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**YIELD RESPONSE TO ZINC
AND THE
ASSESSMENT OF THREE EXTRACTING
SOLUTIONS FOR THEIR ESTIMATION
OF "AVAILABLE" ZINC IN
HAWAIIAN SOILS**

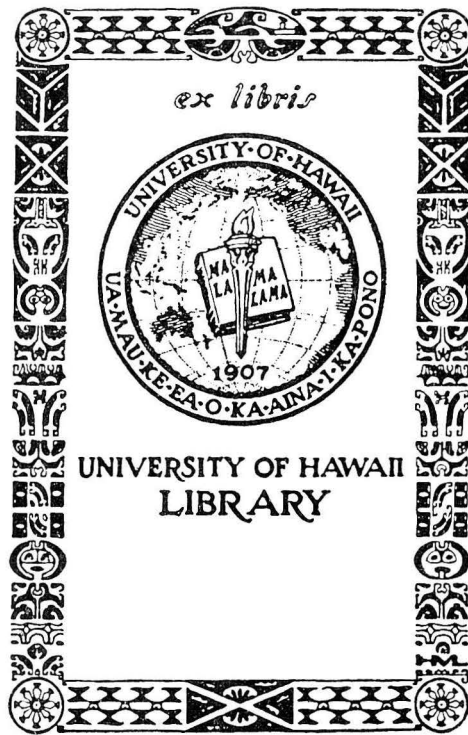
**A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF THE
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INTRODUCTION

The micronutrient status of zinc in soils and in plants has been recognized for many years. Its essential nature was recognized in 1914 and was established in 1926 (39). Zinc deficiency has since been observed in many areas of the world, especially in the United States (11) and in Australia (1). Extensive areas of zinc deficiency are found in the southeastern states, Texas, Washington, and California.

Zinc deficiency in soils affects many annual crops and fruit trees and will result in definite visual symptoms. Seatz and Jurinak (34) and Thorne (39) reviewed the symptoms as follow: mottling, dieback, rosetting, "little leaf", abnormal fruits in fruit trees, and chlorosis and stunting in field crops including "white bud" of field corn (Zea maise). Lyman and Dean (24) reported zinc deficiency in pineapples in Hawaii as shown by blistering and mottling of leaves and by curvatures of the "heart" leaves, also termed "crockneck" (1). Shoji and Ota (37) reported chlorosis and stunting of coffee trees in certain coffee areas of the island of Hawaii which were corrected by foliar applications of zinc.

Research on zinc deficiency in Hawaii is presently being conducted by the University of Hawaii Agricultural Experiment Station, the Pineapple Research Institute, and

the Hawaiian Sugar Planters' Association. This interest in zinc research in Hawaii shows that zinc deficiency is recognized as an important problem in Hawaii.

The need for a rapid chemical means of estimating "available" zinc in Hawaiian soils initiated this study to determine whether or not there is a correlation of zinc extractable by hydrochloric acid, ethylenediamine-tetraacetic acid, or acetic acid with the zinc uptake of plants. The results should determine whether any of the extracting solutions mentioned would reasonably estimate "available" zinc in soils. It should also show whether one of the extracting solutions could be used for further studies on available zinc in the different types of Hawaiian soil.

The information found through this study could lead to further research on zinc availability to plants in Hawaiian soils. It could also aid in further studies on improvement and ease of zinc determination.

REVIEW OF LITERATURE

Extractable and "Available" Zinc

Since zinc was established as essential for plant growth, there has been a need for a method of estimating the zinc in soils which is available to plants. Comparisons of extractable zinc with plant uptake of zinc or the

occurrence of zinc deficiency symptoms in the field have been used for this purpose. The extraction of zinc using neutral normal salt solutions has been found unsatisfactory. Brown and Krantz (5), Tucker and Kurts (40), and Jones et al. (16) obtained unsatisfactory results using normal ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$). This indicates that small amounts of zinc exist as exchangeable ions in soils. Hibbard (11) investigated the use of neutral normal salt solutions, dithionite, acid solutions, and 0.5M KCl-acetic acid solutions. He obtained a good relationship of a modified 0.5N KCl-acetic acid extraction with the occurrence of zinc deficiency symptoms in the field.

