AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

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Batch 72

1. SUBJECT CLASSIFICATION

A. PRIMARY
Food production and nutrition — AF22-0000-G190

B. SECONDARY
Soil chemistry and physics--West AFrica

2. TITLE AND SUBTITLE

Soluable and exchangeable aluminum in ultisols and alfisols in west Africa

3. AUTHOR(S)

Juo,A.S.R.

4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1977	21p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

IITA

8. SUPPLEMENTARY NOTES *(Sponsoring Organization, Publishers, Availability)*

(In IITA j.ser.80)
(In Commun.in soil science and plant analysis,v.8,no.1,p.17-35)

9. ABSTRACT

10. CONTROL NUMBER

PN-AAE-617

11. PRICE OF DOCUMENT

12. DESCRIPTORS

Aluminum
Exchange reactions
pH
Solubility
Tropics

13. PROJECT NUMBER

14. CONTRACT NUMBER

AID/ta-G-1185 GTS

15. TYPE OF DOCUMENT

AID 590-1 (4-74)

AID/ta-G-1185 GTS
IITA
PN-AAE-617

reprint series

Soluble and exchangeable aluminum in Ultisols and Alfisols in West Africa

by A. S. R. Juo

References:
IITA Journal Series No. 80
Commun. in Soil Sc. & Plant Analysis
8(1), 17–35 (1977)

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COMMUN. IN SOIL SCIENCE AND PLANT ANALYSIS, 8(1), 17-35 (1977)

SOLUBLE AND EXCHANGEABLE ALUMINUM IN ULTISOLS AND ALFISOLS IN WEST AFRICA

KEY WORDS: saturation extracts, percent exchangeable Al saturation

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ABSTRACT

Aluminum in soil saturation extracts and exchangeable Al determined by N KCl extraction were studied using a large number of Ultisol and Alfisol samples from West Africa.

The concentration of soil solution Al ranged from 0.05 to 4.5 ppm. Solution Al content was generally higher in the surface horizon (Ap and A_1) than in the lower horizons within the same profile; whereas the reverse was true for exchangeable Al.

For subsoil samples, the percentage exchangeable Al saturation was highly correlated with soil pH measured both in water and in N KCl. But for surface soil samples, the correlations were poor.

INTRODUCTION

High levels of soluble and exchangeable Al are among the major causes of soil infertility of strongly leached mineral soils in the

IITA Journal Paper No. 80

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tropics. For successful crop growth, liming becomes an indispensable practice not only to neutralize the toxic level of Al but also to supply Ca as a plant nutrient. Kamprath[12] and Evans and Kamprath[6] established the use of degree of exchangeable Al saturation instead of soil pH as a criterion for predicting the lime requirement for acid soils; whereas Pearson[16] suggested that the measurement of soil solution composition should provide the most direct information reflecting the soil chemical environment governing plant growth.

While little information is available regarding the Al status in the highly weathered acid soils in the lowland tropics, neither of the above concepts could be quantified with a wide range of applicability. This paper examines the relationships among soils pH, soil solution Al and exchangeable Al status in a large number of Ultisols and Alfisols derived from different parent materials in the lowland tropics of West Africa.

MATERIALS AND METHODS

Eighty-six surface soil samples (Ap and A_1 horizon) and 193 subsoil samples from Liberia, Sierra Leone, Ivory Coast, Togo and southern Nigeria were selected for this study. About 10 percent of the samples are Alfisols while the remaining are Ultisols.

These soils were derived from a wide range of parent materials which included banded gneiss, granitic gneiss, quartzite, mica-schist, amphibolites, basalts, sand-stones, shales and coastal sediments. Pedological descriptions of the soils were made by F.R. Moormann (unpublished data, IITA). Chemical and mineralogical properties of selected profiles from southern Nigeria were reported by Gallez, Juo, Herbillon and Moormann[9].

Exchangeable Al in soil was determined by extraction with 1 N KCl according to the procedure given by Black[2]. Total exchange acidity (Al + H) in the KCl extract was determined by titration and the Al content in the same extract was measured colorimetrically using the modified aluminon method[11].

Soil solution (saturation extract) was obtained by equilibrating 200 g of air-dry soil with deionized water at saturation in a pyrex glass column. After 24 hours, the soil solution was then gradually displaced with an equal volume of deionized water required initially to bring the soil to moisture saturation. The concentration of Al in the saturation extract was determined colorimetrically. The concentrations of Ca and Mg in the extracts were determined on an EEL flame photometer and a Perkin Elmer Model 403 atomic absorption spectro-photometer, respectively.

