

Beneficial and Toxic Effects of Nickel in Relation to Medicinal and Aromatic Plants

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ABSTRACT

Nickel (Ni) is a constituent of urease, and small quantities of Ni (0.01 to 5 g/g dry weight) are essential for some plant species. Ni has been considered as an essential micronutrient, which is required by urease for hydrolysing urea. Ni has a role in plant growth and N uptake in crops supplied with urea in calcareous soils. Ni deficiency affects plant growth, plant senescence, nitrogen metabolism, and iron uptake and it may play a role in disease resistance. Ni is absorbed and redistributed in plants *via* cation and/or metal-ligand complex transport systems. However, excessive Ni inhibits growth and development of plants, induces leaf chlorosis and wilting, and reduces total plant yields. Several investigators have performed several studies on the residual levels of heavy metals (HMs) in medicinal herbs. According to a study, the level of essential elements in MAPs is conditional, being affected by the geochemical characteristics of the soil and by the ability of plants to selectively accumulate some of these elements. The use of hyperaccumulators or wetland plants to remove and/or sequester Ni from soil and water has been proposed by various workers. The accumulation of HMs such as Ni in some desert plants may open a new perspective for the application of these species as ‘accumulators’ of HMs to clean-up contaminated soils in dry environments. The researchers still debate over the causes and mechanisms of hyperaccumulation, which may depend on the morphological and physiological characteristics of particular plant species and the capacity of Ni to overcome the physiological barriers. We have reviewed the information regarding occurrence, sources, essentiality, toxicity and tolerance of Ni regarding medicinal and aromatic plants (MAPs), supporting our view discussing the effects of Ni on other plants.

Keywords: distribution, essentiality, hyperaccumulators, MAPs, Ni, toxicity

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INTRODUCTION

Currently a metal is considered to be an essential nutrient when plants cannot complete their life cycle in its absence and it cannot be substituted with any other nutrient (Eskew *et al.* 1993; Andreeva *et al.* 2001). Ni is a constituent of urease, and small quantities of Ni (0.01 to 5 g/g dry weight) are essential for some plant species. On the other hand, Ni is not as important for plant metabolism as Zn and Cu. However, as with other heavy metals (HMs), high Ni concentrations may become toxic to plants. Ni was discovered in 1975 as a component of the enzyme urease, which is present in a wide range of plant species (Takishima *et al.* 1988). Since then, there has been renewed scientific interest and research concerning the role of Ni in higher plants. Several researchers have since reported growth responses of

plants to Ni fertilization under field conditions (Takishima *et al.* 1988) and in plants grown in nutrient solutions (Gerendas *et al.* 1999) or in tissue culture media furnished with urea as the sole N source (Gerendas *et al.* 1997b). Eskew *et al.* (1983) reported that Ni-deficient soybean (*Glycine max* L.) accumulate toxic levels of urea in their leaflet tips because of a depression in urease activity in their leaves. Walker *et al.* (1985), working with cowpea (*Vigna unguiculata* L. Walp), suggested that Ni (and urease) participates in N metabolism of legumes during the reproductive phase of growth. Checkai *et al.* (1986) reported that Ni-deficient tomato plants (*Lycopersicon esculentum* L.) developed chlorosis in the newest leaves and, ultimately, necrosis of the meristem. The earliest report of a growth response to Ni addition under controlled experimental conditions (Brown *et al.* 1987b) indicated that Ni deficiency has a wide range

of effects on plant growth and metabolism (Marschner 2000; Bai *et al.* 2006; Seregin and Kozhevnikova 2006; Ali *et al.* 2009; Chen *et al.* 2009; Yusuf *et al.* 2011). These include effects on (a) plant growth, (b) plant senescence, (c) N metabolism, and (d) Fe uptake. Preliminary investigations also indicate that Ni may have a role in phytoalexin synthesis and plant disease resistance (Graham *et al.* 1985). Thus, low levels of Ni are known to be beneficial to plant growth. Previously, however, no study satisfied all of the essential criteria for establishment of Ni as an essential element for all higher plants. For an element to be proven essential, one must demonstrate that a plant cannot complete its life cycle in the absence of the element, and that no other element can substitute for the test element (Arnon and Stout 1939). Ni satisfies these criteria and, therefore, should be classified as a micronutrient element essential for all higher plant growth, including medicinal and aromatic plants (MAPs).

The roles of Ni in plant metabolism remain mostly unknown. The broad range of effects attributable to Ni deficiency suggests that it may be involved in several physiological processes. These may include the transport of nutrients to the seed or grain and movement of Fe into plant cells as well as the various metabolic effects described earlier (Eskew *et al.* 1983; Walker *et al.* 1985; Brown *et al.* 1987b). Evidence presented here, and in the literature, indicates that Ni may also have essential functions in grain maturation and plant senescence (Brown *et al.* 1987b). Ni is not likely to be deficient in experiments using conventional solution culture techniques because of contaminant-Ni in the nutrient salts used to prepare the nutrient solutions and/or in the water used for irrigation. High levels of chelating agents (e.g. EDTA), particularly when used together with low levels of Fe (Brown *et al.* 1987a) may, however, result in incipient Ni deficiency that might go unrecognized, especially when nutrient salts of very high purity are used. Under these conditions, the authors recommended that nutrient solutions be supplemented with at least 1.0 gM NiSO₄ to negate the possibility of Ni deficiency. Their evidence demonstrates that barley plants could not complete their life cycle without adequate Ni. Further, Eskew *et al.* (1983) demonstrated that Ni could not be replaced by aluminium (Al), cadmium (Cd), selenium (Sn) or vanadium (V) for the growth of soybeans. This evidence, in conjunction with the findings that Ni is essential for cowpeas, produced beneficial growth responses in oats (*Avena sativa* L.; Brown *et al.* 1987b), wheat (*Triticum aestivum* L.; Brown *et al.* 1987b), tomato (*Lycopersicon esculentum* Mill.; Checkai *et al.* 1986) and other plant species (Shimado and Ando 1980; Welch 1981), providing conclusive evidence that Ni must now be considered essential for all higher plants. This is the first micro-nutrient to be discovered to be essential since chloride (Cl) was reported to be essential in 1954 (Broyer *et al.* 1954). The significance of Ni deficiency in agriculture has yet to be investigated intensively. The potential exists, however, for low Ni availability under some soil conditions (Dalton *et al.* 1985) and therefore, Ni deficiency in food and feed crops is a possibility. Since Ni is required for normal grain development, agricultural scientists should be cognizant of the potential implications of Ni deficiency on grain quality.

