

Full Length Research Paper

Liming and fertiliser P interaction effects on some indices of fertility of selected Malawi acidic soils

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Received 16 March, 2015; Accepted 7 July, 2015

Laboratory investigations were conducted to determine effects of liming materials and inorganic phosphatic fertilisers on some indices of soil fertility. Results showed that soil bulk density decreased with increasing additions of liming materials and that interaction effects of dolomitic limestone and mineral fertiliser P increased soil pH from 4.4 for the unlimed top-soils to 6.3 after 3 t ha⁻¹ of dolomitic limestone and 300 kg ha⁻¹ Super D (a compound fertiliser) were added. Inverse statistically significant relationships were observed between exchangeable Al and lime ($P \leq 0.01$); exchangeable Al and pH ($P \leq 0.01$); and exchangeable Al and extractable P ($P \leq 0.01$). About 98% of the total variation in exchangeable Al was accounted for by the applied dolomitic limestone. The present investigations have demonstrated that the observed low fertility of the acidic soils may be attributed to its association with low P availability; reduced nutrients such as K, Mg and Ca; and adverse effects of exchangeable aluminium.

Key words: Liming effects, exchangeable aluminium, indices of soil fertility.

INTRODUCTION

The average yield for maize obtained by subsistence farmers in Malawi is 1 tonne per hectare (t ha⁻¹) for unimproved cultivars. The minimum requirement of maize per person per year is estimated at 200 kg and yet it has been demonstrated that potential yields of about 10 t ha⁻¹ are attainable in Malawi for hybrid maize, 5 t ha⁻¹ for open pollinated varieties (OPVs), and 3 t ha⁻¹ for unimproved maize cultivars (Government of Malawi, 2007). One of the major factors that contribute to the failure of even the high-yielding varieties to express their yield potentials on smallholders' farms is the status of soil fertility in Malawi.

Like in any other country where rainfall exceeds

evapotranspiration, loss of basic cations and soil acidification in Malawi are ongoing natural processes. Over 40% of the total land in Malawi is covered by Oxisols (Ferralsols) and Ultisols (Acrisols) which are highly weathered, leached and therefore acidic in their reactions, and dominated by clay fractions that consist of low activity minerals such as kaolinite, and Al and Fe oxides. The low activity minerals possess surface charge that is partly variable (pH-dependent) which causes the anion exchange capacity of the soils to increase as pH decreases, and the Al and Fe oxides contents cause the soils to have a greater affinity for phosphate ions, and therefore a high P sorption capacity. The inherent fertility

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Table 1. Geographic distribution of soil orders in the tropics, based on the dominant soil in FAO maps at a scale of 1:5 million (Szott et al., 1991).

Soils	Tropical America		Tropical Africa		Tropical Asia and Pacific		Total	
	Area (ha)	%	Area (ha)	%	Area (ha)	%	Area (ha)	%
Oxisols	502	33.6	316	27.6	15	1.4	833	22.7
Ultisols	320	21.4	135	11.8	294	28.4	749	20.4
Entisols	124	8.3	282	24.7	168	16.2	574	15.7
Inceptisols	204	13.7	156	13.7	172	16.6	532	14.5
Andisols	31	2.1	1	0.1	11	1.1	43	1.2
Alfisols	183	12.3	198	17.3	178	17.4	559	15.2
Vertisols	20	1.3	46	4.0	97	9.3	163	4.4
Aridisols	30	2.0	1	0.1	56	5.4	87	2.4
Mollisols	65	4.4	0	0	9	0.9	74	2.0
Histosols	4	0.2	5	0.4	27	2.6	36	1.0
Spodosols	10	0.7	3	0.3	7	0.7	20	0.5
Total	1493	100	1143	100	1034	100.0	3670	100.0

status of these acidic soils is low. The fertility of the Malawi soils continues to worsen. The annual net nutrient depletion exceeds 30 and 20 kg K ha⁻¹ and crop responses to fertilizers are only 17 kg grain kg⁻¹ N on many smallholders' farms whose fertility has been severely degraded, which is far much less than the 40 kg grain kg⁻¹ N obtainable from relatively more fertile sites (Report No. 98/036 CF. MLW, 1998). The continued application of ammonium sulphate fertilisers by smallholder farmers during the 1960s under conditions of excessive leaching has caused most of the soils in Malawi to become more acidic.

Acidity has been observed to be associated with N and P deficiencies in the soil, aluminium (Al) toxicity, low extractable bases (Ca, Mg, K and Na), and reduced microbial activity which is, therefore, conducive to low crop yield and land productivity (Crawford et al., 2008). The need to improve the fertility of the soils through liming was recognised during the 1960s. Initial investigations conducted during the early 1970s, however, showed that the adjustment of the pH (1:1 soil:water) of selected Malawi Ferralsols from 4.5 to 5.5 required inordinate quantities of liming materials (Maida, 1974). It was widely pointed out (for example: McLean, 1971) then that the structure of tropical soils was very stable and this was attributed to the fact that soil aggregates were stabilised by sesquioxides (oxides of Al and Fe). It was further noted that overliming tropical soils could cause a destabilisation of the structure which, in turn, could result in soil aggregates breaking apart resulting in reduced permeability and lack of adequate drainage.

