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Toxicities and Tolerance of Mineral Elements Boron, Cobalt, Molybdenum and Nickel in Crop Plants

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ABSTRACT

The minerals boron (B), cobalt (Co), molybdenum (Mo) and Nickel (Ni) are beneficial to plant in trace amounts, but excess levels of these cause toxicity limiting crop production. An attempt was made to review the phytotoxicity symptoms, effects on growth and physiology and tolerance and amelioration of these toxicities in crop plants. Though, chlorosis and necrosis of leaves are the common expression of toxicities of these minerals and except B the critical toxic concentration of Co, Mo and Ni in soil has been worked out only for a few crops, the toxicity responses of these minerals in soil and plant tissues vary considerably across the soils and crop genotypes. These toxicities reduce chlorophyll, affect cell metabolites and enzymes specially antioxidant and lipid peroxidation, alter nutrient transport and have negative effects on cellular functioning, these all result in reduced growth and yield. Existence of genetic variation among the crop genotypes highlight the differences in tolerance and scoring for toxicity symptoms and biomass at early growth stages can be considered as reliable criteria for screening for tolerance to toxicity. The *Bo1* gene provides a major source of B toxicity tolerance. The restriction of uptake and transport and internal tolerance mechanisms are the two important criteria which plants employ to combat high external concentrations and hence tolerance could be attributed to the lower B, Co, Mo and Ni content of seed and lower uptake or accumulation of these in the root and shoot and high yield in toxic soils. Ameliorating high-mineral soils using soil amendments is expensive and extremely difficult. Use of tolerant crop genotypes, phytoremediation by tolerant crops, and inoculations of beneficial microorganisms are the solutions.

Keywords: accumulator, critical toxicity level, excess mineral, phytoremediation, phytotoxicity

Abbreviations: **APX**, Ascorbate peroxidase; **ATP**, Adenosine triphosphate; **CAT**, Catalase; **Chl**, Chlorophyll; **DTPA**, Diethylene triamine penta acetic acid; **EC_{50}**, concentration causing 50% inhibition; **EDTA**, ethylene diamine tetra acetic acid; **GPX**, Guaiacol peroxidase; **GR**, Glutathione Reductase; **GS**, Glutamine synthetase; **GSH-Px**, Glutathione peroxidase; **GST**, Glutathione *S*-transferase; **H_2O_2**, hydrogen peroxide; **LOX**, Lypoxigenase; **MDA**, malondialdehyde; **NADPH**, Nicotinamide adenine dinucleotide phosphate; reduced; **O_2^-**, superoxide anion; **PAL**, Phenylalanine ammonia lyase; **POD**, Peroxidase; **PPO**, Polyphenol oxidase; **QTL**, quantitative trait locus; **RAPD**, randomly amplified polymorphic DNA; **RFLP**, restricted fragment length polymorphism; **RNase**, Ribonuclease; **RWC**, relative water content; **SNP**, single nucleotide polymorphism; **SOD**, Superoxide dismutase

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INTRODUCTION

Minerals naturally occur in soil, rock, air, water and are part of biological systems. In natural soils the mineral toxicities do not occur in their native vegetation as these adapt over time to the locally elevated levels of element. However, anthropogenic disturbance such as mining and addition of high amounts of mineral and introduction of new plants by

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humans on the toxic soils, cause mineral toxicity in plants. The main sources of mineral toxicities in crop plants are, soil parent materials, windblown dusts, sewage sludges, pesticides and irrigation water, emissions of factories, mining and smelting, recycling operations, urban and industrial wastes, combustion of petroleum fuels. As a result the mineral toxicities are more common in the agricultural crops at mining and industrial sites, and in naturally elevated soils. Besides these, soil acidity cause mineral toxicities due to increase of their solubilities (Singh 2000).

The toxicities of various elements, in plants occurring world-wide, are due to excess of either plant nutrients or other mineral elements. Though excess of all the mineral elements are harmful to plants, the toxicities of Al, As, B, Cd, Co, Ni, Fe, Mn, Mo and Se are of paramount importance in crop plants and are becoming increasingly common worldwide, in agriculture. Although of considerable agronomic importance, our understanding of toxicities of these elements is rather fragmented and limited (Singh 2008). In a series of review, the toxicities of all these elements and their resistance in crop plants will be covered. In this review, the B, Co, Mo and Ni are discussed.

The toxic soil concentrations of B, Co, Mo and Ni cause major limitations to crop production worldwide. Although B and Mo are essential micronutrients and Ni has been added to the list of essential trace elements for the growth of crop plants (Hutchinson 1981; Eskew *et al.* 1983; Brown *et al.* 1987) and Co is beneficial for plant and human and essential for animals, when present in excessive amounts all these reduce growth and yield. The effect of cobalt on plants are discussed in details by Palit *et al.* (1994) the essentiality, toxicity and physiology and biochemistry of Co and Ni by Bollard (1983) and physiological functions of beneficial elements by Pilon-Smits *et al.* (2009). Among these minerals, B toxicity is most important in the field crops decreasing yields in arid and semi arid environments throughout the world. Though, B-toxic soils are of lesser prevalence than B deficient soils, high levels of subsoil B in alkaline soil limit production of dry land crops in the semi-arid region. The highest naturally occurring soils B are derived from marine evaporites and marine argillaceous sediment (Erd 1980). Boron toxicity is more injurious in the calcareous soils than in the alluvial soils (Elsokkary and Chatby 1974) and has been found a common nutritional disorder in dry areas, where excessive B tends to accumulate in the subsoil. Also, various anthropogenic sources such as irrigation with ground water rich in B, wastes from surface mining, fly ash, industrial waste and fertilizers may increase soil B to the toxic levels for plants. Fly ash because of high silicate is used for rice cultivation, but it also contains considerable B and plants grown on soils amended with fly ash may face B toxicity (Lee-Seul *et al*. 2008). Though research on B Toxicity has increased considerably in the dry areas of the world, especially Mediterranean region and parts of Australia, the importance of B Toxicity was recognized only, when it caused significant reductions in crop yield in South Australia (Yau and Ryan 2008).

Cobalt is a natural earth element present in the soil, dust, seawater, volcanic eruptions and in trace amounts in plants and in our diets. Natural sources of Co also released to the environment from burning coal and oil, from car, truck and airplane exhausts, and from industrial processes that use the metal or its compounds. It usually occurs in association with other metals such as Cu, Ni, Mn and As in many different chemical forms throughout our environment. Small amounts of Co are essential for good health for human life and also in animals as it is part of vitamin B_{12} and plays a key role in its synthesis, produce red blood cells and used for treatment of anaemia. However, high concentration of Co is a possible carcinogen to humans and animals exposed to high Co during pregnancy have problems with the foetus development. Mo occurs in the earth crust with an abundance of 1.0-1.4 mg kg^{-1}. Molybdenum is one of the micronutrients whose toxicity is least investigated (Singh 1994; Singh *et al*. 2004). Though danger of Mo toxicity in plants is small, weathering soils of granite, porphyry, gneiss and Rotliegendes produce an Mo-rich vegetation (Anke and Seifert 2007). On soil derived from ultrabasic rocks of New South Wales, Ni toxicity is common in subterranean clover, lucerne and oats (Anderson *et al.* 1973).

In this paper an attempt has been made to review the available literature on the occurrence of B, Co, Mo and Ni toxicities, phytotoxicity symptoms, effects on growth and physiology, tolerance and management in crop plants, exploring the physiology and genotypic variation for tolerance to toxicity and utilization to maximize plant growth on high toxic soils. The readers are referred to excellent earlier reviews on B toxicity (Gupta *et al*. 1985; Leyshon and Jame 1993; Nable *et al.* 1997; Yau and Ryan 2008) and Ni toxicity (Chen *et al*. 2009).

PHYTOTOXICITY SYMPTOMS, SOIL AND PLANT TOXICITY LEVELS

Phytotoxicity symptoms

The reported visible symptoms of B, Co, Mo and Ni toxicities in various crops are given in **Table 1**. The phytotoxicity symptoms of B toxicity are characterised by chlorosis and necrosis of leaves beginning at their margins in groundnut (*Arachis hypogaea* L.) (Gopal 1973; Blamey and Chapman 1979; Sinha *et al.* 2002; Singh *et al*. 2004) and grapevines (Yermiyahu *et al*. 2006), chlorosis and necrotic spots in the leaf blade in kiwifruit (*Actinidia deliciosa*) vines (Sotiropoulos *et al*. 2006), marginal necrosis in tomato (*Lycopersicon esculentum* L.) leaves (Sinha *et al*. 2006), necrotic leaves in rice (*Oryza sativa* L.) (Cayton 1985), reduced plant size, leaf size and internodal distance between adjacent leaves in groundnut (Singh *et al*. 2004) and grapevines (*Vitis vinifera* L.) (Yermiyahu *et al*. 2006), and brown spotting and scorch on older leaf tips in barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.) (Gupta *et al.* 1973) and leaf edge burning and necrosis in wheat (Sonmez *et al*. 2009). However, due to B accumulation at the end of the transpiration stream in a wide variety of crop plants, the typical visible symptom of B toxicity is leaf burn-chlorotic and necrotic patches, often at the margins and tips of older leaves (Nable *et al.* 1997; Bergmann 1992). In castor bean (*Ricinus communis* L.), a marginal leaf burn at edge and tips of oldest leaves and absence of starch granules in chloroplasts were noted at B toxicity (5.4 mg l^{-1} B) treatment (da Silva *et al*. 2008). Many a times the B toxicity causes leaf cupping (Loomis and Durst 1992; Singh *et al*. 2004) due to inhibition of cell wall expansion, and disturbance of cell wall crosslinks (Loomis and Durst 1992). The visual toxicity effects of excess B were tip burn in corn, leaf mottling and necrosis in beans and peas and leaf mottling and cupping in cucumbers (*Cucumis sativus* L.) (Brinton *et al*. 2008), chlorosis of margins of old leaves in bittergourd (*Momordica charantia* L.) (Sinha *et al*. 2009), yellowing and necrosis in patches between veins and tips and margins of leaves on older leaves first in cotton (*Gossypium* spp.) (Niaz *et al.* 2008). In chickpea (*Cicer arietinum* L.) B toxicity appeared as marginal necrosis of old leaflets along with growth depression, later the necrotic leaflets became completely dry and shed (Chatterjee *et al.* 2005). In banana (*Musa paradisiaca* L.) plants excess B caused continuous necrosis developed from an irregular chlorotic area, from the edge towards the internal part of the leaf blade, but the central portion of the leaf remained green (Vargas *et al.* 2007). Symptoms of B toxicity in crops have been identified in many dry land areas of west Asia and North Africa (Yau and Ryan 2008).

Cobalt toxicity caused chlorosis of the younger leaves in mung beans (*Vigna radiata* L.) (Liu *et al.* 2001), interveinal chlorosis in young leaves of tomato (Chatterjee and Chatterjee 2005), chlorosis with pale white colour and necrosis of young leaves in groundnut (Singh *et al*. 2004), diffused chlorosis of young leaves from base, necrotic spots on chlorotic areas, the necrotic spots enlarge in size,

Table 1 Mineral toxicity symptoms in crops.

Minerals	Crops	Visible symptoms	References
B	Barley, wheat	Brown spotting and scorching on tips of old leaf	Gupta *et al.* 1973
B	Barley	Yellow margins with small brown lesions near the tips and margins	Lacey and Davies 2009
B	Bean, pea	Leaf mottling and necrosis	Brinton *et al*. 2008
B	Banana	Continuous irregular chlorosis and necrosis from the edge towards the internal part of the leaf blade leaving the central portion green	Vargas *et al*. 2007
B	Bitter gourd	Margins of old leaves became chlorotic	Sinha *et al.* 2009
B	Canola	Yellow and dead patches at the margins of the leaves	Lacey and Davies 2009
B	Castor bean	Marginal leaf burn at edge and tips of oldest leaves	da Silva *et al*. 2008
B	Chick pea, lentil	Tips of the leaflets of the oldest leaves start to yellow then die. Necrosis spreads along the margins of the leaflet from the tip towards the base. Dead leaflets often fall off. Older leaves are worst affected	Lacey and Davies 2009
B	Chick pea	Marginal necrosis of old leaflets, later the necrotic leaflets became dry and shed	Chatterjee *et al*. 2005
B	Corn	Tip burn	Brinton *et al*. 2008
B	Cotton	Yellowing and necrosis in patches between veins and tips and margins of leaves first appear on older leaves	Niaz *et al*. 2008
B	Cucumber	Leaf mottling and cupping	Brinton *et al*. 2008
B	Field pea	Yellowing followed by necrosis along the margins of the oldest leaves gradually progressing to the leaf centre	Lacey and Davies 2009
B	Grape	Chlorosis and necrosis of leaves beginning at margins, reduced size and internodal distance	Yermiyahu *et al*. 2006
B	Groundnut	Leaflets with marginal chlorosis and necrosis	Blamey and Chapman 1979; Singh *et al*. 2004
B	Kiwifruit	Chlorosis, necrotic spots in the leaf blade	Sotiropoulos *et al*. 2006
B	Rice	Necrotic leaves	Cayton 1985
B	Wheat	Leaf edge burning and necrosis	Sonmez *et al*. 2009
B	Wheat	Yellowing at the tips of the older leaves progressing down the leaf margins	Lacey and Davies 2009
Co	French bean	Chlorosis of young leaves from the apex toward the base which changed to necrosis, dried and withered	Chatterjee *et al.* 2006
Co	Groundnut	Chlorosis with pale white colour and necrosis of young leaves	Singh *et al*. 2004
Co	Mung bean	Chlorosis of the younger leaves	Liu *et al*. 2001
Co	Tomato	Diffused chlorosis of young leaves from base, necrotic spots and marginal scorching, distorted leaves hook like with rudimentary leaflets at the top	Gopal *et al*. 2003
Co	Tomato	Interveinal chlorosis of young leaves, fruits developed black patches	Chatterjee and Chatterjee 2005
Mo	Forage crops	Yellowing and rolling, curling, and scorching of the leaves	Gupta and Gupta 1997
Mo	Groundnut	Young leaves complete yellow with brilliant yellow colour and dry from the margin	Singh *et al*. 2004
Mo	Flax, soyabean, pea	Induced iron deficiency chlorosis	Warington 2008
Mo	Flax, tomato, *Solanum nodiflorum*	Leaves showing golden colour typical characteristic of Mo poisoning	Brenchley 2008
Ni	Barley	Chlorosis and necrosis of leaves, browning of the root system	Rahman *et al.* 2005
Ni	Lettuce	Interveinal chlorosis of leaves	Bansal and Khurana 2006
Ni	Maize	Leaves became chlorotic at low level and necrotic at high levels	Baccouch *et al.* 1998
Ni	Oat	Chlorosis and chlorosis lesions	Crooke and Knight 2008; Hunter and Vergnano 2008
Ni	Oat	Necrosis and chlorosis	Crooke *et al.* 2008
Ni	Potato	Chlorosis on young leaves initiating from the base, gradually spreading downward leaves	Shukla and Gopal 2009
Ni	Rice	Wilting and leaf necrosis	Llamas *et al.* 2008
Ni	Tomato	Brown spots on the fruit	Foroughi *et al*. 1976
Ni	Tomato	Wilting, necrosis of older leaves, small fruits and early ripening	Foroughi *et al*. 1976
Ni	Wheat	Chlorosis and necrosis of leaves	Gajewska and Skodowska 2007

coalesces and in due course the entire leaf turn necrotic and withered in tomato (Gopal *et al.* 2003). With excess Co, in tomato there was loss of lamina and marginal scorching of affected leaves which became distorted and appeared hook-like with rudimentary leaflets at the top (Gopal *et al.* 2003). Accumulation of Co in tomato fruits developed brown spots and black patches with prolonged Co supply, and in severe cases, young fruits became brown (Chatterjee and Chatterjee 2005). In French bean (*Phaseolus vulgaris* L.) symptoms of excess Co (0.50 mM) appear as chlorosis in young leaves developed from the apex leading toward the base which intensified, changed to necrosis, and the infected leaves dried and withered (Chatterjee *et al.* 2006). In oat excess Ni, Co, Mo and Al produce chlorosis and other specific symptoms to the element, although the specific symptoms of Co and Ni are confused (Hunter and Vergnan 2008).

The Mo toxicity symptoms for a limited number of crops are described by Gupta and Gupta (1997). Common symptoms of Mo deficiency and toxicity in plants include a general yellowing and scorching of the leaves however Mo-toxicity rarely occurs in field conditions (Gupta and Gupta 1997; Singh *et al*. 2004). The yellowing with golden colour are the typical characteristic of Mo toxicity in many crops (Brenchley 2008). In groundnut the Mo toxicity caused chlorosis of young leaves showing complete yellow with brilliant to sulphur yellow colour which in severe case became amber yellow and start drying from the margin leaving golden yellow brown colour (Singh *et al*. 2004). In soybean, flax (*Linum usitatissimum* L.) and pea plants excess Mo induced iron deficiency chlorosis as the symptoms of Mo toxicity (Warington 2008), however in flax, tomato and *Solanum nodiflorum* leaves showed golden colour as the characteristic of Mo poisoning (Brenchley 2008).

The chlorosis and necrosis of leaves, and browning of the root system, are the typical visual symptoms of Ni toxicity in barley (Rahman *et al.* 2005), chlorosis and necrosis in wheat (Gajewska and Skodowska 2007) and oat (Crooke *et al*. 2008). However, wilting and leaf necrosis have been described as typical visible symptoms of Ni^{2+} toxicity by several workers. In coffee (*Coffea arabica*), Ni toxicity

symptoms included chlorosis and necrotic spots on younger leaves and internodes, premature leaf fall, dieback, and streak necrosis of the leaves, petioles and branches (Pavan and Bingham 1982). Lettuce (*Lactuca sativa* L.) plants showed interveinal chlorosis as the characteristic symptoms of Ni toxicity (Bansal and Khurana 2006). The maize leaves became chlorotic at low Ni (<50 µM Ni) level and necrotic at 100 µM Ni and above (Baccouch *et al.* 1998). Nickle toxicity decreased water uptake which is used as an indicator of the progression of Ni toxicity in the birch seedlings (Jones and Hutchinson 1988). The decrease in water content is a typical symptoms of Ni toxicity in Rice (cv. 'Bahia') at 0.5 mM Ni caused by disturbances of membrane functionality (Llamas *et al*. 2008). In potato (*Solanum tuberosum* L.), cv. 'Chandramukhi' excess Ni caused chlorosis on young leaves initiating from the base, gradually spreading downward and intensified with age and brown necrotic areas developed irregularly on the affected lamina (Shukla and Gopal 2009). During a 70-day period from germination to maturity in oat plants, necrosis due to Ni toxicity varied little with time, while chlorosis increased in severity for 40 days then decreased until unfolding young leaves were no longer chlorotic due to change in the Ni-Fe ratio in the plant (Crooke and Knight 2008). Further Crooke *et al*. (2008) found that Ni-toxicity symptoms (both necrosis and chlorosis) in oat plants were less severe at high Fe concentration in the nutrient solution with reduction in degree of necrosis related to a reduced Ni content in the leaf blades, whilst that of chlorosis was related to the Ni/Fe ratio in the leaf blades – an internal antagonism being indicated in the latter case. Autoradiographs of oat leaves from plants supplied with radioactive Fe showed that necrotic areas in the leaf showed very low Fe, the chlorotic areas showed Fe content lower than that of healthy tissue, however more Fe was found in the veins than in the interveinal tissue (Crooke and Knight 2008).

Toxic concentrations in soil

Plant toxicity responses to various minerals are dose dependent and the tolerance of crop plant species. A critical or threshold toxicity concentration, the point at which these mineral cause significant decrease, are often defined as the concentrations corresponding to a yield decrease of 10%. This principle is used to determine both the critical soil and the critical foliar concentrations. Critical concentrations vary considerably across minerals, soils and plant species. The reported toxicity and threshold toxicity levels of B, Co, Mo and Ni in soil for various crops are given in **Table 2**. Plants can access directly the soluble minerals from soil solution the only soil fraction directly available for plant uptake and hence, factors affecting the concentration of these minerals in the soil solution will affect the bioavailability to plants. However, change in the concentration of elements in the matrix of soil minerals is slow relative to exchange and desorption reactions between clays, hydrous oxides, organic matter and the soil solution (Fageria *et al*. 1991; Marschner 1995; Whitehead 2000).

The B soil tests using hot water soluble B are essential as it can predict yield reductions in the B-toxic soil at the beginning of the growing season in most of the crops. However, the ability of the soil B extractants (ammonium acetate, DTPA-sorbitol, saturation and 1:1 soil:water) to predict B content of cotton, melons (*Citrullus vulgaris* L.) and lucerne (*Medicago sativa* L.) under conditions of potential B toxicity indicated that all these extractants were well able to predict B content of container-grown melons, but gave only poor predictability of B content of field-grown crops (Goldberg *et al*. 2005). In another study available B when assessed using three extractants: hot water, HCl (0.05 M), and Mehlich-1, the best extractant was HCl which correlated with the B content in corn (*Zea mays* L.) plant, followed by Mehlich-1 and hot water (Lima *et al*. 2007). Both available B assessed by HCl and plant B contents in corn were inversely related to clay and organic matter concentrations in soils and the soils on which the plants with highest B contents grew presented the most acute B toxicity symptoms with sandy and low organic matter soils (Lima *et al.* 2007). Boron behaviour in soils depends on organic matter, pH and minerals in soils. Boron is essential to crop growth in small soil concentrations of 0.2-1.5 ppm, but may produce plant toxicity symptoms readily as the amount in the soil solution increases over 2 ppm. Ideally, based on the response of agronomic crops to B, the soils containing more than 5 ppm of hot water soluble B is unsuitable for growing crops. However, this value is not an accurate reflection of the plant species and growing conditions as many native species are well adapted to soil at more than 5 ppm B. A survey of 104 crops of spring barley cv. 'Stirling' for B toxicity in south-western Australia having 0.7-130 mg B kg^{-1} soil mannitol-extractable B in sub-soils (>30 cm), the symptoms of B toxicity developed in the later stages of 'Stirling' barley growth, i.e. boot stage to maturity, on duplex soils with high concentrations of B in the sub-soils where soil B increased with soil depth, particularly in the 50 to 80 cm layer, and were highest at soil pH >8 (Brennan and Adcock 2004). In pot experiments on B toxicity, as the B is mixed uniformly in soil and does not detect the subsoil B, use of subsectioned pots was useful (Yau 2010).

In Redlands Crimson strawberries (*Fragaria vesca* L.) the hot water extractable B greater than 1.9 ppm in soil caused B toxicity and in a soil with 1.6 ppm B, B application at 0.32 kg ha^{-1} produced toxicity symptoms in leaves (Haydon 1981). French bean (cv. 'Contender') crop showed B toxicity symptoms at more than 1.0 kg B ha^{-1} (Singh *et al.* 1989). Wood shavings mulch containing 17 ppm B caused B toxicity in older leaves in strawberries (Haydon 1981). In greenhouse 10-20 ppm soil B was toxic in tomato cv. 'Lale' (Gunes *et al.* 1999). In high subsoil B, 0.5 ppm extractable B was non-toxic to barley (variety 'Clipper' and breeders' line 'VB9953') and fababean (*Vicia Faba* L.) (var. 'Fjiord'), but increasing the extractable B (2.4-12.2 ppm) decreased root and shoot biomass among species, however, the symptoms of B toxicity in shoots of all the species were observed at subsoil-extractable B of 12.2 ppm (Choi *et al*. 2006).

In sand-culture, 10 ppm B was injurious to groundnut cv. 'TMV-2' plants which became chlorotic and necrotic (Gopal 1973). In field the B toxicity was observed after the application of a total of 24.5 kg B ha^{-1} over the previous 6 seasons in groundnuts (Blamey and Chapman 1979) and at 5 ppm soil available B (Singh 1994; Singh *et al*. 2004, 2007). On sandy clay loam soil mixed with compost at soil pH 6.3-6.6 and hot-water-soluble B 1-2.26 ppm in glasshouse, the barley cv. 'Volla' and wheat cv. 'Opal', showed symptoms of B toxicity, which were more severe at high rates of compost due to increased tissue B concentration, but decreased with increase in applied N due to decreased tissue B concentration (Gupta *et al.* 1973). In IRRI farm, excess B due to irrigation with high-B deep well waters, especially during dry seasons when rainfall was nil, caused typical necrotic symptoms of B toxicity in rice when the soil had more than 5 ppm hot water soluble B (Cayton 1985). Potential B toxicity exists when fertilizer application rates are more than 3 kg B ha^{-1} for oilseed crops (Murthy 2006). Symptoms of B toxicity in leaves were apparent in kiwifruit vines orchard irrigated with 3.2 mg B l^{-1} (Sotiropoulos *et al*. 2006). In bittergourd (*Momordica charantia* L.) toxicity symptoms developed at 3.3 mg l^{-1} of B in nutrient solution (Sinha *et al*. 2009). In tomato and pepper (*Capsicum annuum* L.) plants B toxicity occurred at 5 and 50 ppm B levels, respectively (Eraslan *et al*. 2007a). Wheat growing at 3-6 mg B l^{-1} showed leaf edge burning and necrosis (Sonmez *et al*. 2009). However, very high critical toxicity concentration of soil soluble B for early vegetative growth of three wheat cultivars, 'Frame', 'BT Schomburgk' and 'Schomburgk' was 53, 32 and 27 ppm, respectively (Nuttall *et al*. 2006).

Toxicity symptoms appeared on older leaves of cotton at 5 mg B kg^{-1} soil level on which 90% of the maximum dry matter yield was obtained (Niaz *et al*. 2008). The toxic

Table 2 Toxicity levels of mineral elements in soil and crop plants (leaves).

