American-Eurasian Journal of Agronomy 2 (3): 144-151, 2009
ISSN 1995-896X

Evaluation of Locally-Sourced Liming Materials for Acid Soils in Akwa Ibom State, Southeastern Nigeria

G.S. Effiong, T.O. Ibia, P.I. Ogban and N.D. Inyang

Department of Soil Science, University of Uyo, Bag 1017, Uyo, Nigeria

Abstract: A greenhouse experiment was conducted to evaluate the shells of molluscs, which are known to have high contents of calcium carbonate ($CaCo_3$) and which are abundant in the coastal area of Akwa Ibom State, for acid soils using yellow maize as test crop. The shells evaluated were those of snail (*Achatina achatina*), periwinkle (*Turilella*), clam (*Cardium edule)* and oyster (*Spondylus spinosus*). Commercial lime ($CaCo_3$) was included in the study to serve as a basis for comparison. Results indicated high neutralizing equivalent values of 89.4, 93.9, 92.8 and 87.6% for oyster (OY), snail (SN), clam (CL) and periwinkle (PR) compared to 96.0% for $CaCo_3$. Chemical composition of mollusc shells show high mean calcium (Ca) contents ranging from 337.1±14.7 in PR to 524.6±2.3gkg^{-1} in $CaCo_3$; magnesium (Mg) concentration was highest in $CaCo_3$ (56.0±4.9gkg^{-1}) and least in SN (22.8±6.4gkg^{-1}). The shells and $CaCo_3$ when incubated with soil appreciably raised the soil pH, basic nutrients (Ca, Mg, Fe), organic carbon, effective cation exchange capacity (ECEC) and percent base saturation (BS), but drastically reduced the exchange acidity. Available P level was also reduced probably a result of formation of insoluble Ca-phosphate and an increased soil pH. Results of incubating molluscs shells with soil revealed no significant differences ($P > 0.05$) among the shells and $CaCo_3$ since they produced almost the same effect on maize plant height and dry matter yield, implying that any of the shells could be used to replace unavailable and sometimes unaffordable $CaCo_3$, to solve acidity problems of soils in Southeastern Nigeria.

Keywords: Mollusc shells • Chemical composition • Neutralizing value • Acid soil management • Nigeria

INTRODUCTION

Soils formed on Coastal Plain Sands (CPS), Beach Ridge Sands (BRS) and Sandstone/Shale (SS) parent materials are generally referred to as "Acid Sands" [1], because they are strongly weathered, leached and highly acidic. These soils which occupy > 27000km^2 of agricultural lands in the southern part of Nigeria [2], are characteristically poor in fertility manifesting in low cation exchange capacity (CEC), low base saturation and high concentration of exchangeable Al^{3+}, which saturates the adsorption complex. Consequently, attainment of good yields of many crops is contingent on increasing the pH of acid soils which then improves plant availability of macronutrients while reducing the solubility of elements such as aluminium (Al) and manganese (Mn). Soil acidity is commonly corrected by applying limestone. However, liming soil is not a common practice in the traditional subsistence farming system due to lack of awareness of the importance of lime and unavailability of the products at critical period. In addition, lime sources of sufficient fineness and purity are a major practical problem in the country. The limestone found in Akwa Ibom State has not been exploited so far for any purpose. Therefore, there is lack of limestone for agricultural purposes in the area. In addition, the commercial lime which can be used is sometimes unavailable and unaffordable at critical farming periods. There is, therefore the need to look for cheap and alternative sources of liming materials which can reduce the concentration of exchangeable Al and increase that of Ca to bring about high yield of arable crops.

The use of mollusc shells (the hard coated coverings of small, soft-bodied sea animals found on the seashore of coastal areas), may provide the needed solution. Mollusc sea animals are sources of protein to Akwa Ibom people and the shells are found at their dumpsites near market places and around homes. They include the shells from snail (*Achatina achatina*), periwinkle *(Turilella)*, clam (*Cardium edule*), slug (*Ampullela)* and oyster (*Spondylus spinosus*). These shells are found to contain high percentage of calcium carbonate, which is the active agent of liming materials.

Corresponding Author: G.S. Effiong, Department of Soil Science, University of Uyo, Bag 1017, Uyo, Nigeria

Recently, Effiong *et al.* [3] and Effiong and Okon [4] observed drastic reduction in soil acidity and increased Ca and Mg concentrations in soils treated with $CaCo_3$ and some mollusc shells. Earlier, Ibia *et al.* [5] observed considerable reduction in exchange acidity when an ultisol was treated with by-products obtained from Delta steel mills. Based on the above observations of liming materials ameliorating soil acidity and supplying Ca, our objectives were to evaluate the nutrient supplying potentials of some mollusc shells, assess the chemical effects of amendment on soil properties, growth and dry matter yield of maize (Zea mays).

