EVALUATION OF TWO BUFFER METHODS FOR THE DETERMINATION OF SOIL BUFFERING CAPACITY

OLUFEMI, T., *ADESANWO, O. O. AND AZEEZ, M. O.

Department of Soil Science and Land Resources Management, Faculty of Agriculture, Obafemi Awolowo University, Ile-Ife, Nigeria.

***** *oadesanwo@oauife.edu.ng / adesanwo62@gmail.com; +2348038898578*

ABSTRACT

A study was carried out to evaluate two buffer methods for the determination of soil pH buffering capacity. Soil samples (0-15 cm) were collected from four sites with varying land use practices (cacao, plantain, oil palm and cashew plantations) at the Teaching and Research Farm, Obafemi Awolowo University, Ile-Ife, Nigeria. The physical and chemical properties of the samples were determined. Titration method which involves shaking for 1 hour and Equilibration method for 7 days, were used to determine soil pH buffering capacity. The result of physical and chemical analyses showed textural classes ranging from Sandy Loam to Sandy Clay Loam, soil pH ranged between 4.7 and 6.5. Soil under cacao plantation had the highest values for pH (6.5), organic matter (6.2%) and calcium saturation (32.5%) than soil samples from other sites. There was significant difference in buffering capacities between the two methods, higher values were obtained with equilibration method compared with 1 hour titration method. For instance, buffering capacities of soil samples under the following cropping systems for titration and equilibration method respectively were: cacao (2.61, 5.09) and cashew (1.84, 2.18). In addition, higher correlation coefficient (R^2) was recorded for Titration method compared with Equilibration method. Similarly, results from titration method correlated more with the selected soil properties compared to equilibration method for all the soil samples. Similar observation was recorded with calculated lime requirement. Therefore, titration method proved a better way of determining soil pH buffering capacity and estimating lime requirement. However, more detailed study is required to support the results of this study.

Keywords: Soil acidity, soil pH, buffering capacity, titration method, equilibration method

INTRODUCTION

Soil acidification is one of the limiting factors to agricultural production and sustainability in Africa (Nduwumuremyi *et al.,* 2013) and throughout the world (Goulding, 2016). This is because soil acidification leads to elevated aluminum concentration and micronutrient toxicity, including loss of essential plant nutrients with consequent reduction in crop yields (Haynes, 1982). Approximately 50% of Nigerian agricultural land is affected by soil acidity because of the kaolinitic nature of our soils and high susceptibility to weathering. In some parts of Nigeria especially the humid tropical areas, soil acidity is further aggravated by high rainfall which leads to leaching of the basic cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) that are released into

the soil during the process of weathering (Obi, 1976). Also, continuous cropping, use of ammonium-based fertilizers (Aduayi, 1980), microbial and plant roots respiration with the release of CO_2 which reacts with water to produce carbonic acid (Murphy *et al.,* 1979, 2003), nitrogen fixation and decomposition of organic matter, are all sources of soil acidity.

Management of low soil pH occasioned by acidification involves application of liming materials (oxides and hydroxides of Ca and Mg compounds) to ameliorate soil acidity and to increase nutrient availability for plant uptake (Goulding, 2016). In addition, application of lime increases the concentration of Ca in soils. Measurement of soil pH indicates the need to lime but cannot be used to estimate the amount of lime to neutralize the soil acidity. Soil pH buffering capacity (pHBC) is an important parameter for proper management of soil acidity (Kissel *et al*., 2012). It is a routine analysis in most laboratories in developed countries but rarely a routine analysis in most of our laboratories in Nigeria probably because of the laborious and time-consuming processes associated with the conventional method which involves incubation of the soil for 7 days to attain equilibration. Several buffer methods have been used to estimate pH buffering capacity in the previous years. These include Dunn Titration Method (Dunn, 1943), SMP Buffer Method (Shoemaker *et al.*, 1961), Woodruff Method (Woodruff, 1948), Adams and Evans Method (Adams and Evans 1962), Modified Mehlich Buffer Method (Mehlich, 1976) and buffer solution methods (Aitken *et al*. 1990). However, these methods have been proven to be hazardous, time consuming and expensive (Kissel *et al.,* 2012). In addition, some of them have been reported to overestimate soil buffering capacity (Liu *et al.,* 2004). Recent findings showed that equilibrium was attained after shaking for 1 hour on a mechanical shaker (Titration method) (Aitken and Moody 1994; Aitken *et al.,* 1990; Liu *et al.,* 2004, 2005). This method is free of hazardous chemicals and involved the use of 0.022 M $Ca(OH)_2$ to measure the soil pH Buffering Capacity with single addition of 0.01 M $CaCl_2$ after which the pH is taken at 1 hour equilibration.

