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REVIEW PAPERS

NICKEL IN THE ENVIRONMENT*

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Abstract

The importance of nickel (Ni) in the environment is an issue that is gaining broader recognition. While nickel is an element essential for plants, it is also a heavy metal. Nickel is a component of nine metalloenzymes, including urease, which participates in urea hydrolysis. It also helps some plants to protect themselves against pathogens and herbivorous insects. There are many sources of Ni in the environment, which can be a problem because at higher concentrations this element is toxic to plants and other living organisms. Therefore, standards have been defined for the Ni content in air, water, soil and plants. Its content is monitored in the air. More and more frequently, attention is paid to this element as an allergen in humans. In the world, attempts have been made to phytoextract nickel from contaminated soils using nickelphilous plants, the so-called hyperaccumulators, and even to recover the metal from these plants by so-called phytomining. On the other hand, nickel-containing fertilizers are marketed and used in cases of nickel deficiency in plants. In industry, this element is primarily used for the production of steel and alloys. The most recent application of nickel is related to graphene, which was invented 10 years ago. Although nickel contamination does not occur in Poland, we cannot rule out this risk in the future. Thus, it is important to monitor the fate of nickel in the environment.

Key words: Ni, micronutrient, heavy metal, allergen.

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INTRODUCTION

Nickel is the fifth most common element on the Earth, after iron, oxygen, silicon and magnesium. This metal has widespread distribution in the environment, as there are almost 100 minerals of which it is an essential constituent and which have many industrial and commercial uses (Cempel, Nikel 2006). It occurs mostly in minerals such as pentlandite, garnierite, millerite, niccolite and ulmannite. Nickel is commonly present in two principal ore types: sulphide or laterite. In 1751, the Swedish scientist Baron Axel Frederich Cronstedt isolated nickel from an ore. Nowadays, most of the world's supply of nickel is mined in Canada, Cuba, the former Soviet Union, China and Australia. Until 1982, Ni had also been mined in Poland. In 2012, the global Ni production reached 1.76 million tonnes and its demand has nearly doubled in the last decade. In industry, Ni is mainly used for the production of nickel steel, iron alloys and electroplating.

Essentiality

Brown et al. (1987) proved that nickel, next to Fe, Mn, Cl, B, Zn, Cu, Co and Mo, is essential for higher plants. Currently, the metal is considered to be an essential nutrient for plants which cannot complete their life cycle in its absence and cannot substitute it with any other nutrient. It is an essential element for the normal growth of many species of microorganisms and plants as well as several vertebrates. Nickel deficiency in field-grown crops is rare, but in recent years numerous findings have confirmed cases of its deficiency. Nickel is the most recent of the essential micronutrients for which field production responses have been confirmed, and first it was the report of Ni deficiency in orchard trees of pecan in the southeast USA. It is concluded that Ni deficiency in pecan orchards is likely to be partially due to either Zn or Cu fertilization-induced reductions in the physiological availability of Ni, perhaps *via* either competitive inhibition or sequestration (Wood 2010). Only low levels of nickel are known to be beneficial (Brown et al. 1987). High concentrations of this element in growing medium may exert adverse effects on plants (Molas, Baran 2004). Gad et al. (2007) observed that the tomato fruit quality improved with an increasing Ni level (30 mg kg^{-1} soil). However, an adverse effect was caused by raising the Ni level from 30 to 45 and 60 mg kg^{-1} soil.

Environmental toxicology

Although Ni is an essential element in plants and many other biota, there has been much more concern about the toxicity of Ni than about its deficiency. Field observations have indicated a significant increase in heavy metal concentrations in agricultural and forest soils as well as in marine and inland water sediments during the last century (Pacyna, Pacyna 2001), which explains why excess Ni rather than its deficiency is more common in plants. The soil-plant system plays an important role in the circulation of nickel in ecosystems.

Nickel is one of many trace metals widely distributed in the environment, being released from both natural sources and by anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material (CEMPEL, NIKEL 2006). Environmental pollution with nickel is caused by transport, industry, increasing consumption of liquid and solid fuels, as well as municipal and industrial waste.

As for most metals, the toxicity of nickel is dependent on the route of exposure and the solubility of a nickel compound (COOGAN et al. 1989). The exposure of the general population to nickel mainly includes oral intake, primarily through water and food, as a contaminant in drinking water or as both a constituent and contaminant of food (HABER et al. 2000). Many harmful effects of nickel are due to the interference with the metabolism of essential metals, such as Fe(II), Mn(II), Ca(II), Zn(II), Cu(II) or Mg(II), which can suppress or modify the toxic and carcinogenic effects of nickel. The toxic functions of nickel probably result primarily from its ability to replace other metal ions in enzymes and proteins or to bind to cellular compounds containing O-, S-, and N-atoms, such as enzymes and nucleic acids, which are then inhibited (COOGAN et al. 1989, SCOTT-FORDSMAND 1997).

