Effect of phosphate fertilizer application on manganese adsorption by some soils in Borno state

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***Abstract*-The study was carried out to investigate the effect of phosphate fertilizer application on manganese (Mn) adsorption. Composite sandy loam and loam soil samples (0-20 cm) were collected from Dalori and Gongulong and analysed for their texture and chemical properties. Mn adsorption experiment was carried out. Loamy soil collected at Gongulong was moderately acidic in reaction, moderate in electrical conductivity (EC), high in base saturation, moderate in organic carbon, low in available phosphorus, and low in DTPA extractable Mn. While sandy loam soil collected at Dalori is neutral in reaction, low in EC, high in base saturation, low in organic carbon and low in DTPA extractable Mn. For sandy loam soil, there was no definite trend in the equilibrium Mn concentration with and without phosphate (P) fertilizer treatment, with increasing application of Mn concentrations. There was however no difference in the amount of Mn adsorbed by the soils when P fertilizer was added. For loam soil, there was no definite trend in the equilibrium Mn ion concentration of the soils with increasing application of Mn levels to the soils with and without P fertilizer treatments. There was however an increase in the amount of Mn adsorbed by the soils. There was no difference in the amount of Mn adsorbed by the soils when P fertilizer was applied. Data were fitted into Langmuir and Freundlich equations. Loam soil without P conformed to Langmuir equation, while for Freundlich isotherm, loam soil with P treatment conformed to the equation. The results showed that maximum adsorption (b) for loam soil without P was 0.99mg/g and binding strength (K) of -214.92 ml/µg. While for Freundlich, the adsorption constant (K) and (n) were 1.28 and -0.21 respectively. This study have revealed that there is no observable effect on the amount of Mn adsorbed by the soils after P fertilizer was applied and on the other hand do not reduce bioavailability of Mn in soil.**

Key words: Manganese, Adsorption, Phosphate, Freundlich, Langmuir.

Introduction

Manganese (Mn) is a naturally occurring element that is found in rock, soil, and water. Manganese (Mn) is present in the soil in greater quantities than other trace elements, with the exception of iron. It is ubiquitous in the environment and comprises about 0.1% of the Earth's crust (Siegel and Siegel, 2000). Manganese is present in soil as a result of mineral weathering and atmospheric deposition, originating from both natural and anthropogenic sources. There are three possible oxidation states of manganese in soil, namely Mn(II), Mn(III) and Mn(IV). The divalent ion is the only form that is stable in soil solution, while Mn(III) and Mn(IV) are only stable in the solid phase of soil (McBride, 1994). The bioavailability of Mn in soils is generally adequate at pH < 6.5 but it becomes significantly lower in soils with higher pH values (Ducic and Polle, 2005).

Manganese is used in plants as a major contributor to various biological systems including photosynthesis, respiration, and nitrogen assimilation. Manganese is also involved in pollen germination, pollen tube growth, root cell elongation and resistance to root pathogens. It also serves as electron storage and delivery to the chlorophyll reaction centers (Diedrick, 2010; Millaleo *et al*., 2010).

Manganese deficiency symptoms, which often look like those of iron deficiency, appear as interveinal chlorosis on the young leaves, and sometimes tan, sunken spots that appear in the chlorotic areas between the veins. Plant growth may also be reduced and stunted. Manganese deficiency can occur when the pH of the growing medium exceeds 6.5, because it is tied up and unavailable for uptake. Manganese toxicity symptoms begin with the burning of the tips and margins of older leaves or as reddish-brown spots across older leaves. Severe toxicity may result in spots becoming more numerous and larger, forming patches on the older leaves. At pH levels below 5.5, manganese is very soluble and toxicity symptoms are probable (EdBloodnick, 2015).

Adsorption is another potential process controlling bioavailability of manganese in soil. Adsorption is the accumulation of gases, liquids, or solutes on the surface of a solid or liquid. It is the process by which molecules of a substance, such as a gas or a liquid, collect on the surface of another substance, such as a solid. The molecules are attracted to the surface but do not enter the solid's minute spaces, as in absorption (AHDSS, 2014). Adsorption of Mn has been shown to conform to the Langmuir or Freundlich isotherm (Willett and Bond, 1995). Adsorption increases with increasing pH, due to the increased hydrolysis species of Mn^{2+} that is preferably adsorbed and increased negative charge on the exchange complex (Reddy and Perkins, 1976).

In well aerated soils, phosphates are of major importance in controlling the level of micronutrients in soils and they are a limiting factor in the soils of arid and semi-arid regions of the world. For optimum utilization of manganese by the crops, knowledge of behavioural interaction of phosphate fertilizers and manganese is essential. Information on adsorption characteristics of manganese as affected by phosphate fertilizers in soils are scarce in literature despite its relative importance as essential micro nutrient. Therefore the objective of this study is to determine the effect of application of 100ppm phosphorus on manganese adsorption by some soils in Borno State.

