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Nickel: A Heavy Metal and an Essential Micronutrient

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ABSTRACT

Nickel is a metal of widespread distribution in the environment: there are almost 100 minerals of which it is an essential constituent and which have many industrial and commercial uses. Nickel and nickel compounds belong to the classic noxious agents encountered in industry but are also known to affect non-occupationally exposed individuals. The general population may be exposed to nickel in the air, water and food. Inhalation is an important route of occupational exposure to nickel in relation to health risks. Most nickel in the human body originates from drinking water and food; however, the gastrointestinal route is of lesser importance, due to its limited intestinal absorption. The toxicity and carcinogenicity of some nickel compounds (in the nasal cavity, larynx and lungs) in experimental animals, as well as in the occupationallyexposed population, are well documented. The objective of this paper is to summarize the current overview of the occurrence and sources of nickel in the environment, and the effect of this metal and its compounds on living organisms.

Introduction

Heavy metals are toxic pollutants in the environment. Some even at low concentration pose toxicity in plants grown in polluted soils. The many uses of heavy metals in several applications lead to their wide distribution in soil, silt, waste and waste water. Such a pollution of the environment by toxic metals and radionuclide arises as result of many human activities, largely industrial, although sources such as agriculture and sewage disposal also contribute. Though several metals are essential for biological systems and must be present in a certain concentration range, too low concentrations lead to a decrease in metabolic activity, at too high concentrations these metals lead to toxicity. Non essential metals are tolerated at very low concentrations and inhibit metabolic activity at higher concentrations. Heavy metals and other pollutants in the environment causes damage to the plants. A pollutant is any substance in the environment which causes objectionable effects, impairing the welfare of the environment, which reduces the quality of plant life and eventually death of the plant. Such substance has to be present in the environment beyond a set or tolerance limit. Heavy metals in high concentrations inhibit seed germination, the growth and development of plants and disturb many biochemical and physiological processes like cell membrane injury, reduce transpiration, breakdown of protein synthesis, damage the photosynthetic apparatus and inhibit photosynthetic rate, raises lipid peroxidation (Foy et al. 1978; Sanita di Toppi and Gabbrielli 1999; Talanova et al. 2000; Monni et al. 2001; Atıcı et al. 2003). Excessive levels of heavy metal in the soil environment adversely affect the germination of seeds, plant growth, alter the levels of bio-molecules in the cells and interfere with the activities of many key enzymes related to normal metabolic and developmental processes (Jha and Dubey. 2005; Li et al. 2005; Leon et al. 2005; Maheshwari and Dubey 2007; Ahsan et al. 2007; Kuriakose and Prasad 2008).

Heavy metal contamination of the environment is currently a major global environmental problem, threatening the health of vegetation, wildlife, and humans (Singh et al. 1997; Salt et al. 1998; Taiz and Zeiger 1998). Plants exposed to high levels of heavy metals typically accumulate the metals in their tissues (both roots and shoots), often to toxic levels that decrease growth or reproduction. The mechanisms utilized by plants to protect cells from excess heavy metals are not completely understood, but are known to include internal and external chelators, efflux pumping, vacuolar compartmentalization, and heat-shock proteins (Salt et al. 1998; Cobbett 2000; Hall 2002). Although, some metals like Cd, Cr, Zn, Ni^{2+} are involved in a variety of processes in the cell, their excessive concentrations are highly toxic to many organisms including higher plants (Verkleij and Prast 1990). Houshmandfar and Moragheb (2011), studied the effect of mixed cadmium, copper, nickel and zinc on seed germination and seedling growth of safflower, study was conducted to evaluate the effect of mixed cadmium, copper, nickel and zinc on seed germination and seedling growth of safflower under controlled light and temperature conditions. The heavy metal mixture treatment showed toxic effects on seed germination and seedling growth of safflower. Elevated levels of heavy metals in contaminated soils are widely spread and concerns have been raised over the potential risks to humans, animals and agricultural crops. Both toxic effects of heavy metals and their detoxification are the complex processes involving numerous related and interacting mechanisms. The efficiency of these mechanisms is probably the primary factor of plant tolerance and plant capacity for hyper accumulation. The elucidation of common and specific mechanisms of heavy metal toxicity and the characteristic plant responses to the excess of heavy metals, 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 heavy metals and avert their entry into human and animal organisms. Among metals, nickel toxicity has become of great concern due to its excessive use in different industries

