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Full Length Research Paper

Effects of cow-dung and rock phosphate on heavy metal content in soils and plants

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Field trial was conducted with the view to determining the ideal rock phosphate (RP) and the level of cow dung fertilizer combination with respect to heavy metal contamination of soil and crops. Soils amended with Ogun rock phosphate (ORP) were subjected to 1-4 tha^{-1} of cow dung on which maize (*Zea mays* (L) _ and okra (*Abelmuscus esculentum)* were planted. The amended soils were found to be enriched with heavy metals (Pb, Zn, Cu and Cd) more than the unamended soil but were still within the tolerable level with the exception of Cd which had a high value of 5.30 ∝g g^{-1} above the critical value of 3∝g g^{-1}. The application of RP in combination with various levels of cow dung elevated the Pb, Zn and Cu content in the tissue of maize relative to the control. The Zn and Pb content of okra were not affected except for Cu and As in soil amended with RP and various levels of cow dung relative to the control. Transfer factor (TF) was higher in the treatment with RP supplemented with 2 t ha^{-1} of cow dung particularly for Pb and Zn for both crops relative to other treatments. Except for Cu and Zn, increasing the level of cow dung while RP did not increase the TF value of the heavy metals to the crops.

Key words: Rock phosphate, cow dung manure, heavy metal contamination, tolerable level, transfer factor.

INTRODUCTION

In the sub- Saharan Africa, increasing attention is being paid to the development of a low input nutrient management strategy without degrading the resource base. Peasant farmers are increasingly finding it difficult to access the inorganic chemical fertilizers for soil productivity improvement due to high cost of procurement and logistic problems. Although, various options are being used to overcome these problems, the most pressing challenge among the farmers is the utilization of rock phosphate (RP) as a low cost input in a low phosphate (p) soil.

The inherent capability of the rock phosphate to supply plant-available phosphate under a specified set of conditions may provide an advantage of increasing crop production in a low P soil. The main pitfalls of direct application of RP identified include poor dissolution of rock phosphate and naturally occurring metallic contaminants such as: Cd and Zn (Carnelo et al., 1997) that could elevate the normal background content of these elements in the soils. Mortvedt et al. (1981) and Oyedele et al. (2006) associated the increase in soil Cd in agricultural soils compared to non agricultural soil with the application of phosphate fertilizer. Cadmium is not required by plants, but is easily absorbed by some plants if available and at higher levels it could be toxic (Oyedele et al., 2006). Health hazards associated with heavy metals entering food chain through soil is demanding attention.

Farmyard manure has been found to have a strong driving force for the dissolution of phosphate rock thereby increasing the available phosphate for crops (Singh et al., 1991). The efficacy of cow dung in facilitating the release of phosphate from applied rock phosphate has been reported by Akande et al. (2005, 2006). Cow dung, a type of farmyard manure is mainly the excreta collected from cattle. It can be applied as manure in the form of slurry or dried to soils (Akande et al., 2006). The changes in soil properties with the application of cow dung could affect the form and bioavailability of metals, and need to be considered in decisions on the management of polluted

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soils. High agricultural inputs are unlikely to be sustain-nable for a long period unless the inputs are correctly judged in terms of both their quality and environ-mental implications. The influence of organic fertilizer such as cow dung manure in combination with RP on soil and crops heavy metal content needs to be investigated. This study was therefore designed to determine the influence of cow dung as a modifier of Ogun rock phosphate (ORP) on the heavy metal content of soil cropped with maize and okra. It was also aimed at evaluating the optimum ORP and level of cow dung fertilizer combinations with respect to Zn, Cu, Pb, Cd and As metal contamination of soil and the crops.

MATERIALS AND METHODS

Study site

The study was carried out on an existing experimental site for 4 years in the Institute of Agriculture Research and Training (IART) Moor Plantation, Ibadan, Nigeria. The experimental site lies between Latitude 7º 31¹ and Longitude 3º 54¹ with annual rainfall of 1350 mm bimodally distributed throughout the year (Awotoye and Matthew, 2010). The soil is an Aquic Arenic Haplustalf. The experiment had been on going for four years before samples were collected. The site was established in the year 2001 and the cropping history revealed that mixed cropping of maize (*Zea mays)* and okra (*Abelmuschus esculentum)* were the only cropping system on the experimental units. Crop rotation was occasionally done with the planting of groundnut (*Arachis hypogeal*) to replenish the nitrate content of the soil.

