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Research Article

Potentials of Unconventional Liming Materials in Reducing Soil Acidity

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Abstract

The shells of molluscs (oyster- *Spondulus spinosus* and snail - *Achatina achatina*), which are known to contain high amounts of calcium carbonate and which are abundant in the state were compared with commercial lime in the management of soils developed on acid sands in Akwa Ibom State. Results showed high neutralizing equivalent value of 65 and 75% for oyster and snail shells, respectively compared to 76% for $CaC0_3$. Chemical composition of mollusc shells indicated high mean Ca contents of 461.0 ± 28.4 and 441.0 ± 56.6gkg^{-1} for oyster and snail shells while $CaC0_3$ contained 541.1 ± 41.7gkg Magnesium contents were higher in oyster (215.2 ± 5.1 gkg^{-1}) than in snail (182.4 ± 17.2gkg^{-1}) shells and $CaC0_3$ (91.2 ± 8.7gkg^{-1}). Iron content was 796mgkg^{-1} for oyster, 127mgkg-1 for snail and 292mgkg-1 for $CaC0_3$. The mollusc shells and $CaC0_3$, drastically reduced the exchange acidity and increased the soil pH, basic nutrients (Ca and Mg), effective cation exchange capacity and percent base saturation of the studied soil. Mollusc shells compared favorably with $CaC0_3$ and could serve as alternative liming materials for soil developed on acid sands in Akwa Ibom State.

Keywords: Mollusc shells; Liming equivalence; Acid sands; Chemical composition

Introduction

Soil acidity is a major problem in the production of arable crops in the humid tropical soils. Yields of many crops are highly reduced by soil acidity. Most of agricultural soils in Akwa Ibom State are derived from Coastal plain sands and Beach ridge sands and are generally referred to as 'Acid sands' [1], because they are strongly weathered, sandy and highly acidic. Most arable crops give poor yields and for the crops to do well the soils will have to be limed to remove the adverse effects of high acidity. The source of limestone close to Akwa Ibom State is M famosing in Cross River State and this limestone is used mainly for the manufacture of cement and a raw material in the iron and steel industry. The limestone in Ini Local Government Area of Akwa Ibom State has not been exploited so far for any purpose. There is therefore lack of limestone in the area for agricultural purposes. There is also the problem of lack of awareness of the farmers about the importance of lime in reducing soil acidity and thus bringing about high yields of arable crops in the high acidic soils of the area. The high cost and unavailability of commercial lime underscores the need to look for cheap and alternative sources of liming materials for management of soils developed on acid sands in Akwa Ibom State. It was also to create the awareness of the importance of liming to the farmers. The use of mollusc shells may provide the solutions since the shells are found to contain high percentage of calcium carbonate, which is the active compound in liming materials. Mollusc sea foods are. sources of animal protein to Akwa Ibom people and beyond, and for many coastal inhabitants. Their shells are commonly found thrown away in the market places and around homes. They include snail, slug, periwinkle, clam, oyster and other shells.

The objectives of this study were

(i) To determine calcium carbonate equivalence of oyster and snail shells.

(ii) Evaluate the chemical composition of snail and oyster shells as liming materials for soils developed on acid sands in Akwa Ibom State and

(iii) Examine the effects of these shells relative to commercial lime on selected soil chemical properties.

Materials and Methods

Study area

Soil samples were taken from the University of IJyo Teaching and Research Farm while mollusc shells were collected at their dumping site near Etuk Market, along Aka Road in Oyo Metropolis. Uyo is situated at latitude 4030' and 5030'N and longitude 7075' and 7093'E. The area experiences two distinct seasons: the wet and dry seasons. The wet or rainy season begins from April and lasts till October. It is characterized by heavy rainfall of about 2500-4000mm per annum. The rainfall is bimodal with peaks in July and September and a relatively moisture stressed period in August, known as "August break". The dry season starts from November till March. It is characterized by high temperature with a mean annual temperature of 28 °C. The highest temperatures are experienced between January through March, the period described by Enwezor et al. [2] as overhead passage of the sun. Relative humidity is between 75% and 95%. The soil in the area is formed on coastal plain sands parent materials and has been described as Typic Paleudult [3].