OCCURRENCE AND SOURCES

Ni was the first micronutrient to be discovered as essential since Cl was added to the list in 1954. Ni, first isolated by the Swedish chemist Cronstedt in 1751, is the 22nd most abundant element in the earth's crust (Sunderman and Oskarsson 1991), where it occurs in igneous rocks as a free metal or together with iron (Fe). It is the 24th most abundant element in the Earth's crust, comprising about 3% of the composition of the earth. It is the 5th most abundant element by weight after Fe, oxygen (O), magnesium (Mg) and silicon (Si). It has an atomic number of 28 in the periodic table and an atomic weight of 58.71. Ni is a hard,

ductile and silvery-white HM that can take a high polish. In general, naturally occurring concentrations of Ni in soil and surface waters are lower than 100 and 0.005 ppm, respectively (McIlveen and Negusanti 1994; McGrath 1995). Ni is also released into the environment from anthropogenic activities, such as metal mining, smelting, fossil fuel burning, vehicle emissions, disposal of household, municipal and industrial wastes, fertilizer application and organic manures (Alloway 1995; Salt and Krämer 2000). Ni is mainly used as a raw material in the metallurgical and electroplating industries, as a catalyst in the chemical and food industry, and as a component of electrical batteries (Easton *et al.* 1992). In recent years, Ni pollution has been reported from across the world, including Asia (Zarcinas *et al.* 2004; Ahmad *et al.* 2007; Zhao *et al.* 2008; Ali *et al.* 2009; Chen *et al.* 2009; Yusuf *et al.* 2011), Europe (Anderson 1992; Kozlov 2005; Papadopoulos *et al.* 2007) and North America (Kukier *et al.* 2004). Pollution mainly results from effluent disposal from mining, smelting and electroplating industries, and from sewage sludge and compost (Barcan and Kovnatsky 1998). Ni concentrations may reach 26,000 ppm in polluted soils (Alloway 1995; McGrath 1995) and 0.2 mg/L in polluted surface waters (Guo and Marschner 1995); 20 to 30 times higher than found in unpolluted areas. Soil and water contamination with Ni has become a worldwide problem (Guo and Marschner 1995; Salt *et al.* 1995).

Ni is one of many trace metals widely distributed in the environment, being released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material. Natural sources of atmospheric Ni levels include wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation. Ni finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources (Clayton and Clayton 1994; Wuana and Okieimen 2011).

Ni is generally distributed uniformly through the soil profile but typically accumulates at the surface from deposition by industrial and agricultural activities. It may present a major problem in land near towns, in industrial areas, or even in agricultural land receiving wastes such as sewage sludge. Its content in soil varies in a wide range from 3 to 1000 mg/kg (Bencko 1983; Scott-Fordsmand 1997; Salt and Krämer 2000; Chen *et al.* 2009). Ni can exist in soils in several forms: inorganic crystalline minerals or precipitates, complexed or adsorbed on organic cation surfaces or on inorganic cation exchange surfaces, water-soluble, free-ion or chelated metal complexes in soil solution (Bennett 1982; Scott-Fordsmand 1997). This metal apparently does not seem to be a major concern outside urban areas at this time but may eventually become a problem as a result of decreased soil pH caused by reduced use of soil liming in agriculture and mobilization as a consequence of increased acid rain (Bencko 1983; Scott-Fordsmand 1997; Karagianidis *et al.* 2002; Seregin and Kozhevnikova 2006; Gad *et al.* 2007; Ali *et al.* 2009; Chen *et al.* 2009; Ezeh and Chukwu 2011; Sabir *et al.* 2011; Yusuf *et al.* 2011). Mielke *et al.* (2000) investigated the effect of anthropogenic metals on the geochemical quality of urban soils.

Ni: Essentiality, toxicity and tolerance in medicinal and aromatic plants

Marschner (1995) listed Ni as an essential micronutrient, which is required by urease for hydrolysing urea. Singh *et al.* (1990) observed an improvement in plant growth and N uptake of wheat (*Triticum aestivum* L.) from urea by Ni application on a calcareous soil. Several investigators have also shown beneficial effects of Ni on urease activity and improving N use efficiency by plants in hydroponic studies (Gerendas and Sattelmacher 1999; Gerendas *et al.* 1999). However, deficiency of Ni in soils has rarely been reported (Dalton *et al.* 1985). Brown *et al.* (1987a) showed that Ni deficiency affects plant growth, plant senescence, nitrogen

Table 1 Concentration of Ni present in the medicinal plants of Ghana region.

Family	Species	Common use	Formulation	Ni concentration
Euphorbiaceae	<i>Alchornea cordifolia</i>	Septicemia	Decoction	Nd
Nyctaginaceae	<i>Boerhavia diffusa</i>	Fevers	Infusion	Nd
Casealpiniaceae	<i>Cassia siamea</i>	Pains	Decoction	16.5 ± 0.005
Lauraceae	<i>Cinnamomum zeylanicum</i>	Dyspepsia	Decoction	Nd
Rutaceae	<i>Clausena anisata</i>	Diabetes	Decoction	25.0 ± 0.012
Papilionaceae	<i>Desmodium adscendens</i>	Jaundice	Decoction	13.5 ± 0.002
Boraginaceae	<i>Gymnema sylvestre</i>	Diabetes	Decoction	Nd
Euphorbiaceae	<i>Heliotropium indicum</i>	Convulsion	Decoction	Nd
Verbenaceae	<i>Jatropha gossypifolia</i>	Migraine	Decoction	Nd
Verbenaceae	<i>Lippia multiflora (Ateububu)</i>	Hypertension	Infusion	14.0 ± 0.010
Verbenaceae	<i>Lippia multiflora kaso</i>	Hypertension	Infusion	Nd
Verbenaceae	<i>Lippia multiflora (kadjebi)</i>	Hypertension	Infusion	Nd
Lamiaceae	<i>Ocimum basilicum (ABF017)</i>	Flatulence	Infusion	36.5 ± 0.000
Lamiaceae	<i>Ocimum basilicum (ABF042)</i>	Flatulence	Infusion	Nd
Lamiaceae	<i>Ocimum basilicum (2)</i>	Flatulence	Infusion	23.0 ± 0.013
Lamiaceae	<i>Ocimum canum (8)</i>	Flatulence	Infusion	Nd
Lamiaceae	<i>Ocimum gratissimum</i>	Flatulence	Infusion	Nd
Lamiaceae	<i>Ocimum sanctum (1)</i>	Flatulence	Infusion	Nd
Asclepiadaceae	<i>Pergularia daemia</i>	Pneumonia	Decoction	Nd
Euphorbeaceae	<i>Phyllanthus amarus</i>	Thrush	Decoction	Nd
Apocynaceae	<i>Rauwolfia vomitoria</i>	Insomnia	Decoction	Nd
Meliaceae	<i>Turrea heterophylla</i>	Impotence	Decoction	Nd
Asteraceae	<i>Vernonia amygdilina</i>	Diabetes	Decoction	3.5 ± 0.000
Apocynaceae	<i>Vinca roseus</i>	Jaundice	Decoction	Nd
Apocynaceae	<i>Vocanga africana</i>	Dental Caries	Decoction	Nd
Rutaceae	<i>Zanthoxylum xanthoxyloides</i>	Impotence	Decoction	Nd
LSD (0.05)				0.012

Source: modified from Annan *et al.* (2010)

Data are mean ± SD ($\mu\text{g/g}$) of n=3. LSD (0.05) was also employed; Nd = below detection limit

(N) metabolism, and Fe uptake and may play a role in disease resistance.

