZnL^{-1}), Teprosyn Zn P F-3090 (300 g Zn + 200 g P_20_5 L^{-1}), Teprosyn Mn F-2157 (500 g Mn L^{-1}) and Teprosyn Mo F-1837 (250 g Mo L^{-1})] found that seed treatment with TeprosynZn+P at the recommended level (8 mL/kg seed) increased the yields of several crops having bigger seed size and found beneficial. It is not suitable for small seed crops. Masuthi et al. (2009) reported increase in seed yield and yield-related traits of vegetable cowpea (*Vigna unguiculata* L.) through pelleting of seeds with $ZnSO_4$ (250 mg kg^{-1} seed) and borax (100 mg kg-1 seed). Seed pelleted with $ZnSO_4$ produced significantly higher 100 seed weights leading to 32.1% seed yield increase over non-pelleted control. Pod weight, seeds/pod and pod weight/plant were substantially improved by treatment with borax compared to control which showed 37.25% pod yield gain over non-pelleted control (Masuthi et al. 2009).

7.3 Heavy Metal Stress in Plants

Heavy metal is defined as metals with specific gravity of 5 g cm^{-3} (Tchounwou et al. 2012). They are also known as trace metals since their requirement by plants and animals is below 10 ppm. Heavy metals like copper (Cu), zinc (Zn), molybdenum (Mo), cobalt (Co), iron (Fe) and manganese (Mn) are required by plants as well as animals in the form of enzymes or cofactor or in structural molecules with specific roles and thus they are necessary nutrients which are required for normal metabolic functioning of life (Plant et al. 2012). Along with these there are some heavy metals like cadmium (Cd), chromium (Cr), lead (Pb), arsenic (As) and mercury (Hg) which exert toxic effect on plants and animal's system and affect their metabolic functioning. Heavy metals are environmental concern as they are non-degradable and persist in the environment, reaching via soil to plants and ultimately human through food chain (Sidhu 2016).

7.3.1 Sources of Heavy Metal Contamination

Rapid industrialization and urbanization has led to soil contamination with heavy metals. In soil, heavy metal accumulates via wet and dry deposition of dust from industries, mine tailing, dumping of metal-contaminated wastes, paints, gasoline, fertilizer application (mainly phosphate fertilizers), sewage sludge, wastewater irrigation, pesticides, etc. (Wuana and Okieimen 2011).

Source of heavy metal in soil can be natural or anthropogenic. Natural sources are mainly by weathering of parent rock along with which heavy metals also reach to the environment while anthropogenic sources of heavy metals are through mining, industrialization and urbanization. In the following section, we will discuss one by one impact of different metals on the plants and soil.

7.3.2 Heavy Metals and Its Impact on Crops

Heavy metal affects crop plants in many ways. Figure 7.1 shows a schematic diagram how in general heavy metals interact in plants. Below we will discuss about how heavy metal affects different plant processes.

7.3.2.1 Arsenic

Arsenic belongs to group V of periodic table and is a metalloid but still it is studied with heavy metals because of its similar toxicity level. Arsenic contamination is mostly geogenic but its widespread prevalence is manmade due to more groundwater withdrawal for irrigation. Arsenic in the environment reaches through natural weathering of parent rocks and anthropogenic sources are smelting, mining, ore processing, fertilizers and chemicals manufacturing, coal-based thermal power plants, pesticides, preservatives and seed dressing (Nriagu et al. 2007). Depending on the redox potential and pH, arsenic in groundwater is found in three forms, i.e.

