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Full Length Research Paper

Neutralization of soil acidity by animal manures: mechanism of reaction

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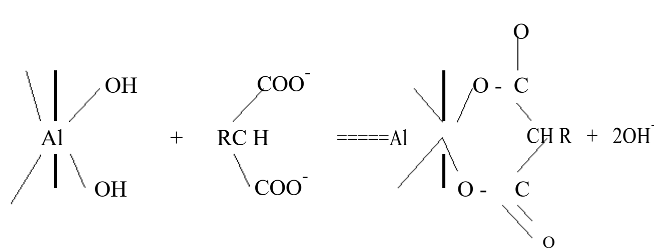
The mechanism of reaction leading to neutralization of soil acidity by animal manures was studied in the laboratory. Five animal manures; rabbit manure (RBM), swine manure (SWM), goat manure (GTM), poultry manure (POM), and cow manure (COM) were respectively added at rates equivalent to 10, 20, 30, and 40 t ha^{-1} to an Ultisol having soil-water pH of 4.6 and KCl extractable acidity of 3.00 cmol kg^{-1}. The amended soils were incubated at 70% water holding capacity for 3 weeks. Animal manures significantly increased the soil pH from 4.6 to values above 5.6 and also reduced exchangeable acidity from 3.00 cmol kg^{-1} to values below 0.35 cmol kg^{-1}. The mechanism that best explained the neutralization reaction was found to be microbial decarboxylation of calcium-organic matter complex leading to the release and subsequent hydrolysis of calcium ions. The hydroxyl ions released in the hydrolytic reaction then reacts with both the exchangeable hydrogen and aluminum ions to form water and insoluble aluminum hydroxide ($Al(OH)_3$) respectively.

Key words: neutralization, soil, acidity, animal, manures.

INTRODUCTION

One of the major factors that limit productivity of many tropical soils is soil acidity. Application of conventional liming materials such as $CaCO_3$ and $MgCO_3$ is used for the amelioration of this problem. These conventional liming materials are scarce, very expensive and beyond the reach of resource poor farmers. However, several studies have shown that addition of some materials of organic origin such as plant materials and poultry manure to acid soils increases the soil pH appreciably (Hue and Amien, 1989). Even though soluble aluminum and hydrogen ions have been established to be responsible for soil acidity in tropical soils, considerable controversy exists from studies carried out by several workers on the actual mechanisms of reactions that lead to neutralization of soil acidity by organic materials. A lot of workers have postulated various reaction pathways: Complexation of aluminium (Al) in soil solution by decomposition products of organic materials, particularly low-molecular weight organic acids as indicated below has been suggested by Bartlett and Riego (1972) and Hue et al. (1986):



Adsorption of soluble Al on the surface of organic material has also been postulated as a mechanism of soil

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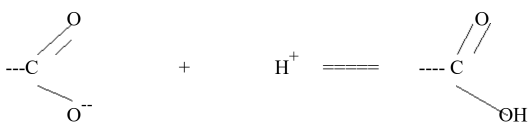
acidity reduction by plant materials (Asghar and Kanehiro, 1980) while Bessho and Bell, (1992) attributed the phenomenon to protonation of organic anions as indicated below:



From the foregoing it is clear that the mechanism involved in the neutralization of soil acidity by organic materials has not been clearly understood. A good understanding of the chemistry of the reactions that occur when animal manures are applied to the soil will enable Scientists develop management strategies for the efficient use of this biological resource in environmental management. The objective of the present study is to elucidate the mechanism of reaction leading to amelioration of soil acidity by animal manures.

MATERIALS AND METHOD

Soil

The soil (0 – 20 cm) used for the study was an Ultisol derived from coastal plain sands and was collected from the National Root Crops Research Institute, Umudike research farm. The soil was air dried and passed through 2 mm sieve. The soil had pH in water of 4.3, KCl extractable acidity of 3.00 cmol/kg and exchangeable K of 0.19 cmol/kg while the effective cation exchange capacity and organic carbon were 5.96 cmol/kg and 0.89%, respectively.

