

# Nickel: The last of the essential micronutrients

## Níquel: el último de los micronutrientes esenciales

Miguel Ángel López<sup>1,3</sup> and Stanislav Magnitskiy<sup>2</sup>

### ABSTRACT

The knowledge about the role of Ni (Ni) in the nutrition, physiology and metabolism of the majority of crops is limited, whereas is considered to be an essential element for the higher plants starting from the 80's of the twentieth century. The primary function of Ni in plants is defined in terms of its importance for the hydrolysis of urea; however, Ni may have an importance in other physiological processes, such as nitrogen fixation. Although the deficiencies of Ni in plants are relatively rare events, the positive response of yield and nitrogen use efficiency to applications of Ni are shown for different species. The present work summarizes the data about the essentiality of Ni and its function in plant metabolism as well as its agronomic importance for the crops.

**Key words:** mineral nutrition, essential element, mineral deficiencies, nitrogen cycle.

### RESUMEN

El conocimiento sobre el rol del níquel (Ni) en la nutrición, fisiología y metabolismo de la mayoría de los cultivos es limitado; no obstante, desde los años 80 del siglo xx este elemento se considera esencial para las plantas superiores. La función principal del Ni en las plantas se define en términos de su importancia para la hidrólisis de urea, aunque también interviene en otros procesos fisiológicos como la fijación de nitrógeno. Si bien las deficiencias de Ni en las plantas cultivadas son relativamente escasas, las aplicaciones de este micronutriente presentan, en diversas especies, respuestas positivas en el rendimiento y la eficiencia del uso de nitrógeno. El presente trabajo revisa la esencialidad del Ni y su función en el metabolismo de las plantas, así como su importancia agronómica para los cultivos.

**Palabras clave:** nutrición mineral, elemento esencial, deficiencias minerales, ciclo del nitrógeno.

## Introduction

Knowledge about the role of Ni in nutrition, physiology and metabolism of most crops is currently limited (Bai *et al.*, 2006). However, the evidence of essentiality of this element for higher plants is not a new issue, but still goes back to the 70's of the twentieth century, when a group of researchers suggested the possible role of Ni in the metabolism of nitrogen through its participation in the structure of the enzyme urease (Dixon *et al.*, 1975). Already in the 80's Eskew *et al.* (1984a), through studies of soybeans, demonstrated the essential role of Ni in nitrogen metabolism of leguminous plants, a role that was independent of the form of available nitrogen ( $\text{NO}_3^-$  or  $\text{NH}_4^+$ ). The evidence generated by this research suggested the essentiality of Ni for higher plants (Eskew *et al.*, 1984b).

The lack of evidence for the role of Ni in non-leguminous plants was caused by the fact that at that time the studies about the essentiality were incomplete and, therefore, its essentiality was not accepted. This gap of knowledge was

supplied by Brown *et al.* (1987) who established the essential role of Ni in non-leguminous plants, specifically in barley. These results together with those obtained previously by Eskew *et al.* (1984a) led Brown *et al.* (1987) to propose a more support towards the addition of Ni to the group of micronutrients. Although these studies were, possibly, the most significant ones in determining the essentiality of Ni, there also stood out the studies forwarded by Roach and Barclay (1946) in plants of potato (*Solanum tuberosum*), wheat (*Triticum aestivum*) and bean (*Phaseolus vulgaris*) in England that indicated an increase in plant production as a result of foliar application of Ni. Additionally, Cataldo *et al.* (1978) studied the dynamics and transport of Ni in soybean plants, while Eskew *et al.* (1983) founded toxic levels of urea in the tips of soybean leaves poor in Ni, a behavior similar to that reported by Walker *et al.* (1985) in plant *Vigna unguiculata*.

The previous studies allowed including Ni within the group of essential mineral nutrients (Marschner, 2002; Taiz and Zeiger, 2004; Epstein and Bloom, 2005; Azcon-

Received for publication: 1 December, 2010. Accepted for publication: 2 February, 2011.

<sup>1</sup> Universidad de Ciencias Aplicadas y Ambientales –U.D.C.A. Bogota (Colombia).

<sup>2</sup> Department of Agronomy, Agronomy Faculty, Universidad Nacional de Colombia. Bogota (Colombia).

<sup>3</sup> Corresponding author: milopez@udca.edu.co.

Bieto and Talón, 2008) and, therefore, it is understood that plants may not complete the life cycle in the absence of this nutrient (Arnon and Stout, 1939). Recently, the Department of Agriculture of the USA and the Association of American Plant Food Control Officials included Ni as an essential element for plants, making it possible in the USA the manufacture and sale of fertilizers containing Ni (Bai *et al.*, 2006).

Due to the fact that this mineral element is a new one in the list of essential micronutrients, the objectives of the present review were to illustrate the current state of research on functions of Ni in plants, in particular, describe the dynamics of Ni in non-accumulator and accumulator species, clarify the physiological functions of Ni in plants as well as symptoms of deficiency and toxicity caused by Ni in plants and identify plant responses to the applications.