Wear and Sommer (42) and others (5, 14, 21) found 0.1N HCl-extractable zinc highly correlated with the occurrence of zinc deficiency symptoms. Viets et al. (41) and Leyden and Toth (21) found more acid-extractable zinc in untreated soils than in treated soils. They attributed this to the conversion of the applied zinc to an insoluble form. Motooka (27) found the acid-extractable zinc to increase with increased soil applications. Beawn et al. (4) found that the availability of zinc to beans and sorghum was greatest with those zinc compounds which were most soluble with 0.1N HCl regardless of their solubilities in water. Tucker and Kurts (40) recommended a 10:1 acid-soil ratio with a 45 minute shaking time sufficient for extraction of "available" zinc which correlated with the

estimate of the Aspergillus niger bio-assay method. Viets et al. (41) found more 0.1N HCl-extractable zinc in non-deficient soils than in deficient soils.

Butler and Bray (6) used 0.1N HNO₃ with unsatisfactory results due to the strong oxidizing action of the acid. They got an increase of zinc uptake using zinc-EDTA as a soil application.

Shaw and Dean (35) used a two phase dithionite-NH₄Ac procedure for extraction which appears to be the most satisfactory method so far. They have shown (36) that dithionite-extractable zinc is correlated with the zinc uptake by plants. Satisfactory correlation of zinc uptake by plants with dithionite-extractable zinc has been obtained by many other workers (9, 10, 40).

Tucker and Kurts (40) compared the removal of zinc from soil by A. niger with soil extractions by 0.1N HCl, acetic acid, EDTA, and dithionite. The various extractants removed about the same amounts of zinc. They considered the A. niger, dithionite, and 0.1N HCl procedures most convenient and rapid. The EDTA and acetic acid extractions correlated with the A. niger estimate but not as well as the dithionite or the 0.1N HCl.

It has been shown that both the dithionite and the 0.1N HCl gave good estimates of the zinc available to plants. The 0.1N HCl does extract more zinc than dithionite and is not realistic when working with calcareous soils (14). The

HCl method is, however, more rapid and simpler than the dithizone procedure.

For this study 0.1N HCl, EDTA, and 2.5% acetic acid were chosen as the extracting solutions. The selection was based on the simplicity and rapidity of the methods, on the ease of handling of the reagents involved, and on the more acidic nature of Hawaiian soils.

MATERIALS AND METHODS

Soils Used (19, 26)

1. Lualualei clay. This soil is a dark magnesium clay from Lualualei Valley, island of Oahu. It is found in low lying areas of poor drainage and receives bases from rock weathering of surrounding uplands, under a rainfall of 20 inches. It is high in 2:1 montmorillonite clays with the accumulations of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystals in the profile. It has a high base saturation and a high pH. Zinc deficiency has not been reported on this soil.

2. Henuaulu clay loam. This soil is a humic latosol from a zinc experiment check plot at the Kona branch station of the University of Hawaii Agricultural Experiment Station, island of Hawaii. It is formed on a thin layer of ash under an uneven rainfall of 65 inches a year and is very young and shallow. The clay fraction contains

kaolin, gibbsite, hematite, and goethite. It is one of the soils which has shown zinc deficiency.

3. Paaloa silty clay, subsoil. This soil is a humic latosol from Helemano, island of Oahu. It is formed from basalt weathered in place under 85 inches of rainfall a year. It has a low base saturation and an acid pH. It has a kaolin-illite clay fraction with goethite, hematite, and gibbsite as free iron and aluminum oxides. Zinc deficiency has been reported on this soil.

4. Wahiawa silty clay. This soil is a low humic latosol from the Poamoho Branch Station of the University of Hawaii Agricultural Experiment Station on the island of Oahu. It was formed from basaltic lavas under 40 inches of rainfall a year. It has a moderate base saturation and an acid pH. It has a kaolin clay fraction with hematite and allophane as dominant free oxides. No zinc deficiency has been reported.

Experimental Procedure

The soils were ground, sieved through a 10-mesh sieve and consolidated. Two pound samples of each soil were placed in one quart plastic freesette containers in four replicates for each of five zinc sulfate treatments.

Complete fertilizer (NPK) was applied initially and mixed thoroughly according to the recommendations of Clarence Lyman, the extension specialist in soil management at the University of Hawaii Extension Service.