Animal manures

The animal manures which comprised rabbit manure (RBM), swine manure (SWM), goat manure (GTM), poultry manure (POM) and cow manure (COM) were collected from Michael Okpara University of Agriculture, Umudike research farm. The manures were air dried, crushed with wooden roller and passed through 2 mm sieve.

Incubation studies

The incubation study was a 5 x 4 factorial, replicated three times. Five hundred grams of the sieved soil were weighed into each of sixty plastic containers. The capacity of each container was one liter. Quantities of each manure equivalent to 10, 20, 30, 40 t/ha were respectively weighed in triplicate into the soils in the buckets. The manure and soil in each bucket were mixed thoroughly and moistened to 70% field capacity with distilled water. Control (in triplicate) which contained only soil without manure was included. The sixty three buckets comprising of sixty with treatments and three without treatment (control) were arranged on the laboratory table in a randomized complete block design with three replications. The soils were maintained at 70% field capacity with distilled water for 21 days after which the soils were air dried and passed through 2 mm sieve.

Analyses

Organic carbon in the animal manures was determined by the wet oxidation method as modified by Nelson and Sommers (1982). 5 mg of each of the animal manures were weighed into conical flasks, 20 ml of conc sulphuric acid and 10 ml of 0.5 M $K_2Cr_2O_7$ solutions were then added to each of the samples. The solutions were allowed to stand for 1 h and thereafter titrated against 0.5 M ferrous ammonium solution.

Nitrogen in the manures was determined according to the method of Bremner (1965). Two hundred milligrams of each of the animal manures were weighed into a Kjeldahl digestion tube, a Kjeldahl digestion tablet was then added followed by 3.0 ml conc. H_2SO_4. The tubes were then placed in a heating block for 4 h and then transferred quantitatively into 50 ml volumetric flasks. The solutions were made up to the mark with distilled water. 10 ml of each of the solution were pipetted into a Kjeldahl distillation unit and 10 ml of 50% NaOH solution were then added. The distillation unit was heated and the ammonia liberated was passed into 5% boric acid. The ammonium borate formed was titrated against 0.01 M H_2SO_4 solution.

Calcium and magnesium in each of the manures were determined by weighing 0.5 g of each manure sample into platinum crucible. The crucible was then placed in a muffle furnace and the sample was allowed to ash for 4 h at 400^{o}C. The ashes from each manure was dissolved in 20 ml of 5 M HCl and thereafter filtered through Whatman No 42 filter papers into 50 ml volumetric flasks. The solution in each flask was made up to the mark with distilled water. Calcium and magnesium in the solutions were determined by EDTA titration.

Organic carbon in the soils after incubation was determined as described for animal manures. In this case soil samples were used in place of animal manure.

The pH of the soil samples was determined according to Mclean, (1982). 10 g of each of the samples were weighed into a beaker and 25 ml of distilled water were added to each of the beakers. The suspensions were stirred intermittently and allowed to stand for 30 min after which the pH was taken using a pH meter.

Exchangeable calcium and magnesium were extracted with one molar ammonium acetate solution of pH 7.0. Five grams of each of the soil samples were weighed into plastic containers and 100 ml of ammonium acetate solution were added into each bottle. The suspensions were shaken for 2 h and thereafter filtered into 100 ml volumetric flasks. The solutions were made up to the mark with ammonium acetate solution. Calcium and magnesium in the solutions were determined by EDTA titration.

Exchangeable acidity of the soils was determined by the method of Mclean (1965). 5 g of each of the soil samples were weighed into plastic bottles and 100 ml of 1 M KCl were added into each bottle. The suspensions were shaken for 1 h and filtered into 100 ml volumetric flasks. The filtrates were made up to the mark with 1 M KCl solution and then titrated against 0.02 M NaOH solution.

RESULTS AND DISCUSSION

Chemical composition of the animal manures

The chemical composition of the manures is shown in Table 1. Calcium content of the manures ranged from 1.12 to 1.37% with a mean value of 1.29%. Rabbit manure (RBM), swine manure (SWM) and goat manure (GTM) had the highest calcium content followed by poultry manure (POM) and lastly cow manure (COM). Mean magnesium content of the manures was 1.12%,

Table 1. Chemical properties of the manures.

