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Extraction Methods for Estimating Available Manganese to Maize (*Zea mays* L.) in Acid Soils

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Twenty surface soil samples were used to evaluate status of soil Mn using five extraction procedures (Coca-cola, EDTA, HCl, EDTA + NH_4OA_C and NH_4OA_C methods). The results show that Coca-cola method extracted the highest amount of the Mn while NH_4OA_C extracted the least amount of Mn. The results also showed that among the five extractants examined, the highest regression coefficients were found between Coca-Cola and HCl, HCl and EDTA+NH_4OAc and, EDTA and EDTA+NH_4OAc-extractable Mn for Mn uptake, respectively. Accordingly, the study indicates that, the comparative extraction capacity of these extractants followed the order: Coca-cola> HCl> EDTA> EDTA+NH_4OAc> NH_4OA_C.

Keywords: Acid soil; critical limits; extractants; grain yield; maize; Mn sulphate, Mn uptake; optimum levels.

1. INTRODUCTION

Maize (*Zea mays L.*) is one of the world's leading cereal grains next to rice and wheat [1,2]. It is very common due to its diverse functionality as a major food source for both man and livestock [3] and it contribute greatly to the economic growth of many developing countries [4]. It is estimated

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that maize together with rice and wheat provide at least 30% of the food calories to more than 4.5 billion people of developing countries [5]. Nigeria has great potential for the expansion of maize production beyond the present level due to its bimodal rainfall pattern, high solar radiation and favourable temperature during the growing season.

In Nigeria maize crop is widely cultivated by farmers in the tropical rainforest of southeastern Nigeria [6,7]. The soils in this region are highly weathered, predominantly lateritic and mostly acidic in reaction, which often have low exchangeable bases due to intensive nutrient depletion [8]. The soils are also low in organic matter content, with low activity characteristics of the clay fraction but, high sandy in nature and leaching due to high rainfalls regimes resulting in deficiency of major and minor nutrient elements specifically micronutrients [9]. Thus, the availability of these nutrient elements to maize crop is conditioned by the soils characteristic under review.

Among various micronutrients, manganese is especially importance owing to its typical and complex behavior in soils besides its vital and indispensable role in plant growth. Manganese (Mn) is a micronutrient which exists in soils as insoluble oxides of trivalent and tetravalent Mn, exchangeable and water soluble divalent Mn [10,11]. Uptake of Mn by plant roots is in divalent ion Mn^{2+} which is needed in small amount and uptake usually is less than 1.0 kg Mn ha^{-1} in cereals [12]. It is an established fact that only a small fraction of total manganese in soil is made available to plants in during the growing season. Application of Manganese fertilizer increases the crop yield and quality, due to improved plant nutrition and increasing photosynthesis in plants [13].

According to [14], total content of manganese in surface in tropical soils ranged from 37-115 mg kg^{-1}. However, 0.1 HCl extractable manganese of 8-29 mg kg^{-1} was reported by [15] in some soils of Samaru, Zaria, Nigeria. [16] reported that available Mn in soil ranged from 1.2 to 30.3 mg kg^{-1} with mean values of 9.8 mg kg^{-1}. [17] observed that the available Mn in upper soil layer ranged from 5.4 to 15.4 mg kg^{-1} which was higher than the critical limits.

A proper soil test is the only proven diagnostic tool that estimates plant nutrient availability in soil [18]. It is underutilized in most developing countries because of lack of rapid and reliable soil testing procedures and related facilities [19]. Soil tests measure the quantity of nutrient element that is extracted from a soil by a particular chemical extracting solution. The measured quantity of extractable nutrient in a soil is then used to predict the crop yield response to application of the nutrient as a fertilizer, manure or other amendments [18].

In this study, the function of acid extractants (0.1M HCl and Coca-Cola) is founded on lowering the pH and the outcome solubilization of some compounds containing these elements [20]. On the other hand, chelating extractant (0.005M EDTA) and neutral salt (1M NH_4OAc) has the capability of reducing the activity of dissolved metals, resulting in the release of more soluble compounds in buffered pH [21]. The use of chelating agent such as EDTA, salt and chelate mix (NH_4OAc+ EDTA) and acid such as HCl and Coca-Cola as extraction methods, have longed been reported for soils elsewhere, to estimate the potential availability and mobility of metals [18,22,23,24], respectively.

Numerous attempts have been made in the past to develop a simple and meaningful soil test method which can predict manganese in soils. Such a soil-Mn-test can prove to be of great help as a diagnostic technique for demarcating accurately the areas of manganese deficiency. Since the suitability of a soil test is more likely to vary depending upon the extractants, soil properties and plant species, the evaluation of soil-test methods of manganese with soils of wide variability in respect of their characteristics, thus, assumes great importance. However, the information on a suitable soil-test method regarding the use of five extractants such as, Coca-Cola 0.05 M EDTA, 0.1M HCl 1M NH_4OAc, NH_4OAc+ EDTA for proper prediction of available Mn for maize production is not available in respect of acid soils of southeastern, Nigeria hence, this evaluation is to develop a best suited method by comparing a number of soil test for available manganese.

Keeping in view the facts enumerated above, the present study was carried out with the following main objectives: (i) to assess the status of different forms of Mn in soils; (ii) to develop a soil test method for estimating available Mn in soils; (iii) to determine the critical limits of Mn in soil for maize plant; and (iv) to estimate the response of maize to manganese application and recommended Mn rate for maize production in acid soils of southeastern, Nigeria.

2. MATERIALS AND METHODS

2.1 Description of Sample Location and Collection

Soil samples were collected from maize farmlands with no history of micronutrient fertilizer application for the past 12 years for laboratory and greenhouse experiments. The sampling sites which have a high potential for dual season's maize production and suitable for production of vegetable crops, upland/swamp rice, okra, yam, citrus, oil palms, plantain/banana, pineapple genotypes (GV. III), and some new cassava varieties, were selected to cover a wide range of soil types of different properties representing, contrasting soil of southeastern, Nigeria (Table 1). The sample location lies between Latitude 4°20' and 7°25 North of the Equator and Longitude 5°25' and 8°51' East of the Greenwich meridian [25,26]. The mean minimum and maximum temperatures ranged from 21-30°C in the Coast and from 29-33°C in the interior. The rainfall pattern is bimodal and decreases from over 3000 mm in the south to 1,700 mm in the north, this has given rise to double cropping (early and late) seasons. The vegetation stretches from mangrove swamp in the coastal region through rainforest to derived savanna in the interior.

2.2 Laboratory Study

To achieve the set objectives, a laboratory procedure was conducted on these soils to determine some physico-chemical properties and status of available forms of manganese by the different extractants. Before the laboratory analyses, the soil samples collected were air-dried and screened through a 2 mm sieve for particle size and chemical analyses. 150 g of each sample was crushed with Agate mortar and pestle and, later sieved to 0.5 mm sieve for the determination of organic carbon, total nitrogen and total manganese. The 2 mm sieved soils were used to analyse for particle size analysis by the Bouyocous hydrometer method using sodium hexametaphosphate as dispersing agent [27]; Soil pH in 1:2.5 soil-0.1 calcium chloride

Table 1. Location of sample collection, soil classification and land use system

Sample no.	Sampling site	Classification*	Land use system
1	Abriba	Psamment Paleudults	Grasses (Andropogon)
2	Afikpo	Typic Ustiflurents	Yam/Sugar cane farm
3	Akamkpa	Typic Paleudults	Gmelina Plantation
4	Akpabuyo	Psammentic Paleudults	Pineapple
5	Akpet	Typic Hapludlts	Cassava/Maize farm
6	Bende	Aquic Hapludlts	Cocoa plantation
7	Betem	Typic Paleudults	Virgin forest
8	Etiti	Udic Psamment	Maize/cassava
9	Igbariam	Udic Haplustalfs	Cassava farm
10	Ikot Ekpene	Typic Paleudults	Telfairia/Water leaves
11	Nsukka	Typic Psammaquent	Cashew plantation
12	Oban	Typic Hapludlts	Plantain/Banana farm
13	Odukpani	Aquic Haplustalfs	Cassava/maize farm
14	Ofodua	Typic Ustpsamments	Eggplant/Telfairia
15	Okigwe	Aquic Ustiflurents	Upland/Swamp rice
16	Owerri	Udic Haplustalfs	Oil palm (E. Guineesis)
17	Umudike	Typic Paleudults	Cassava (Manihot)
18	Uturu	Psammentic Paleudults	Fallow (bush)
19	Uyanga	Typic Paleudults	Cassava/Yam farm
20	Uyo	Psammentic Paleudults	Maize (Zea mays L.)