The fertilizer rates were: 370 lbs./acre $(\text{NH}_4)_2\text{HPO}_4$ and 277 lbs. per acre KCl to all soils initially. This rate was doubled and applied in solution once a week thereafter. Two and a half tons lime was applied as calcium hydroxide $(\text{Ca}(\text{OH})_2)$ to all soils except the Lualualei soil. Magnesium sulfate (MgSO_4) was applied in solution to the Wahiawa and the Paaloa soils at the rate of 200 lbs. per acre.

Zinc was applied as $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ at the rates of 0, 25, 50, 100, and 200 lbs. per acre (based on the assumption that one acre of soil weighs 2.5 million pounds). The zinc sulfate was applied in solution to the Lualualei and Honuauulu soils and was applied as a powder to the Wahiawa and Paaloa soils. (Although there is a difference in the method of zinc fertilization, no difference in zinc uptake was anticipated because of the size of the pots and because of the prolific root development expected after 3.5 weeks of growth.)

Field corn (Zea mays variety Hawaiian Sweet) was selected as the test plant because it is reported as the most widely affected of all annual crops (28). The soil from each pot was hand crushed to break up the relatively large aggregates and was thoroughly mixed. The soils were then left to air dry for two days. The air-dried samples were then saved in polyethylene bags for analysis. Ten seeds were planted in each pot. This was thinned to three plants after one week to obtain uniform growth in each pot.

The corn plants were harvested 24 days after planting. This gave enough plant material for analysis and allowed enough time for the roots to emerge at the surface of the soil. Before harvesting, the plants were rinsed with distilled water and allowed to dry for one hour. After harvesting, the plants were weighed and placed in a forced draft oven at a temperature of 70° C. for 48 hours to dry. They were then weighed again and ground with a Wiley mill through a 20-mesh sieve. The ground plant samples were then placed in the oven at 70° C. until weighed for analysis.

Analytical Procedure and Methods

The dithizone colorimetric procedures as modified by Shaw and Dean (35), Holmes (12), and Wear and Semmer (42) have been the most widely used method for the measurement of micro amounts of zinc. Other methods include polarographic and spectrographic techniques.

Rush and Yoe (35) in 1954 introduced a colorimetric procedure using zincon (2-carboxy-2'-hydroxy-5'-sulfonyl benzene) as the reagent for determining zinc. Interfering elements such as Fe, Mg, Cd, and Ca are removed by the anion exchange resin (DowexI) as proposed by Kraus and Moore (20). Satisfactory results were obtained with this exchange resin-zincon method when applied to the analysis of zinc in plants by Jackson and Brown (14) and to soils by Pratt and Bradford (31) and Hunter and Coleman (15).

The advantages of the Rush and Yoe method over the older dithizone method were also pointed out by Jackson and Brown (14). They are: (1) the zincon method is more simple and rapid; it saves time and lessens the possibilities of contamination or loss of zinc during the analysis; (2) the use of carbon tetrachloride (CCl_4), a toxic compound with a cumulative effect, is not necessary in the zincon method, thus eliminating the hazards of a toxic compound when doing many sets of zinc analyses; and (3) the range of zinc in samples can be greater for the Rush and Yoe method, a range of up to 2.4 ppm for the zincon method as compared to a range up to 1.4 ppm for the dithizone method. Motooka (27) reported satisfactory recovery of added zinc using once-distilled water as compared with triple-distilled water with not more than four percent error.

Where accuracy and sensitivity are required, the zincon-resin method is not as sensitive as the dithizone method but the results obtained are satisfactory when the basic variability of soils and plants are considered.

The zincon-resin method of Rush and Yoe was selected for this study because of its rapidity, convenience, and safety. Modifications were made according to the procedures of Jackson and Brown (14), Pratt and Bradford (31), Motooka (27), Bertramson (3), and the Department of Plant Physiology, University of Hawaii.

The principle of the Rush and Yoe method is that the cations retained by the anion exchange resin is quantitatively removed with different strengths of hydrochloric acid. Zinc (Zn^{++}) is the last ion to be removed if the column is washed with decreasingly dilute portions of acid.