Animal manure	Chemical properties				C:N
	Ca	Mg	N	Organic C	
	%				
Rabbit manure (RBM)	1.37	2.16	0.25	23.03	16.8
Swine manure (SWM)	1.37	1.30	0.52	27.13	19.8
Goat manure (GTM)	1.37	0.83	0.32	28.43	20.8
Poultry manure (POM)	1.24	0.89	0.36	29.63	23.9
Cow manure (COM)	1.12	1.94	0.49	31.30	27.9

Table 2. Effect of manure source and rate of application on soil pH.

Animal manure	Rate of application of manure (t/ha)				mean
	10	20	30	40	
	Soil pH				
Rabbit manure (RBM)	5.57	6.18	6.34	6.41	6.13
Swine manure (SWM)	6.12	6.28	6.54	6.92	6.44
Goat manure (GTM)	5.24	5.57	5.93	5.97	5.68
Poultry manure (POM)	6.18	6.61	6.49	6.66	6.49
Cow manure (COM)	5.38	5.87	6.03	6.36	5.91
Mean	5.69	6.10	6.24	6.46	
LSD (0.05)					
Animal Manure (M)	0.33				
Rate (R)	0.30				
M x R	0.61				
Control (no manure application)	= 4.34				

RBM also had the highest magnesium content, and SWM had the highest nitrogen content of 0.25% while the least value was obtained with RBM. The chemical composition of these manures was highly related to the feed being fed to the animals. Rabbit and poultry were fed with highly nutritious concentrates; pigs (swine) were being fed with food rich in nutrients while the cow and goat were fed with relatively less nutritious browse materials.

Effect of animal manures on soil chemical properties

The effect of animal manure and rate of application on soil pH is shown on Table 2. Animal manure application increased soil pH. Poultry manure (POM), rabbit manure (RBM) and swine manure (SWM) had significantly the greatest effect on soil pH followed by cow manure (COM) and lastly by goat manure (GTM). Increasing the rate of application of these manures also increased the soil pH. Application of animal manures significantly decreased soil exchangeable acidity (Table 3). Exchangeable acidity defined, as the sum of exchangeable H and exchangeable aluminum in the soil, was reduced from 3.00 cmol/kg to values less than 0.50 cmol/kg by the animal manures. Swine manure which the most had pronounced effect reduced the exchangeable acidity of the soil from 3.00 cmol/kg to 0.13 cmol/kg. The order of the ability of the various manures to reduce exchangeable acidity conforms to the same order of their ability to increase soil pH. It therefore follows that the ability of the manures to improve soil pH lies on their capability to reduce exchangeable acidity which comprises exchangeable hydrogen and aluminum ions. Increasing the rate of application of these manures significantly reduced the exchangeable acidity (Table 3).

With the exception of GTM, application of animal manures reduced the soil organic carbon compared to the control (Table 4). Marchner and Noble (2000) also obtainned reduction in soil organic carbon when an acid soil was incubated with leaf litter materials and attributed the observation to increased microbial respiration stimulated by the added manure.

Application of animal manures slightly increased the soil exchangeable Mg (Table 5). The highest effect was obtained with COM followed by RBM. Exchangeable Ca was highly increased by the application of the manures. Swine and poultry manures increased soil exchangeable Ca more than 3 folds. Rate of application of the manures

Table 3. Effect of manure source and rate of application on soil exchangeable acidity.

Animal manure	Rate of application of manure (t/ha)				mean
	10	20	30	40	
	Exchangeable acidity (cmol/kg)				
Rabbit manure (RBM)	0.27	0.23	0.10	0.23	0.21
Swine manure (SWM)	0.17	0.10	0.13	0.10	0.13
Goat manure (GTM)	0.37	0.33	0.23	0.20	0.28
Poultry manure (POM)	0.13	0.17	0.13	0.17	0.15
Cow manure (COM)	0.43	0.37	0.33	0.20	0.33
Mean	0.27	0.24	0.23	0.18	
LSD(0.05)					
Animal Manure (M)	0.09				
Rate (R)	0.05				
M x R	0.12				
Control (no manure application) = 3.00 cmol/kg					

Table 4. Effect of animal manure on soil organic carbon.

