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Zinc in Soil and Corn Leaves in a Calcareous *Rhodic Luvisol* from Yucatan Mexico with Acid and Subsoiling

Jorge Humberto Ramírez Silva, Alejandro Cano González*, Nelda Guadalupe Uzcanga Pérez

Centro de Investigación Regional Sureste del Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias (INIFAP), Mérida, México
Email: *cano.alejandro@inifap.gob.mx

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Abstract

The productivity of corn in Yucatan Mexico is continually threatened by deficiencies of several essential microelements such as Zinc (Zn). The problem is limited to the alkalinity of the soil driving to an unavailable Zn in the soil which is not used by the plants. Another problem facing is the compaction of lower layers in the red *Rhodic Luvisols* that have been plowed, in an intensive use, for more than 30 years. Several studies have addressed the advantages of using acids to release zinc trapped by carbonates as well as the subsoiling to break up the underground to increase aeration and microbial activity. This work aimed to evaluate the effect of the application of sulfuric acid and sub-soiling on the Zinc contents of both soil and foliage of the CHICHEN ITZA Variety and the commercial HYBRID H-443A in a red arable *Rhodic Luvisol* in the state of Yucatan Mexico. Eight treatments were replicated by twice, and the results were subjected to an Analysis of Variance (ANOVA). The Determination Coefficients ($\mathbf{r^2}$) was calculated to evaluate the relationship between zinc in the soil and in the foliage. Zinc deficiencies were graded by comparing the results with the Critical Limits (**CL**) given by the literature and the Relative Sufficiency (%) was calculated. No variable showed significant statistical differences between treatments. However, Zinc, in the soil, is reduced with Sub-soiling in both cultivars. The acid, by itself, increased the availability of Zinc. The highest Zinc contents in the soil were found in CHICHEN. The HYBRID showed the lowest Zinc contents in the leaves (12.5 to 15 ppm) corresponding to 83% and 100% of Relative Sufficiency with respect to the **CL**. In CHICHEN the ranges of foliar Zinc were higher (14.5 to 19 ppm) with 97% and 127% of the Relative Sufficiency.

Subject Areas

Agricultural Engineering

Keywords

Deficiencies, Alkalinity, Compaction, Nutrition, Critical Levels

1. Introduction

The soils of the Yucatan Peninsula (YP), in Mexico, are of calcareous origin with many chemical and physical limitations. One third of the world's soils have the same genesis. In Yucatan, more than 200 thousand hectares of corn are grown in this type of soils, showing important deficiencies of some specific essential microelements like Zinc. By instance, Ramírez-Silva *et al.* (2015) [1] stated that 87.5% of eight arable soils in the state of Quintana Roo in the YP presented strong Zn deficiencies in soil and foliage. The fact is that Zinc studies have been very limited since the preference studies on nitrogen and phosphorus as primary essential elements.

High concentrations of Hydroxides (OH^-), in calcaric soils, usuallyform Low-Zinc solubility complexes such as the Zinc Hydroxide [$Zn(OH)_2$] and its availability decreases 100 times for each pH unit increased. The problem is mainly caused by the presence of high concentrations of alkaline earth carbonates; but the solubility can increase if the soil medium is acidified (Rivera Ortiz *et al.* 2003) [2].

On the other hand, beside the problem of alkalinity, the red arable *Luvisols* of Yucatan with better productive potential, than the stony *Leptosols*, are being used intensively for more than 30 years for corn production and rarely are being subsoiled to break up deep compact layers so there are constraints for low aeration, reduction of microbial activity and nutritional availability. The problem of soil compaction is a problem identified in the corn strip of Frailesca, Chiapas in Mexico (López Baez *et al.*, 2018) [3].

Therefore, the problem can be ameliorated if studies are to be carried out by implicating both acid applications and subsoiling to break out compact subsoil layers.

This work aimed to evaluate the effect of the application of sulfuric acid and sub-soiling on the Zinc contents of both soil and foliage of the CHICHEN ITZA Variety and the commercial HYBRID H-443A in a red arable *Rhodic Luvisol* in the state of Yucatan Mexico.

2. Materials

The work was carried out at the UXMAL-Experimental Station located in the south of the state of Yucatan Mexico in the Autumn-Winter 2022/2023 crop season using drip irrigation.

Two genetic materials established with 56 thousand plants ha^{-1} were used as phytometers: CHICHEN ITZA variety and the commercial HYBRID H-443A, both with yellow grain, subjected to the following eight treatments:

T1 = Without Acid + Sub-soiling + CHICHEN
T2 = Without Acid + No Sub-soiling + CHICHEN
T3 = With Acid + Sub-soiling + CHICHEN
T4 = With Acid + No Sub-soiling + CHICHEN
T5 = Without Acid + Sub-soiling + HIBRID
T6 = Without Acid + No Sub-soiling + HIBRID
T7 = With Acid + Sub-soiling + HIBRID
T8 = With Acid + No Sub-soiling + HIBRID

3. Methods

The sub-soiling was carried out with a vertical chisel plow at a depth of 40 cm. A base fertilization was applied with Di-ammonium Phosphate (18 N-46 P_2O_5-00 K_2O) buried 10 cm from the stem. Watering with drip irrigation was every day, adding sulfuric acid (H_2SO_4) at 98% concentration (agricultural quality) twice a week.