MATERIALS AND METHOD

Environment of the Study Area: Akwa Ibom State which is located within the Niger Delta region of Nigeria is washed by the lower parts and tributaries of Imo, Qua Iboe and Cross Rivers which empty into the Atlantic Ocean. The area lies between latitudes 4°33' and 4°29'N and longitudes 7°35' and 8°25'E. The area experiences two distinct seasons: the wet season (April-October) characterized by heavy annual rainfall (about 3000-4000mm) (6); the rainfall pattern is bimodal with peaks in July and September and a relatively moisture stress period in August called 'August break'. The dry season (November-March) experiences the harmattan (dry dusty wind blowing over the Sahara desert) in the months of December through January. Temperatures are generally high throughout the year (mean-29.31°C), but the influence of the ocean however, tends to reduce the effect of heat during the very hot period (January-March) which coincides with the overhead passage of the sun [7]. Relative humidity is between 75 and 95%.

The major geologic formations of the study area are located on a wide level coastal plain overlying coastal plain sands geologic formation of tertiary era.

Collection and Preparation of Mollusc Shells: Mollusc shells (oyster-*Spondylus spinosus,* snail-*Achatina achatina,* clam-*Cardium edule* and periwinkle-*Turrilella*) were collected from their dump sites near the central market in Uyo metropolis. Besides these shells, commercial lime ($CaCo_3$) was included in the study to serve as a standard for comparison. The shells were washed thoroughly with warm water and rinsed with distilled water; placed in clean watch glasses and oven-dried at 80°C until brittle enough for grinding. The shell samples were separately crushed to powdery form using an agate mortar and pestle; then sieved to obtain particles < 2mm and stored in airtight, properly labeled container for the following mineral/elemental analyses: calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), phosphorus (P) and organic carbon. The shells were also analyzed for micronutrients: [Iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), boron (B) and molybdenum (Mo)].

Analytical Procedure: One gram (1g) of each liming material was placed in a 100 ml conical flask. A mixture of concentrated trioxonitrate (v), tetraoxochlorate (VII) and hydrofluoric acids in the ratio 1:1:1 (5ml each) was added and digested in a fume cupboard at 130°C until solution became colourless. The flasks were removed, cooled and 20ml of distilled water added to each flask. The solution was filtered into a 100ml volumetric flask and made to the mark with distilled water. A blank solution was also prepared using the same procedure but without sample. Sodium and K in the digest were measured using flame analyzer while Ca and Mg were determined by EDTA (ethylene diamine tetra acetic acid) titration with NaOH. Micronutrients (Fe, Mn, Zn, Cu, B and Mo) were measured with atomic absorption spectrophotometer (AAS) (model 939/959). Phosphorous was determined colorimetrically with vanadomolybdate procedure while organic carbon was done by the wet oxidation dichromate method [8].

Determination of Liming Equivalence of Mollusc Shells: The liming equivalence of each mollusc shells (powdery form) was separately placed in a 250ml flask, 50ml of 0.5M HCl added, swirled gently to mix and boiled gently on a steam bath for 5 minutes. The flask was cooled and 2-3 drops of phenolphthalein indicator added. The surplus acid was back titrated with 0.25M NaOH. The calcium carbonate equivalence was calculated using the equation: $\%CaCo_3$ equivalence of sample = 2.5 (mlHCl-mlNaOH)/2.

Field Studies: Composite soil samples were taken at 0-30cm depth from Acid sand soil formed on Coastal Plain sands parent materials in the Teaching and Research farm of the University of Uyo; samples processed for chemical analysis of pH, organic carbon, total Nitrogen, available phosphorus, exchange acidity and exchangeable bases (Ca, Mg, K, Na) using standard methods [9]. Effective cation exchange capacity (ECEC) and percent base saturation were obtained by calculations.