Therefore, the aim of this study was to evaluate the two buffer methods (1-hour titration and 7 days equilibration) on Nigeria soils with the aim of including it as a soil parameter for routine analysis in Nigeria.

MATERIALS AND METHODS

Soil sampling and treatment

The soil samples (0–15cm) were collected randomly from the Teaching and Research (T&R) Farm, Obafemi Awolowo University Ile- Ife, Osun State, Nigeria based on different crop management practices (cacao (*Theobroma cacao*), plantain (*Musa sapientum*), Oil palm (*Elaeis guineensis*) and cashew (*Anacardium occidentale*) plantations). The experimental site is situated within the rain forest zone and located between latitude 7º 32ʾ N and 7º 33' N and longitude 4º 32' E and 4º 40' E, at 200 m above sea level. The soil samples were air-dried, crushed gently, and passed through 2 mm sieve to separate gravel content from other components. The soil particle that is less than 2 mm fraction is retained for laboratory analysis.

Soil physical and chemical analysis

The following physical and chemical properties of the soil samples were determined at the Soil Science Laboratory, Obafemi Awolowo University, Ile-Ife prior to incubation experiment; pH in 0.01 M $CaCl_2$ in ratio 2:1 (Schofield and Taylor, 1955). Organic matter (OM) was determined using a modified chromic acid digestion method (Nelson and Sommer, 1996). Exchangeable cations were determined using 1 N NH_4OAc (Peech, 1941), humic acid extraction, exchangeable acidity using titration method (Mclean, 1978), available phosphorous using Bray 1 method (Bray and Kurtz, 1965) and Particle size distribution using modified Bouyocous method (Bouyocous, 1962).

Determination of Soil Buffering Capacity

Titration Method

Soil Buffering Capacity was measured through the construction of buffer curves to determine the precise effect of 0.022 M $Ca(OH)_2$ on soil solution pH (Kissel *et al.*, 2012). Five grams of soil were weighed into pH cups in duplicate and 25 ml of 0.01 M $CaCl_2$ were added. Each soil sample was treated with increasing amounts of $Ca(OH)_2$ solution (0 ml, 1 ml, 1.5 ml, 2.0 ml, 2.5 ml, 3 ml). After shaking the mixtures for one hour with mechanical shaker, the pH values were recorded. The result was plotted to produce a buffer curve (pH vs volume of $Ca(OH)_2$ added in Mg $CaCO_3$ ha^{-1}). The reciprocal of the slope of the buffer curve is the buffering capacity of the soil.

Equilibration Method

The procedure followed the method described by Liu *et al* (Liu *et al.*, 2005). After thoroughly mixing of soil suspensions for 1 hour with mechanical shaker, the mixtures were left to equilibrate for seven days before reading the pH values. The incubation data were plotted and regressed with base addition in units of Mg $CaCO_3$ ha^{-1} (Liu *et al.*, 2005).

STATISTICAL ANALYSIS

Data obtained from the two buffer methods were analyzed using SAS software version 9.4 (SAS Institute Inc, 2013) and means were separated using Duncan Multiple Range Test at 5% level of probability.

