Nickel – from Toxic to Essential Nutrient

By E. Malavolta and M.F. Moraes

Nickel was long considered as either a non-essential or toxic element. However, more is being learned about the role of Ni as a nutrient and its activity in plants. It has shown benefits in pecan production.

"Mouse-ear" is the expression used to describe peculiar symptoms shown by leaves of pecan (*Carya illinoinensis*) and a few other plants. The tip of affected young leaves has dark spots and is rounded, resembling the ear of a mouse. The disorder, known since 1918, has affected orchards in the Southeastern U.S. Gulf Coast and Coastal Plain (Wood et al., 2004a).

The disorder initially was attributed to various causes, such as spring cold injury, viral disease, or either Mn or Cu deficiency. Leaf analysis of affected and healthy leaves revealed that the symptoms were due to Ni deficiency, caused in turn by low levels in the soil or induced by excess Zn (Wood et al., 2004b). Foliar spray of nickel sulfate ($NiSO_4 \cdot 6H_2O$) in the fall is transported into dormant tissues of shoots and buds, in a proportion sufficient for normal growth. The next spring, leaves from treated plants appear normal in shape with 7 mg Ni/kg, whereas those with symptoms showed 0.5 mg/kg. Soils of orchards exhibiting severe Ni deficiency had from 0.4 to 1.4 kg/ha of Ni (Wood et al., 2006a).

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 proposed by Arnon and Stout (1939). It meets also the direct criterion: urease is an ubiquitous metalloenzyme containing Ni (Dixon et al., 1975). Eskew et al. (1983, 1984) and Brown et al. (1987) placed Ni in the list of micronutrients. As early as 1946, Roach and Barclay - in field trials carried out in England with wheat, potato, and broad beans - obtained increases in yield thanks to the application of sufficient Ni sprays.

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 Ni may play a multitude of roles in higher plants. The necrotic spots associated with the deficiency correspond to local accumulation of either urea or oxalic and lactic acids, the latter indicating changes in carbon (C) 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). Field experiments described as early as 1973 showed that the addition of up to 40 g Ni/ha increased nodulation and grain yield (Bertrand, 1973). In extensive reviews, Mishra and Kar (1974) and Gerendas et al. (1999) mention that sprays with Ni salts are very affective against rust infection in cereals due to its toxicity to the pathogen and also due to changes caused in the host physiology that lead to resistance.

Photo: USDA-ARS, Dr. Bruce Wood

This pecan tree was deficient in Ni. The right branch was treated in early spring with a single foliar spray of nickel sulfate, whereas the left branch was not treated. Growth effects were visible by about 14 days after the treatment.

Plants grown in uncontaminated soils have a Ni concentration in the wide range of 0.05 to 5 mg/kg dry weight. The amplitude of the variation is due to availability in the soil and the species analyzed. Different organs or parts of the same plant may have different contents. According to Gerendas et al. (1999), the content in leaf blade is high during vegetative growth. At harvest, however, grains contain more Ni than the straw. At spring flowering, the partitioning of micronutrient in the branches of citrus disclosed a surprisingly high content of Ni, half of the total in the flowers (**Figure 1**). It is known that increasing the level of NH_3 in the leaves could cause an increase in flower induction (Lovatt et al., 1988). This might suggest that high levels of Ni in the flowers, not previously reported, could increase urease activity and generate NH_3 which would increase flowering and percentage of fruit set (Malavolta et al., 2006).

Abbreviations and notes for this article: Ni = nickel; Mn = manganese; Cu = copper; Zn = zinc; Fe = iron; Mo = molybdenum; Co = cobalt; P = phosphorus; Mg = magnesium; Ca = calcium; N = nitrogen.

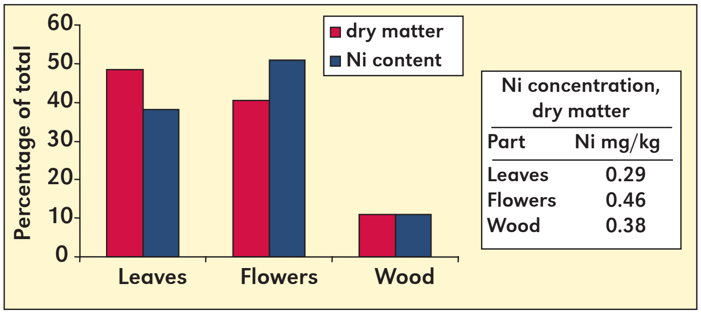

Figure 1. Nickel content of citrus in various plant parts in spring (Malavolta et al., 2006).

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). 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 hyperaccumulators. These plants prosper in Ni-rich, usually serpentine or contaminated soils. *Alyssum bertolonii*, found in Italy and the country of Georgia (in the former USSR), contains 4,000 mg/kg in its leaves and 2,500 in seeds. In plants collected in Ni-rich soils of central Brazil, Brooks et al. (1990) found several species of hyperaccumulators: *Vellozia* spp with more than 3,000 mg/kg in its leaves and *Sebertia acuminate* with 1.17%.