Ni is essential for plants (Eskew *et al.* 1983; Brown 1987a; Ragsdale 1998), but the concentration in the majority of plant species is very low (0.05–10 mg/kg dry weight) (Nieminen *et al.* 2007). Further, with increasing Ni pollution, excess Ni rather than a deficiency, is more commonly found in plants (Alloway 1995; Salt and Krämer 2000). Toxic effects of high concentrations of Ni in plants have been frequently reported, for example inhibition of mitotic activity of pigeonpea (*Cajanus cajan* (L.) Millspagh) (Madhava Rao and Sresty 2000), reductions in plant growth of cabbage (*Brassica oleracea*) (Molas 2002) and adverse effects on fruit yield and quality of wheat (*Triticum aestivum* L.) (Gajewska *et al.* 2006). Extremely high soil Ni concentrations have left some farmland unsuitable for growing crops, fruits and vegetables of Lisbon, Portugal (Duarte *et al.* 2007).

Accumulation and distribution of Ni in medicinal and aromatic plants

There are two major reasons (De Smet 1993) for monitoring the levels of toxic metals in MAPs. The first reason, contamination of the general environment with toxic metals, has increased (Ali 1983). Several studies on the residual levels of toxic metals have been conducted in Egyptian MAPs (Schilcher 1982; Ali 1983, 1987; Schilcher *et al.* 1987; Abou-Arab and Abou Donia 2000). The highest Ni concentration (120 μM) particularly affected the leaf content of mineral nutrients (e.g., decrease in K and increase in Fe) and activities of selected antioxidative enzymes (34 and 135% increase of ascorbate peroxidase (APX, EC 1.11.1.11 and guaiacol peroxidase (GPX, EC 1.11.1.7)) of chamomile (*Matricaria chamomilla* L.) roots. Malondialdehyde accumulation was not influenced. Among 17 detected free amino acids, the accumulation of histidine, proline, methionine, and cysteine was most distinct in the leaf rosettes and/or roots, indicating their involvement in Ni detoxification (Kováčik *et al.* 2009). Annan *et al.* (2010) reported that the concentration of Ni present was rarely detected in Ghanaian MAPs (Table 1). Narendhirakannan *et al.* (2005) re-

ported that certain inorganic trace elements such as Ni play an important role in maintaining normoglycemia by activating the β -cells of the pancreas. The level of Ni in the leaves of four MAPs (*Murraya koenigii*, *Mentha piperitae*, *Ocimum sanctum* and *Aegle marmelos*) was 0.9, 1.01, 0.73 and 0.81 μg , respectively (Narendhirakannan *et al.* 2005). These MAPs are widely used in the treatment of diabetes-related metabolic disorders. In another study conducted at Manipur (India), Ni concentration in *Catharanthus roseus*, *Embillica officinalis*, *Azadirachta indica*, *Solanum anguivi*, *Artemisia nilagirica* and *Elsholtzia communis* was 6.8 ± 18.4, 7.0 ± 12.8, 4.1 ± 24.9, 4.1 ± 20.9, 5.6 ± 20.0 and 7.6 ± 16.0, respectively (Singh *et al.* 2010). According to Abudarwish *et al.* (2009), the level of essential elements in MAPs is conditional, being affected by the geochemical characteristics of the soil and by the ability of plants to selectively accumulate some of these elements. Their study showed that thyme (*Thymus serpyllum*) grown in northern (Jeresh) and southern (Al-Karak, Al-Shouback and Aqaba) regions of Jordan are characterized by low HM contents without Ni contamination and can safely be used for pharmaceutical and edible purposes without any hazardous effect on human health. Prasad *et al.* (2008) reported the beneficial effects of a foliar application of a 0.5% aqueous solution of nickel sulphate ($\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) on the chemical composition and yield of essential oil of rose-scented geranium (*Pelargonium* sp. cultivar 'CIM-Pawan'). They noted that the content of linalool, geraniol and 10-*epi*-eudesmol in the geranium oil significantly increased and that of geraniol and β -bourbonene decreased after the application of $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ compared to control plants. The content of linalool and geraniol increased 54.2 and 38.8% more than the control, respectively. The level of *cis*- and *trans*-rose oxide in geranium oil significantly increased and that of neral decreased after the application of $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ compared to the control (Table 2). Furthermore, they also reported significant increase caused by $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ on herbage and essential oil yield (21.6 and 41.9%, respectively more than the control) (Table 2). The accumulation of HMs such as Ni in some desert plants may open a new perspective for the application of these species as 'accumulators' of HMs to clean-up contaminated soils in arid environments (Sathiy-

Table 2 Effect of foliar application of nickel sulphate on the composition of essential oil of geranium (*Pelargonium* spp.).

Compounds	RI ^a	RI ^b	Control	Nickel sulphate	Identification
<i>Cis</i> -3-Hexanol	860	857	0.11 ± 0.006	0.13	GC-MS
Linalool	1101	1098	1.20 ± 0.06	1.85	GC-MS, CO-GC
<i>Cis</i> -rose oxide	1113	1111	1.67 ± 0.04	2.15	GC-MS, CO-GC
<i>Trans</i> -rose oxide	1129	1127	0.90 ± 0.03	1.07	GC-MS, CO-GC
Isomenthol	1168	1164	8.16 ± 0.92	8.15	GC-MS, CO-GC
Neo-isomenthol	1186	1188	0.34 ± 0.06	0.28	GC-MS
Citronellol	1231	1228	44.46 ± 1.90	42.57	GC-MS, CO-GC
Neral	1242	1240	0.64 ± 0.04	0.50	GC-MS, CO-GC
Geranial	1255	1255	8.84 ± 1.02	12.27	GC-MS, CO-GC
Geranial	1270	1275	1.88 ± 0.19	1.48	GC-MS, CO-GC
Citronellyl formate	1274	1270	8.94 ± 0.44	9.12	GC-MS, CO-GC
Geranyll formate	1300	1300	1.95 ± 0.09	1.91	GC-MS, CO-GC
β -Bourbonene	1392	1384	0.57 ± 0.01	0.42	GC-MS
2-phenylethyl tiglate	1581	1584	1.56 ± 0.015	1.36	GC-MS
10-epi-Eudesmol	1623	1619	4.22 ± 0.44	5.22	GC-MS
Geranyl tiglate	1693	1700	1.46 ± 0.15	1.40	GC-MS, CO-GC

Source: Modified from Prasad *et al.* (2008)