Soil pH was measured both in water and in 1 N KCl at 1:1 soil to solution ratio using a Beckman Expandomatic pH meter. Organic C in soil was determined by the dichromate-oxidation method of Walkley and Black[2]. Effective CEC was calculated from the summation of exchangeable bases determined by N NH_4OAc extraction and the exchange acidity by N KCl extraction.

RESULTS AND DISCUSSION

1. Soil Solution Aluminum

The relationship between Al in solution and soil pH of ten Ultisol and five Alfisol profiles is shown in Figure 1. Data of surface soils and subsoils clearly separate into two populations.

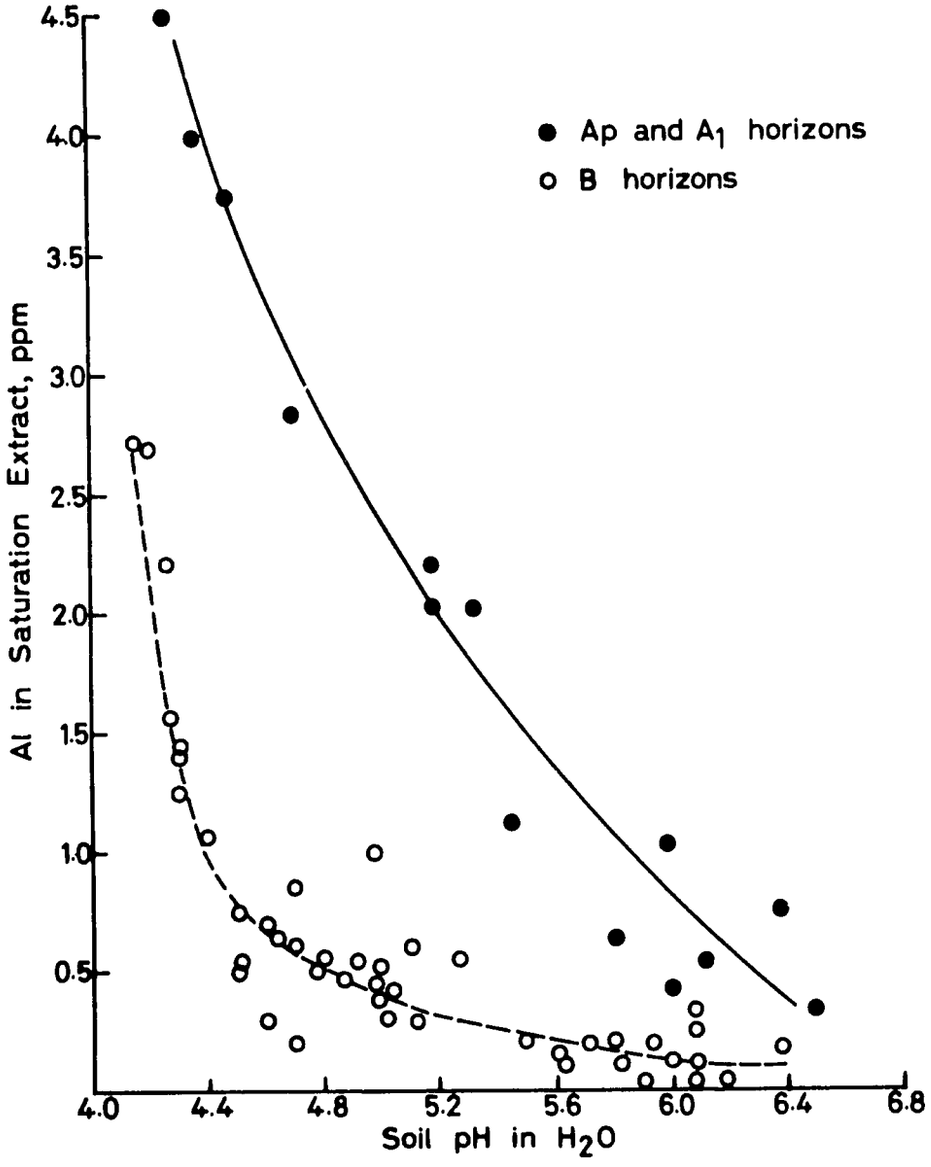


FIG. 1

Concentration of soil solution Al in surface and subsoil horizons of Ultisols and Alfisols as a function of soil pH(H_2O).