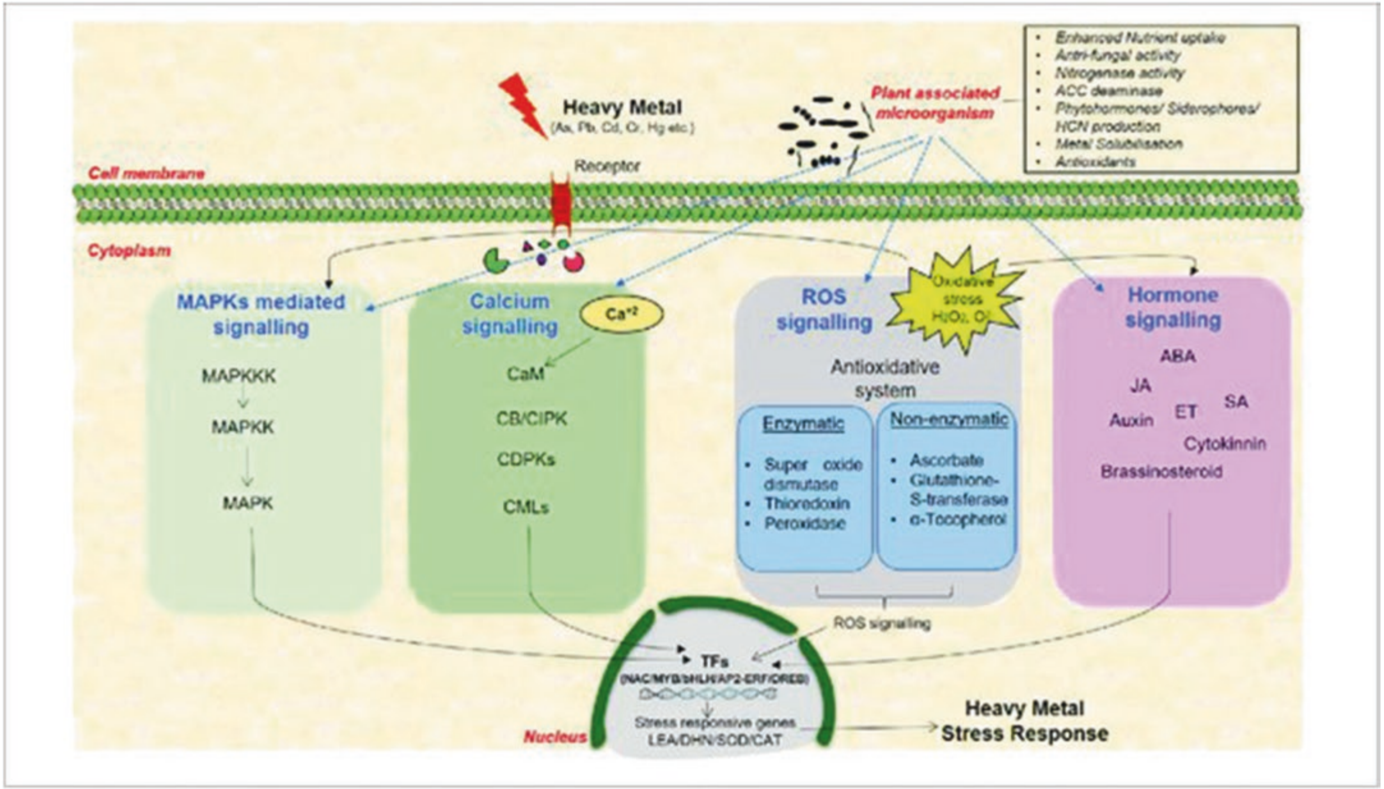

Fig. 7.1 Heavy metals and plant interaction in plants. (Source: Tiwari and Lata 2018)

organic form, arsenate (V) and arsenite (III). As (III) (arsenite) is much more toxic than As (V) (arsenate) form (Hossain et al. 2015). In oxidized condition (Eh = 0.2–0.5 V), arsenate is dominant form while under reducing environment in aqueous phase (Eh = 0–0.1 V) arsenite is found (Hossain et al. 2015). In India, plains adjoining Ganga-Brahmaputra-Meghna are arsenic-contaminated area which are now known worldwide and at many places arsenic concentration has been found above the WHO (World Health Organization) recommended level of 10 ppb in drinking water (Dubey et al. 2018). In soil, most of arsenic source is arsenic-contaminated irrigation water (Roychowdhury et al. 2005). In plants, first exposure of arsenic occurs to roots where root growth and spread is restricted (Garg and Singla 2011). As (V) is analogue of phosphate (PO_4^{2-}) ion. If concentration of arsenic is high compared to phosphate ion, then it will easily outcompete phosphate and enter into plants through transporter proteins. Arsenic in plant organ can restrict growth and biomass development, and impacts heavily on its reproductive ability by making it sterile (Finnegan and Weihua 2012). Very high arsenic concentration can hamper metabolic functions in plants like damaged cellular membranes with increased concentration of malondialdehyde (have role in oxidative stress), and interferes P role like oxidative phosphorylation and energy synthesis (Finnegan and Weihua 2012). Rice is the major crop affected by arsenic contamination and it has put more danger to rice eater towards arsenic exposure. Since rice is mostly grown under puddled and anaerobic condition, arsenic present in groundwater gets converted from As (V) to As (III). When it reaches to plants, it binds with –SH (sulphydryl) group disrupting its functioning in plant organs. Similarly, it produces reactive oxygen species (ROS) and reduces reparation rate by attaching to thiol group in pyruvate dehydrogenase and 2-oxo-glutarate dehydrogenase (Tiwari and Lata 2018). In general, plants have mechanism to restrict arsenic in the roots, so that it is not translocated to upper plant parts but in hyperaccumulator plants more arsenic concentration and accumulation is found in aerial parts of the plants (Finnegan and Weihua 2012). In rice crop, in general, arsenic contamination follows order of root>shoot>grains (Hassan et al. 2017).

7.3.2.2 Lead

Lead (Pb) is one of the most hazardous and ubiquitous heavy metals (Fahr et al. 2013). Pb presence in the environment has become widespread mainly due to human activities. Pb enters into the environment through weathering of parent rocks, mining, smelting, burning of fossil fuels, lead batteries, industrial processes, fertilizer and alloys. Pb is a concern as it persists in the environment and gets accumulated in soil, sediment, water and remains in the environment for 150–2000 years (Fahr et al. 2013). Although in last few years, the use of lead has gone down in paints, as antiknocking agent, pipes, etc., but due to its persistence it is still a problem.