Experimental set up

The field layout was complete randomized plot design consisting of 6 treatments including control and having 3 replicate treatments each. The treatments were done using Ogun rock phosphate (ORP) and four levels of cow dung (1, 2, 3 and 4 tons). The cow dung was collected from the livestock unit of the Institute. The chemical analysis of both the cow dung and ORP fertilizers are shown in Table 1. The ORP treatments were given a basal rate of 100 kg ha^{-1} of P_2O_5 and the application rates are shown in Table 2.

Sampling

Soil samples were collected using a Dutch soil auger in composite replicates of soil core samples at different depths of 0 to 15 cm (top soil) and 15 to 30 cm (sub soil). On each experimental unit, 15 to 25 soil cores per composite samples were collected and thoroughly mixed in clean plastic buckets. Sub samples were then taken to the laboratory, air dried and sieved through 2 mm sieve. Recently mature leaf samples of maize and okra plants were collected before fruiting of crops, dried and prepared for heavy metal analysis.

Laboratory analysis

The plant samples were digested with concentrated H_2SO_4 and 50% (v/v) H_2O_2 at about 90°C as described by Oyedele et al. (2008). The digests were analyzed for Cd, Pb and Hg, using a Perkin Elmer flame atomic absorption spectrophotometer (FAAS). Phosphorus in the digest was analysed using the vanado-molybdate method The soil P content was extracted using Bray No 1 method (Bray and Kurtz, 1945) and the P content in the extract was determined colorimetrically using a Spectron $20D^+$ spectrop-hometer.

To extract the heavy metals, 1 g of sieved soil sample was digested with 10 ml of aqua regia (12 M HCl and 6 M HNO_3 that was in ratio 3:1) and heated to dryness at a temperature of 100°C in a fume cupboard as described by Warren and Dela (1959). This was then leached with 5 ml HCl, filtered and made up to 25 ml and Cd, Pb and Hg contents determined with a Perkin Elmer FAAS. One gram of 2 mm sieved air dried soil was weighed into a conical flask and 1 ml of HNO_3 and 3 ml of HCl (*aqua regia*) were added to the samples. The content was heated on a hot plate in fume cupboard to dryness at 100°C (Warren and Dela, 1959). The residue was allowed to cool and leached with 5 ml of 2 M HCl . The extract was then used for the determination of the total metals (Zn, Pb, Mg, Cd, Ca and As) using atomic absorption spectrophotometer (AAS) while K and Na were determined using the flame photometer (Oyedele et al., 2008). The soils pH was determined by the electrometric method using a glass electrode pH meter (Model 20 of Denver instrument, Dallas, USA). To be able to determine the degree of soil contamination, the soil enrichment factor was computed as the ratio of concentration of the metals in plants relative to that of the soil according to the method by Oyedele et al. (1995).

Statistical analysis

The data obtained were subjected to analysis of variance (ANOVA) to test for treatment effect. Test of significance for differences in means was done using least square differences (LSD) method. Correlation coefficient was used to determine the association between soil heavy metals, pH and phosphorus content and plant shoots. The statistical analysis was carried out using the SAS package for windows (2000).

RESULTS AND DISCUSSION

Heavy metal levels in soils

The effects of the application of ORP and various levels of cow dung fertilizer on nutrient composition on both top soil and sub soil were similar and therefore pooled together (Table 3). The complementary applica-tion ORP fertilizer plus cow dung did not affect the concentration of the exchangeable cations of the soil. Although application of sole ORP fertilizer elevated the soil Pb level, however, with increase in the level of cow dung combination, the soil Pb content decreased (Table 3). In contrast, the combination of ORP with different levels of organic fertilizers did not alter the Zn, Cu and As contents of the soil, the Cd content of the soil was raised with increasing in organic fertilizer application (Table 3). This is not unexpected probably because the ORP treatments increased their retention through adsorption to the mineral and soil particles. The high value of 5.30 μg g^{-1} of dry soil observed for Cd was above the tolerable limit of 3 μg g^{-1} for Cd recommended by Kabata-Pendias and Pendias (1984).

Table 4 depicts the nutrient content of *Zea mays* following the combined application of ORP with various

Table 1. Some chemical properties of Ogun rock phosphate and cow dung.

