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Review
NICKEL IN SOILS AND PLANTS OF CUBA

Reseña bibliográfica
El níquel en suelos y plantas de Cuba

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ABSTRACT. Soil Nickel (Ni) content is very dependant of the parental material that originated it. Besides, Ni in the soil surface could reveal also its contamination. The international bibliography shows total Ni values in soils of the world between 0,2 and 450 mg kg^{-1}. At present it is known that despite Ni is essential for higher plants, an excess in available forms could be toxic and it is considered a Heavy Metal. In Cuba, studies indicate a total Ni mean content of 122,3 mg kg^{-1}, much higher than the one pointed out by the bibliography and extreme values up to 2850,0 mg kg^{-1} in soils developed over ultrabasic rock (serpentinite). Nevertheless, there are no reports of high values (toxic) in crops. In present paper, it is discussed the origin and forms of Ni in Cuban soils, and its possible toxic effect for plants and animals that feed with them. Finally, it was concluded that it is necessary to establish Permissible Limits of Ni in soils, according to the soil type and use.

Key words: pollution, heavy metals, soil

RESUMEN. El contenido de Níquel (Ni) en el suelo es muy dependiente del material parental que le dio origen. Por otra parte, el Ni existente en su superficie, puede ser también un reflejo de su contaminación. La literatura internacional señala valores de Ni total en los suelos del mundo entre 0,2 y 450 mg kg^{-1}. Se conoce en la actualidad, que aunque el Ni es esencial para las plantas superiores, su exceso en forma disponible puede ser tóxico, por lo que se considera un Metal Pesado. En Cuba las encuestas realizadas reflejan un contenido medio de 122,3 mg kg^{-1} de Ni total, muy superior al señalado por la literatura internacional y valores extremos de hasta 2850,0 mg kg^{-1} en suelos desarrollados sobre rocas ultrabásicas (serpentinita). Sin embargo, no existen reportes de valores elevados (tóxicos) del elemento en los cultivos. En el trabajo se discute el origen y formas en que se encuentra el Ni en los suelos cubanos; así como su posible efecto tóxico para las plantas y animales que se alimentan de ellas. Finalmente, se concluyó planteando la necesidad de establecer Límites Permisibles de Ni en el suelo, diferenciados de acuerdo al tipo de suelo y su uso.

Palabras clave: contaminación, metales pesados, suelo

INTRODUCTION

Nickel (Ni) as a chemical element has atomic number 28, atomic weight 58,69, density 8,20 g cm^{-3} and its main oxidation state is +2. Ni belongs to iron (Fe) family, which includes cobalt (Co), both having a geological feature of siderophylic type, so it is easily combined with metallic Fe. In addition, it readily forms sulfur compounds and sulfo arsenides (1). Average Ni abundance in the terrestrial crust is estimated of about 20 mg kg^{-1}, whereas in ultrabasic (ultramafic) rocks such as serpentinite, it varies between 1400-2000 mg kg^{-1} and its concentration decreases when increasing rock acidity; in granite, it contains from 5 to 20 mg kg^{-1}. Sedimentary rocks have Ni range between 5 and 90 mg kg^{-1}, the highest value being recorded in clayey sediments (1, 2, 3, 4).

The first article known about the significance of Ni, Cr and Co dates back to 1935 (5), when ultrabasic soils of Cuba, Puerto

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Rico and the United States were studied, in order to explain soil infertility based on their high contents of these metals. However, today it is known that this is mainly due to high Mg contents, higher than Ca contents. Furthermore, the metal contents of plants growing in them are lower than those found elsewhere (6).

Ultrabasic (ultramafic) rocks are igneous essentially constituted of ferromagnesian minerals. In the eastern part of Cuba, there are significant soil areas developed on this type of rock (5). Cuban ultramafic rocks (serpentine) are the largest in the Caribbean, covering approximately 7 % of the total land area (7).