The environmental mobility of Ni is considered to be low under neutral to alkaline and reducing conditions, but in acidic organic rich soils, where Ni can be quite mobile, Ni contamination may pose a risk to groundwater quality. Although the ionic form of Ni^{2+} is taken up relatively easily by plants, chelated high molecular-weight compounds are less available. Therefore, Ni does not appear to be subjected to biomagnification in terrestrial food webs, with the exception of Ni hyperaccumulating plants. However, frequent application of sewage sludge on agricultural fields may result in substantial Ni absorption by some crop plants (NIEMINEN et al. 2007).

Ni in the air

There are large amounts of natural Ni present in the atmosphere, derived from windblown dust, volcanic ashes, forest fires, meteoric dust and sea salt spray. On a global scale, windborne soil particles from eroded areas can account for (30-50%) of natural Ni emissions (NIEMINEN et al. 2007). Currently, almost 90% of the global anthropogenic Ni emissions originate from oil combustion (PACYNA, PACYNA 2001).

In 2012, forty areas in Poland were included in an assessment of Ni in the air. The threshold level of nickel, 20 ng m^{-3}, was not exceeded in any of these sites (*State Environmental Monitoring* 2012).

Ni in the water

The fate of heavy metals in aquatic systems depends on partitioning between soluble and particulate solid phases. Adsorption, precipitation, coprecipitation, and complexation are processes that affect partitioning. These same processes, which are influenced by pH, redox potential, the ionic strength of the water, the concentration of complexing ions, and the species and concentration of the metal, affect the adsorption of heavy metals to soil (Richter, Theis 1980).

The Baltic water contains 0.09-1.08 µg Ni dm^{-3} (Szefer 2002), while the mean Ni content in river water is 0.7 µg dm^{-3} (Gaillardet et al. 2003).

The mean Ni content in 80 samples of drinking water in Poland collected from an area affected by industrial emissions (Stalowa Wola) was 17 µg dm^{-3} and in most of the analyzed water samples did not exceed the allowable concentration of 20 µg dm^{-3} (Kocjan et al. 2002*a*). Also, the nickel content in bottled mineral waters (0.71-3.20 µg dm^{-3}) stayed below the maximum allowable concentration (Długaszek et al. 2006).

Ni in the soil

Nickel is associated geochemically with iron and cobalt, and soils with a high content of these elements generally contain the large amount of nickel. The mobility of nickel in soils is dependent on texture composition and structure of soil mineralogy (Kabata-Pendias 2001).

In soil, the most important sinks for nickel other than soil minerals are amorphous oxides of iron and manganese. The mobility of nickel in soil is site-specific, depending mainly on the soil type and pH. The mobility of nickel in soil is increased at low pH. The sulphate concentration and the surface area of soil iron oxides are also key factors affecting nickel adsorption (Richter, Theis 1980).

In most soils, Ni is bound to ion exchange sites, and it is specifically adsorbed or adsorbed on or coprecipitated with aluminum and iron oxyhydroxides. These are the dominant processes in neutral to alkaline soils. In acidic, organic-rich soils, where fulvic and humic acids are formed by the decomposition of organic material, Ni may be quite mobile, possibly because of complexation by these ligands (Kabata-Pendias 2001).

The soil content of nickel may be as low as 0.2 mg kg^{-1} or as high as 450 mg kg^{-1} (Ahmad, Ashraf 2011). According to Terelak and Motowicka-Terelak (2000) based on the analysis of 40,000 soil samples, 95.1% of the agricultural land in Poland are characterised by the natural content of nickel and 4.4% have a slightly increased content of this element. A general conclusion was that the heavy metal (Cd, Co, Ni, Pb, Zn) status of agricultural soils in Poland was lower than that of most other countries in Europe and in the world. The average content of nickel in Poland is 6.5 mg kg^{-1} (Siebielec et al. 2012), while in the world it reaches 13-37 mg kg^{-1} (Kabata-Pendias, Szteke 2012).

The mean content of nickel in soil affected by the Bolesław Mining and Metallurgical Plant was 19.62 mg kg^{-1} (Trafas et al. 2006). In 60 samples of the soil collected from a territory affected by industrial emissions from Stalowa Wola, the level of nickel was higher (average 17.20 mg kg^{-1}) than that in reference samples (average 9.72 mg kg^{-1}). All the values, however, were below the highest allowable content (Kocjan et al. 2002*b*).

