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Importance of nickel in crops

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Abstract
Prolonged and unbalanced use of chemicals, leads to destruction of physical structure of soil, disturbed biological condition of soil and also change the chemical equilibrium of soil, which in turn affects the availability of other essential nutrients in the soil matrix. Out of seven essential micronutrient (Fe, Zn, Cu, Mo, Mn, B, and Ni) Ni is one of the recently added essential plant nutrient. Nickel is an important metal for plants, which fulfils a variety of vital roles in plants functions. Also, Ni is a constituent of several metallo-enzymes which are actively engaged in Nitrogen metabolism and biological Nitrogen fixation. As it plays a major part in plant metabolism and other mechanisms, Ni deficiency can produce variety of negative impacts on growth and metabolism of plants. A very limited data is available on uptake of Ni in crop plants as most of the studies were conducted by keeping its toxicity problem in view rather than its deficiency.

Keywords: nickel, micronutrient, crops, deficiency, toxicity

Introduction

Nickel is a d-block element occupying 1st row of transition series. It lies in the 10th group of the periodic table with other group members including palladium (Pd), platinum (Pt) and darmstadtium (Ds). Nickel exists as silvery-white lustrous metal with a slight golden tinge. It typically exists in the 0 and +2 oxidation states, but also establish less frequently in the -1, +1, +3 and +4 oxidation states. It is relatively prolific and naturally occurring metal, widely scattered in the earth crust. It is the 24th most copious element found in the earth's crust as well as the 5th most profuse element by weight following iron (Fe), oxygen (O), magnesium (Mg) and silicon (Si), constituting a total of about 3% of the earth composition (Cempel and Nikel, 2006) [11].

The prominence of Nickel in soils highly depends upon the its content in the parent rocks, but in surface soils, its amount is also a result of soil- forming processes and pollution (Kabata-Pendias and Pendias, 1992; McGrath, 1995) [27, 37]. The contents are lowest in case of sedimentary rocks that are comprised of clays, lime stones, sandstones and shales, while the highest concentrations exist in basic igneous rocks (Kabata- Pendias and Mukherjee, 2007) [26]. The average concentration of Ni in the earth's crust is 0.008% and Agricultural soils contain Ni at levels of 3–1000 mg kg^{-1} (Nagajyoti *et al.*, 2010; Iyaka, 2011) [41, 25]. The actual concentration of nickel in any particular soil sample may vary widely; for example, sandstone and granite may contain less than 0.0001% nickel, whereas, the so-called ultramafic or ultra basic rocks can contain substantially more than 0.3% nickel. Those soils carrying less than 5 mg kg^{-1} Ni are too acidic to support normal plant growth. Nickel content in soils varied widely and has been estimated to range from 3 to 1000 mg kg^{-1}; for the world soils, the grand range is between 0.2 to 450 mg kg^{-1}, while the grand mean is calculated to be 22 mg kg^{-1} (Kabata and Pendias, 1992; Cempel and Nikel, 2006) [27, 11] Most frequently Ni is present as hydrated complex (Ni $(H_2O)^{+6}$, in the soil solution. Other than this, it also exists in many different forms in soils such as adsorbed or complex on organic cation surfaces or on inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, water soluble, free-ion or cheated metal complexes in soil solution (Seregin and Kozhevnikova, 2006) [54].

Nickel is found in all soil types and is also emitted from volcanoes. In the environment, it is found in combination with oxygen or sulphur as oxides or sulphides (Baralkiewicz and Siepak, 1999) [4]. The rocks having low silica, are high in nickel (except for carbonate), and those high in silica are relatively low in nickel. Generally, it is uniformly distribution in soil profile. It is typically accumulated at the surface soil due to deposition through many anthropogenic activities (Cempel and Nikel, 2006) [11]. Nickel can also exist in several other forms in soils that include adsorbed or complex on organic cation surfaces or on inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, water soluble, free-ion or cheated metal complexes in soil solution (Bennett, 1982) [5]. The complexes are much more mobile in the presence of fulvic and humic acids, and may be prominent than the hydrated divalent cation in soil solution (ATSDR, 2005) [3].

