

# CHANGES IN SOIL pH AND MAIZE CONTENTS OF ZINC AND PHOSPHORUS UNDER ZINC SULPHATE AND ORGANIC WASTE APPLICATIONS

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## ABSTRACT

Zinc (Zn) fertilizer application is common in field crop production in many areas of the world. This study evaluated effects of zinc sulphate, ZnSO<sub>4</sub> (22.8 % Zn), a commercial organic fertilizer (O.F) produced from market wastes (0.02 % Zn, 0.36 % Ca, 2.30 % N, 0.55 % P, 0.47 % K) and organo-mineral combination (O.F + ZnSO<sub>4</sub>) on P and Zn nutrition of maize (*Zea mays*, L. var. TZEEY-SR EC5). Plants were grown in pots using a medium acid (pH 5.9) sandy clay Oxic Paleustalf from Zaria (Southern Guinea Savannah zone) and a weakly acid (pH 6.6) sandy Typic Paleudalf from Epe (Rainforest zone). Fertilizer materials (each applied at 0, 20 and 40 mg Zn kg<sup>-1</sup> soil) were replicated three times in completely randomised design for the soils. Crop leaf area, shoot weight, P and Zn concentration and uptake by the crop were determined after 28 days of growth. Triplicates of 400 g treated soil samples were also incubated and soil pH, 0.1N HCl extractable-Zn as well as Bray-1 P determined after 7 and 28 days. Soil type, Zn source and application rate influences were similar on plant leaf area and biomass production. Plants had significantly ( $P < 0.05$ ) more shoot yield on slightly acid Typic Paleudalf than on medium acid Oxic Paleustalf while O.F and O.F + ZnSO<sub>4</sub> applications resulted in similar yields that were higher than was produced with sole ZnSO<sub>4</sub>. Soil type and fertilizer treatments had no appreciable effect on Zn content in maize tissue while only fertilizer sources failed to tangibly influence Zn-uptake but both had pronounced effects on P nutrition. Uptake of Zn and P by plants fertilized with 20 and 40 mg Zn kg<sup>-1</sup> were essentially similar but notably higher than for untreated ones. After incubation for 7 days, both soil types had negligible increases in pH and extractable Zn but slight reductions in available-P. However, by the 28<sup>th</sup> day, pH decreased while Zn and P availability increased. Application of ZnSO<sub>4</sub> fortified organic fertilizer produced from market waste proved to be a good antidote for Zn deficiency and / or toxicity in crop plants.

**KEY WORDS:** Organic wastes, Zinc sulphate, Oxic Paleustalf and Typic Paleudalf soil types, Soil-P-Zn-pH changes.

## INTRODUCTION

Micronutrient malnutrition affects a lot of people worldwide. This is especially manifest in adults as well as children in developing countries and particularly severe with zinc (Zn) deficiency. Welch and Graham (1999) reported overwhelming concerns over the effects of low levels of micronutrients (Zn inclusive) in human diets. Zinc (Zn) deficiency is known to cause growth retardation and delay in skeletal maturation. Improving human Zn nutrition would mean enhancing Zn concentrations in plant foods (WHO, 1995). Applications of Zn fertilizers have been reported to effectively increase Zn concentrations in the edible portion of crops (Rengh *et al.* 1999).

Zinc deficiency in agricultural crops is a frequent disorder on a wide variety of tropical soils and areas with recognized deficiency increase with time (Lindsay, 1972; Sillampaa, 1990). The problem may arise through the use of purified, highly concentrated fertilizers (Munkholm *et al.* 1993) and the use of high yielding and more nutrient demanding improved crop cultivars (Chude and Ango, 1988). Maize is more sensitive to Zn supply than most other crops (Mallarino and Web, 1995). Bukvie *et al.* (1999) reported maize growth disturbance due to Zn deficiency or toxicity. The deficiency is characterized by stunted growth, overall reduction in photosynthetic efficiency and disrupted metabolism (Kanwar and Young Dahl, 1985).

Corrales *et al.* (1990) observed yield advantages accruing from the application of inorganic fertilizers but cautioned on the negative influence of their cost and availability that tend to popularise the use of organic materials as means of supplementing soil fertility in tropical areas. Organic fertilizers are particularly preferred as they contain high levels of Fe, Mn,

and Zn (Singh and Balasubramanian, 1980; Adediran, *et al.* 1996). Agboola *et al.* (1982) opined that organic and inorganic fertilizer mixtures (organo-minerals) are best for tropical soils while De Ridder and Van Keulen (1990) noted that they reduce the undesirable effects of pure inorganic fertilizers such as acidification and increased removal of nutrients other than the one supplied by the fertilizers. Significant interactions have particularly been observed between P and Zn (Marschner, 1995; Li *et al.* (2003). Organic materials applied to supplement soil Zn oftentimes supply P that may induce Zn deficiency in plants by altering both the physico-chemical and biological factors in soil-plant systems. Reduction in the bioavailability of Zn in grains and plant tissue concentrations can also occur in organic material applications (Buerkert *et al.* 1998). The work reported here sought to compare the effectiveness of organic manure (OF), ZnSO<sub>4</sub> and their mixture (OF + ZnSO<sub>4</sub>) as Zn fertilizer sources for maize growth on two tropical alfisols. Soil pH and P / Zn release dynamics as well as changes in plant tissue concentrations of P and Zn resulting from Zn fertilizer treatments were also evaluated.