Soil analysis

Composite soil samples were taken at (0-30cm) depth. The samples were air dried and sieved (< 2mm). The samples were processed for chemical analysis. The soils were analyzed using the procedures described in Il TA [4]. Soil pH was determined in 1:2.5 soil to water ratio using the glass electrode pH metre and organic carbon was determined using wet oxidation method. Total Nitrogen (N) was determined by the Kjeldahl digestion method, available phosphorus (P) was extracted with Bray P-1 method and P in the extract measured by the blue colour method. Exchange acidity (EA) was extracted with IN KCI and estimated in the extract by titration. Exchangeable bases were extracted using INNH40Ac. Potassium (K) and Sodium (Na) were determined by flame photometer while calcium (Ca) and magnesium (Mg) were determined by EDTA (ethylene diamine tetraacetic acid) titration using NaOH. Effective cation exchange capacity (ECEC) was taken as the sum of the exchangeable bases and exchangeable acidity.

Percentage base saturation was computed using the formula:

%BS = x 100

Collection and preparation of mollusc shells

Mollusc shells (snail and oyster) were collected from the dumping site near *Etuk* Market in Uyo metropolis. Commercial lime (calcium carbonate) was bought and used as control sample. The shells were washed in warm water and rinsed thoroughly with distilled water. They were placed in clean watch glasses, oven-dried at 80 °C for 48 hours, and were separately crushed to powder in a hammer mill and sieved to obtain particles less than 2mm. The samples and commercial lime were analyzed for Ca, Mg, K, Na, P, and organic carbon. The iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), boron (B), and molybdenum (MO) contents were also determined using the procedures recommended by the Association of Official Analytical Chemists [5]. One gram (lg) of each material was digested with a mixture of concentrated trioxonitrate (v), tetraoxochloroate (Vll) and hydrofluoric acids in the ratio of 1:1:1 in a fume cupboard at 130 °C, the digests were cooled and 20ml of distilled water added, filtered and made up to mark with distilled water. Na and K in the digest were measured using flame analyzer while Ca and Mg were determined by EDTA. Fe, Mn, Zn, Cu, B, and MO were measured with atomic absorption spectrophotometer (AAS) while P was determined by the molybdenum blue method.

Determination of liming equivalence of oyster and snail shells

Measured 0.5g of milled snail and oyster shells were placed in a 250ml flask, and 50ml of 0.5M HCI added, swirled gently and then 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 as follows:

Effect of mollusc shells (snail and oyster) on pH and other chemical properties

The method adopted was described by Jacobs and Reed [6], The soil sample was oven-dried at 105 °C, ground into powder and sieved. One hundred grams (100 g) of sieved soil sample was placed in each beaker thus. (i) Soil (100 g), (ii) $CaC0_3$ only (1g), (iii) Snail only (1g), (iv) Oyster only (1g), (v) Snail (lg) + 100g of soil, (vi) Oyster (lg) + 100g of soil, (vii) CaC03 (lg) + 100 g of soil.

Twenty (20)ml of distilled water was added and stirred to mix. The mixture was allowed to stand for 1 hour with occasional stirring. The pH was measured using glass electrode pH metre. Similar experiment was set up thus:

a. snail (2g) + 100g soil

b. oyster (2g) + 100g soil

c. $CaC0_3$ (2g) + 100g soil

To assess the effect of liming materials on chemical properties of the soil and the experiment was left for 21 days with occasional stirring. The soil samples were taken and analyzed for exchangeable bases, exchange acidity, available P, organic carbon and total N. Effective cation exchange capacity (ECEC) and percent base saturation were obtained by calculation. Other parameters were Fe, Mn, Cu, Zn, B and MO, using atomic absorption spectrophotometer after digestion.

Statistical analysis

The study used mean and standard deviation (X ± SD).