Greenhouse Studies and Experimental Design: Determination of effect of mollusc shells and calcium carbonate on soil chemical properties and plant growth and dry matter yield: Two (2) kg of soil samples were placed in plastic buckets and an equivalent amount (2g) of shell materials and $CaCo_3$ was added to each bucket thus:

2kg soil + 2g oyster; 2kg soil + 2g snail; 2kg soil + 2g clam; 2kg soil + 2g periwinkle and 2kg soil + 2g $CaCo_3$ (control). Fifty (50)ml distilled water was added to each bucket and stirred to mix. Two weeks after application of lime, four grains of yellow maize were planted per bucket and thinned down to two plants two weeks after germination; and then left for 30 days. The experiment was laid out in a randomized complete block design with four replications with mollusc shells as treatment and $CaCo_3$-control. The plastic buckets were perforated to aid drainage. Plant height (measured weekly for six weeks) and dry matter yield (obtained after six weeks growth) were used to evaluate the effect of mollusc shells on plant productivity. The plants were harvested at blooming stage, the period which tissue nutritional concentration appears to better correlate with yield.

Soil Analysis: Soil samples were taken after harvest and analysed for exchangeable bases (Ca, Mg, K, Na), exchange acidity, available P, organic carbon and total N, using standard methods (Sparks, 1996). Effective cation exchange capacity (ECEC) and percent base saturation were obtained by calculations. Other parameters analysed were Fe, Mn, Cu, Zn, B and Mo, using atomic absorption spectrophotometer (model 939/959).

Plant samples, taken six weeks after germination, were washed using 2% P-free detergent solution to remove dust and soil particles eventhough they were not clearly visible; then quickly washed with flowing pure water [10]. The residual moisture was evaporated and oven-dried at 80°C for 48 hrs. The dried plant samples were crushed using an agate mortar and pestle and then sieved through a 40 mesh sieve, digested using a combination of trioxonitrate (v) and tetraoxochlorate (IIV) acids as described by Mills and Jones [11] for Ca, Mg, K and Na. Potassium and Na in the digest were measured by flame analyzer while Ca and Mg were estimated by titration method,

Mean and standard deviation were employed in this study. Correlation coefficients calculated for elemental contents of liming materials and their concentrations in maize plants were not significant (not included).

RESULTS AND DISCUSSION

Liming Equivalence and Nutrient Contents of Mollusc Shells and Calcium Carbonate: Results of analysis of the various liming materials (oyster, snail, clam, periwinkle and calcium carbonate) for liming equivalence are presented in Table 1. The results indicate that mollusc shells studied have high neutralizing equivalent values: 89.4% for oyster (OY), 93.9% for snail (SN), 92.8% for clam (CL) and 87.6% for periwinkle (PR) shells compared to calcium carbonate ($CaCo_3$) with a value of 96.0% Snail and clam shells had the same neutralizing value which was higher than those of OY and PR. The highest value was found in $CaCo_3$ (96.0%) being slightly lower than 100, an index of pure $CaCo_3$. These values compared favourably with those obtained by Tisdale *et al.* [12] and Effiong and Okon [4]. This result also indicates that mollusc shells studied are good liming materials for acid soils in Southeastern Nigeria.

Table 2 contains data for macro-nutrients in mollusc shells and $CaCo_3$ that consist of total nitrogen, Ca, Mg, K, Na and P as well as organic C and ash. Total N value was relatively low in the studied liming materials. Among the four shells, PR (0.79gkg^{-1}) and SN (0.62gkg^{-1}) had the highest values, followed by CL (0.57gkg^{-1}) and OY (0.050gkg^{-1}) N. Calcium carbonate had the least value of 0.38gkg^{-1} N. Calcium contents of SN (488.5gkg^{-1}), CL (428.5gkg^{-1}), OY (417.0 gkg^{-1}) and PR (377.1 gkg^{-1}), were statistically ($P < 0.05$) lower than that found for $CaCo_3$ (524.6 gkg^{-1}). Like Ca, Mg contents in CL (35.3 gkg^{-1}) were relatively higher than those found for PR (27.5 gkg^{-1}), OY (24.3 gkg^{-1}) and SN (22.8 gkg^{-1}) with the commercial lime (56.0 gkg^{-1}) having the highest content. In a similar study, Inyang [13] found Ca and Mg concentrations of 373 and 27.1 gkg^{-1} for OY, 536 and 27.3 gkg^{-1} for PR shells, respectively. Commercial lime had Ca and Mg concentrations of 508 and 20.8 gkg^{-1}. In a recent study (4) found a relatively higher Ca value of 461 gkg^{-1} for OY and a much lower content of 441 gkg^{-1} for SN shells. The differences may be attributed to the shells age.

The high concentrations of Mg in the shells would be of significance to plants since it is vital in the synthesis of chlorophyll (4). Potassium content in the shells was quite low with values ranging from 0.19 gkg^{-1} in CL to 1.19 gkg^{-1} in SN while P level was similarly low with the lowest level found in $CaCo_3$ (Table 2). Sodium content was relatively higher in the mollusc shells than those of K and P and this may have contributed to the slightly alkaline reaction of the treated soil (Table 4).