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Nickel

The analysis of published evidence on Ni toxicity towards plants shows that, in addition to general toxicity displayed by all heavy metals, Ni manifests the specific characteristics due to its characteristic physical and chemical properties. The toxicity of heavy metals may depend on their binding to various ligands; among such ligands in the biological systems, carboxylate ion, imidazole, sulfhydryl group, and aliphatic amine are the most important.

Nickel is considered to be an essential micronutrient for leguminous plants (Eskew et al. 1983), it has also been proved that growth of other plants is stimulated by the low concentrations of this element (Atta-Aly 1999). However at excess concentrations Nickel becomes toxic for most plant species. Sinha et al (2011), worked on the effects of nickel salts on the growth and yield of *Vigna radiata* and their findings indicate that initially the growth and yield increases with the slight increase in nickel concentration but shows decreasing trend at its higher concentration. High doses of nickel have a negative effect on the metabolism of the plants. While Ni used to be considered non-essential or toxic to plants, work on pecan and other crops reveal that Ni fulfills the indirect criteria of essentiality. It meets also the direct criterion. Urease is an ubiquitous metallo-enzyme containing Ni (Dixon et al. 1975). Eskew et al (1983; 1984) and Brown et al (1987), placed Ni in the list of micronutrients. In general, naturally occurring concentrations of nickel in soil and surface waters are lower than 100 and 0.005ppm, respectively. In recent years, nickel pollution has been reported from across the world, including Asia, Europe and North America. Nickel concentration may reach 26,000 ppm in polluted soils and 0.2mg/L in polluted surface waters, 20 to 30 times higher than found in unpolluted areas. Soil and water contamination with nickel has become a worldwide problem. Further, with increasing nickel pollution, excess nickel rather than a deficiency, is more commonly found in plants (Alloway 1995; Salt et al. 2000). Toxic effects of high concentrations of nickel in plants have been frequently reported. Nickel is essential for plants (Eskew et al.1983; Ragsdale 1998) but the concentration in the majority of plant species is very low, i.e. 0.05-10mg/kg dry weight (Nieminen et al. 2007).

Occurence Of Nickel

Nickel is one of the ubiquitous elements and ranks 22nd in order of abundance. It is more abundant than other common metals like tin, lead and copper. Nickel is a hard, malleable and ductile metal, is silvery white and belongs to iron group. It is magnetic and frequently accompanied by cobalt. Nickel has a lot of compounds and complex which present the oxidation states -1,0,+1,+2,+3,+4. The oxidation state +2 is most common, being known a great number of compounds. The first coin of pure nickel metal was made in 1881. Isotopes of nickel ranges in atomic weight from 52 amu to 74 amu. The atomic number of nickel is 28 and the atomic weight is 58.6934 amu. Nickel belongs to the IV period in the periodic table. Its melting and boiling point are 1728(2651^0 F) and 3186(575^{0}F) respectively. Nickel is metallic and lustrous in appearance.

