REVIEW ARTICLE

Nickel in Environment and Plant Nutrition: A Mini Review

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Abstract

Nickel (Ni) with iron forms the inner core of earth and is ranked seventh element responsible for causing health hazards and 9th in environmental degradation. Nickel is omnipresent. It is in air, water, plant foods and easily gets in the living bodies. Nickel is recently added as an essential plant micronutrient. It is a constituent of enzyme urease and is now known to be involved in several plant physiological processes including nitrogen metabolism, water relations, germination, photosynthesis, growth and senescence. It is present in soil, water systems, industrial effluents, fertilizer and manures in fairly good amounts to meet the requirements of crop plants. It is more known for its toxicity than for its deficiency. Nevertheless, there are Ni deficient soils and Ni fertilization has helped the crop plants. Most of the studies on Ni have been in pot-cultures and solution cultures. When required foliar application of Ni as nickel sulphate is preferred.

Key words: Germination, Legumes, Nickel, Nickel Sulphate, Soybean, urease.

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Introduction

Nickel as an element is in group 10 of the periodic table. It has an atomic weight of 28 and is in the group of transition metals between cobalt (Co) and zinc (Zn). It has an atomic configuration of $1s_2 2s_2 2p_6 3s_2 3p_6 3d_8 4s_2$. The 2 electrons in the fourth's' sub-shell take part in chemical reactions. In soil solution it behaves like zinc. It was first isolated by Swedish Chemist Akel Fredrik Corstedt from the mineral nicolite (Iyaka, 2011). It is universally present in very small amounts in soil, plants and environment. Amounts of Ni in soil and air in the vicinity of Ni mines are very high. The average Ni content for soils is 30 mg kg^{-1}, but could be higher than 10,000 in ultramatic soils (Tsadilas *et al.*, 2018). It is quite low in sedimentary rocks but fairly high in basic igneous rocks. In atmosphere, it is spread by natural causes such as forest fires and burning of vegetation or waste materials (Clayton and Clayton, 1993) as well as by anthropogenic sources, such as burning of coal for generating power and in other plants and mineral oil in combustion. An iron and nickel mixture forms the powder and inner core of earth (Stixrude and Wasserman, 1997).

Ni combines well with several metals. Its alloy with gold is known as white gold. It is used in steel manufacture and coating iron kitchenware and utensils. It is used in making coins in US and Canada. About 2.3 million tonnes of Ni is annually produce, Indonesia being the biggest producer (9560,000 tonnes) followed by Philippines.

Nickel in Environment

Nickel does not breakdown in the environment and can bio-accumulate for many years after exposure to low levels of this metal. It is black listed by the European community. The environmental degradation caused by Ni is not directly but through mineral oil and other sources of energy used in its mining, emanating greenhouse gases. In 2017 Government of Philippines closed 23 Ni mines (Cruz and Serapio, 2017). It is non-essential and highly toxic in the aquatic environment released by industrial sources such as Ni-Cd batteries, plating processes, refining of ores, etc. Effluents from such industries are sources of nickel in aquatic systems. Ni has more health related problems. Safe limit of Ni in air and water is 20 mg L^{-1}. A survey of river waters in India indicated that 25 rivers had water containing more than the safe limits and were not suitable for drinking (Arita and Costa, 2012; DPDO, 2018).

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Ni and Human Health

Ni is known to cause allergy to the skin, and inhaling large amounts leads to lung problems including fibrosis and even lung cancer (Zhao *et al.*, 2009). Ni has also been associated with cardiovascular disease, neurological deficits, and developmental deficits in childhood, and high blood pressure (Zambelli and Ciurli, 2013.). Ni can replace several matalloenzymes and thus interferes with the functioning of several enzymes. Most foods contain <0.5 mg Ni kg^{-1} fresh weight, but foods from legumes including soybeans and spinach may contain 8.5-12.0 mg kg^{-1} fresh weight (Aleksandra and Blaszezk, 2008).