RESULTS AND DISCUSSION

Soil samples collected from cacao plantations consistently had higher values in most of the selected soil properties as compared to other soil samples from other plantations. In cacao plantation, higher values were obtained in soil pH (6.5), exchangeable K (0.43 cmol kg^{-1}), Ca (0.35 cmol kg^{-1}), effective cation exchange capacity (ECEC) (1.87) and organic matter (6.2%) with lowest percent aluminum saturation (5%) (Table 1). This is consistent with rating of soil sensitivity to acidification (Nawaz *et al*; 2011). Huge quantities of organic materials produced in cacao plantation as compared to other plantations considered in this study could account for low percent aluminum saturation. During decomposition of organic matter, various organic acids are produced, and this can form stable chelate complexes with Al and other polyvalent cations, with consequent reduction in Al concentration in soil (Barrow, 2017; Haynes, 1982). This could also explain high exchangeable cations in cacao plantation due to adsorption of cations on the negative charge of organic materials compared to other plantations.

Buffering capacity values for titration method were lower compared with equilibration method for samples from all the sites (Table 2), similar to the report of Liu *et al.* (2004). Variation in soil organic matter content influences soil pH buffering capacity due to high CEC contained in the organic materials added to soil (Xu *et al*., 2012). Significant higher values in buffering capacity were obtained with soil samples from cacao plantation using the two methods than soil buffering capacities from other sites.

TABLE 1. SOIL PHYSICAL AND CHEMICAL PROPERTIES OF SOIL SAMPLES FROM DIFFERENT PLANTATIONS

Soil properties	**Plantations**			
	Cacao	**Cashew**	**Plantain**	**Oil palm**
pH in 0.01M $CaCl_2$	6.5	5.2	4.7	5.5
Organic matter (%)	6.21	5.04	3.49	4.83
Humic acid (%)	0.088	0.0504	0.054	0.077
Exch. Na^+ ($cmolkg^{-1}$)	0.15	0.20	0.16	0.15
Exch. K^+ ($cmolkg^{-1}$)	0.43	0.29	0.28	0.26
Exch. Ca^+ ($cmolkg^{-1}$)	0.35	0.21	0.29	0.27
Exch. Mg^+ ($cmolkg^{-1}$)	0.14	0.18	0.1	0.08
Exch. H^+ ($cmolkg^{-1}$)	0.7	0.6	0.55	0.75
Exch.Al^{3+} ($cmolkg^{-1}$)	0.1	0.15	0.1	0.1
ECEC	1.87	1.63	1.48	1.61
Available P (mg kg^{-1})	1.73	1.63	2.08	1.76
%Al saturation	5	9	6	6
Sand (%)	62	68	74	75
Clay (%)	22	24	17	17
Silt (%)	16	8	9	8
Textural Class	Sandy clay loam	Sandy clay loam	Sandy loam	Sandy loam

ECEC: Effective cation exchange capacity

For example, 2.61 and 5.09 were obtained for titration and equilibration with samples from cacao plantation while 1.84 and 2.18 were obtained with soil samples from cashew plantation (Table 2). This could be due to higher organic matter content in cacao plantation. The values of pHBC obtained with titration method were in close conformity with the selected soil properties compared with equilibration method. Little or no lime is required for soil samples from cacao plantation, the order of lime required follows the order cacao < oilpalm < cashew < plantain with titration method, while the order of increasing lime requirement for equilibration method was: cacao < oilpalm < plantain < cashew (Table 3). The higher the organic matter, exchangeable K and layer silicate clay content, the higher the buffering capacity and the lower the sensitivity to acidification (Nawaz *et al*., 2011).