**[28,29]*

suspensions was determined using a digital glass electrode pH meter [30]; Soil organic carbon was determined by Walkley-Black method of wet combustion involving oxidation of organic matter with potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4) method as described by [31] and the content of the organic carbon (OC) was converted to organic matter by multiplying the OC values by Van Bremelen factor of 1.724 based on the assumption that SOM contains 58% carbon. Available P was determined by Bray I method [32], total N was determined by Kjeldahl procedure of [33], Exchangeable bases (Ca^{+2}, Mg^{+2}, K^+ and Na^+) were extracted with 1N neutral ammonium acetate (NH_4OAc) solution and amounts of K and Na in solution was measured using a Flame Photometer while Ca and Mg were determined by EDTA titration method.

Exchangeable cations in the samples were extracted with neutral ammonium acetate and contents of K and Na was determined with a flame photometer, while Ca and Mg were determined by EDTA titration method. Total exchangeable acidity (TEA) was determined by method of [34]. The effective cations exchange capacity (ECEC) was calculated as the summation of exchangeable bases and exchangeable acidity as described by [35] while, base saturation was by calculation (dividing the sum of exchangeable bases by the ECEC then multiplied by 100).

The total Mn contents in the soil samples were determined after tri-acid digestion of samples in Teflon crucible heated on a hot plate according to [36]. To compare the use of the different extractants (Coca-Cola, EDTA, NH_4OAC +EDTA, 1N NH_4OAC and 0.01N HCl) for assessment of available manganese of the soils were carried out. Soil samples were shaken with respective extractants of various properties (Table 2). After shaking, the soil-solution was centrifuged and filtered through Whatman filter paper No. 42. The quantity of manganese in each soil was determined with an atomic absorption spectrophotometer (AAS) (UNICAM model SOLAAR 32: Mn ASTM D1068).

2.3 Greenhouse Study

The greenhouse experiment was conducted at the National Root Crop Research Institute (NRCRI), Umudike, Nigeria (Latitude 05°29'N and Longitude 07°33'E, and at an elevation of 122 m above sea level), to evaluate the influence of manganese application on Mn uptake in maize plants.

One kilogramme of the air-dried soils was weighed into plastic containers of 2 liter capacity, placed on flat plastic receiver. A total of 400 plastic containers (20 soil samples x 5 levels of Mn x 4 replications) were arranged in a complete randomized design (CRD). The containers were watered using distilled-deionized water as required during the growth period. Before planting, the soils were watered to field capacity (adjusted to 70 %) with distilled water and allowed to stand for about 48 hours in the greenhouse.

Five levels of Mn (0, 4, 8, 12 and 16 kg ha^{-1}) converted to mg kg^{-1} were applied as $MnSO_4.5H_2O$ in solution. Based on previous studies in the region by [12], a dosage of 120 kg N ha^{-1} (mg N kg^{-1} soil) as Urea, 60 kg P_2O_5 ha^{-1} (mg P kg^{-1} soil) as single super phosphate (SSP) and 60 kg K_2O ha^{-1} (mg K kg^{-1}) as muriate of potash (MOP) were applied as basal (NPK) fertilizer uniformly to all the containers in solution form at two weeks after planting (WAP).

Maize variety Oba Supper II yellow was used as a test crop during the dry season. Six maize seeds were sown in each pot and the stand was thinned to four plants, two weeks after germination. The crops were irrigated with tap water as and when required throughout the growing period. The reason for the small quantity of soil and the number of maize seedlings planted per pot was for the soils to be depleted of the nutrients so that, the levels of manganese applied would be used to establish a response curve.

2.4 Plant Sample Collection and Analysis

Plant shoots were harvested at 42 days (6 WAP) by uprooting the entire maize plant (shoots and roots) from the soil, washed in an acidified detergent solution and rinsed with deionized water, pre-dried under shade to remove excess water and later packed in large brown envelopes. Plant materials were oven- dried at 70℃ for 48 hrs to constant weight and the dry matter yield (DMY) were recorded. The dried plant tissues were then cut into small pieces, grind to pass through a 0.5 mm sieve and digested in Teflon crucible, heated on a hot plate using a tri-acid

Table 2. Chemical properties and procedures of extraction used in the study

S/No	Extractant	Groups	pH	Soil-solution ratio	Shaking time (min)	Reference
1	Coca-cola	Acid	2.7	1:10	10	[22]
2	0.01N HCl	Acid	4.8	1:10	60	[37]
3	0.05M EDTA	Chelate	7.0	1:2	30	[21]
4	1N NH_4OAc	Salt	7.0	1:10	60	[38]
5	0.05M EDTA+1N NH_4OAc	Chelate+salt	4.8	1:10	60	[39]

mixture of sulphuric acid (H2SO4)-nitric acid (NHO_3)-perchloric acid ($HClO_4$) at a ratio of 1:2:1 [36]. The content of manganese in the dilute aqua regia, were determined by Unicam model 939 AAS. Dry matter yield, Mn concentration and Mn uptake values from the experiment were used as yield parameters of maize plants. Nutrient uptake (mg·plant^{-1}) of maize plant was determined by multiplying the values of dry matter yield (g·plant^{-1}) and concentrations of manganese (mg kg^{-1}) in plant shoots [40].

2.5 Field Calibration Studies

2.5.1 Location of the field study

The field study was sited at a community farm land in Odukpani LGA of Cross River State, in the southern part of the tropical rain forest zone of Nigeria (Latitude 4°N' and 7°N', and Longitude 8°E' and 8.30°E'), where soil samples were previously collected and used for the laboratory and greenhouse studies (Table 1). The field calibration studies for the maize plant were conducted after the greenhouse studies at two cropping seasons to evaluate the effects of various rates of Mn on maize grain yield and some other yield components. The field was fairly flat and had been under continuous and intensive cultivation without the micronutrient fertilization for over 15 years. The site experiences the southwesterly and northeasterly winds which is associated with the warm humid Maritime Tropical (MT) air mass respectively. As a result of the movement of these air masses winds, the region is characterized by two seasons-the wet season and the dry season. The wet season starts about March and last till October. This region has 2 - 3 months of dry seasons during which the total rainfall is less than 60 mm. The annual rainfall of the area was recorded as 3063 mm [41]. The field study was conducted two cropping seasons.

2.5.2 Experimental design, field plan, and treatments

Seven levels of Mn (0.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 kg ha^{-1}) converted to mg kg^{-1} were applied as $MnSO_4.5H_2O$ in solution. This was arranged in a randomized complete block design (RCBD) replicated 4 times to give 28 (7 levels of Mn × 4 replications) experimental plots. Each experimental plot received a basal application of N, P and K at 120, 90 and 60 Kg·ha^{-1}, respectively and were applied uniformly as Urea, SSP, MOP to all the plots [7]. The NPK were applied at planting as band placement covered while, the Mn treatments were applied two weeks after planting as side dressing. The reason for the selection of such high range of rates of Mn was to observe the response curve mainly for academic research purposes.

The dimension of each experimental plot was 6 m × 10 m (60 m^2), with inter-block and inter-plot spacing of 2.5 and 2.0 m, respectively. A 2-m wide pathway was maintained around the entire experimental area. Maize seeds were sown at the spacing of 75 by 25 cm. Four seeds of Oba Supper ll maize cultivar were sown manually and were thinning to two plants, 14 days after sowing, which gives a plant population of 106,666 plant·ha^{-1}.

During land preparation, seven core soil samples were obtained at the 0-20 cm depth from the site, bulked together and mixed. The samples were air-dried and mixed through a 2 mm stainless steel sieve. The soil sample taken was subjected to the same analysis as described for the greenhouse study.

Plants were sampled at 9 weeks after planting by taking three ear leaves (4th leaf) per row from the net plot, giving a total of 18 leaves per plot [42], when about 50% silking, after maize plants had tasseled. The ear leaf samples were rinsed with tap water, enveloped and oven dried at 65˚C for 48 hours to constant weight, cut into small pieces, and ground to pass through a 0.5 mm sieve, ashed and subjected to chemical analysis as previously mentioned to in the greenhouse study.