Table 1: Mean and standard deviation of liming equivalence of mollusc shells

Liming Materials	Liming Equivalence (%)
Oyster (OY) Shell	89.4±2.6c
Snail (SN) Shell	93.9±2.2b
Clam (CL) shell	92.8±2.2b
Periwinkle (PR) Shell	87.6±2.2d
$CaCo_3$	96.0±2.3a

Each data is a mean and standard deviation (X±SD) of three determinations

Table 2: Mean and Standard deviation of major nutrient contents of mollusc shells and commercial lime

Liming material	TN Nutrients	OC Concentration	Ca	Mg	K	Na	P ($mgKg^{-1}$)	Ash (%)-
			(g Kg^{-1})					
Oyster (OY) Shell	0.50±0.27c	70.9±2.5a	417.0±6.2d	24.3±3.9c	0.20±0.08b	0.69±0.89d	0.17±0.14b	98.2±0.85a
Snail (SN) Shell	0.62±0.37b	36.4±0.0d	488.5±6.7b	22.8±6.4c	1.19±1.40a	1.92±2.50b	0.18±0.19a	98.4±0.71a
Clam (CL) Shell	0.57±0.04b	45.5±2.6c	428.5±10.2c	35.3±1.6b	0.19±0.08c	1.32±1.53c	0.17±0.17b	95.9±3.39c
Periwinkle (PR) Shell	0.79±0.14a	60.0±2.5b	377.1±14.7c	27.5±0.9c	0.26±0.007b	1.54±1.93c	0.18±0.19a	97.9±0.07b
$CaCo_3$	0.38±0.18d	54.5±0.0b	524.6±2.3a	56.0±4.9a	0.35±0.13b	1.97±2.59a	0.15±0.15c	98.4±1.13a

Each data is a mean and standard deviation (• ±SD) of three determinations

TN-total N, OC-organic C

Table 3: Mean and Standard deviation of micronutrient contents of mollusc shells and commercial lime

	Micronutrients concentration (mg kg^{-1})					
Liming material	Fe	Mn	Zn	Cu	B	Mo
Oyster (OY) Shell	795±7.5a	0.192±0.12c	0.301±0.06a	0.012±5.660b	2 x 10^{-3}d	6 x 10^{-3}a
Snail (SN) Shell	127±2.8d	0.227±0.02b	0.266±0.07a	0.011±0.010a	6 x 10^{-3}a	2 x 10^{-3}b
Clam (CL) Shell	300±4.7b	0.281±0.05a	0.213±0.16b	0.062±0.080a	3 x 10^{-3}c	1 x 10^{-3}c
Periwinkle (PR) Shell	186±5.9cd	0.203±0.03c	0.248±5.66b	0.010±0.065b	4 x 10^{-3}b	2 x 10^{-3}b
$CaCo_3$	292±3.9bc	0.157±0.07d	0.066±0.01c	0.012±0.007b	2 x 10^{-3}d	2 x 10^{-3}b

Each data is a mean and standard deviation (• ±SD) of three determinations

Ash contents, often regarded as an index of mineral element contents in biomass were high in the shells with mean values: 98.2±0.85, 98.4±0.71 and 98.4±1.13% for OY, SN and $CaCo_3$ compared to values obtained for CL and PR (Table 2). The high ash content implies that mollusc shells, apart from reducing soil acidity, could also serve as good sources of mineral elements to plants if properly ground and applied to soils. Organic carbon contents were high too and varied widely in the shells. The least value was found for SN (36.4±0.0gkg^{-1}) and highest (70.9±2.5gkg^{-1}) for OY. Commercial lime had 54.5gkg^{-1}, a value which was statistically different from those of CL and SN.

Mean values of micronutrient contents of mollusc shells and commercial lime presented in Table 3 indicate very high values of Fe (795±7.5, 127±2.8, 300±4.7, 186±5.9 and 292±3.9$mgkg^{-1}$) for OY, SN, CL, PR and $CaCo_3$, respectively and relatively low contents for Mn and Zn while B and Mo were found in trace amounts.