The mean and standard deviation values for titration method (1.85, 0.55) were lower than equilibration method (2.69, 1.65). This was in agreement with the work of (Mike and Kathy, 2010) that the lower the standard deviation, the more accurate and precise the result. Correlation

coefficient (R^2) of buffering capacity was higher in titration method than equilibration method (Figs. 1, 2, 3 and 4). This was in line with Kissel *et al*. (2012) who obtained highest correlation coefficient in 30 minutes for titration method than 7 days equilibration. The results of this study confirmed earlier work done that equilibration can be attained within one hour of shaking the soil sample with acidic or alkaline solution based on initial soil pH (Aitken and Moody 1994; 1997; Aitken *et al.*, 1990; Liu *et al.*, 2004, 2005; Lesturgez *et al.*, 2006).

TABLE 2: BUFFERING CAPACITIES OF SOIL SAMPLES FROM DIFFERENT PLANTATIONS WITH THE TWO BUFFER METHODS.

Plantations	Titration method	Equilibration method
Cacao	2.61b	5.09a
Cashew	1.84b	2.18a
Plantain	1.36a	1.28b
Oil palm	1.57b	2.24b
Mean	1.85	2.69

Samples for each plantation for Titration and Equilibration methods within a row are compared. Means with different letters within a row for each plantation are significantly different ($p<0.05$) according to Duncan's multiple range test

TABLE 3: ESTIMATED LIME REQUIREMENT (LR) USING TITRATION AND EQUILIBRATION METHODS.

Plantations	LR (Titration) kg/ha	LR (Equilibration) kg/ha
Cacao	0	0
Cashew	2.395b	2.835a
Plantain	2.44a	2.305a
Oil palm	1.570b	2.240a

Samples from each plantation for Titration and Equilibration methods within a row are compared. Means with different letters within a row for each plantation are significantly different ($p<0.05$) according to Duncan's multiple range test.

CONCLUSION

The titration method for determination of soil buffering capacity and estimating lime requirement proved to be a better method than the equilibration method. Titration method is faster, easier, more economical, more precise and conformed more with the soil chemical properties compared to equilibration method. However, more studies should be carried out to establish the research findings on other Nigerian soils.

