

Mathematical Modeling of the Behavior of Nickel and Copper in a Contaminated Agroecosystem

Modelación matemática para el comportamiento del níquel y cobre en un agroecosistema contaminado

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ABSTRACT: The need to control the contamination caused by heavy metals is increasingly urgent, which is why it is necessary to study the quality of the soil in order to preserve or improve its productivity for the protection of the environment, animal and human health, and to guarantee food safety. Trace elements in high concentrations in soils are food toxins with negative effects on health that manifest in the long term. The action of some of them has been reported on the increase in cases of cancer, nervous system lesions and genetic diseases in humans, etc. as a result of the consumption of contaminated water and food, whether of animal or plant origin. The objective of this work is to propose mathematical models to predict the behavior of nickel and copper concentrations in an agroecosystem adjacent to the dumping of industrial waste in the municipality of San José de las Lajas. For this purpose, the data on the concentration of heavy metals nickel (Ni) and copper (Cu) provided by the Scientific Group of the Faculty of Agronomy of the UNAH from 2005 to 2018 were taken to predict their behavior based on the use of statistical-mathematical tools until 2034. It was obtained that, according to the mathematical models obtained, these soils should not be used to grow vegetables for consumption, nor allow free grazing of cattle, at least until 10 years after this research.

Keywords: Phytoremediation, Food Safety, Toxics.

RESUMEN: La necesidad de controlar la contaminación que provocan los metales pesados es cada vez más apremiante por lo que es necesario el estudio de calidad del suelo para conservar o mejorar su productividad para la protección del ambiente, la salud animal y humana, que garantice la inocuidad alimentaria. Elementos traza en concentraciones elevadas en suelos son tóxicos alimentarios con efectos negativos sobre la salud que se manifiestan a largo plazo. Se ha reportado la acción de algunos sobre el incremento de casos de cáncer, lesiones del sistema nervioso y enfermedades genéticas en humanos, etc. como resultado del consumo de aguas y alimentos contaminados, de procedencia animal o vegetal. En el presente trabajo se plantea como objetivo: proponer modelos matemáticos para predecir el comportamiento de las concentraciones de níquel y cobre en un agroecosistema aledaño al vertimiento de residuos industriales en el municipio San José de las Lajas. Para ello se tomaron los datos de concentración de metales pesados níquel (Ni) y cobre (Cu) cedidos por el Grupo Científico de la Facultad de Agronomía de la UNAH desde el año 2005 al año 2018 para predecir su comportamiento a partir del uso de herramientas estadístico-matemáticas hasta el año 2034. Se obtuvo que, según los modelos matemáticos obtenidos, estos suelos no deben emplearse para cultivar hortalizas con objeto de consumo, ni permitir el libre pastoreo de vacunos, al menos hasta 10 años después de esta investigación.

Palabras clave: fitorremediación, inocuidad alimentaria, tóxicos.

INTRODUCTION

In a context in which industrial environmental pollution is a source of conflict, there is a need to promote social responsibility committed to the preservation, restoration and care of the environment as a central strategy to promote the health of the inhabitants of the affected areas (Guzmán *et al.*, 2019). This problem is undoubtedly one

of the most important ones affecting 21st century society according to CEPAL (2021).

This environmental situation could compromise the fulfillment of some of the millennium goals and affect the process of updating the economic and social model in Cuba, which would guarantee a more just, equitable and inclusive society, moving along the path of sustainable development, which integrates its three dimensions: economic, social and environmental (NN.UU., 2021).

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This is influenced by the development of certain industrial activities that constitute a moderate risk of environmental pollution, given the leaks of components that accumulate in the soil from the natural channel and irrigation with wastewater and as a consequence, "contaminated soil" may appear (Valdés *et al.*, 2017). One of the most persistent pollutants are heavy metals (HM), although their negative effects on animal and human health are manifested in the long term (Alarcón *et al.*, 2015; Doležalová *et al.*, 2019).

To solve these problems that arise, there are treatment techniques based on the ability of different organisms (plants and microorganisms) to degrade, extract or immobilize pollutants from water or soil. These techniques have been called Bioremediation and, as a particular case when using different plants, Phytoremediation (Becerril *et al.*, 2002; Ardizzi, 2018).