In soil, Pb comes from nearby area or through wet and dry deposition of lead particulate matter. Plants take up lead from soil mainly through roots which usually accumulates it in aerial parts of the plant (Sharma and Dubey 2005). Generally, with increase in pH and cation exchange capacity lead absorption in the plant increases (Pourrut et al. 2011). Lead which is present in soil solution enters into roots and gets

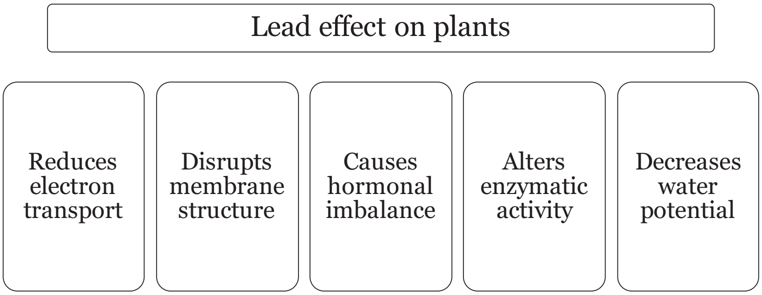

Fig. 7.2 Lead effect on plant. (Copied from: Sharma and Dubey 2005)

attached with carboxyl group present on rhizoderm surface (Pourrut et al. 2011). From rhizoderm they follow passive process and move with water flow through xylem (Sharma and Dubey 2005). In plants, lead affects various metabolic processes as shown in summarized form in Fig. 7.2. It shows that due to lead in plant electron transport, hormonal balance, enzymatic activities and water potential are negatively affected.

Overall if we say, lead impacts and restricts seed germination, seedling elongation, chlorophyll synthesis as it impedes Fe and Mg uptake, transpiration, changes membrane permeability by change in enzymatic activities (mainly –SH group), replaces essential nutrient ions resulting stunted plant with less yield or no yield (Tiwari and Lata 2018).

7.3.2.3 Cadmium (Cd)

Cadmium, a heavy metal, toxicity is known worldwide due to *itai-itai* disease in Japan in 1912 where severe pain in humans occurred in joints due to osteoporosis of bones (Kobayashi 1970). Cadmium is a persistent heavy metal which is very harmful to higher trophic level organisms especially to those with longer life cycle and hence we are at more risk than plants and animals due to longer life cycle. Cadmium enters into environment by anthropogenic activities like mining, plastic manufacture, electroplating industries, producing pigments, Ni-Cd batteries and in nuclear reactors as neutron stabilizer (ASTDR 2011). Cd enters into soil through wet and dry deposition of fine Cd particles in the air, sewage sludge, composts, phosphatic fertilizers, runoff from nearby roads, etc. (Andresen and Küpper 2013).

Cd is a non-essential element as it is not required by plants for any of its metabolic activities. When Cd reaches to plants from soil via roots, it negatively affects growth and development of plants (Sanita di Toppi and Gabbrielli 1999; Benavides et al. 2005). Cd can cause nutrient imbalance in crops and alters uptake of calcium, magnesium, phosphorous, potassium and water in plants. It affects gas exchange traits like photosynthesis, stomatal conductance and transpiration rate by inhibiting Fe (III)-reductase enzyme to Fe (II) (Benavides et al. 2005). Due to induced iron deficiency or Cd toxicity, leaf rolling, chlorosis and stunted growth and development of plants are seen. Cd interrupts nitrogen and sulphur metabolism in plants

(Gill and Tuteja 2011) and produces ROS which leads to early senescence (Benavides et al. 2005).

People who smoke cigarettes have more chances for Cd toxicity since tobacco concentrates high level of Cd in their leaves (Benavides et al. 2005).

7.3.2.4 Mercury (Hg)

Hg is a metal which is liquid at room temperature. It exists in various oxidation states basically as Hg (0): elemental mercury; Hg^+ (mercurous ion) and Hg^{2+} (mercuric ion) are inorganic forms while R-Hg^+ is organic form of Hg. High water solubility and easy change of phase from liquid to vapour form makes its use in wide application (Azevedo and Rodriguez 2012).

Hg^+ has affinity for thiol group in plants and animals and in water forming soluble salts it becomes a powerful poison (Clarkson and Magos 2006). Hg^{2+} induces production of ROS causing cellular interference and this form also plays a major role in Hg cycle as well. Hg^{2+} enters the environment through Hg cycle and under favourable environment by the action of microbial activity gets converted into organic form mainly CH_3-Hg. This methyl mercury can bio-accumulate and biomagnify in the successive trophic levels in food chain making it a neurological poison; minamata disease is one such example showing its toxicity level (Azevedo and Rodriguez 2012). Mercury has variety of applications in electronics, battery, explosives, medicine, cosmetics and agriculture. Industrial activities like chlor-alkali plant, copper and lead extraction, paints and dyes are sources of Hg pollution which finds its way to nearby soil and water.

In soil, Hg is deposited from fertilizer, sewage sludge, manures, composts, seed dressing, etc. Depending on soil pH (more pH less Hg absorption), cation exchange capacity, aeration and type of plant, Hg accumulation will differ in plants (Azevedo and Rodriguez 2012). In plants, Hg changes the cell membrane permeability and reacts with sulphydry group and phosphate group (Azevedo and Rodriguez 2012). Hg interferes with functioning of glutathione, thiols, superoxide dismutase, ascorbate peroxidase and glutathione reductase (Israr et al. 2006). By reacting with sulphydryl group it forms –S-Hg-H which makes it unstable compound and affects seed germination and growth of embryo (Azevedo and Rodriguez 2012). It also affects nutrient balance and competes with Fe, Mn, K and Mg and hence interrupts functioning of photosynthesis, transpiration, chlorophyll synthesis and water uptake processes in plants by binding to water channel protein (Boening 2000).