Sample	Exchangeable cation			Heavy metal						
	P	Ca	Mg	Mn	Pb	Zn	Cu	Fe	Cd	As
	------- %-----			-------∝g g^{-}-------						
ORP	11.3	0.17	0.30	0.11	0.004	0.02	0.01	0.13	0.08	0.01
Cow dung	0.5	1.67	0.22	0.20	0.10	0.26	0.28	0.13	0.00	0.01

ORP = Ogun Rock phosphate.

Table 2. Treatments and application rates of ORP and cow dung fertilizers.

Treatment	Application rate
- ORP-CD (Control)	No ORP and cow dung were applied
ORP	ORP only
ORP-CD 1	ORP + 1 t ha-1 of cow dung
ORP-CD 2	ORP + 2 t ha-1 of cow dung
ORP-CD 3	ORP + 3 t ha-1 of cow dung
ORP-CD 4	

ORP + 4 t ha-1 of cow dung, ORP = Ogun Rock phosphate, CD = Cow dung, 1, 2, 3 and 4 represent tons of cow dung.

Table 3. Effects of the combined application of ORP and various levels of cow dung fertilizer on the pH, exchangeable cations, available P and heavy metals content of sub- surface (0-30 cm) soil.

Treatment	Exchangeable cation						Heavy metal				
	pH	Ca	Mg	K	Na	P	Pb	Zn	Cu	Cd	As
	----cmol kg^{-1}----						-----∝g g^{-1}-----				
- ORP-CD	5.7^{b}	1.53^{ab}	1.30^{a}	0.80^{ab}	2.16^{a}	9.34^{c}	6.07^{b}	7.55^{a}	6.68^{a}	3.53^{bc}	0.87^{a}
ORP	5.9^{ab}	1.33^{b}	1.27^{a}	0.54^{b}	2.34^{a}	10.53^{bc}	7.30^{a}	8.72^{a}	6.93^{a}	3.30^{c}	0.87^{a}
ORP-CD$_1$	6.1^{a}	1.64^{a}	1.21^{a}	0.78^{ab}	2.13^{a}	11.72^{abc}	6.70^{ab}	8.74^{a}	7.42^{a}	3.76^{bc}	0.92^{a}
ORP-CD$_2$	6.0^{a}	1.63^{a}	1.20^{a}	0.42^{b}	2.49^{a}	12.90^{ab}	6.50^{b}	8.20^{a}	8.20^{a}	4.10^{b}	0.65^{a}
ORP-CD$_3$	5.9^{ab}	1.65^{a}	1.20^{a}	1.02^{a}	1.90^{a}	12.90^{ab}	6.37^{ab}	8.17^{a}	7.57^{a}	4.40^{ab}	0.93^{a}
ORP-CD$_4$	5.8^{ab}	1.71^{a}	1.11^{a}	1.02^{a}	1.90^{a}	14.17^{a}	6.05^{b}	8.67^{a}	7.77^{a}	5.30^{a}	0.97^{a}

Means within the same column followed by the same letters are not significantly different from each other at P <0.05 according to the New Duncan multiple range test (NDMRT), ORP = Ogun Rock Phosphate, CD = Cow dung, ORP-CD 1 – 4 = Represent Ogun Rock Phosphate at different levels, 1, 2, 3 and 4 represent tons of cow dung, - ORP-CD represents no organic rock phosphate and cow dung application.

Table 4. Effect of the combined use of ORP and various levels of cow dung on the nutrient content of *Zea mays*.

Treatment	Exchangeable cation					Heavy metal				
	Ca	Mg	K	Na	P	Pb	Zn	Cu	Cd	As
	-------%-------					------ ∝g g^{-1}------				
-ORP-CD	0.20^{b}	5.50^{a}	0.35^{b}	0.33^{b}	0.41^{a}	116.67^{ab}	246.67^{a}	246.33^{a}	0.77^{c}	0.77^{a}
ORP	0.39^{ab}	3.34^{a}	0.25^{c}	0.43^{a}	0.43^{a}	83.33^{b}	310.00^{a}	163.33^{a}	0.86^{c}	0.53^{a}
ORP-CD$_1$	0.34^{ab}	4.83^{a}	0.27^{c}	0.46^{a}	0.44^{a}	98.33^{b}	318.33^{a}	148.33^{a}	1.02^{b}	0.57^{a}
ORP-CD$_2$	0.53^{a}	4.71^{a}	0.41^{a}	0.36^{b}	0.38^{a}	158.33^{a}	282.00^{a}	141.67^{a}	1.19^{b}	0.50^{a}
ORP-CD$_3$	0.50^{a}	5.17^{a}	0.34^{b}	0.35^{b}	0.42^{a}	161.67^{a}	353.33^{a}	153.33^{a}	1.38^{ab}	0.73^{a}
ORP-CD$_4$	0.48^{a}	3.92^{a}	0.27^{c}	0.31^{b}	0.44^{a}	161.67^{a}	375.00^{a}	176.66^{a}	1.60^{a}	0.83^{a}