## MATERIALS AND METHODS

The work involved a laboratory incubation study and a greenhouse pot experiment designed to determine the effects of ZnSO<sub>4</sub>, OF and OF + ZnSO<sub>4</sub> on soil pH changes and the availability of Zn and P for the performance of maize (Var. TZEEY-SR BC5).

Surface (0-15cm) samples of medium acid (pH 5.9) sandy clay Alfisol (Oxic Paleustalf), A from Zaria (Southern Guinea Savannah) and a weakly acid (pH 6.6) sand Alfisol (Typic Paleudalf), B from Epe (Rainforest zone) were used. The samples were air-dried, crushed and passed through a 2mm

sieve. Some characteristics of the soils determined by standard methods (Juo, 1981) are given in Table 1.

The experiments involved a split-split plot arrangement in completely randomised design with three replicates. The two soil types formed the main treatment; the Zn fertilizer sources ( $ZnSO_4$ , OF and OF +  $ZnSO_4$ ) formed the sub-treatment while the Zn application levels (0, 20 and 40 mg kg<sup>-1</sup>) formed the sub-sub treatment.

#### Incubation study

Four hundred gram-samples of each soil type were weighed into 27 Neubauer cultivation vessels, thoroughly mixed with fertilizer materials according to treatment and covered with polythene sheets to reduce evaporation while field capacity (FC) moisture content was maintained at 60 % during incubation. The soils were sampled at 7 and 28 days after incubation (DAI) and processed for the determination of available P by Bray P-1 method (Bray and Kurtz, 1954), Zn extractable by 0.1N HCl (Baker and Amagher, 1982) and soil pH at a ratio of 1:2 in distilled H<sub>2</sub>O.

#### Greenhouse experiment

The fertilizer materials were also thoroughly mixed with one-kilogram samples of the soils in plastic pots, moistened to 60 % FC and allowed to equilibrate for four days prior to planting of five pre-germinated maize seeds (*Zea mays*, L. var. TZEEY-SR EC5). Nitrogen and K were applied uniformly to all pots at the rate of 60kg N/ha (urea) and 30kg K/ha (muriate of potash, KCl) to avoid nutrient imbalance. After 28 days of growth, the above ground plant portions were harvested for the determination of leaf area (using VISTA area meter MK 2) and shoot weights. After grinding dried plant samples and wet digesting with a mixture of 25ml of HNO<sub>3</sub>, 5ml of H<sub>2</sub>SO<sub>4</sub> and 5ml of HClO<sub>4</sub>, contents of P and Zn in plant tissue were determined by absorption spectrophotometer and atomic absorption spectrophotometer (AAS), respectively. Nutrient uptake was estimated by multiplying the nutrient content values by the respective shoot dry matter.

All statistical analyses were performed using the Statistical Analysis System (SAS, 1985).

Table 1. Some physico-chemical properties of the experimental soils and fertilizer materials used.

| Properties  | Soil type                             |                                     | Fertilizer materials                            |                                      |
|---|---------------------------------------|-------------------------------------|---|--------------------------------------|
|   | A (Zaria location)<br>Oxic Paleustalf | B (Epe location)<br>Typic Paleudalf | Organic fertilizer, O.F<br>(from market wastes) | Inorganic<br>Zinc sulphate, $ZnZO_4$ |
|   |                                       |                                     | ← (%) →   |                                      |
| pH (H <sub>2</sub> O)   | 5.9                                   | 6.6                                 | ND  | ND                                   |
| Organic C (g/kg)  | 4.3                                   | 8.3                                 | ND  | ND                                   |
| Total N (g/kg)  | 1.52                                  | 0.80                                | 2.30  | ND                                   |
| Bray-1 P (mg/kg)  | 1.5                                   | 8.77                                | 0.55  | ND                                   |
| <b>Exch. bases and extractable zinc (c mol kg<sup>-1</sup>)</b> |                                       |                                     | <b>Exch. bases and some micronutrients</b>      |                                      |
| Ca  | 2.30                                  | 2.35                                | 0.36  | -                                    |
| Mg  | 1.00                                  | 0.90                                | 0.13  | -                                    |
| K   | 0.25                                  | 0.26                                | 0.47  | -                                    |
| Na  | 0.30                                  | 2.44                                | -   | -                                    |
| Fe  | ND                                    | ND                                  | 0.86  | 0.005                                |
| Pb  | ND                                    | ND                                  | -   | 0.002                                |
| Cl  | ND                                    | ND                                  | -   | 0.002                                |
| Zn  | 0.013                                 | 0.092                               | 0.019   | 22.76                                |
| Mn  | ND                                    | ND                                  | 0.034   | -                                    |
| Cu  | ND                                    | ND                                  | 0.003   | -                                    |
| <b>Particle size analysis (g kg<sup>-1</sup>)</b>               |                                       |                                     |   |                                      |
| Sand  | 400                                   | 933.3                               | -   | -                                    |
| Clay  | 130                                   | 13.3                                | -   | -                                    |
| Silt  | 470                                   | 53.4                                | -   | -                                    |
| Textural class  | Sandy loam                            | Sand                                | -   | -                                    |