Functions of nickel

Nickel as a micronutrient

Nickel is a key component of selected enzymes involved in N metabolism and biological N fixation and is generally accepted as an essential ultra-micronutrient (Marchner, 1993; Freyermuth *et al.*, 2000) [34, 19]. It is a well known functional constituent of seven enzymes, many of which occurring in bacterial and animal systems, but not known to be active in plants. A seventh enzyme, urease, is widely distributed in biology which catalyses the hydrolytic cleavage of urea to give ammonia and carbon dioxide. It is widely distributed in higher plants (Welch, 1981; Marschner, 2003) [59, 35]. Ni usually works as a cofactor to enable urease to catalyse this conversion. It is used as a source of Nitrogen for plant life. Its metabolism is very critical for certain enzyme activities other than urease, such as glyoxalases (family I), peptide deformylases, methyl-CoM reductase, some superoxide dismutases and hydrogenases, in maintaining proper cellular redox state and various other biochemical, physiological and growth responses (Kutman *et al.*, 2013) [31].

It gets accumulated in plant organs or tissues, such as leaves. A broader biological significance of nickel is also implied in the demonstration that nickel is essential for animal life and for a range of bacterial enzymes, including key enzymes in the nitrogen-fixing symbiont, *Bradyrhizobium japonicum.* Evidence of Ni roles in biological systems were also reviewed by Mishra and Kar, (1974); Welch, (1981) [39, 59]. Many examples were cited for yield increases in field-grown crops in response to Ni application to the crop and to the soil. It was clearly explained by Bertrand and Dewolf, (1967) [6], that Ni application benefited the growth of nitrogen-fixing plant species. It was reported that soil-Ni application to field-grown soybean resulted in a significant increase in nodule weight and seed yield. The role of nickel in plant growth and metabolism emerged as a topic of interest after the discovery of Ni as an important component of the plant urease in 1975 (Dixon *et al.,* 1975) [16]. Shimada and Ando, (2004) [55] reported that when tomato and soybean plants were grown in hydroponic cultures with insufficient Ni and supplied with urea as the nitrogen source, urea accumulated in their tissues and developed leaf tip necrosis. Ni also play vital role in urea metabolism in plant as reported by Walker and his co-workers, (1985) [58]. Until then, there was no proven record for Ni as being an essential element for higher plants. Brown *et al.*, (1987) [10] revealed that Ni is an essential nutrient for both monocotyledons and dicotyledons for completion of plant life cycle, based upon the criteria for essentiality. It is the 17^{th} element recognized as essential for plant growth and development (Liu, 2001) [33]. Plants Ni requirement is the lowest of all essential elements at < 0.5 mg kg^{-1} of dry weight, which makes it an essential plant micronutrient. Generally, Nickel is required for plants at very low concentrations such that analytical technologies were not available to detect it until the mid- 1970s. Nickel occupies a unique position among all the plant nutrients because its functions in plant growth and development. Ni is available in the form of divalent cation (Ni^{2+}) for uptake in plants, however total Ni concentration is not a useful measure for Ni bioavailability. It is the only oxidation state of Ni that is likely to be of any importance to higher plants. Generally, about 0.1-5 mg kg^{-1} of Ni is present in the plants. The values in excess of 200 mg kg^{-1} may occur in some plant species in case of serpentine soils. Such levels may be toxic to plants which are not adapted to these soils. It is a well known fact that almost all the transition elements have a unique property to form coordination compounds. In the similar way Nickel is also found to form variety of coordination complexes and chelates. All these complexes formed are of biological importance. One of the major complexes of Ni-DMG complex is having various medicinal uses and a variety of applications in analytical processes.

Deficiency

From the above discussion it can be concluded that the element Nickel is a key component for. plants and their metabolic performance. Insufficiency of Ni might be due to low levels of this element in the soil or be introduced by interaction with other elements. Nickel deficiency symptoms are characterized by marginal chlorosis of leaves, premature senescence, and diminished seed set (Epstein and Bloom, 2005) [17]. Nickel deficiency can be induced by various factors involving:

a) Excessively high soil zinc, copper, manganese, iron, calcium, or magnesium,
b) Root damage by root-knot nematodes or
c) Dry or cool soils at the time of bud break.

The conditions of Ni deficiency occurs also commonly result in a deficiency of zinc or copper and this fact has resulted in the extensive use of copper and zinc fertilizers over many years further exacerbating the nickel deficiency.