The surface soils maintain higher concentration of Al^{3+} in the soil solution than the subsoil samples at any given pH value; and the differences are greater when the soil pH values are below 5.5. In subsoils, Al concentration is well below 1 ppm when soil pH is above 4.5. There is a near linear relationship between Al in solution and soil pH in the surface soils. But in the subsoils, the relationship is curvilinear.

Results given in Table 1 show that the high solution Al concentration in the surface soil within each profile is apparently associated with organic matter. This seems to be in disagreement with the results reported by Evans and Kamprath[6] who showed that the Al^{3+} concentration in soil solution in the surface layer of several acid soils from North Carolina decreased with increasing organic matter content. But they did not compare the solution Al and organic matter relationship within the same profile. The distribution patterns of solution Al, exchangeable Al and percent saturation within two Ultisol profiles are further shown in Fig. 2. In both profiles, solution Al and exchangeable Al remain fairly constant in the B horizons. Whereas the high solution Al concentration in the surface layer is in contrast to the low content of exchangeable Al and to the low percent exchangeable Al saturation.

The high Al solubility in the surface soils may be attributed to the presence of substantial amount of soluble organo-Al complexes, such as, $Al(OH)_2^+$-fulvic acid complexes[19] and a higher electrolyte concentration in the soil solution than its corresponding subsoil horizons. The total electrolyte concentration in

TABLE 1

Soluble and exchangeable Al contents and subsoil horizons of five Ultisols

Profile No.	Soil Group	Horizon	Soil pH H_2O	Org. C %	Solution Al* ppm	Exch. Al me/100g	Effective CEC me/100g	Exch Al Sat. %	Exch. Ca Sat. %
097	Plinthic Paleudult	A_1	4.7	0.95	2.83	0.10	2.49	4	41
		$B_{21}t$	4.6	0.40	0.73	1.55	2.67	58	16
099	Orthoxic Tropudult	Ap	5.2	3.00	2.20	0.02	9.51	0.2	68
		$B_{21}t$	4.8	0.35	0.56	1.98	3.13	63	19
100	Oxic Plinthudult	A_1	5.3	2.00	2.02	0.02	7.59	0.3	62
		B_2t	5.0	0.15	0.46	0.40	2.15	19	15
118	Oxic Paleudult	A_1	4.2	1.04	2.72	1.83	2.86	64	9
		$B_{21}t$	4.3	0.40	0.49	1.94	2.54	76	6
119	Plinthic Paleudult	A_1	4.5	1.25	3.73	0.56	2.17	26	31
		$B_{21}t$	4.4	0.72	1.43	1.07	1.97	54	14