Minerals	Crops and genotypes	Reported toxicity levels (ppm)		Threshold/ Critical toxicity levels (ppm)		References
		Soil	Plant	Soil	Plant	
B	Barley, shoots at booting stage				50-60	Riley 1987
B	Barley	12.2				Choi *et. al*. 2006
B	Barley				80	Davis *et al.* 1978
B	Bittergourd		120	3.3	58	Sinha *et al*. 2009
B	Cotton				198	Niaz *et al*. 2008
B	Chick pea		310		190	Chatterjee *et al*. 2005
B	Groundnut	5				Singh *et al*. 2004
B	Groundnut		106		74	Sinha *et al*. 2002
B	Maize	1.8-8.3	43.3-372		13.8-130	Lima *et al.* 2007
B	Maize	4.0				Aydn *et al*. 2005
B	Pepper	50				Eraslan *et al*. 2007
B	Rice	>5	>35			Cayton 1985
B	Soyabean		63			Murthy 2006
B	Strawberry	>1.9	123			Haydon 1981
B	Sunflower		160			Murthy 2006
B	Tomato	10-20				Gunes *et al.* 1999
B	Tomato	5				Eraslan *et al*. 2007
B	Wheat	3-6				Sonmez *et al*. 2009
B	Wheat 'Frame'			53		Nuttall *et al*. 2006
B	Wheat 'BT Schomburgk'			32		Nuttall *et al*. 2006
B	Wheat 'Schomburgk'			27		Nuttall *et al*. 2006
Co	Barley				6	Davis *et al.* 1978
Co	French bean		72		26	(Chatterjee *et al*. 2006
Co	Maize			2		Kamenova *et al.* 1983
Co	Mung bean	5 µM				Liu *et al.* 2000
Co	Tomato	0.5 mM	0.5 mM			Chatterjee and Chatterjee 2005
Mo	Barley				135	Davis *et al.* 1978
Mo	Soybean, flax, pea		40			Warington 2008
Ni	Barley				26	Davis *et al.* 1978
Ni	Barley	52-1929				Rooney *et al.* 2007
Ni	Bilberry				10–50	Tahkokorpi *et al.* 2010
Ni	Lettuce	>60		9.08	13.7	Bansal and Khurana 2006
Ni	Lettuce (cv. 'Climax')			20 µeq l^{-1}		Heikal *et al.* 1989
Ni	Pakchois			8.59	20.5	Ma *et al.* 2006
Ni	Ryegrass	30	50			Khalid and Tinsley 1980
Ni	Tomato	17-920				Rooney *et al.* 2007
Ni	Wheat			20 mmol m^{-3}		Pandolfini *et al.* 1992

levels of B in soils were 1.8-8.3 mg kg^{-1} for corn plants (Lima *et al.* 2007). The fly ash added to soil increases hot-water soluble B in proportion to the rate. Addition of 33% fly-ash compost to growing media (28 ppm total B) reduced the biomass for bean and cucumber by 45 and 55%, respectively while plant tissue B increased by 6- and 4-fold, respectively, but the economic yield depressions for corn, beans, peas (*Pisum sativum* L.) and cucumber appeared at levels of hot-water soluble in compost media exceeding 5 ppm (Brinton *et al*. 2008). However, application of 6.25% fly ash caused B toxicity in barley cv. 'Leduc' and accumulated B in shoots, fodder cut for silage and straw to levels in excess of amounts considered adequate for most plant species (Sale *et al*. 1996).

Cobalt is not a very abundant element on the earth and as mentioned by Pilon-Smits *et al* (2009) its concentration ranges between 15 and 25 ppm in soils, and is around 0.04 ppm in natural waters. Even though Co has been recognized as a micronutrient for animals, there has been no conclusive evidence of its essentiality for higher plants. As early as in 1957, Bolle-Jones and Mallikarjuneswara (1957) have shown that addition of small amounts of Co to tomato and rubber plants increased dry weight and plant height and the requirement of Co for N_2 fixation in legumes and in roots nodules of legumes was established in 1960 (Ahmed and Evans, 1960; Delwiche 1961). Kliewer and Evans (1963a) isolated a cobalamin coenzyme B_{12} from root nodules of legumes and further demonstrated a close correlation between Co supply, the B_{12} content, formation of leghemoglobin and N_2 fixation (Kliewer and Evans 1963b). The average concentration of Co in soils throughout the world is around 8 ppm, and in general plants show toxic effects at soil Co concentrations above 40 ppm, but, in Ontario, soils around mine sites have been reported as high as 6,450 ppm Co (MOEE 1996). However, plant species vary in their sensitivity to Co, and soil type and soil acidity greatly influence Co toxicity. The more acidic the soil, the greater is the potential for Co toxicity, at any concentration. Soils with high Co usually have high arsenic and Ni which are more toxic to plants than Co.

There are only a few studies on the Co toxicity in crop plants which occurred at 0.5 mM Co in tomato (Gopal *et al.* 2003; Chatterjee and Chatterjee 2005) and at 5 µM Co in mung beans (Liu *et al.* 2001), however threshold toxic concentration of Co for maize was 2 mg Co l^{-1} in nutrient solution (Kamenova *et al.* 1983). The phytotoxicity and bioavailability of Co was investigated using a standardised shoot biomass assay in ten soils varying widely in soil properties where the concentration of added Co causing 50% inhibition (EC_{50}) ranged 40- 1708 mg kg^{-1} for barley, 7-966 mg kg^{-1} for oilseed rape (*Brassica napus* L.) and 7-733 mg kg^{-1} for tomato, representing 43-, 138-, and 105-fold variation among soils (Li *et al*. 2009). The EC_{50} based on the Co concentration in soil solution varied less among soils (4–15 fold) than that based on the total added Co, suggest that solubility of Co is a key factor influencing its toxicity to plants (Li *et al*. 2009). Further study on the barley root elongation, the soil properties greatly influenced the expression of Co toxicity and the EC_{50} ranged from 45-863 mg kg^{-1}, representing almost 20-fold variation among soils, the EC_{50} values of Co toxicity showed variation among soils of 17- and 29-fold, based on the Co concentration in soil solu-

tion and free Co^{2+} activity, respectively (Micóa *et al*. 2008). Regressions of soil Co toxicity threshold values with various soil properties, showed that exchangeable calcium (Ca) was the most consistent predictor for risk assessment suggesting that Co toxicity threshold values for plants be normalised using the soil exchangeable Ca (Li *et al*. 2009). However, in further study, soil effective cation exchange capacity (eCEC) and exchangeable Ca were the most consistent single predictors of the EC_{50} values based on soil added Co (Micóa *et al*. 2008). Thus Soil eCEC and exchangeable Ca were the best predictors of the toxicity threshold values of Co to barley root growth on different soils.

There is comparatively little knowledge of the conditions in which Mo is toxic to plants, though obvious differences in response to Mo poisoning in different soils were observed without adequate explanation. Also the reaction of different crops varied considerably in the same soil with similar treatments. While working on Mo poisoning, Brenchley (2008) reported that on old cucumber soil, tomatoes showed no sign of toxicity even with the heavy dressing, flax was progressively damaged with increasing doses, while *Solanum nodiflorum* was most seriously affected even with the lighter dressing of molybdate; the growth of flax was greatly impeded on a Mn-deficient fen soil, and the Mo toxicity was masked in consequence, but if the deficiency was corrected the poisonous effect of Mo on this soil was very marked, even with the lower dressing. Tomatoes grown in ordinary loam showed little outward sign of Mo poisoning with heavy doses of sodium molybdate, but on certain light and fen soils the plants were killed at an early stage with the heavier dressing of molybdate, and seriously injured with the lighter dose (Brenchley 2008). Symptoms of Mo toxicity developed in soybean, flax and pea at 40 ppm Mo (Warington 2008). Recently, McGrath *et al*. (2010b) studied several soil properties influencing Mo toxicity, in four plant species (oilseed rape, red clover (*Trifolium pratense* L.), ryegrass (*Lolium perenne* L.) and tomato) on ten soils, and observed a larger range (66-609 fold) of added Mo concentrations resulting in 50% inhibition of yield (ED_{50}) among soils than among plant species (2-38-fold), indicating that the soils differed widely in the expression of Mo toxicity. Among the soil properties organic carbon or ammonium-oxalate extractable Fe oxides were the best predictors of the ED_{50} of Mo, also Mo concentrations in soil solution and plant uptake increased when pH was raised as sorption of Mo to amorphous oxides is reduced at high pH (McGrath *et al*. 2010a).

The heavy metal Ni is an essential mineral trace nutrient found at low concentrations in most natural soils, however, it may reach toxic levels in certain areas and affect a number of biochemical and physiological processes in plants. Although Ni at concentrations below 0.0001 mM is beneficial, its high levels can detrimentally affect quality and yield of crops. The Ni is readily absorbed by plants and it is found in traces in all plants (Mortvedt *et al*. 1972; Mishra and Kar 1974) and is essential for maximum urease activity in callus cultures of soyabeans (*Glycine max* L.), tobacco (*Nicotiana tabacum*) and rice (Polacco 1977). A hydroponic study at pH 5.5 demonstrated that 1.0-10 µM Ni needs to be added to the nutrient solution for optimum growth of barley plants, but 100 µM Ni showed toxicity (Rahman *et al.* 2005). In wheat, the threshold value of Ni toxicity was 20 mM Ni, which depressed root and shoot length, dry matter production and water content in seedlings (Pandolfini *et al.* 1992). In a dose-response curves, lettuce (cv. 'Climax') seedlings showed a threshold Ni toxicity at 20 µeq Ni l^{-1} and 50% reduction in yield at 30 µeq l^{-1} Ni, however, if the available Ca was increased from 1.0 to 257 meq l^{-1}, most of the reduction in growth and yield due to Ni toxicity at 30 µeq l^{-1} was reversed (Heikal *et al.* 1989). In perennial ryegrass cv. 'S23' grown in a Seaton loam soil Ni (as $NiSO_4$) at more than 30 ppm depressed shoot yield, but Ni concentration of 50 ppm in shoots, though caused slight chlorosis, did not reduce the dry matter production (Khalid and Tinsley 1980). At 75 mg Ni kg^{-1} soil absorption and phytotoxicity of various forms of Ni in barley plants in medium and heavy clay soils was in the order: $NiSO_4 \cdot 7H_2O$ > Ni(II)-citrate > Ni(II)-Glu > Ni(II)-EDTA, but the morphological and anatomical damages of plants were similar (Molas and Baran 2004). Ni toxicity in seedlings of coffee was observed at 0.5 and 1.0 mg Ni l^{-1} (Pavan and Bingham 1982). In solution culture Ni^{2+} at 100 µM and above were toxic in pea, with complete inhibition of nodulation at 200 µM Ni l^{-1} (Shweta Singh *et al.* 2004). In potato cv. 'Chandramukhi' 0.5 mM Ni, was toxic (Shukla and Gopal 2009). The exposure up to 10 µg ml^{-1} Ni resulted in an increase in top root length, dry weight and chlorophyll contents of the plants but higher doses of Ni affected germination and early seedling growth of chickpea cv. 'Pusa 1103' and 'Pusa 1105' (Yadav *et al*. 2007).

The influence of soil properties on Ni toxicity to barley root and tomato shoot growth on 16 European soils reveals that the effective concentration of added Ni causing 50% inhibition (EC_{50}) ranged from 52-1929 mg kg^{-1} for the barley and 17-920 mg kg^{-1} for tomato, representing 37- and 54-fold variation among soils, respectively (Rooney *et al.* 2007). Soil cation exchange capacity was the best single predictor for the EC_{50}. The EC_{50} based on either the Ni concentration or free Ni^{2+} activity in soil solution varied less among soils (7-14-fold) than that based on the total added Ni, suggesting that solubility of Ni is a key factor influencing its toxicity to plants. The EC_{50} for free Ni^{2+} activity from the barley test decreased with increasing pH, indicating a protective effect of protons (Rooney *et al.* 2007). However, concentrations of Ni in soil solutions as toxicity predictors and the critical concentrations of Ni in maize were all soil-dependent (Guo *et al*. 2010). With the reduction of biomass by 10% as an index in pakchois (*Brassica chinensis*), the critical value of Ni toxicity in drab soil was 57.2 and 8.56 mg kg^{-1} for total Ni and available Ni (DTPA extractable) in the soil, respectively (Ma *et al.* 2006). However, the critical toxicity level of Ni for lettuce in alkaline sandy loam soil was 9 ppm (Bansal and Khurana 2006).

The criterion to assess the toxic levels of elements not standardised world-wide and varies from one country and land use to another (Ross and Kaye 1994). The total mineral provides the maximum pool of these in the soil, but how much of this soil pool will be available to plants is determined by several factors. Moreover minerals in the soil solution are in dynamic equilibrium, and replenishment occurs when these are either removed by plant or by leaching. Soil pH have a large effect on bioavailability of elements (Turner 1994) and with decreases in soil pH the solubility of Co and Ni increases in the soil solution which increases the bioavailability of these and plant uptake. Besides these, the organic matters dissolved in the soil solution are also important for solubility (Norvell 1991). To assess the toxicity in various crops, quantification of the bio available fraction of these minerals in the soil which the plant can access is a must.

Toxic concentrations in plants

The essential metal ions are taken up by plants from the soil solution through metal transporters at the plasma membrane which also give entry to other metals and non-nutritive elements, as well as the essential nutrients at higher than metabolic concentrations, causing phytotoxicity. Besides soil different species or varieties grown on the same soil can have different mineral uptakes. As there are species specific factors affecting plant uptake and a true measure of plant available metals will not be attained unless the extent of soil exploitation by the roots is accounted for. The reported toxicity and threshold toxicity levels of B, Co, Mo and Ni in plant for various crops are given in **Table 2** which indicate that the requirements and expression of toxicity of these minerals vary widely among various crops and cultivars. In plant nutrition studies, the youngest fully expanded leaf is often used as the standard plant tissue for comparison of

foliar concentrations as the element concentrations in this tissue are often independent of plant age, however toxicities of many elements are more pronounced on lower leaves due to its higher accumulation in older leaves than in fresh leaves. The difference in B phloem mobility and expression of B toxicity symptom has significance for its diagnosis. Old leaves are suitable for determining B toxicity only in B-immobile species, but for species in which B is mobile young apical leaves or fruit tissues are needed. More over the pattern of B supply affects the development of leaf injury and other symptoms of B toxicity, the accumulation of B in the grain and in the shoots at maturity, and the relationships between the concentrations of B in the grain and in the shoots at maturity and yield. The barley plants can accumulate relatively high levels of B and express severe leaf injury and other symptoms of B toxicity in the later stages of growth with relatively small effects on grain yield and, thus the grain and shoots, at maturity, are not suitable tissues to diagnose yield depressions due to B toxicity (Riley and Robson 1994).

Boron toxicity is commonly considered in terms of plant B uptake and accumulation, however foliar exposure with high B containing water leads to more severe toxicity reactions in plants as compared to exposure to high B simply through the soil solution. The relative toxicity of B entering through the leaves is greater than that of B entering via roots in maize, tomatoes, onions (*Allium cepa* L.), celery and radish (*Raphanus sativus* L.) (Ben Gal 2007). The sufficiency and toxicity levels of B were 29-125, 160 ppm, respectively in sunflower and 44, 63 ppm, respectively in soyabean (Murthy 2006). Rice plants, in IRRI farm, showed B-toxicity symptoms when plants had more than 35 ppm B (Cayton 1985). In grapevines (cv. 'Sugraone') in Israel's Jordan Valley, excess B, (0.21 and 0.31 mM) caused chlorosis and necrosis, accumulated B in leaves linearly as increased B in irrigation solution with time and with age of leaves with the highest B levels found at the end of each season and in the oldest leaves (Yermiyahu *et al*. 2006). In wheat the B concentrations in shoots ranged from 30.8-589 ppm with the highest shoot B at 6 ppm B in nutrient solution (Sonmez *et al*. 2009).

Critical toxic concentrations of B in barley shoots at booting stage were in the range of 50-70 ppm (Riley 1987), which also varied from 2 to 15 ppm in grain and 50 to 420 ppm in shoots at harvest (Riley and Robson 1994). The tissue B concentration at the boot stage in glasshouse grown barley cv. 'Volla' and wheat cv. 'Opal', ranged from 25-62 ppm in barley and 13-25 ppm in wheat and the N:B ratios of 249-520 were associated with severe to medium B toxicity, but not at ratios greater than 682 (Gupta *et al.* 1973). Shoot B concentration in wheat cultivar 'Frame' ranged from 15 to 947 ppm for increasing soil B to toxic level (Nuttall *et al*. 2006). In Redlands Crimson strawberries the B concentration greater than 123 ppm in old leaves caused B toxicity symptoms (Haydon 1981). The B content of roots, mid leaves and apical leaves in groundnut cv. 'TMV-2' grown at toxic level of 10 ppm B, was 116, 3900 and 3750 ppm, respectively, compared with 23, 112 and 65 ppm in the controls (Gopal 1973). The B concentration in leaves and kernel of groundnut increased with increase in B supply but its concentration in kernels was lower (2 to 80 $\mu g\ g^{-1}$) than that in leaves (6.5 to 220 $\mu g\ g^{-1}$). In Spanish groundnut cv. 'Natal' the leaves showing no symptoms of B toxicity, leaflets with marginal chlorosis and those with marginal necrosis showed the tissue concentration of 112, 235 and 281 ppm B, respectively (Blamey and Chapman 1979). The threshold of toxicity and toxicity were 74 and 106 $\mu g\ g^{-1}$ in leaves and 50 and 72 $\mu g\ g^{-1}$ in kernels of groundnut (Sinha *et al*. 2002) and 190 and 310 ppm B, respectively in leaves of chickpea cv. 'Avrodhi' (Chatterjee *et al*. 2005).

The concentration of B increased in leaves and fruits of tomato with an increase in B supply from low to excessive (3.3 mg B l^{-1}) and the values of threshold of toxicity and toxicity were 102 and 250 ppm, respectively in young leaves (Sinha *et al*. 2006). The values for threshold of toxicity, and toxicity were 58 and 120 ppm, respectively, in young leaves of bittergourd (Sinha *et al*. 2009). For, corn plants the critical levels of B varied from 13.8 to 129.6 mg kg^{-1} and the toxic levels from 43.3 to 372.2 mg kg^{-1} (Lima *et al*. 2007). The interactive effects of salinity levels (1.5, 4, 8 and 12 dS m^{-1}) and B (1, 5, 10 and 15 mg l^{-1}) when studied on growth, yield and ion relations of wheat (cv. 'Yecora Rojo'), the symptoms of B toxicity were closely correlated with B concentration in the leaves, and injury became severe when leaf B exceeded 400 mg kg^{-1} (Grieve and Poss 2000). At toxic level of B causing 90% of the maximum dry matter yield of cotton, the leaf tissues contained 198 mg B kg^{-1} and the concentration of B in various plant parts was in the order of leaves > shoot > root (Niaz *et al*. 2008).

The Co concentrations in plants, though ranges 0.1–10 ppm (Palit *et al*. 1994), rarely exceed 1 ppm and 25-100 ppm is considered the threshold for toxicity in plants, however, in areas with soil Co up to 28 ppm, the Co in plant tissue was 11 ppm in beet roots and 4 ppm in beet tops (MOEE 1996). A study on 670 species of terrestrial plants showed that leaf Co concentration was in general less than 0.2 ppm, with the exception of Ericales, Euasterids and Asparagales clades, where 0.3–0.5 ppm of Co was measured (Watanabe *et al*. 2007). The values of threshold of toxicity and toxicity of Co were 26 and 72 $\mu g\ g^{-1}$ in young leaves of french bean, respectively (Chatterjee *et al*. 2006). However, Baker *et al*. (2000) reported a list of 26 Co hyperaccumulators, containing more than 1000 ppm Co in leaf tissues majority belonging to the families of Lamiaceae, Scrophulariaceae, Asteraceae, and Fabaceae.

Nickel is an essential nutrient for plants, but as the amount of Ni required for normal growth of plants is very low, increasing level Ni pollution in the environment cause Ni toxicity in plants. The critical toxicity levels of Ni in lettuce plant, causing 10% reduction in dry matter yield, was 13.7 $\mu g\ g^{-1}$ dry matter at 60 days after sowing (Bansal and Khurana 2006). The critical value of Ni toxicity was 20.51 mg kg^{-1} Ni in stems and leaves of pakchois (Ma *et al.* 2006). Though excess Ni decreased the rhizome biomass in bilberry (*Vaccinium myrtillus* L.), the Ni concentrations in the rhizome were about 10-fold lower (<3 mg Ni kg^{-1}) than those in the soil (<30 mg Ni kg^{-1}) and translocation of Ni from the rhizome to aerial shoots did not occur and Ni concentrations in shoots remained at 1mg Ni kg^{-1}, much below the threshold values of Ni toxicity (i.e. 10–50 mg Ni kg^{-1}) (Tahkokorpi *et al.* 2010). In birch (*Betula papyrifera*) Ni was concentrated in the roots with the highest concentration, but was lowest in stems (Jones and Hutchinson 1988b). At 200-300 µM Ni, the pea foliage accumulated 34 ppm Ni and the root: shoot share of Ni in pea was invariably 60:40 indicating that 40% of Ni accumulated gets translocated to foliar parts (Shweta Singh *et al.* 2004). Leaf Ni concentrations of 30 to 40 and 70 to 80 ppm in coffee were associated with medium and very severe leaf toxicity symptoms, respectively (Pavan and Bingham 1982).

Nickel is a trace metal that exhibits pronounced long-term immobilization reactions in soil and it is not clear whether the slowly decreasing solubility of Ni in soil on aging also correlates with decreased toxicity soil biota, however, testing Ni toxicity to soil microbial processes immediately after spiking soils in the laboratory overestimates Ni toxicity compared to aged soils (Oorts *et al.* 2007). The barley plants absorbed more Ni from the medium soil than from the heavy clay soil and the highest Ni in barley grown at 75 mg Ni kg^{-1} soil was found in the initial growth stages (emergence), and declined with the progressing growth (Molas and Baran 2004). Crooke and Knight (2008) observed that during a 70-day period from germination to maturity, the iron content of oat plants showing symptoms of Ni toxicity changed little, but the Ni content increased rapidly for about 30 days and then decreased slowly. Further, the uptake of Ni in oat plants increases with increasing pH at constant iron level in the substrate, although the degree of necrotic symptoms was similar over pH range 4–7,

the iron uptake was reduced by both Ni and increasing pH and results in chlorosis at pH 5·5 and above (Crooke *et al*. 2008).

Exposure of the wheat plants to 100 µM Ni for only 3 days led to almost 200-fold increase in Ni concentration in the leaf tissue but later the rate of Ni accumulation was much slower (Gajewska and Skodowska 2007). The concentration of Ni in shoot and root of lettuce increased with the increase in the applied Ni and root accumulated much higher amounts of Ni compared to the shoot with overall mean Ni content of the plant tissue increased from 3.2 µg g^{-1} in the control to 95.0 µg g^{-1} dry matter for 200 mg Ni kg^{-1} of soil (Bansal and Khurana 2006). Field experiments in calcareous soil with pH 8.9, and acidic soils with pH of 5.3 have shown that accumulation of Ni in stems and leaves of maize plants increased linearly with the increase concentrations of Ni added to soils, but the accumulation of Ni in the grains was nonlinear (Guo *et al*. 2010). Nanomaterials are of particular interest in environmental chemistry due to their unknown toxicity to living organisms however there is indication that nanoparticles (NPs) affect seed germination (Parsons *et al*. 2010). The biotransformation of nanoparticles by mesquite plants (*Prosopis* sp.) was reported where plants treated for four weeks with 0.10 g of uncoated and coated NPs before and after synthesis had 803, 764, and 400 mg Ni kg dry weight, in the leaves, respectively, but none of the treatments reduced plant size or chlorophyll production (Parsons *et al*. 2010).

EFFECT OF MINERAL TOXICITIES IN CROP PLANTS

Growth, development and yields

The effect of excess mineral occur at cellular level, at the organ level in leaf as symptoms and at the whole plant level in reduced growth and yield. Both the symptoms and growth effects are side effects of the direct mode of action. Excess B adversely affects the growth, yield and yield attributes, the extent of which depends upon the toxicity levels, crop species and the soil. Growth was rapidly inhibited by internal B concentrations in the range 1-5 mM across a range of plant types. In contrast, mature cells were able to withstand up to 60 mM B for several days (Reid *et al.* 2004). In wheat, rapid inhibition of root growth occurred if high B was applied to the root tip, but not if high B was applied to mature sections of the root. In leaves, there were gradations in B concentrations that correlated with visible symptoms of toxicity (Reid *et al.* 2004). In barley root growth was reduced much more than shoots growth (Riley 1987). Increasing B in soil increased symptom of B toxicity in barley cv. 'Stirling' and decreased the growth of shoots and grain yield, accumulated B in the older leaves and increased the rate of leaf senescence (Riley 1987). In groundnut cv. 'TMV-2', 10 ppm B was toxic which reduced root growth by 50% and the moisture content of mid leaves by 24% (Gopal 1973). In another study on Spanish groundnuts cv. 'Natal' excess B fertilizer decreased pod yields by 10% in the first 2 seasons and by 29% in the 3rd season (Blamey and Chapman 1979). Excess B adversely affected the yield and yield attributes of fababean cv. 'VH-82-1' (Mola *et al.* 1998). In tomato cv. 'DL-3', excessive B (3.3 mg B l^{-1}) reduced growth, number and size of lamina and old leaves developed marginal necrosis (Sinha *et al*. 2006) reduced total biomass in bittergourd (Sinha *et al*. 2009).

In a field with higher soil B, cotton yield decreased with B fertilizer (Rezaei and Malakouti 2001). Yield reduction due to B toxicity in rice at IRRI farm was 10-20% in tolerant varieties, whereas the susceptible varieties were more adversely affected (Cayton 1985). The salt tolerant 'KRL 1-4' and salt sensitive 'HD 2329' cultivars of wheat when exposed to various B (0.0, 0.3 and 0.9 mM) and levels, the plant height, tiller number, leaf number, leaf area, root volume, and total dry weight of plant decreased with the increase in B concentrations (Rani *et al*. 2008). Increased levels of B in tomato depressed biomass and increased the concentrations of B in plant tissues (Gunes *et al.* 1999). Soil treatments with 1 and 2 mg B kg^{-1} in high B containing (>2 ppm) soils of Ghabdan and Kaheru soil series of Punjab reduced the yields of clover by 11.7 and 20.0% in Ghabdan and 4.0 and 7.5% in Kaheru soils, respectively (Arora and Chahal 2005). Toxic levels of B (20 and 30 ppm) reduced leaf and root growth and increased the B concentration of the leaf and stem, bark and roots of grapevine (Gunes *et al*. 2006). However, in a separate study, at high levels of B (0.21 and 0.31 mM), B toxicity was observed, and the rate of trunk growth of grapevines was reduced, but despite severe visual toxicity damage and reduced overall growth rates, commercial fruit yield of the vines remained unaffected (Yermiyahu *et al*. 2006). Using a moderately B toxicity tolerant barley line from the cross 'Arar/Arabic Aswad' (AA) and the moderately susceptible variety 'Harmal' in pots consisting two sections with provision of adding B to the bottom section only and both sections, Yau (2010) demonstrated that grain yield was much less when B was applied both from bottom and top section than that of B applied to bottom only, also when B was applied to bottom the grain yield reduction (8%) by tolerant barley line AA was less than half of the reduction (18%) suffered by 'Harmal'. Thus subjecting barley crops to high-B soils from germination to maturity exaggerates the effects of B on rainfed crops in the field and high subsoil B levels can cause significant yield reduction even when roots reach it as late as the boot stage (Yau 2010).