Being an important constituent its deficiency in the plant and other living beings can lead to various ill impacts causing various problems. It is stated by Eskew *et al.*, (1984) [18] that Ni deficiency can result in plant necrosis. Also, its deficiency cannot be substituted by other metals such as Aluminium (Al), Tin (Sn), Cadmium (Cd) or Vanadium (V)). Nickel deficiency also resulted in significantly high reduction in germination rates (i.e. 50% less than grain from Ni adequate plants) and depressed seedling vigour of the viable grain. Brown *et al.* (1987) [9] also demonstrated the essentiality of Ni in their experiment where a failure in barley plants to produce viable grain was observed. The probable reason was disruption of the maternal plant's normal grain-filling and maturation processes that occur following formation of the grain embryo. The interpretation that barley plants not succeed to complete their life cycle in the dearth of Ni and addition of Ni to the development medium completely alleviates the deficiency symptoms in the maternal plants satisfies the essentiality criteria of Ni.

Toxicity

Since Nickel comes under the category of micronutrients (trace), its presence is useful only upto a certain limits. Any excess in the concentration than its requirement causes toxicity as many other heavy metals do. Rapid industrialization and urbanization during the recent past have caused accumulation of Ni in varied habitats where from the acquisition by the plants and their further transfer to human and animal population may affect the life forms seriously (Smith, 1996; Bisesser *et al.*, 1983; Hale *et al.*, 1985; Seregin and Kozhevnikova, 2006) [57, 7, 21, 54]. The acceptable limit of naturally occurring concentration of Ni in soil and surface waters is lower than 100 and 0.005 ppm respectively. Any increments from the above stated critical limit are considered toxic to plants as well as soil. During the last decade its concentration has been reported up to 26,000 ppm in polluted soils and 0.2 mg/L in polluted surface waters i.e. 20–30 times higher than found in unpolluted areas (Yusuf M. *et al.*, 2011) [63]. The range of nickel concentrations in plants averages 0.05-5 mg Ni/kg dry weight with concentrations above 50 mg Ni/kg dry weight being toxic (Kramer *et al.*, 2000) [30]. As Ni is mobile in plants, therefore the deficiency symptoms can be observed first in the older leaves. Growth of most plants species is also adversely affected by tissue concentration above 50 μg Ni g^{-1} dry weight. Elevated levels of Ni in the soil and in the plants tissue frequently induce Zn or Fe deficiency which leads to typical symptoms of chlorosis.

In present situations, toxicity of Nickel is much under consideration than its deficiency. Various signs of Ni phytotoxicity involve reduction in growth of roots and shoots, poor branching, deformed plant parts, decreased yield, leaf spotting, abnormality in flower shape, mitotic root tip disturbance, inhibition of germination, and chlorosis (Canadian Environmental Quality Guidelines, 1999) (Crooke, 1956; Khan *et al.*, 2012; Di toro *et al.* 1992; Yang *et al.* 1996) [13, 28, 15, 62]. Earlier, Ni toxicity was not of major concern because of its dual role in plant as a micronutrient and also due to its complex electronic chemistry. Excess of nickel causes phototoxic effects. Nickel toxicity has acquired a serious concern because of agricultural use of sewage sludge that is rich in nickel and the industrial use of nickel production of Ni-Cd batteries which leads to discharge of nickel rich effluents (Coman *et al.*, 2013) [12]. Excess Ni was reported to affect a number of biological and physiological processes resulting in an inhibition of plant growth.

The basic origin of Nickel toxicity in the soils is due to a number of anthropogenic activities such as smelting, burning of fossil fuel, vehicle emissions, disposal of household, municipal and industrial wastes, metal mining, fertilizer application, and organic manures. However, the major part of Ni released into the environment includes raw material used in metallurgical and electroplating industries, as a catalyst in the chemical and food industry and as a major component of electrical batteries (Yusuf *et al.*, 2011) [63].