* Al in saturation extract

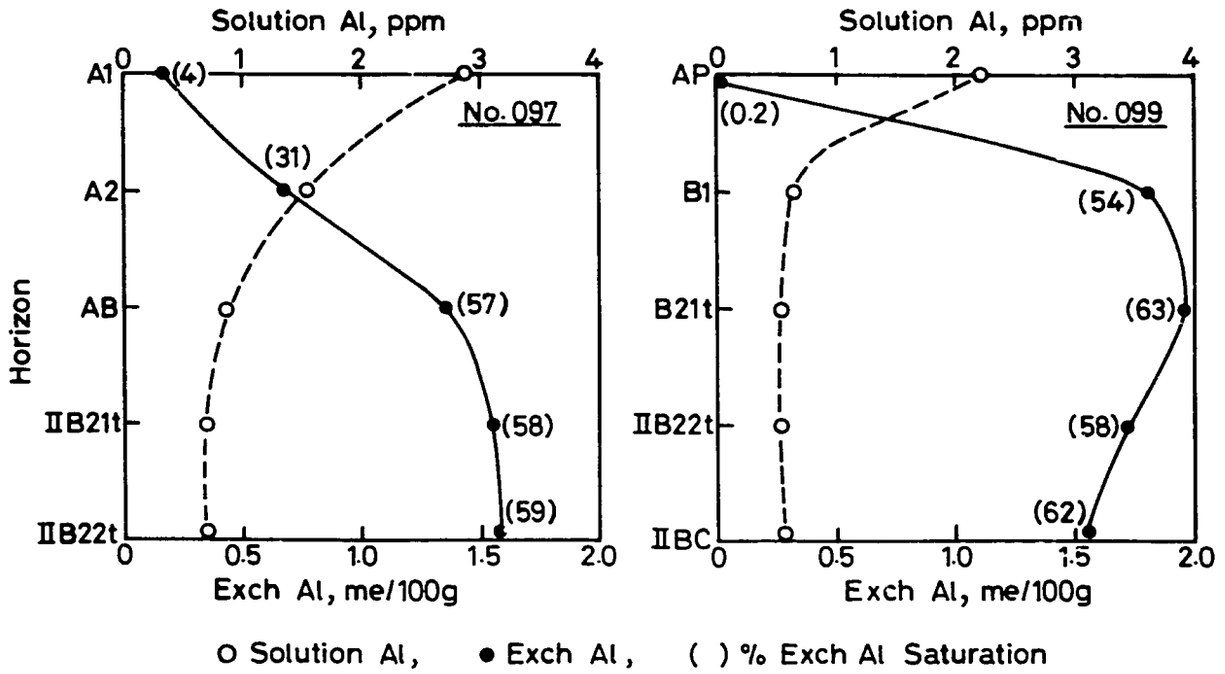


FIG. 2

Distribution of solution Al and exchangeable Al in a Plinthic Paleudult profile (No. 097) and an Orthoxic Tropudult (No. 099).

saturation extracts for the surface soils studied is 10 to 50 times higher than that in the subsoil horizons (Juo, unpublished data).

To compare the Al solubility with respect to gibbsite, the values of (pH-1/3 pAl) were calculated using pH values of saturation extracts which were normally lower than soil pH. The (pH-1/3 Al) values range from 2.92 to 3.38 for surface soils, and 2.62 to 3.05 for subsoils. The surface soils in all cases, show supersaturation with respect to gibbsite which has a (pH-1/3 pAl) value of 2.75 as given by Lindsay et al[13]. For the subsoils, the range of (pH-1/3 pAl) values suggests that in some soils, the system is in equilibrium with gibbsite; whereas others indicate supersaturation. The high (pH-1/3 pAl) values with respect to gibbsite indicate that the solubility of Al in these soils is controlled by more soluble Al compounds, e.g. amorphous Al hydroxides, amorphous Al-silicates, and organo-Al complexes[5,8,19,20].

2. Exchangeable Aluminum

The average values of exchangeable Al within five pH(H_2O) ranges for all soils studied are given in Table 2. Soils with pH values above 5.5 contain little or negligible amount of exchangeable Al. For the group of strongly acidic soils (pH below 5.0), the average values of exchangeable Al are 1.3 and 1.7 me/100g for the surface soils and subsoils, respectively.

Correlation coefficients and regression equations between exchangeable Al and soil pH measured in water and in KCl are given in Table 3. For both the surface soils and subsoils, the correlations between exchangeable Al and soil pH are rather poor although the r

TABLE 2

Mean of exchangeable Al and percent Al saturation for all soil samples within five pH ranges

No. of Samples	pH H_2O Range	pH H_2O Mean	pH KCl Mean	Exch. Al, me/100 g Range	Exch. Al, me/100 g Mean	Al Sat. % Range	Al Sat. % Mean	Mean Effective CEC me/100 g	Mean Org. C %
				Surface Soils					
7	6.5-6.0	6.23	5.56	0-0.19	0.10	0-5	2	6.39	1.11
5	5.9-5.5	5.70	4.10	0-0.13	0.10	0-6	2	6.07	2.23
21	5.4-5.1	5.25	4.42	0-2.04	0.46	0-43	13	4.83	1.80
26	5.0-4.5	4.72	3.92	0.05-3.69	1.34	2-69	41	3.38	1.79
27	4.4-4.0	4.15	3.82	0.05-2.75	1.20	1-67	35	3.65	2.26
				Subsoils					
13	6.5-6.0	6.21	5.39	0-0.28	0.06	0-7	2	3.42	0.24
24	5.9-5.5	5.72	4.73	0-0.19	0.12	0-15	4	3.84	0.46
31	5.4-5.1	5.25	4.12	0.05-0.88	0.38	3-36	13	3.08	0.34
96	5.0-4.5	4.78	3.89	0.42-8.36	1.67	15-90	49	3.49	0.43
29	4.4-4.0	4.25	3.73	0.98-2.20	1.66	34-76	60	2.62	0.52

TABLE 3

Linear correlation coefficients among soil pH, exchangeable Al and percent Al saturation.