These observations were and are still true for those soils that are highly weathered and dominated by low activity minerals such as kaolinite as well as insoluble amorphous 3 hydrous oxides of aluminium and iron. Both Ca²⁺ and Mg²⁺ ions are flocculent and aggregate

stabilizers for negatively charged colloids. In the highly weathered soils, however, these cations lead to formations of smaller aggregates than those formed by the more polyvalent cations (Al³⁺ and Fe³⁺). The introduction of Ca²⁺ and Mg²⁺ ions into soil solutions through the incorporation of dolomitic limestone results in these divalent cations replacing the more polyvalent cations (Al³⁺ and Fe³⁺) from the sesquioxide-stabilized aggregates, thus increasing the number of small aggregates and decreasing the larger aggregates stabilized by Al³⁺ and Fe³⁺.

The sesquioxide-stabilised aggregates are most common in the humid tropics and not in all the tropics. The term "tropics" refers to the continuously warm and frost free zone of the world that lies approximately between the Tropic of Cancer (or latitude 23.5° north of the equator) and the Tropic of Capricorn (or latitude 23.5° south of the equator) (Juo and Franzluebbers, 2003), it may not be correct to assert that soils in this region are, in their physical and chemical characteristics, homogeneous. Because of differences in pedogenesis, soil orders within the tropical region are variable (Table 1) and liming effects on these soils and crop growth will consequently vary with the soil orders.

Field trials conducted in Malawi have shown that unless the soils are very acidic (pH≤5.0) in their reaction, crops do not respond to liming (Mughogho, 1989). A farmer manager of Mpherero Estate, one of the sites in Malawi where the Clinton Development Initiative (CDI) was multiplying seed for Malawian farmers under the Alliance for Green Revolution in Africa (AGRA) project, however, observed that crop yields were far below 2 t ha⁻¹ and that a plant locally known as "Nzobwe" (*Terminalia superba*), which is an indicator of acid soils (Bolan et al., 1988), was thriving well on this site. After incorporating dolomitic limestone into the soil at a rate of 2 t ha⁻¹ and Super D (10.5 N + 24 P₂O₅ + 20 K₂O + (6 S and 0.15 B) at the rate

of 300 kg ha⁻¹) he observed that the crop yield increased significantly to an average of 2.9 t ha⁻¹ of soybean seed from an average of 1.5 t ha⁻¹ that was obtained from the plots that had not been limed (Ngwira, 2011).

It was, however, impossible to conclude on whether the 2 t ha⁻¹ of lime that was applied represented the maximum rate of dolomitic lime required to improve indices of chemical soil fertility such as exchangeable aluminium to optimum yield of the soybean seed at the site. The present study was therefore conducted to establish not only the acidic levels of the soil on the farm but also the effects of lime application on some indices of chemical soil fertility.

MATERIALS AND METHODS

Description of the study site

The study was carried out on Mpherero Estate, one of the sites where the Clinton Development Initiative (CDI) was multiplying seed for Malawian farmers under the Alliance for Green Revolution in Africa (AGRA) project. Mpherero Estate is in Mchinji District (Latitude: 13° 46' 19" S Longitude: 33° 00' 03" E), about 150 km from Lilongwe University of Agriculture and Natural Resources, to the west of Malawi's Capital city, Lilongwe.

The site topographically lies between 1200 and 1829 m above sea level and has two distinct terrains: The hilly western part, comprising the Mchinji Mountain ranges with gentle slopes where almost all rivers found in the district originate from, and the rest of the district lying within a plain of mostly arable land that is generally drained by water ways and there are some *dambos* which are permanently or seasonally inundated wetlands characterized by grasses, rushes and sedges, contrasting with surrounding woodland such as Miombo (*Brachystegia*) woodland. Mchinji experiences mean temperatures ranging from 17 to 20°C per annum. Lowest temperatures are experienced in June while high temperatures are experienced during the months of October and November. The district receives average rainfall of between 800 and 1230 mm per annum with the wet rainy season running from November to April (Mchinji District Assembly, 2008).

Cropping history

The experimental site is an area where the Anchor Farm Project, which is a Clinton Development Initiative (CDI)-operated commercial farm, was conducted. The CDI-sponsored project partners with thousands of neighbouring smallholder farmers and provides them with access to quality inputs for maize and soy production as well as training and market access. Farmers in the project have access to improved soy seed and to training in advanced agronomic techniques. The farmer manager of the commercial farm observed that crop yields were far below 2 t ha⁻¹ and that a plant locally known as "Nzobwe" (*Terminalia superba*), which is an indicator of acid soils (Bolan et al., 1988), was thriving well on this site.

After incorporating dolomitic limestone into the soil at a rate of 2 t ha⁻¹ and Super D (10.5 N + 24 P₂O₅ + 20 K₂O + (6 S and 0.15 B) at the rate of 300 kg ha⁻¹), he observed that the crop yield increased significantly to an average of 2.9 t ha⁻¹ of soybean seed from an average of 1.5 t ha⁻¹ that was obtained from the plots that had not been limed (Ngwira, 2011). It was, however, impossible to conclude on whether the 2 t ha⁻¹ of lime that was applied represented the maximum rate of dolomitic lime required to improve indices of

chemical soil fertility to optimum yield of the soybean seed at the site. The main purpose of the present investigations was to determine effects of different levels of dolomitic lime application on some indices of soil chemical fertility.

Glasshouse incubation experiment

An incubation experiment that was conducted entailed first establishing field capacity (FC) values for each soil by first weighing 3 g of air-dried soil into polythene pots, obtaining the sum of the weight of the polythene pot and the air-dried soil it contained, adding distilled water to the pot placed on a polythene dish until saturation point had been reached, letting the excess water to drain for 24 h, and then re-weighing the pots plus the soil after the excess water had finished draining. The difference in weight between the weight of the soil plus the polythene pots before the soil was saturated with distilled water and the weight of the soil plus the polythene pots after the excess water had drained for 24 h roughly represented FC and aided in establishing the amount of water needed each day. The FC is the water remaining in the soil after draining for 24 h. The difference in weight was divided by the total weight of air-dry soil in the pot and multiplied by 100 to determine the field capacity as percentage of air-dry weight.