Plants were allowed to grow to maturity before the cobs were harvested at 120 days, after which, the cobs were shelled; grain yields were measured in kg $plot^{-1}$ and converted into $tones \cdot ha^{-1}$ at 12.5% moisture, the values were used to determine grain dry meter yield. Grains were later ground using a Willey mill and digested using a tri-acid a mixture at a ratio of 1:2:1 (H_2SO_4: HNO_3: $HClO_4$) as described before, and analyzed for Mn using atomic absorption spectrophotometer (AAS). Nutrient uptake ($mg \cdot plant^{-1}$) of maize plant was determined by multiplying the values of dry matter yield ($g \cdot plant^{-1}$) and concentrations of manganese (mg kg^{-1}) in maize grains. Data interpretation was made by comparing the results with the critical limits recommended for each parameter.

The coefficient of determination (r^2) was used to select the best fitted model. The extractant which displayed the highest correlation coefficient (r) with the maize uptake was recommended for the determination of available Mn content of the acid soils of southeastern Nigeria.

2.6 Statistical Analysis

The data obtained were subjected to analysis of variance (ANOVA) procedure with simple correlation and regression analyses at different probability levels, using the computer software; [43] and PASW Statistics 18 for Window 7.0, to show the relationships between the different extractants and the plant Mn uptake. Significant means were separated using Fisher's Least Significant Different at 5% probability.

3. RESULTS AND DISCUSSION

3.1 Properties of the Study Soils

The contents of some physico-chemical properties of the study soil samples are presented in Table 3. The textural classes for the greenhouse and field experiments were sandy clay loam (SCL) and sandy loam (SL), respectively (Table 3). The soils were strongly acidic in reaction, however, the optimum soil pH range for maize production was reported to be between 4 and 7 [12]. The majority of the soils were low in organic matter content. The low organic carbon could be explained by the fact that acid soils normally have low organic carbon content [44].

The total nitrogen content of the soils was moderately low according to Landon (1991) and Enwerzor (1989). The extractable P content of the soils was rated medium according to [45] while ECEC values of the soils varied widely with a mean of 9.85 and 84.3 cmol kg^{-1}. ECEC of the tested soils were below the average of 12 cmol kg^{-1} and these are rated low according to [46], and this is the range of critical value for soils that are dominated by oxide and hydroxide clays [47]. This suggests that most of the soil may have few exchange sites. [48] noted that ECEC values below a range of 10 to 20 cmol kg^{-1} are considered marginally adequate for crop production. This trend of results is attributed to the nature of the soil types, high rainfall, high leaching and erosion of bases and loss of organic matter as reported by [49].

3.2 Extractable Manganese Contents in Soils by Different Extraction Methods

Results of extractable Mn by different extraction methods are presented in Table 4. The amount of extractable Mn varied remarkably depending on and extractants used and the parent material from which the soils are derived (Yusuf et al., 2005). The lowest content of Mn was extracted by 1M NH_4OAc and the highest by the Coca-cola solution. The amount of extractable Mn in different soils varied from 1.49 to 5.61 5.61 mg kg^{-1} (Table 4).

In this study, higher available manganese content was extracted by the Coca-cola solution, with values which varied widely from 0.92 to 18.24 mg kg^{-1} with a mean of 9.34 mg kg^{-1}, followed by 0.01N HCl extraction method with Mn values which varied widely from 0.87 to 9.81 mg kg^{-1} with a mean of 5.44 mg kg^{-1}. One normal NH_4OAc extraction method extracted the lowest content of Mn relative to the other methods, with Mn values which varied widely from 0.53 to 5.32 with a mean value of 2.95 mg kg^{-1}. 0.05M EDTA-extractable Mn varied widely between 0.52 and 7.26 mg kg-1 with a mean of 4.01mg kg^{-1}. The 0.05M EDTA+1N NH_4OAc extraction method has significantly ($P<0.05$) lower extractable Mn relative to Coca-cola, and 0.01N HCl methods.

Thus, the mean values of available Mn of the acid soils were determined to be 9.34, 4.01, 5.44, 3.79 and 2.95 mg kg-1 (Table 4), on the basis of the mean extractable Mn content in soils, the extractants employed in the study could be arranged in the following order of their Mn extraction capacity: Coca-cola>0.01N

HCl>0.05M EDTA+1N NH_4OAc>0.05M EDTA>1N NH_4OAc methods, respectively. Generally, the variation of extractable manganese obtained in the soils is a reflection of the existing differences in the strengths of the extracting solutions and the availability due to the soil parent materials.

Thus, the quantity of available Mn by 1N NH_4OAc method was three times lower than the amount extracted by Coca-cola and HCl methods, respectively. The results is in line with those reported in previous studies by Kparmwang et al. [17], who reported that 0.01M HCl extracted more Mn than EDTA. [21] also noted that extraction with acid or acid-salts removes "acid soluble Mn" and recommended acetic acid and phosphoric acid which, is a major ingredient of coca-cola solution [50].

However, the amount of extractable Mn obtained in this study, suggests that the soils contain sufficient Mn for successful maize production, since the values are within the critical available range of 3-5 mg kg^{-1} reported by Lindsday and Norvell (1978) and 1-5 mg kg^{-1} reported by [51,52] for the Ustults in Bauchi State, Nigeria. Previous workers noted that soil pH has a dominant effect on the solubility, availability and potential cations (e.g. Mn^{2+}) in soil [53]. [54] noted that, the availability Mn in soil solution as cations (Mn^{2+}) increases with increasing soil acidity, whereas the availability of Mn present as anions (MoO_4^{2-}) increases with increasing pH.

3.3 Critical Limit of Soil Extractable Mn

The relative suitability of different soil extractants could be judged by the statistical significance and the magnitude of R^2-value. To estimate the critical limits (the threshold concentration below which the probability of finding an economic response to the application of a nutrient in a crop is greater) of Mn in terms of soil extractable Mn for maize plants from greenhouse study, the uptake of maize shoots was plotted against soil extractable Mn estimated by different soil extractants. The critical limits of Mn were evaluated following the statistical (R^2-technique) and graphical procedures of [55, 56]. The critical value divides soils as highly responsive and non-responsive to manganese application. The maximum uptake by maize (mg $plant^{-1}$) corresponds to the critical soil extractable Mn values (mg kg-1), under which a high response of added Mn to maize crop is expected. On the basis of highest predictability (R^2) value, a population can easily be partitioned which corresponds to the postulating critical level (Fig. 1). The R^2 indicated in Fig. 1 are coefficients of determination for delineation of responsive soils from non-responsive soils. Simple regression equations between soil extractable Mn (X-axis) and Mn uptake of maize shoots (Y-axis) with their respective coefficient of determination which, could be accounted by extractable Mn for a particular extractant (R^2) are shown in Fig. 2.

Thus, the critical limits of Mn in soil, below which the response of maize to applied Mn could be expected, were determined as 2.82, 4.65, 5.85, 3.10 and 2.46 mg for Coca-Cola, 0.01M HCl, 0.05M EDTA, 0.05M EDTA+1N NH_4OAc and 1M NH_4OAc-extractable Mn kg^{-1} soil, respectively. The R^2 values for Coca-Cola, 0.01M HCl, 0.05M EDTA extractable Mn were significant at P>0.01 while, NH_4OAc and 0.05M EDTA+1N NH_4OAc extractable Mn have R^2 values which are significant at P> 0.05. The observed variation in the critical limit of soil the Mn, could be attributed partly due to contrasting soil properties and in the effectiveness of the extractant.

Considering the magnitude of R^2-values (coefficient of determination for delineation of Mn responsive soils from Mn non-responsive soils), the soil extractants could be arranged in the order of reliability: Coca-Cola> HCl > EDTA > EDTA+NH_4OAc > NH_4OAc. However, keeping in view the rapidity of the extraction procedure (Table 4) with Coca-Cola extractant and in the absence, 0.01M HCl extractants, can be used to achieve the same result. Thus, these would certainly be better extraction methods for soil Mn in acid soils of southeastern Nigeria.