RI^a, Retention indices relative to C₉-C₂₄ n-alkanes on the Equity-5 column

RI^b, values from literature data

GC-MS, identification based on comparison of mass spectra

CO-GC, retention time identical to authentic compounds

moorthy *et al.* 1997; **Table 3**). Abou-Arab and Abou Donia (2000) reported the concentration of Ni in several Egyptian MAPs viz. geranium (*Pelargonium graveolens* L.) (1.1 ± 0.6 µg/g), basil (*Ocimum basilicum* L.) (2.85 ± 0.85 µg/g), marjoram (*Marjorana hortensis* L.) (2.15 ± 0.99 µg/g) peppermint (*Mentha piperita* L.) (0.96 ± 0.14 µg/g) spearmint (*Mentha viridis*) (1.45 ± 0.49 µg/g), Jew's mallow (*Corchorus olitorius*) (0.61 ± 0.26 µg/g), dill (*Anethum graveolens* L.) (1.59 ± 0.69 µg/g), celery (*Apium graveolens* Mill.) (0.64 ± 0.22 µg/g), parsley (*Petroselinum sativum* Hoffm.) (1.93 ± 0.64 µg/g), cumin (*Cuminum cyminum* L.) (0.74 ± 0.20 µg/g) and tea (*Thea sinensis* Linn.) (1.9 ± 0.3 µg/g). Skoula *et al.* (2003) studied Ni uptake in flowers, roots and leaves of chamomile, sage (*Salvia officinalis*) and thymus (*Thymus vulgaris*) (**Table 4**). Yan *et al.* (2008) reported that there is an imbalance between ROS-generating and scavenging enzymes under Ni stress; SOD (Superoxide dismutase, EC 1.15.1.1), POD (Peroxidase, EC 1.11.1.7), CAT (Catalase, EC 1.11.1.6) and PAL (Phenylalanine ammonia-lyase, EC 4.3.1.24) seemed to play an important role in regulation of ROS level upon excessive Ni in cotyledons of *Jatropha curcas* L.

Ni uptake by plants

Ni is delivered into the environment through several pathways: (1) as factory waste of high-temperature technologies of ferrous and nonferrous metallurgy, cement clinker production, and burning liquid and solid fuels; (2) field irrigation with water high in HM content and transfer of sewage residue into soil; (3) transfer of HMs from mine tailings and metallurgical factories by water and air flows; (4) steady application of high rates of organic and mineral fertilizers and pesticides contaminated with HMs (Orlov *et al.* 2002). On the average, the total Ni content in soil varies from 2 to 750 mg/kg soil, with the maximum content reported in serpentine soils (Gerendaas *et al.* 1999). The major Ni ores are garnierite [(Ni, Mg) 6Si₄O₁₀(OH)₂] and penlandite [(Ni, Fe)9S₈] (Emsley 1991). Currently few researches describe the mechanism and kinetics of Ni absorption by plants. Plant absorption of Ni, same as of other metals, may proceed due to passive diffusion and active transport. To elucidate the role of metabolic processes in Ni absorption, the rates of Ni translocation were compared at various temperatures and in relation to the aeration of nutrient solutions. At 23°C, Ni uptake by *Avena sativa* roots directly depended on the incubation period. Low temperature, such as 2°C, considerably lowered Ni absorption from the nutrient solution. The relationship between Ni absorption and temperature was described by an S-like curve, with the maximum

between 23 and 30°C. Both the addition of 20 µM 2,4-dinitrophenol to the nutrient solution and the anaerobic conditions of plant growth inhibited Ni uptake by 91 and 86%, respectively. These data presume that the metabolically active uptake considerably exceeds the passive entry of Ni ions (Aschmann and Zasoski 1987). The ratio between the inputs of active and passive components depends on Ni concentration in the nutrient solution. The former is more important at low Ni concentrations (below 34 MM), and at higher concentrations the role of passive transport mechanism increased due to Ni toxic effect (Temp 1991). The major environmental factors that affect metal uptake by plants are soil acidity, its cation exchange capacity, the contents of organic substance and lime, moisture potential, granulometric composition, and the concentrations of macro- and micro-nutrients (Aschmann and Zasoski *et al.* 1987; Merkusheva *et al.* 2001; Kukier *et al.* 2004). The effects of these factors on the uptake of many HMs are mostly nonspecific. When absorbed by roots, Ni ions may compete with other metal ions. To illustrate, the antagonistic relations were described for Ni and Zn in such hyperaccumulator species as *Thlaspi montanum*, *T. caerulescens*, *Streptanthus poligaloides* and *Dichapetalum gelonioides*, with the addition of Ni-Fe antagonism in *T. montanum*; similar antagonistic relations were reported in *Alyssum bertolonii* between Ni, Zn, and Co and in plant species that exclude HMs, such as *Glycine max* and *Hordeum vulgare*, Ni uptake declined in the presence of Cu and Zn cited after (Boyd *et al.* 1994). As a whole, the inhibitory effect of metal ions on Ni absorption and translocation from roots into shoots decreased in the following order: Fe³⁺ > Co²⁺ > Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ (Temp 1991). Such a range is in good accordance with the evidence for other HMs (Seregin and Ivanov 2001) and apparently signifies their nonspecific effect on Ni uptake. Thus, the specific mechanisms of Ni uptake have not been as yet disclosed. It is not clear whether the hyperaccumulator species acquired particular absorption mechanisms selective towards Ni and the ability to increase its accessibility. It is not known whether the tolerance of particular plant species relies on the lowered Ni uptake or, quite the reverse, depends mostly on the characteristic patterns of Ni translocation and distribution and binding Ni into insoluble complexes.

Physiological role of Ni in higher plants

In 1987, Ni was first established as a nutrient essential for completion of plant life cycle. Ni deficiency decreased the capacity of barley to develop viable seeds because of hindered embryo growth. The embryonic root developed poorly

Table 3 Nickel concentration (mg kg⁻¹ dry weight) in medicinal plants of the Negev desert of Israel.