Plants used for such purposes accumulate in their aerial tissues both essential elements for crops (Fe, Mn, Zn, Cu, Mg, Mo, Ni) and non-essential elements or elements with biological functions yet to be determined (Cd, Cr, Pb, Ag, Se, Hg), reaching very high concentrations that are toxic to most plants (Gonzales *et al.* (2017); Alonso *et al.* (2018); Lama (2018), so those used for such purposes should not be consumed by animals or humans.

In this case, nickel and copper are essential elements for plants that, in high concentrations, cause disorders in the human body such as heart damage and skin irritation, damage to the nervous system, liver and kidney function, the musculoskeletal system, etc., specifically in the child population that is more sensitive to these effects. This situation is exacerbated because the concern for having guaranteed food led man to cultivate and propagate plant species in agricultural areas close to industrialized or contaminated areas, which according to Valdés *et al.* (2017), is a global reality, and Cuba is no exception.

By taking on the challenge, the Faculty of Agronomy-UNAH studies the problems of heavy metal contamination in vulnerable agroecosystems (Guzmán *et al.*, 2021).

Despite the existence of the National Environmental Strategy (EAN) 2021-2030 CITMA-Cuba (2021), in Cuba, there are areas in the country where, for various reasons, the necessary environmental safety is not met, such as the case of the municipality of San José de las Lajas, in Mayabeque, where 78% belongs to the industrial sector, and although it constitutes an important line in the economy, it is considered a source of environmental pollution and an impact on local food security (ONEI-Cuba, 2019).

Taking into account the situation presented, the work aims to propose mathematical models to predict the behavior of nickel and copper concentrations in an agroecosystem, adjacent to the dumping of industrial waste in the municipality of San José de las Lajas.

MATERIALS AND METHODS

The experimental site corresponds to an agricultural area, located 200 m from the source of contamination (Company

Cerámica Sanving S.A.) at 22°57'49.66" N, 82°10'13.02" W and 22°58'7.95" N, 82°10'13.60" W, according to the Cuba Norte coordinate system, and adjacent to the waste dump. The site belongs to farmers who participate in the Urban, Suburban and Family Agriculture Program of the Jamaica People's Council, San José de las Lajas municipality, Mayabeque, on a soil classified as Ferralitic Yellowish Leached, according to Hernández *et al.* (2015). The crop plots produce vegetables and grasses of the Cynodon genus belonging to the Poaceae family, for free animal consumption, which according to Guzmán *et al.* (2021) accumulate high concentrations of these heavy metals in their leaves.

Study of heavy metal content in soil

"The data series corresponding to the values of 42 samples of concentration of heavy metals Nickel and Copper was taken from 2005 to 2018, provided by the FITOPLANT Scientific Group of the Faculty of Agronomy of UNAH". The values were compared with the maximum permissible limits and dangerous levels for soil and plants, proposed by Kabata (2010) & Fadigas *et al.* (2006).

Mathematical analysis to estimate decontamination in the study area of copper and nickel

Taking into account the concentration of the major elements found in the soil analyses (copper and nickel) according to Guzmán *et al.* (2021), the analyzed of the time in which this soil could be decontaminated was carried out.

To characterize the behavior of the concentrations and analysis of the possible decontamination, the data were tabulated in the Microsoft Excel 2003 program. Next, the simple linear regression was performed with the STATGRAPHICS Centurium XVIII program. The estimation was carried out by the interpolation method with the linear equation $Y = a + bx$ Del Valle *et al.* (2022) where "Y" corresponded to the concentration of each variable and "X" years analyzed. In parallel, the behavior and trend for each case were analyzed. In addition, the annual concentration means were analyzed with respect to the Reference Values and Upper Permissible Limit (Fadigas *et al.*, 2006; Kabata, 2010).

The statistical processing for the prediction of pollution consisted of calculating the confidence intervals of the means by treatments of the variables evaluated, for a confidence level of 99%. The calculated and predicted values were taken into account to prepare the prediction graphs, combining the statistical program STATGRAPHICS Plus for Windows 5.1 and the Excel program, taking into account the equations obtained from the models, predicting until the year 2034.

RESULTS AND DISCUSSION

It was found that the concentrations of MP in the contaminated soil samples are higher than those determined in the standard soil, which is presented in Table 1.