Results and Discussion

Mineral composition of oyster and snail shells and calcium carbonate

Liming equivalence of oyster and snail shells

Liming equivalence, which is the measurement of the relative value of the liming material in oyster and snail shells, .is presented in Figure 1. The shells have high neutralizing equivalent values, 65% for oyster shell and 75% for snail shell compared to calcium carbonate with 76.00%. These values are similar to those obtained by Tisdale et al. [7], implying that oyster and snail shells are good liming materials. Mean macronutrient contents of mollusc shells and commercial lime ($CaC0_3$) are presented in Table 1. Ca content of oyster (461.0gkg^{-1}) and snail (441.0gkg^{-1}) shells were lower than that of $CaC0_3$ (541.1gkg^{-1}). Mg content of mollusc shells was higher in oyster (215.2gkg^{-1}) than snail (182.4gkg^{-1}) shells with commercial lime having the least (91.2gkg^{-1}). In a similar study, Inyang (2006) obtained 373gkg^{-1} and 536gkg^{-1} Ca and 27.1gkg^{-1}and 27.3gkg^{-1} Mg for oyster and snail shells, respectively, while commercial lime used advantage in 508gkg^{-1} and 208gkg^{-1}Mg. The relatively high contents of Mg in the shells are of significance because when made available to plants it improves plant growth especially through the synthesis of chlorophyll. All the liming materials were low in K (2.0-2.5gkg^{-1}) while Na was moderate in oyster (3.7gkg^{-1}) and snail (2.4gkg^{-1}) shells but low in CaC03 (1.3gkg^{-1}). The low Na content in commercial lime can be attributed to beneficiation while the shells had not been purified and sodium may be present as silicates.

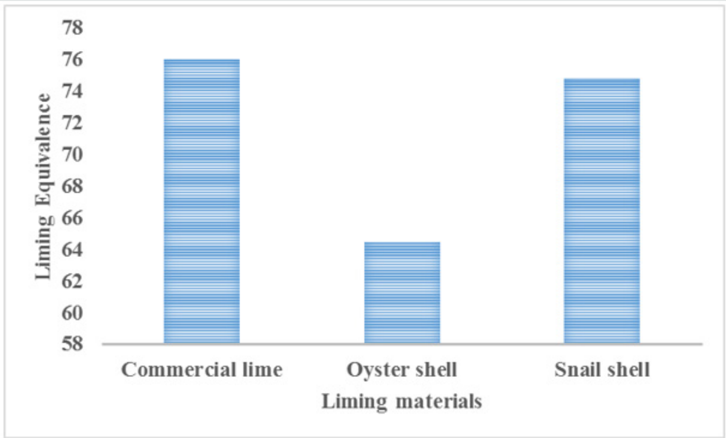

Figure 1: Liming equivalence of mollusc shells.

Table 1: Mean values of macronutrient content of mollusk shell and commercial lime.

Mining material	pH	Ca	Mg	K	Na	p	Ash	TN	Org. C	C/N
Commercial lime	8.23±0.13	541.1±141.7	91.2±87.4	0.25±0.07	1.3±0.7	0.109±0.003	98.40±1.13	0.50±0.02	54.5±0.00	109
Oyster shell	11.36±0.06	461.0±28.4	215.2±5.1	0.25±0.07	3.7±1.6	0.110±0.003	98.20±0.85	0.69±0.03	70.9±2.5	103
Snail shell	8.98±0.79	441.0±56.6	182.4±17.2	0.0±0.00	2.4±0.0	0.114±0.007	98.40±0.71	0.36±0.01	36.4±0.00	101
Each value is a mean and standard deviation (X ±SD) of two determines. TN – total nitrogen, C/N carbon to nitrogen ration										

N and P were low in the shells and $CaC0_3$ (Table 1). However, since liming materials are usually applied in large quantities, (in mega grams per hectare), the low concentration of N and P in the shells may translate into significant level of addition to soils. The ash content, an index of mineral content in biota, was very high and values were the same for the liming materials (98%). This result implies that mollusc shells would be good sources of mineral elements to plants if properly ground and applied to soils. Organic carbon contents of the shells under study and commercial lime were high with the highest value obtained in oyster shell (70.9gkg^{-1}), followed by $CaC0_3$ (54.5gkg^{-1}) and the least value was found in snail shell (36.4gkg^{-1}). These values translate to high organic matter contents of 93.96gkg^{-1} for $CaC0_3$, 122.23gkg^{-1} for oyster shell and 62.75gkg^{-1} for snail shell, respectively. The carbon to nitrogen (C/N) ratio described as an indication of the type of organic matter present and in particular, the degree of humification [8], was very high (in favour of organic C) in mollusc shells and $CaC0_3$ studied. This confirms the fact that mollusc shells are poor sources of N. The micronutrient contents of mollusc shells and commercial lime are presented in Table 2. Fe concentration was highest for oyster shell (795.7mgkg^{-l}) and least in snail shell (127.1mgkg^{-1}) Mn was quite low with values of 0.517mgkg^{-1} , 0.227mgkg^{-1} and 0.192 mgkg^{-1} for $CaC0_3$, snail and oyster shells, respectively. The value of Zn was also low while Cu, B and MO were found in trace amounts in both the shells and commercial lime. The critical levels of 1.0, 0.5, 0.2 and 0.13mgkg^{-1} for Mn, Zn, Cu and B [9] and Oyinlola [10] show that the amount in these materials may not have any significant influence in the soil. However, since limes are usually applied in large quantities, the concentrations of these micronutrients may increase considerably, depending on the pH of the soil and quantity of liming materials supplied. Again, the very high concentration of Fe in the liming materials may not pose any threat to crops grown since the solubility of this element will decline with increase in the pH of the soil.