Family	Species	Plant parts*	Medicinal uses**	***Ni concentration
Apiaceae	<i>Eryngium creticum</i> Lam	WP	Vegetable, diabetes	10.0
	<i>Deverra tortuosa</i> (Desf.) Benth	SF	Stomachache	8.6
	<i>Foeniculum vulgare</i> Mill.	SL	Cough	7.7
Aizoaceae	<i>Mesembryanthemum nodiflorum</i> L.	SL	Fungicide, constipation	15.6
Boraginaceae	<i>Anchusa strigosa</i> Boiss. & Hoheva	WP	Skin disease, wound healing	16.3
Capparaceae	<i>Capparis spinosa</i> L.	AP	Diabetes, toothache	9.6
Caryophyllaceae	<i>Gypsophila arabica</i> Barkodah	SF	Saponin drug, ornamental	6.2
	<i>Paronychia argentea</i> Lam.	AP	Kidney stones	19.3
Chenopodiaceae	<i>Anabasis articulata</i> (Forssk.) Moq.	S	Skin disease, urinary problem	6.3
	<i>Atriplex halimus</i> L.	SL	Stomach worms, fodder	6.7
Cistaceae	<i>Helianthemum ventosum</i> Boiss.	SL	Common cold, flu	12.0
Compositae	<i>Pulicaria crispa</i> (Forssk.) Oliv.	AP	Digestion problems	9.0
	<i>Seriphidium sieberi</i> (Besser)	SL	Stomach pain, blood pressure	7.6
	<i>Achillea santolina</i> Forrsk.	AP	High fever, diabetes	9.0
	<i>Achillea fragrantissima</i> Forrsk.	AP	High fever, diabetes	4.3
	<i>Gundelia tournefortii</i> L.	WP	Liver problem, allergies	3.8
	<i>Echinops polyceras</i> Boiss.	AP	Hemostatic, diaphoretic, abortive	2.6
	<i>Phugnalon rupestre</i> (L.) DC.	SF	Toothache, skin diseases	3.8
	<i>Morkandia nitens</i> (Viv.)	AP	Anti-diarrheal	5.6
Ephedraceae	<i>Ephedra aphylla</i> Forrsk.	SF	Hypertension, asthmatic	3.7
	<i>Ephedra aphylla</i> Forrsk.	S	Hypertension, asthmatic	6.3
Euphorbiaceae	<i>Mercurialis annua</i> L.	WP	Wounds, earache, cut skin	8.3
Juncaceae	<i>Juncus arabicus</i> Adamson	S	Abortive	6.0
Labiatae	<i>Teucrium polium</i> L.	AP	Diabetes, asthma, malaria	3.3
	<i>Balbia undulata</i> (Fresen.) Benth.	AP	Open wounds, scorpion bites	2.0
	<i>Phlomis brachyodon</i> Zohary	AP	Against jaundice	8.0
	<i>Salvia spinosa</i> L.	AP	Diarrhoea, piles, chest pain	5.6
	<i>Urginea maritima</i> (L.) Baker	Bb	Expectorant, abortive, tumors	2.3
Asphodelaceae	<i>Asphodelus tenuifolius</i> Cav.	Bb	Ear ache, jaundice, eye disease	10.6
Asphragaceae	<i>Asparagus aphyllus</i> L.	AP	Vegetable, digestive problems	7.3
Malvaceae	<i>Alcea acaulis</i> (Cav.) Alef	AP	Wounds, coughs	3.3
Papaveraceae	<i>Glaucium arabicum</i> Fressan	AP	Eye infections	10.3
Papilionaceae	<i>Colutea istria</i> Mill.	AP	Leaves purgative, laxative	10.3
	<i>Retama raetam</i> (Forssk.) Green	SFt	Wounds, against infertility	13.0
Polygonaceae	<i>Polygonum palaestinum</i> Delile	AP	Common plant	6.3
Resedaceae	<i>Ochrademus baccatus</i> Delile	AP	Stomachache, muscle pain	5.0
	<i>Caylusea hexagyna</i> (Forssk.) Green	AP	Common plant	2.3
Salicaceae	<i>Populus euphratica</i> Oliv.	SL	Intestinal antiseptic	1.7
Scrophulariaceae	<i>Kickxia aegyptiaca</i> (L.) Nabelek	AP	Common plant	0.8
	<i>Verbascum fruticulosa</i> Sinuatum	AP	Inflammation, eye diseases	1.7
Solanaceae	<i>Hyoscyamus reticulatus</i> L.	AP	Skin diseases, poisonous	1.8
	<i>Solanum elaeagnifolium</i> Cav.	AP	Common plant	0.5
	<i>Lycium shawii</i> Roem. & Schutt.	SL	Diuretic and laxative	2.5
	<i>Nicotiana glauca</i> Graham	AP	Tobacco substitute, insect bites	1.6
Tamaricaceae	<i>Reaumuria negevensis</i> (L.) DC.	AP	Common plant	2.8
Thymelaeaceae	<i>Thymelaea hirsuta</i> (L.) Endl.	SL	Skin inflammation	1.8
Zygophyllaceae	<i>Zygophyllum dumosum</i> Boiss.	AP	Tooth ache, skin irritation	4.7
	<i>Peganum harmala</i> L.	AP	Abortive, skin disease	3.2
	<i>Fagonia mollis</i> Delile.	AP	To treat infections	3.7
Average CV (%)				6.68

Source: Sathiyamoorthy *et al.* (1997)

*Plants parts: WP - whole plant; SF - stem and flowers; SL - stem and leaves; AP - areal parts; S - stem; Bb - bulb; SFt - stem and fruit

**based on Bailey and Danin (1981); Abu-Rabia (1983); Palevitch and Yaniv (1987)

*** Each value is the mean of three independent analyses

or even stayed undeveloped; in addition, several anomalies were reported in endosperm development together with declined dehydrogenase activities. The critical Ni concentration in barley tissues that reduced the yield by 15% was $90 \pm 10 \mu\text{g/g}$ dry weight (Brown *et al.* 1987a). In the middle of the 1970s, Ni was shown to be a constituent of urease, a metalloenzyme from *Canavalia ensiformis* seeds, engaged in urea hydrolysis (Dixon *et al.* 1975). Later Ni was also found in urease from other plant species (Polacco *et al.* 1999; Sirko and Brodzik 2000). In soybean, Ni attachment to the enzyme depends on the activities of two genes, *Eu2* and *Eu3* encoding the auxiliary proteins that activate urease. The mutations in these genes resulted in the loss of urease activity; however, these mutations practically did not affect enzyme content and Ni uptake and translocation (Polacco *et al.* 1999). The *Eu3* gene encodes a 32-kD protein, which interacts with the product of *Eu2* in the course of the embryonic urease activation. When this process was blocked

with the antibodies against the protein *Eu3* accumulating in developing embryos, the urease content did not increase because the enzyme was instable when devoid of Ni in its active center (Sirko and Brodzik 2000). This evidence shows that a sufficient quantity of available Ni is essential for urease activation. A series of experiments with various plant species and growth media was run to demonstrate that Ni and urease are essential for plant vital functions. The deficiency in Ni content in the medium and the low activity of urease resulting from such deficiency upset nitrogen metabolism and led to the accumulation of toxic urea levels in shoots; phenotypically such process was manifested as necroses in leaf tips or chlorosis in older leaves (Welch 1981; Eskew *et al.* 1983; Dalton *et al.* 1985; Walker *et al.* 1985; Gerendas *et al.* 1997a, 1997b; Gerendas and Sattelmacher 1997; Gerendas *et al.* 1999). Similar necrosis of leaf tips was observed following soil dressing with high rates of urea. It was urea and not ammonia that caused the necroses

Table 4 Ni uptake in flowers, roots and leaves of chamomile (*Matricaria recutita*), sage (*Salvia officinalis*) and thymus (*Thymus vulgaris*).

Supply of Ni to the soil ppm	Flowers ppm	Roots ppm	Leaves ppm
Chamomile			
Control (0)	0.15	4.47	1.43
20	1.78	46.25	8.40
60	7.88	148	27.1
200	24.8	206	43.93
600	29.6	288	61.16
Sage			
Control (0)		2.05	0.57
20		29.80	11.95
60		56.15	11.28
200		74.65	16.16
600		248.5	29.53
Thymus			
Control (0)		2.63	0.55
20		21.35	27.86
60		42.55	33.52
200		64.40	57.50
600		154.5	46.53