3.4 Effect of Mn Levels on Dry Matter Production of Maize Shoots

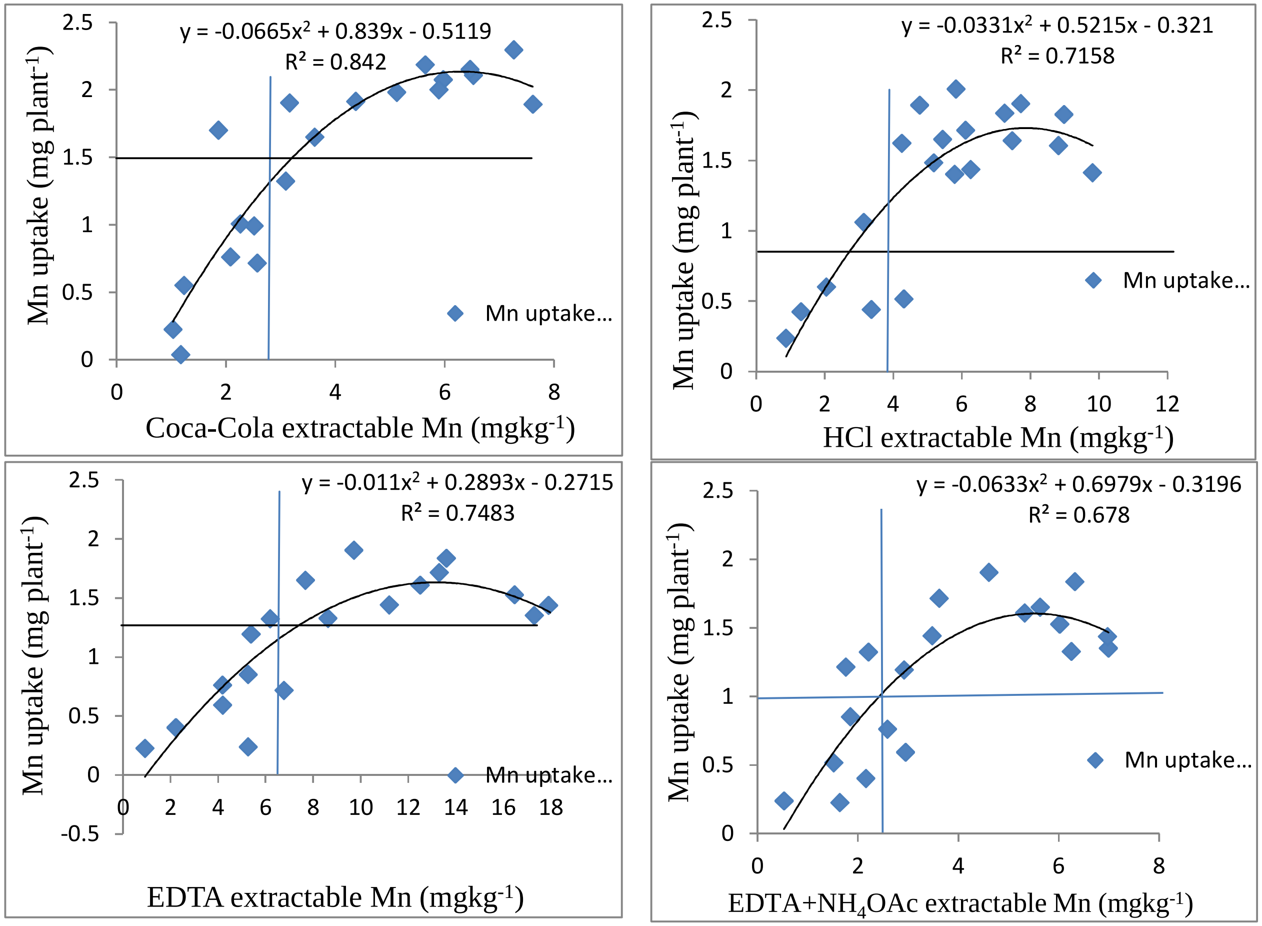
Deficiency symptom of Mn was observed on maize plant shoots which appeared yellow in both intercostal during the emergence of maize tassels. The symptoms first appear on younger leaves because the dynamics of these elements in different plant tissues were limited. It was noted in previous studies by [57,14] that, the major symptom of Mn deficiency is a reduction in the efficiency of photosynthesis leading to a general decline in dry matter productivity and yield. However, a significant result of Mn treatment on dry matter yield of maize shoots was established. In general, wide variation in the dry matter yield of maize shoots was noticed among the soils and differ significantly ($P < 0.05$) among the levels of Mn treatments, and these improved the dry matter yield of maize in some soils ranging from 12.95 to 17.03 g plant^{-1} with a mean of 15.21 g plant^{-1} (Fig. 1).

Table 3. Mean values of some physico-chemical properties of the surface (0-20 cm) soils used for the greenhouse study and the field study

Soil properties	Unit	Greenhouse study (N=25)	Field study
Particle size distribution			
Sand fraction	g kg^{-1}	642.37	661.53
Silt fraction	g kg^{-1}	101.22	153.16
Clay fraction	g kg^{-1}	256.41	185.31
Textural class		Sandy clay loam	Sandy loam
Chemical properties			
pH (1:2.5) H_2O		5.51	5.19
pH (1:2.5) $CaCl_2$		4.78	4.62
Org. Carbon	g kg^{-1}	4.40	1.06
Org. matter	g kg^{-1}	7.59	1.83
Al^+	cmol kg^{-1}	1.91	1.48
H^+	cmol kg^{-1}	3.44	1.16
Effective cation exchange capacity	cmol kg^{-1}	9.85	8.43
Base saturation	%	76.35	84.58
Nutrient concentration (Available nutrient)			
Total nitrogen N	g kg^{-1}	0.56	0.19
Available P	mg kg^{-1}	24.20	12.23
Calcium Ca	cmol kg^{-1}	4.76	3.60
Magnesium Mg	cmo l kg^{-1}	2.46	2.04
Sodium Na	cmol kg^{-1}	0.09	0.15
Potassium K	cmo lkg^{-1}	0.19	1.34
Total Mn in soil	mg kg^{-1}	367.18	115.28

Table 4. Distribution of extractable Mn in soils by different extraction methods

Sample location	Extractable manganese (mg kg-1)					Mean
	Coca-Cola	**EDTA**	**HCl**	**EDTA+NH_4OAc**	**NH_4OAc**	
Abriba	13.62	5.12	7.25	5.61	0.53	6.43
Afikpo	4.19	2.51	5.79	3.62	1.52	3.53
Akamkpa	16.43	5.64	8.82	5.81	1.64	7.67
Akpabuyo	13.31	5.97	6.11	6.75	1.76	6.78
Akpet	18.24	4.37	9.81	2.31	1.85	7.32
Bende	5.26	0.52	0.87	0.71	2.16	1.90
Betem	6.19	3.09	4.25	4.43	2.21	4.03
Etiti	4.18	2.48	3.14	3.06	2.59	3.09
Igbariam	8.62	2.26	8.98	5.32	2.92	3.62
Ikot Ekpene	5.26	1.43	5.18	1.68	2.95	3.30
Nsukka	11.22	5.89	3.36	1.11	3.48	5.01
Oban	9.71	3.16	7.72	4.22	3.62	5.69
Odukpani	5.38	6.61	4.77	2.57	3.03	4.48
Ofodua	2.22	2.16	2.05	1.03	4.61	2.41
Okigwe	12.51	6.52	5.83	5.72	4.97	7.11
Owerri	17.33	6.46	7.47	7.04	4.19	8.49
Umudike	6.77	3.57	4.31	2.41	3.32	4.08
Uturu	7.67	3.62	5.44	3.92	5.32	5.19
Uyanga	17.93	7.26	6.26	6.36	4.02	8.37
Uyo	0.92	1.63	1.31	2.04	2.25	1.63
Min.	0.92	0.52	0.87	0.71	0.53	1.63
Max.	18.24	7.26	9.81	7.04	5.32	8.49
Mean	**9.34**	4.01	**5.44**	3.79	2.95	5.11


y = -0.0665x² + 0.839x - 0.5119
R² = 0.842
Mn uptake (mg plant-1)
Mn uptake...
Coca-Cola extractable Mn (mgkg-1)
y = -0.0331x² + 0.5215x - 0.321
R² = 0.7158
Mn uptake (mg plant-1)
Mn uptake...
HCl extractable Mn (mgkg-1)
y = -0.011x² + 0.2893x - 0.2715
R² = 0.7483
Mn uptake (mg plant-1)
Mn uptake...
EDTA extractable Mn (mgkg-1)
y = -0.0633x² + 0.6979x - 0.3196
R² = 0.678
Mn uptake (mg plant-1)
Mn uptake...
EDTA+NH4OAc extractable Mn (mgkg-1)