Ni in the plants

The uptake of Ni in plants is mainly through roots, either by passive diffusion and by active transport (Seregin, Kozhevnikova 2006). Soluble Ni compounds can be absorbed *via* the cation transport system but could also be absorbed *via* the Mg ion transport system, because of the similar charge/size ratio of the two metal ions (Oller et al. 1997). Secondary active transport of chelated Ni^{2+} is possible, and corresponding proteins that specifically bind Ni^{2+}, such as HoxN (high-affinity nickel transport protein, a permease) (Wolfram et al. 1995).

The uptake of nickel into plants is modulated by the pH of soil. Smith (1994) showed that nickel concentrations in rye grass were reduced by a factor of three as the soil pH was raised from 4 to 7. This is thought to be the consequence of a lesser bioavailability of nickel with an increasing pH. The bioavailability of nickel to plants is also affected by soil type. Weng et al. (2004) found that the bioavailability of nickel to oat plants grown in soil rich in organic matter is half that of plants in sandy or clay soils in the pH range of 4.4-7.0. These differences in bioavailability are attributed to the stronger binding of nickel to organic matter than to silicates and iron hydroxides/oxides in clay and sand under the acidic conditions of the experiment. Absorption and phytotoxicity of Ni by barley plants from these complexes can be put in the following order: $NiSO_4 \cdot 7H_2O$>Ni(II)-citrate>Ni(II)-Glu>Ni(II)-EDTA (Molas, Baran 2004, Molas 2010). Although the root uptake is the main pathway for Ni access in higher plants, there is much evidence showing that Ni is also available to plants through foliage, both in conditions of excess Ni (Gawel et al. 2001) and Ni deficiency (Wood 2010).

According to Matraszek and Hawrylak-Nowak (2010), intensive nutrition of Ni-treated maize plants with Fe or Ca generally did not change the concentration of free Ca in plant organs. Thus, intensive Ca or Fe nutrition presents a promising potential for use in the conditions of Ni contamination by increasing plant growth, reducing Ni translocation from roots to shoots and raising the nutritive value of above-ground parts of spinach and maize plants.

Recent studies have shon that foliar Ni treatment quadrupled the grain yield of wheat plants subjected to glyphosate at booting by preventing nearly 75% of the damage caused by glyphosate. Direct binding of Ni to glyphosate and/or the role of Ni as an ethylene inhibitor may be behind the reported protective effects of Ni, but the exact mechanism remains to be elucidated (Kutman et al. 2013*a*).

Nickel in fertilizers

Although there are no regulations in Poland on the nickel content in fertilizers, amounts of this metal they contain may differ significantly. Considering the analyzed fertilizers, significant quantities of heavy metals were assessed only in phosphorus (Zn>Cr>Ni>Hg>Pb) and multicomponent fertilizers. In nitrogen fertilizers and potassium salt, there were only small amounts of lead, whereas the other metals occurred in trace amounts. Generally, an elevated amount of nickel is determined in fertilizers which also contain magnesium. Nickel in multicomponent fertilizers originates from the used admixtures of ground dolomite, and the Ni content varies from 7.6-396.0 mg kg^{-1} d.m. (Gambuś, Wieczorek 2012). Łukowski and Wiater (2009) found that the nickel content in 11 fertilizers used in the experiment was 0.4-295.1 mg kg^{-1} d.m.

Nowadays, nickel is no longer seen an impurity of fertilizers.Contrary to that, there are even special fertilizers containing nickel for foliar spraying of plants. For example, it may be used for the correction and prevention of the mouse ear disease on pecans (Wood et al. 2004). Nickel also improves the utilization of nitrogen from urea and prevents damage to plants resulting from foliar urea (Kutman et al. 2013*b*).

Pythoremediation and phytomining

Heavy metals, unlike organic pollutants, cannot be chemically degraded or biodegraded by microorganisms. An alternative biological approach to manage this problem is phytoremediation, which removes pollutants, including toxic metals, from the environment by using plants (Salt et al. 1995).

Extracting nickel, cobalt, and other metals, including the platinum and palladium metal families, from soil by cropping it with hyperaccumulating plants that concentrate these metals in aerial parts of the plants, which are then harvested, dried and smelted to recover the metal in a process known as metal phytomining (Chaney et al. 2004).

There is more than 300 taxa of Ni hyperaccumulators, i.e. plants which accumulate more than 1000 mg Ni kg^{-1} of dry weight in their shoots when grown in natural habitats. There are also plants called hypernickelophores, which accumulate >10,000 mg N kg^{-1}, e.g. *Psychotria douarrei* and *Geissois pruinosa* (Grison et al. 2013).