Sources Of Nickel

Nickel is present upto 10kms height in the atmosphere and 45kms down the earth crust in lithosphere. The level of nickel in air samples collected from areas situated in proximity to industries, smelter, power plants and urban centres were significantly higher the unpolluted non urban sites or rural areas. The nickel levels in natural unpolluted surface waters are very low. Nickel is mostly present in all types of soil in various concentrations. Range of total nickel in soil is in between 10-40 ppm. Main source of nickel in soil are mining activities, discharge of sewage sludge, municipal waste application practices, emission from smelters, refineries and other industrial waste, toxic chemicals, agricultural practices means use of fertilizers, pesticides etc. weathering of nickel rich rocks is the main natural resource of increasing the concentration of this metal in soil. Anthropogenic sources of nickel such as burning of fuel and residual oil and natural industrial sources tend to concentrate in the organic residue at sewage treatment work responsible for causing various health and environmental problem to all living organism. Nickel may be released to the environment as an air pollutant, water pollutant or soil contaminant. As an air pollutant Nickel can emanate as part of the stack emissions of large furnaces used to make alloys or from power plants and trash incinerators. The nickel that is emitted from stacks of power plants attaches to small particles of dust that settle to the ground or are precipitated from the atmosphere by rain or snow. If the nickel is attached to minute particulate matter, it can take more than a month to settle out of the air. Nickel can also be released in industrial wastewater. Much of the nickel released into the environment ends up in soil or sediment where it can strongly attach to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and can seep into groundwater. Nickel does not appear to concentrate in fish. Studies show that some plants can take up and accumulate nickel. However, nickel does not seem to accumulate in small terrestrial animals, which are living on land that has been treated with nickel-containing sludge.

Uptake, Transport And Distribution Of Nickel In Plants

The uptake and transport of nickel in plants involves some important physiological processes. It is important to understand the processes that determine plant uptake of nickel from soil. Plant availability of nickel is a complex function of soil and plant parameters. The dynamics of nickel in soil are largely determined by ion exchange reactions (Zehetner and Wenzel 2000) and presence of complexing ligands in soil solution (Dunemann et al.1991). Soil pH is one of the important parameters that determine the mobility of nickel in soil. Ni is readily taken up from acidic soil solutions by plant roots and is transported in free and chelated forms to the transpiring leaves via the xylem (Tiffin 1971; Mishra and Kar 1974; Cataldo et al.1978). Ni ions are reportedly less available to the roots of plants growing on alkaline soils (Dalton et al. 1985; Mishra and Kar 1974) and these plants might therefore be subject to suboptimal rates of supply from the soil. Reduced availability of micronutrients can limit growth and adversely affect new tissue development in plants, especially when mobilization and/or phloem transport of accumulated reserves out of mature sink leaves is restricted (Epstein 1972). However, by contrast with other essential micronutrients, low soil levels of Ni do not limit growth in pot trials (Dalton et al.1985) or seem to produce reports of deficiency symptoms in the field. The uptake of nickel in plants is carried out mainly by root systems by passive diffusion and active transport (Seregin et al. 2006). Root uptake also depends on root density and distribution and on the rate of transfer at root membrane- solution interface (Darrah and Staunton 2000). Absorption may thus be expected to vary between plant species and to depend on their nutritional status. Soluble nickel compounds can be absorbed via the cation transport system. Because of the competition between various metals in the course of their uptake by roots, some metals are absorbed in insufficient quantities, whereas the uptake of other metals is excessive. The soluble metal ions like zinc and copper inhibit nickel uptake competitively and known to absorbed by same system of transport (Kochian 1991). However magnesium ions do not have inhibitory effects on nickel ions absorption and both of these metals have similar charge/size ratio because of which nickel is also absorbed via magnesium ion transport system. It has been reported that secondary active transport of chelated nickel ions is also possible and corresponding proteins that specifically bind nickel ions such as metallo-chaperons (Hausinger 1997; Olson et al.1997; Watt and Ludden 1998), metallothionein (Schor-Fumbarov et al. 2005) and permeases which is high affinity nickel transport protein. However the nickel uptake depends upon the plant metabolism and the concentration of nickel. Nickel is transported through the transpiration stream via xylem from roots to shoots and leaves. This is supplied to the meristematic parts of the plants by re-translocation from old to young leaves and to buds, fruit and seeds via phloem. This transport is regulated by specifically bound proteins to nickel and metal ligand complexes (Ma et al. 2005; Haydon and Cobbett 2007). It has been reported that over 50% of nickel absorbed by plants is retained in the roots (Cataldo et al. 1978). A high percentage of nickel in roots is present in vascular cylinder and the lesser percent in the cortex. It suggests high mobility of nickel in xylem and phloem (Riesen and Feller 2005). The nickel in stems and leaves are mainly located in vacuoles and cell walls. However nickel contents of different organelles and cytoplasm within cells may differ substantially. Many hyper accumulators store Ni in covering and conducting tissues; such localization would protect plants against the pathogens and herbivores and, against drought. Nickel accumulation in covering tissues could also arise from plugged transpiration flow. Such suggestion is supported by the evidence that other heavy metals are non-specifically accumulated in the leaf epidermis and trichomes (Seregin and Ivanov 2001). According to Singh and Pandey (2011), the maximum nickel accumulation was observed in the root than in the leaves of *Pistia stratiotes* (L.) on the nickel exposure, which showed low translocation of nickel towards aerial parts of plants. Their findings indicate that various levels of nickel influence uptake and translocation of nickel.

