Effects of Liming on Dithionate and Oxalate Extractable Aluminium in Acid Soils

Esther Mwende Muindi[1*]

[1]Pwani University, P.O. Box 195-80108, Kilifi, Kenya.

Author's contribution

The author designed, analysed, interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

Liming and phosphorus (P) applications are recommended practices for improving crop production in acid soils of the tropics. Although considerable work has been done to establish liming rates for acid soils in many parts of the world, information on the effects of lime on the forms of aluminium which actively sorb P in such soils is minimal. A greenhouse pot experiment was conducted at Waruhiu Farmers Training Centre, Githunguri to evaluate the effect of liming on oxalate and dithionate extractable aluminium in acid soils. Extremely (pH 4.48) and strongly (pH 4.59) acidic soils were evaluated. Four liming (CaO) rates namely 0, 2.2, 5.2 and 7.4 tonnes ha^{-1} for extremely acidic and 0, 1.4, 3.2, and 4.5 tonnes ha^{-1} for strongly acidic soils were evaluated. The experiment was laid out in a Randomized Complete Block Design (RCBD) and replicated three times. Data collected included: initial soil chemical properties, oxalate (Al_o) and dithionate (Al_d) aluminium levels. The tested soils had high exchangeable Al (> 2 cmol Al kg^{-1}), Al saturation of (> 20% Al) and low extractable P values (< 15 mg P kg^{-1} soil). Liming significantly (p=.05) reduced Al_o by 70% and 68% in extremely and strongly acidic soils respectively and Al_d by 78% in both extremely and strongly acidic soils compared to control. Use of 7.4 tonnes ha^{-1} of lime in extremely acidic soils and 4.5 tonnes ha^{-1} of lime in strongly acidic soils significantly (p=.05) reduced both Al_o and Al_d by > 68% compared to no lime. It was, therefore, concluded that liming contributes to the reduction of soluble Al_o and Al_d in acid soils of the Kenya highlands leading to increased soluble P availability. Studies are required to provide short and long term optimal liming rates that reduce Al_o and Al_d without distabilizing availability of other nutrients in field conditions under wide range of acid soils.

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Corresponding author: Email: e.muindi@pu.ac.ke, muidiede@gmail.com;

1. INTRODUCTION

Approximately 40-50% of the World's total potential arable land consists of acid soils. The acid soils (pH ≤ 5.5) comprise approximately 30% of the total earth area and they are associated with high levels of exchangeable aluminium (Al), hydrogen (H), iron (Fe) and manganese (Mn) in soil solution [1,2,3]. They are also associated with toxicities to plant roots in the soil solution and corresponding deficiencies of the available P, molybdenum (Mo), calcium (Ca), magnesium (Mg) and potassium (K) [4-8]. Although excess H^+ ions are toxic and negatively affect root membrane permeability [9], the main constraint to crop production in highly acid soils is not high H^+ ions but increased concentration of Fe^{3+} and Al^{3+} ions at pH < 5.5 [10,11]. Aluminium toxicity is, however, the most significant threat to plant survival in acid soils [12,13].

Aluminium is a chemical element with the symbol Al and atomic number 13. It is silvery-while, soft, nonmagnetic and ductile metal in the boron group and third most abundant element in the earth's crust after oxygen and silicon making up about 7-8% of the earth's crust [13,14,15]. It is one of the group III elements consisting of aluminium, gallium, indium and thalium which have three electrons in their outer shell. Although the element is metallic in nature, it exhibits both ionic and cuvailent bonding which is dominated by trivalent state. The element has a diameter of 0.57A and it is generally found in sixfold coordination with oxygen in the octahedral layer of many primary minerals such as micas, feldspar, cryolite and secondary phyllosilicates and ores such as bauxite [16,17]. It makes 8.1% of igneous, 8.2% of shale, 2.5% of sandstone and 0.4% of limestone rocks [12]. Despite being ubiquitous and available, Al has no specific biological function in plants [18].

The process of release of Al ions from octahedral co-ordination in minerals through weathering processes [12,19] usually depends on H^+ ion concentration. In acid soils below pH 4.3, Al ions combine with water and solubilizes to form Al (H_2O) 6^{3+}. At pH 4.5-6.5 aluminium-hydroxyls dominates, while in very acidic conditions of pH < 4.5, Al^{3+} dominates [20]. As H^+ ions in the soil solution increases to pH 4 or below, the hydronium ions (OH^{3+}) formed cause the dissolution of Al^{3+} from the edges of the mineral structure. Upon release the Al ions become six fold coordinated with oxygen in OH_2 groups such as $(Al(-OH_2^{0.5+})^6$. This OH_2 groups are Al substituted hydronium ions, the Al having replaced one H from each of the six hydronium ions (OH^{3+}). The Al substituted hydronium ions called aluminohexahydronium ions are often designated as $Al6H_2O^{3+}$. Aluminium can also formulate other species such as Al $(OH)^{2+}$, $Al(OH)_2$, $Al(OH_-^{3-}$, and Al $(OH)_4^-$ where Al^{3+} is considered as the most toxic form that have great impact on plants growth and development [14,21,22].