Phytoremediation

More than 300 taxa of plants are known to be Ni accumulators and *Alysummurale* is recommended as a crop for phytoremediation (Harasim and Filipek, 2015). *Aethionema, Alyssum, Bornmuellera, Cochlearia, Thlaspi* (Brassicaceae) and *Asteraceae* etc. may accumulate 10,000 mg Ni kg^{-1} dry matter or more (Reeves and Adiguzel, 2004). Even in cultivated crops there are Ni accumulators, which do not show harmful effects of excess Ni. Indian mustard is heavy accumulator of Ni (Singh *et al.*, 2001). Prasad *et al.* (1997) reported that even wheat accumulated large amounts of Ni when irrigated with industrial waste and water hyacinth. Some plant species belonging to families.

Ni in Plant Nutrition

Mostly researchers/scientists talks about seven essential micronutrients for the plant nutrients, namely, Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu), Boron (B), Molybdenum (Mo) and Chlorine (Cl). However, recently Ni and Vanadium (V) have been added to this list. Ni is a constituent of enzyme urease (EC 3.5.1.5), which has 2 Ni atoms per 105 kDa or kAMU (One unified atomic mass unit (AMU) or Dalton (Da) is approximately the mass of one nucleon (either a single proton or neutron) (Dixon *et al.*, 1975; Musculus, 1976). The molecular weight for jack-bean urease is either 480 kDa or 545 kDa (calculated mass from the amino acid sequence); 840 amino acids per molecule, of which 90 are cysteine residues (*Krajewska, 2009). In addition to urease,* Ni is a functional constituent of seven other enzymes including Glx I (EC 4.4.1.5) l, ARD (EC 1.13.11.54), Ni-SOD (EC 1.15.1.1.), Hydrogenase (EC 1.12.98.2), MRC (EC 2.8.4.1), CODH (EC 1.2.99.2), and ACS (EC 2.3.1.169) (Ragsdale, 2009).

Urease is present in certain bacteria, fungi, algae, soil and in some plants and even in mammals. It hydrolysis of urea into CO_2 and ammonia and is responsible for ammonia volatilization, when urea is applied to soil surface. The optimum pH is 7.4 and optimum temperature is 60°C. In general, it is present in soils and urea hydrolysis is quite rapid in Indian soils (Reddy and Prasad, 1975). Urease is involved in N-fixation in legumes and is also extremely important to N metabolism in plants, especially legumes. Eskew *et al.* (1983, 1984) reported that legume plants grown in nutrient solutions containing urea as the N source developed necrotic lesions on the leaflet tips due to accumulation of 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. Brown (2015) suggested accumulation of nitrates as a consequence of reduction in malate dehydrogenase activity when Ni supply was reduced to plants. The leaf tip necrosis symptom of Ni deficiency is even more frequent and extensive when plants are highly dependent on biological N fixation for their N.

Nickel as a plant nutrient has not received much attention in India, because it is needed in very small amounts and the requirements are generally met by impurities present in fertilizers and manures. Benson *et al.* (2014) reported from Nigeria that in the samples of fertilizers they studied, single super phosphate contained on average 5.26 mg Ni kg^{-1}, while urea contained 5.87 mg Ni kg^{-1}. Organic manures also contain fairly high amounts of Ni. Chauhan *et al.* (2008) reported values of 9.6 mg Ni kg^{-1} in dairy manure and 7-9 mg Ni kg^{-1} in poultry manure. Sewage sludge may contain 15-815 mg Ni kg^{-1} (Maiti *et al.*, 1992). Industrial effluents may contain 5-80 mg Ni L^{-1} (Sengar *et al.*, 2008). Even natural water bodies contain Ni. The Ni concentration in river water and in sediments in the upper Ganges (India), for example, has been estimated to be 35-211 mg Ni L^{-1} and 70,900-511,000 mg Ni kg^{-1}, respectively (Israili, 1992).

Nickel can be easily determined in aqueous extracts using Dimethylglyoxime ($C_4H_8N_2O_2$), generally abbreviated as $dmgH_2$ (Salman *et al.*, 2011). It forms a bright red complex with Ni, the colour intensity of which can be measured on a spectrophotometer. It can also be determined by Atomic Absorption Spectrometry (Hazer *et al.*, 2009).