Field Use and Response

Would field grown crops respond to Ni addition? Nickel requirements are of the same order as those of Mo and Co, around 0.05 mg/kg. Molybdenum deficiency has been described and response to its use is well known. Cobalt is routinely applied as seed treatment in the case of legumes. Responses to Ni, besides that shown by pecan, could show up in the future.

Nickel occurs in soils in several forms: soil solution, exchangeable and non exchangeable, in minerals, and associated with organic matter. A study of 863 soils from the U.S. gave an average concentration of 20 mg/kg and a range of less than 5 to 700 mg/kg (Uren, 1992). Analyses of 38 samples of Brazilian soils from the State of São Paulo showed soluble (DTPA) Ni in the range of less than 0.5 to 1.4 mg/kg, values considered as low. Total content was from lower than 10 to a maximum of 127 mg/kg (Rovers et al., 1983).

Nickel deficiency could be due either to low levels of available forms in the soil, or could be induced by several factors, particularly the following (Wells, 2005; Wood et al., 2006a): 1) High contents of Ca, Mg, Cu, or Zn inhibit Ni uptake. 2) Availability decreases with excessive application of lime, when pH is raised above 6.5. 3) High rates of phosphatic fertilizers or high levels of soil P reduce the availability either in the soil or within the plant itself. 4) Nematodes damage the root system and lead to severe deficiency.

One or two applications of Ni to foliage, at a concentration of 10 to 100 mg/L (plus urea and surfactant) can correct the deficiency and ensure normal growth, the treatments being made during the early canopy expansion phase, or soon after bud break (Wood et al., 2006-a). This practice, effective for mouse-ear of pecan, could serve as a trial example in other perennial fruit crops, to be checked, of course, through experimental work. Recently, Wood et al. (2006b) were able to correct Ni deficiency in pecan with sprays of an aqueous extract of *Alyssum murale*, a hyperaccumulator.

Several products are available for foliar application, including $NiSO_4 \cdot 6H_2O$ and synthetic chelates. Both the American Association of Plant Food Control Officials and the USDA have placed Ni on the list of essential nutrients. Sale and use of Ni fertilizers in the U.S. are now authorized. A new product, a chelate of ligno sulfonate with 6% Ni and 10% N, is on the market. In Brazil, the law which controls the commerce of fertilizers and amendments lists products for leaf and soil application and establishes the minimum concentration which can be registered. BC

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References

Arnon, D.I. and P.R. Stout. 1939. Plant Physiology 14(2): 371–375.

Bai, C., C.C. Reilly, and B.W. Wood. 2006. Plant Physiology 140 (2): 433-443.

Bertrand, D. 1973. Comptes Rendus Hebdomadaires des Seances de L´Academie des Sciences. Serie D. París 276(12): 1855-1858.

Brooks, R.R., et al. 1990. National Geographic Research 6 (2): 205-219.

Brown, P.H., R.M. Welch, and E.E. Cary. 1987. Plant Physiology 85(3): 801-803.

Dixon, N.E., C. Gazzola, R.L. Blakeley, and B. Zerner. 1975. Journal of the American Chemical Society 97(14): 4131-4133.

Eskew, D.L., R.M. Welch, and E.E. Cary. 1983. Science 222(4624): 621-623.

Eskew, D.L., R.M. Welch, and W.A. Norvell. 1984. Plant Physiology 76(3): 691-693.

Gerendas, J., et al. 1999. Journal of Plant Nutrition and Soil Science 162(3): 241-256.

Klucas, R.V., F.J. Hanus, S.A. Russell & H.J. Evans. 1983. Proceedings of the National Academy of Sciences of the United States of America 80(8): 2253-2257.

Lovatt, C.J., Y.S. Zheng, and K.D. Hake. 1988. Israel Journal of Botany 37(2-4): 181-188.

Malavolta, E., et al. 2006. Revista Brasileira de Fruticultura 28(3): 506-511.

Mishra, D. and M. Kar. 1974. Botanical Review 40(4): 395-452.

Piccini, D.F. and E. Malavolta. 1992. Revista brasileira de ciência do solo 16(2): 229-233.

Roach, W.A. and C. Barclay. 1946. Nature 157(3995): 696.

Rovers, H., O.A. Camargo, and J.M.A.S. Valadares. 1983. Brasileira de Ciência do Solo 7(3): 217-220.

Smith, N.G. and J. Woodburn. 1984. Naturwissenschaften. 71(4): 210-211.

Uren, N.C. 1992. Advances in Agronomy 48: 141-203.

Wells, L. 2005. Mouse-ear of pecan. The University of Georgia, Cooperative Extension 4 p. (Circular, 893)

Wood, B.W., C.C. Reilly, and A.P. Nyczepir. 2004a. Mouse-ear of pecan: I. Symptomatology and occurrence. HortScience 39(1): 87-94.

Wood, B.W., C.C. Reilly, and A.P. Nyczepir. 2004b. HortScience 39(1): 95-100.

Wood, B.W., C.C. Reilly, and A.P. Nyczepir. 2006a. Acta Horticulturae 721: 83-97.

Wood, B.W., R. Chaney, and M. Crawford. 2006b. HortScience 41(5): 1231-1234.