7.3.2.5 Chromium (Cr)

Chromium ranks seventh in abundance in the earth crust. It exists in two major oxidation states: Cr (III) and Cr (VI) in which Cr (VI) is more phytotoxic than Cr (III). In terms of solubility and mobility also Cr (VI) is more soluble and mobile forming chromate and dichromate ions in water, while Cr (III) is sparingly soluble in water. Cr has vast industrial use in industries like steel, tannery and textile, catalytic manufacture and in chromic acid production (Panda and Choudhury 2005). Cr is non-essential element for the plants and does not play any metabolic role in its growth and development. In plants, uptake of Cr follows different route, since Cr (VI) needs energy to reach into plant cells while Cr (III) can move passively along with the nutrient flow in the plant (Singh et al. 2013). Accumulation of Cr occurs in order of root>shoot>leaves> fruits (Sundaramoorthy et al. 2010). Chromium affects seed germination, root and shoot growth and reduces leaf expansion and necrosis of leaf. It also affects photosynthesis and chlorophyll synthesis by degrading δ-aminolaevulinic acid dehydrates (Oliveira 2012). It affects nutrient uptake and balance of both macro- and micronutrients as well as induces production of ROS in plants (Liu et al. 2008) and affects enzymes like SOD, CAT, dehydrogenase and glucose-6-phosphate (Oliveira 2012).

7.3.2.6 Antimony (Sb)

Antimony mainly finds its use in industrial applications for semiconductors, infrared detectors and diodes, alloys, in plastics, pigments, etc. Due to presence of Sb in so many compounds its release in the environment has increased and especially in industrial areas it is posing health risk to human beings (Sundar and Chakravarty 2010). Sb is non-essential element in the plants, therefore plants living in Sb-polluted site can accumulate large amount of Sb in their parts, but it is not proportional to the soil level of contamination and depends on many factors like plant species, Sb speciation, etc. (Feng et al. 2013).

Sb can affect plant process as other heavy metals do, but still information about its impact on plants is very limited and only crop specific. In general, Sb in plants induces production of ROS, which induces malondialdehyde production and enhances lipid peroxidation. It also affects photosynthesis by inhibiting the synthesis of chlorophyll. Sb impacts PS II, enhances flux of dissipated energy, reduces yield and causes nutrient imbalance and uptake of Ca, Mg, N, K, Mg, Fe and Zn (Feng et al. 2013).

7.3.3 Mitigation Measures to Tackle Heavy Metal Stress in Plants

Since the pollution impacts our surrounding soil, water, crops and human and animal health. We need to reduce the pollutant concentration or totally eliminate it. To prevent these contaminant many physical and chemical methods had been envisaged but they were not very environmentally sound and expensive. Hence bioremediation including phytoremediation has emerged a new technique to remediate the contaminated site which in turn will lead to less entry of contaminants into crop plants.

Bioremediation refers to the use of living organism for removal of pollutant. Here we use microorganism in particular which can degrade, detoxify and even accumulate the harmful organic and inorganic compounds (Sharma 2012).

Here we will stress one of the bioremediation type, i.e. phytoremediation, which can be defined as in situ use of plants to stabilize, remediate and reduce or restore contaminated soil, groundwater, sediment or even wastewater. Here phyto means plant and remediation means to correct. It is a solar driven pumping and filtering

Table 7.2 Types of phytoremediation

Phytoremediation category	Technique	Suitable plants
Enhanced rhizosphere degradation	Degradation of contaminant by plant rhizosphere microorganism	Grasses, hybrid poplars, mulberry, alfalfa
Phyto-degradation	Degradation of contaminant via plant metabolism or through release of enzyme by plants	Algae, hybrid poplars, rice
Phytoextraction	Also known as hyperaccumulators where plants accumulate metal and translocate to upper plant parts	Mustard, sunflower, penny grass
Rhizo-filtration	Plants absorb or precipitate metal from soil solution around the root and immobilize the metals	Sunflower, mustard, tobacco, maize
Phyto-volatilization	Uptake and transformation of compounds by the plants and subsequent release in the environment	Poplar, mustard, alfalfa
Phyto-stabilization	Stabilization of metal-contaminated soil by plant roots reducing its offsite movement	Indian mustard, grasses, hybrid poplar

Table 7.3 Metal hyperaccumulator plants

Plants	Metal
Thlaspi caerulescens, Brassica juncea, Helianthus annuus	Zn
Thlaspi rotunifolium, Azolla filiculoides, Brassica oleracea	Pb
Arabidopsis halleri, Rorippa globosa, Azolla pinnata	Cd
Alyssum lesbiacum, Alyssum bertolonii, Alyssum murale	Ni
Pteris vittata, Agrostis capillaris	As
Brassica napus, Eichhornia crassipes, Hydrilla verticillata, Pistia stratiotes	Hg
Dittrichia viscosa	Sb

system which can restore contaminated sites (Sharma 2012). Table 7.2 shows different types of phytoremediation available which can be used under different scenarios.