Content in soils

Nickel (atomic weight 58.6934) is a transition metal close to iron (atomic weight 55.845) and the Ni-Fe alloy forms the inner core of the earth. Other essential cationic micronutrients for plants belonging to transition metal group include Fe, Mn, Cu, Zn, and V. The transition metals are capable of forming paramagnetic and colored compounds of different oxidation states. The general range for total Ni content in world soils varies from 0.2 to 450 mg kg^{-1} soil, however, higher values are up to 1000 mg kg^{-1} soil are reported (Iyaka, 2011). DTPA-extraction (Lindsay and Norvell, 1978) is considered quite suitable for available Ni. In India, data are available on Ni content in Jharkhand soils (Rawat *et al.*, 2019). Surface soil samples were collected from different locations and topo-sequences covering three agro-climatic zones of Jharkhand, viz. zone-IV (Baliapur, Jharia, and Dhanbad), zone-V (Bagru, Pakharpat, Kisko, and Lohardaga), and zone-VI (Moshabani, Jadugonda, and Chandil). A large number (n=225) of soil samples were collected from the surface and examined for nickel. DTPA-extractable nickel in zones IV, V, and VI were 0.06-2.5, 0.06-2.2, and 0.06-4.46 mg kg^{-1} soil, respectively, whereas total content of nickel in zones IV, V, and VI were 147-472, 122-486, and 93-630 mg kg^{-1} soil, respectively. About 0.001% of the total Ni in a soil is in soil solution at field capacity (Chauhan *et al.*, 2008). The order of mobility of Ni as compared to other cations on a sandy loam was reported as: Cu> Zn> Mo> Cd> Ni> Pb = Cr, whereas on a calcareous loam it was Cu> Mo> Cd= Cu = Pb> Cr = Ni = Zn (Davis *et al.* 1988). Availability of Ni decreases with an increase of soil pH above 7.0 and excess liming reduces Ni availability (Chesworth, 2008; de Macedo *et al.*, 2016). In a study Patterson (1971) reported that when soil pH increased from 5.1 to 7.5, Ni content in spring wheat declined from 74 to 1.2 mg Ni kg^{-1} plant material with an addition of 80 mg Ni kg^{-1} soil. Absorption of Ni by plant products is also influenced by pH of the solution. Panda *et al.* (2007) reported that husks of *Lathyrus sativus* had increased Ni absorption up to pH 5 and then it decreased later up to pH 8.0.

Content in Plants

The absorption of Ni^{2+} by the intact plant and its transfer from root to shoot are inhibited by the presence of Cu^{2+}, Zn^{2+} and Fe^{2+}. The competition kinetic studies showed that Cu^{2+} and Zn^{2+} inhibit Ni^{2+} absorption competitively, suggesting that these cations are absorbed using the same carrier site (Cataldo *et al*., 1978).

Plants leaves contain 0.05 to 5 mg Ni kg^{-1} (ppm) dry matter. The critical Ni concentration in plant tissues required for normal shoot growth of urea-fed tomato and zucchini is about 1 mg kg^{-1} (Liu *et al.*, 2015). A concentration of 0.02-0.04 mg kg^{-1} (Eskew *et al.,* 1984) in soybean tissue is considered deficient. Similarly, a concentration of 0.01-0.14 mg kg^{-1} in cowpea tissue is considered deficient (Walker *et al*., 1985). Ni needs attention for soybean cultivation in India, because the crop is grown mostly on above neutral soils and the yield achieved is much below the world average of ~2.3 tonnes.