Correlation (y vs. x)	r	Regresstion Equation
	Surface soils	
pH(H_2O) vs. pH(KCl)	+0.843**	y = 0.917 + 0.935 x
Exch. Al vs. pH(H_2O)	-0.483**	y = 3.801 - 0.597 x
Exch. Al vs. pH(KCl)	-0.616**	y = 4.455 - 0.844 x
% Al Satn vs. pH(H_2O)	-0.497**	y = 111.23 - 17.46 x
% Al Satn vs. pH(KCl)	-0.630**	y = 129.65 - 24.51 x
Log Exch. Al vs. pH(KCl)	-0.676***	y = 5.91 - 1.56 x
	Subsoils	
pH(H_2O) vs. pH(KCl)	+0.824**	y = 1.414 + 0.870 x
Exch. Al vs. pH(H_2O)	-0.482**	y = 6.829 - 1.136 x
Exch. Al vs. pH(KCl)	-0.527**	y = 6.554 - 1.313 x
% Al Satn vs. pH(H_2O)	-0.809**	y = 222.32 - 37.48 x
% Al Satn vs. pH(KCl)	-0.690**	y = 175.07 - 33.76 x
Log Exch Al vs. pH(KCl)	-0.842***	y = 9.48 - 2.44 x

values between exchangeable Al and pH(KCl) are slightly higher than those between exchangeable Al and pH(H_2O). However, the correlations are improved considerably when the values of log(exch. Al) are used (Table 3).

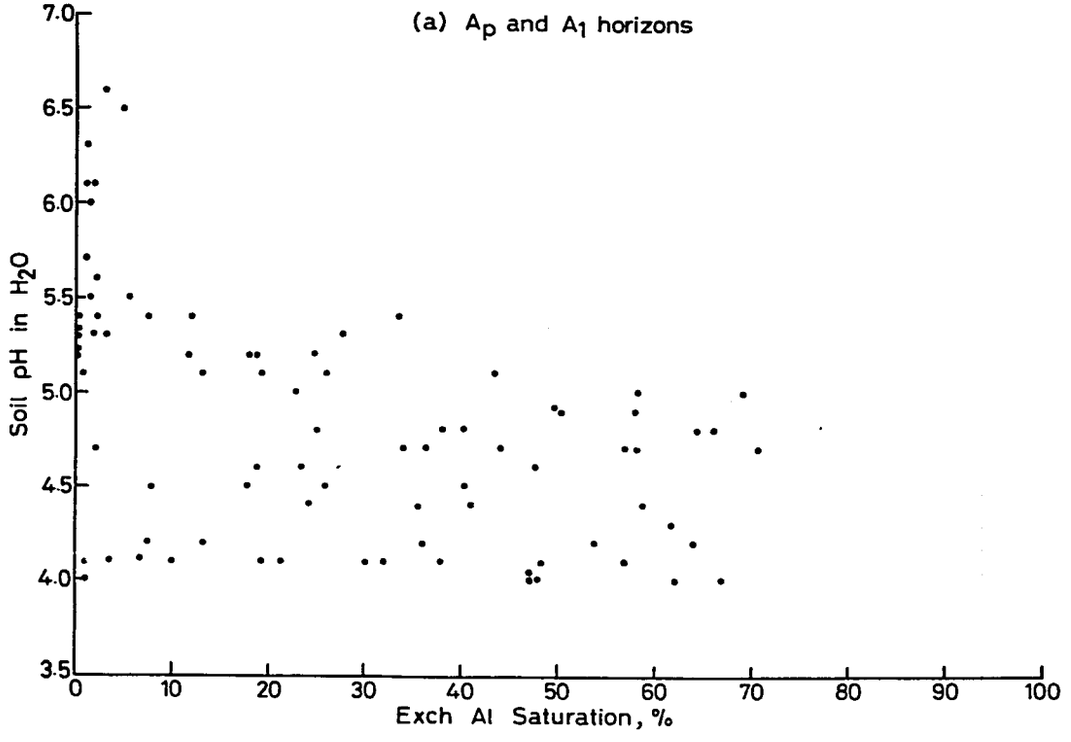
The poor correlation between exchangeable Al and pH(KCl) may be attributed to two factors: the release of exchangeable H^+ associated with soil organic matter and the release (or adsorption) of H^+ at the surface of Fe and Al hydrous oxides. For soils containing moderate amounts of Fe and Al oxides and hydrous oxides, the pH values measured in N KCl reflect not only the amount of exchangeable

Al^{3+} and H^+ in the soil, but also the release (or adsorption) of H^+ ion by the oxide surfaces[14, 15]. Therefore, one would expect better correlation between KCl-exchangeable Al and pH(KCl) for mineral soils dominating in constant-charge colloids (e.g. smectite, vermiculite) than soils dominating in constant-potential colloids (e.g. Fe and Al oxides).