The nickel (Ni) hyperaccumulator *Alyssum murale* has been developed as a commercial crop for phytoremediation/phytomining Ni from metal-enriched soils. Nickel (hyper)tolerance is attained *via* epidermal compartmentalization (i.e. vacuolar sequestration), wheras Co in the xylem or leaf apoplasm is excreted from leaves and subsequently sequestered on leaf surfaces as soluble precipitate(s). Therefore, the specialized biochemical processes linked to Ni (hyper)tolerance in *Alyssum murale* do not confer (hyper)tolerance to Co (Tappero et al. 2007).

Physiological functions of nickel

Nickel is known to participate in some key metabolic reactions such as ureolysis (N metabolism), hydrogen metabolism, methane biogenesis and acitogenesis (Mulrooney, Hausinger 2003).

Small amounts of Ni may also have a role in phytoalexin synthesis and thus confer resistance to diseases and other environmental stresses (Wood, Reilly 2007). Fones et al. (2010) have demonstrated that hyperaccumulation of any of three metals, zinc, nickel or cadmium, by *Thlaspi caerulescens* provides the plant with an elemental defense against the hemibiotrophic pathogen *Pseudomonas syringae* pv. *maculicola* (Psm). Jhee et al. (2005) conclude that Ni in *Streptanthus polygaloides* defends against tissue-chewing insect herbivores (leaf-chewing and root-feeding) and some cell-disruptors but is ineffective against vascular tissue-feeding insects.

Ni is a constituent of nine metalloenzymes, e.g., urease. Therefore, a deficiency of Ni leads to reduced urease activity and disturbs N assimilation. Urease (EC 3.5.1.5) (i.e., urea amidohydrolase) is extremely important to N metabolism in plants. As an Ni-metalloenzyme, urease is involved in the hydrolysis of urea. Nickel as a cofactor enables urease to catalyze the conversion of urea into ammonium ions, which plants can use as a source of N. Without the presence of Ni, urea conversion is impossible (Sirko, Brodzik 2000).

Nickel and graphene

In 2004, two independent research teams have created graphene – a 2-dimensional, crystaline allotrope of carbon. Graphene can be described as a one-atom thick layer of graphite. In 2013, a composite of graphene and nickel was created, which increases the tensile strength of nickel by 180-fold. In 2012, an international team of physicists discovered that in a graphene layer applied to nickel, electrons behave like light and not as particles having mass. The potential application of this discovery is electronics.

Graphene can also find an application in the purification of wastewater containing nickel owing to greater adsorption capacity of graphene than that of conventional adsorbents (Varma et al. 2013).

Allergy to nickel

Nickel is known to induce allergies. It is one of the commonest sensitizers all over the world and the sensitivity to this heavy metal is more common in females than males. Nickel is present in some natural foods and in many articles e.g. costume jewelry, keys, pottery, furniture, clothes accessories but also in soaps. Foods known to be high in nickel include chocolate (cocao), coffee, tea, nuts, soy beans and other legumes. Careful selection of food with relatively low nickel concentration can result in the reduction in the total dietary intake of nickel per day. This can help to control nickel dermatitis. Therefore, sound knowledge of the presence of nickel in food is helpful for the management of nickel allergy (Sharma 2013). Nickel is used in the production of margarine as a catalyst for hydrogenation. This may lead to the presence of its residues in the products and could cause allergic reactions. Ni was determined in 10 brands of margarine, and only in 3 samples its content was below the acceptable limit of 0.2 mg kg^{-1} (Łodyga-Chruścińska et al. 2012).

CONCLUSION

Nickel (Ni) is an important metal in modern infrastructure and technology, with major uses in stainless steel, alloys, electroplating and rechargeable batteries. That is why the major sources of nickel contamination in soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (KHODADOUST et al. 2004). Nickel deficient soils are rare. Nickel is essential for higher plants. Our understanding of the mechanisms of Ni uptake and hyperacumulation by plants has been considerably advanced in recent years. Deficiency of nickel in the plants, if it does occur, is mainly related to inaccessibility of this element from the soil due to high pH and/or disrupted elemental balance (especially elevated content of Zn or Fe). In this case, crops may be supplied with Ni as a foliar spray. The general population is exposed to nickel in nickel alloys and nickel-plated materials, such as coins, steel and jewelry. Although in excess nickel may pose risk to human health, unlike cadmium it does not bioaccumulate (biomagnify) in a food-chain. However, even small amounts of Ni may cause allergies.

In the last decade, much research on the nickel in the environment has been carried out. Up to the present, measurements in many countries, including Poland, indicate that concentrations of nickel in the environment (air, water, soil, food) do not exceed legislative limits and should not be dangerous for the general population (CEMPEL, NIKEL 2006).

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