### Dynamics of nickel in soils and plants

At level of dynamics in soil, Ni is abundant metal in the earth crust with about 3% of the composition of the earth. In agricultural soils, typical contents of this element vary from 3 to 1,000 mg kg<sup>-1</sup>, however, the soils derived from basic igneous rocks can contain from 2,000 to 6,000 mg kg<sup>-1</sup> of Ni. Soil pH plays an important role in the availability of Ni, and at pH > 6.7 Ni exists in form of poorly soluble hydroxides, while at pH < 6.5 increases the presence of relatively soluble compounds (Brown, 2006).

It is considered that the system of Ni<sup>+2</sup> uptake by roots is similar to that of Cu<sup>2+</sup> and Zn<sup>2+</sup>, a conclusion obtained after confirmation of competitive inhibition in absorption of these three nutrients. When the available concentration of Ni<sup>+2</sup> in the substrate is low (0.5 - 30 mkM), the process of its absorption by roots is dependent on the expenditure of ATP, a characteristic that indicates the presence of an active transport of high affinity (Brown, 2006).

Once Ni is absorbed by the root, its movement to the aboveground parts of plants is closely linked to the formation of organic complexes (Cataldo *et al.*, 1978, 1988; Bhatia *et al.*, 2005). In general, potential ligands of metals in plants could be grouped into three classes: oxygen donor ligands (carboxylates: malate, citrate, malonate, succinate, and oxalate), sulfur donor ligands (metallothioneins and phytochelatins), and nitrogen donor ligands (amino acids) (Baker *et al.*, 2000). In the case of Ni (Ni<sup>+2</sup>), there was reported complex formation for its transport in the xylem with amino acids histidine (Krämer *et al.*, 1996; Brown, 2006) and nicotinamine (Mari *et al.*, 2006) and organic

acids citrate, malate, and malonate (Cataldo *et al.*, 1988; Robinson *et al.*, 2003; Bhatia *et al.*, 2005), although in the case of complex with nicotinamine, this one was reported for the species tolerant or accumulators of Ni (Mari *et al.*, 2006). At the same time, Homer *et al.* (1995) suggested that formation of complexes of Ni in the xylem with molecules of high molecular weight, such as metallothioneins and phytochelatins, is an unlikely process.

Complex formation is dependent on pH, such as at low pH the organic acids are better chelating agents for Ni than amino acids, whereas at high pH amino acids increase their capacity to act as ligands (Bhatia *et al.*, 2005). Brown (2006) indicates that at pH below 6.5 histidine is the most significant ligand for Ni, while at pH < 5 citrate is the most important chelating agent. In oak *Quercus ilex*, Araujo *et al.* (2009) evaluated the effect of four different ligands (histidine, oxalic acid, aspartic and citric acids) present in the xylem sap on the movement of Ni<sup>+2</sup> in the xylem. The order of affinity of ligands towards Ni<sup>+2</sup> reported in this research was: oxalic acid > citric acid > histidine > aspartic acid. In contrast, the amount of Ni bound to the walls of the xylem was higher when Ni was present as free cation, followed by Ni-aspartic acid, Ni-histidine, Ni-citric acid, and Ni-oxalic acid (Araujo *et al.*, 2009).

Addition of chelating agents to soils with high contents of Ni may be an effective practice to increase the metal concentration in soil solution, but have a low effect on increasing of Ni absorption by plants, as showed the study of Molas and Baran (2004) in barley. This research evaluated several Ni containing compounds: Ni-citrate, Ni-glutamate, Ni-EDTA and NiSO<sub>4</sub>·7H<sub>2</sub>O and found that the rate of absorption of Ni by plants arranged from highest to lowest as NiSO<sub>4</sub>·7H<sub>2</sub>O > Ni-citrate > Ni-glutamate > Ni-EDTA.

In Ni non-accumulating species, after being absorbed and transported, is used to ensure the functioning of urease, and, thus, to ensure the hydrolysis of urea to produce ammonia and carbon dioxide (Marschner, 2002; Taiz and Zeiger, 2004). Ni in the phloem may be retraslocated rapidly from the leaves to young tissues, especially during reproductive growth (Tiffin, 1971); this movement is associated with the formation of complexes with organic acids and amino acids (Brown, 2006). Thus, Ni is considered an element mobile in the phloem (Cataldo *et al.*, 1978; Page and Feller, 2005), whose mobility is higher than that of cobalt (Zeller and Feller, 1999). In soybeans, over 70% Ni present in the leaves could be retraslocated to the seeds and accumulated mainly in the cotyledons (Tiffin, 1971; Cataldo *et al.*, 1978).