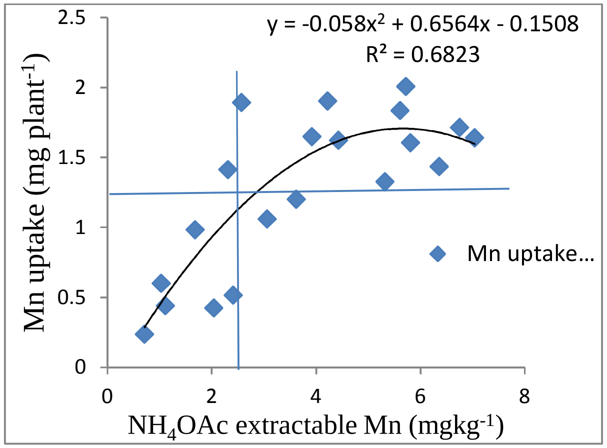
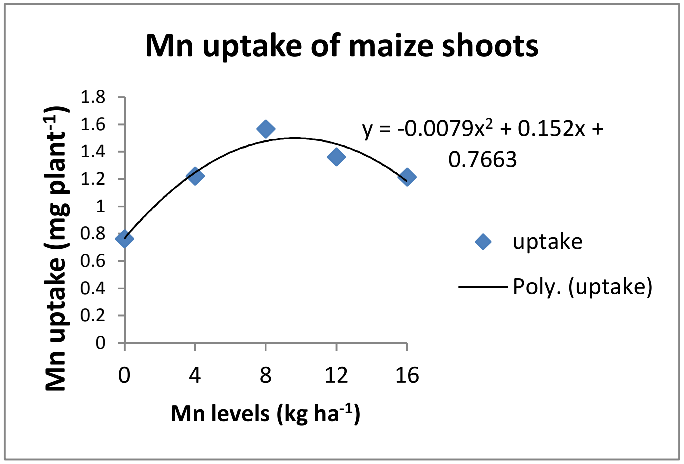
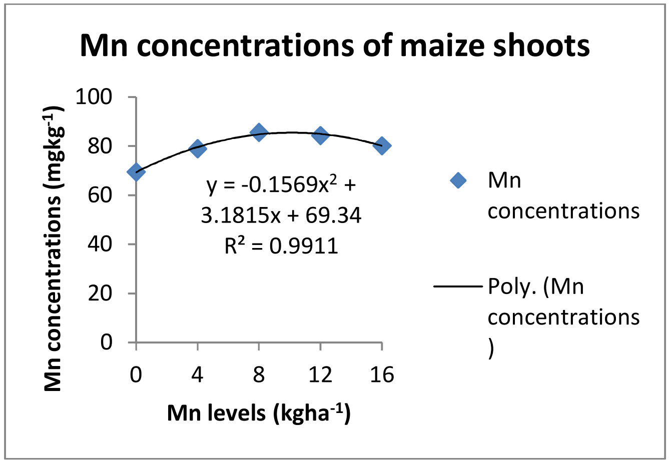
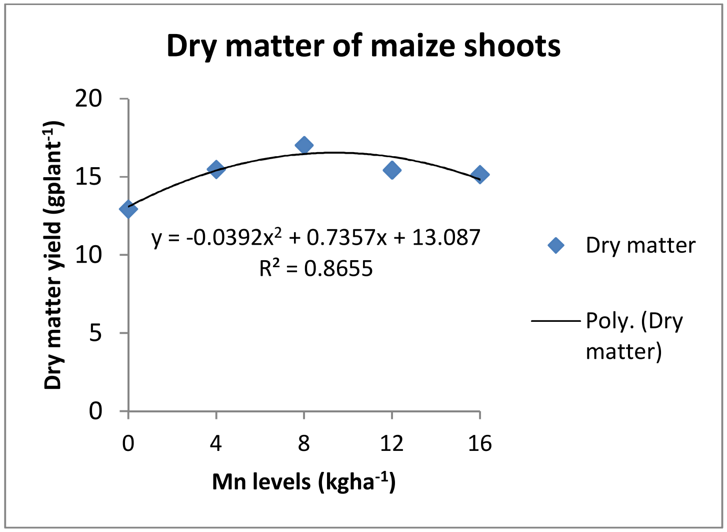


Fig. 1. Scatter diagrams plotted between Mn uptakes of maize shoots versus extractable soils Mn after greenhouse experiment







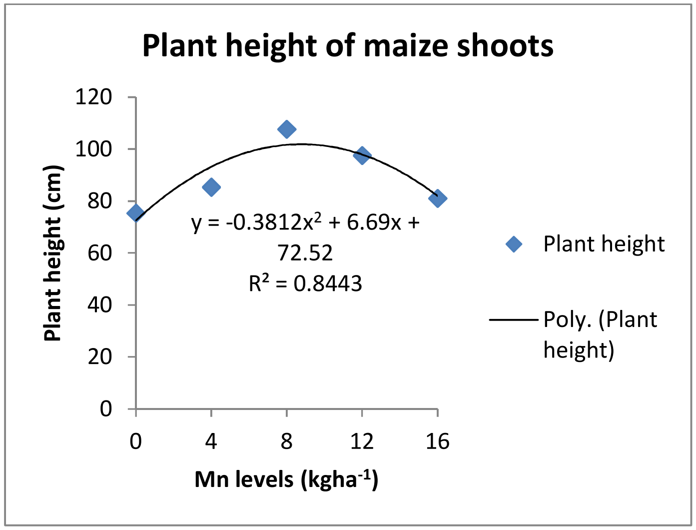


Fig. 2. Graphs showing the effects of Mn levels on yield and growth parameters of maize shots in greenhouse experiment

Dry matter yields obtained at different Mn levels in soils indicated that the application of 8 kg·Mn·ha^{-1} soil brought the highest and significant dry matter yield of maize over the 0 kg·Mn·ha^{-1}soil level (Fig. 2). The significant (P < 0.05) increase in DM yield in the Mn treatments over the control suggests that Mn was one of the limiting nutrients in the soils (Fig. 1). Further addition of $MnSO_4.5H_2O$ salt to 8 kg ha^{-1}, did not significantly improve DM yield of plant shoots. Although, 8 kg Mn ha^{-1} levelsof application gave the highest DM yield of maize, according to the polynomial regression equation analysis (Table 4), a maximum of 9 kg·Mn·ha^{-1} will be required to improve dry matter production of maize in the soil, which in turn will improve maize grain yields. This finding is in agreement with previous result reported by [42,58]. The finding, suggests that 9 kg·Mn·ha^{-1} is the critical nutrient level that will optimize maize production in the acid soils under reviewed.

3.5 Effect of Mn Levels of the Concentration of Manganese in Maize Shoots

The Mn concentration in maize shoots increased with increasing Mn levels (Fig. 1). The content of manganese concentration ranged from 69.50 to 85.61 mg kg^{-1} with a mean of 79.73 mg kg^{-1}, and these were sufficient according to previous studies by [46,59,18,60], respectively. Moreover, Mn application significantly (P<0.05) increased Mn concentration compared to control, indicating that Mn was one of the limiting nutrients in this soil (Fig. 1). Surprisingly, lower levels of Mn also yielded higher concentration in maize shoots. It is noted in Table 3 that, 8 kg·Mn·ha^{-1} level which gave the maximum dry matter production also gave significantly (P < 0.05) higher Mn content relative to lower levels of Mn. However, the polynomial regression equation (Table 5) determined, indicated that it will take about 10 kg·Mn·ha^{-1} to produce optimum Mn concentration in maize plants. The wide variability in Mn concentration in maize shoots as determined in this study may be as a result of higher available Mn content and low Mn fixation in some of the soils. The effect of Mn application on the yield parameter of maize plants was determined to be significant at 5% probability level.

3.6 Effect of Mn Levels on Uptake of Manganese in Maize Plants

The Mn uptake of the maize shoots determined at 6 WAP increased with increasing Mn levels and varied from 0.906 to 1.458 mg plant^{-1} with an average of 1.257 mg plant^{-1} (Fig. 2). The progressive increased in uptake due to the addition of Mn, indicated that the application of 8 kg·Mn·ha^{-1} soil yielded the highest and significant higher uptake of maize over the 0 kg·Mn·ha^{-1}soil level (Fig. 2). However, the significant result obtained at this level of Mn application, may not be unconnected to the increase in either DM yield or Mn concentration which accumulated Mn content in the various plant parts. Supporting this, the polynomial regression analysis ($Y = 0.7663 + 0.0152x - 0.0079x^2$; $R^2 = 0.7663$) computed indicated that the maximum Mn level that gave the optimum Mn uptake as shown in Fig. 1, was 8 kg·Mn·ha^{-1} of application (Table 5). In general, acidic soils with low clay contents appeared to be more responsive to Mn application [61]. Similar results were obtained in previous studies by [58,62,42].