Inhibition of seedling growth occurred at 5 µM Co in mung beans (Liu *et al.* 2001). In tomato excess Co (0.5 mM Co), reduced biomass (Gopal *et al.* 2003) depressed the fruit weight, volume and size of fruits and quality of fruits (Chatterjee and Chatterjee 2005). In Lucerne the Co(II)-Gly chelate was more toxic than the Co(II)-EDTA chelate and reduced the crop of dry matter, the content of nitrogen, protein and essential amino acids and reduced the physiological efficiency of the symbiotic system of Lucerne and caused changes in its structural organization (Molas 2008). Under excess Co at >0.0001 mM (cobalt sulfate) in french bean (cv. 'Anupama'), decreased the biomass, the flowers produced were fewer and smaller, many failed to mature, leading to lower seed yields (Chatterjee *et al*. 2006).

Although beneficial at concentrations below 0.0001 mM, at high levels Ni can detrimentally affect yield and quality of crops. The Ni toxicity in wheat was observed 3rd day of Ni treatment at 100 µM Ni and length and fresh weight of the leaves were substantially reduced (Gajewska and Skodowska 2007). The Ni toxicity in maize seedlings decreased dry matter production most in the root system which accumulated large amounts of Ni (Baccouch *et al.* 1998). In acid soils 120 ppm Ni, decreased dry matter and seed yields in French bean cv. 'Carioca' and rice cv. 'IAC-165' (Piccini and Malavolta 1992). Excess Ni (200, 500 µM) in radish (cv. 'Early menu') caused a considerable reduction in germination percentage, growth and biomass, decreased the different pigments (Yadav *et al*. 2009). The potato (*Solanum tuberosum* L.) takes up Ni easily and can accumulate in tubers and become ingested by humans. Exposure of potato plants to excess Ni show retarded growth, decreased Chlorophyll (Chl) concentration (Shukla and Gopal 2009). The Ni toxicity at 150 ppm Ni in *P. vulgaris* affected root and shoot length, leaf area, and dry biomass (Al-Qurainy 2009). In pea, the Ca, H, and Ni competed for root-binding sites with high pH and low Ca favoring more Ni accumulation in pea and at low pH, Ca accumulation is the key factor determining root growth, while at medium to high pH, root elongation is more sensitive to Ni concentration in pea (Wu and Hendershot 2010). The order of activity of the elements in producing chlorosis in oat plants was found to be Ni >Co > Mo in oat, which is related to yield reduction and is similar to the order of stability of metal complexes (Hunter and Vergnan 2008). The effect of toxic metals on seed germination in 23 cultivars of flax at concentrations 0.01-1 mM by standard ecotoxicity test that Co

was more toxic than Ni (Soudek *et al.* 2010).

A Biotic Ligand Model (BLM) was developed for predicting the effect of Co on root growth of barley in nutrient solutions where with increasing activities of Mg^{+2}, and to a lesser extent also K^+, the EC_{50} Co^{+2} increased linearly, while Ca^{2+}, Na^+ and H^+ activities did not affect Co^{+2} toxicity with the stability constants for binding of Co^{2+}, Mg^{+2} and K^+ to the biotic ligand $\log_K Co^{BL}$=5.14, $\log_K Mg^{BL}$=3.86 and $\log_K K^{BL}$=2.50 (Lock *et al*. 2007). However, this needs further refinement. Using BLM, Li *et al*. (2009) found that Ni toxicity to barley root elongation in solution culture decreased with increases of Mg^{2+} and Ca^{2+} activities, higher H^+ activity decreased the toxicity through H^+ competition with Ni^{2+} bound to biotic ligands at pH <7.0 or through the change of Ni species in solution at pH ≥7.0, however when pH ≥7.0 the Ni^{2+} plus $NiHCO_3^+$ were toxic to barley root elongation. The conditional binding constants for Ni^{2+}, $NiHCO_3^+$, H^+, Mg^{2+} and Ca^{2+} with biotic ligand were 4.83, 5.36, 4.29, 4.01 and 1.60 (Li *et al*. 2009). The study suggest that in solutions with pH ≥7.0 free Ni^{2+} as well as $NiHCO_3^+$, Mg^{2+} and Ca^{2+} competitions with Ni^{2+}, should be considered for BLM development (Li *et al*. 2009).

Physiological processes

1. Photosynthesis

The effect of B, Co Mo and Ni toxicities decreased Chl concentrations, followed by reduced growth, loss of leaf area and decreased CO_2 fixation. Studies on the sensitivity to B of a range of metabolic processes including photosynthesis, respiration and protein synthesis indicated that growth is not restricted by effects of B on energy supply and not directly by inhibition of protein synthesis (Reid *et al*. 2004). Excess B, in bittergourd, reduced total biomass, Chl *a* and *b*, carotenoid (Sinha *et al*. 2009). Exposure of chickpea seedlings at 0, 1.6 and 6.4 mM B (boric acid) for 7 days increased shoot length in the drought-tolerant cultivar 'Gokce' and decreased in the drought-sensitive 'Kusmen' cultivars of chickpea at 6.4 mM B, Chl fluorescence (Fv/Fm) did not change in 'Gokce' at either B level, but dry weights of both cultivars decreased at 6.4 mM B and B concentration in the shoots of both cultivars increased with increasing levels of applied B (Ardc *et al*. 2009a). At higher B concentrations, many cellular activities were partially inhibited and the toxicity to mature tissues was considered not to arise from the disruption of a single process, but from the accumulated retardation of many cellular processes, exacerbated in light by photo-oxidative stress (Reid *et al*. 2004).

Excess Co depressed the concentrations of Chl *a*, *b* and carotene in tomato (Gopal *et al.* 2003; Chatterjee and Chatterjee 2005). Exposure of *Phaseolus vulgaris* cv. 'Kentwood' seedlings to phytotoxic rates of Co and Ni reduced the export of ^{14}C-photoassimilates from the fully expanded unifoliate leaves and only little ^{14}C reached the major sink areas (the young trifoliate leaves and root tips) within 1 or 2 days (Samarakoon and Rauser 1979). Excess Co, Ni and Zn in *P. vulgaris* seedlings, accumulated callose on phloem sieve plates which ranged in thickness and were most pronounced in midribs of unifoliate leaves and their subtending petioles. Lesser callose deposits were found in stems. Although translocation of ^{14}C was reduced drastically in seedlings exposed to excess Co, Ni or Zn, no correlation was found between translocated ^{14}C and the amount of callose in the petioles indicating that the inhibition of phloem translocation was due to effects other than callose deposition (Peterson and Rauser 1979). Excess Co (> 0.0001 mM) decreased concentration of Chl, Hill reaction activity in French bean (Chatterjee *et al*. 2006).

Excess Ni decreased the Chl a and b in durum wheat (Pandolfini *et al*. 1996), total leaf Chl in coffee (Pavan and Bingham 1982) and reduced photosynthetic rates in birch seedlings (Jones and Hutchinson 1988a). The effect of *in vivo* Ni^{2+} toxicity on the photosynthetic system of primary leaves was studied where the leaf area, Chl and total carotenoid content in *P. vulgaris* cv. 'Slowianka' decreased due to Ni- toxicity and there was an indirect effect of Ni on photosystems related to the disturbances in the Calvin cycle reactions and down-regulation or even feedback inhibition of electron transport by the excessive amounts of ATP and NADPH accumulated due to non-efficient dark reactions (Krupa *et al*. 1993). The visual symptom of Ni toxicity was influenced by the length of the light and dark periods and nature of these effects is discussed in length by Anderson *et al.* (1979). Under conditions of Ni toxicity in oats (*Avena byzantina*) cv. 'Algerian', the plants containing high levels of Ni contained higher levels of protochlorophyll and lower levels of Chl than control plants (Anderson *et al*. 1979).

2. Water relations

Excess B caused decline in leaf area, relative water content (RWC), Ca, Mg, Zn, Cu, Ca/B and K/Na ratios and this increase in leaf permeability and osmotic potential led to more accumulation of toxic ions like Na, Cl, S and B in leaf tissues of bean (Mola *et al*. 1998). However, there was no evidence to support the hypothesis that toxicity in leaves is due to osmotic stress induced by the accumulation of B. In order to restrict excessive uptake of B, stomatal resistance of the leaves increased at high B of grapevine (Gunes *et al*. 2006). The stomatal closure is an important response of lettuce against NaCl and B+NaCl stress (Eraslan *et al*. 2007c). Boron-stress induced changes in water status and stomatal morphology in maize (var. '32-A09') plants, compared to B sufficient plants (0.33 mg B l^{-1} supply), B deficient (0.033 mg B l^{-1}) and toxic (3.3 mg B l^{-1} supply) plants showed accumulation of proline, reduced stomatal size and increased stomatal index and increased the leaf water status by increasing the specific and relative water content an decreased water potential (Ψ) (Pandey and Archana 2009). Excess Ni decreased water potential and relative water content in durum wheat (Pandolfini *et al*. 1996). The Ni-toxicity at 200 µM Ni in wheat caused inhibition of shoot growth, a decline in relative water and Chl contents (Gajewska *et al*. 2006). In bilberry under Ni stress, the anthocyanins in aerial shoots responded to Ni concentrations in the rhizome, but anthocyanins are not involved in osmotic regulation despite the lack of water stress (Tahkokorpi *et al.* 2010).

3. Mineral contents and interactions with other elements

The B, Co, Mo and Ni toxicities increases concentration of these elements and also alters the other mineral contents in plants. In bean there was an antagonistic relationship between Ca and B and synergism between K and B uptake (Mola *et al*. 1998), and B increased Zn concentration in tomato plants (Gunes *et al*. 1999). The B toxicity increased Ca, Mn, Zn and Fe, decreased K in leaves but did not alter P, Mg and Cu in groundnut (Blamey and Chapman 1979). In another study on groundnut B toxicity decreased Fe content of roots and leaves and Cu in middle leaves (Gopal 1975b, 1976) reduced Ca in middle leaves and increased P contents and ratio of P:Fe of roots and middle and apical leaves, K in middle leaves (Gopal 1975c). The B toxicity in kiwifruit vines, decreased Ca contents and increased Zn and B contents in fruit, but did not affect fruit N, P, K, Mg, Mn and Fe contents (Sotiropoulos *et al*. 2006). The decrease in B content from the basal part of the fruit towards the apical was observed due to the low mobility of B within the plant, the higher B content in the basal part of flesh suggests that this tissue is the most sensitive indicator of B toxicity in fruit (Sotiropoulos *et al*. 2006). The B toxicity (50 ppm) increased the N, P and K concentrations of tomato and N, P, Mg and S concentrations of pepper (Eraslan *et al*. 2007a). In lettuce, B toxicity increased B concentration, but in the presence of NaCl, the concentration of B was reduced, however, Na concentrations increased (Eraslan *et al*. 2007c). In spinach also the concentration of B in the tissues, which was strongly increased by B treatment, was decreased by NaCl (Eraslan

et al. 2008). In banana the B toxicity was combined with a decrease of Ca in the leaf (Vargas *et al*. 2007). In maize the content of N, Ca, Mg, Fe, Mn, Zn and Cu generally decreased with an increase in B and P fertilizer application, however P and B content increased (Aydn *et al*. 2005). Similarly, higher levels of B caused reduction in N, Ca, Mg, Mn, Zn and Fe contents but P, K and Cu contents increased significantly in leaf tissues of cotton (Niaz *et al*. 2008).

Excess Co (0.5 mM Co) restricted the concentrations of P, S and Fe in tomato where accumulation of Co was greatest in roots and old leaves and lowest in stem (Gopal *et al*. 2003). In mung beans inhibition of seedling growth occurred at 5 μM Co but none of the nutrients except Mn and Fe, were affected, the uptake of Fe into roots was not inhibited by Co, but transport of Fe to the shoot was greatly reduced, thus the effect of Co on growth was additive to that of Co-induced Fe deficiency (Liu *et al*. 2001). The toxic effects of Co, when compared with, Cd, Cu, Ni and Hg at 5 μM in mung bean, all the trace metals showed strong inhibition of Fe transport to the shoot, but Co stimulated the uptake of S into the plant and its transport to the shoots, the leaves S was increased 2-fold (Liu *et al*. 2001).

Though symptoms of Mo toxicity developed at 40 ppm Mo in flax soybean and peas, Ammonium molybdate at 20 or 40 ppm Mo prevented chlorosis caused by low iron in young flax plants and sodium molybdate was effective only at 40 ppm, but with an increase in iron supply, a reduction in Mo toxicity symptoms was observed in soybean and peas (Warington 2008). However, in flax the higher level of iron eventually proved excessive unless it was combined with 40 ppm Mo, thus high Mo seemed able to counteract both iron deficiency and toxicity in this plant (Warington 2008). High iron, (not at excessive) reduced the Mo content of both shoot and root in soybean, peas and also in flax. High Mo usually reduced the iron content of the shoot, but markedly increased it in the root. Mo-induced chlorosis could thus be partly attributed to inhibition in iron translocation, but the beneficial effect of high Mo or high iron on colour was not obviously correlated with the analytical data (Warington 2008).

The effect of Ni toxicity, a non-resource abiotic stress, on intraspecific nutrient competition in wheat appears to be due to an increased demand for nutrients in the presence of toxic levels of Ni (Stadt *et al*. 1994). The combinations of excess Cu, Ni and Co in *P. vulgaris* showed that excess Cu + Ni induced a chlorosis which was not given by Ni or Cu alone, combined Ni + Co + Cu decreased leaf Fe content and induced Fe deficiency (Wallace *et al*. 1981). In acid soils 120 ppm Ni decreased leaf Mn, Ca and Zn concentrations in *P. vulgaris* cv. 'Carioca' and rice cv. 'IAC-165' (Piccini and Malavolta 1992); however, in coffee excess of Ni increased leaf Mn, Fe and Zn, decreased leaf Ca, but did not affect leaf Mg and total N contents (Pavan and Bingham 1982). In birch Ni reduced the concentration of P, Mg, Ca and Fe in shoot tissues (Jones and Hutchinson 1988b). Increasing Ni levels 10, 100 and 1000 ppm in a sandy soil at pH 5.9, decreased nitrification and N and C mineralization (Giashuddin and Cornfield 1978). In barley cv. 'Minorimugi' increase of Ni, increased the concentrations of Cu and Fe in roots, but decreased Mn and Zn in shoots and roots and Cu and Fe in shoots and the shoot concentrations of Cu, Fe, Mn and Zn in plants grown at 100 μM Ni were below the critical levels for deficiency (Rahman *et al*. 2005). The levels of Fe and Zn in shoot and root of lettuce increased, whereas the Cu and Mn contents decreased with the increase in the Ni rate (Bansal and Khurana 2006). The Ni and Fe content of the shoots in ryegrass grown in a Seaton loam soil increased and that of Mn and Zn decreased with increasing rates of Ni application, however, pattern of Ni uptake was different, being highest at the middle level and decreasing on both sides, indicating that the increase of Ni of shoots was not proportional to the reduction in the yield (Khalid and Tinsley 1980). The Ni:Fe ratio rather than Ni and Fe concentration in plants showed a better relationship with the toxic effects of Ni (Khalid and Tinsley 1980).

A reciprocal relationship exists between the Ni and Fe contents of the leaf blades in oat plants; the Ni content is materially reduced by high concentrations of iron in the nutrient solution, and the iron content by Ni, the former being the more pronounced effect (Crooke *et al*. 2008). For a constant level of iron supply the P content of the stem extracts is higher the greater the degree of Ni toxicity in oat plants; the P status of the plant may be a factor in producing Ni toxicity but if so, it has to be considered in relation to other factors (Crooke *et al*. 2008). The concentration of iron in mature leaves from oat plants growing in a Ni toxic soil was lowest in the necrotic areas of the leaf, suggesting a migration of nutrients out of the dying tissue (Crooke and Knight 2008). Exposure of potato plants to excess Ni decreased concentration of Zn and Fe whereas increased the concentration of Ni, P and S in different plant parts of potato (Shukla and Gopal 2009). The toxic effects of Ni, Co and Mo in oat plants are associated with high concentrations of these element in the leaf tissue and toxic effects of Ni and Mo reduced N content of the plant, while Ni and Co increase the concentration of P in the tissue (Hunter and Vergnan 2008). Aluminium reduces the intensity of toxic symptoms produced by Ni—probably by reducing the uptake of Ni and P, the Cu effectively reduces the leaf necrosis produced by Ni, but not the Ni content of the leaf tissue suggesting that one factor in Ni toxicity may be inhibition of one or more functions of Cu (Hunter and Vergnan 2008). In pea, the Ca, H, and Ni competed for root-binding sites with high pH and low Ca favoring more Ni accumulation in pea and at low pH, Ca accumulation is the key factor determining root growth, while at medium to high pH, root elongation is more sensitive to Ni concentration (Wu and Hendershot 2010). Thus the tissue concentration of Ni and Ca can be predicted from total dissolved Ni, pH, and total dissolved Ca in pea.

Enzymes and cell metabolism

The direct mode of action of these minerals is on plant metabolism and each has a different mode of action. One of the physiological roles of B is cross-linking the pectic polysaccharide rhamnogalacturonan II in primary cell walls. Borate cross-linking of pectic networks serves both for physical strength of cell walls and for cell adhesion. In groundnut excess B (10 ppm) increased B accumulation, reducing-sugar, non-reducing and total-soluble sugars in mid leaves (Gopal 1973). The B-toxicity decreased cytochrome oxidase (EC 1.9.3.1), catalase (CAT, EC 1.11.1.6), peroxidase (POD, EC 1.11.1.7), ascorbic acid oxidase (EC 1.10.3.3) and polyphenol oxidase (PPO, EC 1.14.18.1) activities in middle leaves of groundnut (Gopal 1975a). Excess B (300 μM) caused growth reduction, increased the activity of POD, acid phosphatase (APase, EC 3.1.3.2) and PPO, increased the concentration of sugars, starch and phenols in leaves, but decreased that of proteins and oil in kernels of groundnut (Sinha *et al*. 2002). Excess B (6.6 mg B l^{-1}) increased the activity of starch phosphorylase (EC 2.4.1.1) and APase and decreased ribonuclease (RNase, EC 3.1.27.5) and PPO, deteriorated the quality of chickpea seeds (cv. 'Avrodhi') by lowering seed yield, starch and protein concentration, and increasing the accumulation of phenols and sugars (Chatterjee *et al*. 2005).

The N metabolism adversely affected by high B and contents of total N and protein N reduced due to a change in Fe metabolism in groundnut (Gopal 1975a). In low and excessive B, the concentration of reducing, non-reducing and total sugars and phenols were high in tomato fruits (Sinha *et al*. 2006). Leaves of tomatoes grown in a B toxic nutrient solution had a different phenol composition with the absence of caffeic acid and aesculetin in B toxic plants at flowering (Revilla *et al*. 1985). In another study on tomato cv. 'DL-3' excessive B (3.3 mg B l^{-1}), the specific activity of POD, RNase and APase increased while that of PPO and phenylalanine ammonia-lyase (PAL, EC 4.3.1.5)

decreased and concentration of ascorbic acid and lycopene content decreased (Sinha *et al*. 2006).

The B toxicity increased membrane permeability and proline accumulation in tomato and pepper (Eraslan *et al*. 2007a) and bean (Gunes *et al*. 2009). The B-toxicity in lettuce increased H_2O_2 and antioxidant enzymes (superoxide dismutase (SOD, EC 1.15.1.1), CAT, ascorbate peroxidase (APX, EC 1.11.1.11) activities and accumulation of ascorbic acid and proline were involved in order to overcome B-induced oxidative stress (Eraslan *et al*. 2007c). However excess B in bittergourd reduced proline contents and activity of CAT and enhanced activities of the antioxidant enzymes POD, SOD, APX, and PPO in leaves, but lipid peroxidation decreased, and tissue B concentration increased with an increase in B supplied (Sinha *et al*. 2009). In grapevine the concentrations of H_2O_2, lipid peroxidation and membrane permeability increased due to B toxicity while proline and activity of lypoxygenase (LOX, EC 1.13.11.34) decreased (Gunes *et al*. 2006). The B toxicity elevated the antioxidant enzymes to protect the membrane functions from reactive oxygen species injury in grapevine and it was hoped that this study would provide a basis for developing strategies for reducing the risks associated with B toxicity (Gunes *et al*. 2006).

The B toxicity in bean leaves increased the membrane permeability, malondialdehyde (MDA) content, and activities of SOD and LOX while that of CAT was decreased however, application of Zn ameliorated the membrane deterioration, decreased the SOD and increased the CAT and APX activities under toxic B conditions (Gunes *et al*. 2009). The concentrations of H_2O_2 and proline increased by B toxicity of bean, their concentrations were decreased by Zn supply (Gunes *et al*. 2009). Boron toxicity at 20 mg kg^{-1} B decreased proline concentrations and activities of SOD, CAT, APX and non-enzymatic antioxidant activity (AA), increased lipid peroxidation (MDA content) and LOX activity of barley, but application of Si (50-100 mg kg^{-1}) increased the activities of AA, SOD, CAT and APX decreased LOX activity under toxic B conditions (Inal *et al*. 2009). The Si alleviates B toxicity by possibly preventing oxidative membrane damage, both through lowering the uptake of B and by increasing tolerance to excess B within the tissues (Inal *et al*. 2009). Excess B increased B concentrations in shoot and root tissues of bean and application of Zn treatment reduced B and increased the Zn concentration in the roots and shoots (Gunes *et al*. 2009). While the concentrations of H_2O_2 and proline increased by B toxicity of bean, their concentrations were decreased by Zn supply (Gunes *et al*. 2009).

Excess Co (0.5 mM) restricted Chl *a* and *b*, DNA and RNA, reducing and non-reducing sugars, starch, total soluble proteins, protein and non-protein nitrogen and increased phenol and Co concentrations in tomato (Gopal *et al.* 2003), depressed the concentrations of ascorbic acid, lycopene, reducing sugars and starch, and increased acidity and phenols therby reduced quality of tomato fruits (Chatterjee and Chatterjee 2005). In excess Co treated tomato leaves, the activity of CAT and POD decreased and RNase and APase increased (Gopal *et al*. 2003). The unifoliate leaves of *P. vulgaris* seedlings exposed to toxic Co and Ni accumulated sucrose, reducing sugars and starch (Samarakoon and Rauser 1979). The Mg-dependent ATPase activity in maize decreased with the increase in Co levels (Kamenova *et al*. 1983). Excess Co (>0.0001 mM) decreased and activity of CAT, and deteriorated the quality of produce (sugars, starch and protein N), but increased the concentration of phenols and activity of POD, RNase and APase (Chatterjee *et al*. 2006).

The Mo-toxicity (0.4-1.6 µM Mo) increased POD and CAT activities in rice (Rout and Das 2002); however, excess Mo decreased POD activity in groundnut leaves (Singh and Chaudhari 1992). Nitrogenase (EC 1.18.6.1) is the nitrogen fixing enzyme complex, while nitrate reductase (NR, EC 1.6.6.1) requires Mo for its activity (Anke and Seifert 2006). The toxicity of 100 µM Mo in their oxyanionic forms Na_2MoO_4 were studied on NO_3^- assimilation, NR, nitrite reductase (EC 1.7.2.1), glutamine synthetase (GS, EC 6.3.1.2) and glutamate synthase (EC 1.4.7.1) activities, in sunflower (*Helianthus annuus* L. var. 'Kasol') where Mo had no negative effect on the growth (Ruiz *et al*. 2007).

The Ni induced accumulation of soluble phenolics, starch and reducing sugars in maize leaves, the observed accumulation of carbohydrates in shoots was cause of root growth inhibition (Baccouch *et al*. 1998). As potato takes up Ni, accumulate in tubers and become ingested by humans, the affects of Ni on quality of potato when studied on potato cv. 'Chandramukhi' the Ni above 0.1 mM reduced tuber concentrations of sugars, starch, and protein nitrogen and increased accumulation of nonprotein nitrogen and phenols in tubers, but levels of nonreducing sugars, starch and phenols increased in leaves (Sukla 2010). The relationship between Ni toxicity (250 µM $NiCl_2$) and oxidative reactions when studied in maize during metal accumulation in roots, membrane lipid peroxidation enhanced only 6 h after metal treatment before roots revealed a decrease in growth, the activities of SOD and guaiacol peroxidase (GPX, EC 1.11.1.7), were unaffected by Ni stress, however, CAT activity was increased from 24 h after metal treatment (Baccouch *et al*. 2001). The excess Ni increased O_2^- and H_2O_2 contents in wheat leaves with their highest values on the 3rd day and then decreased, increased APX and GPX activities by several-fold and glutathione peroxidase (GSH-Px, EC 1.11.1.9) by 29%, decreased SOD and CAT activities, but did not change the lipid peroxides content in leaves (Gajewska and Skodowska 2007). Despite prolonged increases in O_2^- and H_2O_2 levels, oxidative damage, measured as the level of lipid peroxidation, did not occur in the leaves of Ni treated wheat (Gajewska and Skodowska 2007). Intracellular PODs might act as scavengers of peroxide radicals produced as a result of Ni toxicity in wheat (Pandolfini *et al*. 1992). At 40 mM Ni m^{-3} wheat roots showed enhanced lipid peroxidation and increased leakage of K; enhanced both guaiacol and syringaldazine extracellular POD activity in roots and shoots and stimulated intracellular soluble PODs in shoots (Pandolfini *et al*. 1992). The Ni-toxicity (200 µM Ni) in wheat caused accumulation of proline, decrease in activities of SOD and CAT and several-fold enhancements of POD and glutathione *S*-transferase (GST, EC 2.5.1.18) activities (Gajewska *et al*. 2006).