Modified from Skoula *et al.* (2003)

because the addition of a urease inhibitor augmented the necrosis (Krogmeier *et al.* 1989). Leaf injury was especially manifest in plant species that were capable to develop the symbiosis with nitrogen-fixing bacteria: in such species, nodule development on the roots lagged behind by two or three days (Eskew *et al.* 1983). The addition of Ni salts at low concentrations to the nutrient solution alleviated these symptoms; Ni could not be substituted with other nutrients, such as Al, Cd, Sn, V, Cr and Pb (Eskew *et al.* 1983). Low Ni concentrations were shown to promote seed germination in rice (Das *et al.* 1978), wheat, timothy grass, pea, bean, soybean, and lupine (Welch 1981). In addition to urease, low concentrations of Ni were reported to activate several more enzymes (Welch 1981; Walker *et al.* 1985; Andreeva *et al.* 2001); however, the mechanism of this phenomenon stays unknown. In some legumes, small amounts of Ni are essential for root nodule growth and hydrogenase activation. The efficiency of nitrogen fixation immediately depends on hydrogenase activity because the oxidation of hydrogen by the latter provides ATP required for N reduction to ammonia. Ni deficiency was shown to lower down hydrogenase activity in the nodules. On the contrary, when soybean plants grown in soil culture were irrigated, once in two weeks, with the nutrient solution containing 1 mM NiCl₂, at day 52 the hydrogenase activity of *Rhizobium japonicum* nodules exceeded that of the control plants by about 45%, although the promoting effect disappeared by day 100, apparently as a result of increasing Ni toxicity (Dalton *et al.* 1985). The fact that several enzyme activities depend on the presence of Ni ion can explain the promotional effects of low Ni concentrations on plant growth and development in such species as zucchini, oilseed rape, cotton, sweet pepper, tomato, potato, and Chinese hemp (Walker *et al.* 1985; Gerendas and Sattelmacher 1997a, 1997b, 1999). Thus, spraying cotton plants with Ni₂SO₄·7H₂O solution (234.8 mg/kg) increased the numbers of buds and flowers, the rate of boll formation, and seed oil content (by 4.6%) (Andreeva *et al.* 2001).

Growth and development inhibition and reduction of yield

There have been many reports on the effects of Ni on germination and growth in plants, including the following. The germination of pigeon pea was found to decrease by circa 20% in a 1.5 mM solution of Ni, with the percentage germination related to Ni concentration (Nedhi *et al.* 1990; Madhava Rao and Sresty 2000). Exposure of 42 day-old cabbage plants to 0.5 mM Ni for eight days did not produce any perceptible difference in growth, but their subsequent

growth was retarded (Pandey and Sharma 2002). The shoot growth of wheat was clearly inhibited when treated with 0.2 mM Ni (Gajewska *et al.* 2006). The roots of *Nicotiana tabacum* became dark brown within 7 to 10 days of exposure to 0.43 mM Ni and growth of the plants was severely inhibited (Boominathan and Doran 2002). Other reports show that accumulation of Ni seriously affects the yield of plants, significantly decreasing the numbers of seeds/pod, 100-seed weight and seed-yield per plant (Tripathy *et al.* 1981). The total dry matter accumulation in roots, shoots and the total biomass may also decrease when plants are stressed by Ni (Madhava Rao and Sresty 2000; Pandey and Sharma 2002), probably due to reductions in leaf blade area and leaf density (Molas 1997), with accompanying reductions in numbers of flowers and fruits (Balaguer *et al.* 1998). Overall, reductions in plant yield can be attributed to poor plant development and reduced supply of nutrients to the reproductive parts (Ahmad *et al.* 2007).

It is well known that other metals as well as Ni, such as K, Na, Ca, Mg, Fe, Cu, Zn, and Mn are essential for plants (Taiz and Zeiger 2002). Ni has some similar characteristics to Ca, Mg, Mn, Fe, Cu, and Zn. Therefore, Ni may compete with these metals in absorption and transpiration processes (Cataldo *et al.* 1978; Kochian 1991; Kupper *et al.* 1996). As a result of competition, Ni at high concentrations may inhibit the absorption of these metals, decrease their concentration and even lead to their deficiency in plants (Gabbrielli *et al.* 1990; Van Assche and Clijsters 1990). Subsequently, this may affect important physiological processes, and ultimately result in toxic effects (Gajewska *et al.* 2006). For example, Ni can decrease Mg (or Fe) uptake and its supply to aerial parts via competition, and then induce deficiencies of these elements in plants. This can result in the retardation of germination, growth suppression, and reductions in yields (Boominathan and Doran 2002; Seregin and Kozhevnikova 2006). These inhibitory effects of Ni on the growth of plants can be reduced by supplying additional Mg (or Fe) ions (Ouzounidou *et al.* 2006). Therefore, Ni toxicity in plants is partly due to interference with other essential metal ions. In addition, Ca²⁺ has been shown to reduce the toxic effects of Ni on root development in *Alyssum bertolonii* Desv. (Gabbrielli and Pandolfini 1984), while Cu seemed to increase Ni toxicity in terms of reduced vitality and growth of Scots pine (Nieminen 2004). Many enzymes, such as SOD and CAT, are metalloenzymes containing Fe, Cu, Zn, or Mn in their prosthetic groups. Since excess Ni has been shown to decrease the contents of Fe (Pandey and Sharma 2002), Cu and Zn (Parida *et al.* 2003) in plant tissues, it can be speculated that Ni may reduce the biosynthesis of these metalloenzymes by causing deficiencies of these essential metals (Wisniewski and Dickinson 2003). Further studies on photosynthesis in plant leaves suggest that Ni can competitively remove Ca ions from the Ca-binding site in the oxygen evolution complex and replace the Mg ion of chlorophyll (Kupper *et al.* 1996, 1998), which may eventually inhibit the PSII electron transport chain.

Ni distribution and its hyperaccumulation in plant organs

Plant species vary in their capacity to accumulate HMs. High accumulation of HMs and the ratio of metals in various organs of diverse plant species largely depend on plant morphophysiological characteristics. The current classification divides all plant species into three groups: (1) the accumulators that store metals mainly in the shoots under high and low metal concentration in soils; (2) the indicators, with plant metal concentrations reflecting the metal content in the environment; and (3) the excluders, with restricted transfer of HMs into the shoots whatever high are metal concentrations in the environment and the roots (Baker 1981; Antosiewicz 1992). Among the plants accumulating Ni, there is a discrete group of the hyperaccumulators that accumulate metals in the shoots to the level of over 1000