Increase in soil pH, cause subsequent dissociation into various species of Al [17,23]. The aluminohydronium ions sequentially dissociate H ions as base is added leaving OH ions in place of the OH_2 groups. The resulting Al forms range from simple monomeric species to polymeric species of varying molecular weight, either in combination with Fe or Si or both, depending on soil pH [24,25]. This is because, some of the resulting Al^{3+}, $(OH)Al^{2+}$, and $(OH)_2Al^+$ ions remain in the soil solution and they may be adsorbed as monomers to the cation exchange sites of the soil or polymerized on clay mineral surfaces or adsorbed and then complexed by soil organic matter.

One of the major consequences of aluminium toxicity is growth inhibition in plants. Excess Al inhibits roots cell division, elongation, root hair formation and enhances development of swollen roots apices [26]. It also inhibits water and nutrients uptake of affected plants [13]. Several studies have indicated that excess Al alters nutrient levels such as N, K, Ca, Mg and P and reduces photosynthetic rates, stomatal conductace and leaf transpiration rate in plants [27,21,28,29]. The negative effects of Al in soil and plants can however, be managed by application of organic matter and lime. Soil organic matter has been reported to form stable complexes of Al with humic aliphatic organic acids to supress detrimental effects of Al in soil solution [30]. Lime on the other hand is an important approach of correcting acidity by increasing soil pH, reducing Al toxicity [31,32,4] restoring Ca, P, availability as well as improving soil cation exchange capacity (CEC) [32,33].

The soil iron and aluminium released during weathering can be re precipitated as amorphous
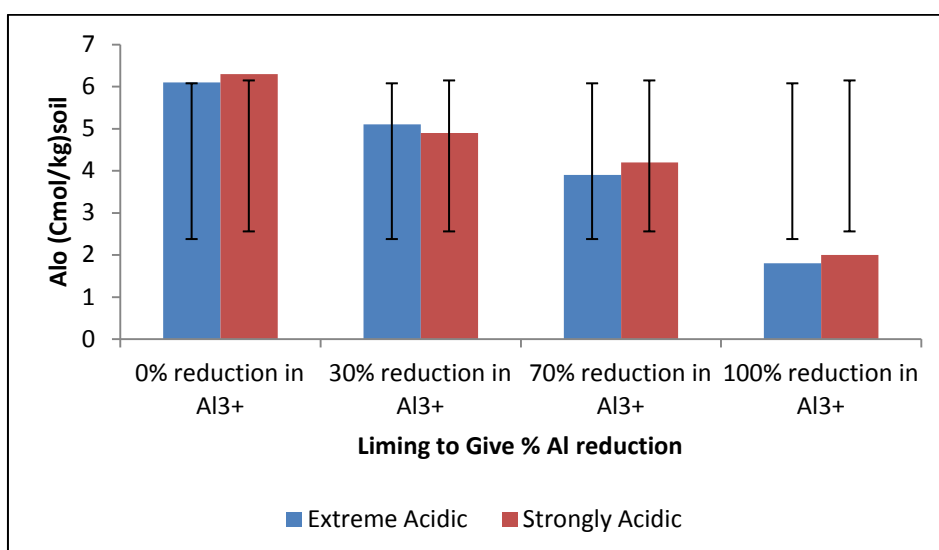
Fig. 1. Effect of liming on oxalate aluminium (Al$_o$) (cmol kg^{-1}) on acid soils

or crystalline oxides, hydroxides or oxhydroxides [34]. The amount, nature and distribution of this various forms of Fe and Al oxides with organic complexes can greatly influence soil physical and chemical properties [35] hence affecting ionic charge chemical characteristics and ionic adsorption especially phosphorus sorption, surface charge and specific surface area. Swelling and aggregate formation may also be significantly modified by the presence of amorphous Fe and Al oxides [36]. The amorphous (short range order) and crystalline (hematite and gibbsite) Fe and Al hydroxides are particularly important to P sorption in soils. Crystalline Fe and Al hydrous oxides sorb 5-10 times more P than crystalline alumina silicates clay minerals where else amorphous Fe oxide gel sorb 10-100 times more P than their crystalline counterparts. Amorphous Fe and AL hydroxides also often occur as coatings on other soil mineral surfaces [37]. Owing to the fact that increased P sorption on limed soils is attributed to formation of active x-ray amorphous Al hydroxyl polymers, which actively sorb more P than Al^{3+} [38]. The active Al hydroxyl polymers formed has also been associated with coating the surfaces of minerals, thereby affecting their surface charge characteristics [39]. Understanding of the amount of crystalline and amorphous forms of Fe and Al in acid soils and the effects of management practices on such forms is an important approach in the management of such soils. Amorphous forms can be evaluated by use of oxalate while dithionate evaluates crystalline forms. This study therefore aimed at evaluating the effects of lime