Phytoextraction or phytoaccumulation is the use of metal accumulating plant to remove metals from soil or water and concentrating them in above-ground plant biomass. Here the plants which are suitable to tolerate high level of metals or hyperaccumulator plant should only be chosen. For example, *Typha latifolia* can remove Cd, Fe, Pb and Zn; *Azolla filiculoides* removes Pb. Some examples are given in Table 7.3.

Another technique is genetically engineered plants which are modified with bacterial genes merB and merA which can convert methyl mercury to elemental mercury; *Brassica juncea* was genetically engineered to express *E. Coli* genes (glutamylcysteine synthetase) (Sharma 2012).

7.4 Air Pollution Stress on Plants

Air pollution refers to the presence of various contaminants such as gases, dust, fumes tar, vapour, suspended particulate matter, etc. in the atmosphere to the level which affect the normal biological process of humans, animals, plants and microorganism.

7.4.1 Air Pollution Types

7.4.1.1 Primary Air Pollutants

These pollutants are directly emitted from various polluting sources such as industries like smelter and roasting, ceramic, fertilizer, cement, thermal power plants, refineries, vehicles, processing, mining, metal coating, electroplating and agricultural activities, etc., e.g. sulphur dioxide, hydrogen fluoride, chlorine, nitric oxide, ammonia, ethylene, hydrogen sulphide, carbon monoxide, carbon dioxide, methane, suspended particulate matter, fly ash, heavy metals, carbon, resin, pollen, crop threshing dust, and bacteria.

7.4.1.2 Secondary Air Pollutants

These pollutants are formed in the atmosphere as a result of interaction between two or more primary pollutants, for example, nitrogen dioxide, ozone, peroxy acetyl nitrate (PAN), photochemical smog, acid mist, formaldehyde, etc.

7.4.2 Effect of Air and Water Pollution on Crops

Any undesirable changes in air, water and soil by means of its physical, chemical and biological characteristics lead to a harmful impact to the all living and nonliving entities known as pollution. So pollution can be say in other words that contamination with injurious or detrimental effects. The detailed effects of air and water pollution are described below.

7.4.2.1 Factors Associated with Plant Response to Air Pollution

Industries, automobiles and power generating sources are the major sources through which pollutants enter into the air eventually disturbing the health and survival of plants and animals through their physical and biochemical interaction. The nature and extent of plant damage by the air pollutants depend upon varieties of factors such as pollutant factors which include the concentration of pollutants and duration of exposure; environmental factors, i.e. climatic (temperature, radiation, humidity and wind velocity), edaphic (soil types, nutrient content and their bioavailability, soil reaction) and biotic factors like insect and pathogenic infestation; and biological factors comprising species and genetic diversity (genetic makeup) of plants, the metabolic activity of plant tissues, growth stage of plants, morphological, anatomical and geometrical features of leaves on plants, etc. The magnitude of plant response to air pollutants is expressed in the forms of acute, chronic and subtle effects as a result of interaction between pollutants, environmental and biological factors followed by the mechanism of action in plant system. The severity of injury/damage depends upon the sensitivity of plants to the exposed pollutants. The plants show marked genetic and genomic variability (both within and between plant species) in their response to air pollution. Based on the dose–response relationship, the plant species have been classified into two major groups, i.e. sensitive (susceptible) and insensitive (tolerant) plants. Generally sensitive plants exhibit visual injury symptoms at low level of pollutant as compared to insensitive plants which generally have high threshold level for the same pollutant.

7.4.2.2 Uptake of Pollutants

The most vulnerable part of a plant to be damaged is the leaf because of the presence of stomata which allows the entrance of toxins into the tissues of the leaves. Limit layer obstruction is the first boundary of vaporous air contaminations which shifts with various factor including wind speed, size, shape and orientation of leaves (Heath et al. 2009). More pollutants enter the leaves at higher wind speed as boundary layer obstruction decays. Waxy and cuticular leaf surface is a potential hindrance to the vast majority of the pollutants; however, the cells most vulnerable to air contamination activity are epidermal cells. In any case, cuticular waxes can be separated by acidic gases and these gases can enter the leaves by infiltrating the cuticle (Rai et al. 2011).