Table 2: Mean of micronutrient content of molusc shell and commercial lime.

Liming material	Fe	Mn	Zn	Cu	B	Mo
Commercial lime	292.0±38.5	o.517±0.07	0.066±0.01	0.012±0.007	0.0023±0.001	0.002±0.001
Oyster shell	795. ±75.3	0.192±0.12	0.301±0.06	0.012±5.006	0.002±0.001	0.006±0.002
Snail shell	127. ±20.9	0.227±0.02	0.266±0.07	0.011±0.010	0.006±0.003	0.002±0.001

Soil properties

Some chemical properties of the soil studied before and after liming are presented in Table 3. The soil was strongly acidic with low total N (0.24gkg^{-1}) and organic carbon content (9.70gkg^{-1}). With a separating index of 25 between fertile and infertile soil [8], the C/N ratio of 40 obtained for this soil indicates that the soil is poor in N. Available P content of the soil was high and far above the (15-25mgkg^{-1}) determined as critical level for this zone [11]. Calcium level was moderate (3.60 cmolkg^{-1}) while K was lower than Na in the soil. Exchange acidity was high (3.6cmolkg^{-1}) and effective cation exchange capacity low (9.14cmolkg^{-1}) show that percent base saturation was high (60%) and within the >50% regarded as critical value for a fertile soil [8].

Effect of liming materials on soil chemical properties

Results of incubating the soils with liming materials for 21 days indicate that all the liming materials significantly raised the soil pH to between 7.58 and 7.72, representing or 61.8, 58.9 and 00.2% by commercial lime respectively, oyster and snail shells. As shown in Table 1, snail shell and calcium carbonate were moderately alkaline (pH 8.98 and 8.23) while was very 'strongly alkaline (pH 11.36) Such that oyster and snail shells could be used as suitable alternative liming materials for acid soils. Inyang [12] and Akpabio [13] noted that mollusc shells were as effective as calcium carbonate in reducing soil acidity. Liming soil with oyster and, snail shells increased organic C content from 9.70gkg^{-1} in the unlimed soil to 12.15 and 10.10gkg^{-1}, respectively but decreased to 9.55gkg^{-1} in $CaC0_3$ treated soil. The liming materials had no effect on total N content of the soil. Available P content in the soil after treatment with mollusc shells was 123.75mgkg^{-1} for oyster and 115.12mgkg^{-1} for snail shells. Commercial lime had the least effect on the P value (95.40mgkg^{-1}) of the three liming materials. These values are many times above the critical level of 15-25mgkg^{-1} P for soils of this zone but lower than the amount of P before application of liming materials. Ibia et al. [14] and Effiong et al. [15] had observed increased availability of P when acid soils were limed, while a report by IlTA [16] indicated that available P decreased as the amount of various liming materials increased, in three Ultisols. The reduction of P content following liming might have resulted from phosphate fixation which is always a problem in alkaline soils due to the formation of complex insoluble calcium phosphates [17]. High pH value and available Ca content are also closely related to low availability of P especially at conditions of low Na content [18].