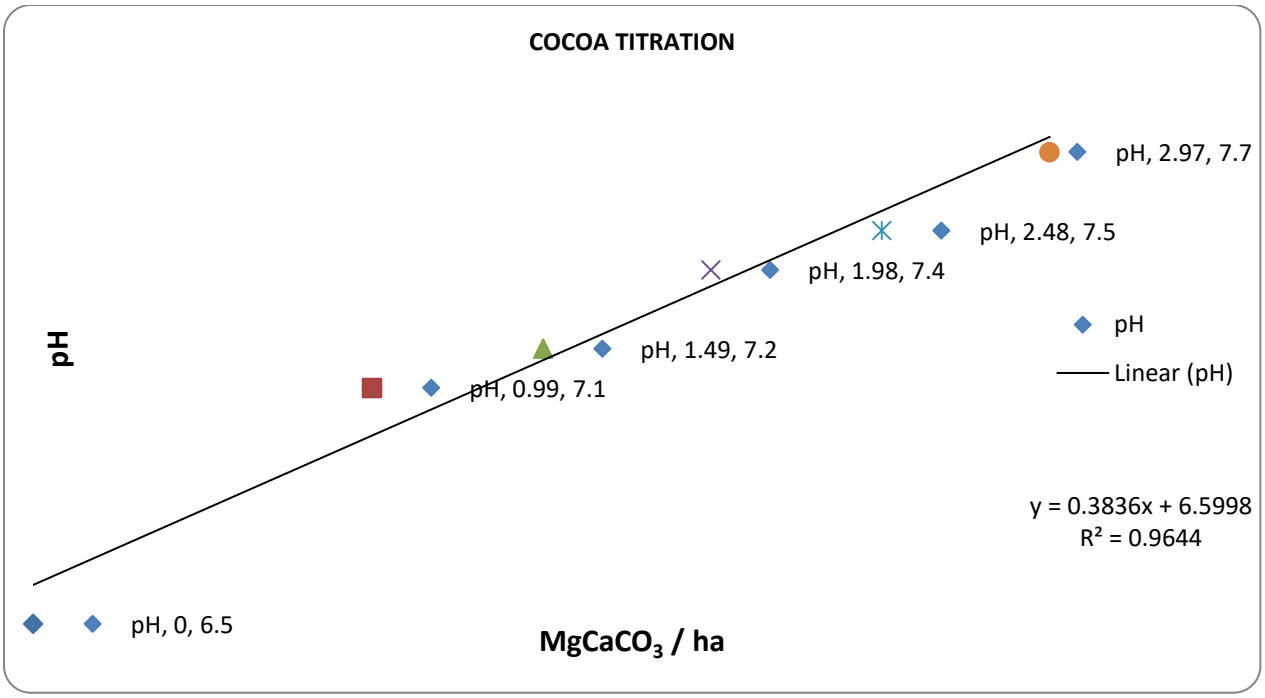

FIG. 1: GRAPH OF PH AGAINST MGCACO3 / HA AT 1HOUR (BC= 1/0.3836 = 2.61)

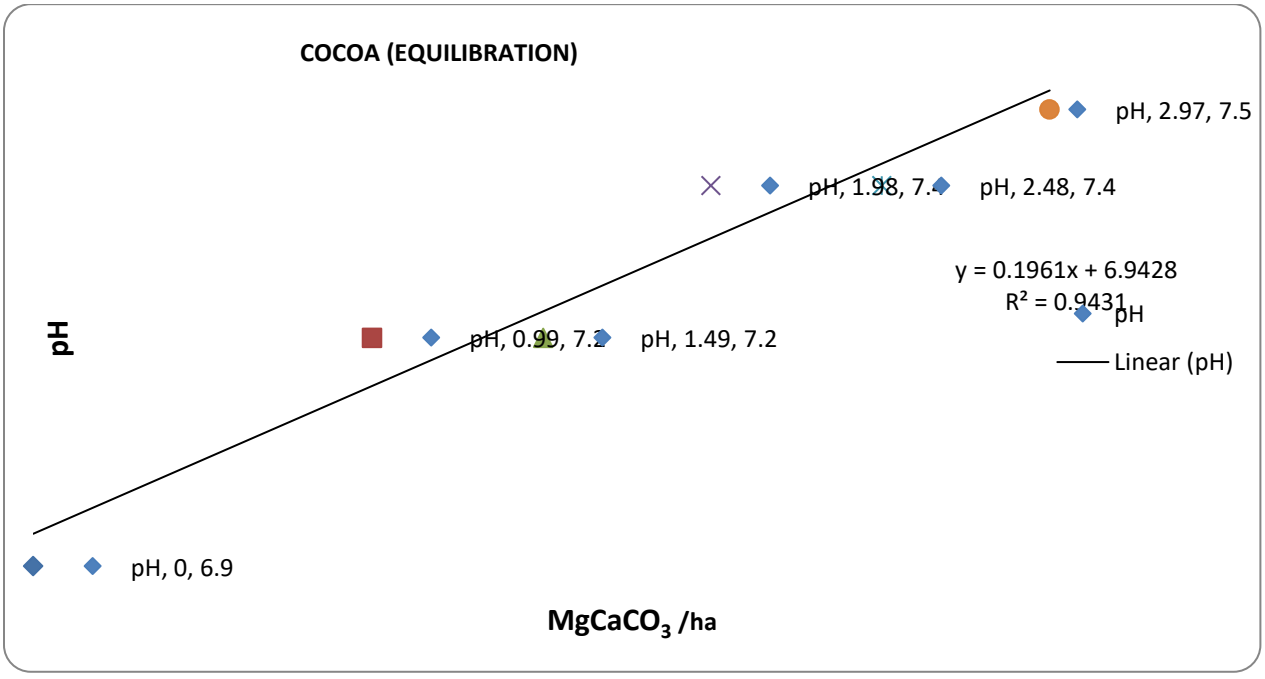

FIG. 2: GRAPH OF PH AGAINST MGCACO3 / HA AT 7DAYS (BC= 1/0.1961 = 5.09)