In roots of rice seedlings the Ni toxicity increased H_2O_2, MDA contents and SOD, APX and diamine oxidase (EC 1.4.3.22) activities, but no effect on CAT and glutathione reductase (GR, EC 1.6.4.2) activities (Lin and Kao 2005a). The Ni toxicity at 200-400 µM Ni^{2+} in rice seedlings suppressed the hydrolysis of RNA and proteins by inhibiting the activity of RNase and protease, respectively (Maheshwari and Dubey 2007). Cell wall stiffening and lignifications are the processes that are enhanced by Ni to reduce growth of rice roots (Lin and Kao 2005b). In rice seedlings $NiSO_4$ (60 µM) inhibited root growth, increased the activities of cell-wall POD against ferulic acid and syringaldazine peroxidase and lignin content in roots, but, did not affect the activity of PAL, the first enzyme of phenylpropanoid pathway (Lin and Kao 2005b). The *Jatropha curcas* L. embryos germinated and grown in vitro under 100, 200, 400 and 800 µ M Ni concentrations have shown that dry biomass of cotyledons increased with increasing Ni concentrations up to 200 µM, the SOD and POD activity increased significantly up to 400, 200µ M Ni, respectively and then decreased at 800 and 400 µ M Ni and above, respectively, however the PAL activity was highest at 400 µ M Ni and a negative link between CAT activity and Ni concentrations was observed (Yan *et al*. 2008). Further the electrophoresis analysis suggested a significant correlation between Ni concentrations and isoenzyme patterns of SOD and POD (Yan *et al*. 2008). At 200-300 µM Ni in pea proline biosynthesis promoted by more than 3-fold and a 40:60 root: shoot share of proline infers that it is synthesized primarily in foliar parts and can be adopted as a reliable metal-stress indicator (Shweta Singh *et al.* 2004). Excess Ni decreased activities

Table 3 Mineral toxicity-tolerant crop cultivars or genotypes.

Minerals	Crops	Tolerant cultivars or genotypes	References
B	Algerian barley	'Sahara 3771'	Sutton *et al*. 2007
	Algerian barley landrace	'Sahara'	Roessner *et al*. 2006
	Barley	'Anadolu', 'Tarm-92'	Torun *et al*. 2003
	Barley	'SloopVic', 'Sahara 3771'	Choi *et al*. 2007
	Barley	'Sahara 3763'	Nable 1988
	Barley	'ICB 104041', 'Tadmor', 'Tokak, Walfajr'	Yau 1997
	Barley	'VB9743'	Emebiri *et al*. 2009
	Bread wheat	Halberd (Wq*KP)*WmH/6/12	Paull *et al*. 1988
	Chickpea	'Gokce'	Ardc *et al*. 2009a
	Durum wheat	'Sabil-1', Stn "S", 'Aconhi-89' 'Wadelmez-2'	Torun *et al*. 2006
	Durum wheat	'Candeal de Grao Escuro no. 7746', 'Senatore Cappelli'	Yau *et al*. 1997
	Durum wheat	'ICDW 7674'	Yau 1997
	Lentil	'ILL 5883', 'ILL 1765'	Yau and Erskine 2000
	Lentil	'ILL 2024', 'ILL 0213A'	Hobson *et al*. 2006
	Pea	'SA 132', 'SA 310'	Bagheri *et al*. 1994
	Rapeseed mustard	'WWY Sarson', 'Local' India	Kaur *et al*. 2006
	Rice	'Koshihikari', 'Nipponbare' 'Sasanishiki	Ochiai *et al*. 2008
	Rice	'IR42', 'IR46', 'IR48', 'IR54', 'IR9884-54'	Dobermann and Fairhurst 2000
	Wheat	'G61450', 'Halberd'	Paull *et al*. 1991
	Wheat	'Greek' (G 6140)	Nable 1988
	Wheat	'India 126', 'Benventuto Inca', 'Turkey1473', 'Abyssinia 10', 'Iraq 22', 'Klein Granador', 'Lin Calel'	Chantachume *et al*. 1995
	Wheat	'Shi#4414/Crow'S'	Yau 1997
Mo	Rice	'Annapurna', 'Kusuma', 'Deepa'	Rout and Das 2002
Mo	*Poinsettia*	'Glory'	Hammer and Bailey 1987
Ni	Sunflower	'Mehran-II', 'Hyssun-33', 'M-3260' 'SF-187'	Ahmad *et al.* 2009

of antioxidative heme enzymes in potato (Shukla and Gopal 2009).

Also there was an indication of positive interaction between Ni and B. Excess Ni (200, 500 µM) in radish (cv. 'Early menu') reduced amylase activity and total proteins, but induced POD and CAT activity, however, B (50-100 µM) addition recovered the negative effect of Ni on pigment, increased protein contents reduced the CAT and POD activity (Yadav *et al*. 2009). The effect of Ni on hydrolyzing enzyme amylase was observed to be inhibitory in radish, resulting into poor germination followed by poor seedlings growth. The stress protecting enzymes POD and CAT seem to be induced under the influence of Ni, and providing protection to the seedlings. The application of B with Ni showed improved germination and growth. The level of CAT and POD were found to be significantly reduced showing normal growth and biomass of seedlings (Yadav *et al*. 2009). The genotoxicity produced by Ni was assessed by RAPD marker in treated plants of *P. vulgaris* and compared from untreated plants and out of 10 primers used, 5 gave monomorphic, 4 gave unique band, and remaining one did not amplify the genomic DNA, indicating that this technique was useful in evaluation of genotoxicity produced by these heavy metals and there is a environmental risk of heavy metals on DNA polymorphism of *P. vulgaris* (Al-Qurainy 2009).

MECHANISM OF TOLERANCE TO MINERAL TOXICITIES

The toxicities of B, Co, Mo and Ni are important for crop productivity. The mechanisms by which plants respond to excess of these though not understood fully, the present knowledge and understanding are mentioned here.

Genetic variation

The existence of genetic variation highlights the differences in tolerance or adaptation among the cultivars to high levels of these elements in soil. The reported highly tolerant genotypes are listed in **Table 3**. Cultivar differences in root elongation under B toxic conditions were observed in barley. An increase in the length and width of the root meristematic zone was observed in a B tolerant 'Sahara 3771' barley grown under excessive B which coincided with an increase in cell width and cell numbers in the meristematic zone, whereas decrease in the length and no effect on the width of the meristematic zone, decrease in cell numbers, increase in the length and width of individual cells present along the meristematic zone was observed in 'Clipper' a B-intolerant genotype under excessive B supply (Choi *et al*. 2007). In a hydroponic assay of 19 *Brassica rapa* genotypes at B concentrations (15-165 µM) two B tolerant genotypes, 'WWY Sarson' and 'Local' were identified (Kaur *et al*. 2006). Because high levels of B and salt usually co-exist in the field, plant tolerance to these limitations need to exist in combination (Nuttall *et al*. 2006).

The scoring for B toxicity symptoms and shoot dry weight at early stage of growth can be considered as reliable criteria for screening cultivars for tolerance to B toxicity in soils (Torun *et al*. 2003). The genotypic variation in tolerance to B toxicity in a soils containing very high soluble B when studied in 10 Turkish barley cultivars, the barley cultivars 'Hamidiye' and 'Bulbul' were the most sensitive, and 'Anadolu' and 'Tarm-92' were the most tolerant (Torun *et al*. 2003). The differences in tolerance to B toxicity showed a very close relationship to the severity of B toxicity symptoms, but not at all to shoot or leaf concentrations of B (Torun *et al*. 2003). Greenhouse screening of 70 durum wheat (*Triticum durum*) cultivars for their tolerance of B toxicity in soil containing 12 ppm B and treated with 25 mg kg^{-1} soil, showed a large genotypic variation in the severity of leaf symptoms and genotypes 'Sabil-1', Stn "S", 'Aconhi-89' and 'Wadelmez-2' were tolerant to B toxicity and the genotypes 'Lagost-3', 'Dicle-74', 'Brachoua/134 x S-61' and 'Gerbrach' were sensitive (Torun *et al*. 2006). The differential responses of 29 bread wheat and 3 durum wheat cultivars to B toxicity was studied with and without application of 40 mg B l^{-1} where detrimental effect of B on root dry matter production was much higher than on shoot dry matter (45 and 26%, respectively) but the symptom scoring for B tolerance was more reliable than measuring plant B concentration (Kalayci *et al*. 1997). At toxic dose of 6.4 mM B, the root length of the drought-tolerant cultivar 'Gokce' increased without affecting root biomass, but in drought-sensitive cultivar 'Kusmen' both root length and biomass decreased, however, B concentration was higher in 'Kusmen' than in 'Gokce' (Ardc *et al*. 2009b).

The B toxicity tolerance in ICARDA barley and CIMMYT/ICARDA durum and bread wheat international nurseries in soils treated with 50 mg B kg^{-1} soil showed largest variation in barley, while least variation in durum wheat and shoot B concentrations varied widely for the entries with lowest symptom scores in all crop species (Yau *et al*. 1994). In rice modern japonica subspecies such as 'Koshihikari', 'Nipponbare' and 'Sasanishiki' were tolerant, whereas indica subspecies such as 'Kasalath' and 'IR36' were intolerant to excessive application of B, even though their shoot B contents under B toxicity were not different (Ochiai *et al*. 2008). Recombinant inbred lines (RILs) of *japonica* 'Nekken-1' and *indica* 'IR36' were used for quantitative trait locus (QTL) analysis to identify the gene responsible for B toxicity tolerance (Ochiai *et al*. 2008).

The rice cultivars 'Annapurna', 'Kusuma' and 'Deepa' were tolerant to Mo-toxicity at 0.4- 1.6 µM Mo (Rout and Das 2002). Based on root length, shoot length, ratio of root:shoot biomass, and root/shoot tolerance index the Mo-toxicity tolerance of 20 rice cultivars ranked: 'Annapurna' > 'Deepa' > 'Kusuma' > 'Vaghari' > 'Hamsa' > 'Vikram' > 'Bharati' > 'Paridhan-2' > 'Aswathi' > 'Subhadra' > 'Sankar' > 'Sakti' > 'Nilgiri' > 'Rudra' > 'Hema' > 'Pragati' > 'Pusa-2-21' > 'Ratna' > 'Paridhan-1'(Rout and Das 2002).

The seedlings of durum wheat cv. 'Adamello' (drought sensitive) and 'Ofanto' (drought tolerant) when exposed to 10-35 µM Ni in hydroponic culture, the Ni decreased the Chl *a* and *b*, water potential and relative water content in both cultivars, but these decreases were greater in 'Adamello' and despite greater Ni tissue content, 'Ofanto' exhibited better growth and nutritional status compared with 'Adamello' (Pandolfini *et al*. 1996). The antioxidative defence enzymes, GPX, APX, and GR, increased activity in Ni-treated 'Adamello seedlings, but not in 'Ofanto' indicating that the different wheat cultivars may markedly differ in Ni uptake and sensitivity and that a enhanced capacity to counteract Ni stress may be associated with drought resistance (Pandolfini *et al*. 1996). Two Graminaceous species *Secale montanum* and *Dactylis glomerata* with different distribution and coverage on Ni-rich soils of Northwest Iran, when studied for their tolerance to Ni, in hydroponic culture at 100 µM Ni, the shoot and root growth of *D. glomerata* was inhibited up to 42 and 69%, respectively, while in *S. montanum* the growth reduction was as low as 20% in shoot but not in root, however the two species showed similar accumulation potential for Ni (Hajiboland 2007).

Differential uptake and transport of minerals

The mineral toxicity tolerance is attributed to their lower content and accumulated in various tissues and high yield in toxic soils. The B tolerance could be attributed to the lower B content of seed and lower uptake or accumulation of B in the root and shoot. In cereal crops low accumulation of B in the shoot or grain is correlated with the maintenance of biomass production and grain yield under high B conditions, suggesting that this trait is an important component of field tolerance. The high B tolerant bread wheat (*Triticum aestivum* L.) and durum wheat subsp. *durum* Husn.) accessions showed low B accumulation (Schnurbusch *et al*. 2008). Five barley and 6 wheat cultivars displaying a broad range of tolerance to B toxicity when grown in nutrient solution at adequate to toxic B levels, the tolerant cultivars developed fewer symptoms, grew better and absorbed less B than sensitive cultivars, but B supply had no effects on the tissue composition of K, S, Mg, P, Ca, Cu, Zn, Mn and Fe, which were normal and adequate for maximum growth, nor was any interaction between B and these nutrients involved in differences in B tolerance between cultivars (Nable 1989). In a filter-paper bioassay method, the differential response of 23 barley genotypes to B toxicity at 100 ppm B indicated a great variation among barley genotypes where B-tolerant genotypes with longer roots had lower B contents in their seed, root and shoot (Rehman *et al*. 2006). The most tolerant and sensitive genotypes of *B. rapa* were assessed for shoot B concentrations in a soil with 4, 29 and 54 ppm B where shoot B uptake and concentrations were 3 and 10 times lower, respectively in the tolerant than sensitive genotypes, indicating that B tolerance involved B exclusion from the shoot (Kaur *et al*. 2006). However, Torun *et al* (2006) in a study of 70 durum wheat genotypes demonstrated that the B exclusion mechanism is not involved in the differential expression of B tolerance in wheat as the most B sensitive durum wheat genotypes had generally much lower amount of B in shoots than the genotypes showing greater tolerance of B-toxicity. The shoot dry matter in B toxic soil can be a consistent parameter for considering barley and fababean varieties for tolerance to B toxicity (Choi *et al*. 2006).

Growth and yield of bell pepper (*Capsicum annuum* L.) at different B and salinity levels and the results from the experiments and from published data for wheat, tomato and chickpea indicated an antagonistic relationship for excess B and salinity (Yermiyahu *et al*. 2008). Thus, toxic effects on growth and yield were less severe for combined B toxicity and salinity than what would be expected if effects of the individual factors were additive. Though the mechanism of relationships between B and salinity in plants is not clear, the possible explanations are reduced uptake of B in the presence of Cl and reduced uptake of Cl in the presence of B (Yermiyahu *et al*. 2008).

To avoid deficiency and toxicity problems, the plants maintain their tissue B concentrations within an optimum range by regulating transport processes. Miwa and Fujiwara (2010) in a recent study identified transporters important for tolerating high B levels in the environment which export B from roots back to the soil and two types of transporters are involved in these processes: NIPs (nodulin-26-like intrinsic proteins), boric acid channels, and BORs, B exporters. The expression of genes encoding these transporters is finely regulated in response to B availability in the environment to ensure tissue B homeostasis. Furthermore, plants tolerant to stress produced by low B or high B in the environment can be generated through altered expression of these transporters.

The root-to-shoot transfer, localization, and chemical speciation of Co were investigated in a wheat and tomato plant in nutrient solution at low (5 µM) and high (20 µM) Co(II) concentrations. Although the root-to-shoot transport was higher for tomato plants exposed to excess Co, both plants appeared as excluders. The oxidation state of Co(II) was not transformed by either plant in the roots or shoots and Co appeared to be present as Co(II) in a complex with carboxylate containing organic acids. Co was also essentially located in the vascular system of both plant species indicating that neither responded to Co toxicity via sequestration in epidermal or trichome tissues as has been observed for other metals in metal hyperaccumulating plants (Collins *et al*. 2010). The influence of Co (1.2 mg l^{-1} Co) in Fe uptake and the Fe-stress response mechanism was studied in Fe-efficient and Fe-inefficient plants of tomato ('T3238' fer+ and 'T3238' fer, respectively) and soybeans ('A6' and 'T203', respectively) in nutrient solutions where Co decreased Chl and leaf Fe and increased leaf and root Co in all cultivars, however, Co effects on root Fe varied among cultivars (Blaylock *et al*. 1985). In presence of Co, the Fe-inefficient cultivars were most susceptible to chlorosis and exhibited true Fe-deficiency, but Fe-efficient cultivars showed a combination of Fe-deficiency and Co-toxicity (Blaylock *et al*. 1985). In Fe-efficient cultivars, due to Co toxicity the Fe uptake was limiting Chl formation as reductant and proton excretion from roots of Fe-efficient cultivars did not occur. However, the Fe-stress response mechanism was not observed in Fe-inefficient cultivars regardless of Co level (Blaylock *et al*. 1985).

A level of 806 mg Mo kg^{-1} was recorded in leaves without adverse effects on plant growth or appearance indicating that Mo toxicity is not a real threat in *poinsettia* production (Hammer and Bailey 1987).

In a study, Ni toxicity (85 µM Ni) in mycorrhizal birch seedlings infected with *Scleroderma flavidum*, a fungus

known to increase Ni tolerance, reduced photosynthetic rates, but increased Ni tolerance in the host not by preventing Ni-induced reductions in photosynthetic rates or by affecting shoot respiration rates, but by high P content in the roots of *S. flavidum*-infected seedlings could be correlated with potential Ni-binding sites, allowing the Ni to be detoxified (Jones and Hutchinson 1988b).

Plant tolerance to Ni toxicity was related to low influx of Ni and its transport from roots to shoots of Ni in four species white clover (*Trifolium repens*) cv. 'California Ladino', cabbage (*Brassica oleracea* var. *capitata* L.) cv. 'Early Jersey Wakefield', ryegrass cv. 'Linn' and maize cv. 'Early Sunglow' (Yang *et al*. 1996a). The white clover had high DM at high Ni levels because of its low influx and transport from roots to shoots of Ni, and at <60 μM, Ni maize had high DM because of its low transport from roots to shoots even though it had high influx of Ni and both showed tolerance. Ryegrass was sensitive to Ni-toxicity because of its high influx and transport of Ni from roots to shoots. The sensitivity of cabbage (var. 'capitata') to Ni toxicity was correlated with high transport from roots to shoots even though it had low influx of Ni (Yang *et al*. 1996a). Ni accumulation in shoots was relatively high for cabbage and low for maize showing about 60-fold less Ni in shoots than cabbage and about 10-fold less than ryegrass at <120 μM Ni (Yang *et al*. 1996a). Further study demonstrated that plant tolerance to Ni toxicity was associated with the influence of Ni on influx into roots and transport from roots to shoots of Cu, Fe and Mn in white clover and cabbage but not in maize and ryegrass (Yang *et al*. 1996b). Excess Ni (>30 μM) decreased both influx and transport from roots to shoots of Zn, Cu, Ca and Mg, but only transport of Fe and Mn from roots to shoots in white clover; decreased both influx and transport from roots to shoots of Cu, Fe, Mn, Mg and S, but increased P in cabbage; decreased transport from roots to shoots of Cu, Fe, Mn, Ca, and Mg, but influx of these elements except Mg was not affected in ryegrass, however the influx and transport of P and S increased in ryegrass with increasing external Ni levels (Yang *et al*. 1996b). Nickel inhibited influx of Cu, Ca and Mg, and transport of Zn, Cu, Fe, Mn, Ca and Mg from roots to shoots in maize (Yang *et al*. 1996b).

Maize belongs to excluder plants as their root systems function as a barrier limiting heavy metal intake by aboveground organs, also the pattern of Ni transport differs from that of Cd and Pb, including an arrest of root branching (Seregin *et al*. 2003). Deposition of an iron oxide plaque or coating on roots of rice cv. 'M-201 84 Biggs' ameliorated the toxic effects of Cu, Ni and Cu + Ni on plant growth and affected patterns of metal uptake and accumulation (Greipsson and Crowder 1992). Plaque was formed on plants during 24 h in an anaerobic solution at pH 5.5, subsequently 2 additional coatings were deposited after new growth of roots, the Cu, Ni and Fe were concentrated in plaque and in roots and lower concentrations of Cu and Ni were found in leaves of plants with a plaque than in plants without plaque (Greipsson and Crowder 1992). The leaf rosettes of chamomile accumulated 174.1 μg Ni g^{-1} at 120 μM Ni treatment and roots contained 3.4, 7.3 and 6.1 times more Ni than leaf rosettes at 3, 60 and 120 μM Ni treatments, respectively indicating that chamomile is a Ni excluder. The results suggest chamomile tolerance to Ni excess and its considerable accumulation in above-ground biomass (*ca*. 30% of whole plant Ni content) (Kováčik *et al*. 2009).

Metabolites

The adaptation of barley plants to B toxicity and tolerance mechanisms was investigated using a metabolomics approach by comparing metabolite profiles in root and leaf tissues of an intolerant commercial cultivar (cv. 'Clipper') and a B tolerant Algerian landrace (cv. 'Sahara') where exposure to elevated B (200 and 1000 μM), the number and amplitude of metabolite changes in roots were greater in 'Clipper' than in 'Sahara'. In contrast, leaf metabolites of both cultivars only responded at 1000 μM at which B toxicity symptoms were visible (Roessner *et al*. 2006). This study provided insights into metabolic differences of two genetically distinct barley cultivars and information about how they respond metabolically to increase B levels (Roessner *et al*. 2006). The metabolite levels were dramatically altered in the tips of leaves of the sensitive cultivar 'Clipper' grown at 1000 μM B compared to those of 'Sahara', which correlates with a gradual accumulation of B from leaf base to tip in B-intolerant cultivars (Roessner *et al*. 2006). Overall, there were always greater differences between tissue types (roots and leaves) than between the two cultivars.

Certain proteins may be related to genotype tolerance to salt and B toxicity. In a salt-tolerant 'Manak' and salt-sensitive 'ICPL 88039' pigeon pea genotypes, the B and NaCl (S) stress alone and in combination with each other at the seedling stage had deleterious effects on shoot growth, the S+B being the most deleterious. The protein profiles of these stress-treated seedlings showed a new 28.3 kDa protein band specific to B in 'Manak' present in B, B+Ca, S+B and S+B+Ca treatments, another 75.8 kDa protein was present in control and Ca treatments but was absent in the stress treatments, however, a 95.6 kDa protein band disappeared in specific response to B treatments (Bishnoi *et al*. 2006). In shoot of 'ICPL 88039', 67.2 and 54.3 kDa proteins were present in all the treatments but were absent in B-, B+Ca-, S+B- and S+B+Ca-treated seedlings and another 34.9 kDa protein was absent whenever S and B treatment was given either alone or in combination (Bishnoi *et al*. 2006). However, alleviatory effects of Ca did not lead to the formation of any new polypeptides.

Boron toxicity enhances the reactive oxygen species in plant tissues, however, as to how B-toxicity affects the plant antioxidant defence system is not clear. This aspect was studied in tomato cultivars 'Kosaco' and 'Josefina' where high B caused oxidative damage in leaves and increased antioxidant enzyme activities particularly ascorbate pool size, L-galactose dehydrogenase enzyme involved in ascorbate biosynthesis, and the activity of enzymes of the Halliwell-Asada cycle (Cervilla *et al*. 2007). The B-toxicity diminished growth and boosted the amount of B, MDA and H_2O_2 in tomato leaves with the trends being more pronounced in cv. 'Josefina' than in 'Kosaco', increased ascorbate concentration in both cultivars and increased glutathione only in 'Kosaco' and also induced activities of antioxidant- and ascorbate-metabolizing enzymes providing a better understanding of the role of ascorbate in the plant response against B stress (Cervilla *et al*. 2007). The ascorbic acid content, and activities of APX, CAT, GR, POD and SOD activities decreased above 0.3 mM B level and this decline in enzyme activity was, in general, greater in the salt sensitive 'HD 2329' than in the salt tolerant 'KRL 1-4' cultivar of wheat. Application of Ca (20 mM $CaCl_2$) caused a partial reversal of the decline in the activity of these enzymes with greater efficacy of alleviation in the salt sensitive cultivar than in the salt tolerant cultivar (Rani *et al*. 2008).

The oxidative stress and the antioxidant response to B in chickpea cultivars differing in their tolerance to drought when investigated the 'Gokce' was tolerant and 'Kusmen' was sensitive to B toxicity, and the tolerance of 'Gokce' was closely related to increased capacity of the antioxidative system (total SOD, CAT and APX) to scavenge reactive oxygen species in the shoot and thus suppress lipid peroxidation under B stress (Ardc *et al*. 2009a). Further increases in total SOD activity were observed in shoots of both cultivars of chickpea due to excess B and shoot extracts exhibited five activity bands, two of which were identified as MnSOD and Cu/ZnSOD. GR activity decreased, while activities of CAT, POX and APX did not change with 6.4 mM B in 'Kusmen'. On the other hand, activities of CAT, APX and SOD increased in 'Gokce' at both B levels. In addition, lipid peroxidation was higher in 'Kusmen' than in 'Gokce', indicating more damage by B to membrane lipids in the former cultivar (Ardc *et al*. 2009a). In another

study differences in the antioxidant systems of the roots of two chickpea (*Cicer arietinum* L.) cultivars differing in tolerance to drought were observed under B toxic conditions (Ardc *et al*. 2009b). There was increase in roots SOD and POX activities due to B toxicity and the root extracts exhibited three SOD and three POX activity bands in both cultivars. The CAT and GR activities in 'Gokce' increased, but Lipid peroxidation did not change suggesting that roots of 'Gokce' are better protected from B-stress-induced oxidative stress due to enhanced SOD, CAT and POX activities under high B levels, however the CAT and GR activities decreased and lipid peroxidation levels increased in 'Kusmen', indicating more damage to membrane lipids due to B toxicity (Ardc *et al*. 2009b).

Nickel toxicity induces oxidative damage in maize roots as part of the overall expression of Ni toxicity in roots of *Z. mays* and that enhanced lipid peroxidation could be a consequence of primary effects of Ni stress (Baccouch *et al*. 2001). Proline appears to act as a protectant of the enzyme RNase against Ni and PEG-induced damages (Maheshwari and Dubey 2007). Two Graminaceous species from Ni-rich soil when grown at 100 µM Ni a higher endogenous and Ni-induced malate accumulation did not cause a higher tolerance to Ni in *Dactylis glomerata*, in contrast, high endogenous and Ni-induced accumulation of cysteine particularly in shoot was observed in Ni tolerant *Secale montana* (Hajiboland 2007).