Total Ni content in the soil is highly dependent on its parent material (forming rock). However, Ni concentration on soil surface may reflect the impact of soil formation and pollution processes (1, 3, 8, 9). It is reported that total Ni in the soils worldwide varies from 0,2 to 450 mg kg^{-1} and its average content between 19 and 22 mg kg^{-1} (1); nevertheless, other authors point out the latter is between 20 and 40 mg kg^{-1} (8).

At present, it is known that although Ni is essential for higher plants, as an urease enzyme cofactor and due to its effect on legume nodulation, nitrification and N mineralization, its available excess amount to plants can be toxic (1, 2, 3, 8), since it is considered heavy metal (HM). Researches indicate that Ni toxicity in human beings cause neurological, reproductive and carcinogenic effects (10, 11). Particular care should be taken at Ni industry, because it is highly toxic when inhaled. Therefore, industrial processes using this metal, as well as coal and oil are considered polluting sources (1, 3, 12).

This work pretends to consistently and chronologically review information coming from different studies and projects made in Cuba about Ni origin, content and forms in Cuban soils, as well as its possible toxic effect on plants and, consequently, on human being. It should be clarified that soil types were named according to a Cuban Classification existing at the time the work was done. However, there are correlations with other prior or subsequent national and international classifications (13, 14).

ANALYTICAL METHODS USED

Total or semi-total Ni contents in the soil were studied, as these forms are usually employed to evaluate soil contamination by HM. The method used for sample mineralization has been changed with time, which is clarified in each particular case. In all cases, the atomic absorption spectrophotometry with flame or coupled plasma (ICP) was used as instrumental analytical technique (12, 15, 16).

NI IN CUBAN SOILS

There is an unpublished doctoral thesis conducted in the former Soviet Union that studied trace elements, including Ni, in profiles of Cuban soils cultivated with sugarcane[A]. A few years later, a survey was performed on some HM contents in soils (17, 18). Determinations were made during 1987 in collaboration with Jena IPE from the former German Democratic Republic (GDR). Thus, 85 soil samples were taken from the topsoil of typical profiles in 10 provinces and the special municipality of Isla de la Juventud, which were processed through extractions with HNO_3 1,5 N (18). Results (Table I) showed an average content of 122,3 mg kg^{-1} total Ni, and extreme values of up to 2850,0 mg kg^{-1}, much higher than those reported by international literature in that moment (1, 8), which mainly corresponded to Ferromagnesian Brownish Red Fersialitic soils developed upon serpentinite (13, 14) of Holguin province, where there are large nickeliferous deposits.

Nevertheless, in the same study, leaf samples were taken from crops growing in some soils of Holguin province and, in all cases, Ni contents were suitable (Table II); thus, the authors concluded that they come from the parent material that gave rise to lithogenic soil, which are largely found in non-available forms to plants.

Furthermore, it was found that Red Ferralitic soils (13, 14), of particular agriculture importance in the provinces of Mayabeque, Artemisa, Matanzas and Ciego de Avila, developed upon limestone sedimentary rocks, have high total Ni contents of about 200 mg kg^{-1}; although they are not as high as the previous ones, they are higher than those reported by international literature of that time.

[A] Companioni, N. *Formas de los compuestos de los microelementos en los suelos de las plantaciones de caña de la República de Cuba*. [Tesis de Doctorado], Moscú, URSS, 1981, 110 p.

Similarly, it was found that most Ni content was non-available to plants, so it was concluded that its origin is also lithogenic (17, 18). These soils are characterized by clayey mineral formation of type 1:1 and Fe-Al oxide and hydroxide accumulation. Soil Ni is strongly associated with Fe and Mn oxides (1). Fe oxides and minerals contain Ni range between 100 and 170 mg kg^{-1}, whereas Fe-Mn concretions accumulate up to 680 mg kg^{-1} (1, 9). Note that about 70 % of Cuban soils are developed on limestone sedimentary rocks, which were enriched during its formation in Ni and Cr derived from rich ultrabasic rock areas (19, 20, 21).

Subsequently, these authors confirm what was earlier stated[B] and prove that large profitable Ni amounts added to both types of soils (Ferromagnesian Brownish Red Fersialitic and Red Ferralitic) are quickly fixed in them and not assimilated by the plant, so that high total Ni contents are not a cause of contamination to crops growing in them (9).