7.4.2.3 Effect on Cuticle and Stomata

Cuticle and stomata are the main receptors or targets where the pollutants experience. Stomata give the immediate way through which the gases enter the leaf, yet the immediate effect on cuticle should likewise be considered. The reaction of stomata to air contaminations is fluctuating and shifts from species to species. It additionally changes with focus, age of the plants and in different environmental conditions (Abeyratne and Ileperuma 2006). Plant species vary in their capacity to moderate traffic contamination because of contrasts in their leaf surface attributes which incorporate epicuticular wax, fingernail skin, epidermis, stomata and trichomes (Neinhuis and Barthlott 1998). Toxins consumed by gatekeeper cells and backup cells may at first influence the stomatal opening. Disruption of cuticular waxes because of air contamination has been found in species, for example, Scots Pine. Because of air pollutants and acid deposition, the weathering of needle cuticle is many times faster in unpolluted forest areas. Comparative perceptions have been depicted in lichens and mosses (Huttunen and Laine 1983). Because of this, evapotranspiration would be more prominent which would be critical in arid conditions. Rai and Kulshrestha (2006) suggested that air pollutants caused inhibited cell extension, leaf area and consequently the expansion in cell recurrence which leads to decrease in the span of stomata and epidermal cells. So as to keep away the entry of hurtful constituents of air which can generally cause bad impacts, the decrease in the size of stomata could be considered as an adaptive approach (Satyanarayana et al. 1990). Distorted shapes of stomata saw in *Pongamia pinnata* populaces exposed to debilitate contamination may have come about because of bringing down of pH in cytoplasm of guard cells and along these lines change in the turgor relations of the stomata complex because of physiological damage inside the leaf. Further, Rai and Mishra (2013) have delineated that the plants developing along the roadsides have adjusted leaf surface characters including stomata and epidermal cells because of the worry of vehicle exhaust discharge with high traffic thickness in urban zones. Rahul and Jain (2014) have detailed that dust particles of a range under 5 mm in breadth can interfere with the mechanism of stomatal pores. These little openings are to a great extent in charge of the fundamental breath and transpiration capacity of plants. A large portion of the air toxins which are known for their impact on stomata are normal segments of the air; however, they are available now in higher fixations in the environment than their regular focus. The adjustments in the stomata because of air toxins which appear to be little can be of extraordinary result as for survival of a plant amid pressure (Robinson et al. 1998). Stomatal opposition ought to be considered as the principle impediment to ozone flux, the immediate response of the poison with cell divider ascorbate is much of the time included (Plochl et al. 2000). The first detoxifying layer which speaks to the antioxidant system found in the cell (apoplasm + symplasm) at the season of ozone assault will rummage ozone and its subordinates. This framework is exceedingly connected to the dimension of ascorbate and particularly apoplastic ascorbate, which was fundamentally proposed as a decent pointer for ozone resilience (Tausz et al. 2007).

7.4.3 Physiological and Biochemical Impact on Plants/Crops

In this regard, we will discuss how the air and water pollutants manipulate the physiological and biochemical processes within the plants/crops.

7.4.3.1 Sulphur Dioxide (SO_2)

SO_2 made entry to plant through stomatal pores, reaches to sub-stomatal air space and dissolved into cellular water and get transformed to sulphite (SO_3) and bisulphate (HSO_3) ions. Even at lower concentration of SO_2 disruption of the cell membrane and chloroplast occurs (Fig. 7.3).

Depletion of cellular pH and competitive inhibition of ribulose bisphosphate (RuBP) carboxylase by SO_3 and HSO_3 at carbon fixation site reflect in decreased photosynthesis. Reduction in the Hill reaction activity accompanies by swelling and disintegration of chloroplast membranes resulting in chlorosis of leaves. SO_2 can also affect the electron transport system and phosphorylation during photosynthesis. It is also reported that SO_2 at high concentration degrades chlorophylls to phaeophytin, which results in early leaf senescence. SO_2 also disrupts the ATP formation in mitochondria therefore at the time of photosynthesis its availability and supply get affected. SO_2 reduced the photorespiration and also depleted the level of sugars and lipids mainly by breaking down the polysaccharides and by enhancing the activity of amylase and lipase enzyme, respectively.

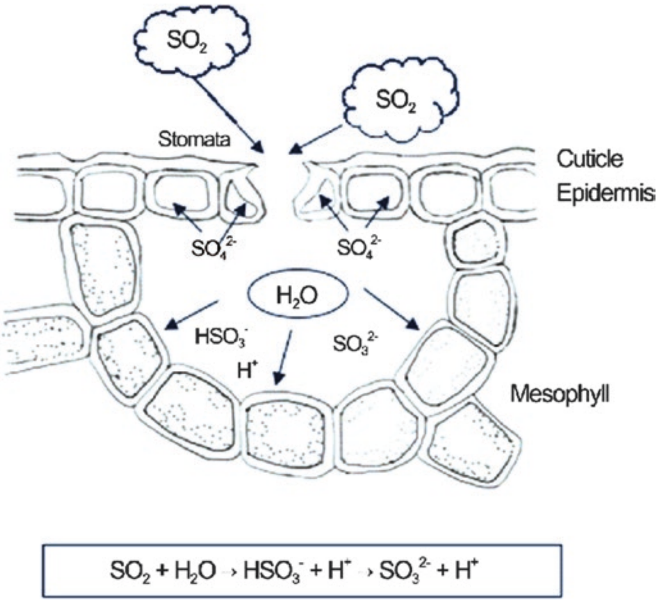

Fig. 7.3 SO_2 toxicity and detoxification reactions in a plant leaf (Knabe 1976)

7.4.3.2 Oxides of Nitrogen

NO_2 has found to be most phototoxic forms among all oxides of nitrogen. Generally, it is seen that NO_2 is 5 times more toxic than SO_2. NOx do reduce photosynthesis by competitive inhibition for NADPH between the processes of nitrite reduction and carbon assimilation in chloroplasts. The acidity produced by NO_2 in the cell has a significant impact on electron flow and photophosphorylation. NO_2 has been seen to inhibit photosynthesis by uncoupling electron transport and by inducing structural alterations. In the manner of NO_2, NO also affects nitrogen metabolizing enzymes. Irreversible swelling of thylakoid membrane of chloroplast is reported at fumigation with $NO_{2.}$ Overall all oxides of nitrogen reduce the photosynthetic activity.