In six plants with complete competition, the foliar concentration of Zinc was measured in the leaf opposite to the ear. Composite soil samples were taken from the rhizophere of the same 6 plants.

The treatments were replicated by twice, and the results subjected to an Analysis of Variance (ANOVA) at 5% of probability (p) to detect statistical differences between treatments. In addition, the Determination Coefficients ($\mathbf{r}^2$) was calculated to evaluate the relationship between zinc in the soil and in the foliage.

Zinc deficiencies were graded by comparing the results with the Critical Limits (CL) given by the literature: As in the case of soil, the references taken from NOM-121 [4] with 1.0 ppm and Phytomonitor Laboratory (2022) [5] with 3.0 ppm were considered; taking 3.0 as the highest and strictest reference as the principal reference in this work. In the case of the foliage, the reference was the standards of Jones Jr. *et al.* (1973) [6] of 15 ppm as the minimum permissible.

4. Results

4.1. Zinc in Soils (Ppm) and Foliage (Ppm) of Corn

Table 1 shows the contents of Zinc in soil and foliage of both corn genotypes. Zinc in the soil is lower when no acid, but sub-soiling, is used for both CHICHEN ITZA (T1) and H-443 (T5) materials, adjusting exactly to 100% of the Critical Limit of 3.0 ppm while the other treatments exceed the LC with a range of 178% to 398%.

The zinc average contents in the soil were higher when acid was applied with 11.90 ppm (T3) and 8.5 ppm (T7) for CHICHEN and HYBRID respectively. This finding suggests that there is a favoring effect of sulfuric acid to release the zinc, in its cation available form (Zn^{2+}) trapped by alkaline earth carbonates. Rivera-Ortiz *et al.* (2003) [2] reported the effect of acids in the soil.

It was detected a detrimental effect of subsoiling in the contents of Zinc in the soil mainly when acid is not applied as it is seen in T1 (3.1) ppm vs. T2 (7.6 ppm) in CHICHEN and T5 (3.0 ppm) vs. T6 (5.3 ppm) in the HYBRID.

Table 1. Zn content (ppm) in soil, leaves (ppm) and Relative Sufficiency (%) in a calcareous *Rhodic Luvisol* with acid and sub-soiling treatments in Chichen Itza and Hybrid H-443A corn. O-I Cycle: 2022/2023.

Tratamientos	Zn in soil (ppm)	Soil Relative Sufficiency (%)	Zinc in foliage (ppm)	Foliage Relativ Sufficiency (%)
T1 = Without Acid + Sub-soiling + CHICHEN	3.0	100	16.5	110
T2 = Without Acid + No Sub-soiling + CHICHEN	5.3	178	18.5	123
T3 = With Acid + Sub-soiling + CHICHEN	11.9	398	14.5	97
T4 = With Acid + No Sub-soiling + CHICHEN	10.9	363	19.0	127
T5 = Without Acid + Sub-soiling + HIBRID	3.1	103	12.5	83
T6 = Without Acid + No Sub-soiling + HIBRID	7.6	255	13.5	90
T7 = With Acid + Sub-soiling + HIBRID	8.5	283	15.0	100
T8 = With Acid + No Sub-soiling + HIBRID	7.2	242	15.0	100
Reference	**3.0 ppm**			**15 ppm**

On the other hand, the highest average Zinc contents in soil were found in CHICHEN more than in the HYBRID; and the same trend was in the leaves. The HYBRID showed lower Zinc contents in leaves (Table 1) fluctuating from 12.5 ppm (T5) to 15 ppm (T7 and T8) corresponding to 83% and 100% of Relative Sufficiency.

The lowest values, in the foliage, were found when acid was not applied, regardless of the sub-soiling; being 12.5 ppm WITHOUT ACID + SUBSOILING (T5) and 13.5 ppm WITHOUT ACID + WITHOUT SUBSOILING (T6).

As in the case of CHICHEN the foliage values ranged from 14.5 (T3) to 19 ppm (T4) with 97% and 127% Relative Sufficiency respectively.

4.2. Statistical Analysis

Regardless of the differences in the absolute values of Zinc in soil and foliage levels, the Analysis of Variance (ANOVA) of the treatments for both variables (Table 2) shows that with a P-value of 0.0678 for soil and 0.052 for foliage, both higher than 0.05 there are NO statistically significant differences between treatments.

On the other hand, the relationship between Zinc-soil vs. Zinc-foliage treatments is shown in Table 3. The Determination Coefficients ($\mathbf{r}^2$) suggest that as in the case of CHICHEN there is no any relationship since the $\mathbf{r}^2 = 0.041$ whilst in the HYBRID the $\mathbf{r}^2$ was an acceptable higher 0.675. This means that the changes in Zinc-foliage can be explained in a 67% by changes in Zinc-soil.