Other works determined the so-called available forms with different extractive solutions (1, 4, 6), DTPA being mostly used (22). However, results have not allowed arriving at conclusive results (1, 2, 3, 6)

Table III shows that although the greatest HM accumulation is often present on topsoil, the uniform distribution of total Ni is evident along soil profile, which confirms its lithological character. Also, note that the available or profitable fraction is a very small part of the total, coinciding with the low leaf Ni contents obtained in different studies[C] (23, 24).

There are other types of Cuban soils, which often have total Ni contents between 100 and 200 mg kg^{-1}; this is the case of Ferritic, Vertisol, Fluvisol and many Sialitic Brown soils. However, those of sandy texture in Pinar del Rio and the special municipality of Isla de la Juventud usually have low or very low contents of this metal[D] (17).

Table I. Ni and Cr contents (mg kg^{-1}) in Cuban soils

Element	Mid value	Range	± s
Ni	122,30	0,5-2850,0	35,56

Table II. Ni content in soils of Holguin province and leaf samples from crops growing in them

Soil				Plant	
Classification	Town	Depth (cm)	mg kg^{-1} de Ni	Crop	mg kg^{-1} of Ni
Reddish Brown Fersialitic	Banes	0-20	75	Banana	1,3
		20-45	74		
Fluvisol	Mayarí	0-20	208	Cassava	13,0
		20-40	302		
Vertisuelo	Banes	0-20	153	Sugarcane	2,0
		20-45	152		
Fluvisol	Mayarí	0-20	420	Sugarcane	12,0
		20-40	426		
Ferromagnesian Brownish Red Fersialitic	Mayarí	0-20	670	Grass	14,0
		20-40	490		
Ferromagnesian Brownish Red Fersialitic	R. Freyre	0-20	914	Sugarcane	1,6
		20-40	856		
Ferromagnesian Brownish Red Fersialitic	R. Freyre	0-20	372	Sugarcane	2,3
		20-50	376		

The critical concentration in plants is from 10 to 100 mg kg^{-1} Ni, depending on the crop (3)

Table III. Total and profitable Ni content (DTPA) (mg kg^{-1}) in Compacted Red Ferralitic soil areas grown with vegetables, tubers and roots in Mayabeque province

Location	Depth (cm)	Ni	
		Total	DTPA
Quivicán	0-20	229	0,15
	20-40	239	0,15
	40-60	232	0,15
	60-80	238	0,15
Güira de Melena	0-20	241	0,20
	20-40	230	0,18
	40-60	233	0,16
	60-80	233	0,16

NI PHYTOTOXICITY IN THREE CUBAN SOILS

During the second half of the 90s, another project[D] studied the addition of growing Ni doses (0, 100, 200, 400 and 800 mg kg^{-1}) as soluble salt, using plastic pots containing 1 kg of soil, using three types of Cuban soils: Red Ferralitic, Low Clayey Activity Alitic (ABAA) and Pelic Vertisol (13, 14), with the purpose to cause toxicity in plants. Once Ni was added, the pot was allowed to rest for 30 days; then, sorghum was seeded (six plants per pot) and harvested 45 days after its germination. Yield (as dry matter produced), heavy metal content in crops and by calculation, as well as its corresponding extraction were evaluated, in order to assess Ni phytotoxicity; thus, the critical soil phytotoxicity level was defined, like the one that gave rise to a statistically significant yield decrease.

In the case of Red Ferralitic soil (13, 14), applying up to 800 mg kg^{-1} Ni to the soil produced 1131,8 mg kg^{-1} total Ni, which neither affected crop yield significantly nor caused visual symptoms in plants. In addition, plant contents were lower than 30 mg kg^{-1}, which is considered a phytotoxicity criterion for this metallic element in the plant (25). It allows inferring that this type of soil is characterized by having mineral type 1: 1 and Fe-Al hydroxides with a high fixing capacity of this metal.