Animal manure	Rate of application of manure (t/ha)				mean
	10	20	30	40	(%)
	Organic carbon (%)				
Rabbit manure (RBM)	0.62	0.70	0.62	0.88	0.71
Swine manure (SWM)	0.55	0.83	0.39	0.70	0.62
Goat manure (GTM)	0.73	0.70	1.10	1.19	0.93
Poultry manure (POM)	0.65	0.74	0.72	0.61	0.68
Cow manure (COM)	0.76	0.56	0.54	0.89	0.69
Mean	0.51	0.71	0.67	0.85	
LSD(0.05)					
Manure sources (M)	0.12				
Rate (R)	0.05				
M x R	0.38				
Control (no manure application) = 0.89					

Table 5. Effect of animal manure on exchangeable Mg.

Animal manure	Rate of application of manure (t/ha)				mean
	10	20	30	40	cmol/kg
	Exchangeable Mg (cmol/kg)				
Rabbit manure (RBM)	2.25	1.47	1.20	2.26	1.80
Swine manure (SWM)	2.20	1.13	1.73	1.33	1.35
Goat manure (GTM)	0.80	1.07	1.07	2.00	1.24
Poultry manure (POM)	1.73	1.87	1.73	2.00	1.83
Cow manure (COM)	1.07	3.07	1.33	2.13	1.90
Mean	1.41	1.52	1.41	1.94	
LSD(0.05)					
Manure sources (M)	0.09				
Rate (R)	0.12				
M x R	0.21				
Control (no manure application) = 1.15 cmol/kg					

Table 6. Effect of animal manure on exchangeable Ca.

Animal manure	Rate of application of manure (t/ha)				mean
	10	20	30	40	cmol/kg
	Exchangeable Ca (cmol/kg)				
Rabbit manure (RBM)	3.87	3.47	4.40	3.07	3.70
Swine manure (SWM)	3.30	4.93	6.40	5.60	5.06
Goat manure (GTM)	3.48	2.80	3.73	3.47	3.37
Poultry manure (POM)	4.40	4.93	5.47	5.60	5.10
Cow manure (COM)	1.60	1.73	2.53	4.27	2.53
Mean	3.38	3.58	4.51	4.40	
LSD(0.05)					
Manure sources (M)	0.69				
Rate	0.60				
M x R	0.16				
Control (no manure application) = 1.60					

also increased the level of exchangeable Ca in the soils (Table 6).

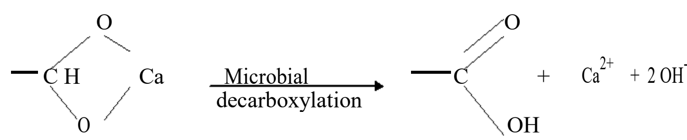
Table 7. Relationship between soil factors and soil pH after manure application.

Soil factors	Correlation coefficient (r)
Exchangeable Mg	0.163 NS
Exchangeable Ca	0.573**
Organic carbon	-0.159 NS

** = significant at $P < 0.01$

Mechanism of neutralization of soil acidity by animal manures

Simple correlation analysis was used to elucidate the mechanism of reaction leading to the neutralization of soil acidity by the animal manures. If complexation of Al^{3+} in soil solution by decomposing organic matter is the mechanism as suggested by Bartlett and Riego (1972) and Hue et al. (1986), the soil organic matter content will be positively correlated with soil pH. Soil organic matter did not correlate positively with pH (Table 7), indicating that this is not the mechanism of the reaction. However exchangeable Ca correlated positively and strongly with soil pH. This indicates that as the organic manures mineralize, Ca ions are released into the soil solution. The released Ca^{2+} ions get hydrolysed. The Calcium hydroxide formed reacts with soluble aluminum ions in the soil solution to give insoluble $Al(OH)_3$. The hydroxide of the calcium hydroxide reacts with hydrogen ions to form water. The mechanism of reaction is therefore as is given below:



(Ca-organic matter complex)

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3\downarrow$$

$$H^+ + OH^- \longrightarrow H_2O$$

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