on oxalate and dithionate extractable Al in acid soils.

2. MATERIALS AND METHODS

2.1 Experimental Layout Design

A greenhouse pot experiment was carried out at Waruhiu Farmers' Training Centre, Githunguri, Kiambu County, Kenya. Two composite soil samples representing extremely acid (pH 4.0-4.5) and strongly acidic (pH 5.0-5.5) soils, as described by Kanyanjua, et al. [40] were used. The experiments were a 4^2 factorial laid down in a Randomized Complete Block Design (RCBD and replicated three times. The treatments were liming rates were chosen to obtain 0, 30, 70 or 100% reduction in amounts of M KCl-extractable Al originally present in the soil and the two levels of acidity (Table 1). Burnt lime (CaO) containing about 21% calcium oxide was used in this study.

Five kilogramme composite soil sample portions for both extremely and strongly acid soils were weighed into ten litre plastic pots. The six (6) lime levels as stipulated in Table 1 were weighed and incorporated into the soil samples by thoroughly mixing and incubating at moist conditions for a period of 21 days. Water was added every 2 days to compensate for evaporative losses. After incubation, soils from each liming level were air-dried, sieved and returned to the plastic pots. The soils were re-incubated at the same conditions for 14 days after which they were air dried. Subsamples of the soils were then used for chemical analyses.

Table 1. Actual amounts of lime added to the acid soils

	Lime added (tonnes ha⁻¹)			
Soil	**0%**	**30%**	**70%**	**100%**
Extremely Acidic	0	2.2	5.2	7.4
Strongly Acidic	0	1.4	3.2	4.5

Table 2. Physicochemical properties of the two soils prior to the pot experiment

	Extremely acidic	**Strongly acidic**
pH (H$_2$O)	4.48	4.59
Exch. Al (cmol kg^{-1})	3.85	3.90
P (mg kg^{-1})	9.25	10.50
Oxalate Al (cmol kg^{-1})	4.61	4.58
Dithionate Al (cmol kg^{-1})	3.85	3.48
Oxalate Fe (cmol kg^{-1})	6.75	6.85
Dithionate Fe (cmol kg^{-1})	3.85	3.82
Al Saturation (%)	55.82	49.66
PSD*		
% Clay	56.32	50.00
% Silt	21.00	17.00
% Sand	22.68	33.00
Textural class	Clay	Clay

Particle size distribution

2.2 Laboratory Analysis

Soil physicochemical analysis and P adsorption were determined before and after application of treatments. Soil pH, exchangeable aluminium, exchangeable Calcium, exchangeable magnesium and particle size distribution were analyzed as described by Okalebo, et al. [41]. Iron and aluminium contents were extracted using ammonium oxalate at pH 4.0 [42] and dithionate-citrate-bicarbonate (DCB) [43]. Extractable P was determined as described by [44]. The lime requirements of the soils were calculated using the equation of Cochrane, et al. [45]. The equation aims at reducing the % Al saturation to a level that is commensurate with crop Al tolerance, and is given as: Lime required (CaCO$_3$ equiv.) tones ha^{-1} = 1.8 [Al - RAS (Al + Ca + Mg) /100] where Al = cmol kg^{-1} soil in the original exchange complex, RAS = Required percentage Al saturation, Ca = cmol kg^{-1} soil in the original exchange complex, Mg = cmol kg^{-1} soil in the original exchange complex. A RAS value of 20% was used. Soil characterization data in Table 2 was used for lime requirement determinations.

2.3 Statistical Analysis

Data obtained were subjected to Analysis of Variance (ANOVA) using the GenStat statistical package [46] and treatment effects were tested for significance using the F-test at 5% level of significance. Means were ranked using Duncan's New Multiple Range Test (DNMRT). Dependency tests were also conducted to find out if there was a relationship between the various variables assessed.