The percentage exchangeable Al saturation calculated on the basis of effective CEC has been shown to be a useful criteria for predicting crop response to liming in acid soils[12, 17]. The mean values of exchangeable Al saturation for five pH(H_2O) ranges given in Table 2, indicate that the largest increase in Al saturation occurs when soil pH is below 5.1.

The drop of mean percentage of exchangeable Al saturation for surface soils below pH 4.5 (Table 2) is due to the increasing degree of exchangeable H^+ saturation in soils within this pH range (exchangeable-H data not given).

The relationships between percentage exchangeable Al saturation and soil pH are shown in Figs 3 and 4. For surface soils, the scattering of the data points in the % Al vs. pH(H_2O) plot indicate that substantial amount of exchangeable Al exists at higher pH in some surface soils (Fig. 3a). Whereas the low Al saturation occurring below pH 4.5 is due to high degree of exchangeable H saturation (not shown) in soils, such as Tropaquults which contain a substantial amount of organic matter. Similar results were shown by Coleman and Thomas[5] for a large number of surface soils from eastern United States.


(a) A_p and A_1 horizons
Soil pH in H_2O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
0
10
20
30
40
50
60
70
80
90
100
Exch Al Saturation, %

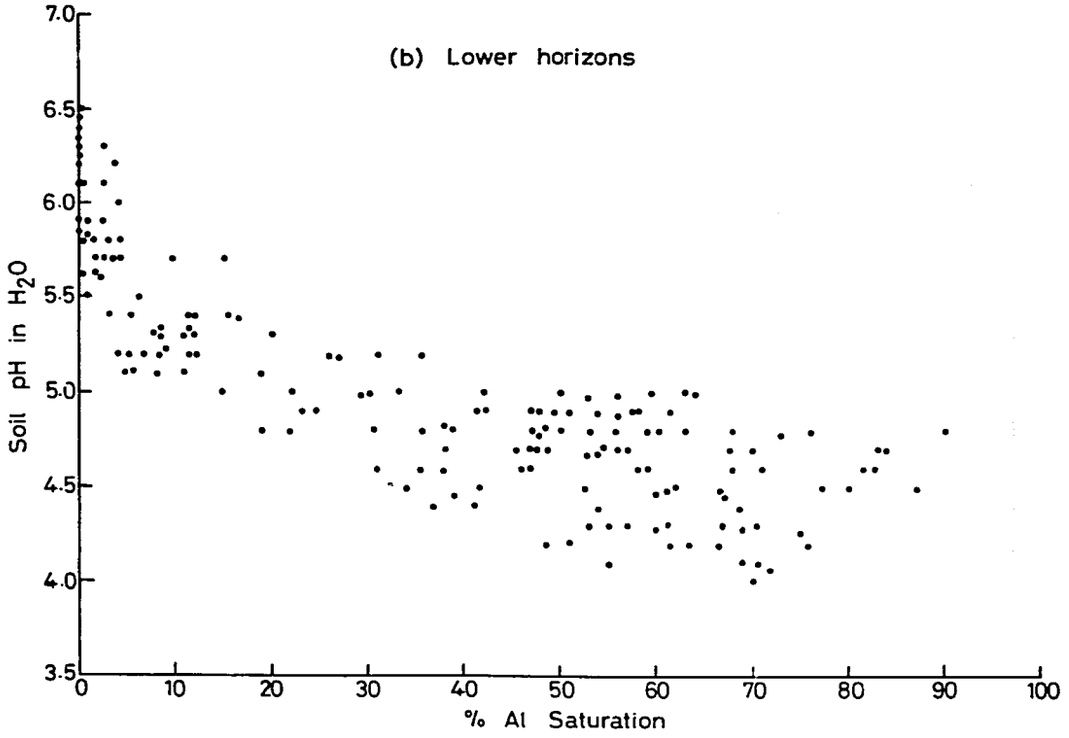
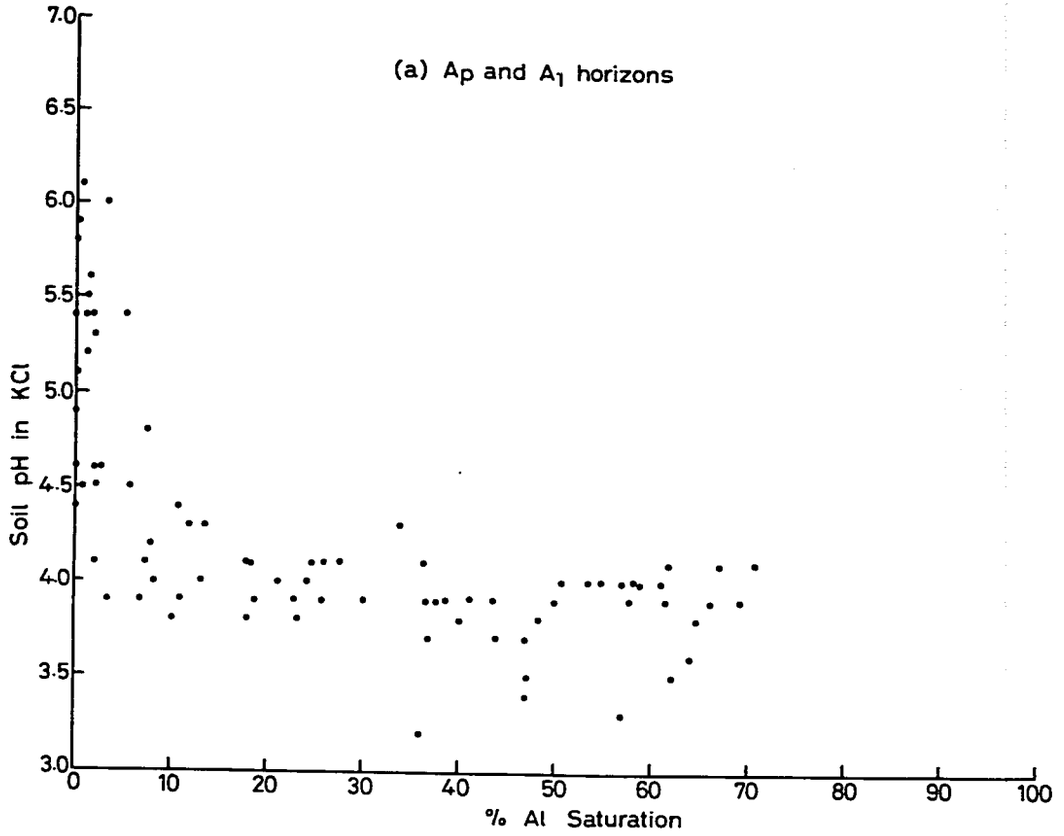