## Nickel hyperaccumulator plants

Ni hyperaccumulator species (metallophytes), such as *Stackhousia tryonii*, *Hybanthus floribundus*, *Thlaspi caerulescens*, *Halimione portulacoide*, *Berkheya coddii*, *Brassica juncea*, and *Typha latifolia* are known to accumulate high concentrations of Ni, among 0.1 and 3.0%, in shoots and leaves (Ye *et al.*, 1997; Robinson *et al.*, 2003; Bidwell *et al.*, 2004; Bhatia *et al.*, 2005; Duarte *et al.*, 2006; Mari *et al.*, 2006; Hsiao *et al.*, 2007). The latex of *Sebertia acuminata* (Sapotaceae), a tree native to New Zealand, contains 25.74% dry weight Ni (Sagner *et al.*, 1998) as well as other cases of exceptionally high accumulation of Ni in the aboveground parts of plants are reported; the explanations for Ni hyperaccumulation are related to the defense role played by high concentrations of Ni in plant tissues against herbivores and pathogens (Baker *et al.*, 2000).

It is known that the members of ZIP protein families (*Zinc Regulated Transporters / Iron Regulated Transporters*), NRAMP (*Natural Resistance Associated Macrophage Protein*), and YSL (*Yellow Stripe Like*) are involved in the transport of Ni in different organisms. The transformation of yeasts with ZNT1 or ZNT2 partially conferred Ni tolerance correlated with the input of Zn, which inhibits the absorption of Ni. In contrast, transformation with NRAMP4 conferred sensitivity to Ni in yeasts explained by a release of Ni from the vacuole (Tejada-Jiménez *et al.*, 2009). In transgenic plants of *Arabidopsis* sp., the overexpression of gene AtIREG2 causes increased tolerance to high concentrations of Ni. Thus, it appears that the physiological function of AtIREG2 may be accumulation of excess of Ni accompanied by a counter ion (nitrate or sulphate) in the vacuole to maintain the ionic balance of cells (Schaaf *et al.*, 2006).

Pianelli *et al.* (2005) suggested that, in response to elevated contents of Ni, nicotinamine is translocated from the leaves of hyperaccumulators to the roots, where it forms complexes with Ni and facilitates its transport to the shoot. In *Arabidopsis* sp., overexpression of nicotinamine synthase confers tolerance to Ni. In addition, the tolerance of plants to Ni also results from the chelating of Ni in the root with histidine or organic acids, such as citrate (Tejada-Jiménez *et al.*, 2009).

Ni hyperaccumulator plants differ from non-accumulators with the route of transport of this element in the root cortex. The absorption of Ni via the apoplast of the roots of corn, a non-accumulating plant, ranged from 81.3 to 88.0%, while that of *Leptoplax emarginata*, a hyperaccumulator of

Ni, was from 90.6 to 95.5% (Redjala *et al.*, 2010). The root cell wall in both species had similar affinity for the Ni but, in hyperaccumulator plants, more Ni was absorbed via the apoplast. This suggests, according to the authors, that symplastic absorption is not the main factor associated with hyperaccumulation, and the transport system of Ni can not be similar in these two species (Redjala *et al.*, 2010).

In hyperaccumulator species, after absorption and transport via xylem, Ni can be accumulated in vacuoles of leaf epidermal cells (Krämer *et al.*, 1996; Küpper *et al.*, 2001; Bidwell *et al.*, 2004; Schaaf *et al.*, 2006), in the cuticle of the upper epidermis (Robinson *et al.*, 2003) or remain in the apoplast occupying certain sites in the cell wall (Krämer *et al.*, 1996; Bidwell *et al.*, 2004). The accumulation of Ni in the vacuole of epidermal cells is related to the decrease in the concentrations of K<sup>+</sup> and Na<sup>+</sup> (Bidwell *et al.*, 2004) as a likely consequence of a competitive effect between these cations.

Montargés-Pelletier *et al.* (2008) reported the carboxylic acids (citric and malic) as the main responsible agents for the transfer of Ni in hyperaccumulator plants *Alyssum murale* and *Leptoplax emarginata*. In their research, citrate was the main ligand of Ni found in stems, whereas in leaves this function corresponded to malate. Histidine was not detected in leaves, stems, and roots of plants under study. In contrast, McNear *et al.* (2010) founded that, in *Alyssum murale*, Ni was in the sap of xylem in a greater proportion together with histidine, followed by malate and other low molecular weight molecules. The authors based on their results adapt a model, in which Ni is transported from roots to leaves in complexes with histidine and then stored in the epidermis of leaves and stem in complexes with malate, other organic acids of low molecular weight and counter-ions, such as sulfate SO<sub>4</sub><sup>2-</sup> (McNear *et al.*, 2010).

## Nickel functions in plants: hydrolysis of urea

Ni is chemically related to iron (Fe) and cobalt (Co). Oxidation state of Ni in biological systems is Ni<sup>+2</sup>, but it could also exist as Ni<sup>+</sup> and Ni<sup>+3</sup> (Marschner, 2002). Ni is a functional constituent of seven enzymes, six of which are present in bacteria and animals, while only one, urease (urea amidohydrolase, EC 3.5.1.5), occurs in plants (Brown, 2006). Constituent participation of Ni in the structure of urease was first documented by Dixon *et al.* (1975) after its isolation and description from *Canavalia ensiformis*. Of the seven Ni-dependent enzymes two have non-redox functions (urease and glyoxylase) and the remaining five are involved in oxidation-reduction reactions (Ni-superoxide

dismutase, methyl coenzyme M reductase, carbon monoxide dehydrogenase, acetyl coenzyme A synthase and hydrogenase) (Brown, 2006).