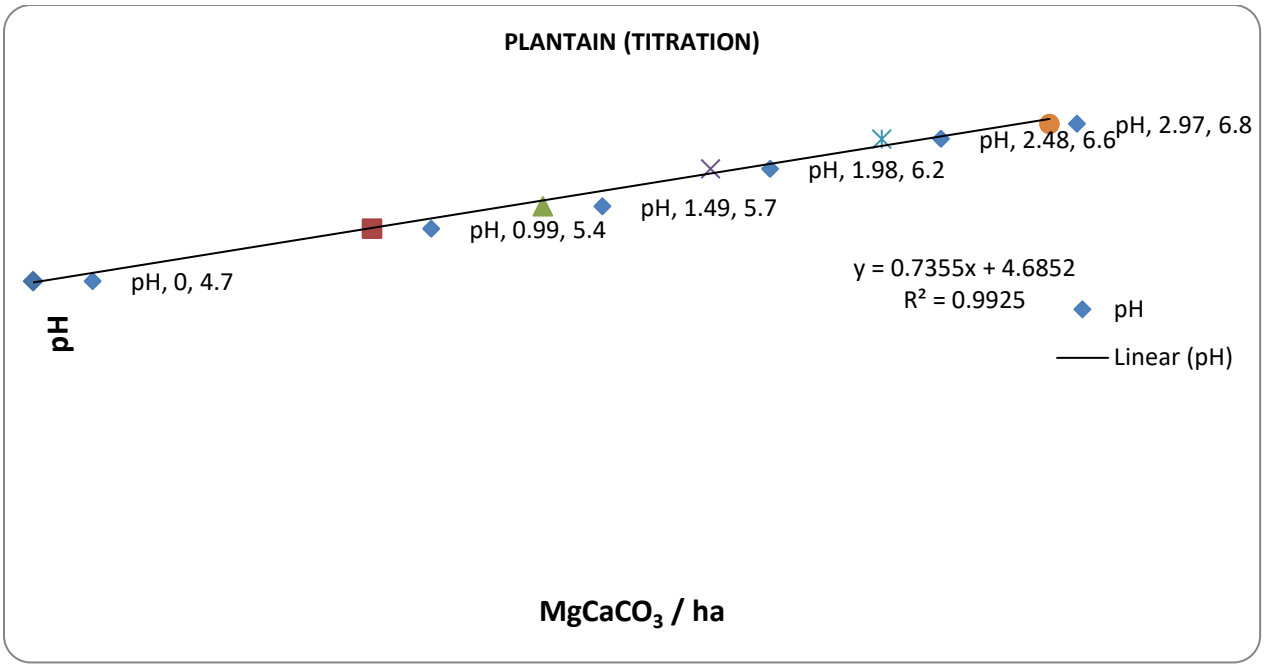

FIG. 3: GRAPH OF PH AGAINST MGCACO$_3$ / HA AT 1HOUR (BC= 1/0.7355 = 1.36)