5. Discussion

The main trend was that Zinc in the soil increased when sulfuric acid was applied. In the case of CHICHEN, the effect of acid on Zinc in the soil is shown when comparing: T1-3.0 ppm (Without Acid + Sub-soiling) vs. T3-11.9 ppm

Table 2. Analysis of Variance (ANOVA) for Zn content in soil (ppm) and leaves (ppm) in a calcareous *Rhodic Luvisol* from Yucatan Mexico with acid and sub-soiling in Chichen Itza and Hybrid H-443A corn. O-I Cycle: 2022/2023.

Treatments	Square Sum (SS)	Degree of Freedom (DF)	Mean Square (MS)	F	P
Zinc in Soil (ppm)	144.69	7	20.67	3.10	0.678 NDS
Zinc in Foliage (ppm)	73.43	7	10.49	3.43	0.052 NDS

Table 3. Determination coefficients (r^2) for average Zn content (ppm) in corn leaves (dependent variable Y) and Zinc content in the soil (ppm) (independent variable X).

Treatments	(Variable Y) Zinc in foliage (ppm)	(Variable X) Zinc in soil (ppm)	Determination Coefficient (r^2)
With Chichen	*16.5, 18.5, 14.5, 19.0*	3.0, 5.35, 11.95, 10.90	0.041
With Hybrid	*12.5, 13.5, 15.0, 15.0*	3.10, 7.65, 8.50, 7.25	0.675

(With Acid + Sub-soiling) maintaining Sub-soiling as a constant factor, and T2-5.3 ppm (Without Acid + No Sub-soiling) and T4-10.9 ppm (With Acid + No Sub-soiling) maintaining No Subsoiling as a constant.

In the HYBRID the effect of acid was more contrasting when Sub-soiling was a constant; T5 (Without Acid + Sub-soiling) with 3.1 ppm was lower than T7 (With Acid + Sub-soiling) with 8.5 ppm.

The acid had a good effect on the availability of Zinc and this can be explained by the next chemical reaction:

$$Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O$$

When Zinc is in an alkaline environment, or when Hydroxide Ions (OH^-) are more dominants than the Hydrogen Ions (H^+), the Hydroxides trap the Zinc to form a no available Zinc complex named Zinc Hydroxide [$Zn(OH)_2$] which can be released by the acid Hydrogen Ions (H^+). The concentration, in both the soil solution and plant, generally decline when the soil pH increased as pointed out by Bohn et al (1979) [7].

The negative effect of sub-soiling on Zinc availability could be related to a leaching effect since tillage could have broken the underground layers, improving the hydraulic conductivity and percolation of water to the underground. However, the main general trend is that the zinc lost through leaching is largely counteracted by the amount of zinc released by the acid.

On the other hand, the Determination Coefficients (**r^2**) suggested a poor relationship between Zinc-soil and Zinc-foliage in CHICHEN but a good correlation in the HYBRID; changes in the content of Zinc-foliage can be explained in a 67% by changes in Zinc-soil.

These differences may be due to the intrinsic genetic variability of the CHICHEN as compared to the HYBRID. The HYBRID has a uniform growth and plant habit than the variety CHICHEN. As it has been mentioned: "In irrigated crops, native plants have been adapted to the natural rates of trace metal recycling" [7] such as the case of the native best adapted CHICHEN. Deficiencies of micronutrients are related to the growth rates of each intrinsic plant genotype or variety and the ability to uptake the essential Zinc from the soil solution [7].

6. Conclusions

Corn is a staple food in the state of Yucatan Mexico but it is continually threatened by deficiencies of microelements such as Zinc (Zn). The problem is aggravated since the soils are alkaline, by nature, with high concentration of Hydoxides (OH^-). Beside the alkalinity problem, the red *Rhodic Luvisols* are facing problems of compaction since they have been plowed for more than 30 years.

Several studies have addressed the advantages of using both acids to release zinc trapped by carbonates and subsoiling to break up the underground to increase aeration and microbial activity. This work aimed to evaluate the effect of applying sulfuric acid and sub-soiling on the available zinc content of the soil and its relationship with zinc in the foliage in CHICHEN ITZA Variety and HYBRID H-443A in a red arable *Rhodic Luvisol* of the state of Yucatan Mexico and the main findings were that:

1) There were not any significant statistical differences between treatments.

2) Zinc, in the soil, is reduced by Sub-soiling in both cultivars.

3) The acid, by itself, increased the availability of Zinc.

4) The highest Zinc contents in the soil were found in CHICHEN.

5) The HYBRID showed the lowest Zinc contents in the leaves (12.5 to 15 ppm) corresponding to 83% and 100% of Relative Sufficiency with respect to the CL.

6) In CHICHEN the ranges of foliar Zinc were higher (14.5 to 19 ppm) with 97% and 127% of the Relative Sufficiency.

7) According to the Determination Coefficients (r^2) there was a poor relationship between Zinc-soil and Zinc-foliage in CHICHEN but a good correlation in the HYBRID. These contrasting findings may be due to the intrinsic genetic variability of each corn material.

For future research work, special attention should be paid to the effect of sub-soiling on the availability of Zinc and other essential nutrients since these results can contradict the conventional results of the advantage of sub-soiling on the availability of nutrients.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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