I. Separation of zinc from interfering ions

A. Reagents

1. Dowex I anion exchange resin, analytical grade, 1-X8 linkage, 50-100 mesh
2. HCl solutions: 2N, N, 0.005N
3. HCl solutions for purification of resin columns 12N, 6N

B. Apparatus

1. Two sets of funnels were used in this study, one set for plant samples and the other for soil extracts. This was in anticipation of greater quantities of interfering ions in the soil extract.

a. Pyrex glass funnels for soil extracts

Dimensions: stem length, 150 mm
diameter at top, 100 mm
inside diameter of stem, 5 mm

b. Kimble "58" glass funnels for plant samples

Dimensions: stem length, 150 mm

inside diameter at top, 65 mm

inside diameter of stem, 5 mm

c. Glass wool - Pyrex brand

C. Preparation of the resin column

A wad of Pyrex glass wool is placed inside the bottom of the funnel stem. Water is added to the funnel and a slurry of resin suspended in water is added before all the water has passed through. Enough resin is added to fill the stem to approximately 140 mm for the larger funnel and to approximately 50 mm for the smaller funnel. Agitation with a thin diameter glass rod will remove all air bubbles that may form. Air bubbles will stop the passage of any solution or water through the column.

By loosening or tightening the wad of glass wool, the flow through the column can be adjusted to a rate of approximately 15 ml. per hour for both columns. Too rapid passage may result in incomplete separation of ions.

To purify the resin column, 10 ml. each of 12N, 6N, and 2N HCl and 50 ml. of zinc-free water are passed through the column successively in that order.

A short length of Tygon plastic tubing is attached to the end of the funnel stem so that

the flow of solution can be closed off with a pinchcock when the column is not in use. The resin is kept wet at all times to prevent air bubbles from forming in the column.

D. Procedure for separation of interfering ions

To separate zinc from interfering ions the unknown solution is made 2N with HCl and passed through the resin column which has been prewashed with 50 ml. of 0.005N HCl and 10 ml. of 2N HCl. After the unknown solution has completely passed through the column, 50 ml. of N HCl is passed through to wash out the interfering ions that remain. Then 10 ml. of N KOI is passed through to wash out the excess acid. All washings are discarded. Then a 50 ml. volumetric flask is placed under the column and 40 ml. of 0.005N HCl is passed through in two portions of 20 ml. to extract the zinc. The eluate is then ready for analysis by the zincon method.

Although the separation procedure is slow, many determinations can be made at the same time by setting up as many columns as desired.

II. The zincon method of zinc analysis

A. Reagents

1. Zincon
2. Buffer solution

a. Boric acid (H_3BO_3), 15N ammonium hydroxide (NH_4OH)

b. 2N sodium hydroxide (NaOH)

B. Preparation of the buffer solution

Twenty grams of H_3BO_3 and 50 ml. of 15N NH_4OH are mixed in a 1000 ml. volumetric flask with 800 ml. water. The pH is adjusted to 9.5 and the solution brought up to volume.

C. Preparation of zincon solution

Dissolve 0.30 gram zincon in 2 ml. N sodium hydroxide and dilute to 250 ml. with water. This solution is good for about four days.

D. Procedure for zinc analysis

After the zinc has been separated from interfering ions, extracted from the resin column, and collected in a 50 ml. volumetric flask, 5 ml. buffer solution and 3 ml. zincon solution are added to the flask and the whole solution is made to volume with water. After standing for 25 minutes, the optical density of the solution is determined colorimetrically on the Klett-Summerson colorimeter using filter number 62 (620 m-microns wave length). The reading is then compared with a standard curve made with concentrations of 0.01, 0.02, 0.05, 0.07, 0.1 mg. of zinc per 50 ml. of solution to determine

the zinc content of the unknown solution.

III. Preparation of plant material for zinc analysis

A 0.70 to 1 g. sample of dried, 20-mesh plant material is weighed into a 30 ml. porcelain crucible and is dry-ashed overnight in a muffle furnace at 450 to 550 degrees C. After the ashed sample has cooled, it is taken up with 2N HCl (3), heated, then filtered hot through S and S 589 white ribbon filter paper. The residue is washed three or four times with 2N HCl to a volume of approximately 50 to 100 ml. of filtrate. The filtrate is then analysed for zinc by the Rush and Yoe method.

IV. Preparation of the soil extracts for zinc analysis

A. Procedure for 0.1N HCl-extractable zinc

Fifteen grams of air-dried soil is placed in a 500 ml. Erlenmeyer flask and 10 ml. of 0.1N HCl is added for each gram of soil (a 1:10 soil to solution ratio). The flask is stoppered and shaken for 45 minutes on a reciprocal action mechanical shaker. The supernatant liquid is then filtered through Number 12 Whatman folded-filter paper. An appropriate aliquot of the filtrate is taken and evaporated to dryness. The residue is then digested with 10 ml. aqua regia (three volumes 12N HCl to one volume 16N HNO₃) to destroy organic matter. After digestion

overnight the solution is evaporated to dryness and the residue is taken up in 2N HCl. The 2N solution is then filtered hot through S and S 589 white ribbon filter paper to remove insoluble substances. The filtrate is then analyzed for zinc by the zincon-resin method.