ND, not determined

RESULTS

The experimental soils

Organic C, total N and available P were 4.3 g kg<sup>-1</sup>, 1.52 g kg<sup>-1</sup> and 1.50 mg kg<sup>-1</sup>, respectively prior to treatment and cropping of the Oxidic Paleustalf from Zaria location soil (Table 1). The respective values for Epe location soil were 8.30 g kg<sup>-1</sup>, 0.8 g kg<sup>-1</sup> and 8.77 g kg<sup>-1</sup>. Total N was marginal for maize production on Zaria location soil and by far less than the critical level of 1.5 g kg<sup>-1</sup> (Enwezor, *et al.*, 1979) in Epe location soil. The available P values were less than the critical level of 10-16 mg kg<sup>-1</sup> (Adeoye and Agboola, 1985). However, exchangeable K values were above the critical level of 0.18 - 0.20 cmol kg<sup>-1</sup> (Agboola and Obigbesan, 1974). The Zn values were above the critical level of 0.003 cmol kg<sup>-1</sup> (Osiname, 1972).

Effects of soil type and fertilizer treatment on plant biomass and nutrition of maize

The effects of the experimental factors (soil type, Zn fertilizer sources and levels) on both the plants' major photosynthetic (leaf) area and biomass production are indicated in Figure 1. Leaf area and dry shoot weights on the slightly acid Typic Paleudalf (Epe location soil) were higher than on the medium acid Oxidic Paleustalf (Zaria location soil). Untreated plants recorded significantly (P<0.5) less values compared with those treated with 40 mg Zn kg<sup>-1</sup> but similar with those of 20 mg kg<sup>-1</sup> soil application rates.

Soil type and fertilizer treatment influences were not appreciable on maize tissue Zn content but only the fertilizer sources failed to tangibly influence Zn-uptake by the crop (Figure 2). Maize plants grown on the slightly acid Typic Paleudalf of Epe averagely accumulated up to 1.10 mg Zn pot<sup>-1</sup> compared with just 38.2 % of this (0.42 mg Zn pot<sup>-1</sup>) for those grown on the medium-acid Oxidic Paleustalf of Zaria. Treatment with 40 mg Zn kg<sup>-1</sup> soil led to mean Zn uptake value that was thrice that of the untreated plants. Zinc uptakes for plants

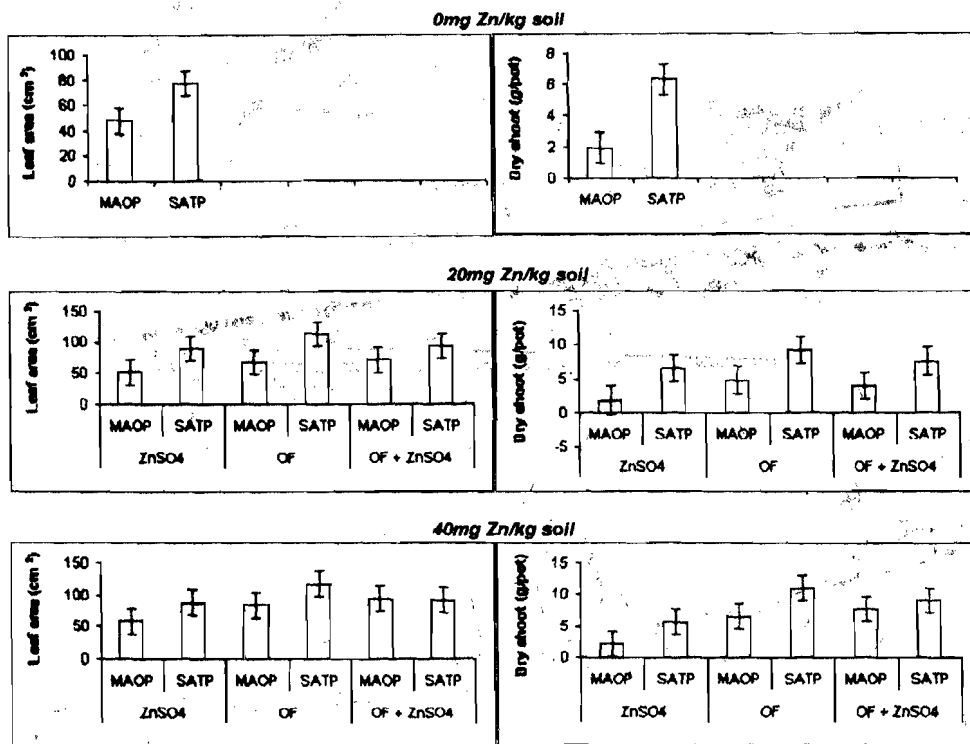


Figure 1. Effects of soil type and fertilizer treatment interactions on leaf area and shoot weight of maize.