Effects of Liming Materials on Soil Chemical Properties: Table 4 contains data for untreated and treated soils that consist of soil pH, organic C, total N, P, exchangeable bases (Ca, Mg, K, Na), exchange acidity, ECEC and percent base saturation. The pH value (4.6) of untreated soil was strongly acidic. Total N level (0.73gkg^{-1}) and organic C (6.8gkg^{-1}) contents were relatively low. With a separating index of 25 between fertile and infertile soil [14], the C/N ratio of 9 obtained for this soil though falls outside the normal range of 10:1 to 12:1 indicates gain of NH_4^+ and NO_3^-. [15]. Available P content (138.9$mgkg^{-1}$) of the soil was high compared to 15-25$mgkg^{-1}$ critical level for this zone [16]. Calcium content was moderate (3.0$cmolkg^{-1}$); Mg level was high while K and Na were low. Exchange acidity value (2.38 $cmolkg^{-1}$) accounts for only 30% of the ECEC. Percent base saturation (61%) was high in the soil. The low contents of basic cations (K, Ca and Mg) in the acid soil probably, result from the small amounts in the parent material, low CEC to retain them against leaching and their removal by erosion [17].

Table 4: Effect of mollusc shells and commercial lime on some soil chemical properties before and after 30 days of incubation

Liming materials	pH	OC (gkg^{-1})	TN $mgkg^{-1}$	P	Ca	Mg	K	Na $cmolkg^{-1}$	EA	ECEC	BS (%)
Untreated soil	4.6±0.2	6.8±4.9	0.73±0.2	138.9±3.9	3.0±0.7	1.5±0.3	0.13±0.08	0.16±0.13	2.38±2.07	7.86±1.50	61.21±1
Treated soil											
OY	7.2±0.4b	17.5±6.9c	1.00±0.6b	101.4±1.4b	20.5±9.8b	6.2±2.4a	0.09±0.06b	0.18±0.19b	0.75±0.33a	27.71±1.50b	97.28±1a
SN	7.3±0.5a	16.4±7.3c	1.05±0.7b	107.5±1.7a	19.9±7.0b	5.7±2.9ab	0.09±0.05b	0.25±0.18a	0.77±0.05a	22.14±3.70d	96.90±1b
CL	7.3±0.4a	24.9±1.8b	3.08±4.3a	107.8±2.5a	18.3±1.6c	3.0±1.1c	0.10±0.05a	0.06±0.03d	0.52±0.26c	21.90±9.50c	96.67±2b
PR	7.1±0.8c	27.9±2.8a	0.76±0.4b	78.3±2.3c	15.1±2.2d	4.2±1.4b	0.09±0.05b	0.05±0.13d	0.65±0.14b	23.92±8.90c	98.44±1b
$CaCo_3$	7.3±0.6a	17.9±2.4c	0.98±0.6b	98.2±3.8b	23.7±9.8a	6.6±2.4a	0.08±0.05c	0.13±0.09c	0.77±0.12a	30.57±9.69a	97.42±0a

Each data is a mean and standard deviation of three determinations.

OC-organic carbon, TN-total nitrogen, ECEC-effective cation exchange capacity.

BS-base saturation, EA-exchange acidity.

Table 5: Effect of mollusc shells and commercial lime on maize plant height

Liming Materials	Plant height (cm)
Oyster (OY) Shell	118.5±12.5a
Snail (SN) Shell	114.6±15.0d
Clam (CL) shell	115.9±15.9c
Periwinkle (PR) Shell	117.0±15.3b
$CaCo_3$	116.1±15.3c

Each data is a mean and standard deviation (X±SD) of three determinations

Results of incubating the soil with liming materials for 30 days indicate considerable changes in soil pH. Calcium carbonate, SN and CL treatments raised the pH of soil from 4.6 to 7.3 while PR and OY raised pH to 7.2 and 7.1, respectively. These values translate to 59% increase for $CaCo_3$, SN and CL treatments. This result implies that mollusc shells studied could be used as suitable alternative liming materials for acid sand soils of Southeastern Nigeria. This study also confirms works by Chichilo *et al.* [18]. Inyang [13] and Akpabio [19] that mollusc shells were as effective as $CaCo_3$ in reducing soil acidity.

Incubating acid soil with various liming materials had considerable effects on exchangeable Ca and Mg, exchange acidity, ECEC and percent base saturation (Table 4). Exchangeable Ca increased appreciably in the treated soils, accounting for 74, 90, 84, 63 and 77% of the CEC in soils amended with OY, SN, CL, PR and $CaCo_3$, respectively as against 58% in untreated soil. Increase in exchangeable Mg followed similar pattern but with lower contributions to cation exchange capacity (CEC): OY (27%), SN (26%), CL (14%), PR(18%) and $CaCo_3$ (22%). Meanwhile SN and CL contributed more Ca while OY and SN released more Mg than $CaCo_3$, indicating the effectiveness of some of the shells over the commercial lime. The high contents of Ca following application of various liming materials was probably a result of slow rate of movement of Ca and the low solubility of $CaCo_3$, which is the active agent in each of the mollusc shells thereby creating an excess of Ca since the products of neutralization by the acid soil were Ca^{2+} and HCO_3^-, the latter decomposing into Co_2 and H_2O.