Metalloenzyme urease is a ubiquitous (everywhere present) (Malavolta and Moraes, 2007) enzyme that consists of six identical spherical subunits, each with two atoms of Ni (Dixon *et al.*, 1980; Hirai *et al.*, 1993) whose molecular mass is reported in the range of 473-590 kDa (Fishbein *et al.*, 1973; Dixon *et al.*, 1980). Within the subunits, the union of Ni is coordinated by ligands containing N- and O- (Marschner, 2002).

Although it is considered that Ni is not required for the synthesis of urease, this element is an essential metal component in the structure and catalytic function of the enzyme (Hirai *et al.*, 1993; Marschner, 2002). In soybean urease, its synthesis is directed by a long chain of RNA consisting of 3,000 to 3,500 nucleotides and their participation on the total weight of extractable seed protein is of the order of 0.2% (Polacco and Sparks, 1982).

The role of urease is to catalyze the hydrolysis of urea  $\text{CO}(\text{NH}_2)_2$  to ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ), a reaction that occurs mainly in leaves (Marschner, 2002; Taiz and Zeiger, 2004; Malavolta and Moraes, 2007; Azcon-Bieto and Talón, 2008). The above statement may indicate that the functionality of Ni is restricted to those crops, where nitrogen inputs are derived from urea, however, this assumption is not correct; the essentiality of Ni is due to the formation of urea interior of plants as a result of metabolic pathways common to all plants that include the catabolism of purines (adenine and guanine), ureides and protein catabolism of arginine via ornithine cycle and conversion of canavanine to canaline in certain plants (Walker *et al.*, 1985).

### Other functions of nickel in plants

Ni is also involved in symbiotic nitrogen fixation through its role as an active center of hydrogenase, a process documented in strains of nitrogen-fixing bacteria *Bradyrhizobium japonicum*, *Bradyrhizobium* sp. (*Lupinus* sp.), *Rhizobium tropici*, *Rhizobium leguminosarum*, and *Azorhizobium caulinodans* (Palacios, 1995). Hydrogenase is an enzyme responsible for oxidizing the hydrogen produced by nitrogenase during symbiotic nitrogen fixation resulting in the production of ATP and, therefore, this enzyme increases the efficiency of symbiotic process, and decreases the inhibitory activity of hydrogen in the bacteroids (Palacios, 1995; Ruiz-Argueso *et al.*, 2000). Thus, the low level

of Ni in agricultural soils may limit the activity of hydrogenase from *R. leguminosarum* and, therefore, the efficiency of symbiotic nitrogen fixation in legumes (Ruiz-Argueso *et al.*, 2000; Malavolta and Moraes, 2007).

Zobiolo *et al.* (2010) in Brazil showed that application of glyphosate can negatively influence symbiotic nitrogen fixation in soybeans grown in soils with low native concentrations of Ni in response to a decrease in the foliar concentration of this element. In *Matricaria chamomilla*, accumulation of chlorogenic acid, an important antioxidant compound, was increased almost fourfold in response to the application of 120  $\mu\text{M}$  Ni to the substrate (sand). It is, therefore, proposed that Ni may have antioxidant properties of phenolic metabolites (Kovacik *et al.*, 2009).

Being similar to cation of iron, cation of Ni may have beneficial functions for the formation of anthocyanins that contain iron or aluminum as structural elements. According to Aziz *et al.* (2007), applications of Ni to soil contributed to accumulation of anthocyanins and flavones in plants of *Hibiscus sabdariffa* when applying 20-25  $\text{mg kg}^{-1}$  Ni.

### Deficiencies and toxicities of nickel in plants

Ni deficiency in legumes and other dicots causes a decrease in the activity of enzyme urease, a condition that causes accumulation of toxic levels of urea and is manifested as necrosis at the tip of the leaves (Eskew *et al.*, 1983; Walker *et al.*, 1985; Malavolta and Moraes, 2007). In soybean, low levels of Ni in soil reduced nodulation (Zobiolo *et al.*, 2010) and seed yield, a phenomenon that is explained by the involvement of Ni in hydrogenase activity of bacteroids (Brown, 2006). At the same time, due to the relatively low requirements of plants in Ni, the events of Ni deficiencies in the field are few, while the toxicities caused by Ni are more common (Mengel and Kirkby, 2001).

Decreased urease activity in non-timber species can induce the deficiency of nitrogen and affect the contents of amino acid amides (asparagine and glutamine) and intermediates of urea cycle (arginine, ornithine, and citrulline) (Bai *et al.*, 2006). In grasses, on the other hand, deficiency symptoms include interveinal chlorosis and necrotic spots on young leaves. In general, urea accumulation in the tip of the leaves (necrosis) of both monocotyledonous and dicotyledonous plants is diagnostically symptom of Ni deficiency (Brown, 2006).