B. Procedure for EDTA-extractable zinc

The procedure is the same as for the 0.1N HCl except that 10 g. of air-dried soil is placed in a 500 ml. Erlenmeyer flask and 0.1 g. disodium EDTA with 50 ml. neutral normal NH_4Ac is added for each 5 g. of soil (a 1:10 soil to solution ratio).

C. Procedure for 2.5% H_2O_2 -extractable zinc

This procedure is the same as for 0.1N HCl except that 2.5 g. of air-dried soil was taken and 40 ml. of 2.5% H_2O_2 was added for each gram of soil (a 1:40 soil to solution ratio).

V. Procedure for pH readings

The pH was determined on a 1:1 soil to water paste using a Beckman Model G pH meter.

RESULTS AND DISCUSSION

The complete results of this study are summarized in the appendix. Statistical analysis was applied to the

data by the methods of Snedecor (38).

Response and Total Plant Yield

There was a good visual response to added zinc. Figure 1 illustrates the differences in growth and color of field corn with different levels of zinc when grown in the Lualualei soil. These same differences were also noted on plants grown in the Paaloa subsoil. The plants without any application of zinc showed poor color, interveinal chlorosis, and stunting. Response to added zinc was apparent on the plants with 25, 50, 100, and 200 lbs. $ZnSO_4 \cdot H_2O$ per acre. The optimum growth response was with the 50 lbs. per acre zinc application. The plants with the 100 and 200 lb. levels of added zinc exhibited a slight degree of chlorosis probably due to excessive zinc (10).

Figure 2 illustrates the response to zinc of the corn plants grown in the Honuaulu soil. This same response was also exhibited by the plants grown in the Wahiawa soil. The visual symptoms and the response to added zinc were not as noticeable on plants grown in the Honuaulu soil as those grown in the Lualualei soil. This was apparently due to an adequate level of original zinc in the former soil. A decrease in growth at the 200 lb. rate of applications of zinc is also illustrated in Figure 2 as a result of excessive zinc.

Figure 3 illustrates still further the differences

between the control Lualualei soil (number 21) with low original soil zinc and the control Honuaulu soil (number 43) with high original soil zinc. There is a contrast in size and vigor between these pots.

Figure 4 shows the response of both soils to 25 lbs. $ZnSO_4 \cdot H_2O$ per acre. There are no apparent differences in growth, color, or vigor between the plants in the two pots.

Plant yields differed significantly with added zinc in three of the four soils (Table I). Yields on the Wahiawa soil, however, did have an increased trend but

TABLE I
THE EFFECT OF SOIL AND ADDED ZINC
ON TOTAL PLANT YIELD OF FIELD CORN (Z. MAIZE)

Soil	$ZnSO_4 \cdot H_2O$ <u>lbs/A</u>	Dry Weight <u>Yield</u> g
Lualualei	0	4.04
	50	5.36
	100	5.62
Honuaulu	0	4.65
	50	5.46
	100	5.65
Paaloa	0	1.62
	50	2.79
	100	2.56
Wahiawa	0	3.48
	50	3.69
	100	3.58
LSD (5%)		0.56

(Each weight is the average of four observations.)