3. RESULTS

3.1 Initial Soil Physical and Chemical Characteristics

The tested soils were acidic with pH < 5.5 (Table 2). Dithionate and oxalate extractable Al and exchangeable Al levels were high >2 cmol kg^{-1} in both soils. Percent aluminium saturation was also high; > 20% and extractable P (< 15 mg kg^{-1}) was low. The tested soils had clay texture.

3.2 Effects of Liming on Soils pH, Aluminium Levels

Liming significantly (*p*=.05) increased soil pH levels and reduced extractable Al and percent Al saturation (Table 3). The reduction of soil pH was in the order: 0 % reduction of Al^{3+} < 30% reduction of Al^{3+} < 70% reduction of Al^{3+}, 100% reduction of Al^{3+}. The significant (*p*=.05) decrease of exchangeable Al on liming followed the order: 0% reduction of Al^{3+} < 30% reduction of Al^{3+} < 70% reduction of Al^{3+} < 100% reduction of Al^{3+} in both extremely and strongly acidic soils. Liming aimed at 100% reduction of exchangeable Al led to 50% reduction of

exchangeable Al in extremely acidic soils and 55% reduction in moderately acidic soils compared to liming aimed at 0% reduction of exchangeable Al. The significant (p=.05) decrease of % Al saturation followed the order: 0% reduction of Al^{3+} < 30% reduction of Al^{3+} < 70% reduction of Al^{3+} < 100% reduction of Al^{3+} in both extremely acidic and strongly acidic soils. Liming to give 100% reduction of exchangeable Al led to 46% and 61% reduction of % Al saturation in extremely and moderately acidic soils respectively.

Liming significantly (p=.05) reduced oxalate extractable aluminium (Al_o) in the acid soils (Fig. 1). The Al_o was reduced from ≥ 6.0 cmol kg^{-1} to < 3 cmol kg^{-1} in both extremely acidic and strongly acidic soils. Oxalate extractable Al was reduced

by 70% in extremely acidic soils and 68% in strongly acidic soils compared to the control (0% reduction in AL^{3+} treatment).

Liming significantly (p=.05) reduced dithionate extractable aluminium (Al_d) in the acid soils (Fig. 2). The Al_d was reduced from > 5.0 cmol kg^{-1} to < 2.5 cmol kg^{-1} in both extremely acidic and strongly acidic soils. Dithionate extractable Al was reduced by 78% in both extremely acidic and strongly acidic soils compared to the control.

A significant (p=.05) positive relationship was observed between soil pH, lime and exchangeable P (Table 4). Lime was also positively correlated with exchangeable P. On the contrary, soil pH, lime, exchangeable P,

Table 3. Effect of liming on the pH $_{(water)}$, exchangeable aluminium and percent aluminium saturation of the acid soils

Lime to give:	Extremely acidic			Moderately acidic		
	pH(water)	Exch. Al	Al Sat.	pH(water)	Exch. Al	Al Sat.
0% reduction in Al^{3+}	4.2a	3.6d	64.1d	4.1a	3.8c	71.5d
30% reduction in Al^{3+}	5.2b	2.9c	49.2c	5.3b	2.8ab	45.5c
70% reduction in Al^{3+}	6.3c	2.3b	42.9b	5.6bc	2.2a	38.1b
100% reduction in Al^{3+}	6.4d	1.8a	34.8a	6.4bc	1.7a	27.6a
% CV	0.6	1.6	7.9	0.9	0.8	3.2

Values followed by the same letter(s) on the same column are not significantly different at p=.05. CV-coefficient of variation
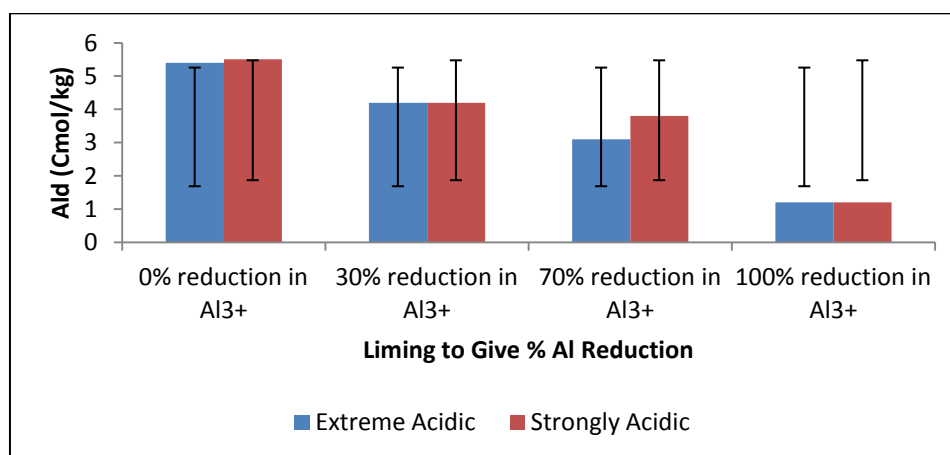