One of the best documented cases of the deficiency of Ni is the perennial timber pecan *Carya illinoensis*. In this

species, Ni deficiency is known as “mouse ear” or “little leaf disorder” (Malavolta and Moraes, 2005; Bai *et al.*, 2006) and was first proved as a deficiency of Ni in 2004 by Wood and colleagues (Malavolta and Moraes, 2007). However, the symptom is reported in the United States since 1918 and is characterized by the presence of round dark spots on the tips of new leaves and curving of leaf blade to make the appearance of the ear of a mouse (Malavolta and Moraes, 2005).

In pecan, Ni deficiency affects nitrogen metabolism via ureide catabolism, amino acid metabolism and ornithine cycle intermediates and metabolism of carbon through the accumulation of lactic acid and oxalic acids that accumulate on the edges of leaf blade and would also be linked to necrosis of the tips of the leaves (Bai *et al.*, 2006).

Ni deficiency in pecan could be corrected by foliar application of Ni; however, the dose of Ni reported in the literature is variable. Thus, Brown (2006) indicates that a dose of Ni equal to 100 mg L<sup>-1</sup> is sufficient to correct the deficiency, while Malavolta and Moraes (2005) recommended spraying a solution of 0.8 g L<sup>-1</sup> Ni mixed with a dose of 4.8 g L<sup>-1</sup> urea.

Malavolta and Moraes (2005) and Brown (2006) indicated that the main factors that favor the development of Ni deficiency are: a) excess of Cu and Zn that competitively inhibits the absorption of Ni by roots, b) soil pH > 6.5 (formation of low soluble hydroxides and Ni oxides), c) soils with high contents of Fe, Mn, Ca, or Mg, d) excessive doses of nitrogen or excessive liming, e) high levels of soil phosphorus that favor the formation of phosphates of Ni and decrease the absorption of Ni by plants; f) inhibition of urease activity by accumulation of Cu in plants.

In soils developed over ultrabasic rocks, high levels of Ni, such as exceeding 250 mg kg<sup>-1</sup> soil, may lead to Ni toxicity in non-accumulator plants (Mengel and Kirkby, 2001). The symptoms of Ni toxicity may resemble the symptoms of iron deficiency due to a reduced absorption of iron in soils high in Ni (Mengel and Kirkby, 2001). The critical level of Ni in leaves varies according to species, but generally a suitable range is considered between 1 and 10 mg kg<sup>-1</sup> dry matter basis (Marschner, 2002), higher than 25 mg kg<sup>-1</sup> lead to Ni toxicity in non-accumulator species (Malavolta and Moraes, 2007) through distortions in the growth of root system and leaf buds (Brown, 2006). In wheat, the addition of 50 and 100 mkM Ni to the growth substrate resulted in decrease of fresh weight of shoot, the nitrate content, a reduction in the activity of nitrate and nitrite reductase,

40 and 80% less, respectively (Gajewska and Skłodowska, 2009). In contrast, an increase in ammonium content, proline concentration, and the activity of NADH-glutamate synthase in plants treated with toxic levels of Ni was reported (Gajewska and Skłodowska, 2009). The toxicity of Ni in plants may be alleviated by liming or application of phosphate fertilizers that reduce availability of Ni to the plants (Mengel and Kirkby, 2001).

## Plant yield response to applications of nickel

The response of plants to applications of Ni is wide and includes effects on nitrogen fixation, seed germination and disease suppression. However, a much higher effect could be seen when nitrogen is provided in the form of urea or symbiotically fixed (Brown, 2006).

The first evidence of the yield response to Ni was documented by Roach and Barclay (1946), who reported a significant increase in crop yields of potato (*Solanum tuberosum*), wheat (*Triticum aestivum*) and bean (*Phaseolus vulgaris*) as a result of foliar application of Ni from dilute solutions.

In soybean, it was found that the addition of 40 g ha<sup>-1</sup> Ni increases nodulation and crop yield (Malavolta and Moraes, 2007), an effect attributed to the proper functioning of the symbiosis between soybean and *Rhizobium* sp. (Brown, 2006). In parsley (*Petroselinum crispum*) growing in plastic containers with clay, the addition of 50 mg kg<sup>-1</sup> soil Ni from NiSO<sub>4</sub> source increases the yield and quality of leaves, reduces the accumulation of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and increases the accumulation of essential oil aroma constituents (Atta-Aly, 1999). On the other hand, in Brazil the application of 0.03 mg L<sup>-1</sup> Ni in nutrient solution of umbu seedlings (*Spondias tuberosa*) increased dry mass production by 81.52% compared to untreated control (Caires *et al.*, 2007).

In rose of Jamaica (*Hibiscus sabdariffa*), Aziz *et al.* (2007) found that a joint application of cobalt and Ni in doses of 20 and 25 mg kg<sup>-1</sup> soil, respectively, increases the total mass of the plants, branch number and dry weight and fresh weight of flowers. In addition, these applications promoted an increase in the concentration of N, P, K, Co, Ni, Mn, Zn, and Cu, both in leaves and flowers of the plants (Aziz *et al.*, 2007).