Liming acid soil with various liming materials increased exchangeable Ca and Mg, exchange acidity, ECEC and percent base saturation (Table 3). Exchangeable Ca increased appreciably from 3.60cmolkg^{-1} in the unlimed soil to 34.80, 25.60 and 25.40 cmolkg^{-1} in soil treated with lime, oyster and snail shells, respectively. Previous studies showed that exchangeable Ca increased with the quantity of lime applied [19,15]. Mg content also increased from 1.60 to 4.40, 3.40 and 4.60 cmol kg^{-1} in soil treated with lime, snail, and oyster shells. The various liming materials had no significant effect on K and Na, because of the very low concentrations of these two nutrients in the liming materials and soil. Brady and Weil [17] noted that the availability of K in soil may decrease or increase due to liming. The reduction of soil acidity is one of the most commonly mentioned specific effects of lime. As indicated in Table 4, exchange acidity was reduced by 80, 76 and 69%, respectively by snail, lime and oyster shells. This reduction raised soil pH and increased ECEC and percent base saturation, remarkably in the soil. Effective cation exchange capacity (ECEC) increased from 9.14cmolkg^{-1} in unlimed soil to 40.36, 31.79 and 30.00cmolkg^{-1} in the soil treated with lime, oyster, and snail shells, respectively. The micronutrient content of the soil after liming are presented in Table 4. Fe was 24.48, 24.66 and 24.24mgkg^{-1} in soils limed with lime, oyster, and snail shells, respectively. These values are many times lower than those found in the mollusc shells and commercial lime. The drastic reduction of Fe contents in the soil probably resulted from the alkaline nature of the soil following liming. This observation calls for proper calculation of the rate of liming to avoid over liming, which is probably responsible for the reduction in Fe content in the soil. Mn content was moderate at 1.98, 2.16 and 1.72mgkg^{-1} in the soil limed with $CaC0_3$, oyster and snail shells, respectively, which are slightly higher than the critical limit of 1.0mgkg^{-1} [8]; and also higher by 74, 91 and 87% than the values found in mollusc shells and $CaC0_3$. Soil Zn content was enhanced by liming though Cu, B and MO values were almost the same following liming with $CaC0_3$, oyster and snail.

Table 3: Selected chemical properties of the soil studied before and after liming.

Liming material	pH	Org.C	TN	C/N	Av. P	Ca	Mg	K	Na	EA	ECEC	BS
		gkg^{-1}			$mgkg^{-1}$			$cmolkg^{-1}$				
Before liming												
	4.77	9.7	0.24	40	148	3.6	1.6	0.04	0.3	3.6	9.14	60.61
After liming												
Commercial lime	7.72± 0.05	9.55± 0.49	0.238± 0.075	40	95.40± 12.20	34.80± 0.00	4.40± 2.83	0.044± 0.003	0.235± 0.049	0.88± 0.11	40.36	97.82
Oyster shell	7.58± 0.08	12.15± 0.21	0.304± 0.038	40	123.75± 21.62	25.60± 2.26	4.60± 0.28	0.044± 0.011	0.409± 0.037	1.12± 0.09	32.77	96.47
Snail shell	7.64± 0.07	10.10± 0.28	0.253± 0.025	40	115.12± 12.20	25.40± 1.41	3.40± 1.41	0.061± 0.028	0.318± 0.006	0.72± 0.00	30	97.59

Each value is a mean and standard deviation (x±SD) of two determines org. c -organic carbon Av.p-available phosphorus EA-exchange acidity, ECEC-effective exchange capacity, BS-percent base saturation

Table 4: Values of micronutrient levels of the soil after liming with commercial and unconventional lime.

Liming materials	Fe	Mn	Zn	Cu	B	Mo
	mgkg-1					
Commercial	24.48	1.98	0.26	0.009	0.006	0.004
Oyster shell	24.66	2.16	0.29	0.069	0.004	< 0.001
Snail shell	24.24	1.72	0.3	0.015	0.001	< 0.001

Conclusion

This study has revealed that mollusc shells (oyster and snail) have high neutralizing values, high contents of Ca and Mg, organic C and ash and Fe while micronutrients (Cu, B and MO) were low. Oyster and snail shells used as liming materials have drastically reduced exchange acidity and appreciably increased the soil pH, basic nutrients, ECEC and percent base saturation of the soil. Mollusc shells compared favorably with lime and so can be used in replacement for neutralizing acidity in soils developed on acid sands in Akwa Ibom State. Lime is unavailable and unaffordable at critical periods, whereas the mollusc shells are common place as wastes around homes and in market places.

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