In order to explore the possible physiological mechanisms of Ca involved in improving adaptation to Ni stress in plants, the effects of external calcium (Ca^{2+}) when investigated by Hu *et al*. (2007) under 0.1 mM Ni treatment, the activities of SOD, CAT and APX and H_2O_2 and MDA in rice leaf tissues decreased, while the activity of POD was enhanced indicating oxidative damage and membrane peroxidation in Ni-treated leaf tissues and external Ca at 10 mM promoted the activities of SOD, CAT, APX and POD, but reduced considerably H_2O_2 and MDA contents and permeability of cell membrane in leaf tissues during the stress period. It was suggested that one of the mechanisms that external Ca enhanced the tolerance to Ni toxicity in rice seedlings was mediated by improving scavenging of active oxygen species and maintaining the integrity of cell membrane under Ni stress (Hu *et al*. 2007). Influence of excess Ni on selected physiological aspects of metabolism when studied in chamomile (*Matricaria chamomilla*), a Ni excluder, high Ni doses elevated root-soluble proteins stimulated accumulation of soluble phenolics in both the rosettes and roots, and hydrogen peroxide in the roots, proline content increased more pronouncedly in the rosettes, histidine was elevated in the roots, suggesting its involvement in Ni retention (Kováčik *et al*. 2009).

Indigenous species and accumulators

High soil B constitutes a major soil problem in many parts of the world, particularly in low-rainfall areas and land under irrigation. In a B-deficient calcareous soils the sunflower genotypes 'S-288' and 'TR-4098' yielded 4.17 and 3.28 t ha^{-1}, respectively at 0 kg B ha^{-1} as against 3.75 and 3.23 t ha^{-1} in the 'AS-615' and 'Coban' genotype, respectively at 7.5 kg B ha^{-1}, hence, 'S-288' and 'TR-4098' can be indicator genotypes for B-toxicity (Ceyhan *et al*. 2008). The accumulation of Fe, Mn, Cu and Zn and heavy metals (Ni, Co, Cr and Cd), their uptake pattern and translocation in wheat, Indian mustard (*Brassica juncea*), cabbage and cauliflower (*Brassica oleracea* var. *botrytis* L.) in fields receiving industrial effluents and sewage sludge showed different pattern of accumulation of all the elements as far as the plant parts are concerned and wheat can, to some extent, tolerate the excess limits of heavy metals and therefore can be treated as an accumulator plant (Dube *et al*. 2004). In *Cannabis sativa* grown in soils, containing 74 and 115 ppm Ni, Ni uptake was limited if compared with that of the Ni-hyperaccumulator *Alyssum murale* (Citterio *et al*. 2003).

Plants growing on serpentine soils are usually Ni-tolerant species. A study have shown that *Cunonia macrophylla*, an endemic species common on Ni-rich soils in New Caledonia, is a Ni-tolerant species that accumulates Ni without any impairment of growth up to 500 mg Ni l^{-1} (Leon *et al.* 2006). In greenhouse plants watered with solutions containing Ni chloride 5-1000 mg Ni l^{-1} for 15 months reveals that *C. macrophylla* plants grown with 5- 100 mg Ni l^{-1} had more leaves, and there was greater stem thickness and fresh shoot biomass and higher Mn, Cu and Zn concentrations at 50 mg Ni l^{-1}, however 1000 mg l^{-1} Ni induced Ni toxicity, and lower concentration of K in the shoots and roots of plants (Leon *et al.* 2006). The Ni concentrations in the plant increased with the level of Ni applied, and the Ni gradient decreased from roots to stem and from stem to leaves, but Ca and Fe levels were lower in roots exposed to higher concentrations of Ni (Leon *et al.* 2006). In the serpentine area in Hokkaido, 46 taxa of serpentine plant species were recognized, and 44 of them were endemic to Hokkaido. The P concentration in the serpentine plants was lower, while K, Ca and N concentrations were higher, than those in nonserpentine plants (Mizuno *et al*. 2009). The Ni concentration of the serpentine plants increased proportionally to that of the exchangeable Ni concentration in the soil up to 10 mg kg^{-1} soil, but did not increase further and a nonserpentine plant, *Thlaspi japonicum*, was recognized for its extraordinary Ni accumulation (1300 mg kg^{-1} on average), indicating that this plant is the first Ni-hyperaccumulator identified in Japan (Mizuno *et al*. 2009).

Alyssum bracteatum is the first Ni hyperaccumulator reported from serpentine soils of western Iran however tolerance to Co of serpentine population was significantly greater than the Co tolerance of this species from the nonserpentine population (Ghaderian *et al*. 2009). The uptake and accumulation of Co by a serpentine and a non-serpentine population of *A. bracteatum* when tested at various Co levels (0, 2, 5, 10, 15 and 30 mg Co l^{-1}) in solution culture (perlite), the concentration of Co in both populations of A. *bracteatum* increased with increasing Co in solution culture, but amounts of Co in the shoots of non-serpentine plants were significantly less than those in serpentine plants (Ghaderian *et al*. 2009). Plants of the serpentine population contained as much as 1830 µg Co g^{-1} dry weight when grown in 15 mg Co l^{-1} conditions, showing that this species is capable of hyperaccumulating Co under solution culture conditions (Ghaderian *et al*. 2009).

Chen *et al*. (2009) briefly reviewed the advances in Ni toxicity research over the past 20 years and summarised that interference with other essential metal ions and induction of oxidative stress are the two indirect pathways of Ni toxicity in plants. Further research needed on the hyperaccumulators plant species that are capable of accumulating high Ni concentration which can provide model systems to study the mechanisms of Ni tolerance and can also be used for phytoremediation by removing Ni from polluted environment (Chen *et al*. 2009).

Compartmentation and complexing within the cell

The plant tolerance of these elements could also be achieved if these elements were sequestered away in places within the cell where these elements cannot react with metabolically active cellular substances. Compartmentation in the vacuole is the most probable site. The B tolerance mechanism is associated with a complex control of sucrose levels between leaf and root tip that assist in maintaining root growth under B-toxicity (Choi *et al*. 2007). Excessive B concentrations led to a lower osmotic potential within the cell sap of the root tip in 'SloopVic' a B-tolerant cultivars, while the opposite was observed in 'Clipper' a sensitive cultivar of barley. Enhanced sugar levels in the root tips of 'SloopVic' were observed between 48 and 96 h after excess B was applied which coincided with an increase in the root elongation rate and 2.7-fold increase in sucrose level within mature leaf tissue, however, a decrease in reducing sugar levels was observed in the root tips of 'Clipper' under

excess B which also coincided with lower root elongation rates and lower sucrose levels in leaf tissues (Choi *et al*. 2007). Under B toxic conditions, as most of the B is accumulated on tips, leaching of B from leaves in wheat and barley by rain had a strong positive effect on growth of both roots and shoots, however concentration of B in guttation droplets indicated small impact of guttation on the alleviation of B toxicity (Reid and Kate 2009).

The crop tolerance to high B has been attributed to reduced uptake of B as a result of B efflux from roots. Salinity interacts with B toxicity by a combined effect on B and water uptake and B partitioning within the plant (Wimmer *et al.* 2001). Salinity usually reduces shoot B concentrations. The whole tissue B concentration is a poor indicator of B tolerance, but the tissue B distribution and subcellular ion compartmentation and B and salinity interactions is important criteria in wheat (Wimmer *et al.* 2001). Under saline conditions, the total B concentration increased in leaf tips, decreased in roots and was not affected in basal leaf parts, however, soluble B concentrations in basal leaf parts increased in the combined salt/high B treatment compared to high B treatment alone in wheat (Wimmer *et al.* 2001). Looking to the complex relations between salinity and B toxicity the interactions of soluble B with salinity was studied on physiological response of plants in tomato plants and several hypotheses are established by (Bastías *et al*. 2010). The increase of aquaporin functionality due to the presence of B and Ca compared with NaCl-treated plants could be the most feasible, whereas there is currently no satisfactory explanation for the results for the cell wall amino acid composition. In addition, the elemental composition results revealed that, in addition the known interactions between B and Ca with respect to cell wall stability, Mg and Mn were also increased in NaCl+B and NaCl+Ca treatments, suggesting their possible involvement in the cell wall function necessary for plant growth (Bastías *et al*. 2010).

The effect of exogenous silicon (Si) in spinach plants when studied, 150 ppm Si supplied to the soil with high B counteracted the deleterious effects of 30 ppm B on root and shoot growth, lowered the severity of B-toxicity and B concentration in the shoots, increased B concentration in the roots, increased the stomatal conductance of the plants which was decreased by B, and brought down concentrations of H_2O_2 and proline increased by B toxicity (Gunes *et al*. 2007a). Boron toxicity increased the membrane permeability, lipid peroxidation and LOX activity and activities of antioxidant, SOD, CAT and APX of spinach and applied Si ameliorated the membrane deterioration and decreased the activities of antioxidant (Gunes *et al*. 2007a).

Ferroportin (FPN) is the iron efflux transporter identified in animals, and there are two closely related orthologs in *Arabidopsis thaliana*, IRON REGULATED1 (IREG1/ FPN1) and IREG2/FPN2. The FPN1 localizes to the plasma membrane and is expressed in the stele, suggesting a role in vascular loading; however, FPN2 localizes to the vacuole and is expressed in the two outermost layers of the root in response to iron deficiency, suggesting a role in buffering metal influx (Morrissey *et al*. 2009). Ferroportins also play a role in Co homeostasis and in study of *Arabidopsis* accessions for ionomic phenotypes showed that truncation of *FPN2* results in elevated shoot Co levels and leads to increased sensitivity to the metal. Conversely, loss of *FPN1* abolishes shoot Co accumulation, even in the Co accumulating mutant *frd3*. Consequently, in the *fpn1 fpn2* double mutant, Co cannot move to the shoot via FPN1 and is not sequestered in the root vacuoles via FPN2; instead, Co likely accumulates in the root cytoplasm causing *fpn1 fpn2* to be even more sensitive to Co than *fpn2* mutants (Morrissey *et al*. 2009).

Using histochemical method of Ni determination, the pattern of Ni distribution when studied in various plant tissues in maize seedlings grown at 15-35 μM $Ni(NO_3)_2$, Ni was found in all root tissues and its content increased with the period of exposure and from the tip to the root base; the Ni penetrated the endodermal barrier and accumulated in the endodermis and pericycle to the highest concentration restricting root branching, however, Ni did not affect the cell length, and root growth inhibition resulted from suppressed cell division (Seregin *et al*. 2003). Distinctive effects of Cd and Ni on membrane function (i.e., Em and membrane permeability) were observed in the short term, the pattern of Em changes caused by Cd and Ni using barley roots and have also followed the effects of both metals in longer term in rice (Sanz *et al*. 2009). It was demonstrated that the distinct effects caused by Cd and Ni are due to differences in cellular responses, triggered when entering the cytoplasm (i.e., an efficient detoxifying mechanism for Cd), more than to different direct effects on membranes (Sanz *et al*. 2009).

The plasma membrane of root cells constitutes the first barrier for the entry of heavy metals but also a target of their toxic action. Addition of Ni^{2+} to the solution bathing the roots induced a concentration-dependent plasma membrane depolarization but the activity of the plasma membrane H^+-ATPase was not inhibited by the presence of Ni^{2+} and the initial resting potential recovered in less than 1 h. In the short term (hours), membrane permeability of root cells was not significantly affected by Ni^{2+} treatments. However, in the long term (days) a drastic loss of K^+ was measured in roots and shoots, which should be responsible for the changes in the water content measured, since stomatal conductance and the transpiration rate remained unaffected by Ni^{2+} treatment. The effects induced by Ni^{2+} were not permanent and could be reverted, at least in part, by transferring the plants to a medium without Ni^{2+} (Llamas *et al*. 2008).

Lignification plays an important role in tolerance to Ni toxicity. The two Graminaceous species from Ni-rich soil when grown at 100 μM Ni and compared, the distribution of Ni among various fractions of plant tissues studied by gel filtration chromatography, suggested an efficient chelation of excess Ni by low molecular weight fraction in *S. montanum* but not in *D. glomerata*, also a higher re-translocation of Ni from mature into growing young leaves was one of the other causes of higher susceptibility of *D. glomerata* to excess Ni (Hajiboland 2007). The activities of POD and CAT was much strongly inhibited in *D. glomerata* than *S. montanum* and activity of PPO was induced in response to Ni toxicity in roots of *S. montanum* indicating its possible role in lignification, for higher Ni tolerance of *S. montanum* (Hajiboland 2007).

Tolerant gene and phytoremediation

Considerable genetic variation in response to high B, Co, Mo and Ni has been identified in a wide range of crop cultivars, most of which share a similar tolerance mechanism – reduced uptake of these in both shoots and roots. However, the tolerance mechanism is under the control of several major additive genes, and specific chromosomal locations were identified for the genes in some species. With the widespread occurrence and importance of B toxicity in dry areas, a considerable amount of progress in identifying B toxicity tolerant genotypes and breeding cultivars with tolerance to B toxicity have been made. The molecular mechanism of B transport allows to develop technology to alleviate B toxicity problems and identification of a boric acid/borate exporter, BOR1, from *Arabidopsis thaliana*, the BOR1 homologs require for B-toxicity tolerance in plant (Takano *et al*. 2008).

Wheat varieties show differential responses to high concentrations of soil B where, *Bo1*, a single major gene is responsible for the higher level of B tolerance in the varieties historically dominant in southern Australia (Moody *et al*. 1993). The genetic control of tolerance of wheat to high soil B when studied in 5 genotypes, the B tolerance was expressed as a partially dominant character, although the response of F1 hybrids varied with the level of B applied (Paull *et al*. 1991). The F_1 hybrids responded similarly to the more tolerant parent at low B treatments and interme-

diate to the parents at higher B treatments. Ratios consistent with monogenic segregation were observed for the F_2 and F_3 generations for the combinations (WI*MMC) x Kenya Farmer, Warigal x (WI*MMC) and Halberd x Warigal. The genetic variation with respect to B tolerance, among these 4 genotypes, could be accounted for by 3 genes, *Bo1, Bo2* and *Bo3*, while transgressive segregation between 2 tolerant genotypes, 'G61450' and 'Halberd', suggested a fourth locus controlling tolerance of B (Paull *et al*. 1991).

Tolerance to B-toxicity in cereals is associated with reduced tissue accumulation of B. *Bot1*, a BOR1 ortholog, is the gene responsible for the superior B-toxicity tolerance of the Algerian barley landrace 'Sahara 3771' (Sutton *et al*. 2007). The high-resolution mapping show that *Bot1* is located at the tolerance locus and compared to intolerant genotypes, 'Sahara' contains about four times as many *Bot1* gene copies, produces substantially more Bot1 transcript, and encodes a Bot1 protein with a higher capacity to provide tolerance in yeast (Sutton *et al*. 2007). Bot1 transcript levels identified in barley tissues are consistent with a role in limiting the net entry of B into the root and in the disposal of B from leaves via hydathode guttation (Sutton *et al*. 2007). Genes from roots of B-tolerant cultivars of wheat and barley, with high similarities to previously reported B-efflux transporters from *Arabidopsis* and rice, were cloned the expression of these genes was strongly correlated with the ability of tolerant genotypes to lower the concentration of B in roots (Reid 2007). The gene from barley is located to chromosome 4 and backcross lines containing a B tolerance locus on chromosome 4 showed tolerance in proportion to the level of expression of the transporter gene, whereas those lacking the locus were sensitive to B and had very low levels of gene expression consistently with a widespread mechanism of tolerance to high B based on efflux of B from root cells (Reid 2007).

Toxicity due to high levels of soil B represents a significant limitation to cereal production in a considerable area of some regions and the *Bo1* gene provides a major source of B toxicity tolerance in bread wheat. In the 16 gene fragments totalling 19.6 kb, SNPs were observed between the two cultivars 'Cranbrook' and 'Halberd' at a low frequency (one every 613 bp) these SNPs were distributed unevenly, being limited to only two genes (Schnurbusch *et al*. 2007). In contrast, RFLP provided a much greater number of genetic markers, with every tested gene identifying polymorphism. *Bo1* previously known only as a QTL was located as a discrete Mendelian locus. The markers and rice colinearity represent tools that will assist B tolerance breeding and the positional cloning of *Bo1* (Schnurbusch *et al*. 2007). Mapping of high B tolerance in the durum wheat population 'AUS14010/Yallaroi' revealed a locus possibly allelic to *Bo1*, a major source of B toxicity tolerance identified in bread wheat. Three bread wheat accessions had tolerance that was independent of *Bo1* and is probably located on chromosome 4A (Schnurbusch *et al*. 2008). Recently, Schnurbusch *et al.* (2010) identified the second B toxicity tolerance gene in barley, describe the cloning of a gene from barley, underlying the chromosome 6H B toxicity tolerance quantitative trait locus. Previously identified gene, *Bot1* functions as an efflux transporter in B toxicity-tolerant barley to move B out of the plant. The gene identified by Schnurbusch *et al.* (2010) encodes HvNIP2;1, an aquaporin from the nodulin-26-like intrinsic protein (NIP) subfamily that was recently described as a silicon influx transporter in barley and rice (*Oryza sativa*). The tolerance to high soil B is mediated by reduced expression of HvNIP2;1 to limit B uptake, as well as by increased expression of *Bot1* to remove B from roots and sensitive tissues. Together with Bot1, the multifunctional aquaporin HvNIP2;1 is an important determinant of B toxicity tolerance in barley (Schnurbusch *et al.* 2010).

Seven independent transgenic *Arabidopsis thaliana* lines producing the BOR4-green fluorescent protein (GFP) fusion were generated under the control of Cauliflower mosaic virus 35S RNA promoter. The 10 mM boric acid was lethal to wild-type plants, but much more vigorous root and shoot growth was observed in all the homozygous Pro35S-BOR4-GFP transgenic lines grown on solid medium containing 10 mM boric acid. Accumulation of BOR4-GFP and tolerance of B were positively correlated and the overproduction of BOR4-GFP improved growth under B toxicity through B efflux (Miwa *et al*. 2007).

DNA microarrays, being high-density and high-throughput, allow quantitative analyses of thousands of genes and their expression patterns in parallel. In a study, Oz *et al.* (2009) used Barley1 GeneChip to investigate transcriptome changes associated with B toxicity in a sensitive barley cultivar (cv. 'Hamidiye') and reported global expression analysis of barley seedlings under B toxicity using DNA microarrays from total RNA of leaf tissues (Oz *et al*. 2009). Among the 22,840 transcripts-each represented with a probe set on the GeneChip - 19,424 probe sets showed intensity values greater than 20th percentile in at least one of the hybridizations. Compared to control, 5 mM $B(OH)_3$ (boric acid) treatment resulted in differential expression of 168 genes at least by two fold. Moreover, 10 mM boric acid resulted in at least two fold induction or reduction in expression of 312 transcripts. Among these genes, 37 and 61 exhibited altered levels of expression under 5 and 10 mM boric acid treatments, respectively. Differentially expressed genes were characterized using expression-based clustering and HarvEST:Barley and expression profiles revealed that B toxicity results in global changes in the barley transcriptome and networks of signaling or molecular responses. A noticeable feature of response to B was that it is highly interconnected with responses to various environmental stresses. Additionally, induction of jasmonic acid related genes was found to be an important late response to B toxicity. Determination of responsive genes will shed light on successive studies aiming to elucidate molecular mechanism of B toxicity or tolerance (Oz *et al*. 2009).

Reid and Kate (2009) showed that the expression of genes encoding B efflux transporters in leaves of wheat and barley is associated with an ability of leaf tissues to withstand higher concentrations of B and in tolerant cultivars, necrosis in leaves occurred at B concentrations more than 2-fold higher than in sensitive cultivars. It was hypothesized that this leaf tolerance is achieved via redistribution of B by efflux transporters from sensitive symplastic compartments into the leaf apoplast and B concentrations in leaf protoplasts, and of B released through infiltration of leaves, support this hypothesis (Reid and Kate 2009). The identification of B transporter indicated that B transport is a process mediated not only by passive diffusion but also by transporters whose activity was regulated in response to B conditions. Recent studies have shown that plants sense internal and external B conditions and regulate B transport by modulating the expression and/or accumulation of these transporters and as the results obtained in model plants are applicable to other plant species, such knowledge may be useful in designing plants or crops tolerant to soils containing low or high B (Miwa and Fujiwara 2010).

MITIGATION OF MINERAL ELEMENT TOXICITIES

Soil amendments

Ameliorating toxic soils containing high B, Co, Mo and Ni is extremely difficult. If feasible, extensive leaching could be adopted using low mineral containing water. On long term, use of soil amendments, tolerant plant genotypes and phytoextraction and phytoremediation using accumulator plant species are the major solution. Soil amendments with lime, gypsum and the planting of plant genotypes that are tolerant of high external B concentrations ameliorate B toxicity (Nable *et al.* 1997).

Dry ploughing, low-B surface water and use of tolerant varieties provided the best means of making B-toxic soils more productive for rice in IRRI farm (Cayton 1985). The $ZnSO_4$ decreased B toxicity in the cotton leaves and apply-

ing micronutrients increased quality and yield of cotton in Varamin (Rezaei and Malakouti 2001). Increasing levels of Si in soil counteracted the deleterious effects of toxic B on barley shoot growth. Application of 20 mg kg^{-1} B, a toxic dose, increased the B and H_2O_2 concentration in barley plants, but, Si application (50-100 mg kg^{-1}) decreased B and H_2O_2 concentrations and increased the Si concentration in barley plants (Inal *et al*. 2009). Application of Si alleviated B-toxicity by preventing oxidative membrane damage and also translocation of B from root to shoots in spinach and wheat (Gunes *et al*. 2007a, 2007c) and soil to plant in wheat (Gunes *et al*. 2007c). In another study the Si alleviated sodicity and B-toxicity in spinach and tomato plants grown in sodic-B toxic soil by preventing both oxidative membrane damage and also translocation of Na, Cl and B from root to shoots and soil to plant, and lowering the phytotoxic effects of Na, Cl and B within plant tissues (Gunes *et al*. 2007b). The Si applied to the sodic-B toxic soil at 2.5 and 5.0 mM increased the Si concentration in the spinach and tomato and counteracted the deleterious effects of high concentrations of Na, Cl and B on root and shoot growth by lowering the accumulation of these elements in the plants (Gunes *et al*. 2007b). Thus Si improved the salt and B tolerance of spinach and tomato in naturally sodic-B toxic soil, which describes membrane-related parameters and antioxidant responses (Gunes *et al*. 2007b). Application of 5.0 and 10.0 mM Si to the B toxic soil increased Si concentration of the wheat and counteracted the deleterious effects of B on shoot growth (Gunes *et al*. 2007c). Spinach is a plant that is naturally reasonably resistant to combined salinity and B toxicity, and exogenous Si application increases stress tolerance by the enhancement of antioxidant mechanisms that reduce membrane damage, however exogenous salicylic acid (SA) application has a less effect in Spinach (Eraslan *et al*. 2008).

Table grape production is popular in arid and semiarid regions of Israel where salinity and excess B are prevalent and recycled wastewater is often saline and contains high B. The potential of this wastewater for irrigation in grapevines were tested in the Jordan Valley of Israel, in a vines grafted on 'Ramsey' rootstock irrigated at two salinity levels (1.3 or 2.7 dS m^{-1}) combined with four concentrations of B (0.03, 0.12, 0.21 or 0.31 mM) and study reveals that exposure to increasing root-zone B led to severe B toxicity, increased B accumulation in the leaves and decreased woody vegetative production, without influencing annual production of biomass and fruit yield, however, higher salinity (EC=2.7 dS m^{-1}) reduced the levels of B accumulated in leaves and decreased the annual pruning biomass, but did not influence fruit production (Yermiyahu *et al*. 2007). In pigeon pea, the B and NaCl (S) stresses at the seedling stage, alone and in combination with each other, had deleterious effects on shoot growth, the S+B being the most deleterious but Ca alleviated the adverse effects (Bishnoi *et al*. 2006).

On a calcareous soil with high levels of B, application of Zn reduced the adverse effects of B-toxicity and increased yield (Hosseini *et al*. 2005). In a greenhouse 4.0 ppm B caused toxicity while addition of P (80 ppm) alleviated B toxicity in maize. The 10-20 ppm B in soil was toxic in tomato cv. 'Lale' which were partially alleviated with application of Zn (Gunes *et al.* 1999). Increased levels of B, in tomato, decreased biomass and increased the concentrations of B in plant tissues; however, Zn treatments reduced the inhibitory effect of B on growth (Gunes *et al.* 1999). In bean plants Zn at 20 mg kg^{-1} supplied to soil counteracted the deleterious effects of 20 mg kg^{-1} B on root and shoot growth alleviates B toxicity of bean by preventing oxidative membrane damage (Gunes *et al*. 2009). The impact of exogenous SA (0.5 mM) on the growth, physiology and antioxidant activity of carrot (*Daucus carota* L. cv. 'Nantes') grown under combined stress of salinity (NaCl and Na_2SO_4), and B toxicity (25 ppm B) when assessed the diameter of the storage root increased by Na_2SO_4 salinity under B toxicity and SA application regulated proline and toxic ion (B, Cl) accumulation in the storage root and shoot (Eraslan *et al*. 2007b). However, in long term the SA was not as effective as in alleviating abiotic stress reported in the literature with short-term studies (Eraslan *et al*. 2007b).

Hydrogen sulfide (H_2S) is emerging as a potential messenger molecule involved in modulation of physiological processes in plants. In a study root elongation was significantly inhibited by exposure of cucumber (*Cucumis sativus*) seedlings to 5 mM B, and this inhibitory effect was substantially alleviated by treatment with H_2S donor sodium hydrosulfide (NaHS) (Wang *et al.* 2010). There was an increase in the activity of pectin methylesterase (PME) and up-regulated expression of genes encoding PME (CsPME) and expansin (CsExp) on exposure to high B concentration which were markedly reduced in the presence of H_2S donor (Wang *et al.* 2010). The increases in activities of PME and expansin may underlie the inhibition of root elongation by toxic B, and that H_2S plays an ameliorative role in protection of plants from B toxicity by counteracting B-induced up-regulation of cell wall-associated proteins of PME and expansin (Wang *et al.* 2010).