[MAOP = medium acid Oxidic Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer]

grown with 20 mg Zn kg<sup>-1</sup> soil were not significantly different from the untreated ones but averagely 74.8 % of the maximum. Soil type, fertilizer sources and application rates had greater influence than this on the content and uptake of P. Except for fertilizer sources, the other experimental factors (soil type and fertilizer application rates) caused significant differences in maize P contents (Figure 3). On the average, maize plants grown on the slightly acid Alfisol (Typic Paleudalf) of Epe recorded 0.58 % tissue P content as against 0.24 % for those grown on the medium acid Alfisol (Oxidic Paleustalf) at Zaria. The control plants had a mean of 0.34 % tissue P content compared with the significantly higher average of 0.45 % for the treated ones. Maize P uptake was affected by soil type in a similar way to that of the tissue P-content as the slightly acid Alfisol (Typic Paleudalf) favoured more uptake (44 mg P pot<sup>-1</sup>) than the medium acid Alfisol (Oxidic Paleustalf) with

10 mg pot<sup>-1</sup>. Organic fertilization (O.F) enhanced greater uptake of P by the crop than ZnSO<sub>4</sub> but had virtually the same effect as O.F + ZnSO<sub>4</sub> (Figure 3). P-uptake by plants fertilized with 20 and 40 mg Zn kg<sup>-1</sup> soil were essentially similar (28 and 34 mg pot<sup>-1</sup>, respectively) but notably higher than estimated for those of the untreated ones (17.5 mg pot<sup>-1</sup>).

Changes in soil pH and availability of phosphorus and zinc in incubated soils

The relevance of soil type, fertilizer sources and application levels was further revealed through the incubation study. Figures 4 - 6 summarize their effects on pH, extractable Zn and available P after 7 or 28 days of incubation. Prior to treatment, the Oxidic Paleustalf was a medium acid soil having lower amounts of extractable Zn and available-P than the Typic Paleudalf. The trend was essentially maintained during

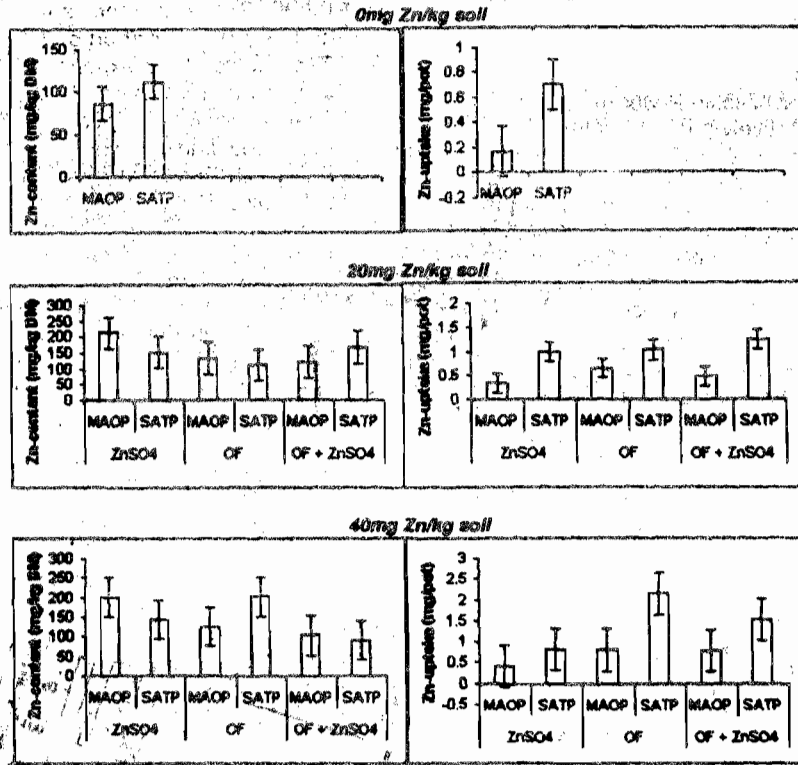


Figure 2. Effects of soil type and fertilizer treatment interactions on zinc content and uptake by maize. (MAOP = medium acid Oxis Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer)

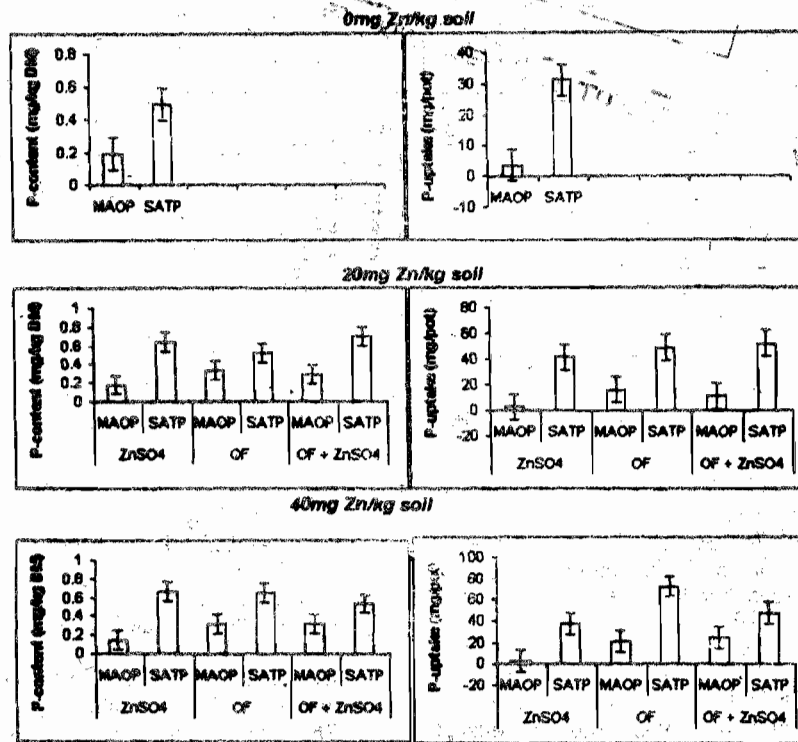


Figure 3. Effect of soil type and fertilizer treatment interactions on phosphorus content and uptake by maize. (MAOP = medium acid Oxis Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer)