However, in the case of Low Clayey Activity Alitic soil of sandy texture (ABAA) (13, 14), due to its chemical and physical characteristics, it keeps a greater Ni proportion available to plants than Red Ferralitic soil, so that the plant absorbs a higher Ni quantity. Thus, there was a significant yield drop for a total Ni content of 407 mg kg^{-1} in the soil that corresponded to a plant content of 49,30 mg kg^{-1} Ni, which surpasses 30 mg kg^{-1} (considered phytotoxic) (25).

Finally, in the case of Pelic Vertisol, a significant yield decrease was recorded for 451 mg kg^{-1} total Ni in the soil, to which corresponded higher plant content than the phytotoxic above mentioned. Results are shown in Table IV.

Chlorosis is the most common visual symptom of Ni phytotoxicity, followed by leaf yellowing and necrosis, which is mainly induced by Fe-Ni interaction, that is, low leaf Fe concentration due to high Ni concentrations in the medium (3). However, these symptoms were not observed in previous experiments.

Ni DISTRIBUTION IN THE PLANT

Ni extracted by plant organs was studied in bean, tomato, potato and tobacco crops grown in Compacted Red Ferralitic soil under intensive agriculture, as well as pepper, watermelon and cabbage growing in greenhouses, all of them from Mayabeque and Artemisa provinces. Some results are shown in Figures 1 and 2. In general, results indicate that Ni contents in edible organs of the crops studied are not a risk to human health, since most of this metal is not transported to the fruit[C] (23, 24).

[B] Irigoyen, H. y Muñiz, O. Contenido de Ni, Cr, Cd, Pb, Cu y Zn en suelos Ferralítico Rojo y Fersialítico Rojo Parduzco Ferromagnesial cubanos. edit. Archivos del Instituto de Suelos, La Habana, 1989, 15 p.

[C] Muñiz, O. Contenido de metales pesados en áreas de agricultura intensiva de La Habana y Pinar del Río. Informe Final del Proyecto 07 perteneciente al PR-11: Recursos Naturales, Inst. Archivos del Instituto de Suelos, La Habana, Cuba, 2004, 37 p.

[D] Muñiz, O.; Molina, J.; Estévez, J.; Quicute, S.; Vega, E.; Montero, A.; Pupo, I. y Padilla, R. Contaminación por metales pesados en algunos de los principales agroecosistemas cubanos. Informe Final del Proyecto 002.042 perteneciente al PNCT Producción de Alimentos por Métodos Sostenibles, Inst. Archivos del CITMA, La Habana, Cuba, 2000, 25 p.

Table IV. Critical phytotoxicity levels of Ni (mg kg-1) obtained in three Cuban soil types

	Red Ferralitic*	Soils ABAA	Pelic Vertisol
Total Ni in the soil	-	407	451
Ni in the plant	< 24	49,3	> 30,0

*Total Ni content in the soil of 1131,8 mg kg-1, it did not affect yield of cultivation