TABLE 1. Concentration of Ni and Cu in soil used for vegetable cultivation and free grazing

Samples	Ni $\pm$ std	Cu $\pm$ std
	mg kg ⁻¹	
Standard	84 $\pm$ 29	364 $\pm$ 98
Contaminated	317 $\pm$ 25	421 $\pm$ 32
VR ^a	35	36
VI ^a	210	190
LSP ^b	75	100
CT ^c	74	55

a- Reference Values (VR) and Intervention Values (VI) of the Dutch Standards.

b- Upper Permissible Limit in soils.

c- Values reported for the Earth's crust.

The following decreasing order in contamination contributions is Ni > Cu, with values of 233 and 57 units of differences respectively between the contaminated soil and the standard soil, which is equivalent to a percentage of 310.66% for Ni above the upper permissible limit, being the one that makes the greatest contribution to the soil, which means that when exceeding the intervention limit of said standards, it is classified as a soil in need of urgent remediation due to these concentrations.

Figure 1 shows a comparison of the intervention limits with respect to the concentration percentages of the metals Ni and Cu to mitigate the excessive increase in these soils, since despite being essential elements for plant growth, when they exceed the standard values they become food toxins with the consequent risk to animal and human health, which is determined by this intervention limit as proposed by Doležalová *et al.* (2019).

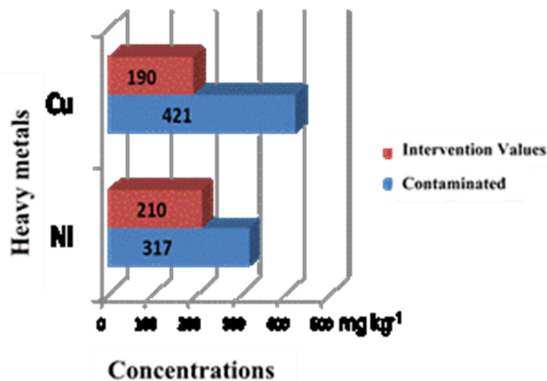
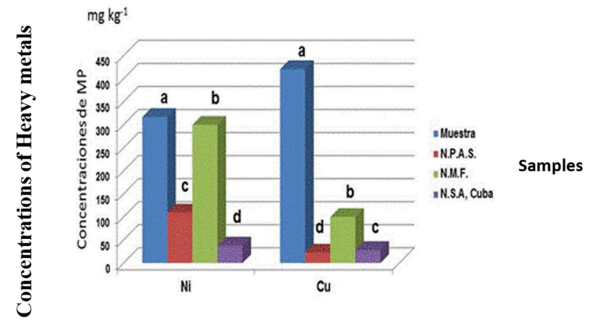

FIGURE 1. Relationship between the intervention limits and the percentages of Ni and Cu in the soil of the agricultural plot under study.

Figure 2 shows the metals compared to the permissible levels for healthy foods (N.P.A.S), average phytotoxic levels (N.M.F) and levels in Cuban agricultural soils (N.S.A, Cuba) (Muñiz, 2008).

It can be seen that these elements are found in concentrations much higher than those required by these established levels, obtaining statistically significant differences with respect to the three values with which



Unequal letters differ significantly with $p < 0.05$ according to Duncan's test

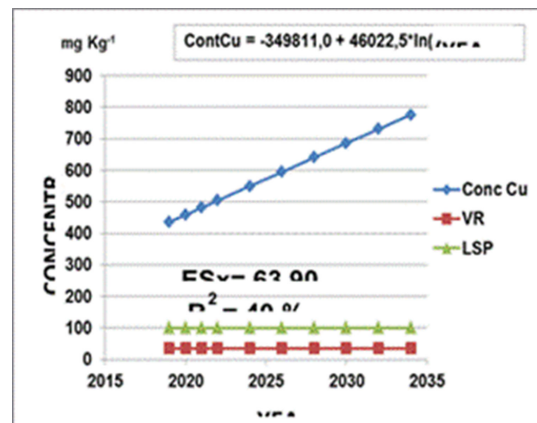
FIGURE 2. Ni and Cu concentration compared to the average acceptable levels for the production of healthy food and phytotoxic levels.

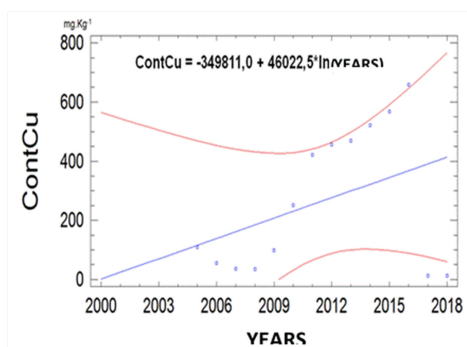
they are compared. The samples with the highest levels with respect to their indicators are those of Cu, which exceed these limits by very high percentages (1 830%, 421% and 1 472%, permissible levels for healthy foods, average phytotoxic levels and levels in Cuban agricultural soils, respectively).