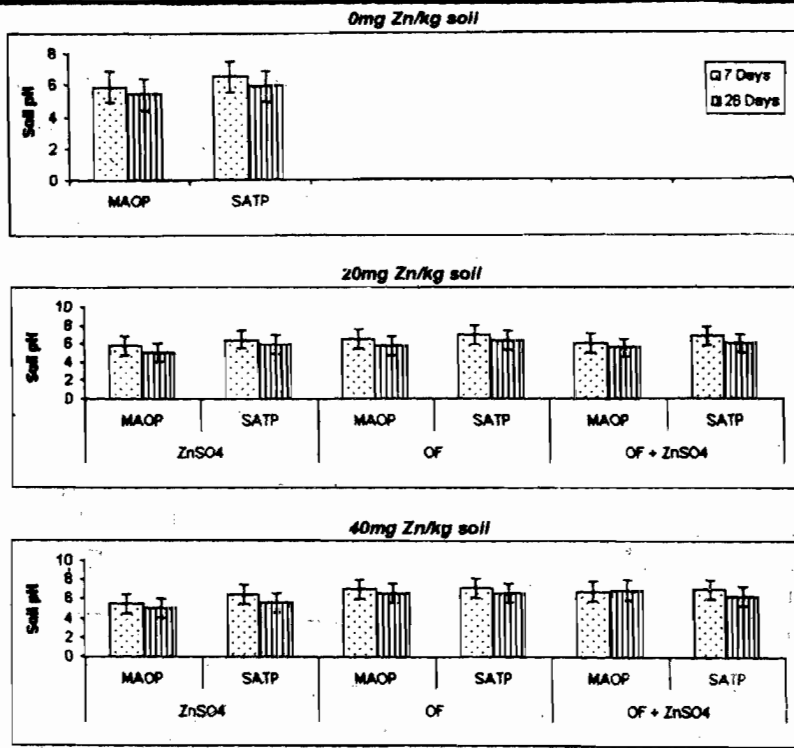


Figure 4. Effects of soil type and fertilizer treatment interactions on soil pH after 7 and 28day-incubation periods. [MAOP = medium acid Oxic Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer]

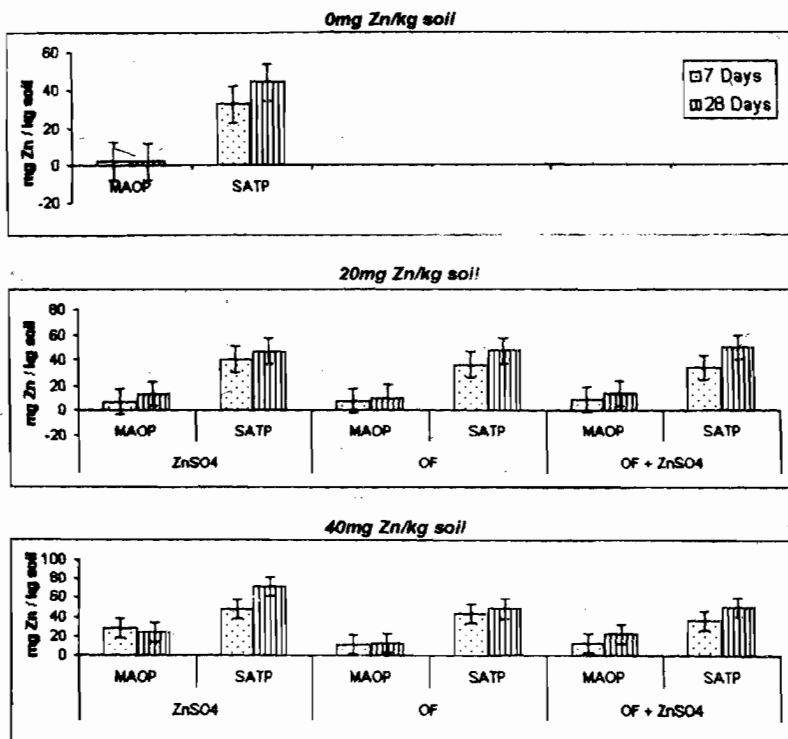


Figure 5. Effects of soil type and fertilizer treatment interactions on extractable zinc after 7 and 28 day-incubation periods [MAOP = medium acid Oxic Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer]

incubation. Initially (after 7 days), both soil types had negligible increases in pH and extractable Zn but slight reductions in available-P. However, by the 28<sup>th</sup> DAI, pH decreased while extractable-Zn increased sharply and P availability rose above the level obtained at 7 DAI though less than the pre-treatment