Role Of Nickel

The physiological role of nickel is starting to unravel but the exact mechanism is still not well understood. The advance science of instrument and analytical methods towards the end of the 20th century has allowed for the determination of the role of certain transition elements in the metabolism of some plant species. Some elements such as copper, molybdenum, nickel and zinc among others are essential for plant growth in low concentration (Reeves and Baker 2000). Dalton et al (1988), reported that nickel has been included in micronutrients in small amounts in normal plant growth. Nickel has recently been defined as an essential micronutrient because of its involvement in enzymatic activities of legumes (Welch. 1995). Nickel is consistently present in RNA, it is bound to several biological substances such as proteins (keratin and insulin), amino acids, serum albumins and it also activate enzymes like arginase, trypsin, carboxylase and synthetase. Nickel containing enzymes catalyse five distinct biological reactions including urea hydrolysis, reversible hydrogen oxidation, interconversion of carbon monoxide and carbon dioxide (often associated with acetate metabolism), methane generation and dismutation of superoxide (Gerendas 1998). The essential role for nickel became evident with the discovery that urease enzyme requires nickel for activation (Dixon et al. 1975). While Ni used to be considered non-essential or toxic to plants, but work on pecan and other crops reveal that Ni is a micronutrient as stated earlier. It is well known phenomenon that low concentrations of nickel are necessary in nitrogen metabolism and the germination of plants, such as cereals and cowpeas (Tan et al. 2000). Nickel may also be required for symbiotic nitrogen fixation by legumes (Gerendas and Sattelmacher 1997). It also influences nitrogen uptake and transport in plants. The role of nickel in plant metabolism is poorly understood. Whereas many proteins contain nickel. Nickel nutrition of higher plants and its physiological significance, especially to woody perennials, have received little attention. There are several enzyme systems in bacteria and lower plants that are activated by nickel (Mulrooney and Hausinger 2003), however the activation of urease appears to be only enzymatic function of nickel in higher plants. Urease contains two nickel ions at the active site. Urease splits urea hydrolytically into ammonia (NH_3) and carbon dioxide (CO_2). Urea $[CO(NH_2)^2]$ originates from the amide arginine due to the activity of the enzyme urease. Nickel deficiency, preventing the action of urease, leads to the accumulation of urea, which causes necrotic spots on the leaves. As further consequences of the deficiency, metabolism of ureides, amino acids, and organic acids is disrupted. Oxalic and lactic acid accumulate (Bai et al. 2006). These effects suggest that nickel may play a multitude of roles in higher plants. The necrotic spots associated with the deficiency correspond to local accumulation of urea or oxalic and lactic acids, the latter indicating changes in carbon metabolism, particularly impaired respiration. Nickel is involved also in symbiotic N fixation, since it increases the hydrogenase activity in isolated nodule bacteroids (Klucas et al. 1983). Nickel ions present in the culture solution of beans and apple inhibited ethylene production (Smith and Woodburn 1984). Nickel can also replace Zn or Fe and other metal ions, in certain other metallo-enzymes of lower plants. Circumstantial evidence indicate that pecan which is a ureide transporting species possess a higher nickel requirement than amide transporting species (Wood 2006) thus raising the possibility that ureide transporters might possess enzymes, other than urease, that require nickel for activation or for enhanced activity (Bai et al. 2006). Najafi et al. (2011), studied the effects of different concentrations of nickel sulphate on some physiological parameters in sunflower (*Helianthus annuus* L.) and observed that total soluble sugars and protein contents were increased at high concentrations of nickel whereas malondialdehyde (MAD) and respiration rate were significantly increased in high concentrations, however, photosynthetic rate and relative water content decreased in all concentrations of Nickel.