Treatments were different levels of dolomitic lime {CaMg(CO₃)₂} and Super D (10.5:24:20:6:0.15) fertiliser (Table 2). Lime was mixed with 3 kg of soil by shaking the mixture in a bag, placing the shaken mixture in a 16.5 cm polythene pot that was placed on polythene dishes, weighing the pot with its contents, and then adding Super D fertiliser in solution (Sarrantonio, 1991) followed by distilled water to field capacity.

Nitrogen and phosphorus sources used for the experiment were calcium ammonium nitrate (CAN) and single superphosphate, respectively. Dolomitic limestone was the liming material used in the present investigations. The twelve treatments were replicated three times. The pots containing the treatments (Table 2) were laid out in a completely randomised factorial design, and the soils were incubated for a period of four weeks to ensure complete dissolution of the liming material even though it was then known that lime effects may be detected after one week in the soil (Millar and Turk, 2006). During the incubation period, the soil moisture content in each pot was maintained at 70% of FC and the room temperature ranged from 23 to 25 with a mean temperature of 24°C.

Laboratory investigations

Soils

Representative soil samples were collected from three blocks at the Mpherero Estate in which soils had not been limed at the study site. The soil samples were collected from the topsoil (0-20 cm) and then from the subsoil (20 to 40 cm), air-dried and passed through 2 mm sieve to remove large particles, debris and stones. Before the sieved soil samples were mixed with lime for an incubation experiment, an aliquot of the samples was taken and subjected to soil analysis. After the incubation experiment, an aliquot of the soil sample was taken from each of the incubated soils and analysed for the soil variables detailed subsequently.

Analytical methods

The soils were analyzed for pH in a 1:2.5 soil to water slurry using a pH electrode as outlined by described by Blakemore et al. (1987), particle size distribution using the Bouyoucos hydrometer method

Table 2. Comparative factors and levels

Treatment number	Treatment code	Treatment combination
1	L ₀ P ₀	0 t/ha dolomitic limestone + 0 g/ha Super D
2	L ₀ P ₁	0 g/pot dolomitic limestone + 0.2 g/pot Super D
3	L ₀ P ₂	0 g/pot dolomitic limestone + 0.5 g/pot Super D
4	L ₀ P ₃	0 g/pot dolomitic limestone + 0.7 g/pot Super D
5	L ₁ P ₀	2.4 g/pot dolomitic limestone + 0 g/pot Super D
6	L ₁ P ₁	2.4 g/pot dolomitic limestone + 0.2 g/pot Super D
7	L ₁ P ₂	2.4 g/pot dolomitic limestone + 0.5 g/pot Super D
8	L ₁ P ₃	2.4 g/pot dolomitic limestone + 0.7 g/pot Super D
9	L ₂ P ₀	4.8 g/pot dolomitic limestone + 0 g/pot Super D
10	L ₂ P ₁	4.8 g/pot dolomitic limestone + 0.2 g/pot Super D
11	L ₂ P ₂	4.8 g/pot dolomitic limestone + 0.5 g/pot Super D
12	L ₂ P ₃	4.8 g/pot dolomitic limestone + 0.7 g/pot Super D

Table 3. Indices of soil physical fertility before and after liming

Block	Depth (cm)	ρ_d (g cm ⁻³)		Sand	Silt % (w/w)	Clay	Textural class
		Before liming	After liming				
1	0-20	1.52±0.01	1.38±0.02	70.33	26.33	3.33	SL
	20-40	1.63±0.02	1.39±0.01	62.00	29.67	3.33	SL
2	0-20	1.55±0.04	1.36±0.05	67.67	28.33	4.00	SL
	20-40	1.61±0.06	1.37±0.02	67.00	28.33	4.67	SL
3	0-20	1.59±0.02	1.32±0.03	67.00	28.33	4.67	SL
	20-40	1.62±0.05	1.33±0.03	68.33	27.67	4.00	SL

SL, Sandy loam and pb denotes soil bulk density. SL = sandy loam; pb = soil bulk density.

(Day, 1965) as described by Anderson and Ingram (1993), and soil bulk density using the method outlined by Gradwell and Birrell (1979). The soil organic carbon contents were determined by the potassium dichromate (K₂Cr₂O₇) oxidation method of Walkley and Black (1934) as described by Anderson and Ingram (1993).

Organic matter was estimated by multiplying the total soil organic carbon with 1.724. Total nitrogen was determined using the Kjeldhal wet oxidation process as described by Anderson and Ingram (1993), while available phosphorus was extracted by the Mehlich 3 method (Mehlich, 1984) and P in the clear extracts was determined colorimetrically by the ascorbic acid method (Murphy and Riley, 1962) on a Perkin Elmer Lambda 25 UV/VIS spectrometer. Exchangeable K was determined by the Mehlich 3 method (Mehlich, 1984) and the K in the extracts was determined by flame emission photometry at a wavelength of 766 nm. Cation exchange capacity was determined by the BaCl₂ Compulsive Exchange Method of Gillman and Sumpter (1986) as outlined by Sumner and Miller (1996). Exchangeable Al was determined using the 1 mol dm⁻³ KCl method outlined by Sparks (1996).