7.4.3.3 Peroxyacetyl Nitrate (PAN)

PAN is a very phytotoxic component of photo-oxidative smog. PAN when treated with isolated chloroplasts show inhibition of electron transport, photophosphorylation and CO_2-fixation. The inhibitory effect of PAN on enzymes has been known to its ability to oxidize SH groups in proteins and metabolites such as cysteine, reduced glutathione, CoA, lipoic acid and methionine. PAN not only oxidizes SH groups, it can also oxidize and reduce nicotinamide adenine di-nucleotides, NADH and NADPH, which would eventually interfere with metabolic reactions involving these reduced coenzymes. The synthesis of cellulose and alkali soluble glucan is inhibited, but there is no significant effect on lipid synthesis in tobacco. PAN also inhibited the starch mobilization in darkness and phosphorylase activity.

7.4.3.4 Fluorides (F)

Fluorides can occur in the air either in gaseous or in particulate form. The gaseous form (HF) is absorbed through the leaves by means of diffusion and does not require any active metabolic process, while the particulate form is generally adsorbed on the outer surfaces of the plant and thus is less injurious to plants. The accumulation of fluoride inside the leaf cells has been reported that, after passing through cell wall, fluoride attacks cytoplasmic membranes and is partially retained there and perhaps transferred to the vacuoles. In gladiolus, fluorides get translocated outward of the leaf surface and to the upward leaf tip. Fluoride at low concentrations (1.3 to 12.4 ppb) generally caused slight depressions in the amounts of chlorophyll a and chlorophyll b. The free sugar content of the leaves reduced when fumigating with fluorides, also leads to fluctuation of non-volatile organic acids level and also reduced the activity of some glycolytic enzymes. Fluorides also reported to inhibit the rate of Hill reaction in plants. In soybean and corn, fluorides are seen to inhibit the oxidative phosphorylation in etiolated leaf discs and sucrose synthesis. Fluorides can be seen to damage and deformed the shape of chlorophyll structure in fir plants.

7.4.3.5 Ozone (O_3)

Ozone is a highly reactive molecule due to having two unpaired electrons and a high redox potential. Ozone first attacks the chloroplast membrane and then enters into leaf. Thylakoid membrane is found to be more sensitive to ozone due to oxidation of sulphydryl group, amino acids and proteins. Ozone reacts with the unsaturated fatty acids and ring containing compounds. Similar to SO_2, O_3 also can give rise to the superoxide radical (O_2^-), which can produce other radicals such as OH^-, $^1O_2$ and H_2O_2 which can oxidize various cellular metabolites. O_3-fumigated tissues show changes in permeability due to leaky plasmalemma; these include changes in permeability to water, glucose and ions. Permeability of mitochondrial and chloroplast membranes is also influenced by O_3. The visible sign of ozone damage has been clearly seen in tobacco plant. Ozone has been reported to reduce pollen tube growth and pollen germination in tobacco and decreased flower production in carnation. Mitochondrial swelling due to ozone is reported in tobacco. During photolysis of water, the electron transport system also gets affected due to ozone. Ozone is also found to reduce the activity of carboxylase enzyme responsible for CO_2 fixation in plants. The activity of both nitrate and nitrite reductase enzymes in plants results in lower availability of nitrogen for photosynthesis.

7.4.4 Toxicity Effects of Pollutants on Plant

7.4.4.1 Sulphur Dioxide (SO_2)

Sulphur dioxide affects the middle aged leaf which is comparably more sensitive than old aged leaf. Mesophyll cell is the main targeted area of sulphur dioxide. Minimum threshold level of SO_2 is 0.30–0.8 ppm for plants. The main injury symptoms of sulphur dioxide are chlorosis, inter-venal chlorosis, tip and marginal necrosis. In many cases, the visible symptoms are similar to drought, insect or chilling injury, for example, acute marginal and intercostal necrosis on alfalfa, marginal and intercostal necrosis on tomato, needle tip necrosis of eastern white pine.

7.4.4.2 Ozone (O_3)

Older most leaves are mainly sensitive to O_3 damage, whereas the young most leaves are less sensitive. Palisade or spongy parenchyma in leaves are target area for ozone attack. Minimum threshold level of O_3 is 0.03 ppm. Major visible symptoms of O_3 are fleck, stipple, bleached and necrotic spotting, pigmentation and browning of conifer tips, for example, weather fleck of tobacco, chlorotic stipple of ponderosa pine, necrosis of corn, ozone stippled lesion on upper surface leaf of avocado.

7.4.4.3 Peroxyacetyl Nitrate (PAN)

Youngest leaves are the most sensitive to PAN. Spongy tissue of leaf is the main target of attack. Minimum threshold level of PAN is 0.01 ppm. Glazing, silvering or bronzing of lower leaf surface are the main symptoms of PAN injury, for example, silvering or bronzing of lower leaf surface on lettuce, glazing of lower leaf surface of petunis.