In soil with more than 40 ppm Co, the Co uptake by plants can be reduced by liming the soil and by incorporating, peat moss, compost or manure into the soil (MOEE 1996). Amelioration of Co toxicity is best with removal or discontinuation of Co sources. In new fruits developed after the discontinuation of the Co supply appeared green and normal, but were few in number (Chatterjee and Chatterjee 2005). Brenchley (2008) reported that composting of loam with peat usually, but not invariably, resulted in a reduction of Mo toxicity however, different results obtained with several crops on a variety of soils failed to show a definite clue to the factors determining the relative toxicity of Mo to plant growth. The addition of sulphate decreased Mo uptake by oilseed rape (McGrath *et al*. 2010).

Nickel toxicity on soil derived from ultrabasic rocks of New South Wales was observed in subterranean clover, Lucerne and oats and clover and lucerne responded to applications of $CaCO_3$, with greater response by lucerne (Anderson *et al.* 1973). Exogenous application of SA alleviated Ni toxicity of plants and decreased the reduction in dry weight, Chl and β-carotene contents, and net photosynthetic rate of the Ni-stressed maize H_2O_2 (Wang *et al*. 2009). Superoxide anion (O_2^-) generation rate, H_2O_2 and MDA contents, and LOX activity significantly increased in the chloroplasts of maize exposed to Ni stress, revealing an oxidative damage occurred in maize chloroplasts, whereas, the values of these parameters were markedly lowered in the SA-treated plants under Ni stress. Application of SA significantly enhanced the activities of SOD, APX, monodehydroascorbate reductase (MDHAR, EC 1.6.5.4), dehydroascorbate reductase (DHAR, EC 1.8.5.1) and GR, and the poll of reduced ascorbate and glutathione in chloroplasts of the Ni-stressed maize. Accordingly, the fact that SA upregulates the capacity of antioxidant defense system in chloroplasts, thus reducing the oxidative damage, is involved in the SA-induced alleviation of Ni toxicity in maize (Wang *et al*. 2009).

Selected bacterial inoculation improved the mycorrhizal benefit in nutrients uptake and in decreasing B and Ni toxicity. These beneficial microorganisms are autochthonous *Brevibacillus brevis* and *Glomus mosseae* which may be used as a tool to enhance plant performance in soil contaminated with Ni (Vivas *et al.* 2006). In clover inoculation with *Rhizobium trifolii*, and combinations of two Ni-adapted indigenous bacterial isolates *B. brevi*s and an arbuscular mycorrhizal (AM) fungus *G. mosseae* in a soil spiked with 11.7, 27.6 and 65.8 mg kg^{-1} Ni reveals that inoculation with the most Ni-tolerant bacterial isolate (*B. brevis*) increased the nodule number that was highly depressed in 11.7 mg kg^{-1} Ni added soil or suppressed in 27.6 and 65.8 mg kg^{-1} Ni supplemented soil, shoot and root biomass at all the three levels of Ni and single colonization of *G. mosseae* enhanced clover dry weight and P-content of the shoots concomitantly with a reduction in Ni in the shoot (Vivas *et al.* 2006). The coinoculation of most Ni-tolerant autochthonous micro-

organisms (*B. brevis* and *G. mosseae*) increased shoot and root plant biomass and substantially reduced the specific absorption rate for Ni thus achieved the highest plant biomass and N and P content and the lowest Ni shoot concentration (Vivas *et al.* 2006). Also there is a report that mycorrhiza infection prevents wheat plants from an excessive concentration and uptake of B (Sonmez *et al*. 2009).

Synthetic chelating agents, such as organic acids and amino acids, are used in remediation of soil contaminated with heavy metals, including Ni. However, it is not clear that the complexation of Ni by organics increases the effectiveness of phytoremediation; the Ni complexation may increase the removable metal concentration, but may decrease its uptake by plants (Molas and Baran 2004). Addition of ion-exchange substrate Biona-312 (2-5%) to nickel (Ni)-polluted soil increased the yield of cherry tomato and cucumber and reduced the Ni content in plant biomass (Matraszek *et al.* 2010). In the presence of Biona the plant yield did not change significantly at 40 mg Ni kg^{-1} of soil, but decreased at 100 mg Ni kg^{-1}. Higher Ni content was observed in the aboveground organs than in roots, but tomato contained more Ni than cucumber (Matraszek *et al.* 2010). Most of the mineral ions can be complexed by organic matter altering their availability to plants as COO^- groups in both solid and dissolved organic matter form stable complexes with metals. The organic matter present in soil forms stable metal-organic matter complexes and, plants are unable to absorb the large metal-complexes with thus decrease their bioavailability.

Use of tolerant and accumulator crop plants

As it is neither practical nor easy to detoxify high mineral containing soils using soil amendments, selecting crops and genotypes with tolerance to these toxicities is the only practical approach to increase yields in these soils. The shift from soil intervention to plant adaptation to solve an intractable crop nutrition constraint is a new paradigm in the agronomic sciences (Yau and Ryan 2008) and the physiological and genetic studies have provided some understanding of genetic variation which have facilitated the breeding of tolerant genotypes for cultivation on high B soils (Nable *et al.* 1997; Yau and Ryan 2008). A review on B toxicity tolerance in crops reveals that in the field, B toxicity usually is more prominent after drought, indicating that both B toxicity and drought tolerance are needed in crops for dry areas having high levels of subsoil B (Yau and Ryan 2008). Plant tolerance to B toxicity has been identified in a range of genotypes and recent research has revealed a physiological mechanism behind this tolerance in cereals. Cultivars with high levels of expression of a gene encoding a B-efflux transporter in roots and shoots have been reported to show tolerance to high B in soils and in solution culture under controlled conditions in glasshouses and growth rooms. However, field trials of tolerant cultivars in rain-fed semiarid environments have been disappointing with few showing even modest improvements in yield, and others showing either no effect or a decrease in yields (Reid 2010).

Amelioration of high B concentrations in soils is expensive and not always feasible, so breeding for B tolerance is the most viable alternative. Emebiri *et al* (2009) reported the marker-assisted (MAS) transfer of favourable alleles from an unadapted six-rowed barley (*Hordeum vulgare* L.) variety, 'Sahara 3771', into two-rowed lines adapted to southern Australia and using a combination of molecular and conventional assays to unequivocally classified the 40 BC6F1-derived DH lines as B tolerant or sensitive, and results showed modest improvements in grain yield of lines carrying B tolerance genes at some B toxic environments without affecting the malting quality profile was not adversely affected through the introgression of the B tolerance allele from 'Sahara 3771', allowing the newly developed material to be used by breeding programs without risk of a penalty on malt quality (Emebiri *et al*. 2009).

Using the perspective of full scale application of phytoremediation techniques, research is focusing on the optimization of agronomic practices. The Jerusalem artichoke, maize, *Sida hermaphrodita*, amaranth (*Amaranthus hypochondriacus*) and industrial hemp are the species capable of taking up harmful elements and producing high yields and with increasing concentration of heavy metals in the soil their uptake by plants increased successively and depended on the plant species (Antonkiewicz and Jasiewicz 2002). Two annual high biomass yielding crops, *Sorghum bicolor* and *Helianthus annuus*, when grown in a polymetallic soil with As 309, Cd 4.29, Co 51, Cu 1527 and Zn 980 ppm in soil, the mineral fertilization and organic amendment increased the biomass yield, but did not heighten the concentration of metals in the harvestable tissue of the plants during the crop cycle, however, these crops showed high removal of metal making them good potential for phytoremediation (Marchiol *et al*. 2007). A number of wheat cultivars were screened for differential root growth, as an indicator of ability to withstand mineral toxicity and 17 out of 270 lines exhibited tolerance (Johnson *et al*. 1991).

The Mo content of the flora decreases with increasing age. Legumes store the highest Mo levels in the bulbs of their roots; on average, they accumulate more Mo than herbs and grasses do (Anke and Seifert 2007). The toxicity of 100 µM Mo as Na_2MoO_4 had no negative effect on the growth in sunflower (*Helianthus annuus* L. var. 'Kasol') suggesting the possibility of using sunflower for the phytoremediation of this metal, mainly in agricultural zones used for grazing where the excess of this element can provoke problems of molybdenosis in ruminants cattle (Ruiz *et al*. 2007). The *Poinsettia* plants have a very good tolerance to Mo and no visible phytotoxic effects and growth upto 320 mg Mo l^{-1} (irrigated biweekly) were observed on any plants in the cv. 'Glory' without any adverse effect on plant height, diameter of display bract at anthesis and nutrient uptake of any element except Mo (Hammer and Bailey 1987).

In a study to determine whether use of recovered sediment as a growth media for garden vegetables promotes the bioaccumulation of undesirable elements in plant tissues revealed that only Zn and Mo, in sediment-grown plants, were more than 3-fold higher than those in plants from the reference soil, except for bean tissues, which showed a >10-fold greater concentration (>20 mg kg^{-1} DW) in sediment-grown plants (Ebbs 2006). The Mo concentrations observed were >3-fold greater than those associated with Mo toxicity to grazing animals, suggesting that use of recovered sediment should be monitored to prevent transfer of this element to terrestrial food webs (Ebbs 2006).

Selecting or developing cultivars with low transport from roots to shoots of Ni might improve plant tolerance to moderate Ni toxicity and reduce the flow of Ni from contaminated soils to shoot organs (Yang *et al.* 1996a). In Ni-contaminated field the transgenic canola (*Brassica napus*) increased growth but decreased shoot Ni concentrations compared to non-transformed canola, resulting in similar total Ni per plant (Farwell *et al*. 2006). Inoculation of *Pseudomonas putida* strain HS-2 enhanced growth and total Ni per plant for non-transformed canola, indicating the potential usefulness of this bacterium in phytoremediation strategies (Farwell *et al*. 2006).

Phytoextraction, using plants to extract heavy metals from contaminated soils is an emerging technology. The phytoremediation efficiency depended both on biomass production and on the metal accumulation in tissues. The effects of various concentrations of four heavy metals including Cd, Cr, Co and Ni when studied in two cultivars of wheat, bean and lucerne based on the biomass, metal content, as well as % recovery values, the bean plant was the most effective crop in removing heavy metals from medium, the lucerne, though had higher tissue concentration, because of a low biomass, was not an effective species (Hajiboland 2005). The possibilities of using nine cultivated crops *Beta vulgaris*, *Cichorium intybus*, *Cucurbita pepo*, *Phaseolus vulgaris*, *Hordeum vulgare*, *Brassica oleracea* var. *capitata*, *Zea mays*, *Medicago sativa*, and *Pastinaca sativa* in re-

moving metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from Eutric Cambisols soil in Poland where the most effective crop in Cd, Mn, Cu, Ni, Pb and Zn remediation was *Cucurbita pepo* (Ciura *et al*. 2005). Examination of 16 plant species from industrial zone of Islamabad, Pakistan reveals that the concentrations of Co, and Ni in soils varied between 7.3-24.7 and, 41.4-59.3 mg/kg, respectively and based on, transfer and accumulation of metals from soil to roots and shoots in terms of biological concentration factor (BCF), translocation factor (TF) and bioaccumulation coefficient (BAC) values, though most of the studied species have potential for phytostabilization and phytoextraction, *Parthenium hysterophoirus* L., and *Amaranthus viridis* L., were good for phytoextraction of Ni (Malik *et al*. 2010).

Severe contamination of vegetation and soil by Ni, Cu and Co has been observed in the vicinity of a Ni refinery in Southern Ontario with more than 2.6% Ni in surface soil near the refinery and 100 ppm Ni in soil are found over 8 km downwind of the refinery (Temple and Bisessar 1981). Foliage samples from trees growing within 1 km of the refinery frequently exceed 200 to 300 ppm Ni, with lesser amounts of Co and Cu. Despite these high concentrations of Ni, overt metal toxicity symptoms are confined to a few extremely susceptible native species such as silver maple (*Acer saccharinum* L.), and to susceptible crops such as oats, lettuce and cabbage (Temple and Bisessar 1981).

Uptake and toxicity of Ni and other metals in crops growing on a soil with Ni content 2000 to 10000 ppm show that the growth of crops such as onions, potatoes, celery, cabbage, and lettuce was more or less normal at 2000 to 3000 ppm Ni, but was severely inhibited with severe toxicity symptoms at 10000 ppm Ni (Temple and Bisessar 1981).

The effect of phytoremediation on microbial communities in soils contaminated with Ni was investigated in pot by planting two Ni hyperaccumulators and one Ni tolerant species on paddy soils with Ni ranging from 100 to 1600 mg kg^{-1} where after 110 days of incubation, the populations of bacteria, fungi and Actinomycetes and biomass of the microorganisms were stimulated at 100 mg kg^{-1} Ni in non-rhizospheric soil, but at Ni higher than 100 mg kg^{-1} in the soil showed adverse effects on microbial communities (Cai *et al.* 2006). Hyperaccumulator plants could increase both the population and biomass of soil microorganisms by absorbing Ni from the soil and excreting root exudates thus reduced Ni toxicity and improved the living environment of soil microorganisms, however, different plant species had different effects on microorganisms in soil (Cai *et al.* 2006). Further studies of randomly amplified polymorphic DNA (RAPD) with 5 primers when used in 25 soil samples of 4 types, a total of 947 amplified bands were obtained, including 888 bands of polymorphic and 59 bands of non-polymorphic indicating that the composition of microbial DNA sequences had changed due to Ni addition to soil (Cai *et al.* 2006). Shannon-Weaver index of soil microbial DNA sequence was reduced in Ni contaminated soils with increasing Ni concentration. The changes in Shannon-Weaver index in the 4 types of soils ranged from 1.65 to 2.32 for *Alyssum corsicum*, 1.37 to 2.27 for *Alyssum. murale*, 1.37 to 1.96 for *Brassica juncea*, and 1.19 to 1.85 for non-rhizospheric soil and with the same amount of Ni added to soils, the Shannon-Weaver index in rhizospheric soil with plant was higher than that in non-rhizospheric soil (Cai *et al.* 2006).

It is also known that natural hyper-accumulators do not use rhizosphere acidification to enhance their metal uptake. Recently, it has been found that some natural hyper-accumulators (e.g. *Thlaspi caerulescens*) proliferate their roots positively in patches of high metal availability. In contrast, non-accumulators actively avoid these areas, and this is one of the mechanisms by which hyper-accumulators absorb more metals when grown in the same soil (McGrath *et al*. 2001). *Cannabis sativa* when grown in soils containing 74 and 115 µg g^{-1} of Ni preferentially accumulated Ni in the roots and only partially translocated to the above-ground tissues, the Ni uptake was limited if compared with that of the Ni-hyperaccumulator *A. murale* (Citterio *et al*. 2003).

The concentration of metal in the growth medium, C_s, the concentration of metal absorbed by the plant, C_p, and the total biomass achieved, M, are factors relevant to the efficiency of phytoremediation of the plant, the implications of these in phytoremediation engineering to maximize C_p and M simultaneously in the same plant have been discussed elsewhere (Dasgupta *et al.* 2007). This inter-relationship between parameters that principally affect the metal uptake in the plant studied via the macro-physiological response of *B. juncea* seedlings to Ni stress reveals that for the metal accumulator *B. juncea* with regard to its capacity to accumulate Ni, the overall metabolic nature of the plant is important – neither rapid biomass increase nor a high metal concentration capability favours the removal of high metal mass from the medium, but rather the plant with the moderate photosynthetically driven biomass growth and moderate metal concentrations demonstrated the ability to remove the maximum mass of metal from the medium (Dasgupta *et al.* 2007).

The crops raya (Indian mustard) and toria (*Brassica campestris*) when irrigated with sewage water containing high Ni, accumulated higher Ni in comparison with other crops, with higher content in roots than shoots, however, transport index suggested that major part of taken up Ni is translocated to top parts of plant (Khurana and Bansal 2008). As the plants take up Ni readily there is danger of its excessive accumulation in plant organs and devaluation of the plant products (Khurana and Bansal 2008). Two plant growth promoting bacteria Ps29C and Bm4C, from a collection of Ni resistant bacterial strains isolated from serpentine soil, with intrinsic ability for the production of indole acetic acid, siderophore and solubilization of insoluble phosphate when inoculated, promoted growth and protected Indian mustard plant from Ni toxicity thus provide a new insight into the phytoremediation of Ni contaminated soil (Mani and Freitas 2008).

The *A. murale*, *A. corsicum* and *Nyssa sylvatica* var. 'biflora' and *N. sylvatica* var. 'sylvatica' are the Ni hyperaccumulators, the phytoextraction of Co by these when compared with that of *B. juncea*, a nonmetal accumulator crop, on Sassafras sandy loam soil (< 2 mg Co and 5 mg Ni kg^{-1} dry soil) amended with 58.9 mg Co kg^{-1} soil, and two Ni smelter-contaminated soils (collected downwind of a Ni-Co refinery) Quarry muck with 24 mg Co and 1720 mg Ni kg^{-1} soil and Welland loam with 37 mg Co and 2570 mg Ni kg^{-1} soil, in Sassafras soil, the maximum concentration accumulated by *A. murale* was 1320 mg Co kg^{-1}, which was 60 times higher than that accumulated by *B. juncea* (Malik *et al*. 2000). Both *Alyssum* species accumulated up to 1% Ni when grown on Ni-contaminated soils and in a single harvest after 60 days of growth, *A. murale* extracted more than 3% of Co from Co-amended soil (Malik *et al*. 2000). The toxicity symptoms, as chlorosis, emerged in first few leaves both in Co-amended and Ni-contaminated soils, but disappeared with growth. The *N. sylvatica* showed significant Ni accumulation, foliar Co concentration was as high as 800 mg kg^{-1} after a second harvest. In Co-amended soil, Co concentration in *N. sylvatica* leaves was 30% of that found in *Alyssum* species, but higher than that of *B. juncea* also the metal accumulation in leaves was much higher than that in stems (Malik *et al*. 2000).

CONCLUSIONS AND FUTURE RESEARCH STRATEGIES

The mineral toxicities issues are becoming increasingly common worldwide in agriculture. The minerals B, Co, Mo and Ni are a natural part of terrestrial systems occurring in soil, rock, air, water and are essential to plant metabolism in trace amounts, however excessive levels of these cause toxicity limiting crop production. Plants can access the soluble form of these minerals from soil solution, which are

directly available for plant uptake. The total mineral provides the maximum pool of these in the soil. The free ion is the most toxic form of mineral for plant, however, the bioavailable fraction of a metal is somewhere between the total amount in the soil solution and the free ion activity. Also minerals in the soil solution are in dynamic equilibrium, and replenishment occurs when these are removed either by plant or by leaching. To assess the toxicity of minerals to plants, quantification of the bioavailable fraction in the soil which the plant can access is essential. There is a strong need for quality testing, and comparisons of all promising soil tests against plant responses for various crops.

The expression of toxicity of these minerals varies widely among various crop plants and cultivars depending upon soils, tolerance of crop and the growth stages. Though the critical toxic concentration of Co, Mo and Ni in soil has not been worked out, most of the crops show toxicity if the soil concentrations of B increase over 2 ppm. Ideally, the soils containing more than 5 ppm of hot water soluble B is unsuitable for growing crops, however, many species grow well at more than 5 ppm B (Choi *et. al*. 2006; Nuttall *et al*. 2006; Eraslan *et al*. 2007a). With decreases in soil pH the solubility of Co and Ni increases in the soil solution which increases the plant uptake. The effect of excess mineral occurs at cellular level, at the organ level in leaf as symptoms and at the whole plant level in reduced growth and yield. Both the symptoms and growth effects are side effects of the direct mode of action. An early effect of B, Co, Mo and Ni toxicities decreased Chl and reduced growth, leaf area and CO_2 fixation well before the development of visible toxicity symptoms.

The mineral toxicities are accompanied by specific leaf symptoms useful in diagnosis. The typical visible symptom of B-toxicity is characterised by chlorosis and necrosis of leaves beginning at their margins followed by leaf burn-chlorotic and necrotic patches, often at the margins and tips of older leaves. Cobalt toxicity caused chlorosis to diffused chlorosis of young leaves from base with necrotic spots on chlorotic areas, which enlarge in size, coalesces and in due course the entire leaf turn necrotic. Mo toxicity caused complete chlorosis of young leaves showing brilliant yellow to golden yellow colour which start drying from the margin with scorching of the leaves, however Mo-toxicity rarely occurs in field conditions. The chlorosis and necrotic spots on younger leaves and internodes, streak necrosis of the leaves and petioles, premature leaf fall and dieback and browning of the root are the typical visual symptoms of Ni toxicity.

The critical toxicity levels of B in leaves were 190 ppm B in chickpea (Chatterjee *et al.* 2005), 160 ppm in sunflower (Murthy 2006), 123 ppm in old leaves of redlands Crimson strawberries (Haydon 1981), 74 ppm in leaves and 50 ppm in kernels of groundnut (Sinha *et al*. 2002), 63 ppm in soyabean (Murthy 2006), 35 ppm in rice (Cayton 1985), 25-62 ppm in barley and 13-25 ppm in wheat (Gupta *et al.* 1973), however, 50-70 ppm in barley shoots at booting stage and 2 to 15 ppm in barley grain (Riley 1987). The Co concentrations in plant rarely exceed 1 ppm and 25-100 ppm is considered the threshold for toxicity in plants (MOEE 1996). However level of toxicity varied with crop and was 26 ppm Co in young leaves of French bean (Chatterjee *et al.* 2005). The critical toxicity level of Ni in leaf was 13.7 ppm in lettuce (Bansal and Khurana 2006) and 20.5 ppm in pakchois (Ma *et al.* 2006).

The B, Co, Mo and Ni toxicities have been shown to reduce photosynthesis, affect enzyme and, alter nutrient transport and cell metabolites and negative effects on cellular functioning. Excess of these minerals adversely affect the growth, yield and yield attributes, the extent of which depends upon the toxicity levels, crop species and the soil. Growth is rapidly inhibited by internal concentrations of these minerals. Research on the excess soil B has increased considerably in the dry areas of the Mediterranean region and parts of Australia where B toxicity caused significant reductions in crop yield. The B toxicity reduced leaf and root growth and increased the B concentration of the leaf and stem, however, in grapevines despite severe visual toxicity damage and reduced growth, fruit yield remained unaffected (Yermiyahu *et al*. 2006). The grain and shoots, at maturity, are not suitable tissues to diagnose yield depressions due to B toxicity as plants accumulate relatively high B and express severe leaf injury in the later stages of growth with relatively small effects on grain yield. Excess Co inhibited seedling growth, reduced biomass, and depressed the size and quality of fruits.

Boron toxicity increases B, N, P and K concentration and also alters the other mineral contents in plants. There was an antagonistic relationship between Ca and B and synergism between K and B uptake and B and Zn concentration, but in the presence of NaCl, the concentration of B was reduced. Excess Co restricted the concentrations of P, S and Fe in leaves and accumulation of Co was greatest in roots and old leaves and lowest in stem. Excess Ni, decreased the Cu, Fe, Mn and Zn in plants and root accumulated much higher amounts of Ni compared to the shoot. Salinity interacts with B-toxicity by a combined effect on B and water uptake and B partitioning within the plant. Evidences show that there is migration of nutrients out of necrotic areas and dying tissue to young leaves.

Excess B increased the activities of POD, APase and PPO, concentration of sugars, starch and phenols in leaves and decreased RNase and protein concentration. The B toxicity also increased H_2O_2 and activities of antioxidant enzymes (SOD, CAT, APX) and in order to overcome B-induced oxidative stress accumulation of ascorbic acid and proline were involved. Excess Co depressed the activities of CAT and POD and concentrations of ascorbic acid, DNA and RNA, reducing and non-reducing sugars, starch, protein and non-protein nitrogen and increased phenol, acidity and activities of POD, RNase and APase. The Mo-toxicity increased POD and CAT activities. The Ni toxicity induced accumulation of proline, soluble phenolics, starch and reducing sugars in leaves and increased O_2^- and H_2O_2 contents and activities of POD, GST, APX, GPX and GSH-Px, but decreased SOD and CAT activities and did not change the lipid peroxides content.

The differences in tolerance among the cultivars highlight the existence of genetic variation in adaptation to high levels of these elements in soil. The known highly tolerant crop genotypes are listed. However screening for more crops and genotypes is essential for having diversified crops on problem soils. Scoring for B toxicity symptoms, shoot weight at early stage of growth and root elongation can be considered as reliable criteria for screening cultivars for tolerance to B toxicity in soils. Some of the B-toxicity tolerant genotypes include, barley cultivars, 'Sahara 3771' , 'Anadolu' and 'Tarm-92', durum wheat cultivars 'Sabil-1', Stn "S", 'Aconhi-89' and 'Wadelmez-2' and modern japonica rice subspecies 'Koshihikari', 'Nipponbare' and 'Sasanishiki'. The rice cultivars 'Annapurna', 'Kusuma' and 'Deepa' were tolerant to Mo-toxicity.

The restriction of uptake and transport and internal tolerance mechanisms are the two main functions to which plants employ a number of strategies to combat high external metal concentrations. Now it is evident that plants sense internal and external B conditions and regulate B transport by modulating the expression and/or accumulation of these transporters, thus useful in designing plants tolerant to soils low or high B (Miwa and Fujiwara 2010). However, the complex nature of crop responses to mineral toxicity invites argument and common consensus on the possible mechanisms of tolerance. The tolerance to B, Co, Mo and Ni toxicities could be attributed to the lower content in seed and lower uptake or accumulation of these in the root and shoot and high yield in toxic soils. However, various other mechanisms are also involved. In cereal crops low B in the shoot or grain is correlated with the maintenance of biomass production and grain yield under high B conditions. Boron toxicity triggers the formation of reactive oxygen species in plant tissues and ascorbate could be important against B

stress. The tolerance to Ni toxicity was related to low influx of Ni and its transport from roots to shoots and influence of Ni on influx into roots and transport from roots to shoots of Cu, Fe and Mn. Deposition of an iron oxide plaque or coating on roots of rice ameliorated the toxic effects of Ni and affected patterns of metal uptake and accumulation. Certain proteins may be related to genotype tolerance to various minerals, an efficient chelation of excess Ni by low molecular weight fraction in tolerant indigenous species was reported. Maize belongs to excluder plants as their root systems function as a barrier limiting heavy metal intake by aboveground organs.