mg/kg dry weight (Brooks *et al.* 1977). Presently about 300 such species have been described; they mostly belong to the families Asteraceae (Merkusheva *et al.* 2001), Brassicaceae (Van Assche and Glijsters 1990), Buxaceae (Dalton *et al.* 1985), Euphorbiaceae (Kositsin 1991), Flacourtiaceae (Krogmeier *et al.* 1989), Rubiaceae (Gerendas and Sattelmacher *et al.* 1997a), and Violaceae (Welch 1981) and grow on serpentine soils in the tropical and subtropical zones of Cuba, New Caledonia, Indonesia, Philippines, Brazil, Australia (Queensland), the South Africa (Zimbabwe), and the Mediterranean region (Raskin and Ensley 2000). Thus, the Cuban flora comprises 130 hyperaccumulators mostly representing the *Buxus*, *Phyllanthus*, *Leucocroton*, *Euphorbia*, *Pentacalia*, *Senecio*, *Psychotria*, *Ouratea*, and *Tetralix* genera (Reeves *et al.* 1999). The number of species that hyperaccumulate other HMs is considerably lower, and elucidating the cause of this phenomenon is an inviting problem. There are contradictory hypotheses as to the mechanism of hyperaccumulation. Thus, Boyd and Martens (1998) presumed that the hyperaccumulators possess the most efficient system of ion absorption with yet unknown functions. There are also several hypotheses explaining the role of hyperaccumulation in plant vital functions. Within the removal hypotheses, the hyperaccumulation is seen as a mechanism of tolerating high levels of metal in the environment: in this case, the absorbed metal is transferred into the compartments of low physiological activity or into plant organs to be shed in future (Boyd *et al.* 1994; Brooks 1998). Indeed, the old leaves of the hyperaccumulator species *Psychotria douarrei* stored considerably more Ni than the young leaves (Davis *et al.* 2001). The drought resistance hypothesis claims that Ni accumulation in plant tissues would enhance plant tolerance to moisture deficit by reducing the cuticular transpiration (Boyd *et al.* 1994; Brooks 1998; Severne 1974). According to the hypothesis of elementary allelopathy, shedding plant organs with high HM content, such as leaves, would enrich soil surface with these metals and inhibit the growth of competing neighbor species that are not tolerant to the corresponding HMs (Boyd *et al.* 1994; Brooks 1998). According to the most widely accepted defense hypothesis, the elevated concentrations of HMs, especially in the plant dermal tissues, would avert the penetration and propagation of pathogenic microorganisms. In addition, such hypothesis supports the view that the accumulator plant species are in advantage over non-accumulators because the former spend less nitrogen and carbon on organic substances, such as tannins and phenolics that protect plant tissues against the herbivores, mostly insects (Boyd *et al.* 1994; Brooks 1998; Sagner *et al.* 1998; Davis and Boyd 2000). The defense hypothesis was supported by several experimental studies. Thus, the pathogenic strain of *Xanthomonas campestris* pv. *campestris* did not develop in *Streptanthus polygaloides* plants when they accumulated Ni, and the growth of the parasitic fungus *Erysiphe polygoni* and the necrotrophic fungus *Alternaria brassicola* was inhibited (Boyd *et al.* 1994). However, when Ni accumulation exceeds a characteristic limit, plant mechanisms of detoxification that keep low the shoot metal concentrations become less efficient. As a result, the control over metal entry into the shoots is lost, and such plants perish.

Ni distribution in plants depends on their developmental stage. Thus, most Ni accumulation in the roots of *Avena sativa* was registered at the tillering and booting stages, while the maximum accumulation in the reproductive organs proceeded at the heading stage and at the stages of milky and full maturity (Andreeva *et al.* 2000). This evidence leads to an important practical question: what is the mechanism that determines the capacity of the hyperaccumulator species to hoard Ni in the shoots and to avoid its toxic effects. Apparently, no sole mechanism exists for Ni accumulation in the shoots and no sole mechanism stands for the tolerance of these particular plant species towards the excess of Ni. As a whole, the process of hyperaccumulation seems to depend on the characteristic patterns of metal translocation and distribution, while their concomitant tol-

erance to the excess of metal relies on several detoxification mechanisms.

Ni hyperaccumulators

The growing concerns about environmental pollution and interest in phytoremediation have stimulated several recent studies on Ni hyperaccumulator plants, reflecting their potential to survive and sequester high levels of Ni in tissues (from several thousands of mg/kg up to 5% of dry biomass) without exhibiting phytotoxicity (Baker *et al.* 2000; Prasad 2005; Milner and Kochian 2008). More than 310 species of Ni hyperaccumulators have been identified (Chaney *et al.* 1997; Baker *et al.* 2000; Chaney *et al.* 2005; Ahmad *et al.* 2007), including members of the Acanthaceae, Asteraceae, Brassicaceae, Caryophyllaceae, Fabaceae, Flacourtiaceae, Meliaceae, Myristicaceae, Ochnaceae, Poaceae, Rubiaceae, Sapotaceae and Stackhousiaceae (Reeves and Baker 2000). The family with the most such species is the Brassicaceae, with more than 80 species which are capable of accumulating Ni to concentrations as high as 3% of shoot dry biomass (Reeves and Baker 2000). These species have higher requirements for Ni (e.g., up to 500 mg Ni/kg) than normal plants (Kupper *et al.* 2001). *Stackhousia tryonii* Bailey (Stackhousiaceae), an herbaceous species from Australia, has been shown to accumulate Ni in dry leaves at concentrations exceeding 4% (Batianoff and Specht 1992). In addition, it is notable that many aquatic plants such as *Typha* (Hadad *et al.* 2006), *Phragmites* (Bragato *et al.* 2006), *Eichhornia* (El-Gendy *et al.* 2006), *Azolla* (Khosravi *et al.* 2005), and *Lemna* (Axtell *et al.* 2003), have the potential to remove HMs from water (Rai 2008). The Ni removal efficiencies of these particular species are 80% higher than those of non-accumulators (Axtell *et al.* 2003). Ni hyperaccumulator species are thought to have strategies similar to allelopathy that reduce interspecific plant competition, e.g., increasing Ni availability to other plants by depositing locally Ni rich senescent leaves (Boyd 2004). In addition, these species have efficient root absorption mechanisms which allow them to specifically accumulate metals from soils and/or water. After root absorption, Ni can be transported quickly into shoots and leaves of hyperaccumulators and then sequestered in the vacuole (Milner and Kochian 2008). For these reasons, Ni hyperaccumulators has been extensively used to remove Ni from polluted soils and/or water; a so-called 'green' technology (Boyd 2004). Recent developments of analytical techniques have allowed some of the mechanisms of Ni tolerance in hyperaccumulators to be explored and described. For example, exceptionally high endo-DNase activities (Abou Auda *et al.* 2002) and elevated concentrations of protective amino acids and proteins, such as free histidine (Kramer *et al.* 1996), serine decarboxylase (SDC) (Fujimori and Ohta 2003) and metallothionein (Schor-Fumbarov *et al.* 2005), appear to contribute to the high Ni tolerance of some species, by chelation and/or facilitating the export of Ni from root to shoot in the xylem. ROS and Ca ions have also been demonstrated to participate in Ni induced alterations in the expression of various proteins and genes in animal cells (Denkhaus and Salnikow 2002).

Effect of Ni on mineral nutrition

HMs curb cation and anion absorption by plant roots; this is one of nonspecific mechanisms of their toxicity (Seregin and Ivanov 2001). However, the published evidence on the effects of Ni on plant mineral nutrition is rather contradictory. In the presence of Ni, the contents of mineral nutrients in plant organs may increase, decrease, or stay even. One of the probable mechanisms for decreasing the uptake of macro- and micronutrients relies on the competition for the common binding sites due to the comparable ionic radii of Ni and other cations. Such mechanism may operate (Barsukova and Gamzikova 1999) when the uptake of Mg (78 pm), Fe (82 pm), and Zn (83 pm) is decreased in the presence of