Toxicity Of Nickel

Symptoms of toxicity develop when excessive levels of Ni are taken up. Symptoms include chlorosis due to reduced absorption of Fe, stunted growth of the root and shoot, deformation of various plant parts, and unusual spotting of the leaves (Mishra and Kar 1974). The effects of nickel on the gram plants subjected to nickel toxicity showed decrease in growth and adverse effects on the metabolism (Misra et al. 2010). Plants do vary in their sensitivity or tolerance to excess Ni. For instance, beans are more sensitive than rice (Piccini and Malavolta. 1992). Toxic levels in plants are commonly of the order of 25 to 50 mg/kg. Nevertheless, there are species which withstand exceedingly high levels of Ni in the substrate and in their tissue – the hyper-accumulators. These plants prosper in Ni-rich, usually serpentine or contaminated soils such as ***Alyssum bertolonii*** **and** ***Vellozia*** **species.**

Nickel is a micronutrient for most organisms but its excessive quantities have toxic effects. Nickel is toxic for animals and plants both. In animal studies, the dietary nickel deficiency has caused pigmentation changes, thicker legs with swollen locks, less friable liver, enhanced accumulation of trace amount of nickel in the liver, bone and aorta. It causes dermatitis and respiratory disorders including lung cancer. Nickel tetra carbonyl is the poisonous derivative of nickel. The humans are also affected by nickel. The main route by which nickel enters the human body is oral ingestion via food and drinking water. Breathing also contributes to the intake of nickel into the body. Dermatitis was recognized to be the most common symptom of industrial exposure to nickel, although high occupational exposures have been associated with renal problems and lung cancer. Epidemiological studies conducted on the refinery workers indicated that nickel compound induce nasal, laryngeal and lung cancer. Emphasized location for nickel accumulation in human being is the kidney tissue. Nickel toxicity has become of great concern due to its excessive use in different industries.

Effect Of Nickel On Plant Growth And Morphogenesis

Nickel is known to produce symptoms of stunting growth, leaf chlorosis and occasionally vein necrosis in plants (Seregin and Kozhevnikova 2006). Nickel significantly retards germination; inhibits growth and dry matter production (Nedhi et al.1990) and affects nutrient uptake potassium, calcium and magnesium in the different plant parts, particularly in shoot (Rubio et al. 1994). Similarly, it decreases number of flowers and fruits and subsequently yield (Balaguer et al. 1998) in different plant species. Nickel concentrations that are toxic to plants vary in magnitude according to plant species. In early stages of nickel poisoning there are no definite symptoms, only dwarfing or a repression in growth. More advance stages produces chlorosis followed by necrosis and death of the plant. Degree of necrosis depends on the metal supply and genotype of the species. Root and shoot injury, stunted growth of plant and patchy discolouration are the morphological symptoms of the excess supply of this metal. While working on nickel toxicity in wheat Setia et al. (1989), observed the decrease in the fresh and dry matter production of the plant and the inhibition in the length of internodes. Increasing concentrations of nickel chloride in plant inhibited the lignifications of hypodermal cells in the internodes and a significant reduction was also observed in number of parenchymatous layer with the nickel chloride compound. The cross section area covered by vascular bundle of xylem phloem per vascular bundle was drastically changed with increasing level of nickel in plants. It was also observed that he length, fresh weight and dry weight of total ear and number of spikelet in the ear declined with increasing concentration of nickel.