3.7 Calibration and Correlation for Greenhouse Study

The usefulness of any soil extractant to estimate the availability of micronutrient element is dependent on the ability to determine (from the extractant) the extent to which plants will accumulate a given nutrient element. Although, comparisons between various chemical extractants can be problematic due to variations in soil types, properties and treatment duration [18]. An effective extractant will be able to predict the availability of these trace elements under a variety of soil conditions [42,18].

Significant correlation coefficients (r) were determined between all the extractants and Mn uptake at P<0.05 and 0.01 probability levels (Table 6). The highest significant correlation coefficients (r) were determined between Coca-Cola method which correlated significantly with dry matter yield (r = 0.875**), and Mn uptake (r = 0.783**) but negatively correlated with Mn concentration (r = -0.699*) of maize, followed by HCl method which correlated negatively with dry matter yield (r = -0.657*) and positive correlation with Mn uptake (r = 687*). The EDTA-extractable Mn had significant negative correlation with Mn concentration (r = -0.509*) of maize. While EDTA+NH_4OAc- extractable Mn had negative correlation with dry matter yield (r = -0.586*) but correlated positively with uptake (r = 0.546*). These significant positive correlations with plant parameters suggest that the amount of Mn extracted by these extractants have strong association with plant uptake [63]. This may be due to Mn transformation and availability in soils which depends on various forms of this nutrient element with which Mn have significant and positive correlation [64]. The results obtained from NH_4OAc method followed the above methods regarding the correlation coefficients (r) but, had no significant correlation with either of the yield parameter of maize shoots.

The low values obtained by EDTA , NH_4OAc and EDTA+NH_4OAc methods respectively may be attributed to the soil factors such as, redox potential conditions of the soils which determined the final behavior of Mn in the soils and its availability to maize plants. Moreover, chemical properties of the soils (Table 3) suggests that they were strongly acidic, low in organic matter and ECEC, coarse in texture as reported in the previous study by [24]. Thus, the use of salt and chelate mix (NH_4OAc+ EDTA) extraction method was not adequate in the determination of available Mn, rather, the used of acid methods (Coca-Cola and HCl) was shown to be more suitable in the prediction of available Mn content in the soils. The result obtained in this study with Coca-Cola method is similar to the result reported by [22] in soils on the Island of Ruegen. This is supported by the result with higher correlation coefficients (r) which were obtained from acid methods (Table 5 and 7). Therefore, when considering the physical and chemical properties of the soils studied, the acid method can be used with satisfaction in the determination of available Mn contents in soils of southeastern Nigeria. Besides the better results obtained with the Coca-Cola method, in extracting available Mn fractions from these soils, the correlations with plant uptake was superior to the other extracting solutions. Further advantages of Coca-Cola as an extractant are its ubiquitous availability and readiness for us but also its easy and safe handling and the fact that the procedure has no harmful impacts as compared to the other extracting solutions [50].

3.8 Prediction of Mn Uptake of Maize Shoots by Soil Extractable Manganese

Manganese uptake of maize under 0 mg Mn kg^{-1} soil was regressed on soil extractable Mn contents estimated by different soil extractants (Table 7). The regression analysis between Mn extracted by different soil extractants (Table 7) and the Mn uptake by maize shoots showed that the Mn extracted by Coca-cola, 0.05M EDTA, 0.01M HCl, EDTA+NH_4OAc and 1N NH_4OAc extractants (Table 4) accounted for 86.6, 51.1, 77.2, 60.1 and 33.0 percent variations in Mn uptake by maize plants, respectively.

Table 5. Maximum levels of Mn (kg ha^{-1}) that gave the optimum growth/yield parameters of maize shoots

Maize shoot parameter	Maximum rates of Mn (kg ha^{-1}) required	Polynomial regression (R^2) values
Plant height	8.8	0.844
Dry matter yield	9.4	0.865
Mn content in plant shoot	10.2	0.991
Mn uptake	8.0	0.766

Table 6. Correlation coefficients (r) between extractable Mn in soils and uptake by maize shoots (N=20)

Extraction methods	Yield parameters of maize plants (non-application of soils Mn)		
	Dry matter yield of plant (g $plant^{-1}$)	Mn concentration of plant (mg kg^{-1})	Uptake of Mn in plant (mg $plant^{-1}$)
Coca-Cola	0.875**	-0.699*	0.783**
0.005M EDTA	0.496^{ns}	-0.509*	0.107^{ns}
0.1M HCl	-0.657*	-0.153^{ns}	0.687*
EDTA-NH_4OAc	-0.586*	-0.204^{ns}	0.546*
1M NH_4OAc	0.279^{ns}	-0.179^{ns}	0.361^{ns}

*Ns: not significant at P < 0.05, * significant at P < 0.05, ** significant at P < 0.01*

Table 7. Regression equations for the prediction of Mn uptake in maize by different extractants in acid soils of southeastern Nigeria (N=20)

Soil extractant (X)	Mn uptake (Y, mg pot^{-1}) Regression equation	R^2 value
Coca-Cola	Y = 243.20 +180.74X	0.866**
EDTA	Y = 607.17 + 1592X	0.511*
HCl	Y = 245.27 + 418.18X	0.772**
NH_4OAc+EDTA	Y = 348.36 – 123.75X	0.601**
NH_4OAc	Y = 446.32 + 70.16X	0.330^{ns}

*Ns: not significant at P < 0.05, * significant at P < 0.05, ** significant at P < 0.01*

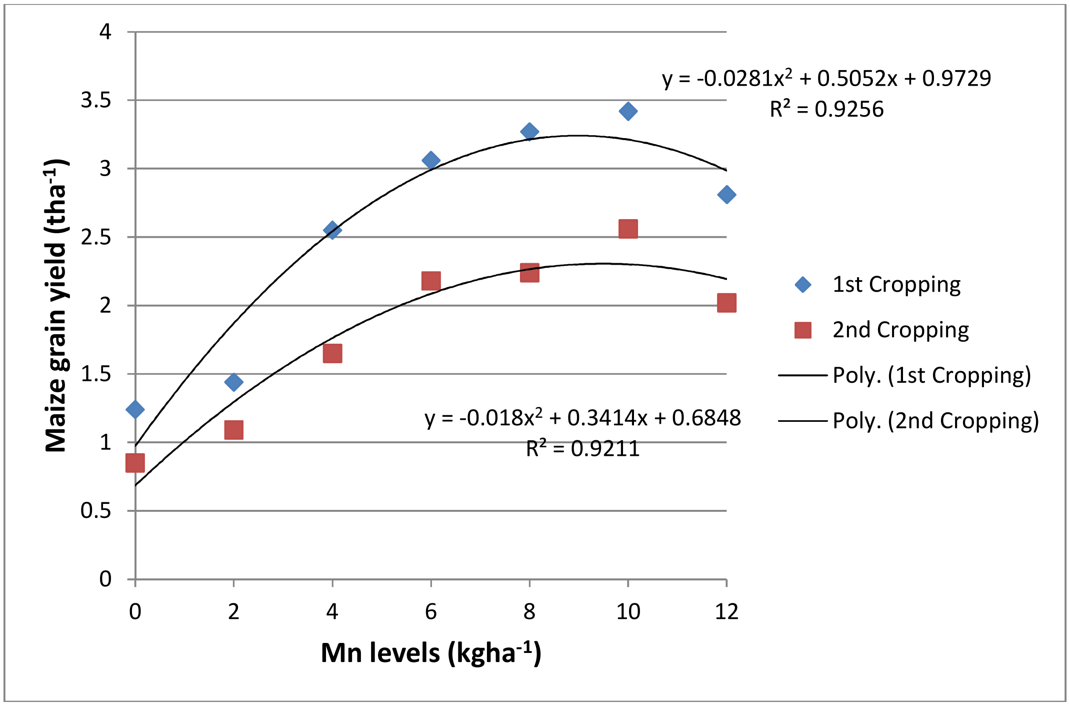


Fig. 3. Optimum Mn levels for maize grain yield in field experiment

Similar to the predicted results establish from the correlation analysis (Table 6), the linear regression analysis conducted showed that, all the predicted equations regarding Mn uptake and extractants were statistically significant with exception of NH_4OAc (Table 7). In these evaluations, uptake results were very similar to those determined for dry matter yield and Mn concentration of maize plants. The linear regression equation that is not significant indicates that the material did not significantly increase Mn uptake. Though, 0.01M HCl methods performed equally well, the Coca-cola method performed better. Based on the correlation and regression analyses (Tables 6 and 7), this study has proven that Coca-cola and 0.01M HCl extraction methods which performed better among others tested, are the most suitable extractants and are therefore highly recommended for the estimation available manganese in acid soils of southeastern Nigeria. These findings are in agreement with previous studies by [65].