Results of soil analysis described above and of an incubation experiment described below were subjected to statistical analysis using Genstat 14th edition statistical package. Analysis of variance was used to determine the statistical significance of treatment effects. Differences between and within treatments were determined using least significant difference (LSD) tests. Correlations and linear regressions were used to determine relationships between treatments.

RESULTS AND DISCUSSION

Soil physical properties

Table 3 shows physical properties of the soil samples before liming. The soils were sandy loam (SL) sand, silt, and clay particles are intrinsic soil properties and were therefore not expected to be affected by the treatment effects. Bulk density (ρ_b) is, however, dynamic and dependent on soil texture and the densities of soil mineral (sand, silt, and clay) and organic matter particles, as well as their packing arrangement. It increases as the ratio of solids in a soil increases, and conversely decreases as the ratio of solids decreases. If looked at from the porosity (the ratio of pore volume to its total volume) perspective, bulk density increases as pore space decreases.

The relationship of bulk density and porosity is reciprocal. Bulk density indirectly provides a measure of the soil porosity. Soil porosity (ϕ) is the ratio of the volume of soil pores (V_p) to the total soil volume

Table 4. Mean indices of soil chemical fertility before liming.

Block	Depth (cm)	Mean pH	OM	Total soil N	Available P	Exchangeable K	Exchangeable Al	CEC
			(%)	(%)	(mg kg ⁻¹)	(mg kg ⁻¹)	(cmol _c kg ⁻¹)	
1	0-20	4.4	1.40	0.08	12.0	69	28	3.8
	20-40	4.6	1.02	0.04	9.0	52	26	3.01
2	0-20	4.0	1.60	0.05	12.5	73	30	4.5
	20-40	4.2	1.04	0.06	11.0	61	25	3.20
3	0-20	4.0	1.8	0.07	15.0	58	27	4.6
	20-40	4.5	1.08	0.05	12.0	59	26	3.00

$$\left(\sum V_P\right):$$

$$\phi = \frac{V_P}{\sum V_S}$$

The bulk density of a soil is inversely related to the soil porosity through the following relationship:

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

Where ρ_b and ϕ are as defined earlier and ρ_s = particle density. Results of soil analysis obtained before incubation show that the mean soil bulk densities increased with increasing depth (Tables 3), suggesting that compaction increased with an increase in depth.

One commonly used relationship between porosity and depth is given by the Athy (1930) equation:

$$\phi(z) = \phi_0 e^{-kz}$$

Where ϕ_0 is the surface porosity, k is the compaction coefficient (m⁻¹) and z is depth (m). An increase in bulk densities with increasing profile depth is due to changes in organic matter content, porosity and compaction. Soil compaction is an important process of soil degradation affecting soil productivity. A compacted soil has low porosity and low water and air permeability thus causing the soil to be susceptible to soil erosion, and this also causes soil water availability and microbial activity to be adversely affected. Bulk density can therefore be regarded as an indicator of the state of soil health. The data given in Table 3 show that bulk density (ρ_b) values of the soils that had been limed were lower than those of the unlimed soils, thus suggesting that the introduction of the divalent cations (Ca²⁺ and Mg²⁺) into the soils, through the application of dolomitic limestone to the soils,

was conducive to an improvement of soil aggregation. It has earlier been noted earlier that replacement of the more polyvalent cations (Al³⁺ and Fe³⁺) by Ca²⁺ and Mg²⁺ from the sesquioxide-stabilized aggregates has a negative impact on the structure of tropical soils when the soil pH is raised beyond pH 6 which is said to be the target pH (MacLean, *op cit.*). The rates of dolomitic limestone used in the present investigations managed to increase pH values to levels that were below the target pH (Table 4).

Soil chemical properties

Soil reaction

Given in Table 4 are soil chemical variables obtained from the present investigations before dolomitic lime and fertiliser P were added to the soils. The results show that the soils collected from the experimental site in Mchinji are strongly acidic in their reaction, ranging from pH 4.0 to 4.4 in the topsoils (0-20 cm) and from pH 4.2 to 4.6 in the subsoils (Table 4), which is consistent with previous observations (Ngwira, 2011). These are well-drained soils.

The acidic status of these soils may be due to the fact that under periods of high temperatures and heavy rainfall, intensive weathering on such well-drained soils leads to the release and leaching of basic cations leaving behind an increased effective H⁺ ion concentration in the soil solution, and causing some of the protons to become adsorbed on surfaces of soil colloids where they can attack mineral structures and release cations such as Si⁴⁺, Fe³⁺, Al³⁺ and other ions from the minerals. The Al³⁺ ions thus released hydrolyse to produce more protons that cause the soil to be more acidic. Continued use of acidifying fertilisers by farmers in the long run causes soils to become much more acidic.

During the 1950 to late 1960 period, smallholder farmers in Malawi used to apply continuously ammonium sulphate (sulphate of ammonia) fertiliser as a means of correcting N deficiencies that were observed to cause a

Table 5. Liming effects on mean soil chemical properties.