Plants growing on serpentine soils are usually Ni-tolerant species and lignification plays an important role in tolerance to Ni toxicity. Interference with other essential metal ions and induction of oxidative stress are the two indirect pathways of Ni toxicity in plants. The tolerance mechanism is under the control of several major additive genes, and specific chromosomal locations were identified for the genes in some species. The B tolerance was expressed as a partially dominant character in wheat (Paull *et al*. 1991). Bot1, a BOR1 ortholog, is the gene responsible for the superior B-toxicity tolerance of the Algerian barley landrace 'Sahara 3771' (Sutton *et al*. 2007). Genes from roots of B-tolerant cultivars of wheat and barley were cloned, the expression of which has ability of tolerant genotypes to lower the concentration of B in roots (Reid 2007, 2010). Recently, Schnurbusch *et al.* (2010) identified the second B toxicity tolerance gene in barley, which encodes HvNIP2;1, an aquaporin.

An understanding of crop responses in relation to management practices is required to utilise potentially toxic soils. The physiological and genetic studies have provided some understanding of genetic variation in crops in response to high concentrations of B, Co, Mo and Ni which have facilitated the breeding of tolerant genotypes for cultivation on toxic soils. Considerable success has been achieved in breeding for tolerance to B toxicity. Dry ploughing, use of low-B surface water and tolerant varieties provided the best means of making B toxic soils more productive. Using the perspective of full scale application of phytoremediation techniques, research is focusing on the optimization of agronomic practices. The Jerusalem artichoke, maize, *Sida hermaphrodita*, amaranth (*A. hypochondriacus*) and industrial hemp are the species capable of taking up harmful elements and producing high yields. The Si improved the salt and B tolerance in naturally sodic-B toxic soil. The beneficial microorganisms autochthonous *Brevibacillus brevis* and *Glomus mosseae* inoculation improved the mycorrhizal benefit in nutrients uptake and in decreasing Ni-toxicity (Vivas *et al.* 2006), which may be used as a tool to enhance plant performance in soil contaminated with Ni. The B, Co and Ni are present in significant amounts in recycled materials such as municipal solid waste (MSW) and coal fly ash, and therefore composts containing these ingredients may potentially exceed toxic levels, especially when used at heavy rates. There is need for careful management of exogenous factors that may be present in composts to reduce potential negative growth effects.

Finally, most research of B, Co, Mo and Ni toxicities has been undertaken on a few crops and genotypes with little attention on the mechanism of toxicity tolerance. It is essential to understand the toxicity responses of various crops and popular cultivars to these minerals to utilise appropriate one in the problem soils.

REFERENCES

Ahmed S, Evans HJ (1960) Cobalt: A micronutrient element for the growth of soyabean plants under symbiotic conditions. *Soil Science* **90**, 205-210

Al-Qurainy F (2009) Toxicity of heavy metals and their molecular detection on *Phaseolus vulgaris* (L.). *Australian Journal of Basic and Applied Sciences* **3**, 3025-3035

Anderson AJ, Meyer DR, Mayer FK (1973) Nickel toxicity in subterranean clover, lucerne and oats. *Annual Report 1972*, Division of Plant Industry, CSIRO, pp 96-97

Anderson AJ, Meyer DR, Mayer FK (1979) Effects of the environment on the symptom pattern of nickel toxicity in the oat plant. *Annals of Botany* **43**, 271-283

Anke M, Seifert M (2006) The biological and toxicological importance of molybdenum in the environment and the nutrition of plants animal and man. Trace elements in the food chain. In: *Proceedings of an International Symposium on Trace Elements in the Food Chain*, 25-27 May, Budapest, Hungary, pp 1-5

Anke M, Seifert M (2007) The biological and toxicological importance of molybdenum in the environment and in the nutrition of plants, animals and man: Part 1: Molybdenum in plants. *Acta Biologica Hungarica* **58**, 311-324

Antonkiewicz J, Jasiewicz C (2002) Estimation of usefulness of different plant species for phytoremediation of soils contaminated with heavy metals. *Acta Scientiarum Polonorum Formatio Circumiectus* **1**, 119-130

Ardc M, Sekmen AH, Tokur S, Ozdemir F, Turkan I (2009a) Antioxidant responses of chickpea plants subjected to boron toxicity. *Plant Biology* **11**, 328-338

Ardc M, Sekmen AH, Turkan I, Tokur S, Ozdemir F (2009b) The effects of boron toxicity on root antioxidant systems of two chickpea (*Cicer arietinum* L.) cultivars. *Plant and Soil* **314**, 99-108

Arora S, Chahal DS (2005) Toxic effect of high boron content in soils on clover (*Trifolium alexandrinum*). *Environment and Ecology* **23**, 255-257

Aydn A, Kant C, Ataoglu N (2005) Effect of boron and phosphorus application on the growth and mineral content of corn in Erzurum and Rize soils. *Ziraat Fakultesi Dergisi Ataturk Universitesi* **36**, 125-129

Baccouch S, Chaoui A, El Ferjani E (1998) Nickel toxicity: effects on growth and metabolism of maize. *Journal of Plant Nutrition* **21**, 577-588

Baccouch S, Chaoui A, El Ferjani E (2001) Nickel toxicity induces oxidative damage in *Zea mays* roots. *Journal of Plant Nutrition* **24**, 1085-1097

Bagheri A, Paull JG, Rathjen AJ (1994) The response of *Pisum sativum* L. germplasm to high concentrations of soil boron. *Euphytica* **75**, 9-17

Bailey DA, Hammer PA (1988) Evaluation of nutrient deficiency and micronutrient toxicity symptoms in florists' hydrangea. *Journal of the American Society for Horticultural Science* **113**, 363-367

Baker AJM, McGrath SP, Reeves RD, Smith JAC (2000) Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal polluted soils. In: Terry N, Bañuelos GS (Eds) *Phytoremediation of Contaminated Soil and Water*, CRC Press, Boca Raton, pp 85-107

Bansal RL, Khurana MPS (2006) Effect of nickel on yield and mineral composition in lettuce (*Lactuca sativa* L.) and its critical toxicity levels. *Environment and Ecology* **24**, 1140-1144

Bastías E, Alcaraz-López C, Bonilla I, Martínez-Ballesta MC, Bolaños L, Carvajal M (2010) Interactions between salinity and boron toxicity in tomato plants involve apoplastic calcium. *Journal of Plant Physiology* **167**, 54-60

Ben GA (2007) The contribution of foliar exposure to boron toxicity. *Journal of Plant Nutrition* **30**, 1705-1716

Bergmann W (1992) *Colour Atlas: Nutritional Disorders of Plants*, Gustav Fischer, New York, pp 204-239

Bishnoi SK, Kumar B, Datta KS, Sheoran IS, Angrish R (2006) Effect of NaCl and boron stress and alleviatory effects of Ca^{+2} on protein profile of pigeonpea genotypes. *Physiology and Molecular Biology of Plants* **12**, 313-316

Blamey FPC, Chapman J (1979) Boron toxicity in Spanish groundnuts. *Agrochemophysica* **11**, 57-59

Blaylock AD, Jolley VD, Brown JC, Davis TD, Walser RH (1985) Iron-stress response mechanism and iron uptake in iron-efficient and inefficient tomatoes and soybeans treated with cobalt. *Journal of Plant Nutrition* **8**, 1-14

Bollard EG (1983) Involvement of unusual elements in plant growth and nutrition. In: Lauchli A, Bieleski RL (Eds) *Inorganic Plant Nutrition*, Springer-Verlag, Berlin, Germany, pp 695-744

Bolle-Jones EW, Mallikarjuneswara VRA (1957) A beneficial effect of cobalt on the growth of *Hevea braziliensis*. *Nature* **179**, 738-739

Brenchley WE (2008) The toxic action of molybdenum in relation to soils and crops. *Annals of Applied Biology* **35**, 139-160

Brennan RF, Adcock KG (2004) Incidence of boron toxicity in spring barley in southwestern Australia. *Journal of Plant Nutrition* **27**, 411-425

Brinton WF, Evans E, Blewett C (2008) Extractability, plant yield and toxicity thresholds for boron in compost. *Compost Science and Utilization* **16**, 114-118

Brooks R, Anderson C, Stewart R, Robinson B (1999) Phytomining: growing a crop of a metal. *Biologist London* **46**, 201-205

Brown PH, Welch RM, Cary EE (1987) Nickel: A micronutrient essential for higher plants. *Plant Physiology* **85**, 801-803

Cai XD, Qiu RL, Chen GZ, Zeng XW, Fang XH (2006) Response of microbial communities to phytoremediation of nickel contaminated soils. *Acta Pedologica Sinica* **43**, 919-925

Cayton MTC (1985) Boron toxicity in rice. *IRRI Research Paper Series* **113**, 5 pp

Cervilla LM, Blasco B, Juan JR, Lous R, Juan MR (2007) Oxidative stress and antioxidants in tomato (*Solanum lycopersicum*) plants subjected to boron

toxicity. *Annals of Botany* **100**, 747-756

Ceyhan E, Onder M Ozturk O, Harmankaya M, Hamurcu M, Gezgin S (2008) Effects of application boron on yields, yield component and oil content of sunflower in boron-deficient calcareous soils. *African Journal of Biotechnology* **7**, 2854-2861

Chantachume Y, Smith D, Hollamby GJ, Paull JG, Rathjen AJ (1995) Screening for boron tolerance in wheat (*T. aestivum*) by solution culture in filter paper. *Plant Soil* **177**, 249-254

Chatterjee C, Gopal R, Dube BK (2006) Physiological and biochemical responses of French bean to excess cobalt. *Journal of Plant Nutrition* **29**, 127-136

Chatterjee C, Sinha P, Dube BK (2005) Biochemical changes, yield, and quality of gram under boron stress. *Communications in Soil Science and Plant Analysis* **36**, 1763-1771

Chatterjee J, Chatterjee C (2005) Deterioration of fruit quality of tomato by excess cobalt and its amelioration. *Communications in Soil Science and Plant Analysis* **36**, 1931-1945

Chen C, Huang D, Liu J (2009) Functions and toxicity of nickel in plants: recent advances and future prospects. *CLEAN - Soil, Air, Water* **37**, 304-313

Choi EY, McNeill A, Coventry D, Stangoulis J (2006) Whole plant response of crop and weed species to high subsoil boron. *Australian Journal of Agricultural Research* **57**, 761-770

Choi, EY, Kolesik P, McNeill A, Collins H, Zhang QS, Huynh BL, Graham R, Stangoulis J (2007) The mechanism of boron tolerance for maintenance of root growth in barley (*Hordeum vulgare* L.). *Plant Cell and Environment* **30**, 984-993

Citterio S, Santagostino A, Fumagalli P, Prato N, Ranalli P, Sgorbati S (2003) Heavy metal tolerance and accumulation of Cd, Cr and Ni by *Cannabis sativa* L. *Plant and Soil* **256**, 243-252

Ciura J, Poniedziaek M, Sekara A, Jedrszczyk E (2005) The possibility of using crops as metal phytoremediants. *Polish Journal of Environmental Studies* **14**, 17-22

Collins RN, Bakkaus E, Carrire M, Khodja H, Proux O, Morel JL, Vergnano O (2010) Uptake, localization, and speciation of cobalt in *Triticum aestivum* L. (wheat) and *Lycopersicon esculentum* M. (tomato). *Environmental Science and Technology* **44**, 2904-2910

Crooke WM, Hunter JG, Vergnano O (2008) The relationship between nickel toxicity and iron supply. *Annals of Applied Biology* **41**, 311-324

Crooke WM, Knight AH (2008) The relationship between nickel-toxicity symptoms and the absorption of iron and nickel. *Annals of Applied Biology* **43**, 454-464

Dasgupta, Schubert N, Alexander S, Sommer L, Whelan T, Cuevas VRA, Mendez LME, Persans MW (2007) The light quanta modulated physiological response of *Brassica juncea* seedlings subjected to Ni(II) stress. *Engineering in Life Sciences* **7**, 259-267

da Silva DH, Rossi ML, Boaretto AE, de Nogueira NL, Muraoka T (2008) Boron affects the growth and ultra structure of castor bean plants. *Scientia Agricola* **65**, 659-664

Delwiche CC, Jihnson CM, Reisenauer HM (1961) Influence of cobalt on nitrogen fixation by *Medicago*. *Plant Physiology* **36**, 73-78

Dobermann A, Fairhurst T (2000) *Rice. Nutrient Disorders and Nutrient Management*, handbook series, Potash and Phosphate Institute, Atlanta, GA, Potash & Phosphate Institute of Canada, and International Rice Research Institute, Los Baños, the Philippines, 191 pp

Dube BK, Sinha P, Chatterjee C (2004) Crop plants as biological tools for assessing and monitoring agricultural lands inundated with sewage and sludge. *Bulletin of Environmental Contamination and Toxicology* **72**, 429-436

Ebbs SD (2006) Metal bioaccumulation by garden vegetables grown on soil derived from Peoria Lake sediment. In: *Research Report Illinois Waste Management and Research Center* (RR-109) viii, 40 pp

Elsokkary IH, Chatby A (1974) Leaf analysis as a guide to the nutritional status of orange trees in some alluvial and desert calcareous soils in Egypt. *Beitrage zur Tropischen Landwirtschaft und Veterinarmedizin* **12**, 249-262

Emebiri LC, Michael P, Moody DB (2008) Enhanced tolerance to boron toxicity in two-rowed barley by marker-assisted introgression of favourable alleles derived from Sahara 3771. *Plant and Soil* **314**, 77-85

Eraslan F, Inal A, Gunes A, Alpaslan M (2007b) Boron toxicity alters nitrate reductase activity, proline accumulation, membrane permeability, and mineral constituents of tomato and pepper plants. *Journal of Plant Nutrition* **30**, 981-994

Eraslan F, Inal A, Gunes A, Alpaslan M (2007c) Impact of exogenous salicylic acid on the growth, antioxidant activity and physiology of carrot plants subjected to combined salinity and boron toxicity. *Scientia Horticulturae* **113**, 120-128

Eraslan F, Inal A, Pilbeam DJ, Gunes A (2008) Interactive effects of salicylic acid and silicon on oxidative damage and antioxidant activity in spinach (*Spinacia oleracea* L. cv. 'Matador') grown under boron toxicity and salinity. *Plant Growth Regulation* **55**, 207-219

Eraslan F, Inal A, Savasturk O, Gunes A (2007a) Changes in antioxidative system and membrane damage of lettuce in response to salinity and boron toxicity. *Scientia Horticulturae* **114**, 5-10

Erd RC (1980) The minerals of boron. In: R Thompson (Ed) *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Vol V), Longman, New York, pp 7-71

Eskew DL, Welch RM, Cary EE (1983) Nickel: An essential micronutrient for legumes and possibly all higher plants. *Science* **222**, 621-623

Fageria NK, Baligar VC, Jones CA (1991) *Growth and Mineral Nutrition of Field Crops*, Marcel Dekker, New York, 476 pp

Farwell AJ, Vesely S, Nero V, Rodriguez H, Shah S, Dixon DG, Glick BR (2006) The use of transgenic canola (*Brassica napus*) and plant growth-promoting bacteria to enhance plant biomass at a nickel-contaminated field site. *Plant and Soil* **288**, 309-318

Gajewska E, Skodowska M (2007) Effect of nickel on ROS content and antioxidative enzyme activities in wheat leaves. *BioMetals* **20**, 27-36

Gajewska E, Skodowska M, Saba M, Mazur J (2006) Effect of nickel on antioxidative enzyme activities, proline and chlorophyll contents in wheat shoots. *Biologia Plantarum* **50**, 653-659

Ghaderian SM, Movahedi M, Ghasemi R (2009) Uptake and accumulation of cobalt by *alyssum bracteatum*, an endemic Iranian Ni hyperaccumulator. *Northeastern Naturalist* **16**, 131-138

Giashuddin M, Cornfield AH (1978) Incubation study on effects of adding varying levels of nickel (as sulphate) on nitrogen and carbon mineralisation in soil. *Environmental Pollution* **15**, 231-234

Goldberg S, Shouse PJ, Lesch SM, Grieve CM, Poss JA, Forster HS, Suarez DL (2005) Soil boron extractions as indicators of boron toxicity. In: *International Salinity Forum. Managing Saline Soils and Water, Science Technology and Social Issues*, Poster Presentation, Abstracts Riverside Convention Center, Riverside, California, USA, pp 55-58

Gopal NH (1973) Physiological studies on groundnut plants with boron toxicity. 1. Effect on dry weight, moisture, boron, respiration and carbohydrate metabolism. *Turrialba* **23**, 410-419

Gopal NH (1975a) Physiological studies on groundnut plants with boron toxicity. 2. Effect on nitrogen metabolism. *Turrialba* **25**, 144-147

Gopal NH (1975b) Physiological studies on groundnut plants with boron toxicity. 3. Effect on chlorophyll, iron and copper metabolism. *Turrialba* **25**, 306-315

Gopal NH (1975c) Physiological studies on groundnut plants with boron toxicity. 4. Effect on phosphorus, potassium and calcium. *Turrialba* **25**, 436-439

Gopal NH (1976) Physiological studies on groundnut plant with boron toxicity. 5. Effect on boron and iron distribution. *Turrialba* **26**, 288-294

Gopal R, Dube BK, Pratima Sinha, Chatterjee C (2003) Cobalt toxicity effects on growth and metabolism of tomato. *Communications in Soil Science and Plant Analysis* **34**, 619-628

Gopal R, Dube BK, Sinha P, Chatterjee C (2003) Cobalt toxicity effects on growth and metabolism of tomato. *Communications in Soil Science and Plant Analysis* **34**, 619-628

Greipsson S, Crowder AA (1992) Amelioration of copper and nickel toxicity by iron plaque on roots of rice (*Oryza sativa*). *Canadian Journal of Botany* **70**, 824-830

Grieve CM, Poss JA (2000) Wheat response to interactive effects of boron and salinity. *Journal of Plant Nutrition* **23**, 1217-1226

Gunes A, Alpaslan M, Cikili Y, Ozcan H (1999) Effect of zinc on the alleviation of boron toxicity in tomato. *Journal of Plant Nutrition* **22**, 1061-1068

Gunes A, Inal A, Bagc EG, Coban S, Sahn O (2007c) Silicon increases boron tolerance and reduces oxidative damage of wheat grown in soil with excess boron. *Biologia Plantarum* **51**, 571-574

Gunes A, Inal A, Bagci EG (2009) Recovery of bean plants from boron-induced oxidative damage by zinc supply. *Russian Journal of Plant Physiology* **56**, 503-509

Gunes A, Inal A, Bagci EG, Coban S, Pilbeam DJ (2007b) Silicon mediates changes to some physiological and enzymatic parameters symptomatic for oxidative stress in spinach (*Spinacia oleracea* L.) grown under B toxicity. *Scientia Horticulturae* **113**, 113-119

Gunes A, Inal A, Bagci EG, Pilbeam DJ (2007a) Silicon-mediated changes of some physiological and enzymatic parameters symptomatic for oxidative stress in spinach and tomato grown in sodic-B toxic soil. *Plant and Soil* **290**, 103-114

Gunes A, Soylemezoglu G, Inal A, Bagci EG, Coban S, Sahin O (2006) Antioxidant and stomatal responses of grapevine (*Vitis vinifera* L.) to boron toxicity. *Scientia Horticulturae* **110**, 279-284

Guo XY, Zuo YB, Wang BR, Li JM, Ma YB (2010) Toxicity and accumulation of copper and nickel in maize plants cropped on calcareous and acidic field. *Plant and Soil* **333**, 365-373

Gupta UC (1997) Symptoms of molybdenum deficiency and toxicity in crops. In: *Molybdenum in Agriculture*, Cambridge University Press, Cambridge, UK, pp 160-170

Gupta UC, Jame YW, Campbell CA, Leyshon AJ, Nicholaichuk W (1985) Boron toxicity and deficiency: A review. *Canadian Journal of Soil Science* **65**, 381-409

Gupta UC, Sterling JDE, Nass HG (1973) Influence of various rates of compost and nitrogen on the boron toxicity symptoms in barley and wheat. *Canadian Journal of Plant Science* **53**, 451-456

Hajiboland R (2005) An evaluation of the efficiency of cultural plants to remove heavy metals from growing medium. *Plant, Soil and Environment* **51**, 156-164

Hajiboland R (2007) Uptake, transport, re-translocation and chelation of Ni in

one tolerant and one susceptible Graminaceous species. *Pakistan Journal of Biological Sciences* **10**, 1011-1019

Hammer PA, Bailey DA (1987) Poinsettia tolerance to molybdenum. *HortScience* **22**, 1284-1285

Haydon GF (1981) Boron toxicity of strawberry. *Communications in Soil Science and Plant Analysis* **12**, 1085-1091

He ZL, Yang XE, Stoffella PJ (2005) Trace elements in agro-ecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology* **19**, 125-140

Heikal MMD, Berry WL, Wallace A, Herman D (1989) Alleviation of nickel toxicity by calcium salinity. *Soil Science* **147**, 413-415

Hobson K, Armstrong R, Nicolas M, Connor D, Materne M (2006) Response of lentil (*Lens culinaris*) germplasm to high concentrations of soil boron. *Euphytica* **151**, 371-382

Hosseini SM, Maftoun M, Karimian N, Ronaghi A, Emam Y (2005) Effects of different levels of boron and zinc, and two zinc sources on rice growth and chemical composition. *Iranian Journal of Agricultural Sciences* **36**, 869-883

Hu ZY, Deng XB, Peng XX, He Y, Liu WH, Dai GY, Wang HH (2007) Effects of external calcium on activities of antioxidant enzymes and membrane lipid peroxidation in rice seedlings under nickel stress. *Chinese Journal of Rice Science* **21**, 367-371

Hunter JG, Vergnano O (2008) Trace-element toxicities in oat plants. *Annals of Applied Biology* **40**, 761-777

Hutchinson TC (1981) Nickel: Effect of heavy metal pollution on plants (Vol I). In: Lepp NW (Ed) *Effects of Trace Metals on Plant Function,* Applied Science Publishers, Barking, Essex, UK, pp 71-211

Inal A, Pilbeam DJ, Gunes A (2009) Silicon increases tolerance to boron toxicity and reduces oxidative damage in barley. *Journal of Plant Nutrition* **32**, 112-128

Jayakumar K, Jaleel CA, Azooz MM, Vijayarengan P, Gomathinayagam M, Panneerselvam R (2009) Effect of different concentrations of cobalt on morphological parameters and yield components of soybean. *Global Journal of Molecular Sciences* **4**, 10-14

Johnson JW, Box JE Jr., Manandhar JB, Ramseur EL, Cunfer BM (1991) Breeding for rooting potential under stress conditions. In: Acevedo E Conesa AP, Monneveux P, Srivastava JP (Eds) *Physiology Breeding of Winter Cereals for Stressed Mediterranean Environments*, Montpellier, INRA, Paris, France, pp 307-317

Jones MD, Hutchinson TC (1988a) Nickel toxicity in mycorrhizal birch seedlings infected with *Lactarius rufus* or *Scleroderma flavidum*. I. Effects on growth, photosynthesis, respiration and transpiration. *New Phytologist* **108**, 451-459

Jones MD, Hutchinson TC (1988b) Nickel toxicity in mycorrhizal birch seedlings infected with *Lactarius rufus* or *Scleroderma flavidum*. II. Uptake of nickel, calcium, magnesium, phosphorus and iron. *New Phytologist* **108**, 461-470

Kalayci M, Alkan A, Cakmak I, Bayramoglu O, Yilmaz A, Aydin M, Ozbek V, Ekiz H (1997) Studies on differential response of wheat cultivars to boron toxicity. *Developments in Plant Breeding* **6**, 189-195

Kamenova YSM, Kudrev TG, Apostolova-Shakhpazova LK (1983) Effect of cobalt and mercury on some maize plant reactions. *Fiziologiya Rastenii* **9**, 78-82

Kaur S, Nicolas ME, Ford R, Norton R, Taylor PWJ (2006) Selection of *Brassica rapa* genotypes for tolerance to boron toxicity. *Plant and Soil* **285**, 15-123

Khalid BY, Tinsley J (1980) Some effects of nickel toxicity on rye grass. *Plant and Soil* **55**, 139-144

Khurana MPS, Bansal RL (2008) Impact of sewage irrigation on speciation of nickel in soils and its accumulation in crops of industrial towns of Punjab. *Journal of Environmental Biology* **29**, 793-798

Kliwere M, Evans HJ (1963a) Identification of cobamide coenzyme in nodules of symbionts and isolation of the B12 coenzyme from *Rhizobium meliloti*. *Plant Physiology* **38**, 55-59

Kliwere M, Evans HJ (1963b) Cobamide coenzyme content of soyabean nodules and nitrogen fixing bacteria in relation to physiological conditions. *Plant Physiology* **38**, 99-104

Kováčik J, Klejdus B, Kaduková J, Bačkor M (2009) Physiology of *Matricaria chamomilla* exposed to nickel excess. *Ecotoxicology and Environmental Safety* **72**, 603-609

Krupa Z, Siedlecka A, Maksymiec W, Baszynski T (1993) In vivo response of photosynthetic apparatus of *Phaseolus vulgaris* L. to nickel toxicity. *Journal of Plant Physiology* **142**, 664-668

Lee SB, Lee YB, Lee CH, Hong CO, Kim PJ, Yu C (2008) Characteristics of boron accumulation by fly ash application in paddy soil. *Bioresource Technology* **99**, 5928-5932

Leon V, Fogliani B, Bouraima Madjebi S, Pineau R (2006) Effects of nickel on growth and nutrient concentrations in a serpentine endemic *Cunoniaceae*. *Journal of Plant Nutrition* **29**, 219-234

Leyshon AJ, Jame YM (1993) Boron toxicity and irrigation management. In: Gupta UC (Ed) *Boron and its Role in Crop Production*, CRC Press, Boca Raton, FL, USA, pp 207-226

Li B, Zhang X, Wang XD, Ma Y (2009) Refining a biotic ligand model for nickel toxicity to barley root elongation in solution culture. *Ecotoxicology and Environmental Safety* **72**, 1760-1766

Li HF, Gray C, Mico C, Zhao FJ, McGrath SP (2009) Phytotoxicity and bioavailability of cobalt to plants in a range of soils. *Chemosphere* **75**, 979-986

Lima JCP de S, Nascimento CWA do, Lima JG da C, Lira Junior M de A (2007) Critical and toxic boron levels in corn plants and soils of Pernambuco, Brazil. *Revista Brasileira de Ciência do Solo* **31**, 73-79