4. FIELD CALIBRATION STUDY

4.1 Optimum Mn Levels for Maize Grain Production

The application of Mn fertilizer to soil significantly (P<0.05) influenced maize grain yield of both the first and second cropping (Fig. 3). However, the polynomial regression analysis determined for maize grain yield as a function of Mn application was also significant (R^2=0.925 and 0.921) for first and second cropping seasons, respectively. The maximum increase (150%) in maize grain yield was determined when the Mn was applied at 9.0

kg ha^{-1}, for the first cropping season, while, the second cropping season exhibited maximum increase (278%) in grain yield when Mn was applied at 9.5 kg ha^{-1}. These results imply that the second cropped maize required nutrients in greater amounts to attain full yield potential compared to that grown in the first cropping season. In the present study, maize grain yields of both seasons were reduced at the highest rate of Mn application (12 kg ha^{-1}). The reduction in maize grain yields in both cropping seasons after application at 9.0 kg ha^{-1} and 9.5 kg ha^{-1} respectively is attributed to their optimum levels of Mn requirement. These values are higher than the optimum rate of 8.0 kg Mn ha^{-1} (Table 6) estimated in the greenhouse study for Mn uptake in maize shoots. Thus, the result illustrated in (Fig. 3) suggests that 9.0 and 9.5 kg Mn ha^{-1} respectively is the estimated optimum Mn rate for maximum maize grain yields in the study area.

5. CONCLUSION

The results obtained in this study shows that the Coca-cola method extracted the highest amount of the Mn (5.61 mg kg^{-1}) while, 1N NH_4OA_C extracted the least amount of Mn (1.49 mg kg^{-1}) with an average of 3.78 mg Mn kg^{-1}. Coca-Cola, followed by 0.01M HCl extractants is highly recommended for the determination of available Manganese for the acid soils. Levels of Mn applied to the soils significantly ($P < 0.05$) increased maize plant height, dry matter production, concentration and uptake in maize plants. The optimum rate of applied Mn that promoted Mn uptake in maize shoots was established at 8 kg Mn ha^{-1}. The critical limits of Mn in soil that produced responses for maize plants were determined to be; 2.82, 4.65, 5.85, 3.10 and 2.46 mg Coca-Cola, 0.01M HCl, 0.05M EDTA, 0.05M EDTA+1N NH_4OAc and 1N NH_4OAc-extractable Mn kg^{-1} soil, respectively. The results obtained based on the two year field studies, suggests that, the rate of Mn required to produce maximum maize grain yield in the acid soils of southeastern Nigeria is recommended as 9.0 kg ha^{-1}.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Šimić D, Zdunić Z, Jambrović A, Ledenčan T, Brkić I, Duvnjak V, Kovačević V. Relations among six micronutrients in grain determined in a maize population. Poljoprivreda. 2009;15(2):15-19.
2. FAO FAOSTAT–Agriculture Database. Available:http://faostat3.fao.org/faostat-gateway/go/to/download/Q/*/E (Accessed 2013 Sep 15)
3. Nuss ET, Tanumihardjo SA. Maize: A paramount staple crop in the context of global nutrition. Compr Rev Food Sci F. 2010;9:417–436.
4. FAOSTAT. FAO production year book. Food and Agricultural Organization, Rome; 2010.
5. Shiferaw B, Prasanna B, Hellin J, Bänziger M. Crops that feed the world 6. Past successes and future challenges to the role played by maize in global food security. Food Sec. 2011;3:307–327.
6. Enwezor WO, Ohiri OC, Opuwaribu EE, Udo EJ. A review of fertilizer use on crops in southeastern zones of Nigeria (in Five Vols.) (FFDD Eds). Boboma Publ, Ibadan. 1990;47-70.
7. Chude VO, Malgwi WB, Amapu IY, Ano AO. Manual on soil fertility assessment. federal fertilizer department/National Special Food Programme for Security, Abuja. 2004;89.
8. Ogban PI, Akwue IP, Mauako O. Properties and management of catenary soils on coastal plain sands in Southeastern Nigeria. In: Babalolu, O., Omoti, U. and Isenmila, A.E., Eds., Management of the Soil Resources of Nigeria for Sustainable Agricultural Production in the 21st Century. Proceedings of the 25th Annual Conference of the Soil Science Society of Nigeria, Benin. 1999;45-52.
9. Sillanpaa M. Micronutrients and the nutrient status of soils: A global study. FAO Soil Bulletin No. 48, FAO/Finnish International Development agency, Rome; 1982.
10. Shuman LM. Effects of organic matter on the distribution of manganese, copper, iron and zinc in soil fractions. Soil Sci. 1988; 146:192-198.
11. Havlin JL, Beaton JD, Tisdale SL, Nelson WL. Soil fertility and fertility and fertilizers: An introduction to nutrient management 7th rd. Asoke K-Ghosh, Prentice Hall Publishers, New Delhi, India; 2005. Available:http://dx.doi.org/10.1097/00010694-198507000-00003
12. Aduayi EA, Chude VO, Adebusuyi BA, Olayiwola SO. Fertilizer use and

management practices for crops in Nigeria. Federal Fertilizer Distribution Department. Federal Ministry of Agriculture and Rural Development, Abuja. 2002;126.

13. Mortved TJ. Micronutrients in crop production, overview of micronutrients and their sources. Colorado State Univ; 2010. Available:http://www.back-to-basics.net/archives/articles/pdf/micronutrients.pdf
14. Marschner. Mineral nutrition of higher plants, 3rd edn. Academic, London. Elsevier Science Ltd. Academic Press. New York. 2011;123.
15. Yaro DT, Kparmwang T, Aliyu SM, Wuddivira HN, Tarfa BD. Status of DPTA and Hcl extractible cationic micronutrient in soils of the long term DNPK plot at Samaru Zaria. Nigerian Journal of Soil Research. 2006;3:27-32.
16. Ibrahim AK, Usman A, Abubakar B, Aminu UU. Extractable micronutrients status in relation to other soil properties in Billiri LGA. Journal of Soil Science and Environmental Management. 2011;3(10): 282-285.
17. Kparmwang T, Chude VO, Esu IE. Hydrochloric acid (0.1N HCl) and DTPA extractable and total iron and manganese in basaltic soil profiles of the Nigeria savanna. Comm. Soil Sci. Plant Anal. 1995;26:2235-2245.
18. Menzies NW, Donn MJ, Kopittke P. Evaluations of extractants for estimation of the phytoavailable trace metals in soils. Environ. Pollut. 2007;145:121-130.
19. Porter GS, Bajita-Locke JB, Hue NV, Strand D. Manganese solubility and phytotoxicity affected by soil moisture, oxygen levels, and green manure additions. Comm. Soil Sci. Plant Anal. 2004;35:99-116.
20. Grava I. Importance of soil extraction techniques. 1980;9-11. In: W. C. Dahuke et al. (ed). Recommended soil test procedures for the North Central Region (revised). North Central Regional Publication. 221. ND. Agric. Exp. Stn. Bull. 499 (revised).
21. Gronflaten LK, Steines E. Comparison of four different extraction methods to assess plant availability of some metals in organic forest soil. Comms in Soil Sci and Plant Anal. 2005;36(19 & 29):2699-2718.
22. Schnug E, Fleckenstein J, Haneklaus S. Coca-Cola extractant for the evaluation of available micronutrient concentrations in soils for oil seed rape. Institute of Plant Nutrition and Soil Science, Fed Agric. Research Centre, Germany; 2001.
23. Ivezić V, Lončarić Z, Engler Meri D, Kerovec D, Singh BR. Comparison of different extraction methods representing available and total concentrations of Cd, Cu, Fe, Mn and Zn in soil. Poljoprivreda. 2013;15(2):53-58.
24. Eteng EU, Asawalam DO, Ano AO. Total and available micronutrients in soils of contrasting parent materials in Southeastern Nigeria. Journal of Agriculture, Biotechnology and Ecology. 2014;7(2):1-16.
25. Odurukwe SO, Anuebunwa FA, Iloka AW, Udeabor A, MA Ibedu M. Physical environmental of Southeastern Nigeria. I: Indigenous fallow and multipurpose tree and shrub species in the farming system of southeastern zone of Nigeria. A report of diagnostic survey. NRCRI, Umdike Publications; 1995.
26. Ojanuga AG. Agroecological Zones of Nigeria manual. In: Berding, F. and Chude, V.O., Eds., National Special Programme for Food Security (NSPFS) and FAO. 2006;124.
27. Gee GW, Or D. Particle size analysis. In: Methods of Soil Analysis. Soil Sci. Soc. Of Am. Book Series No. 5 ASA and SSSA Madison, Wis. 2002;225-293.
28. USDA. Keys to soil taxonomy. 10th Edition, United States Department of Agriculture, NRCS Soil Conservation Service, Washington DC; 2006.
29. FDALR. Federal Department of Agriculture and Land Resources. The Reconnaissance Soil Survey of Cross River State, Nigeria. FDALR, Abuja. 1995;43.
30. Thomas GW. Soil pH and soil acidity. In: Sparks, D.L., Ed., Methods of Soil Analysis Part 3: Chemical Methods, SSSA Book Series 5, Soil Science Society of America, Madison, Wisconsin. 1996;475-490.
31. Nelson DW, Sommers LE. Total carbon, organic carbon and organic matter. In: Sparks, D.L., Ed., Methods of Soil Analysis Part 3: Chemical Methods, SSSA Book Series 5, Madison, Wisconsin, Soil Science Society of America. 1996; 961-1010.
32. Kuo S. Phosphorus. In: Sparks, D.L., Ed., Methods of soil analysis Part 3: Chemical methods, SSSA Book Series 5, Soil