Effect of nickel on crops

Like other essential nutrients, Nickel is also one of the most vital element required in very low concentrations. It is highly responsible for enhancement in plant growth and various other associated growth components. The discovery of Nickel as a component of the plant urease in 1975 by Dixon *et al.*, 1975 [16] lead to enhanced research interests in studying nickel as essential nutrients in plants. After this various experiments were also conducted to determine the other beneficial effects too. In 1977, it was examined by Polacco [47] that tissue-cultured soybean cells could not develop in the lack of Nickel when applied with urea as the single nitrogen source. Similarly, an absolute nickel requirement was demonstrated for tissue-cultured rice (*Oryza sativa* L.) and tobacco (*Nicotiana tabacum* L.) by Mishra and Kar (1974) and Welch (1981) [39, 59]. Nickel is also involved in the function of at least nine proteins (Li and Zamble, 2009) [32] including methyl-coenyme M reductase, superoxide dismutase, Ni dependent glyoxylase, aci-reductone dioxygenase, NiFe-hydrogenage, carbon monoxide dehydrogenase, acetyl-CoA decarbonylase synthase and methyleneurease, of which urease and the Ni-urease accessory protein (Eu3) (Freyermuth *et al.*, 2000) [19].

It is also an essential micronutrient for higher plants like legumes (Marschner, 2003) [35] being an integral component of urease enzyme which is involved in hydrolysis of urea. Soybean plants grown with urea as N source showed necrosis of leaf tips which was associated with deficiency of Ni and due to accumulation of urea to toxic levels in plant shoots. Bertrand and Dewolf, 1967 [6], reported clear evidence that Ni application benefited the growth of nitrogen-fixing plant species. It was reported that soil-Ni application to field-grown soybean resulted in a significant increase in nodule weight and seed yield. The very first evidence of a response of a field crop to the application of a Ni fertilizer was demonstrated in 1945 for potato, wheat and bean crops (Roach and Barclay, 1946) [55] it was reviewed by Mishra and Kar, (1971); Welch, (1981) [40, 59] that the evidence of Ni roles in biological systems and cited many examples of yield increases in field-grown crops in response to Ni application to the crop and to the soil. The role of Ni in urea metabolism in plant was reported by Walker *et al*., (1985) [58] in 1985. Until then, there was no proven record for Ni as being an essential element for higher plants. Similarly, Shimada and Ando, 2004 [55] reported that when tomato and soybean plants were grown in hydroponic cultures with insufficient Ni and supplied with urea as the nitrogen source, urea accumulated in their tissues and developed leaf tip necrosis. Toxic symptoms of Ni in oats, a Ni-sensible plant species, were observed when Ni concentration was higher than 100 mg kg^{-1} tissue dry matter (Crooke, 1956) [13].

Biomass production

Biomass production in plants was also significantly affected by the concentration of nickel present. Biomass (fresh and dry weights of root and shoot) of chickpea was impeded by the nickel treatments. Fresh weights of root and shoot were more affected by Nickel. Significant reduction in the fresh weight of root of the plants grown in 100, 200 and 400 ppm Ni was observed. Significant reduction in fresh weight of shoot occurred with 400 ppm of Ni. Similar reduction in dry weight of root was noticed with the application of 200 and 400 ppm of Ni in comparison to untreated plants (control). Higher concentrations (100, 200 and 400 ppm) of nickel was significantly effective in reducing the dry weights of chickpea shoots. It was concluded that all the three concentrations were equally harmful as reductions caused by the concentrations did not differ significantly (Khan and Khan, 2010) [29]. Another study revealed that dry matter yield of maize was decreased at 10 mg L^{-1} nickel in solution culture, while in pot culture study, a decrease in dry matter weight at 50 mg kg^{-1} nickel concentration was recorded and also symptom of chlorosis was observed at nickel dose above 100 mg kg^{-1}. Rathor *et al.*, (2014) [50]. Sabir *et al*., (2011) [53] revealed that an improved dry weight production was also observed with Nickel addition to maize at all applied levels (0, 17, 51 and 68 µM) compared to control, however maximum increase in shoot and root was observed at 68 µM. Plant growth, nodulation and yield of grain and straw increased at lower doses up to 3 mg Ni kg^{-1} but decreased at higher doses. At higher level, the accumulation of Ni in root was mostly two times greater than in grain (Maurya *et al.*, 2008) [36]. More number of leaves were found in the plants grown with 5, 10, 50, and 1000 mg Ni L^{-1} and there was a tendency toward greater stem thickness and fresh shoot biomass at 50 mg Ni L^{-1}. It was observed by Parida *et al*. (2003) [45] that the dry matter yields of fenugreek increased slightly up to 20 mg Ni kg^{-1}. A green house experiment was conducted by Rabie *et al.*, (1992) [49] with wheat, faba beans and sorghum on loamy soil treated with varying concentrations of Nickel as nickel sulphate. An obvious accumulation of nickel in plants and a slight increase in the dry matter production was observed with Nickel levels of 15, 30, 45, and 60 mg kg^{-1}. Another glasshouse experiment was conducted by Singh *et al.* (1990) [56] to study the effect of Ni on the growth of wheat *(Triticum aestivum* Cv. WH 291) in the presence and absence of nitrogen as urea. Responses to N application were observed only up to 120 µg N g^{-1} soil while no response was observed in the dry matter yield of wheat tops (leaves + stem) in case of absence of applied N. While in the presence of applied N, significant yield increases were obtained at 12.5 µg N g^{-1} soil. Highest shoot dry weight of maize plant was obtained with 0.05 and 0.1 mg Ni L^{-1} supplied Ni levels. Poulik (1997) [48] performed a pot experiment taking different doses of Ni as 0, 14, 28, 56, 84 and 168 mg Ni kg^{-1} soil. The kernel yields of oats grown on soil incubated with concentrations of up to 56 mg kg-1 Ni showed a highly significant increase by 15.5-25.1%.