Materials and Methods

Sampling site

The study was carried out with the soils of Borno state with coordinates 11°30′N 13°00′E and about 350m above sea level (Encyclopedia, 2013). with annual mean rainfall and temperature of 650mm and 32^0C. The soils of Borno State vary in colour, texture, structure, physico-chemical and other essential characteristics from the hilly south to the northern dune landscape (Nigerian Wiki, 2008). The vegetation is a mixture of Sudan Savannah and Sahel Savannah dominated with Acacia species (Nigerian Wiki, 2008).

Soil Sampling and Handling

Composite sandy loam and loam soil samples (0-20cm) were collected from two different locations namely; Dalori (11.78574^{0}N and 13.27079^{0}E) and Gongulong-Lawanti Agricultural Area (11.89629^{0}N and 13.19534^{0}E). The soils were air dried, ground to pass through 2mm stainless steel sieve and the texture was confirmed in University of Maiduguri Soil Science laboratory and used for routine physico-chemical properties determination and for the adsorption experiment.

Manganese adsorption experiment

2g of soil was weighed into series of plastic bottles. 25mls of double strengthed manganese concentrations (0, 50, 100, 150, and 200 ppm) were added to the bottles. 5mls of 1000 ppm P was added to the appropriate bottles. 20mls of 0.02M $CaCl_2$ was added to the bottles containing P and 25mls to those without P. The final concentrations of manganese were 0, 25, 50, 75 and 100 ppm and the final strength of $CaCl_2$ and P were 0.01M and100 ppm respectively. The bottles were shaken with WS-2 100A SERADON platform shaker at 27^0C at 400rpm for one hour and equilibrated for 24 hours and Mn concentrations in equilibrium solutions were determined using uv smart spectrophotometer. The amount of adsorbed Mn was calculated by the difference between Mn added and that remained in the equilibrium solutions multiplied by soil solution ratio. The obtained results of adsorption experiments were tested with Langmuir and Freundlich adsorption equations. Langmuir equation is as follows:

X =kbc/1+kc

Where C and X are the equilibrium ion concentration and the amount of ion adsorbed and the constants b and k which are related to adsorption maximum and binding strength of the adsorbent. Using the Langmuir isotherm, a graph of C/X against C was plotted where the slope (1/b) and intercept (1/Kb) from which both binding energy (K) and maximum adsorption (b) were found.

Freundlich adsorption equation is as follows:

Log X= Log K+ n Log C,

Where X is the amount of substance adsorbed per unit weight of adsorbent, C is the equilibrium concentration of the adsorbate, K and n are constants. Using Freundlich isotherm, a graph of Log X versus Log C was plotted giving a straight line from which the slope(n) as adsorption intensity and intercept (Log K) can be used to obtain the adsorption constant (K) by taking the antilog for soils that have conformed to the model.

Results and Discussion

The particle size of the soil sample collected at Gongulong had 47.10% sand, 43.20% silt and 9.70% clay with textural class of loam and soil at Dalori contained 64.60% sand, 28.20% silt and 7.20% clay and with textural class of sandy loam (Table 1).

Table 1: Particle size distribution of the soil samples

Soil sample	Sample Location	%			Textural class
		Sand	Silt	Clay	
1	Dalori	64.60	28.20	7.20	Sandy-loam
2	Gongulong	47.10	43.20	9.70	Loam

Loamy soil collected at Gongulong was moderately acidic in reaction, moderate in electrical conductivity (EC), high in base saturation, moderate in organic carbon, high in calcium, very high in magnesium, moderate in potassium, high in sodium, low in available phosphorus, and low in DTPA extractable Mn. While sandy loam soil collected at Dalori is neutral in reaction, low in EC, high in base saturation, low in organic carbon, low in calcium, high in magnesium, low in potassium, high in sodium, low in available phosphorus, and low in DTPA extractable Mn as in Table 2.

Table 3 shows the results obtained from adsorption studies. There was no adsorption of Manganese (Mn) as to the treatments with 0 level Mn. But amount of Mn adsorbed increase with increase in Mn level from 25µg/ml to 100µg/ml for all the soils with and without phosphorus (P). For example in loamy soil from Gongulong without P when no Mn was applied there was no adsorption but when 100µg/ml level of Mn was applied, the amount of adsorbed

Mn was 2.50mg/g. This shows that as the Mn concentration increases Mn adsorption also increases in the soils.

There was no difference in amount of Mn adsorbed by soils with P and without P for both sandy loam and loam.