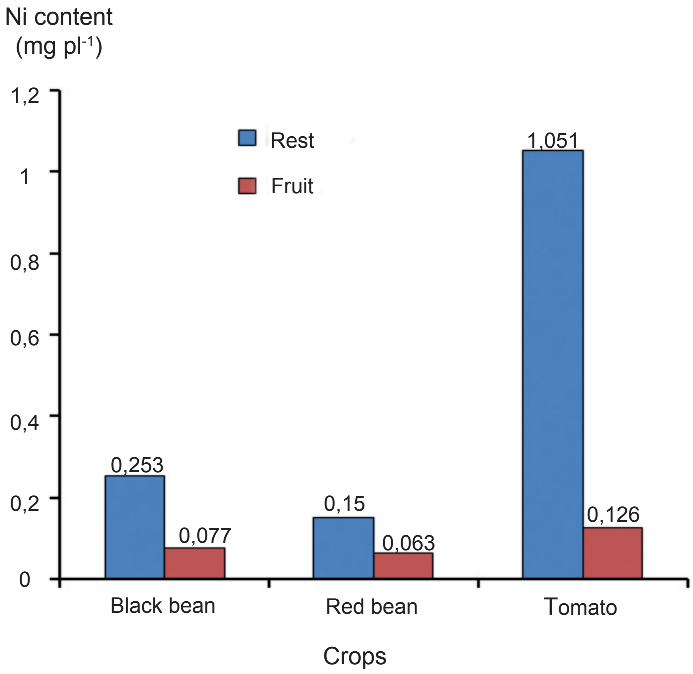

Figure 1. Ni (mg plant-1) extracted by bean and tomato in Red Ferralitic soil

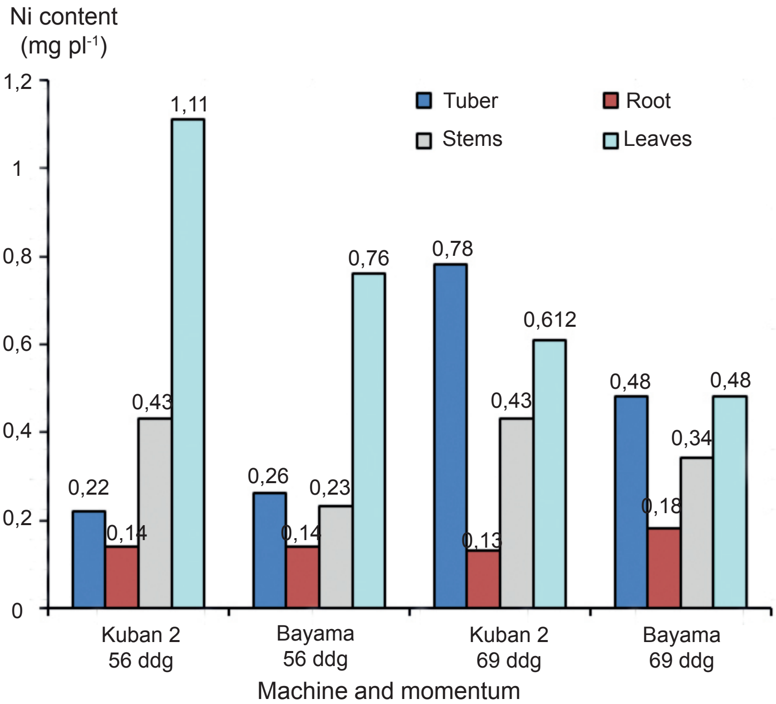

Figure 2. Ni (mg plant-1) extracted at two potato cycle stages in Red Ferralitic soil

However, it should be made clear that, unlike what happens to HM as arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg), the feeding codex does not establish permissible limits for Ni in fresh or preserved foods (26).

Ni forms are diverse in the soil, ranging from highly mobile until nonreactive ones (4, 12, 27). Ni content in plants is highly dependent on its origin and soil properties, which control Ni behavior and its availability to plants, such as clay, organic matter content and pH (1, 3, 9). Regarding cereals, it varies between 0,34 and 14,6 mg kg-1 whereas average values, depending on the crop, does not generally exceed 1,28 mg kg-1 (3).

There are also methodologies that allow the sequential extraction (fractionation) of HM in the soil. In general, all of them start by extracting water-soluble fraction, followed by the interchangeable, adsorbed or occluded ones in carbonates, and those occluded in organic matter, Mn oxides, amorphous and crystalline Fe oxides and finally, the residual one (28, 29, 30, 31). It is logical that predominant forms in each case will depend on the balance existing between factors such as pH, mineralogy, quantity and type of humus, etc. Results obtained when deepening the forms in which Ni appears in Red Ferralitic and Gley Ferralitic soils of Havana and Pinar del Río, respectively, indicate that most Ni is found as non-profitable to plants (24).

On the other hand, a large number of plants (317 taxas and 37 families) classified as Ni accumulative and hyperaccumulative are reported to extract 10000 mg kg-1 Ni or more. The best known are *Alyssum* sps.