Ni (78 pm) (ionic radii in parentheses are from (Emsley 1991). One should emphasize that the lowered uptake of Mg and Fe is one of the causes of chlorosis produced by the excess of Ni in the environment (Piccini and Malavolta 1992). The decline in nutrient uptake may also result from the Ni-induced metabolic disorders that affect the structure and enzyme activities of cell membranes (Seregin and Ivanov 2001). Thus, Ni affected the sterol and phospholipid composition of the plasma membrane in *Oryza sativa* shoots, with concomitant changes in the ATPase activity. Apparently, these changes affected the membrane permeability and in this way changed the ion balance in the cytoplasm. The effects of Ni on nutrient uptake depend in many aspects on Ni concentration in the environment. The experiments with ryegrass plants demonstrated that Fe content in the shoots increased at low Ni concentrations and decreased at higher concentrations (Khalid and Tinsley 1980). An increase in soil Ni content from 50 to 200 mg/kg soil decreased the contents of Cu and Mg in the caryopses and Mg and Ca in the shoots of *Triticum aestivum*. At high Ni concentrations (about 0.1 to 1 mM), the contents of macro- and micronutrients in plant tissues are usually lowered down because of disordered absorption and transport (Pandolfini *et al.* 1992). At the same time, at low Ni concentrations in the environment (10 to 1 μ M), the contents of nutrients did not change and in some cases even increased (Barsukova and Gamzikova 1999). Such phenomenon was described as the concentrating effect; these effects are seen as the result of growth inhibition (dry biomass decreases) in the plants grown on the nutrient solutions low in Ni, while the rate of metal absorption stays the same as in the control plants; consequently, the contents of HMs increase per unit of dry matter (Piccini and Malavolta 1992). The effects of the same Ni concentration would vary in diverse plant species. Thus, when the plants of *T. aestivum* and *T. durum* were kept on 67 μ M Ni, the contents of Ca and Mg increased and that of Zn decreased in the leaves of the former species and did not change in the latter (Barsukova and Gamzikova 1999). The toxic Ni concentrations specifically affect the ionic balance in various plant organs. The contents of Fe, Mn, and Zn decreased in *T. aestivum* leaves at the tillering stage, while only Mn content declined in the roots (Barsukova and Gamzikova 1999). Plant species tolerant and susceptible to Ni may differ by the changes in their mineral contents as affected by Ni. When two cultivars of *T. aestivum* were grown in the soil contaminated with Ni (50–200 mg/kg soil), Fe concentration in grain declined in both cultivars and the contents of Cu, Ca, and Mg, only in the susceptible genotype. The latter also manifested Mn and Mg deficiency in the leaves, apparently resulting in chlorosis (Barsukova and Gamzikova 1999). This evidence and some additional data presume that the resistance of transport systems to HMs provides one of the mechanisms of plant tolerance.

SUMMARY AND FUTURE PROSPECTS

Scientific advances over the past 20 years suggest that Ni is absorbed and redistributed in plants *via* cation and/or metal-ligand complex transport systems. The toxic effects of Ni in plants are reviewed here. However, the mechanisms operating at both protein and molecular levels that result in these toxicity symptoms remain largely unknown and require further study. Growing concerns about Ni pollution in the environment have led to research on phytoremediation, i.e., the use of hyperaccumulator or wetland plants to remove and/or sequester Ni from soil and water. However, many such plants have limited utility for phytoremediation, because of their slow growth, difficult propagation, seasonal growth, and low biomass. Solutions to these problems are important and require further research. In addition, although many studies regarding the mechanisms of Ni tolerance in hyperaccumulators have been conducted, further studies are needed to fully understand their details at both biochemical and molecular levels. As an example, unique

genes encoding the Ni-chelated proteins in Ni hyperaccumulators could be transferred to fast growing species. This type of genetic modification may allow the development of a plant specifically tailored for Ni phytoremediation with enhanced abilities to tolerate, accumulate and detoxify Ni.

CONCLUSION

Our analysis of the published data on Ni distribution, translocation, and toxic effects and on plant responses to Ni excess showed the characteristics that are peculiar for Ni or common with other HMs. The specific mechanisms of Ni absorption by plant root systems have not been yet elucidated. Soil is the major source of Ni for plants, and similar to other soils of low humus content, light granulometric composition, and low pH of the soil solution. The ions of other metals decrease Ni availability, although the effects of Ca may vary. The great number of plant species that hyperaccumulate more than 1 g Ni per kg of dry shoots is a characteristic aspect of Ni distribution in plant organs. The researchers still debate over the causes and mechanisms of hyperaccumulation, which may depend on the morphological and physiological characteristics of particular plant species, the capacity of Ni to overcome the physiological barriers, etc. Plants comprise several such barriers that curb the entry of HMs into the shoots, primarily the plasma-membrane and endodermis at the cell and tissue levels, respectively. However, these barriers are not universal: most of Cd and Pb are translocated via the apoplast, and their entry into the central cylinder is limited at nonlethal concentrations, while Ni freely enters the stele via the symplast. The specific carriers providing for Ni uptake in plants have not been yet identified. The uptake of HMs into plant cytoplasm is mediated by various transport systems localized at the plasmalemma. In grasses, the uptake of Ni and other HMs was shown to employ Ca-channels and the phytometallophore mechanism. The intracellular localization of HMs and their distribution in plant tissues determine the profile of their toxicity affecting various physiological processes. Ni exerts both general and specific toxicity. The former manifestations characteristic of most HMs include the disorders in mineral nutrition, water regime, photosynthesis, growth and developments, etc. The specific pattern of Ni toxicity is illustrated by the inhibition of lateral root development: it is in this aspect where Ni toxicity differs from that of other HMs, such as Ag, Cd, Pb, Zn, Cu, Tl, Co, and Hg, which blocked root growth at nonlethal concentration without inhibiting root branching. The inhibition of root branching by Ni stems from its accumulation in the endoderm and pericycle and the interruption of cell divisions in the latter. When HMs enter plant cells, they incite several specific and nonspecific systems of protection and detoxification, such as the immobilization in the cell walls and vacuoles or the induction of catalase, peroxidase, and superoxide dismutase, which account for the neutralization of free radicals and peroxides that are progressively accumulated in the course of metal induced oxidative stress; other protection systems include the synthesis of osmolites, such as proline, the changes in the cell wall composition such as callose and suberin deposition, the imbalance of plant hormones, primarily ethylene and ABA, the synthesis of metallothioneins, phytochelatins, etc. All these changes are the links in one and the same chain of events representing cell responses to the entry of HMs and aimed at maintaining cell homeostasis. The accumulation of HMs in plant vacuoles as the complexes with organic acids is a universal mechanism of detoxification. As different from other HMs (Cd, Ag, Cu, Zn, Bi, and Hg), Ni does not activate the synthesis of phytochelatin synthase; as a result, phytochelatins are not of great importance for Ni detoxification. Another mechanism of detoxification is employed to neutralize Cu and Zn ions: they induce the synthesis of metallothioneins, which, in contrast to phytochelatins, are the primary gene products.

The efficiency of Ni mechanisms is probably the pri-

mary factor of plant tolerance and plant capacity for hyperaccumulation. The elucidation of common and specific mechanisms of HM toxicity and the characteristic plant responses to the excess of HMs, which stem from plant morphology and physiology and the physical and chemical properties of metal ions, is an important research problem; solving this problem would help cleanse the environment from HMs and avert their entry into human and animal organisms. Further investigation on a cellular or molecular level is necessary to understand the mechanism that causes these positive effects at low concentrations of Ni, as well as the changes in free radicals induced by Ni stress.

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