FIGURE 1
RESPONSE OF CORN TO ZINC APPLICATIONS
ON THE LUALUALEI SOIL



FIGURE 2
RESPONSE OF CORN TO ZINC APPLICATIONS
ON THE HONUAAULU SOIL

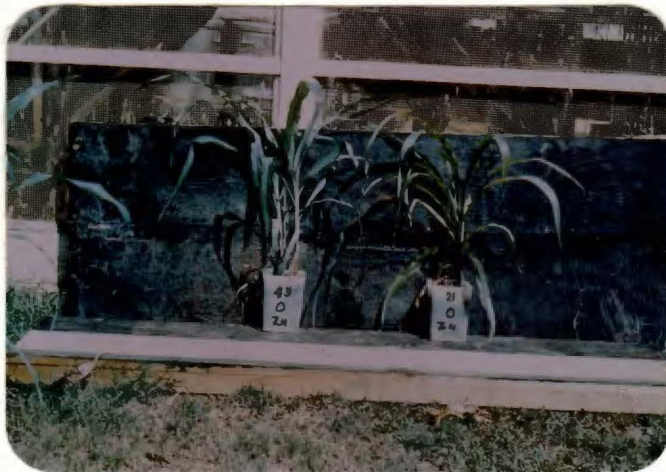


FIGURE 3

COMPARISON OF THE CONTROL PLANTS ON THE
LUALUALEI (21) AND HONUAAULU (43) SOILS



FIGURE 4

COMPARISON OF PLANT RESPONSE TO 25 lbs. ZINC
ON THE LUALUALEI (26) AND HONUAAULU (48) SOILS

non-significantly. This soil probably had sufficient zinc in its original condition. About 50 lbs. $ZnSO_4 \cdot H_2O$ per acre appeared to be adequate. Yield increase, therefore, is dependent on the amount of zinc applied and the soil in which the crop is grown.

The total plant yield was found to be correlated with 0.1N HCl-extractable zinc ($r=0.63^*$) and with plant zinc ($r=0.57^*$) in the Lualualei soil. No significant correlations of plant yield with any other factor was found other than those on the Lualualei soil.

Plant Uptake of Zinc

The uptake of zinc by field corn increased significantly with added zinc depending on the soil in which the crop was grown. The increase in the plant content of zinc was significant for all soils used in this study (Table II). Increased uptake of zinc by plants on acid soils was reported by Epstein and Stout (9) and others (2, 4, 22). According to Viets et al. (41), 15 ppm of zinc in corn leaves was adequate for the production of 100 to 125 bushels of corn. The lowest concentration found in this study was 28.1 ppm in plants grown on the Paalca soil. This means that all four soils used in this study were adequately supplied with zinc for good corn production. However, as stated earlier, the plants grown in these soils responded to applications of zinc. The linear increase

in zinc uptake by plants was found to be highly dependent on both the soil used and the added zinc.

The total plant zinc was found to be highly correlated with 0.1N HCl-extractable zinc (Lualualei, $r=0.80^{**}$; Paaloa, $r=0.83^{**}$; and Wahiawa, $r=0.88$). Total plant zinc was also significantly correlated with EDTA-extractable zinc for the Paaloa soil ($r=0.73^{**}$). These differences in linear correlation may be a reflection of the inherent differences in physical and chemical properties of these soils (26).

TABLE II
EFFECT OF SOIL AND ADDED ZINC
ON PLANT UPTAKE OF ZINC

Soil	$ZnSO_4 \cdot H_2O$ <hr/> lbs/A	Zn in Plant <hr/> ppm
Lualualei	0	33.4
	50	46.8
	100	66.4
Honuaulu	0	54.6
	50	65.9
	100	77.5
Paaloa	0	35.9
	50	68.8
	100	84.8
Wahiawa	0	39.2
	50	51.3
	100	66.7
LSD (5%)		8.7

(Each number is the average of four observations.)

Comparisons of different extractants

The quantities of zinc extracted by the three procedures are shown on Table III. The results give a clear indication of the relative amounts of zinc each extractant released from each of the four soils.

The 0.1N HCl extracted the least zinc from the calcareous Lualualei soil, while it extracted the most zinc from the strongly acid Honuaulu soil. This coincides with the reports of Motooka (27), and others (10, 28, 30) who found that calcareous soils and high pH decreased the amounts of extractable zinc in soils. The amounts of 0.1N

TABLE III

EFFECT OF SOIL AND ADDED ZINC ON ZINC
EXTRACTABLE WITH HCl, EDTA, AND HAc

Soil	ZnSO ₄ ·H ₂ O	HCl	EDTA	HAc
	<u>lbs/A</u>	<u>extractable Zinc ppm</u>	<u>extractable Zinc ppm</u>	<u>extractable Zinc ppm</u>
Lualualei	0	10.8	33.8	22.4
	50	13.2	58.0	14.8
	100	15.6	45.6	21.2
Honuaulu	0	32.2	70.2	34.5
	50	34.9	83.5	35.5
	100	44.4	54.5	72.2
Paaloa	0	11.9	11.9	22.6
	50	20.6	39.9	27.2
	100	30.4	51.8	37.0
Wahiawa	0	9.6	46.6	11.6
	50	15.7	39.8	18.0
	100	24.6	67.9	21.1
LSD (5%)		4.2	31.7	11.8

(Each number is the average of four observations.)