Limestone effects (t ha ⁻¹)	Depth (cm)	pH	OM Percent (w/w)	Total soil N	Exchangeable			
					Available P	Al	K	CEC
					mg kg ⁻¹			cmol _c kg ⁻¹
0	0-20	4.4 ^a	1.40 ^a	0.08 ^a	12 ^a	30 ^a	69 ^a	3.8 ^a
	20-40	4.3 ^a	1.10 ^a	0.04 ^b	9.00 ^a	28 ^a	53 ^a	3.01 ^a
1.5	0-20	5.4 ^b	2.40 ^{ab}	0.09 ^a	18.14 ^b	20 ^a	74 ^b	4.6 ^b
	20-40	5.3 ^b	2.03 ^b	0.05 ^a	17.80 ^b	20 ^a	61 ^{ab}	4.5 ^b
3.0	0-20	5.6 ^b	3.12 ^{bc}	0.07 ^a	20.24 ^b	11 ^b	59 ^{ab}	6.0 ^{ab}
	20-40	5.5 ^b	2.71 ^b	0.08 ^a	19.25 ^b	14 ^b	60 ^{bc}	5.8 ^{ab}

Means with the same letters in a column are not significantly different at P<0.001

Table 6. Liming (t ha⁻¹) and super D (kg ha⁻¹) interaction effects on mean pH in the topsoils.

Treatment effects	pH values			
	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
L ₀	4.1 ± 0.0012	4.0 ± 0.0010	4.0 ± 0.0010	4.0 ± 0.0010
L _{1.5}	4.2 ± 0.0021	4.3 ± 0.0020	4.3 ± 0.0020	4.3 ± 0.0020
L _{3.0}	5.2 ± 0.0030	5.4 ± 0.0031	6.3 ± 0.0041	5.3 ± 0.0390

decline in crop yields and it was further observed that soil acidity increased with continued application of the fertiliser in some parts of Malawi. The levels of dolomitic lime added to the soils, however, have resulted in decreasing the activity of hydrogen ions in the soil solution from a mean pH value of 4.4 for the unlimed topsoils, to a mean pH value of 5.6 for the topsoils to which 3 t/ha dolomitic limestone was added (Table 5). It is widely believed that the target pH should not exceed about 6.0, with optimum being more in the range of 5.0 to 5.5 (Harter, 2007). The levels of dolomitic limestone used in the present investigations therefore raised the pH slightly above the optimum level of pH 5.5 by 0.1 unit. The interaction effects of dolomitic limestone and mineral fertiliser P on soil reaction caused the pH to increase from 4.4 for the unlimed topsoils, to 6.3 for the topsoils to which 3 t ha⁻¹ of dolomitic limestone and 300 kg ha⁻¹ super D were added (Table 6), thus suggesting that an application of liming materials and P fertiliser at the rates used in the present study caused the pH of the soils to increase to pH 6.3, which was beyond the pH 6 target, without any adverse effect on the soil structure.

Relatively large amounts of limestone can be incorporated into acid soils of the temperate region without impacting negatively on the soil structure whereas over-liming acid soils in the tropical region leads to dispersion of soil aggregates. This is mainly due to the replacement of the polyvalent aluminium (Al³⁺) on the soil colloid with a divalent cation (Ca²⁺) and the peptising effect of hydroxyl ion (OH⁻) "overshadowing the

flocculating effect of Ca²⁺ in soils predominantly positively charged" (McLean, 1971). The benefits of liming effects under the tropical region are attributable to phosphorus being available to crops and to the reduction of root damage by aluminium due to the precipitation of aluminium as gibbsite which eventually enhances nutrient uptake by crops.

Under field conditions, the increase in soil pH with increasing depth (Table 4) is attributable to the increase in the organic matter in the topsoil. Being weak acids, organic acids such as carboxylic acid (R-COOH) and phenolic acid (R-OH) do not protonate easily. When limestone is added to acidic soils, however, the organic acids facilitate the transport of the limestone to deeper soil layers where the soil pH consequently increases. The differences in the pH values due to treatment effects were statistically significant at the 0.1% probability levels (Table 5). The pH of the topsoil also increased with treatment effects, ranging from 4.1 for the unlimed subsoil to 6.3 for the topsoil that received 3 t ha⁻¹ dolomitic limestone and 300 kg ha⁻¹ super D (Table 6).

Soil exchangeable aluminium

In acid soils, an appreciable portion of the cation exchange complex is satisfied by Al³⁺ ions. What is referred to as exchangeable Al³⁺ ions are actually a mixture of monomeric aluminium ions [Al³⁺, AlOH²⁺, Al(OH)₂⁺] with an average charge per Al between 2 and

Table 7. Interaction effects of liming (t/ha) and super D (kg ha⁻¹) on mean exchangeable Al (mg kg⁻¹) in top soil.

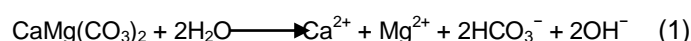
Treatment effects	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
L ₀	30 ± 1.3	29 ± 1.2	28 ± 1.2	30 ± 1.5
L _{1.5}	20 ± 1.4	18 ± 1.3	24 ± 1.3	22 ± 1.4
L _{3.0}	11 ± 1.7	10 ± 1.5	5 ± 0.4	9 ± 1.2

Table 8. Interaction effects of liming and Super D on mean CEC in top soils

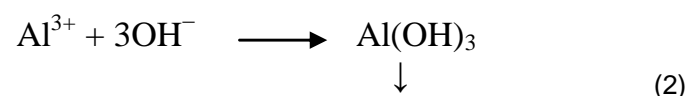
Liming effects (t ha ⁻¹)	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
	(k ha ⁻¹)			
L ₀	3.8 ± 0.3	4.5 ± 0.2	5.4 ± 0.2	4.4 ± 0.5
L _{1.5}	4.6 ± 0.4	5.4 ± 0.3	6.1 ± 0.3	6.4 ± 0.4
L _{3.0}	6.0 ± 0.7	6.1 ± 0.5	7.0 ± 0.4	6.1 ± 1.2

3, decreasing as pH increases (Wild, 1988). It has been observed that soils having contents of exchangeable Al above 25 mg kg⁻¹ usually are strongly acidic in their reaction (Haynes, 1984). Results of the present study indicate that the unlimed topsoils have high contents of exchangeable aluminium ranging from 26 to 30 mg kg⁻¹ (Table 5). After liming, however, the exchangeable aluminium was significantly reduced from 30 mg/kg to 11 mg kg⁻¹ in the topsoils and from 28 to 14 mg kg⁻¹ in the subsoils and the differences were statistically significant (Table 5).