values (Figure 6). Similarly, there were significant changes in soil acidity and P availability caused by the application of the fertilizer materials. At 7 DAI, O.F and O.F + ZnSO<sub>4</sub> treated soils were less acidic than ZnSO<sub>4</sub> treated soils, sole O.F application caused the highest P availability while the quantity

of extractable Zn was essentially the same irrespective of the fertilizer material applied. At 28 DAI, the pH of O.F, ZnSO<sub>4</sub> and O.F + ZnSO<sub>4</sub> treated soils declined to average values of 6.2, 5.4 and 5.8, respectively (Figure 4) while the extractable-Zn values increased (Figure 5). Both O.F and O.F + ZnSO<sub>4</sub> caused lower pH decline than sole ZnSO<sub>4</sub> during incubation but all the three fertilizer sources had similar amounts of extractable-Zn and available-P. With respect to fertilizer application rates, the pH, extractable-Zn and available-P of the untreated and treated soils were similar but increased with incubation. However, 40 mg Zn kg<sup>-1</sup> soil treatment resulted in pH of 6.2, extractable-Zn of 38.5 mg kg<sup>-1</sup> and available-P of 6.8 mg kg<sup>-1</sup> at 28 DAI. These were significantly different from the control (Figures 4-6).

## DISCUSSION

The remarkable differences in leaf area and biomass production of maize plants grown on the two soil types are attributable to the differences in the physico-chemical properties of the soils. The slightly acid Typic Paleudalf (Soil B) was more fertile, having almost neutral pH (even after incubation of treated soil samples) compared with the medium acid Oxidic Paleustalf (Soil A). The higher inherent fertility and favourable pH facilitated the release of higher amounts of nutrients for plant growth on soil B (of Epe) than on soil A (of Zaria).

Soil fertility can be maintained with the use of organic manures alone (Dennison, 1961) or in combination with inorganic fertilizers (Klausner and Guest, 1981; Agboola, 1982;

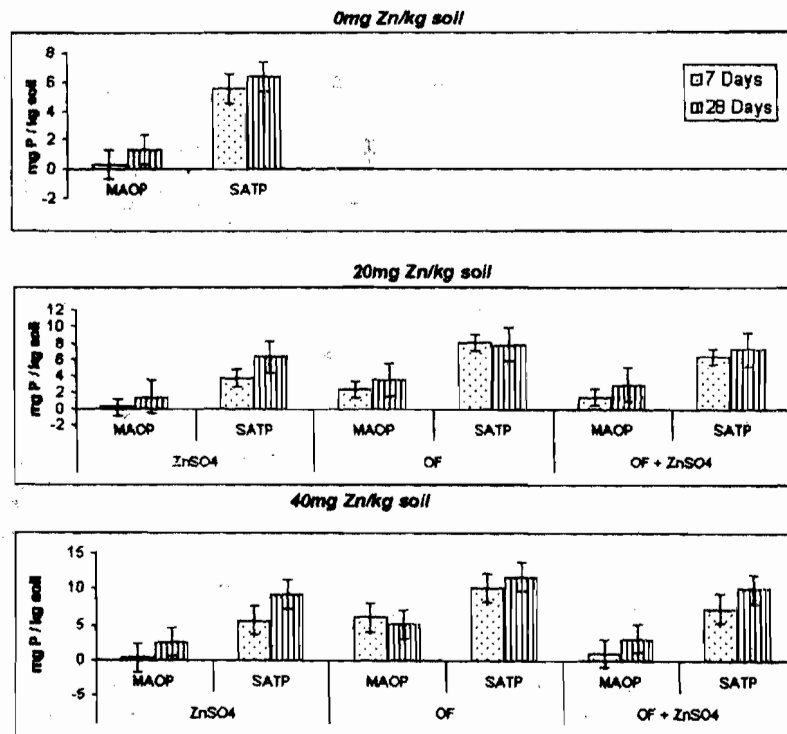


Figure 6. Effects of soil type and fertilizer treatment interactions on available phosphorus after 7 and 28 incubation periods (MAOP = medium acid Oxidic Paleudalf; SATP = slightly acid Typic Paleudalf; OF = Organic fertilizer)

Mantovalli, *et al.* 1989). The use of organic manure in combination with inorganic fertilizers serves to reduce the negative effects of inorganic fertilizers, particularly in respect of acidification and increased removal of nutrients other than the one supplied by the fertilizer (De Ridder and Van Keulen, 1990). Thus, the fortification of O.F with ZnSO<sub>4</sub> in this study could have directly reduced the negative effects of, and improved the efficiency of ZnSO<sub>4</sub> but had no negative effect on the efficiency of O.F. This was evidenced by improved photosynthetic surface area and higher dry shoot yield of the crop. The significant reduction of the effects of sources of Zn fertilizers on these parameters should have been due to the toxicity effects of high concentrations of Zn in the soils. This is particularly so in soil B (slightly acidic Typic Paleudalf of Epe). Li *et al.* (2003) similarly attributed the reduction in plant biomass as Zn addition was made under low P conditions to Zn toxicity. They further reported the resumption of plant biomass increases when high P addition was made. In this study, it seems obvious that ZnSO<sub>4</sub>-fortified O.F ameliorated the condition of Zn toxicity caused by ZnSO<sub>4</sub> in line with the earlier stated view of De Ridder and Van Keulen (1990). In an

earlier study on tomato plant (Adediran *et al.* 1996), it was explained that O.F acted as a reservoir of nutrients. Vanlauwe *et al.* (2001) reported recently that application of urea-fortified organic materials significantly increased dry matter accumulation of maize stover in Zaria (Guinea Savanna zone), Nigeria.