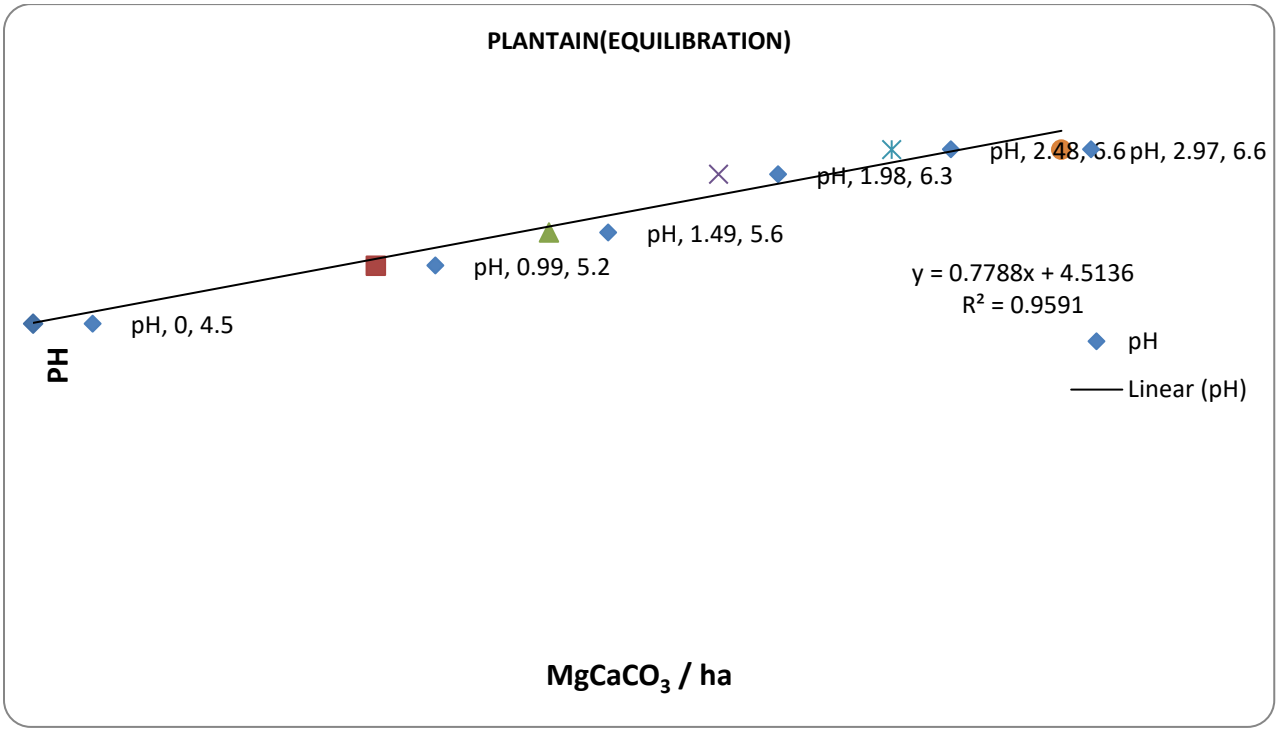

FIG. 4: GRAPH OF PH AGAINST MGCACO$_3$ / HA AT 7DAYS (BC= 1/0.7788 = 1.28)

REFERENCES

Adams, F., and Evans, C. E. (1962). A rapid method of measurement of lime requirement of red-yellow podzoic soils. *Soil Science Society of America Proceeding*, 26: 355-357.

Aduayi, E. A. (1980). Effect of ammonium sulphate fertilization on soil chemical composition fruit yield and nutrient content of okra. *Ife Journal of Agriculture*, 2: 16-34

Aitken, R.L., Moody, P.W. (1994). The effects of valence and ionic strength on the measurement of buffering capacity. *Australian Journal of Soil Research*, 32: 975 – 984.

Aitken, R. L., Moody, P. W., McKinley, P. G. (1990). Lime requirement of acidic Queensland soils. II. Comparison of laboratory methods for predicting lime requirement. *Australian Journal of Soil Research*, 28: 703–715. doi:10.1071/SR9900703

Barrow, N. J. (2017). The effects of pH on phosphate uptake from the soil. *Plant Soil*, 410:401-410. https://doi.org/10.1007/s11104-016-3008-9

Bouyoucos, G.J. (1962). Hydrometer method improved for making particle size analysis of soils. *Soil Science Society of America Proceeding*, 26: 917-925.

Bray, R. H. and Kurtz, L. T. 1945. Determination of total organic and available forms of P in soils. *Soil Science*, 59: 39-45

Dunn. L.E. (1943). Lime requirement determination of soils by means of titration curves. *Soil Science*, 56: 341- 351.