These species can extract up to 400 kg ha^{-1} Ni. The mechanism of Ni hyperaccumulation by plants is not well known, but it is considered associated with metallic-organ complexes which transport the metal inside the plant (7, 32, 33, 34). These plants are characteristic of soils developed upon serpentinite. Cuba has the largest ultramafic rocks (serpentines) in the Caribbean, covering approximately 5300 km^2, which represents 7 % of the total land area; Cuba is the Antillean country having the greatest number of hyperaccumulative species (35, 36, 37).

An alternative to prevent contaminated areas is by extracting heavy metals through hyperaccumulative plants. This technique is known as phytoremediation, phytoextraction or bioremediation, which involves plants and microorganisms in environmental sanitation (12, 38, 39, 40, 41).

Ni IN ORGANIC MANURES

When European socialist field disappeared, there was a sharp decline in the consumption of mineral fertilizers and other inputs in Cuba, with the resulting negative effect on agricultural production. However, the use of different sources of organic manures (OM) has been an alternative to recover agricultural production (42, 43). It is sometimes considered that every OM is adequate, but it is not. The prior assessment of its quality is required, including the possible content of pathogens and HM. This is much more important when considering heavy OM loads supporting urban agriculture and especially organoponics. In this way, during the last 10 years, studies were performed involving HM monitoring in different organic sources (44).

In the case of Ni, values are usually higher than those reflected by international literature, similar to what happened in soil samples, which indicates the influence of soil on soil-plant-animal system; to high Ni contents in the soil usually correspond high contents of different OM produced. However, Ni amounts are low in crops grown using them, which indicates once again that it is found as a non-assimilable form to plants. Something similar happens with OM substrates used in organoponics (44).

The Ministry of Agriculture, Livestock and Supply of Brazil sets 70 mg kg^{-1} Ni (as dry weight) as the maximum allowable limit of organic manures to use in agriculture. In Cuba, it is being worked to this aim.

As it was discussed, Ni is almost immobile in the soil and mainly found in its residual fraction. There is evidence that in the topsoil, Ni can be strongly linked to the organic form, therefore, it is nearly immobile. Nevertheless, its remobilization seems possible when humic and fulvic acids are present (1).

DEVELOPING STUDIES

At present, it is being worked with the collaboration and experience of Brazilian institutions, in order to perform researches that enable to prepare a legislation containing the permissible HM limits, including Ni in the soils of Cuba, based on international methodologies that consider modeling and risk analysis (45, 46).

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Many Cuban soils are characterized by high values of total Ni. However, there is no evidence of toxic contents for human being, or phytotoxic for crops grown in them, as most Ni in the soil is found in unavailable forms to plants. The highest values are characteristic of Ferromagnesian Brownish Red Fersialitic soils (more than 2000 mg kg^{-1}), developed upon serpentinite rocks, which are unproductive soils due to the reverse Mg/Ca relationship, among other limiting factors, rather than to high Ni content.

Ni industry is the main source of soil contamination of this metal. Since it is very important to Cuban economy, particular care should be considered, because Ni is too much toxic when inhaled.

Other important soils for agriculture, such as Red Ferralitic, which are plenty in Havana-Matanzas plains and Ciego de Avila, also have high Ni contents, although without high values (100 and 200 mg kg^{-1}). Ferritic, Vertisol, Fluvisol and many Sialitic Brown soils often have values within this range. Although researches have indicated that Ni contents are low the edible part of economically important crops, it is advisable to study the possible effect of soil properties, such as pH, organic matter and clay contents on the improvement of its available forms to plants. In this sense, the sequential extraction (fractionation) of its different forms in the soil will give rise to new elements.

Ni contents of organic sources used as manures are higher than those reported by many countries, which are undoubtedly affected by the corresponding high values in soils; nevertheless, its toxic effects have not been detected in human being. However, it should be noted that Ni is not an element regulated by feeding codex, so there is not any international criterion in this regard. But it is essential to keep monitoring HM content (not only Ni) in all organic sources used. Likewise, it is advisable to continue studying the potentialities of phytoextraction or phytoremediation as a promising technique for the sanitation and recovery of soils contaminated by metals such as Ni.

Finally, we recommend deepening on further researches with Ni and other HM, in order to reach an early version of Cuban legislation on the permissible limits of heavy metals in Cuban soils.

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