In marked contract to Ca and Mg, treatments had little or no effect on K and Na contents in the soil (Table 4). This may be attributable to the very low concentrations of these elements in the liming materials used for amendment or due to the low absolute levels of K and Na in the soil. However, the low Na content is beneficial in that Na ions if found in high concentrations in soils can be destructive to soil structure and thus becomes detrimental to plant growth [20].

Exchangeable Ca values have been reported to increase with increase in the quantity of lime applied [3, 21]. Effective cation exchange capacity (ECEC) and percent base saturation levels of the treated soils increased markedly above levels found in the untreated soils. For example, ECEC level increased from 7.86 $cmolkg^{-1}$ in the untreated soil to mean values of 27.71±1.50, 22.14±3.70, 21.90±9.50, 23.92±8.90 and 30.57±9.70 $cmolkg^{-1}$ in the soil treated with OY, SN, CL, PR and $CaCo_3$, respectively. Similarly, percent base saturation increased from 61% to 97% in soil treated with OY, SN, CL and $CaCo_3$ and 96% for PR. The above observations show mollusc shells to be effective

Table 6: Effect of mollusc shells and commercial lime on dry matter yield of maize

Liming Materials	Dry matter yield (ha•[1])
Oyster (OY) Shell	22.5±7.5a
Snail (SN) Shell	21.8±7.6b
Clam (CL) shell	21.3±5.9c
Periwinkle (PR) Shell	21.0±6.8d
$CaCo_3$	21.0±6.8d

Each data is a mean and standard deviation (X±SD) of three determinations

Table 7: Effect of mollusc shells and commercial lime on major nutrients concentrations in maize plant shoot

	Nutrients concentration (gk g•[1])			
Liming material	Ca	Mg	K	Na
Oyster (OY) Shell	3.9±3.2b	2.8±2.2a	25.0±3.1a	0.1±0.00b
Snail (SN) Shell	4.1±3.3b	1.8±0.5d	10.5±10.2c	0.15±0.07a
Clam (CL) Shell	3.4±2.5c	2.6±1.7b	21.8±8.1b	0.15±0.07a
Periwinkle (PR) Shell	3.0±3.0d	1.7±0.4d	21.1±2.5b	0.15±0.07a
$CaCo_3$	4.5±4.9a	2.3±2.8c	20.0±3.0b	0.1±0.00b

Each data is a mean and standard deviation (X±SD) of three determinations

Table 8: Effect of mollusc shells and commercial lime on major nutrients concentrations in maize plant root

	Nutrients concentration (gk g•[1])			
Liming material	Ca	Mg	K	Na
Oyster (OY) Shell	1.7 0.1a	1.7±1.8c	22.8±9.9b	0.1±0.0b
Snail (SN) Shell	1.5±0.7b	2.4±1.9a	28.9±8.2a	1.5±0.0a
Clam (CL) Shell	0.8±0.00c	1.4±0.4d	16.5±0.5c	0.1±0.0b
Periwinkle (PR) Shell	0.8±0.5c	2.1±1.9b	28.7±7.9a	0.1±0.0b
$CaCo_3$	1.6±0.32ab	1.4±0.8d	17.6±1.5c	0.15±0.7b

Each data is a mean and standard deviation (X±SD) of three determinations

amendments for supplying the needed Ca and Mg to the studied soils. Apart from pH, effect of mollusc shells and commercial lime was marked in the reduction of exchange acidity (EA). Clam and periwinkle shells reduced EA by 78 and 73%, respectively, closely followed by OY, SN and $CaCo_3$ with 69, 68 and 68%.

Mollusc shells and commercial lime had considerable effect on organic carbon contents (Table 4), with values increasing from 6.8gkg•[1] in the untreated soil to 17.5, 16.7, 24.9, 27.9 and 17.9gkg•[1] in soils amended with OY, SN, CL, PR and $CaCo_3$, respectively. The results imply that OY and SN shells were as effective as $CaCo_3$ while CL and PR shells were more effective in producing organic C than $CaCo_3$. In other words, mollusc shells which are usually applied in tons per hectare could add considerable quantity of organic C to soils.