All these results have a chemical-biological influence on the crops produced in these areas since, as can be seen, the values with which they are compared are related to food safety Muñiz *et al.* (2015); GOC-Cuba (2020) a property that is of interest in local food safety, in addition to confirming the importance of these studies because under normal conditions these elements are essential for the growth and development of plants.

Analysis of statistical-mathematical models for the description of decontamination in the study area

Figures 3 and 4 for copper and 5 and 6 for nickel present the mathematical statistical models for predicting the minimum time required for the recovery of contaminated soil or the possible reduction of PM concentrations under the study conditions presented. To do so, the company must regulate its discharges of waste to the exterior, taking the necessary measures to meet this objective.


FIGURE 3. Predictive model for Cu, from minimum time to soil recovery to 99% confidence level.



Trend lines (blue color), Prediction limits (pink color), Confidence limits (red color) at 99% confidence level.

FIGURE 4. Mathematical models fitted for the prediction of copper decontamination in the study area.

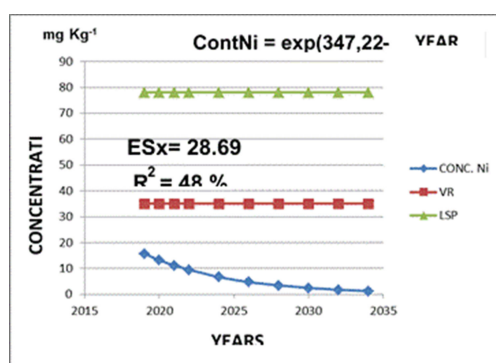
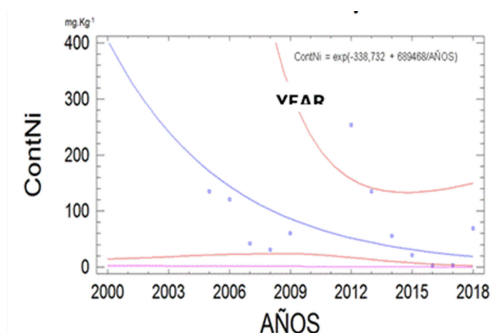


FIGURE 5. Predictive model for Ni, from minimum time to soil recovery to 99% confidence level.



Trend lines (blue color), Prediction limits (pink color), Confidence limits (red color) at 99% confidence level.

FIGURE 6. Mathematical models fitted for the prediction of nickel decontamination in the study area.

The elements studied show a differentiated behavior, according to the predictions made.

In the case of Cu, according to the logarithmic model and the adjusted models (Figure 4), it shows that its concentrations will probably not begin to decrease until 2035, so the company must review its production process according to UNAH-Cuba (2017), and the possibilities of recycling or using raw materials with less of this element, coinciding with what was proposed by Alarcón et al. (2015) & González et al. (2017), who report that the pollutant load can be reduced if its presence in the raw materials used in the production process is reduced.

In the case of Nickel (Figures 5 and 6), the best-fitting model is the exponential one, and it can be seen that since 2019 the levels of this substance have begun to decrease, reaching 0 by 2035, which shows the possibility offered by the regulations complied with regarding the use of raw materials imported from other places in the country such as Moa, which in their nature provide large volumes of nickel, as reported in the UNAH-Cuba (2017).

For all the above, it must be taken into account that, according to Alloway (2013), one of the most serious problems presented by PM contamination is the half-life of the same, which in the case of copper (Cu) is 740 to 5 900 years, so the effects due to accumulation are more drastic than those produced by contamination caused at a specific time.

CONCLUSIONS

The inclusion of mathematical models in contamination studies allowed us to evaluate agricultural areas contaminated with heavy metals and to define that the soils are unusable for agricultural production for consumption, both animal and human, and are classified as requiring urgent remediation due to the concentrations of Ni and Cu.

The mathematical statistical models allowed us to predict that the heavy metals studied have a different behavior; for Ni, their contents have decreased since 2019, but not for Cu, although the areas should not be used for agricultural purposes (at least to grow vegetables or allow free grazing) in the next 10 years.

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