Fig. 2. Effect of liming on dithionate aluminium (Al_d) (cmol kg^{-1}) on acid soils

Table 4. Relationship between soil pH, P, aluminium saturation, Al_o, Al_d and lime in the two acid soils

	pH	Lime	Al_o	Al_d	Al. Sat.
pH	-	0.94	-0.95	-0.96	-0.84
Lime	0.94	-	-0.98	-0.97	-0.86
P	0.38	-	-0.29	-0.33	-0.28

All correlations had high significant relationship of p=.05

aluminium saturation, Al_o and Al_d, were observed to have a significant (p=.05) negative correlation.
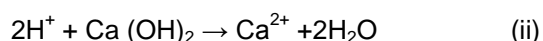
4. DISCUSSION

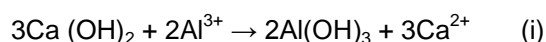### 4.1 Soil Chemical and Physical Characteristic of the Soils

As per the rating suggested by Landon [47] the soils had low levels of P (< 10 bicarbonate extractable P) and high levels of exchangeable aluminium (> 2.0 cmol kg^{-1}) and Al saturation (> 20%) implying that they were of high acidity levels and low fertility status. The soils also had high levels of crystalline and amorphous aluminium (> 2.0 cmol kg^{-1}). The high levels of Al and Al saturation are considered to be toxic to maize plants [41,47]. According to Kanyanjua, et al. [40], the soils were strongly to extremely acidic with pH of 4.48-4.58. Such acid soils with high Al^{3+} ions, low bases and CEC are characteristic of highly weathered soils, which have lost most of the basic cations through the process of leaching [47]. As a result, their high levels of Fe and Al sesquioxides may lead to high P fixation, resulting in low available P [47,48,49,50]. Additionally, the acidity could be attributed to the mineralogy of the parent materials [50] because most of these soils are developed from non-calcareous parent materials such as syenites, phololites, trachytes and nepholites which are acidic in nature [51].

4.2 The Effects of Lime on Soil pH and Aluminium

The significant increase of soil pH with liming in the present study could be attributed to the presence of Ca^{2+} ions contained in the lime. The Ca^{2+} ions displaces H^+ and Al^{3+} ions from the soil adsorption sites (Equation i and ii) which are subsequently neutralized resulting in increased soil pH [52].

$$3Ca\,(OH)_2 + 2Al^{3+} \rightarrow 2Al(OH)_3 + 3Ca^{2+} \qquad \text{(i)}$$

$$2H^+ + Ca\,(OH)_2 \rightarrow Ca^{2+} + 2H_2O \qquad \text{(ii)}$$

The significant reduction of exchangeable Al and aluminium saturation, oxalate Al and dithionate Al upon liming could be attributed to reaction of the calcium oxide with carbon dioxide and water in the soil to yield Ca bicarbonate ($CaHCO_3$). The resulting Calcium bicarbonate reacts with exchangeable and residual soil acidity, hence replacing H^+ and Al^{3+} on the colloidal complex [6, 53] that is subsequently neutralized.

The negative correlation between extractable P and Al_d and Al_o could be attributed to the fact that Al oxyhydroxides act as sinks for soluble phosphates [54]. According to Gasparatos, et al. [55] Vaananen, et al. [56], aluminium iron enriched concretions are major sinks of P, which control P dynamics in agricultural soils by maintaining high sorption capacity. Oxalate extraction method has the ability to extract poorly crystalline oxyhydroxides of Al, which are directly associated with P sorption and while dithonate extraction extracts the amorphous Al forms [54].

5. CONCLUSIONS AND RECOMMENDATIONS

Liming significantly increased soil pH and decreases exchangeable Al, % Al saturation, Al_o and Al_d levels. High rates of lime which resulted into 100% reduction of Al^{3+} were more effective as compared to lower rates in both extremely and strongly acidic soils. Liming significantly reduced Al_o by 70% and 68% in extremely acidic and strongly acidic soils respectively while Al_d was reduced by 78% in both extremely and strongly acidic soil compared to control. This implies that liming aimed at reducing 100% exchangeable Al is effective in the reduction of both crystalline and amorphous forms of Al. Further research is however required to evaluate the short and long term effects of the rates hence their interactions on crop yields, other plant nutrients and the environment under field conditions. The research will also evaluate the rates that are effective in management of Al in acid soils with highest return per capital.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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