HCl-extractable zinc found in this study were all higher than those found by Notooka (27) for the same soils. This may have been caused by an increased soil to solution ratio due to high soil moisture contents of up to 50%. This would give a larger amount of extraction solution per unit of soil, thereby increasing the chances of extracting more zinc from a given unit of soil.

The disodium salt of EDTA extracted larger amounts of zinc than either of the other two extractants. Viro (42) stated that EDTA extracts adsorbed ions more effectively than ammonium acetate. Metals such as copper, zinc, and iron can be almost completely chelated by EDTA. Viro (43) also reported that EDTA extracts more zinc at pH 9 than at pH 7, the amount being a function of pH of the extractant. The high measurements could also have been caused by incomplete washing of the interfering ions from the column.

The 2.5% H_2O_2 extractions showed a progressive increase of extractable zinc with increased rates of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ applications. Soils with the exception of the Lualualei soil showed a decrease with the 50 lb. rate. The Lualualei soil has a high buffering effect which may explain why there was no significant difference in HAc-extractable zinc. Again, the nature of the soil explains to some extent the variations in the extracting capabilities of the extractant. The linear increases in extractable zinc for the other soils were found to be non-significant but the

overall treatment was found highly significant.

SUMMARY AND CONCLUSIONS

This study was conducted to compare three methods of zinc extraction with plant uptake of zinc and to determine whether any of the extractants may be useful in assessing "available" zinc in Hawaiian soils. A study was also conducted to determine the plant response to zinc applications.

A pot experiment was set up using four Hawaiian soils: the Lualualei clay, the Honolulu clay loam, the Paaloa silty clay, and the Wahiawa silty clay. Zinc was added at the rates of 0, 25, 50, 100, and 200 lbs. $ZnSO_4 \cdot H_2O$ per acre in four replicates. The soils were fertilized and limed according to their known acidity and fertility status. Corn was planted as the indicator plant for this study. The green yields and the dry yields were recorded after harvesting. The plants were then analyzed for total zinc and the soils were analyzed for extractable zinc, using 0.1N HCl, EDTA, and 2.5% $H_2C_2O_4$ as extractants.

The findings from this study may be summarized as follows:

1. There was a significant yield response to added zinc in three of the four soils tested.
2. There was a significant linear increase in plant

uptake of zinc from the applications of $ZnSO_4 \cdot H_2O$.

3. There was a highly significant correlation between plant uptake of zinc and HCl-extractable zinc in three of the four soils tested.

4. The EDTA-extractable zinc depended almost entirely on the soil.

5. There was no significant correlation between the plant uptake of zinc and the H_2O_2 -extractable zinc.

6. The extractants in general, extracted more or less zinc depending on the nature of the soil.

The results of this study indicate a need for further research into the forms of zinc in soils as related to chemical, physical, and environmental factors. There also is an indication that the EDTA extracting could be refined as to the soil to solution ratio, shaking time, and moisture content of the soil sample.

The moisture content of the air-dried soil may have influenced the amounts of zinc extracted with either 0.1N HCl or EDTA. The dilution with soil moisture causes great variations in the amounts of zinc extracted.

The addition of zinc as a sulfate nullified to some extent the effect of the lime and decreased the pH.

The visual response to added zinc with respect to the plant uptake of zinc indicates that the corn plant can tolerate different levels of zinc depending on the type of soil. This also implies that soil zinc has different

degrees of "availability" in each type of soil.

It is concluded that none of the extractants used is fully satisfactory for all Hawaiian soils when the "available" zinc is estimated by correlation of plant uptake with extractable soil zinc. However, the 0.1N HCl-extractable zinc can be used to assess the available zinc in most Hawaiian soils because of its high correlation with plant uptake for three of the four soils used. The correlation for the only soil exception, the Honuauulu clay loam, was close to being significant.

It is further concluded that the EDTA procedure of extraction warrants further study because of the high metallic ion content of Hawaiian soils and the strong chelating action of the compound.