FIG. 3

The relationship between percentage exchangeable Al saturation and soil pH measured in water. (a) surface soils, (b) lower horizons.


(a) Ap and A1 horizons
Soil pH in KCl
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
0
10
20
30
40
50
60
70
80
90
100
% Al Saturation

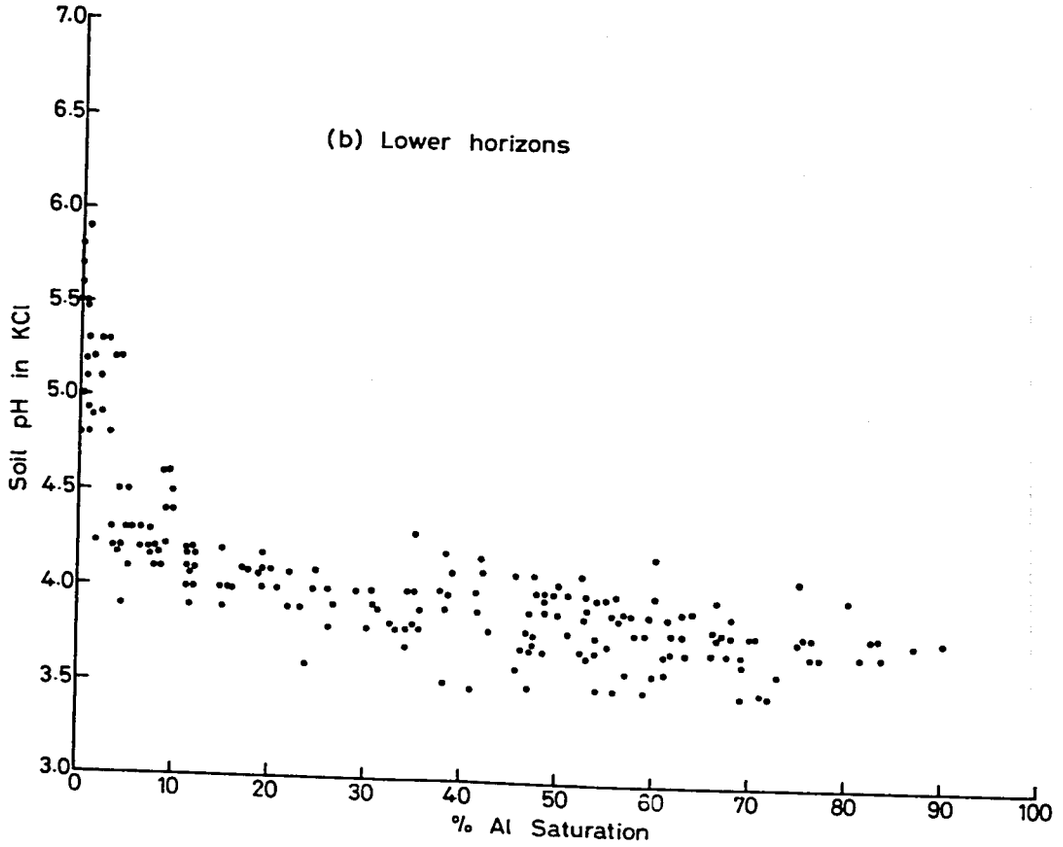


FIG. 4

The relationship between percentage exchangeable Al saturation and soil pH measured in N KCl. (a) surface soils, (b) lower horizons.

For subsoils, the percentage exchangeable Al saturation is highly correlated with pH(H_2O), where the pH value of 5.1 corresponds to approximately 30% Al saturation (Fig. 3b and Table 3). Similar relationships were obtained by Kamprath (personal communication) and by Abruna et al.[1] for Ultisols and Oxisols from Central America and Puerto Rico.

Linear regression equations and correlation coefficients between % exchangeable Al saturation and soil pH for both surface and subsoil samples are given in Table 3. Curvilinear regression analysis was non-significant for both surface and subsoil groups.

The relationships of exchangeable Al saturation and pH(KCl) are shown in Figs. 4a and 4b. The correlation coefficients are considerably higher than for pH(H_2O) for both the surface soils and subsoils (Table 3). The pH(KCl) for all soil samples is lower than the pH values of the corresponding samples measured in water (Table 2) indicating that these soils bear net negative charge[10, 14].

GENERAL DISCUSSION AND CONCLUSION

Results obtained from the present study may be summarized as follows:

1. There is a good correlation between percentage exchangeable Al saturation and pH(H_2O) for subsoil samples but not for surface soil samples.
2. The concentration of Al^{3+} in soil solution (saturation extract) in surface soils is generally higher than their corresponding subsoil horizons within the same profile.

Published results have shown that exchangeable Al and the percentage exchangeable Al saturation calculated on the basis of effective CEC are more reliable criteria than soil pH for predicting crop response to liming in leached mineral soils[12, 17, 18]. Based on a number of field trials on acid soils in southern United States, Kamprath[12] indicated that exchangeable Al saturation of 40% or less was required for optimum growth of maize, while 20% or less was required for soybean.

The question remains whether the growth response is because of the elimination of Al toxicity, or it is simply due to increased supply of Ca and/or Mg to the plant. Greenhouse experiments on maize using a number of Ultisols from Nigeria (pH 4.3 to 4.7) failed to show symptoms of Al toxicity in the unlimed treatment where essential nutrient elements other than Ca were applied. But the plants showed severe Ca deficiency symptoms (Juo, unpublished data). The relatively low levels of soluble and exchangeable Al in most of the Ultisols used in this study also suggest that nutrient deficiencies are probably more critical limiting factors than Al toxicity for crop growth.

Little information is available relating soil solution Al to crop growth and response to liming in acid tropical soils. Results published by Evans and Kamprath[6] indicated that maize growing in several coastal plain soils from North Carolina responded to liming when the concentration of soil solution Al was greater than 3.6 ppm. For soybean, the critical value for solution Al was 1.8 ppm. Moreover, the level of Al in solution required to be

toxic varies with soil, with the concentration of other ions, and with plant species or variety. More sensitive plants will grow satisfactorily at Al concentrations in the order of 1.0 ppm[17].

Addition of fertilizer salts, such as chloride and sulfate will increase the concentration of Al in soil solution[3,4]. Thus, soil solution Al may be too variable to be used as a criterion for predicting Al toxicity and crop response to liming.

ACKNOWLEDGEMENT

The author wishes to thank Dr. Morris Garber for his help in statistical analysis. Acknowledgement is also due to Mr. Fabian Chukwuma and Miss Celestina Okogun for their laboratory assistance.

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