Gad *et al.* (2007) in tomato (*Lycopersicon esculentum*) grown in sand found that the addition of 30 mg kg<sup>-1</sup> sand Ni significantly increased the total mass of the plant,

number of branches, leaf area, root length, contents of auxins and gibberellins. Similarly, the addition of Ni in the aforementioned doses improved fruit quality variables such as size, fresh weight, diameter, dry weight, contents of vitamin C, total soluble solids, and soluble sugars. In addition, the application of Ni caused the decrease in the contents of  $\text{NO}_3^-$  and  $\text{NH}_4^-$  as well as acidity, favorable characteristics for consumer health (Gad *et al.*, 2007).

Finally, it has been shown a beneficial effect of Ni in the management of agents causing fungal diseases, such as rust of cereal crops (Brown, 2006; Malavolta and Moraes, 2007). The beneficial effect is attributed to the alleged role of this element in reactions involving enzymes, such as superoxide dismutase, changes in nitrogen metabolism due to the contribution of Ni (Brown, 2006) and the possible toxicity of Ni to the pathogen (Malavolta and Moraes, 2007).

Changes in nitrogen metabolism may involve the decrease in amount of free amino acids, a substrate used by most pathogens for growth and proliferation (Strengbom *et al.*, 2002). The accumulation of free amino acids, such as valine, leucine, isoleucine, tyrosine, tryptophan, and arginine, in response to Ni deficiency was reported by Bai *et al.* (2006). In practical terms, the efficiency of foliar sprays of urea in different crops can be improved by their joint application with Ni ( $\text{NiSO}_4$ ) at levels not exceeding  $40 \text{ g ha}^{-1}$  of Ni for crop cycle.

The application of Ni may have positive effects on nitrogen use efficiency in crops that extract high content of this mineral nutrient from soil and where nitrogen fertilizers are applied using urea as the main source, such as in case of rice. However, such effects could only be verified by conducting a research involving Ni as a case study.

## Conclusions

The current state of research dedicated to physiology of Ni in plants illustrates the essentiality of this micronutrient for plants, in particular, its importance for the processes related to the metabolism of nitrogen. The primary function of Ni is defined in terms of its importance for the hydrolysis of urea; however Ni may have an importance in other physiological processes, such as nitrogen fixation and synthesis of anthocyanins. Although the deficiencies of Ni in plants are relatively rare events, the positive response of crop yield and nitrogen use efficiency to applications of Ni are shown for different species.

## Literature cited

- Araujo, G.C.L., S.G. Lemos and C. Nabais. 2009. Ni sorption capacity of ground xylem of *Quercus ilex* trees and effects of selected ligands present in the xylem sap. *J. Plant Physiol.* 166, 270-277.
- Arnon, D.I. and P.R. Stout. 1939. The essentiality of certain elements in minute quantity for plants with special reference to copper. *Plant Physiol.* 14, 371-375.
- Atta-Aly, M.A. 1999. Effect of Ni addition on the yield and quality of parsley leaves. *Scientia Hort.* 82, 9-24.
- Azcon-Bieto, J. and M. Talón. 2008. *Fundamentos de fisiología vegetal.* 2<sup>nd</sup> ed. Mc Graw Hill Interamericana, Barcelona, Spain. pp. 83-97.
- Aziz, E., N. Gad and N. Badran. 2007. Effect of cobalt and Ni on plant growth, yield and flavonoids content of *Hibiscus sabdariffa* L. *Aust. J. Basic Appl. Sci.* 1, 73-78.
- Bai, C., C. Reilly and B.W. Wood. 2006. Ni deficiency disrupts metabolism of ureides, amino acids, and organic acids of young pecan foliage. *Plant Physiol.* 140, 433-443.
- Baker, A.J.M., S.P. McGrath, R.D. Reeves and J.A.C. Smith. 2000. Metal hyperaccumulator plants: A review of the ecology and physiology of a biochemical resource for phytoremediation of metal-polluted soils. pp. 85-107. En: Terry, N., G. Bañuelos and J. Vangronsveld (eds.). *Phytoremediation of contaminated soil and water.* Boca Raton, FL.
- Bidwell, S.D., S.A. Crawford, I.E. Woodrow, S. Knudsen and A.T. Marshall. 2004. Sub-cellular localization of Ni in the hyperaccumulator, *Hybanthus floribundus* (Lindley) F. Muell. *Plant Cell Environ.* 27, 705-716.
- Bhatia, N.P., K.B. Walsh and A.J.M. Baker. 2005. Detection and quantification of ligands involved in Ni detoxification in a herbaceous Ni hyperaccumulator *Stackhousia tryonii* Bailey. *J. Exp. Bot.* 56, 1343-1349.
- Brown, P.H., R.M. Welch and E.E. Cary. 1987. Ni: A micronutrient essential for higher plants. *Plant Physiol.* 85, 801-803.
- Brown, P.H. 2006. Ni. pp. 329-350. En: Barker, A.V. and D.J. Pilbeam (eds.). *Handbook of plant nutrition.* CRC Press, Boca Raton, FL.
- Caíres, O.S., E.V. de Oliveira, J.G. de Carvalho and C.R. Fonseca. 2007. Adição de níquel na solução nutritiva para o cultivo de mudas de umbuzeiro. *Rev. Bras. Ci. Solo.* 31, 485-490.
- Cataldo, D.A., T.R. Garland, R.E. Wildung and H. Drucker. 1978. Ni in plants. II. Distribution and chemical form in soybean plants. *Plant Physiol.* 62, 566-570.
- Cataldo, D.A., T.R. Mc Fadden, T.R. Garland and R.E. Wildung. 1988. Organic constituents and complexation of Ni (II), cadmium (II) and plutonium (IV) in soybean xylem exudates. *Plant Physiol.* 56, 734-739.
- Dixon, N.E., C. Gazzola, R.L. Blakeley and R. Zerner. 1975. Jack bean urease. A metalloenzyme. A simple biological role for Ni. *J. Am. Chem. Soc.* 97, 4131-4133.
- Dixon, N.E., R.L. Blakeley and R. Zerner. 1980. Jack-Bean urease (EC 3.5.1.5.3.). III. The involvement of active site Ni ion in inhibition by b-mercaptoethanol and phosphoramidate, and fluoride. *Can. J. Biochem.* 58, 481-488.