APPENDIX

DATA FROM THE ZINC STUDIES ON THE PAALOA (Paa.) AND WAHIWA (Wah.) SOILS

Soil	Rep.	Treatment lbs/A ZnSO ₄	pH Soil after harvest	Yield dry wt. grams	Zinc in plants ppm	Ext. Zinc 0.1N HCl ppm	Ext. Zinc EDTA ppm	Ext. Zinc 2.5% HAc ppm
Paa.	1	0	5.35	1.33	35.7	13.2	10.9	19.5
	2	0	5.35	1.08	28.1	16.4	9.6	23.1
	3	0	5.35	1.57	38.5	10.6	13.9	27.9
	4	0	5.20	2.54	41.4	7.6	13.1	20.0
Paa.	1	50	5.25	2.72	65.4	22.6	22.2	33.7
	2	50	5.25	2.03	65.6	22.9	84.5	30.5
	3	50	5.10	3.41	71.2	20.0	23.9	22.7
	4	50	5.15	3.02	72.9	17.1	28.9	22.1
Paa.	1	100	5.30	2.14	97.8	35.9	76.3	34.4
	2	100	5.25	2.20	69.9	23.0	32.9	41.9
	3	100	5.25	2.44	98.6	29.4	54.4	38.4
	4	100	5.25	3.46	72.9	33.2	43.4	33.3
Wah.	1	0	5.85	3.84	44.2	13.7	53.5	11.2
	2	0	5.90	3.59	37.1	9.9	33.7	12.1
	3	0	6.00	3.48	37.0	7.5	36.9	11.4
	4	0	5.95	3.03	38.5	7.4	62.5	11.8
Wah.	1	50	6.00	3.73	42.7	15.4	30.1	17.3
	2	50	5.90	4.11	61.2	11.8	33.3	20.0
	3	50	6.05	3.30	48.5	12.4	59.0	16.3
	4	50	6.00	3.61	52.8	15.1	36.6	18.5
Wah.	1	100	6.00	3.56	71.4	27.7	26.9	19.3
	2	100	6.05	3.03	62.9	21.2	31.0	17.1
	3	100	5.95	3.41	65.5	22.5	136.4	22.7
	4	100	5.95	4.34	67.1	27.1	77.3	25.4

DATA FROM THE ZINC STUDIES ON THE LUALUALEI (Lua.) AND HONUAULU (Hon.) SOILS

Soil	Rep.	Treatment lbs/A ZnSO ₄	pH Soil after harvest	Yield dry wt. grams	Zinc in plants ppm	Ext. Zinc 0.1N HCl ppm	Ext. Zinc EDTA ppm	Ext. Zinc 2.5% HAc ppm
Lua.	1	0	6.80	4.06	31.4	10.8	44.4	34.6
	2	0	6.80	4.06	34.0	13.9	36.4	25.4
	3	0	6.70	3.58	37.1	8.1	35.2	14.5
	4	0	6.90	4.45	31.2	10.5	19.0	15.2
Lua.	1	50	6.80	5.21	43.4	13.9	106.8	12.7
	2	50	6.80	5.66	5.25	14.1	52.3	16.4
	3	50	6.95	5.27	54.2	12.9	45.4	17.1
	4	50	6.75	5.32	37.0	12.1	27.7	13.5
Lua.	1	100	6.80	5.91	68.1	15.0	32.9	25.4
	2	100	6.95	4.69	73.6	16.8	35.2	24.5
	3	100	6.85	6.17	48.4	14.0	70.1	13.8
	4	100	6.85	5.70	75.7	16.4	44.3	20.9
Hon.	1	0	3.90	5.45	38.6	41.6	50.9	36.9
	2	0	4.65	4.91	52.9	34.8	93.9	34.4
	3	0	4.55	5.00	58.3	28.2	89.1	40.6
	4	0	4.60	3.25	68.4	24.3	47.3	26.1
Hon.	1	50	4.65	4.52	75.6	4.80	6.54	43.1
	2	50	4.55	5.96	65.6	29.7	193.2	43.2
	3	50	4.65	5.67	65.5	34.3	41.2	27.0
	4	50	4.45	5.70	57.1	27.7	34.4	28.8
Hon.	1	100	4.45	5.49	92.0	36.4	49.2	54.8
	2	100	4.60	5.54	69.8	45.1	45.2	43.9
	3	100	4.55	5.24	84.2	49.3	76.9	126.0
	4	100	4.60	6.32	74.0	46.7	46.7	64.0

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