Nutrient content

A marked enhancement in plant senescence and reduced tissue-iron concentrations was observed by Nickel deficiency. It can also reduce Fe levels in plant tissues (Wood and Reilly, 2007) [61]. Since excess Ni has been shown to decrease the contents of Fe (Pandey and Sharma, 2002) [44], Cu and Zn (Parida *et al*., 2003) [45] in plant tissues, it can be speculated that Ni may reduce the biosynthesis of these metalloenzymes by causing deficiencies of these essential metals (Gajewska, 2006) [20]. (Wisniewski and Dickinson, 2003; Nieminen, 2004) [60, 42], Studied photosynthesis in plant leaves and suggested that Ni can competitively remove Ca ions from the Ca-binding site and replaced the Mg ion of chlorophyll which eventually inhibited the PS-II electron transport. It was observed that Ni-treated lettuce plants accumulated lower concentrations of nitrate ($NO3^{-}$) in their leaves compared with untreated plants. Hosseini and Khoshgoftarmanesh (2013) [24] Nickel supplementation increased the leaf total N concentrations in the urea-fed plants (Amir *et al.* 2011) [2]. Ni in higher levels (40 mg L^{-1}) decreased the concentrations of Ca, Mn and Fe in achenes of sunflower. In contrast, achene N, K, Zn, Mn and Cu decreased consistently with increasing level of Ni, even at lower level (10 mg L^{-1}). Ahmad *et al.* (2011) [1].

Cholorophyll content

Chlorophyll content of various photosynthetic plants was also affected by the presence of Nickel in variable concentration. Metal ions may replace Mg ion from the tetrapyrol ring of the chlorophyll molecule leading to denaturing of the pigments. Many researchers found significant reduction in leaf contents of chlorophyll under the application of nickel (Hilmy and Gad, 2002; Hilmy *et al*., 2002; Reddy, 2003; Boularbah *et al*., 2006; Ogundiran, 2007) [22, 23, 51, 8, 43].

A study has revealed that 10 and 50 ppm as a damage threshold level of Ni or Co respectively for chickpea cultivation. Reqirment of appropriate efforts to maintain the metal concentration below the damaging level in the areas close to nickel or cobalt source was observed by (Khan and Khan, 2010) [29]. Milosevic *et al.* (2002) [38] noticed the decreased Chlorophyll content at each level of applied Ni rate. Parlak, (2016) [46] also observed that chlorophyll content in wheat decreased statistically at both 25 and 50 g Ni L^{-1}. The seedlings grown at 50g Ni L^{-1} was affected most compared with the control. Their chlorophyll content was reduced by 50%. Dhir *et al.*, (2009) [14] was explained that this decline in chlorophyll levels was due to a lowering in Fe content, reduced efficiency of enzymes for chlorophyll biosynthesis and replacement of central Mg^{2+} by the heavy metals. Similarly several other authors reported decreased chlorophyll contents in the leaves of Ni-treated plants (Pandey and Sharma, 2002; Gajewska *et al.* 2006; Seregin and Kozhevnikova; 2006) [44, 20, 54].

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