Goulding, K. W. (2016). Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom. *Soil Use Management*, 32, 390-399.

Haynes, R. J. (1982). Effects of liming on phosphate availability in acid soils. *Plant and Soil*, 68(3): 289-308.

Kissel, D. E., Sonon, L. S., and Cabrera, M. L. (2012). Rapid measurement of soil pH Buffering Capacity. *Science Society of America Journal*, 76(2), 694-699

Lesturgez, G., Poss, R., Noble, A., Grünberger, O., Chintachao, W. and Tessier, D. (2006). Soil acidification without pH drop under intensive cropping systems in Northeast Thailand. *Agriculture, Ecosystems & Environment*, 114: 239–248. doi:10.1016/j.agee.2005.10.020

Liu, M., Kisel, D. E., Vendrell, P. F. and Cabrera, M. L. (2004). Soil lime requirement by direct titration with Calcium hydroxide. *Science Society of America Journal*, 68: 1228-1233.

Liu, M., Kisel, D. E., Vendrell, P. F. and Cabrera, M. L. (2005). Soil lime requirement by direct titration with a single addition of calcium hydroxide. *Science Society of America Journal*, 69: 522-530.

McLean, E. O. (1978). Principles underlying the practice of determining lime requirements of acid soils by use of buffer methods, *Communications in Soil Science and Plant Analysis*, 9(8): 699-715, DOI: 10.1080/00103627809366845

Mehlich, A. (1976). New buffer method for rapid estimation of exchangeable acidity and lime requirement. *Communication Soil Science and Plant Analysis*, 7(7): 637–52.

Mike, T. F. W. and Kathy, W. (2010). Evaluation of rapid buffer methods to estimate pH buffer capacity of highly weathered soils from

south west of Western Australia. *19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia*. 57-60.

Nawaz, R. H. (2011). Soil Acidity Ranking, Soil Sensitivity and Vulnerability to Acid Deposition in the Northeast Region of Thailand. *2010 International Conference on Biology, Environment and Chemistry IPCBEE vol.1 (2011) IACSIT Press, SingapoNre*.

Nduwumuremyi A., Mugwe, J. N., Ruganzu V., Rusangwa, K. C., Nyirinkwa, B. (2013). Effects of Travertine in improving Selected Soil Properties and Yield of Irish Potato (*Solanum tuberosum L.*) in Acidic Soils. *Journal of Agricultural Science and Technology, A* 3: 175 – 182.

Nelson, D. M and Sommers, L. E. (1996). Total carbon, organic carbon and organic matter. *In: Spark, D. L. (eds). Methods of Soil Analysis Part 3- Chemical methods, SSSA Book Series 5, madison, Wisconsin, USA*- pp 61-1010.

Obi, A. O. (1976). Relative effects of different N-fertilizers on soil pH and crop yield in Western Nigeria soils. *Nigeria Agricultural Journal*, 13:95-101

Peech, M. (1941). Determination of Exchangeable Bases in Soils. *Industrial and Engineering Chemistry Analytical Edition*, 13(6), 436-441

Schofield, R. K. and Taylor, A. W. (1955). The measurement of soil pH. *Soil Science Society of America Proceedings*, 17: 164-167.

Shoemaker, H. E., E. O. McLean, and P. F. Pratt. (1961). Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. *Soil Science Society of America Proc*eedings, 25:274–277

SAS Institute Inc. 2013. SAS/ACCESS® 9.4 Interface to ADABAS: Reference. Cary, NC: SAS Institute Inc.

Woodruff, C. M. (1948). Testing soils for lime requirement by means of a buffer solution and glass electrode. *Soil Science*, 66: 53-63.

Xu, R., Zhao, A., Yuan, J. and Jiang, J. (2012). pH buffering capacity of acid soils from tropical and subtropical regions of China as influenced by incorporation of crop straw biochars. *Journal of Soils Sediments* 12, 494–502. https://doi.org/10.1007/s11368-012-0483-3