Ni concentrations > 10 mg kg^{-1} in plant tissue in sensitive species (soybean, cowpea, pecan etc.) are generally considered to be toxic (Brown, 2015), while the toxicity limit in less sensitivity species (barley, wheat and spinach etc.) could be > 50 mg kg^{-1} (Asher, 1991). Excess Ni toxicity is illustrated by the inhibition of lateral root development, photosynthesis, mineral nutrition and enzymatic activity and it is in this aspect where Ni toxicity differs from that of other heavy metals such as Zn, Cu and Co (Bhalerao *et al*., 2015). Samantray *et al.* (1997) screened tolerance of six cultivars of rice to different concentrations of nickel (0, 6, 12, 18, 24 and 30 µg dm^3). Based on the standard growth parameters (root and shoot length, root and shoot dry matter production tested after 7, 10 and 13 days of treatment), six cultivars of rice were ranked in respect of their tolerance to nickel: Nilgiri > Annapurna > Subhadra > Khandagiri > Rudra > Sankar.

Functions in Plants

Functions of Ni in plants include: 1. Germination (Brown, 1987a), 2. Hydrolysis of urea in plants, when fed with urea (Eskew *et al.,* 1983), 3. Nitrogen metabolism (Polacco,1977), 4. Water relations (Bishnoi *et al.*, 1993), 5. Photosynthesis (Bishnoi *et al.*, 1993), 6. Plant growth (Brown, 2006), 7. Resistance to disease (Graham *et al.*, 1985) and 8. Senescence (Brown *et al.*, 1987b). Ni has been identified as one of the components for number of enzymes, including glyoxalases (family I), peptide deformylases, methyl-CoM reductase and ureases, and a few superoxide dismutases and hydrogenases (Ermler *et al.*, 1998). Therefore, Ni plays a role in various important metabolic processes, including ureolysis, hydrogen metabolism, methane biogenesis and acitogenesis (Ragsdale, 1998; Mulrooney and Hausinger 2003; Maier *et al.*, 1993; Collard *et al.,* 1994). Ni may also have other functions that have yet to be discovered in plants, but that may be revealed with further study and use of new techniques. Since Ni is essential for plant metabolism, its uptake and transport in plants is involved in some important physiological processes.

Deficiency Symptoms

Deficiency symptoms of Ni in plants include: 1. Leaf tip burning in legumes (Eskew *et al.*, 1983); 2. Mouse-ear leaves, cupping of leaves and rosetting in pecan (Bai *et al.,* 2006; Wood, 2006); and 3. Interveinal chlorosis and stunted growth in cereals (Kumar *et al.*, 2018).

Toxicity symptoms

Toxicity symptoms of Ni in plants include: 1. Grey spots in the leaves in beans, which may coalesce and become necrotic (Campanharo *et al.*, 2010); 2. Marginal chlorosis in leaves in *Brassicae* (Sachan and Lal, 2017); 3. Leaf chlorosis in barley (Sachan and Lal, 2017) and 4. Pale yellow stripes running the length of leaves in oats (Crooke and Inkson, 1955).

Nickel Fertilization

Most studies on Ni fertilization have been in pots or in solution cultures. In USA, barley plants grown from low Ni seed and Ni-deprived had significantly (30%) lower root and shoot weights than +Ni-plants and displayed deficiency characteristic symptoms that could be eliminated by Ni supplementation (Brown *et al.*, 1987b). Siqueira *et al.* (2018) from Brazil reported that a Ni supply of 0.5 mg of Ni kg^{-1} of soil recorded yield gains in soybean up to 2.9 g per plant in greenhouse and up to 1,502 kg ha^{-1} in field conditions and observed that these were associated with a promoted N metabolism. However, Oliveira *et al.* (2013) in Brazil failed to obtain a response to Ni fertilization in pot culture studies with lettuce.

In India, results from a pot experiment at Varanasi (Kumar *et al.*, 2018) showed that growth and yield attributes viz. plant height, leaf greenness index, number of tillers, number of ears pot^{-1}, number of grains ear^{-1}, straw yield, grain yield and of 1000-grain weight of barley was the highest with 3 foliar application of 0.2% of $NiSO_4.7H_2O$ (T_4-Ni 0.2%) at 20, 40, and 60 days after sowing.

Conclusion

Nickel in environment and as an essential plant nutrient has not received much attention in India. It may be deficient in some soils and may affect legume, especially, soybean. It is hoped that to begin with, Soil Scientists and Agronomists in the country need to initiate a general survey on Ni content in air, waters and soils and plants.

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