Means with the same value column followed by the same letters are not significantly different from each other at P < 0.05 according to the New Duncan multiple range test (NDMRT), ORP = Ogun Rock Phosphate, CD = Cow dung, ORP-CD $_{1-4}$ = Represent Ogun Rock Phosphate and cow dung at different levels, 1, 2, 3 and 4 represent tons of cow dung, - ORP-CD represents no organic rock phosphate and cow dung application.

Table 5. Effect of the combined application of ORP and various levels of cow dung on the nutrient contents of *Abelmuschus esculentum*.

Treatment	Exchangeable cation					Heavy metal				
	Ca	Mg	K	Na	P	Pb	Zn	Cu	Cd	As
	------%-----					------∝g g^{-1}-----				
- ORP-CD	0.39^{a}	4.83^{a}	1.10^{a}	0.27^{c}	0.35^{a}	133.33^{a}	350.00^{a}	123.33^{b}	1.49^{a}	1.10^{a}
ORP	0.52^{a}	3.80^{a}	0.92^{ab}	0.27^{c}	0.36^{a}	105.50^{b}	340.67^{a}	206.67^{a}	1.49^{a}	1.43^{a}
ORP-CD_1	0.45^{a}	3.67^{a}	1.05^{a}	0.40^{ab}	0.32^{a}	126.67^{ab}	310.67^{a}	170.00^{ab}	0.99^{ab}	1.23^{a}
ORP-CD_2	0.48^{a}	4.33^{a}	0.50^{b}	0.35^{b}	0.35^{a}	123.33^{ab}	320.33^{a}	126.67^{b}	0.73^{b}	1.33^{a}
ORP-CD_3	0.30^{a}	4.83^{a}	0.73^{ab}	0.63^{a}	0.36^{a}	108.00^{b}	360.00^{a}	156.67^{ab}	1.16^{ab}	1.23^{a}
ORP-CD_4	0.32^{a}	5.54^{a}	0.73^{ab}	0.33^{b}	0.34^{a}	105.50^{b}	330.00^{a}	150.67^{b}	1.09^{ab}	1.20^{a}

Means with the same value column followed by the same letters are not significantly different from each other at $P < 0.05$ according to the New Duncan Multiple range test (NDMRT), ORP = Ogun Rock Phosphate, CD = Cow dung, ORP-CD $_{1-4}$ = Represent Ogun Rock Phosphate and cow dung at application.

Table 6. Comparative effects of the application of ORP and various levels of organic fertilizer on *Abelmuschus esculentum* and *Zea mays* nutrient contents.

Crop	Exchangeable cation					Heavy metal				
	Ca	Mg	K	Na	P	Pb	Zn	Cu	Cd	As
	----- %----					------∝g g^{-1}------				
Okra	0.41a	4.50a	0.84a	0.38a	0.34b	110.06a	347.78a	150.00a	1.11a	1.19a
Maize	0.41a	4.58a	0.31b	0.37a	0.42a	125.50a	313.39a	171.11a	1.13a	0.66b

Means with the same value column followed by the same letters are not significantly different from each other at $P < 0.05$ according to the New Duncan Multiple Range Test (NDMRT).

levels of cow dung fertilizers. No definite trend was observed on the exchangeable cations content of *Zea mays* with respect to ORP and cow dung treatments.

However, the Pb and Cd contents of maize were elevated by the combined application of ORP with cow dung. Cadmium content increased with increase in cow dung levels, the content doubles as the cow dung application increased to 4 tha^{-1}.