The increase in extractable-Zn during incubation and a rise in available-P at 28 DAI after a fall at 7 DAI were suggestive of a possible negative relationship between Zn and P. This is common knowledge and Singh *et al.* (1988) reported the mechanism using bean (*Phaseolus vulgaris* L) plant tissues:

The fact that maize plants performed best at 40 mg Zn kg<sup>-1</sup> is indicative of positive interactive effect of Zn and P at that rate of Zn fertilizer application. This was evidenced by both the content and uptake of the nutrient elements by maize plants after 28 DAP as well as the extractable-Zn and available-P values especially at 28 DAI. Apart from containing 0.02 % Zn, the organic manure had 0.55 % P and reasonably high proportions of other nutrient elements (2.30 % N and 0.47 % K) (Table 1). This is an indication that for every gram addition of Zn through O.F, about 27.5 g of P is also added. These

observations were also supported by Li *et al.* (2003) who demonstrated that nutrient deficiency is a relative measure of soil fertility dependent on the balance of the limiting nutrients. These workers observed deleterious effects of Zn-P imbalance on barley only at a high Zn concentration of 150 mg Zn kg<sup>-1</sup>. Huang *et al.* (2000) explained that Zn deficiency caused an increase in the expression of P transporter genes both in P-deficient and P-sufficient barley roots, and this condition may induce P toxicity in plants (Loneragan *et al.*, 1982). In this work, however, the significantly reduced content and uptake of P in the untreated maize plants is attributable to P deficiency in the original soils.

The pronounced effects of soil type on the content and uptake of tissue P and uptake of tissue Zn as well as the extractable-Zn and available-P upon incubation was a further confirmation of the superior or better fertility status of soil B (of Epe) over soil A (of Zaria). Nevertheless, a fertile soil may still require further addition of Zn for maximum plant growth if high levels of P fertilizer are applied (Li *et al.* 2003).

Reduction in uptake and content of tissue P and uptake of tissue Zn of the test crop grown on soil A, together with similar reduction in soil extractable Zn and available P upon incubation, are further reflections of the low fertility status of the soils as evidenced by pH decline to 5.5 at 28 DAI. Besides, the insignificant difference in the extractable-Zn from soils treated with inorganic Zn fertilizer (ZnSO<sub>4</sub>) compared with that from soils treated with the other fertilizer sources (O.F and O.F + ZnSO<sub>4</sub>) might have partly resulted from the reduced pH values at 28 DAI and partly from the increased concentrations of Zn (relative to native P) in soil B, which might have induced Zn toxicity (Li *et al.*, 2003). It is probable that the reservoir of nutrients in organic manure (O.F) (Adediran *et al.* 1996) and the ameliorative capacity of organic manure – inorganic fertilizer mixtures (De Ridder and Van Keulen, 1990) remarkably increased the uptake of P and Zn in the maize plants. This was further substantiated by the higher amounts of Zn (31mg Zn kg<sup>-1</sup>) and P (5.2 mg P kg<sup>-1</sup>) determined at 28 DAI. It is obvious, therefore, that combined use of organic and mineral fertilizers such as ZnSO<sub>4</sub> fortified O.F could be a good antidote for the antagonistic interaction between P and Zn that may result in Zn deficiency or toxicity in crop plants.

REFERENCES

Adediran, J. A., Taiwo, L. B. and Sobulo, R.A. 1996. Comparative nutrient values of some solid organic wastes and their effect on tomato (*Lycopersium esculentus*) yield. Institute of Agricultural Research and Training (IAR&T), Obafemi Awolowo University, Moor Plantation, Ibadan, Nigeria. Pp. 99-116.

Adeoye, G.O and Agboola, A.A. 1985. Critical levels for soil pH, available P, K, Zn and Mn and ear-leaf content of P, Cu and Mn in sedimentary soils of South Western Nigeria, Fertilizer Research 6: 65-71.

Agboola, A.A. and G. O. Obigbesan. 1974. The response of some improved food crop varieties to fertilizers in the forest zone of Western Nigeria. In: Report of FAO/NORAD/FAD seminar on fertilizer use development in Nigeria, Ibadan

Agboola, A.A. ; G. O. Obigbesan, and A. A. Fayemi. 1982. Effect of organic matter (farm yard manure), lime and phosphorus fertilizer on the yield of cowpea. FAO Soil Bulletin. 27 : 339.

Baker, D. E., and Amacher, M. C. 1982. Nickel, copper, zinc and cadmium, In: Methods of Soil Analysis. Part 2 pp. 323-326. Agronomy 9. Soil Sci. Soc. Amer. Madison, Wisc. USA.

Bray, R. H. and Kurtz, L. T. 1954. A nutrient mobility concept of soil-plant relationships. Soil Sci. 78 : 9-22.

Buerkert, A., Haake, C., Ruckwied, M. and Marschner, H., 1998. Phosphorus application affects the nutritional quality of millet grain in the Sahel. Field Crops Res. 57: 223-235.