Table 2: Chemical properties of the 2 soil samples

SS	ST	SD (cm)	pH	EC (ms/cm)	Meq/100g Soil							%		P (mg/g)	av. Mn (µg/g)
					EA	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC	ECEC	BS	O.C		
1	SL	0-20	7.06	0.220	0.20	4.40	7.40	0.18	0.87	12.85	13.05	98.47	0.49	5.60	0.82
2	L	0-20	5.85	0.268	0.20	10.20	11.00	0.40	1.39	22.90	23.19	99.14	1.21	15.40	0.84

SS soil sample, ST soil texture, SD sampling depth, EC electrical conductivity, EA exchange acidity, BS base saturation, OC organic carbon, av. available

Table 3: Manganese adsorption data

Soil sample	Soil texture	Treatments	Initial Mn concentration (µg/ml)	Equilibrium concentration (µg/ml)	(C) Equilibrium concentration- Zero concentration (µg/ml)	(X) Amount of Mn adsorbed (mg/g)	C/X	Log X	Log C
1	Sandy loam	100	0	0.18	0.00	0.00	0.00	0.00	0.00
	Without P	101	25	0.39	0.21	0.62	0.34	-0.21	-0.68
		102	50	0.16	-0.02	1.25	-0.016	0.0969	1.70
		103	75	0.46	0.28	1.87	0.15	0.27	-0.55
		104	100	0.20	0.02	2.50	0.008	0.39	-1.70
	Sandy loam	110	0	0.19	0.00	0.00	0.00	0.00	0.00
	With	111	25	0.46	0.27	0.62	0.44	-0.21	-0.57
	100 ppm P	112	50	0.65	0.46	1.24	0.37	0.09	-0.34
		113	75	0.14	-0.05	1.88	-0.027	0.27	1.30
		114	100	0.09	-0.10	2.50	-0.04	0.40	1.00
2	Loam	200	0	0.25	0.00	0.00	0.00	0.00	0.00
	without P	201	25	0.42	0.17	0.62	0.27	-0.21	-0.77
		202	50	0.22	-0.03	1.25	-0.024	0.0969	1.52
		203	75	0.43	0.18	1.87	0.096	0.27	-0.74
		204	100	0.32	0.07	2.50	0.028	0.40	-1.15
	Loam	210	0	0.05	0.00	0.00	0.00	0.00	0.00
	With	211	25	0.01	-0.04	0.63	0.063	-0.20	1.40
	100ppm P	212	50	0.62	0.57	1.24	0.46	0.093	-0.24
		213	75	0.14	0.09	1.87	0.048	0.27	-1.05
		214	100	0.64	0.59	2.49	0.24	0.40	-0.23

With regards to the equilibrium concentration, for sandy loam soil without P treatment and loam soil with P treatment, as concentration of Mn increases, the equilibrium concentration increase and then decreased with no observable definite trend. While for sandy loam soil with P treatment, as the Mn level increases, there was increase first and then decrease in equilibrium concentration as shown in figures 1 and 2.

Harter (1991), in a review of the subject, concluded that, adsorption isotherms have provided the majority of information about micronutrient adsorption by soils. For Langmuir adsorption isotherm, only loam soil without P conformed (Fig. 3) while for Freundlich adsorption isotherm, only loam soil with P treatment conformed (Fig. 4) and these have agreed with the findings of Willett and Bond (1995) who concluded that adsorption of Mn has been shown to conform to the Langmuir or Freundlich isotherm. While sandy loam soil with P treatment and without P have not conformed to either of Langmuir or Freundlich isotherm and this may be due to their difference in adsorption behaviours that can be attributed to physiochemical properties of the adsorbents and the cation anion pairs, solution pH, surface adsorption coverage as stated by Wang and Xing (2002).

Using the Langmuir and Freundlich equations, adsorption constants for loam soil without P and loam soil with P which conformed to the models were evaluated. The results showed that maximum adsorption capacity (b) for loam soil without P was 0.99mg/g and binding strength (K) of -214.92ml/µg. While for Freundlich, the adsorption constant (K) and (n) were 1.28 and -0.21 for loam soil without P. This study have revealed that there is no observable effect on the amount of Mn adsorbed by the soils after phosphate fertilizer was applied and on the other hand do not reduce bioavailability of Mn in the soils as to the findings of Ajouri *et al.*, 2004 who concluded that phosphorus induced micronutrients deficiency is not common to all soils, crop species and environmental conditions, but it has been proved in various soils and crops. Also John (1999) stated that phosphorus/Mn interactions can develop when soil Mn availability increases with higher soil P levels. On some soils this is believed partially due to increased soil acidity from high rates of P.