The decrease in exchangeable Al from 30 mg kg⁻¹ of the unlimed topsoil to 5 mg kg⁻¹ the topsoil to which 3.0 t/ha limestone and 300 kg/ha Super D were added (Table 7) suggests that the exchangeable Al was inactivated by the dolomitic limestone. The differences in the exchangeable Al due to liming effects are statistically significant at the 0.1% probability level (Table 5). The increase in the pH of the soils may be due to the reaction of the dolomitic limestone after its incorporation into the soil:

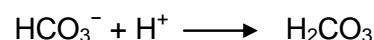


The Ca²⁺ and Mg²⁺ ions thus introduced into soil solution (Equation 1) replace Al³⁺ ions adsorbed on the surface of soil colloids. Equation (1) shows that the reaction of dolomitic limestone in the soil with water yields Ca²⁺ and Mg²⁺ ions and alkalinity in the bicarbonate (HCO₃⁻) and hydroxide (OH⁻) anion forms. The hydroxide anion thus yielded may neutralise aluminium ions (Al³⁺) in the soil solution and precipitate the Al³⁺:



For the reaction in Equation (2), which is

thermodynamically favourable, the enthalpy is highly exothermic and the Al in the form of gibbsite is no longer available for toxicity in the plants (Millar and Turk, 2006). The reaction in Equation (2) explains the low exchangeable aluminium (5 mg kg⁻¹) following the incorporation of 3 t ha⁻¹ dolomitic limestone and 300 kg ha⁻¹ Super D (10.5:24:20 + 6 S, 0.15 B) (Treatment 11). The bicarbonate anion may have neutralized or consumed H⁺ ion in the soil solution through the following reaction:



Resulting in carbonic acid, a weak dibasic acid, as the product of the reaction, which may have reduced the effective concentration of H⁺ in the soil solution.

Cation exchange capacity (CEC)

The cation exchange capacity (CEC) increased from 3.8 cmol_c kg⁻¹ of the unlimed topsoil to 6.0 cmol_c/kg of the topsoil to which 3 t ha⁻¹ of dolomitic limestone was added (Table 8). The increase in CEC with increasing rates of lime limestone additions may be attributed to the fact that as the aluminium hydroxy ion, for example Al(H₂O)₅(OH)²⁺, is precipitated due to the liming effects, the two negative sites on the clay surface that are blocked due to the adsorption of the aluminium hydroxy ion become exposed, resulting in an increase of the CEC. An increase in CEC causes the chemical fertility of the soil to improve as its capacity to hold in reserve essential elements against leaching is improved.

Total soil nitrogen, organic matter and available P

Results obtained from the study of effects of liming and P

Table 9. Liming x Super D interaction effects on mean total soil N (%w/w) in topsoil (0-20 cm).

Treatment effects	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
L ₀	0.05 ± 0.001	0.012 ± 0.002	0.013 ± 0.003	0.013 ± 0.003
L _{1.5}	0.08 ± 0.002	0.014 ± 0.003	0.015 ± 0.003	0.014 ± 0.003
L _{3.0}	0.09 ± 0.002	0.015 ± 0.003	0.018 ± 0.005	0.015 ± 0.003

Table 10. Interaction effects of liming and super D on mean soil organic matter (%w/w) in top soil.

Liming effects (t ha ⁻¹)	D ₀ (kg ha ⁻¹)	D ₁₅₀	D ₃₀₀	D ₄₅₀
L ₀	1.39 ± 0.02	1.39 ± 0.02	1.39 ± 0.02	1.39 ± 0.02
L _{1.5}	1.40 ± 0.01	1.41 ± 0.02	1.41 ± 0.02	1.42 ± 0.03
L _{3.0}	1.42 ± 0.02	1.43 ± 0.03	1.45 ± 0.03	1.40 ± 0.01

Table 11. Interaction effects of liming and super D on mean available P in top soil.

Liming effects (t ha ⁻¹)	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
		(kg ha ⁻¹)		
L ₀	12 ± 0.10	14 ± 0.12	15 ± 0.14	17 ± 0.17
L _{1.5}	19 ± 0.12	23 ± 0.11	25 ± 0.19	33 ± 0.14
L _{3.0}	29 ± 0.18	38 ± 0.19	70 ± 0.09	42 ± 0.15

treatments on total soil nitrogen and soil organic matter contents are given in Tables 9 and 10 respectively while those on Mehlich 3-extractable P and exchangeable K are given in Tables 11 and 12, respectively. Total soil nitrogen (N) contents increased with increasing rates of applications of dolomitic limestone and fertiliser phosphorus (P) suggesting that the treatments resulted in the creation of an edaphic environment that was favourable for soil mineralisation. Mineralisation is commonly taken to be a first order reaction of the form:

$$Y = Mo(1 - e^{-kt})$$

Where Y = cumulative amount of an element (e.g., N, C, P or S) mineralized in time (t), Mo is potentially mineralisable element, and k is a rate constant (Ellert and Bettany, 1988; Campbell et al., 1993).