Bukvie, G., Teklic, T. and Marketic, M., 1999. The influence of P and Zn fertilization on some morphological characteristics of maize inbred lines (*Zea mays* L.). Cereal Research Communication. 27, 3

Chude, V. O and Ango, A. M., 1988. Relative efficiency of three zinc sources for maize (*Zea mays* L.). Paper presented at the 16th. Annual Conference of the Soil Science Society of Nigeria, University of Science and Technology, Minna, 27-30 Nov. 1988.

Corrale, G., Guerra, A. and Montes de Oca, F., 1990. Potassium fertilization effect on yield and its components in banana vicands in a brown with carbonates soil ciencia. Technica enla Agric. 13 : 7-16.

Dennison, E. B., 1961. The value of farmyard manure in maintaining fertility in northern Nigeria. Empir. Journ. Exper. Agric. 29:330-336.

De Ridder, N. and Van Keulen, H., 1990. Some aspects of the role of organic matter in sustainable intensified arable farming system in West African Semi-Arid Tropics (SAJ). Fertilizer Research 26:299-310.

Enwezor, W.O., Udo, E. J., Usoroh, N. J., Ayotade, K. A., Adepetu, J. A., Chude, V. A and Udegbe, C. I. 1979. Fertilizer use and management for crops in Nigeria. Series 2, pp. 163.

Huang, C.Y., Barker, S.J., Langridge, P., Smith, F. W. and Graham, R. D. 2000. Zinc deficiency up-regulates expression of high affinity-deficient barley (*Hordeum vulgare* L. CV Weeah) roots. Plant physiol. 124:415-422.

Juo, A. S. R., 1981. Automated and semi-automated methods for soils and plant analyses. IITA, Manual series, No. 7, Ibadan, Nigeria. pp. 155

Kanwar, J. S and Youngdahl, L. J., 1985. Micronutrient needs of tropical food crops. Fertilizer Research, 7: 131-150.

Klausner, S.D. and Guest, R.W. 1981. Influence of NH<sub>3</sub> conservation from dairy manure on the yield of corn. Agron. J. 73: 720-723.

Li, H. Y., Zhu, Y. G., Smith, S. E. and Smith, F.A., 2003. Phosphorus-zinc interactions in two barley cultivars differing in phosphorus and zinc efficiencies.

Lindsay, W. L., 1972. Inorganic phase equilibria of micronutrients in soils. p. 41-58. In: J. J. Mortvedt *et al.* (eds). Micronutrients in Agriculture. Soil Sci. Soc. Amer., Madison, Wis.

- Loneragan, J. K., Grunes, D.L., Welch, R. M., Aduayi, E. A., Tengah, A., Lazar, V.A. and Gary, E.E., 1982. Phosphorus accumulation and toxicity in leaves in relation to zinc supply. *Soil Sci. Soc. Am. J.* 46:345-352.
- Mallarino, A. P and Webb, J. R. 1995. Long term evaluation of P and Zn interaction in corn. *J. Prod. Agric.*, 8 (1): 52-55
- Marschner, H., 1995. Mineral nutrition of higher plants. Academic Press, London
- Montavalli, P.P., Kelling, K. A. and Converse, J. C., 1989. First-year nutrient availability from injected dairy manure. *Journ. Environ. Qual.* 18:180-185.
- Munkholm L. J., Esu, J. and Moberg, J. P., 1993. Trace elements in some northern soils. *Commun. Soils Sci. Plant Analysis.* 24, 657-672.
- Osiname, O. A., 1972. Soil test for available Cu and Zn in soils of western Nigeria. Ph.D Thesis, University of Wisconsin, Madison.
- Rengh, Z., Batten, G.D. and Crowley, D. E., 1999. Agronomic approaches for improving the micronutrient density in edible portions of field crops. *Field Crop Res.* 60:27-40.
- SAS, Institute, 1985. SAS user's guide: Statistics. 5<sup>th</sup> ed. SAS Inst. Cary, NC.
- Sillampaa, M., 1990. Micronutrient assessment at the country level: an international study. *Soils Bulletin.* 63, FAO, Rome.
- Singh, J. P and Balasubramanian, V., 1980. Organic recycling in Asian agriculture. In *FAO organic recycling in Africa.* FAO Soils Bulletin, 43: 235-278.
- Singh, J.P, Karamanos, R.E. and Stewart, J.W.B., 1988. The mechanism of phosphorus-induced zinc deficiency in bean (*Phaseolus vulgaris*, L.). *Canadian J. Soil Sci.* 68:345-358.
- Vanlauwe, B., Aihou, K., Aman, S., Iwuafor, E.N.O., Tossah, B.K., Diels, J., Saginga, N., Lyasse, O., Merckx, R. and Deckers, J. 2001. Maize yield as affected by organic inputs and urea in the West African Moist Savanna. *American Society of Agronomy, Agronomy Journal* 93:1191-1199.
- Welch, R. M and Graham, R.D., 1999. A new paradigm for world agriculture: Meeting human-needs, productive, sustainable and nutritious. *Field Crops Res.* 60: 1-10.
- WHO, 1995. World Health Organisation: Trace Elements in Human Nutrition and Health. Geneva, 343 pp.