- Duarte, B., M. Delgado and I. Caçador. 2007. The role of citric acid in cadmium and Ni uptake and translocation, in *Halimione portulacoides*. *Chemosphere* 69, 836-840.
- Epstein, E. and A. Bloom. 2005. Mineral nutrition of plant: principles and perspectives. Sinauer Associates, Inc. Publishers. Sunderland, MA.
- Eskew, D.L., R.M. Welch and E.E. Cary. 1983. Ni an essential micronutrient for legumes and possibly all higher plants. *Sci.* 222, 621-623.
- Eskew, D.L., R.M. Welch and E.E. Cary. 1984a. A simple plant nutrient solution purification method for effective removal of trace metals using controlled pore glass-8 hydroxyquinoline chelation column chromatography. *Plant Physiol.* 76, 103-105.
- Eskew, D.L., R.M. Welch and W.A. Norvell. 1984b. Ni in higher plants: further evidence for an essential role. *Plant Physiol.* 76, 691-693.
- Fishbein, W.N., K. Nagarajan and W. Scurzi. 1973. Urease catalysis and structure. IX. The half-unit and hemopolymers of jack bean urease. *J. Biol. Chem.* 248, 7870-7877.
- Gad, N., M.H. El-Sherif and N.H.M. El-Gereendly. 2007. Influence of Ni on some physiological aspects of tomato plants. *Aust. J. Basic Appl. Sci.* 1, 286-293.
- Gajewska, E. and M. Skłodowska. 2009. Ni-induced changes in nitrogen metabolism in wheat shoots. *J. Plant Physiol.* 166, 1034-1044.
- Hirai, M., R. Kawai-Hirai, T. Hirai and T. Ueki. 1993. Structural change of jack bean urease induced by addition of surfactants studied with synchrotron-radiation small-angle X-ray scattering. *Eur. J. Biochem.* 215, 55-61.
- Homer, F.A., R.D. Reeves and R.R. Brooks. 1995. The possible involvement of amino acids in Ni chelation in some Ni-accumulating plants. *Curr. Topics Phytochem.* 14, 31-37.
- Hsiao, K.H., P.H. Kao and Z.Y. Hseu. 2007. Effects of chelators on chromium and Ni uptake by *Brassica juncea* on serpentine mine tailings for phytoextraction. *J. Hazard. Materials* 148, 366-376.
- Kováčik, J., B. Klejdus and M. Backor. 2009. Phenolic metabolism of *Matricaria chamomilla* plants exposed to Ni. *J. Plant Physiol.* 166, 1460-1464.
- Krämer, U., J.D. Cotter-Howells, J.M. Charnock, A.J.M. Baker and J.A.C. Smith. 1996. Free histidine as a metal chelator in plants that accumulate Ni. *Nature* 379, 635-638.
- Küpper, H., E. Lombi, F.J. Zhao, G. Wieshammer and S.P. McGrath. 2001. Cellular compartmentation of Ni in the hyperaccumulators *Alyssum lesbiacum*, *Alyssum bertolonii* and *Thlaspi goesingense*. *J. Experim. Bot.* 52, 2291-2300.
- Malavolta, E. and M.F. Moraes. 2005. Niquel: "Orelha de raton". *Informações Agronômicas* 112, 2.
- Malavolta, E. and M.F. Moraes. 2007. Ni – from toxic a nutrient essential. *Better crops with plant food* 91, 26-27.
- Marschner, H. 2002. Mineral nutrition of higher plants. 2<sup>nd</sup> ed., Academic Press, London, 889 p.
- Mari, S., D. Gendre, K. Pianelli, L. Ouerdane, R. Lobinski, J.F. Briat, M. Lebrun and P. Czernic. 2006. Root-to-shoot long-distance circulation of nicotianamine and nicotianamine-Ni chelates in the metal hyperaccumulator *Thlaspi caerulescens*. *J. Exp. Bot.* 57, 4111-4122.
- McNear, D.H., R.L. Chaney and D.L. Sparks. 2010. The hyperaccumulator *Alyssum murale* uses complexation with nitrogen and oxygen donor ligands for Ni transport and storage. *Phytochem.* 71, 188-200.
- Mengel y Kirkby, 2001. Principles of plant nutrition. 5<sup>th</sup> ed., IPI, Bern, 687 p.
- Molas, J. and S. Baran. 2004. Relationship between the chemical form of Ni applied to the soil and its uptake and toxicity to barley plants (*Hordeum vulgare* L.). *Geoderma* 122, 247-255.