Lin YC, Kao CH (2005a) Nickel toxicity of rice seedlings: Cell wall peroxidase, lignin, and $NiSO_4$-inhibited root growth. *Crop Environment and Bioinformatics* **2**, 131-136

Lin YC, Kao CH (2005b) Nickel toxicity of rice seedlings: The inductive responses of antioxidant enzymes by $NiSO_4$ in rice roots. *Crop Environment and Bioinformatics* **2**, 239-244

Liu J, Reid RJ, Smith FA (2001) The mechanism of cobalt toxicity in mung beans. *Physiologia Plantarum* **110**, 104-110

Llamasa A, Ullrich CI, Sanz A (2008) Ni^{2+} toxicity in rice: Effect on membrane functionality and plant water content. *Plant Physiology and Biochemistry* **46**, 905-910

Lock K, de Schamphelaere KAC, Because S, Criel P, Eeckhout HV, Janssen CR (2007) Development and validation of a terrestrial biotic ligand model predicting the effect of cobalt on root growth of barley (*Hordeum vulgare*). *Environmental Pollution* **147**, 626-633

Loomis WD, Durst RW (1992) Chemistry and biology of boron. *BioFactors* **3**, 229-239

Ma JJ, Zhu JT, Yu FM, Liu YJ, Zhang SX (2006) Biological impact of nickel pollution on pakchois in drab soil and its critical value. *Journal of Ecology and Rural Environment* **22**, 75-79

Maheshwari R, Dubey RS (2007) Nickel toxicity inhibits ribonuclease and protease activities in rice seedlings: Protective effects of proline. *Plant Growth Regulation* **51**, 231-243

Malik M, Chaney RL, Brewer EP, Li YM, Angle JS, Li YM (2000) Phytoextraction of soil cobalt using hyperaccumulator plants. *International Journal of Phytoremediation* **2**, 319-329

Malik RN, Husain SZ, Nazir I (2010) Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. *Pakistan Journal of Botany* **42**, 291-301

Mallick N, Singh AK, Rai LC (1990) Impact of bimetallic combinations of Cu, Ni and Fe on growth rate, uptake of nitrate and ammonium, $^{14}CO_2$ fixation, nitrate reductase and urease activity of *Chlorella vulgaris*. *Biology of Metals* **2**, 223-228

Mani R, Freitas H (2008) Effects of inoculation of plant-growth promoting bacteria on Ni uptake by Indian mustard. *Bioresource Technology* **99**, 3491-3498

Marchiol L, Fellet G, Perosa D, Zerbi G (2007) Removal of trace metals by *Sorghum bicolor* and *Helianthus annuus* in a site polluted by industrial wastes: A field experience. *Plant Physiology and Biochemistry* **45**, 379-387

Marschner H (1995) *Mineral Nutrition of Higher Plants* (2nd Edn), Academic Press, London, 889 pp

Matraszek R, Szymańska M, Chomczyńska M, Soldatov VS (2010) Productivity and chemical composition of tomato and cucumber plants growing in nickel-polluted soils fertilized with Biona-312. *Communications in Soil Science and Plant Analysis* **41**, 155-172

McGrath SP, Zhao FJ, Lombi E (2001) Plant and rhizosphere processes involved in phytoremediation of metal-contaminated soils In: Powlson DS, Bateman GL, Davies KG, Gaunt JL, Hirsch PR, Barlow PW (Eds) *Interactions in the Root Environment: An Integrated Approach. Proceedings of the Millennium Conference on Rhizosphere Interactions*, IACR Rothamsted, UK, pp 207-214

McGrath SP, Micó C, Curdy R, Zhao FJ (2010a) Predicting molybdenum toxicity to higher plants: Influence of soil properties. *Environmental Pollution* **158**, 3095-3102

McGrath SP, Micó C, Zhao FJ, Stroud JL, Zhang H, Fozard S (2010b) Predicting molybdenum toxicity to higher plants: Estimation of toxicity threshold values. *Environmental Pollution* **158**, 3085-3094

Micóa C, Lia HF, Zhaoa FJ, McGrath SP (2008) Use of Co speciation and soil properties to explain variation in Co toxicity to root growth of barley (*Hordeum vulgare* L.) in different soils. *Environmental Pollution* **156**, 883-890

Mishra D, Kar M (1974) Nickel in plant growth and metabolism. *Botanical Review* **40**, 395-452

Miwa K, Fujiwara T (2010) Boron transport in plants: Co-ordinated regulation of transporters. *Annals of Botany* **105**, 1103-1108

Miwa K, Takano J, Omori H, Seki M, Shinozaki K, Fujiwara T (2007) Plants tolerant of high boron levels. *Science* **318**, 1417

Mizuno T, Horie K, Nosaka S, Obata H, Mizuno N (2009) Serpentine plants in Hokkaido and their chemical characteristics. *Northeastern Naturalist* **16**, 65-80

MOEE (Ontario Ministry of the Environment and Energy) (1996) Rationale for the development and application of generic soil, groundwater and sediment criteria for use at contaminated sites in Ontario. PIBS 3250E01, Queen's Printer for Ontario

Mola DY, Datta KS, Angrish R, Dayal J, Kumari P, Kumar B (1998) Mineral ion uptake characteristics during boron toxicity under saline conditions in broad bean (*Vicia faba* L.). *Plant Physiology and Biochemistry, New Delhi* **25**,

114-121
Molas J (2008) Comparison of the toxicity of Co(II)-Gly and Co(II)-EDTA chelates to lucerne (*Medicago sativa* L.). *Proceedings of ECOpole* **2**, 71-75
Molas J, Baran S (2004) Relationship between the chemical form of nickel applied to the soil and its uptake and toxicity to barley plants (*Hordeum vulgare* L.) *Geoderma* **122**, 247-255
Moody DB, Rathjen AJ, Cartwright B (1993) Yield evaluation of a gene for boron tolerance using backcross-derived lines. In: Randall PJ, Delhaize E, Richards RA Munns R (Eds) *Genetic Aspects of Plant Mineral Nutrition. The 4th International Symposium on Genetic Aspects of Plant Mineral Nutrition*, Canberra, Australia, pp 363-366
Morrissey J, Baxter IR, Lee J, Li L, Lahner B, Grotz N, Kaplan J, Salt DE, Guerinot ML (2009) The ferroportin metal efflux proteins function in iron and cobalt homeostasis in *Arabidopsis. The Plant Cell* **21**, 3326-3338
Mortvedt JJ, Giordano PM (1972) Micronutrients in agriculture. In: Lindsay WL (Ed) *Soil Science Society of America*, Madison, Wisc., USA
Murthy IYLN (2006) Boron studies in major oilseed crops. *Indian Journal of Fertilisers* **1**, 11-20
Nable RO (1988) Resistance to boron toxicity amongst several barley and wheat cultivars: A preliminary examination of the resistance mechanism. *Plant and Soil* **112**, 45-57
Nable RO (1989) Effects of boron toxicity upon the mineral nutrient composition of barley and wheat cultivars. Divisional Report, Division of Soils, CSIRO **104**, 17 pp
Nable RO, Banuelos GS, Paull JG (1997) Boron toxicity. *Plant and Soil* **193**, 181-198
Niaz A, Muhammad A, Fiaz A (2008) Boron toxicity in irrigated cotton (*Gossypium hirsutum* L.). *Pakistan Journal of Botany* **40**, 2443-2452
Norvell WA (1991) Reactions of metal chelates in soils and nutrient solutions. In: Mortvedt JJ, Cox FR, Shuman LM, Welch RM (Eds) *Micronutrients in Agriculture* (2nd Edn), Soil Science Society of America, Madison, pp 187-227
Nuttall JG, Armstrong RD, Connor DJ (2006) Early growth of wheat is more sensitive to salinity than boron at levels encountered in alkaline soils of south-eastern Australia. *Australian Journal of Experimental Agriculture* **46**, 1507-1514
Ochiai K, Uemura S, Shimizu A, Okumoto Y, Matoh T (2008) Boron toxicity in rice (*Oryza sativa* L.). I. Quantitative trait locus (QTL) analysis of tolerance to boron toxicity. *Theoretical and Applied Genetics* **117**, 125-133
Oorts K, Ghesquiere U, Smolders E (2007) Leaching and aging decrease nickel toxicity to soil microbial processes in soils freshly spiked with nickel chloride. *Environmental Toxicology and Chemistry* **26**, 1130-1138
Oz MT, Ylmaz R, Eyidogan F, Graaff Lde, Yucel M, Oktem HA (2009) Microarray analysis of late response to boron toxicity in barley (*Hordeum vulgare* L.) leaves. *Turkish Journal of Agriculture and Forestry* **33**, 191-202
Palit S, Sharma A, Talukder G (1994) Effect of cobalt on plants. *Botanical Review* **60**, 149-181
Pandey N, Archana (2009) Boron-stress induced changes in water status and stomatal morphology in *Zea mays* L. and *Catharanthus roseus* L. *Indian Journal of Plant Physiology* **14**, 310-314
Pandolfini T, Gabbrielli R, Ciscato M (1996) Nickel toxicity in two durum wheat cultivars differing in drought sensitivity. *Journal of Plant Nutrition* **19**, 1611-1627
Pandolfini T, Gabbrielli R, Comparini C (1992) Nickel toxicity and peroxidase activity in seedlings of *Triticum aestivum* L. *Plant, Cell and Environment* **15**, 719-725
Parsons JG, Lopez ML, Gonzalez CM, Peralta-Videa JR, Gardea-Torresdey JL (2010) Toxicity and biotransformation of uncoated and coated nickel hydroxide nanoparticles on mesquite plants. *Environmental Toxicology and Chemistry* **29**, 1146-1154
Paull JG, Cartwright B, Rathjen AJ (1988) Response of wheat and barley genotypes to toxic concentrations of soil boron. *Euphytica* **39**, 137-144
Paull JG, Rathjen AJ, Cartwright B (1991) Major gene control of tolerance of bread wheat (*Triticum aestivum* L.) to high concentrations of soil boron. *Euphytica* **55**, 217-228
Pavan MA, Bingham EFT (1982) Toxicity of metals in plants II. Nickel toxicity in coffee. *Pesquisa Agropecuaria Brasileira* **17**, 323-328
Peterson CA, Rauser WE (1979) Callose deposition and photoassimilate export in *Phaseolus vulgaris* exposed to excess cobalt, nickel, and zinc. *Plant Physiology* **63**, 1170-1174
Piccini DF, Malavolta E (1992) Nickel toxicity in rice and beans on acid soil. *Revista Brasileira de Ciência do Solo* **16**, 229-233
Pilon-Smits EAH, Quinn CF, Tapken W, Malagoli M, Schiavon M (2009) Physiological functions of beneficial elements. *Current Opinion in Plant Biology* **12**, 267-274
Polacco JC (1977) Is nickel a universal component of plant ureases? *Plant Science Letters* **10**, 249-255
Rahman H, Shamima S, Shah A, Kawai S (2005) Effects of nickel on growth and composition of metal micronutrients in barley plants grown in nutrient solution. *Journal of Plant Nutrition* **28**, 393-404
Rani C, Sharma PK, Kumar B, Angrish R, Datta KS (2008) Alleviation of boron-salt toxicity by calcium in wheat through associated changes in antioxidant defense system. *Indian Journal of Plant Physiology* **13**, 21-28
Rehman S, Park TI, Kim YJ, Seo YW, Yun SJ (2006) Inverse relationship between boron toxicity tolerance and boron contents of barley seed and root. *Journal of Plant Nutrition* **29**, 1779-1789
Reid R (2007) Identification of boron transporter genes likely to be responsible for tolerance to boron toxicity in wheat and barley. *Plant and Cell Physiology* **48**, 1673-1678
Reid R (2010) Can we really increase yields by making crop plants tolerant to boron toxicity? *Plant Science* **178**, 9-11
Reid R, Kate F (2009) Influence of leaf tolerance mechanisms and rain on boron toxicity in barley and wheat. *Plant Physiology* **151**, 413-420
Reid RJ, Hayes JE, Post A, Stangoulis JCR, Graham RD (2004) A critical analysis of the causes of boron toxicity in plants. *Plant, Cell and Environment* **27**, 1405-1414
Revilla E, Ciruelos A, Apaolaza A, Sarro MJ (1985) Influence of boron toxicity on single phenols of tomato leaves. *Plant and Soil* **88**, 295-297
Rezaei H, Malakouti MJ (2001) Critical levels of iron, zinc and boron for cotton in Varamin region. *Journal of Agricultural Science and Technology* **3**, 6-10
Riley MM (1987) Boron toxicity in barley. *Journal of Plant Nutrition* **10**, 2109-2115
Riley MM, Robson AD (1994) Pattern of supply affects boron toxicity in barley. *Journal of Plant Nutrition* **17**, 1721-1738
Roessner U, Patterson JH, Forbes MG, Fincher GB, Langridge P, Bacic A (2006) An investigation of boron toxicity in barley using metabolomics. *Plant Physiology* **142**, 1087-1101
Rooney CP, Zhao F-J, McGrath SP (2007) Phytotoxicity of nickel in a range of European soils: Influence of soil properties, Ni solubility and speciation. *Environmental Pollution* **145**, 596-605
Rout GR, Das P (2002) Rapid hydroponic screening for molybdenum tolerance in rice through morphological and biochemical analysis. *Rostlinna Vyroba* **48**, 505-512
Ruiz JM, Rivero RM, Romero L (2006) Boron increases synthesis of glutathione in sunflower plants subjected to aluminium stress. *Plant and Soil* **279**, 25-30
Ruiz JM, Rivero RM, Romero L (2007) Comparative effect of Al, Se, and Mo toxicity on NO_3^- assimilation in sunflower (*Helianthus annuus* L.) plants. *Journal of Environmental Management* **83**, 207-212
Sale LY, Naeth MA, Chanasyk DS (1996) Growth response of barley on unweathered fly ash-amended soil. *Journal of Environmental Quality* **25**, 684-691
Samarakoon AB, Rauser WE (1979) Carbohydrate levels and photoassimilate export from leaves of *Phaseolus vulgaris* exposed to excess cobalt, nickel, and zinc. *Plant Physiology* **63**, 1165-1169
Sanz A, Llamas A, Ullrich CI (2009) Distinctive phytotoxic effects of Cd and Ni on membrane functionality. *Plant Signal and Behaviour* **4**, 980-982
Schnurbusch T, Collins NC, Eastwood RF, Sutton T, Jefferies SP, Langridge P (2007) Fine mapping and targeted SNP survey using rice-wheat gene colinearity in the region of the *Bo1* boron toxicity tolerance locus of bread wheat. *Theoretical and Applied Genetics* **115**, 451-461
Schnurbusch T, Langridge P, Sutton T (2008) The *Bo1*-specific PCR marker AWW5L7 is predictive of boron tolerance status in a range of exotic durum and bread wheat. *Genome* **51**, 963-971
Schnurbusch T, Hayes J, Hrmova M, Baumann U, Ramesh SA, Tyerman SD, Langridge P, Sutton T (2010) Boron toxicity tolerance in barley through reduced expression of the multifunctional aquaporin HvNIP2;1. *Plant Physiology* **153**, 1706-1715
Seregin IV, Kozhevnikova AD, Kazyumina EM, Ivanov VB (2003) Nickel toxicity and distribution in maize roots. *Russian Journal of Plant Physiology* **50**, 711-717
Shukla R (2010) Nickel level and toxicity and metabolism of potato. *International Journal of Vegetable Science* **16**, 160-166
Shukla R, Gopal R (2009) Excess nickel alters growth, metabolism, and translocation of certain nutrients in potato. *Journal of Plant Nutrition* **32**, 1005-1014
Singh AL (1994) Micronutrient nutrition and crop productivity in groundnut. In: Singh K, Purohit SS (Eds) *Plant Productivity under Environmental Stress*, Agro Botanical Publishers India, Bikaner, India, pp 67-72
Singh AL (2000) Mechanism of Tolerance and Crop Production in acid Soils. In: Hemantaranjan A (Ed) *Advances in Plant Physiology (Vol III), Plant Physiology, Biochemistry and Plant Molecular Biology 2000*, Scientific Publishers (India), Jodhpur, India, pp 353-394
Singh AL (2006) Macronutrient stresses and their management in crop plants. In: Trivedi PC (Ed) *Advances in Plant Physiology*, IK. International Publishing House Pvt. Ltd, New Delhi, India, pp 198-234
Singh AL (2008) Mineral stresses and crop productivity. In: *International Symposium on Natural Resource Management in Agriculture*, Agricultural Research Station, RAU, Durgapura, Jaipur, pp 9-23
Singh AL, Basu MS, Singh NB (2004) *Mineral Disorders of Groundnut*, National Research Centre for Groundnut (ICAR), Junagadh, India, 85 pp
Singh AL, Chaudhari V (1992) Enzymatic studies in relation to micronutrient deficiencies and toxicities in groundnut. *Plant Physiology and Biochemistry* **19**, 107-109
Singh AL, Chaudhari V, Basu MS (2007) Boron deficiency and its nutrition of groundnut in India. In: Xu F, Goldbach H, Brown PH, Bell RW, Fujiwara T,

Hunt CD, Goldberg S, Lei Shi (Eds) *Advances in Plant and Animal Boron Nutrition*. Springer Publishers, pp 149-162

Singh AL, Hariprasanna K, Solanki RM (2008) Screening of groundnut genotypes for tolerance of salinity stress. *Australian Journal Crop Science* **1**, 69-77

Singh BP, Singh B, Singh BN (1989) Influence of phosphorus and boron on picking behaviour and quality of French-bean (*Phaseolus vulgaris*), under limited irrigation, grown in Alfisol deficient in P and B. *Indian Journal of Agricultural Sciences* **59**, 541-543

Singh S, Kayastha AM, Asthana RK, Singh SP (2004) Response of garden pea to nickel toxicity. *Journal of Plant Nutrition* **27**, 1543-1560

Sinha P, Dube BK, Chatterjee C, Sinha P (2002) Influence of boron stress on biomass, yield, metabolism and quality of groundnut. *Indian Journal of Plant Physiology* **7**, 131-134

Sinha P, Dube BK, Singh MV, Chatterjee C (2006) Effect of boron stress on yield, biochemical parameters and quality of tomato. *Indian Journal of Horticulture* **63**, 39-43

Sinha P, Nautiyal N, Khurana N, Gupta S (2009) Development and physiological response of bittergourd to boron level. *International Journal of Vegetable Science* **15**, 303-311

Sonmez O, Aydemir S, Kaya C (2009) Mitigation effects of mycorrhiza on boron toxicity in wheat (*Triticum durum*) plants. *New Zealand Journal of Crop and Horticultural Science* **37**, 99-104

Soudek P, Katrusáková A, Sedlácek L, Petrová S, Kocí V, Marsík P, Griga M, Vanek T (2010) Effect of heavy metals on inhibition of root elongation in 23 cultivars of flax (*Linum usitatissimum* L). *Archives of Environmental Contamination and Toxicology* **59**, 194-203

Sotiropoulos TE, Therios IN, Dimassi KN (2006) Seasonal accumulation and distribution of nutrient elements in fruit of kiwifruit vines affected by boron toxicity. *Australian Journal of Experimental Agriculture* **46**, 1639-1644

Stadt KJ, Taylor GJ, Dale MRT (1994) Measuring the effect of an abiotic stress on competition. *Oecologia* **100**, 221-228

Sutton T, Baumann U, Hayes J, Collins NC, Shi BJ, Schnurbusch T, Hay A, Mayo G, Pallotta M, Tester M, Langridge P (2007) Boron toxicity tolerance in barley arising from efflux transporter amplification. *Science Washington* **318**, 1446-1449

Tahkokorpi M, Korteniemi A, Taulavuori E, Roitto M, Laine K, Huttunen S, Taulavuori K (2010) Trace amounts of nickel in belowground rhizomes of *Vaccinium myrtillus* l. Decrease anthocyanin concentrations in aerial shoots without water stress. *Environmental and Experimental Botany* **69**, 338-342

Takano J, Miwa K, Fujiwara T (2008) Boron transport mechanisms: Collaboration of channels and transporters. *Trends in Plant Science* **13**, 451-457

Temple PJ, Bisessar S (1981) Uptake and toxicity of nickel and other metals in crops grown on soil contaminated by a nickel refinery. *Journal of Plant Nutrition* **3**, 473-482

Torun AA, Yazc A, Erdem H, Cakmak I (2006) Genotypic variation in tolerance to boron toxicity in 70 durum wheat genotypes. *Turkish Journal of Agriculture and Forestry* **30**, 49-58

Torun B, Kalayci M, Ozturk L, Torun A, Aydin M, Cakmak I (2003) Differences in shoot boron concentrations, leaf symptoms, and yield of Turkish barley cultivars grown on boron-toxic soil in field. *Journal of Plant Nutrition* **26**, 1735-1747

Turner AP (1994) The responses of plants to heavy metals. In: Ross SM (Ed) *Toxic Metals in Soil-Plant Systems*, John Wiley and Sons, Chichester, pp 153-187

Vargas A, Arias F, Serrano E, Arias MO (2007) Boron toxicity in banana (*Musa* AAA) plantations of Costa Rica. *Agronomia Costarricense* **31**, 21-29

Vivas A, Biro B, Nemeth T, Barea JM, Azcon R (2006) Nickel-tolerant *Brevibacillus brevis* and arbuscular mycorrhizal fungus can reduce metal acquisition and nickel toxicity effects in plant growing in nickel supplemented soil. *Soil Biology and Biochemistry* **38**, 2694-2704

Wallace A, Romney EM, Alexander GV (1981) Multiple traces element toxicities in plants. *Journal of Plant Nutrition* **3**, 257-263

Wang HH, Feng T, Peng X, Yan ML, Tang XK (2009) Up-regulation of chloroplastic antioxidant capacity is involved in alleviation of nickel toxicity of *Zea mays* L. by exogenous salicylic acid. *Ecotoxicology and Environmental Safety* **72**, 1354-1362

Wang BL, Shi L, Li YX, Zhang WH (2010) Boron toxicity is alleviated by hydrogen sulfide in cucumber (*Cucumis sativus* L.) seedlings. *Planta* **231**, 1301-1309

Warington K (2008) The influence of high concentrations of ammonium and sodium molybdates on flax, soybean and peas grown in nutrient solutions containing deficient or excess iron. *Annals of Applied Biology* **43**, 709-719

Watanabe T, Broadley MR, Jansen S, White PJ, Takada J, Satake K, Takamatsu T, Tuah SJ, Osaki M (2007) Evolutionary control of leaf element composition in plants. *New Phytologist* **174**, 516-523

Whitehead DC (2000) *Nutrient Elements in Grasslands: Soil-Plant-Animal Relationships*, CABI Publishing, Wallingford 369 pp

Wimmer MA, Muehling KH, Lauchli A, Brown PH, Goldbach HE (2001) Interaction of salinity and boron toxicity in wheat (*Triticum aestivum* L.). In: Horst WJ, Schenk MK, Burkert A, Claassen N, Flessa H, Frommer WB, Goldbach H, Olfs HW, Romheld V (Eds) *Plant Nutrition Food Security and Sustainability of Agro Ecosystems through Basic and Applied Research. 14th International Plant Nutrition Colloquium*, July 27-August 3, 2001, Hannover, Germany, pp 426-427

Wu Y, Hendershot WH (2010) The effect of calcium and pH on nickel accumulation in and rhizotoxicity to pea (*Pisum sativum* L.) root-empirical relationships and modeling. *Environmental Pollution* **158**, 1850-1856

Yadav R, Kumar J, Jain V, Singh IB, Mishra JP, Kumar R (2007) Nickel dose for development of mapping population for nickel resistance in chickpea (*Cicer arietinum* L.). *Indian Journal of Crop Science* **2**, 399-402

Yadav SS, Rajni S, Sharma YK (2009) Nickel toxicity on seed germination and growth in radish (*Raphanus sativus*) and its recovery using copper and boron. *Journal of Environmental Biology* **30**, 461-466

Yan R, Gao S, Yang W, Cao M, Wang S, Chen F (2008) Nickel toxicity induced antioxidant enzyme and phenylalanine ammonia-lyase activities in *Jatropha curcas* L. cotyledons. *Plant Soil and Environment* **54**, 294-300

Yang X, Baligar VC, Martens DC, Clark RB (1996) Plant tolerance to nickel toxicity: I. Influx, transport, and accumulation of nickel in four species. *Journal of Plant Nutrition* **19**, 73-85

Yang X, Baligar VC, Martens DC, Clark RB (1996) Plant tolerance to nickel toxicity: II. Nickel effects on influx and transport of mineral nutrients in four plant species. *Journal of Plant Nutrition* **19**, 265-279

Yau SK (1997) Differential responses of barley, durum and bread wheat to high levels of soil boron. In: Ryan J (Ed) *Accomplishments and Future Challenges in Dryland Soil Fertility Research in the Mediterranean Area*, Institute Mondial du Phosphate, Casablanca, Morocco, and ICARDA, Aleppo, Syria, pp 208-216

Yau SK (2010) Boron toxicity in barley genotypes: Effects of pattern and timing of boron application. *Communications in Soil Science and Plant Analysis* **41**, 144-154

Yau SK, Erskine W (2000) Diversity of boron-toxicity tolerance in lentil. *Genetic Resources and Crop Evolution* **47**, 55-61

Yau SK, Nachit MM, Ryan J (1997) Variation in boron toxicity tolerance in a durum wheat core collection. In: Bell RW, Rerkasem B (Eds) *Boron in Soils and Plants*, Kluwer Academic Publishers, Dordrecht, the Netherlands, pp 117-120

Yau SK, Ryan J (2008) Boron toxicity tolerance in crops: A viable alternative to soil amelioration. *Crop Science* **48**, 854-865

Yermiyahu U, Ben GA, Keren R, Reid RJ (2008) Combined effect of salinity and excess boron on plant growth and yield. *Plant and Soil* **304**, 73-87

Yermiyahu U, Ben GA, Sarig P (2006) Boron toxicity in grapevine. *HortScience* **41**, 1698-1703

Yermiyahu U, Ben GA, Sarig P, Zipilevitch E (2007) Boron toxicity in grapevine (*Vitis vinifera* L.) in conjunction with salinity and rootstock effects. *Journal of Horticultural Science and Biotechnology* **82**, 547-554