No visible effect of the various liming treatments was noticed on the total N level of the soil (Table 4). This observation could be attributable to increased Ca content and near neutral pH value of the soil which stimulate microbial growth and activity, resulting in rapid loss of the soil organic matter and negatively affected N availability. Available phosphorus contents of the limed soils were 101.4mgkg•[1] for OY, 107.5mgkg•[1] for SN, 107.8mgkg•[1] for CL, 78.3mgkg•[1] for PR and 98.2mgkg•[1] for $CaCo_3$. These values were high compared to 15-25mgkg•[1] regarded as critical level for soils of this zone. However, there was considerable reduction in the value of P for the untreated soil. On the contrary, Ibia *et al.* [5]and Effiong *et al.* [3] observed increased availability of P following application of lime to an acid soil. However, IITA [22] reported a decline in phosphate availability when three ultisols were treated with various liming materials. The reduction in phosphate levels following liming in this study probably results from the formation of insoluble Ca-phosphates and increased soil pH. High pH value and enhanced Ca contents in soils are closely related to low availability of P, especially under this condition of low Na content.

Effect of various Mollusc Shells on Plant Height and Dry Matter Yield of Maize: Results presented in Tables 5 and 6 revealed that all the liming materials produced almost the same effect on plant height and dry matter yield with OY having slightly higher effect than the rests, implying that any of the mollusc shells could be used to replace $CaCo_3$ which is sometimes scarce at critical farming periods. It could also mean that liming beyond pH value of 6.5 (as in this study) may induce deficiency of some nutrients which could limit the growth and hence, dry matter yield of maize. Plant tissue analysis presented in Tables 7 and 8 indicates that K was the most abundant element in maize plant shoot, with mean concentration ranging from 10.5±10.2 in SN treatment to 25.0±3.1gkg^{-1} in OY; the value for CL, PR and $CaCo_3$ was the same. The value of K in plant root varied widely and ranged from 16.5±0.5 in CL treatment to 28.9±8.2gkg^{-1} in SN shells. Calcium carbonate, OY and PR had K values of 17.6±1.5, 28.8±9.9 and 28.7±7.9gkg^{-1}, respectively. These values are in lime with those obtained by Mills and Jones [11] for corn. Calcium levels varied slightly with higher values in maize shoot than the roots. Soil treated with $CaCo_3$ produced the highest mean concentration of Ca in maize shoot (4.5±4.9gkg^{-1}), closely followed by SN (4.1±3.3gkg^{-1}) and Oy (3.9±3.2gkg^{-1}) shells. The least values were obtained from PR (3.0±3.0gkg^{-1}) and CL (3.4±2.5gkg^{-1}). In roots, Ca contents ranged from 0.8±0.0gkg^{-1} in CL and PR to 1.7±0.1gkg^{-1} in OY, while the values of 1.5±0.7 and 1.6±0.3gkg^{-1}, were found for SN and $CaCo_3$. Magnesium contents were higher in maize shoot than the root, with values varying from 1.4gkg^{-1} in CL and $CaCo_3$ to 2.4gkg^{-1} in SN and from 1.7 in PR to 2.8gkg^{-1} in OY for root and shoot, respectively. Sodium content was least in both the shoot and root of the test crop with values ranging from 0.1 to 1.5gkg^{-1}.

CONCLUSION

This study was conducted to evaluate the liming effectiveness of mollusc shells using oyster, snail, clam and periwinkle. The shells had high neutralizing equivalence, high contents of nutrients (Ca, Mg, Fe), Organic C and ash, compared to $CaCo_3$. These liming materials also reduced markedly the soil exchange acidity and increased appreciably the pH, basic nutrients (Ca and Mg), effective cation exchange capacity (ECEC) and percent base saturation of the acid soil. Applying at the same rate, the mollusc shells and $CaCo_3$ had no significant differences ($P < 0.05$) as their effects were similar on maize plant height and dry matter yield. Based on chemical compositions, effects on soil properties, growth and dry matter yield of maize plants, mollusc shells compared favourably with the commercial lime ($CaCo_3$) and could be used to solve acidity problems of acid sand soils in Southeastern Nigeria.