- Montargés-Pelletier, E., V. Chardot, G. Echevarria, L.J. Michot, A. Bauer and J.L. Morel. 2008. Identification of Ni chelators in three hyperaccumulating plants: An X-ray spectroscopic study. *Phytochem.* 69, 1695-1709.
- Page, V. and U. Feller. 2005. Selective transport of zinc, manganese, Ni, cobalt and cadmium in the root system and transfer to the leaves in young wheat plants. *Annals Bot.* 96, 425-434.
- Palacios, J.M. 1995. Sistema de oxidación de hidrogeno de *Rhizobium leguminosarum*: control de la expresión génica por NiFe y F<sub>n</sub>Rn. En: Universidad Politécnica de Madrid. <http://wwwedu-micro.usal.es/sefin/Palacios.html>, consulta: mayo de 2009.
- Pianelli, K., S. Mari, L. Marques, M. Lebrun and P. Czernic. 2005. Nicotianamine over-accumulation confers resistance to Ni in *Arabidopsis thaliana*. *Transg. Res.* 14, 739-748.
- Polacco, J.C. and R.B. Sparks. 1982. Patterns of urease synthesis in developing soybeans. *Plant Physiol.* 70, 189-194.
- Redjala, T., T. Sterckeman, S. Skiker and G. Echevarria. 2010. Contribution of apoplast and symplast to short term Ni uptake by maize and *Leptoplax emarginata* roots. *Environ. Exper. Bot.* 68, 99-106.
- Roach, W.A. and C. Barclay. 1946. Ni and multiple trace-element deficiencies in agricultural crops. *Nature* 157, 696.
- Robinson, B.H., E. Lombi, F.J. Zhao and S.P. McGrath. 2003. Uptake and distribution of Ni and other metals in the hyperaccumulator *Berkheya coddii*. *New Phytol.* 158, 279-285.
- Ruíz-Argueso, T., J. Imperial and J.M. Palacios. 2000. Prokaryotic nitrogen fixation. pp. 489-507. En: Triplett, E.W. (ed.). *Horizon Scientific Press*, Wymondham, U.K.
- Sagner, S., R. Kneer, G. Wanner, J.P. Cosson, B. Deus-Neumann and M.H. Zenk. 1998. Hyperaccumulation, complexation and distribution of Ni in *Sebertia acuminata*. *Phytochem.* 41, 339-347.
- Schaaf, G., A. Honsbein, A.R. Meda, S. Kirchnert, D. Wipf and N. von Wiren. 2006. AtIREG2 encodes a tonoplast transport protein involved in iron-dependent Ni detoxification in *Arabidopsis thaliana* roots. *J. Biol. Chem.* 281, 25532-25540.
- Strengbom, J., A. Nordin, T. Näsholm and T. Ericson. 2002. Parasitic fungus mediates change in nitrogen-exposed boreal forest vegetation. *J. Ecol.* 90, 61-67.
- Taiz, L. and E. Zeiger. 2004. *Plant physiology*. 3<sup>th</sup> ed. Sunderland: Sinauer Associates. 723 p.
- Tejada-Jiménez, M., A. Galván, E. Fernández and Á. Llamas. 2009. Homeostasis of the micronutrients Ni, Mo and Cl with specific biochemical functions. *Curr. Opin. Plant Biol.* 12, 358-363.
- Tiffin, L.O. 1971. Translocation of Ni in xylem exudates of plants. *Plant Physiol.* 48, 273-277.

- Walker, C.D., R.D. Graham, J.T. Madison, E.E. Cary and R.M. Welch. 1985. Effects of Ni deficiency on some nitrogen metabolites in cowpeas (*Vigna unguiculata* L. Walp.). *Plant Physiol.* 79, 474-479.
- Ye, Z.H., A.J.M. Baker, M.H. Wong and A.J. Willis. 1997. Copper and Ni uptake, accumulation and tolerance in *Typha latifolia* with and without iron plaque on the root surface. *New Phytol.* 136, 481-488.
- Zeller, S. and U. Feller. 1999. Long-distance transport of cobalt and Ni in maturing wheat. *Europ. J. Agron.* 10, 91-98.
- Zobiolo, L.H.S., R.S. Oliveira, R.J. Kremer, J. Constantin, T. Yamada, C. Castro, F.A. Oliveira and A. Oliveira. 2010. Effect of glyphosate on symbiotic N<sub>2</sub> fixation and Ni concentration in glyphosate-resistant soybeans. *Appl. Soil Ecol.* 44, 176-180.