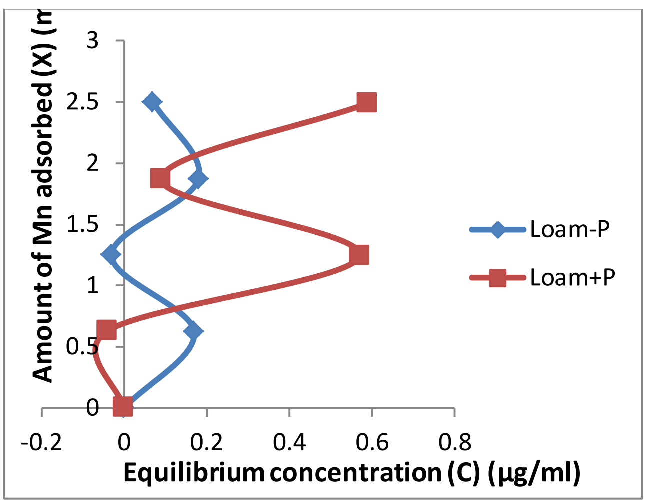

Fig. 1: Adsorption isotherm for loam soil with P and without P

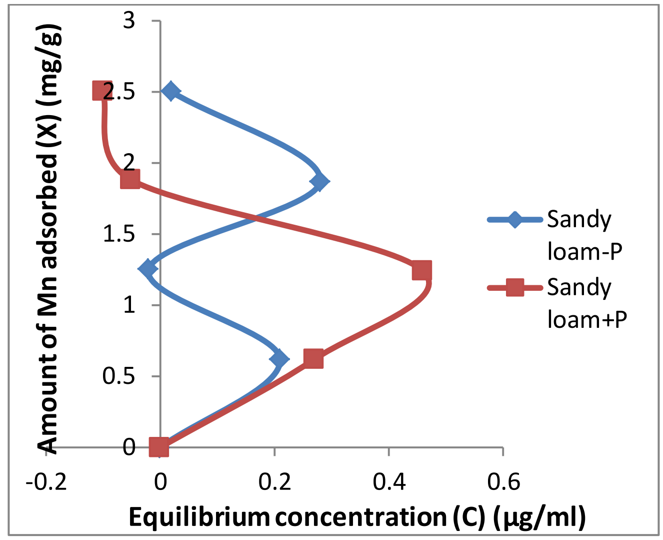

Fig. 2: Adsorption isotherm for sandy loam soil with P and without P

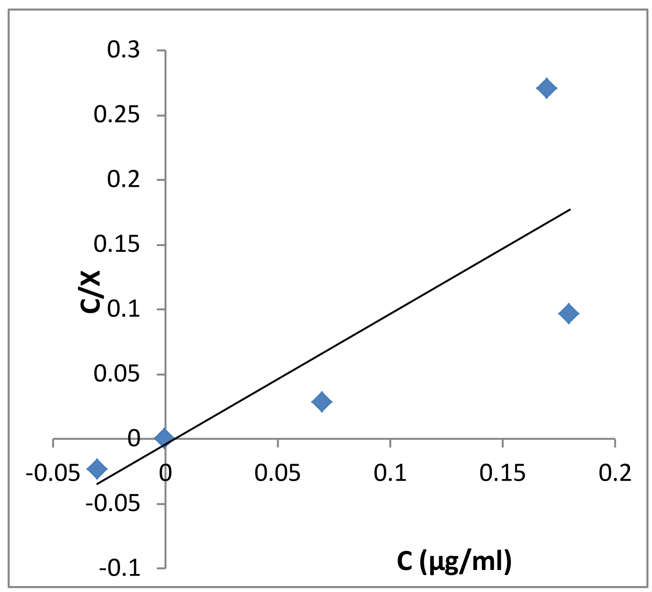

Fig. 3: Langmuir isotherm for loam soil without P

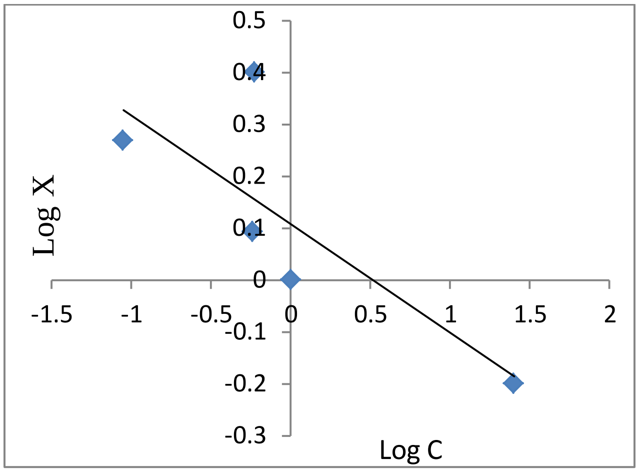

Fig. 4: Freundlich isotherm for loam soil with P

Conclusion

The application of 100 mgkg^{-1}P had no effect on the adsorption of Mn by both loam and sandy loam soils studied.

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