The response of *Abelmuschus esculentum* to ORP at various levels of cow dung application (Table 5) was similar to that of *Zea mays*. Ogun rock phosphate significantly elevated the Cu content of *A. esculentum* by 68% when compared with unfertilized plants. The sole application of ORP to *A. esculentum* plants did not influence the Pb content, however, the combined use of ORP with high levels of organic fertilizers elevated Pb content in the plant. The concentration of Cd in the *A. esculentum* showed that only the treatment ORPCD2 was significantly different. Neither sole application of ORP nor combined use of ORPCD$_2$ and cow dung had an appreciable effect on the As content of *A. esculentum*.

Table 6 shows the comparative effect of the application of ORP and various levels of cow dung on basic cations and heavy metal contents of *Zea mays* and *A. esculentum*. The complementary use of ORP and cow dung enhanced the K content appreciably in *A. esculentum* compared with Zea mays. The P content was affected by the application of the fertilizers and was higher in maize than okra. Except for As content, the effect of complementary use of ORP and cow dung on the heavy metals content in both *Zea mays* and *A. esculentum* was not significantly different. However, according to Stewart et al. (1974), the naturally occurring concentrations of heavy metals in the tissue of plants are as follows; 0.01 to 0.03 ∝g g^{-1} for Cd; 0.5 to 3 ∝g g^{-1} for Pb; 2.5 to 25 ∝g g^{-1} for Cu, 15 to 100 ∝g g^{-1} for Zn, 0.01 to 1.0 ∝g g^{-1} for As and the element P is 0.05 to 0.3 ∝g g^{-1}. Results from this study indicated that Pb, Zn, Cu and Cd contents of *Zea mays* plant tissue were above the normal range recommended by Kabata-Pendias and Pendias (1984).

Table 7 depicts the extent of heavy metals contamination of the soil as influenced by the complementary use of RP and organic fertilizer. The transfer factor indicates that the uptake of metal varied from one treatment to the other and from one plant species to the other. Chambers and Sidle (1991) found that plant metal levels were highly variable when related to soil metal levels. Similarly Fleming and Parle (1977), observed that uptake of heavy metals vary widely depending on the plant species studied. Alternatively, metal uptake could be controlled by such variables as pH, organic matter content and the degree of soil moisture (Fleming and Parle 1997). In *Zea mays*, complementary use of RP and

Table 7. Transfer factor of heavy metals from soil to *Zea mays* and *Abelmuschus esculentum* as influenced by ORP and cow dung applications.

Plant specie	Treatment	Pb	Zn	Cu	Cd	As
Zea mays	- ORP-CD	11.40	32.70	36.40	0.20	0.90
	ORP	14.70	35.60	25.60	0.30	0.60
	ORP-CD_1	17.90	35.90	20.00	0.30	0.02
	ORP-CD_2	32.10	34.40	17.30	0.30	0.10
	ORP-CD_3	25.40	43.20	20.30	0.30	0.80
	ORP-CD_4	19.20	43.30	22.70	0.30	`0.50
Abelmuschus	- ORP-CD	14.40	39.80	19.20	0.40	1.30
	ORP	22.80	44.40	29.80	0.50	1.70
	ORP-CD_1	18.20	35.70	22.90	0.30	1.30
	ORP-CD_2	25.00	39.40	14.80	0.50	2.10
	ORP-CD_3	12.60	44.10	20.70	0.30	0.90
	ORP-CD_4	16.20	38.10	15.00	0.20	1.20

ORP = Ogun Rock Phosphate, CD = Cow dung, ORPCD $_{1-4}$ = Represent Ogun Rock Phosphate and cow dung at different levels, 1, 2, 3 and 4 represent tons of cow dung. - ORP-CD represents no organic rock phosphate and cow dung application.

organic fertilizer increased the transfer factor of Pb without any corresponding increase in the level of organic fertilizer used. For example, transfer factor of Pb in *Zea mays* with sole ORP application increased by 30% relative to the unfertilized crop and, with the complimentary application with cow dung the transfer factor increased between 70 to 270% depending on the rate of application of cow dung. The high T/R of the heavy metals into the crop samples and eventual consu-mption by man poses grave health consequences not only to crops but to man and animals when consu-med directly or indirectly through plant product. This is because high transfer ratios mean high bioaccumulation in the crops. Lead is toxic to pregnant women and children while Cd is carcinogenic.

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