The rate constant, k, is dependent on edaphic conditions such as temperature, moisture and other soil conditions that influence microbial activity (Campbell et al., 1994). Soil pH is one of the edaphic factors recognised as an important regulator of microbial activity (Haynes, 1986) and the composition of the microbial population (Paul and Clark, 1996). Suboptimal pH values reduce the value of k, and in their liming study, Dancer et al. (1973) showed that nitrification decreased 3- to 5-fold as pH decreased with increasing acidity effects in the pH range 4.7 to 6.6. Results obtained from the present

investigations show that soil contents of total N decreased with increasing liming x fertiliser P interaction effects (Table 9) but that the increases were not statistically significant within the experimental error.

Organic matter (OM) contents of the soils are given in Table 10. The increases in OM with increasing rates of dolomitic limestone and fertiliser P applications were, within limits of experimental error, not statistically significant ($P \leq 0.01$). The data given in Table 11 and Figure 1 show that available P increased from 12 mg kg⁻¹ of the soil that was not limed to 70 mg kg⁻¹ of soil to which 3.0 t/ha dolomitic lime and 300 kg ha⁻¹ Super D were added. The low extractable (available) P values may be ascribed to the fact that in acid soils, any phosphate ions added to acidic soils can be dominantly adsorbed by oxides and hydroxides of Al and Fe such as gibbsite, haematite, and goethite (Parfitt, 1989). The phosphate ions can be first adsorbed on the surface of clay minerals and Fe and Al oxides by forming various complexes.

Non-protonated and protonated bidentate surface complexes may coexist at pH ranging from 4 to 9, while protonated bidentate inner-sphere complex is predominant under acidic soil conditions (Luengo et al., 2006; Arai and Sparks, 2007). The adsorption of soil P is enhanced with increasing ionic strength. With further reactions, P may be occluded in nanopores that frequently occur in Fe and Al oxides, and thereby

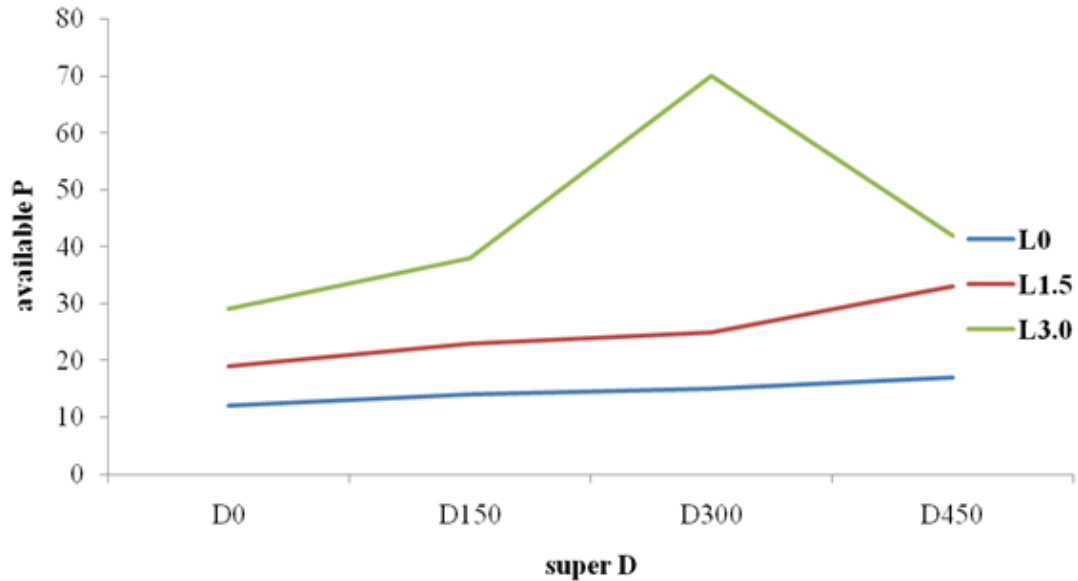


Figure 1. A plot showing liming ($t\ ha^{-1}$) \times Super D ($kg\ ha^{-1}$) on mean available P ($mg\ kg^{-1}$) in top soil.

become unavailable to plants (Arai and Sparks, 2007).

The sorption of phosphate anions occurs by both specific adsorption and precipitation reactions (Sample et al., 1980; Sanchez and Uehara, 1980). At low soil pH, that is, from less than 4.5 to 5.0, additions of P to soils can result in precipitation of Al and Fe phosphates, whilst at high pH (>6.0–6.5) insoluble calcium phosphates can form (Haynes, 1984). The form of P and the levels of Al, Fe and Ca in soil solution are all governed by soil reaction and the effective concentrations of the cations in solution influence the sorption of phosphate ions. Results of Lemare and Leon (1989) have shown phosphate adsorption on the Oxisols and Dystropept to decrease with limestone adsorption, while Haynes (1982) has observed that an incorporation of liming materials into highly weathered soils generally causes the adsorption of phosphate by amphoteric soil surfaces to decrease slowly as the effective concentration of protons in the soil solution is decreased from pH 4.0 to 7.0.