Science Society of America, Madison, Wisconsin. 1996;869-920.
33. Bremner JM. Nitrogen total. In: Sparks, D.L., Ed., Methods of Soil Analysis Part 3: Chemical Methods, SSSA Book Series 5, Soil Science Society of America, Madison, Wisconsin. 1996;1085-1122.
34. McLean EO. Soil pH and lime requirement. In A.L. Page, R.H. Miller & D.R. Keeney (Eds), Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Madison, Wisconsin, USA. 1982; 199–224.
35. Sumner ME, Miller WP. Cation exchange capacity and exchange coefficients. In: Sparks, D.L., Ed., Methods of Soil Analysis Part 3: Chemical Methods, SSSA Book Series 5, Soil Science Society of America, Madison, Wisconsin. 1996;1201-1230.
36. Shuman LM. Fractionation method for soil micronutrients. Soil Sci. GEOBASE. 1985; 140:11-22.
37. Lindsay WL. Chemical reactions in soils that affect iron availability to plants. A quantitative approach. Iron Nutrition in Soils and Plants, Kluwer Academic Publishers. 1995;7-14.
38. Olsen SR. Micronutrients interaction. In: Micronutrients in Agriculture. Mortvedt , J. J., Giordano, P. M. and Lindsay, W. L. (eds). Soil Science Society of American, Madison, W. 1992;248.
39. Adiloglu A. Determination of suitable chemical extraction methods for available iron content of the soils of Edirne province in Turkey. Pakistan Journal of Biological Sciences. 2003;6(5):505-510.
40. Whitney DA. Micronutrient soil test zinc, iron, manganese and copper. In: Dahuke, W.C., Ed., Recommended Chemical Soil Test Procedures for the North Central Region, North Dakota Agric. Exp. Stn. Bull. 1988;499:20-22.
41. NIMETS. Nigeria meteorological services, Calabar Station, Margerate Ekpo International Airport Calabar, Nigeria; 2009.
42. Lisuma JB, Semoka JMR, Semu E. Maize yield response and nutrient uptake after micronutrient application on a volcanic Soil. Agronomy Journal. Madison, W.I. 2006;98:402-406.
43. GenStat. GenStat for Windows. Release 7.2. 7th Edition, VSN International Ltd, Oxford; 2004.
44. Ibanga IJ, Udo EJ. Soil Survey and fertility baseline data collection of Akwa Ikot Effangha farm, Akpabuyo LGA, Cross River State Nigeria. National Agricultural Land Development Authority, Abuja; 1996.
45. Landon JR. Tropical soil manual. A handbook for soil survey and agricultural land evaluation in the tropics and sub tropics. Longman Scientific & Technical Publ., Harlon; 1991.
46. Melsted SW, Motto HL, Peck TR. Critical plant nutrition composition values useful in interpreting plant analysis data. Agronomy Journal. 1969;61:17-20.
47. Omueti JAI, Lavkulich LM. Identification of clay minerals in soils: The effect of sodium-pyrophosphate. Soil Sci. Soc. Am. J. 1988;52:285-287.
48. Aluko AP, Owunubi JJ, Fagbero JA. Physico-chemical properties and potentials of some wetland soils of the mangrove ecolosystem for sustainable forest trees establishment. In: Management of wetland soils for sustainable agriculture and environment Proceedings of the 7th Annual Conference of the Soil Science Society of Nigeria. 2001;237-240.
49. Asawalam DOK. The human element in soil erosion and the campaign for hunger in Southern Nigeria. Proc. of the 17th Ann. Conf. of the SSSN. 1989;50-55.
50. Schnug E, Fleckenstein J, Haneklaus S. Coca-Cola is it! The ubiquitous extractant for micronutrients in soils. Commun. Soil Sci. Plant Ana. 1996;27:1721-1730.
51. Esu IE. Detailed soil survey of NIHORT farm at Bunkure Kano State, Nigeria. Institute. Agric. Res., Zaria. 1991;72.
52. Mustapha S, Loks NA. Distribution of available Zn, Cu, Fe and Mn in Fadama soils from two District Agro-ecological zones in Bauchi State, Nigeria. J. Environ. Sci. 2005;9(2):22-28.
53. Clark RB, Baligar VC. Acidic and alkaline soil constraints on plant mineral nutrition. In: R.E. Wilkinson (ed.) Plant-Environment Interactions. Marcel Dekker Inc, New York. 2000;133-177.
54. Rengel Z. Role of pH in availability of ions in soil. In: Z. Rengel (ed.) Handbook of Plant Growth. pH as a Master Variable in Plant Growth. Marcel Dekker, New York. 2002;323-350.
55. Cate RB Jr, Nelson LA. A rapid method for correlation of soil test analysis with plant response data. North Carolina Agric. Exp. Stn. Inst. Soil Test Serv. Tech. Bull., No. 1: 1965;67-69.

56. Cate RB, Nelson LA. A simple statistical procedure for partitioning soil-test correlation data in two soils. Soil Sci. Soc. Am. Proc. 1971;35:658-659.
57. Sharma PC, Sharma PN, Chatterjec C, Agarwald SC. Manganese deficiency in maize effect on pollen viability. Plant and Soil. 1991;138:139-147.
58. Fageria NK. Influence of micronutrients on dry matter yield and interaction with other nutrients in annual crops. Pesq. Agropec. Bras., Brasília. 2002;37(12):1765-1772.
59. Tandon HLS. Micronutrients in soils, crops and fertilizer: A source book-cum-directory. Fertilizer Development and Consultation Organ, New Delhi; 1995.
60. Rastija M, Rastija D, Simic D, Mihaljevic I. Yield and concentration of maize Mn and Zn in grain of maize parameter inbred and hybrids. Poljoprivreda. 2009;15(2):20-25.
61. Enwezor WO, Udo EJ, Usoro NJ, Ayotade JA, Chude VO, Udegbe CC. Fertilizer use and management practices for crops in Nigeria. Series 2. Federal Ministry of Agriculture, Water Resources and Rural Development. 1989;52-56.
62. McBride MB, Richards BK, Steenhuis T. Bioavailability and crop uptake of trace elements in soil columns amended with sewage sludge products. Plant and Soil. 2004;262:71-84.
63. Lindsay WI, Schwab AP. The chemistry of iron in soils and its availability to plants. J. Plant Nutr. 1982;5:821-840.
64. Dahnke WC, Olson RA. Soil test correlation, calibration, and recommendation. In: R. L. Westerman (3rd ed.) Soil Testing and Plant Analysis. SSSA, Madison, Wisconsin. 1990;45-71.
65. Aydinalp C, Katkat AV. The comparison of extraction methods for evaluating some heavy metals in polluted soils. Plant Soil Environment. 2004;50(5):212-217.

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