7.4.4.4 Fluorides (F)

Tip and marginal leaf burning is the one of the major symptoms of fluorides. The other visible effects of flourides are dwarfing and leaf abscission; narrow brown-red band separating necrotic tissues from green tissues. Flourides toxicity shows similar symptoms as fungal, cold and high thermal injuries. For fluorides, youngest leaves are most sensitive. Epidermal and mesophyll cells of leaf are the main area of attack. Minimum threshold level for fluorides is 0.0001 ppm. Some of the symptoms of fluorides in crops are marginal leaf necrosis in apricot, chlorotic stipple injury in corn etc.

7.4.4.5 Oxides of Nitrogen

NO_2 is most harmful phytotoxic among the oxides of nitrogen. NO_2 mainly attacks the mesophyll cells of middle aged leaf. Minimum threshold level for NO_2 is 2.5 ppm. Visible symptoms of NO_2 injury are irregular, white or brown collapsed lesions on near leaf margin and around intercostal leaf tissue.

7.4.5 Stress Management in Plants

Levitt (1972) defines stress as any environmental factor with the capacity to elicit from plants a harmful chemical or physical change; this change or strain may be either reversible (elastic) or permanent (plastic). Plant resistance to stress is result of two possible mechanisms: stress avoidance or stress tolerance. In the stress avoidance mechanism, the plant excludes partially or completely the environmental stress and therefore avoids the specific strain induced by the stress, while in stress tolerance the plant may experience stress internally and try to adapt towards it. Stress tolerance is defined by Levitt (1972) as resistance via the plant's ability 'to come to

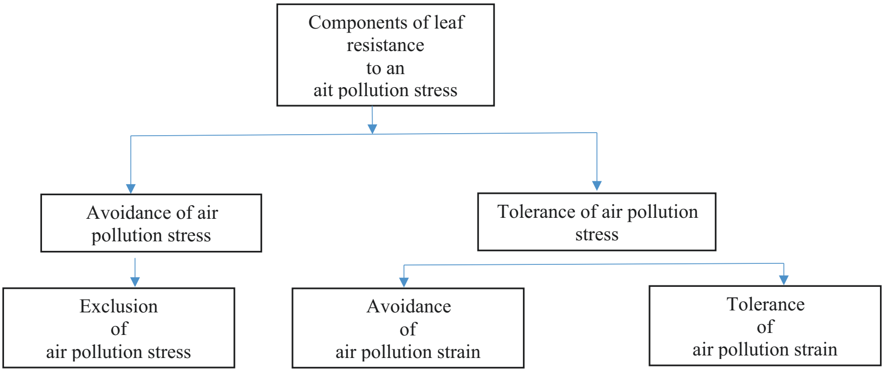

Fig. 7.4 Scheme of alternative components determining a plant's resistance to gaseous air pollution stress. (Adapted from Taylor (1978))

thermodynamic equilibrium with the stress' without being killed. The plant activity is reduced in strain tolerance, but the plant survives (i.e. the strain is tolerated) as a consequence of either reparative or compensatory processes which counters the toxic effect of the strain. In strain avoidance, the plant does not exhibit any morphological or physiological strain even though the stress is experienced thermodynamically.

7.4.5.1 Stress Avoidance

When plant is exposed to pollutants, leaf response is determined generally by two factors. First is internal concentration level of pollutants in leaf and second is threshold level of pollutants to plants. If the leaf internal concentration is exceeds the threshold level, leaf may die but this effect is mostly reversible until and unless plants are exposed to pollutants for longer duration. The response of pollutants to plants depends on the constituents (tissue, cell, molecule, etc.), so it may vary accordingly, therefore, the same internal pollutant concentration may result variable outcome depending on the affected constituent. This scheme of alternatives accounting for variation in resistance to air pollution stress is given in Fig. 7.4.

Air Pollution Stress: Presence in the environment of an air pollution dosage capable of inducing leaf strain.

Air Pollution Strain: Elastic (physiologic) of plastic (chronic or acute) leaf damage induced by an air pollution stress.

7.5 Emerging Pollutants Stress

Till yet we talked about the different chemical stress including micronutrients, air pollutants and heavy metal impact on plant crop. A new category has been recently added to this group of chemical pollutants which is known as emerging pollutants or contaminants (EC).

EC includes antibiotics, personal care products, veterinary medicines, nanomaterials and many more. Emerging contaminants can be defined as those substances which may or may not be present in the environment for long time but their proper pathway is still unknown and no regulatory guidelines is mentioned (Boxall 2012).

In agriculture, there are some EC which are of great concern which includes:

(a) Biowarfare agents
(b) Cosmetics or personal care products
(c) Flame retardants, dioxins
(d) Artificial hormones
(e) Antibiotics
(f) Nano-compounds
(g) Intermediate products from degradation of manufactured chemicals

The proper pathway and mechanism of many above-mentioned EC is still not very clear and it is an emerging area of research in recent times. In general, it is assumed that EC follows the same fate as other contaminants like heavy metals.

One of the mitigation options to some extent is bioremediation where different microorganisms are used to remediate or degrade these emerging pollutants. There are two main approaches for bioremediation, one is biostimulation where modification of environment is enhancing microbial activity and second is bioaugmentation where microbial cultures are added to increase biodegradation. Another tool can be biomonitoring and use of biosensors. Biomonitoring with bioassays, markers can advance the risk assessment process and detailing of how these EC move in the biosphere, while biosensor can enhance detection process of presence of EC in any system like plant or soil or water (Gavrilescu et al. 2015).

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