The results given in Table 11 and summarised in Figure 1, however, show that the extractability of the soil P improved after 3 t/ha of dolomitic limestone was added and that the dolomitic limestone \times Super D interaction effects caused an amount of 35 mg P kg^{-1} to be extractable by the Mehlich 3 method (Mehlich, 1984) after 3 t ha^{-1} dolomitic limestone and 450 $kg\ ha^{-1}$ Super D were incorporated into the soils. This suggested that the dolomitic limestone \times Super D interaction effects were conducive to an increase in the mineralisation of organically bound P which contributed to the observed increase in extractability and therefore bioavailability of P. In an incubation study, Lelei et al. (2000) also observed that liming and P application enhanced soil N and P mineralization, respectively. Chimdi et al., (2012)

observed that the P extracted by the Bray P 2 method (Bray and Kurtz, 1945) increased with increasing rates of lime application.

Exchangeable K

The liming effects caused exchangeable potassium (K) to increase with increasing rates of dolomitic limestone application (Table 12). This is as was expected because raising the pH through liming soils particularly those with pH-dependent charge such the ones used in this study increases the soils' cation exchange capacity (CEC) as has been observed in this study and thus increases the soils' capacity to adsorb K.

It has also been shown that more exchangeable K has been caused by the liming \times Super D interaction effects (Table 12) but that the differences due to treatment effects were not statistically significant.

Interrelationships among soil analytical data

Exchangeable Al is positively related at 1% probability level to CEC and organic matter but negatively correlated at 1% probability level with dolomitic limestone, pH, and extractable P. In reaction with water, the Al^{3+} ions become hydrolysed and then precipitated, thus causing the inverse statistically significant relationships observed (Table 13) between the exchangeable Al and the dolomitic limestone ($r = -0.99$; $P \leq 0.01$); between the exchangeable Al and pH ($r = -0.93$; $P \leq 0.01$); between the exchangeable Al and extractable P ($r = -0.97$; $P \leq 0.01$); between the exchangeable Al and grain yield ($r = -$

Table 12. Liming × Super D interaction effects on mean exchangeable K in top soil.

Liming effects (t ha ⁻¹)	D ₀	D ₁₅₀	D ₃₀₀	D ₄₅₀
	(mg kg ⁻¹)			
L ₀	69 ± 0.0407	72 ± 0.0411	75 ± 0.0413	80 ± 0.0415
L _{1.5}	92 ± 0.0504	93 ± 0.0515	94 ± 0.0599	90 ± 0.0421
L _{3.0}	86 ± 0.0839	88 ± 0.0840	96 ± 0.0731	91 ± 0.0576

Table 13. Matrix of correlation coefficients.

Variable	Al	N	P	K	OM
N	0.00				
P	-0.97**	0.00			
K	0.00	0.00	0.00		
OM	0.69**	0.76**	0.81**	0.79**	
Lime	-0.99**	0.82**	0.83**	0.88**	0.73**

Al_{ex} = Exchangeable Al (mg kg⁻¹); N_{total} = total soil N (%); P_{extr} = extractable P (mg kg⁻¹); K_{ex} = exchangeable K (mg kg⁻¹);
 **Significant at the 0.01 level of probability; *significant at the 0.05 level of probability.

0.91; $P \leq 0.01$); and between the exchangeable Al and harvest index ($r = -0.89$; $P \leq 0.01$). Since the solubility of Al is highly pH-dependent, when an acid soil is limed, exchangeable and soluble Al precipitate as hydroxy-Al species.

The positively charged monomeric AlOH_2^+ and $\text{Al}(\text{OH})_2^+$ species can polymerize to form both large and small positively-charged polynuclear complexes [$\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ (aq), $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+$ (aq)] which become sorbed to clay mineral and organic matter surfaces (Rengasamy and Oades, 1978; Stole et al., 1976). Thus, liming an acid soil to above about pH 5.5 results in concentrations of soluble and exchangeable Al being lowered to negligible levels and Al toxicity no longer limits crop growth.

The present observations are consistent with previous findings that showed that liming acidic soils raises soil variables such as the soil pH, which reduces aluminium, hydrogen, manganese and iron toxicity to nontoxic levels and creates a favourable environment for Rhizobium bacteria which decompose organic matter to release nutrients such as N and P for crop use (Kryzanowski, 2002).

Conclusions

The overall results of the present investigations indicate that the soils in the Mchinji district of Malawi, from which the soil samples were collected, are acidic in their reactions and low in CEC, suggesting that the loss of cations and silica through leaching from these highly weathered soils whose left a preponderance of H^+ ions adsorbed on the soil colloidal surfaces and induced the

soils to be dominated by low activity minerals. On the basis of the reaction of the un-limed soils (pH 4), it may be concluded that both excess levels of exchangeable Al and the unavailability of plant nutrients such as N, P, K, Ca, and Mg contribute to observed low crop yields obtained from this area. The findings of the present investigations suggest that the observed improved crop production may be attributed to the favourable soil environment that might have been caused by the amount of 2 t ha⁻¹ of the liming materials the farm manager of applied to the soils. There is, however, need for additional research aimed at establishing the rate of dolomitic limestone required for the farmer to obtain maximum economic crop yield from these acidic soils.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGEMENTS

The research whose findings are summarised in this paper was conducted with financial support from the Soil Health Programme (SHP) of the Alliance for Green Revolution in Africa (AGRA). The authors also acknowledge the support provided by Mr. Austin Ngwira, Director of the Clinton Development Initiative (CDI) Anchor Farm Business Development Project, which made it possible for the investigations to be conducted on one of the CDI-funded farmers' farms in the Mchinji district of Malawi. The authors would like to thank Messrs L. K. Chirwa, B. Msukwa and S. Khombe for their assistance during the execution of the laboratory investigations.

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