REFERENCES

1. Obiora, C.H., 1961. The Acid sands of the Eastern Nigeria. Part 1-Extent. The Nigerian Scientists Journal Eastern Nigeria Science Association, 1(1): 54-64.
2. Ojanuga, A.G., G. Lekwa and F.R.O. Akamigbo, 1981. Survey, Classification and Genesis of 'Acid Sands' In: E. J. Udo and R. A. Sobulo (eds.) Acid Sands of Southern Nigeria, Soil Science Society of Nigeria, pp: 1-18.
3. Effiong, G.S., N.O. Isirimah and U. Eshiet, 2006. Influence of Liming on Extractable P. Growth and Yield of Okra (*Abelmoschus esculentus* (L.) Moench). Nig. J. Agric. Food and Environ., 3(1 and 2): 131-134.
4. Effiong, G.S. and I. Okon, 2009. Evaluation of Mollusc Shells as Liming Materials for Acid Sands of Akwa Ibom State, Southeastern Nigeria. Soil Sci. Soc. Nigeria Jour (in press).
5. Ibia, T.O., E.J. Udo and U. Omoti, 1997. Evaluation of Slag by-products from Delta Steel Plant, as liming materials. Global J. Pure and Appl. Sci., Vol. 3. No. 3.
6. Uniuyo Consult, 2001. Soil Potentials of Akwa Ibom State. Soils of the Coastal Zone, Ministry of Agriculture, Uyo, pp: 116.
7. Enwezor, U.O., A.C. Ohiri, E.E. Opuwaribo and E.J. Udo, 1990. A review of fertilizer use on crops in the South Eastern Zone of Nigeria. In: Literature Review on Soil Fertility Investigation in Nigeria. Fed. Min. of Agriculture and Nat. Resources, Lagos.
8. Nelson, D.W. and L.E. Sommers, 1996. Total Carbon, Organic Carbon and organic matter. In: D.L. Sparks, Methods of Soil Analysis. Part 3. Chemical Methods-SSSA Book Series no. 5.
9. Sparks, D.L., 1996. Methods of Soil Analysis. Chemical properties. Soil Science Soc. of America. Bk. Series, 5. Madison, WI.
10. Sonnerveld, C. and P.A. van Dijk, 1982. The effectiveness of some washing procedures on the removal of contaminates from plant tissues of glass house crops. Comm.. in Soil Sci. and Plant Analysis, 13: 487-496.

11. Mills, H.A. and B. Jones, 1996. Plant Analysis Handbook ll. A Practical Sampling, Preparation, Analysis and Interpretation Guide. Micro-Publishing, Inc., pp: 116-124.
12. Tisdale, S.L., W.L. Nelson, J.D. Beaton and J.L. Havlin, 1993. Soil acidity and basicity. In: Soil Fertility and Fertilizers (Tisdale, S. L. and Nelson, W.L. eds), 5th Edition, Mac. Publishing Co., N.Y., pp: 364-404.
13. Inyang, N.D., 2006. Use of mollusc shells as liming materials for acid soils of Akwa Ibom State. Unpublished M. Sc. Thesis, Dept. of Soil Sci. University of Uyo, Uyo, pp: 87.
14. Landon, J.R., 1984. Booker Tropical Soil Manual. A handbook for soil survey and agricultural land evaluation in the tropics and subtropics. Booker Agriculture International Limited, USA, New York, pp: 450.
15. Stevenson, F.J. and M.A. Colė, 1999. Cycles of Soil. C, N.P.S. Micronutrients. John Wiley and Sons, pp: 427.
16. Ibia, T.O. and E.J. Udo, 1993. Phosphorus Forms and fixation of representative soils in Akwa Ibom State of Nigeria. Geoderma, 58: 95-106.
17. Amberger, A., 2006. Soil fertility and plant nutrition in the tropics and subtropics. IFA/IPI, pp: 96.
18. Chichilo, P.P., H.W. Armiger and A.W. Specht, 1954. Plant nutrients from slag-furnace. Slag as a source of plant nutrients and its liming effectiveness relative to limestone. J. Agr. Food Chem., 2: 258-462.
19. Akpabio, E.S., 2007. Determination of the chemical properties and liming equivalence of mollusc shells. Unpublished M.Sc. Thesis. Dept. of Chemistry, University of Uyo, Uyo, pp: 56.
20. Richards, L.A., 1969. Diagnosis and improvement of saline and alkaline soils. Agricultural Handbook 60, Salinity Laboratory, Riverside, California.
21. Mascarenhas, H.A., J.R. Crallo, B. van Raij, J. Ique and O.C. Batalgia, 1976. Effects of liming on chemical characteristics of soil and the nutrition of soybeans on a red latisol., pp: 30.
22. IITA, 1975. Management of Ultisols and Oxisols in the tropics. International Institute of Tropical Agriculture, Ibadan, Nigeria, pp: 12-14.