Effect Of Nickel On Mineral Nutrition Of Plants

The effects of Ni on nutrient uptake depend in many aspects on Ni concentration in the environment. At high Ni concentrations the contents of macro and micronutrients in plant tissues are usually lowered down because of disordered absorption and transport (Rubio et al. 1994; Pandolfini.1992). At the same time, at low Ni concentrations in the environment, the contents of nutrients did not change and in some cases even increased (Piccini and Malavolta 1992; Barsukova and Gamzikova 1999). Such phenomenon was described as the concentrating effect; 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^{2+} and other cations. 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).

Effect Of Nickel On Photosynthesis

Nickel damages the photosynthetic apparatus and decrease chlorophyll content. It also damages the thyllakoid membrane and chloroplast grana structure. At the biochemical level, nickel affects light harvesting complex II. The diminished rate of photosynthesis is related to disrupted chloroplast structure, blocked chlorophyll synthesis, disordered electron transport, inhibited activities of the Calvin cycle enzymes, and CO_2 deficit caused by stomatal closure.

Induction Of Oxidative Stress

The production of reactive oxygen species in plant cells is another universal mechanism of heavy metal toxicity. Plants respond to oxidative stress by elevating the activity of the antioxidant enzymes of the ascorbate–glutathione cycle, such as catalase, peroxidase, superoxide dismutase, glutathione reductase, and ascorbate oxidase, which protect plant cells against free radicals (Das et al. 1978; Schickler and Caspi 1999). Excessive nickel leads to significant increase in the concentration of hydroxyl radicals, superoxide anions and hydrogen peroxide (Hao et al. 2006). Nickel directly cannot generate reactive oxygen species(ROS) but it interferes indirectly with a number of antioxidant enzymes (Gajewska et al. 2005). Exposure of plants to low nickel has been shown to increase the activities of SOD, POD and GR in order to enhance the activation of other antioxidant defences and hence lead to the removal of ROS (Gajewska et al. 2005). However excess nickel has been found to reduce the activity of many cellular antioxidant enzymes, both in vitro and in vivo, and plant's capability to scavenge ROS, leading to ROS accumulation and finally oxidative stress in plants (Gajewska and Sklodowska 2007). ROS have been shown to damage cell membrane, proteins, lipids and DNA resulting in lipid peroxidation, genetic instability and developmental defects in plant species.

Effect Of Nickel On Enzyme Activity

Ni affects several enzyme activities. Total decline of enzyme activities is sometimes observed due to decreased enzyme contents. Depending on its concentration, nickel ion can both stimulate and inhibit enzyme activities in plant tissues at high Ni concentrations, most of enzyme activities were diminished, whereas some activities, especially those of the antioxidant enzymes, increased. In most cases, we do not know whether these changes in enzyme activities stem directly from Ni^{2+} effects, such as binding to SH-groups or histidine or displacing the metals from metal–enzyme active centers, or indirectly, when mediated by the chain of reactions that affect the expression of the corresponding genes or exhaust their substrate pools. The inhibition of enzyme activities by heavy metals is one of the causes of declining cell metabolism. Maheshwari and Dubey (2011), determined the effects of nickel on the phosphate pool and the activity of phosphorolytic enzymes in rice germinating seeds and growing seedlings, their results suggested that alteration in the level of phosphate pool and inhibition in the activities of phosphorolytic enzymes might contribute to reduced metabolic activities, delayed germination of rice seeds and decreased vigour of seedlings in Nickel polluted environment.

Future Prospects

Growing concerns about nickel pollution in the environment have led to research on phyto-remediation, the hyper-accumulators to remove nickel from soil and water can be use to minimise the effects of nickel. Further studies are needed to fully understand the details regarding the mechanisms at molecular and biochemical level. At the molecular level further research is required regarding the genetic modification of the plant in which specific genes having nickel chelated proteins of nickel hyper-accumulator can be transferred. This genetically modified plant can be used as a hyper-accumulator with enhanced abilities to detoxify and tolerate nickel.

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