



COMPARISON OF SOIL ALUMINIUM METHODS AND THEIR RELEVANCE TO THE SOILS OF PAPUA NEW GUINEA

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PAPUA NEW GUINEA**

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ABSTRACT

Three methods for determining extractable aluminium in soils were investigated. Two of these methods involved extraction with potassium chloride and differed only in extraction technique and method of determining the final solution aluminium concentration. These methods were highly correlated ($r = 0.94$, $P < 0.001$) and are equally suitable for determining exchangeable aluminium.

The third method, involving ammonium acetate as extractant, was not highly correlated with the potassium chloride methods and extracted larger quantities of aluminium from the soils.

Potassium chloride aluminium was negatively correlated with soil pH. Multiple regression showed it to be related to pH, hydrogen ion concentration and NaF pH.

Ammonium acetate aluminium was also correlated with pH and NaF pH, but multiple regression showed that P retention accounted for the largest part of the variation, and that organic carbon and calcium also made significant contributions to the correlation.

Soils with potentially toxic levels of potassium chloride aluminium were found to have $\text{pH} < 5.5$ together with low levels of organic carbon, exchangeable calcium and available phosphorus. No soils with $\text{pH} > 5.5$ had toxic levels of potassium chloride aluminium.

No clear criteria for toxic levels of ammonium acetate aluminium could be drawn from the work reported. Ammonium acetate aluminium levels imply that more soils may contain aluminium at toxic levels than is indicated by the potassium chloride tests, especially those derived from Volcanic Ash.

INTRODUCTION

Extractable aluminium is determined routinely by the Chemistry Department of D.P.I., at Konedobu, by the method of McLean, et al (1965). This involves leaching the soil with unbuffered 1M potassium chloride at a 1:10 soil solution ratio, with aluminium in the extract being determined on a Varian 875 atomic absorption spectrophotometer. This last procedure uses an acetylene/nitrous oxide mixture, at very high temperatures, and involves a certain amount of danger, especially considering the parlous state of the present wooden Chemistry laboratory buildings. It has been found often that requests for aluminium determinations have borne little relationship to the type of soil and whether or not significant quantities of aluminium will be found. Obviously, no aluminium is expected in near neutral or alkaline soils, and in fact, some authors claim that aluminium is unlikely to be important above pH 5.5 (Thomas, 1982).

Potassium chloride aluminium may also be used in the calculation of effective cation exchange capacity (ECEC) and aluminium saturation where:-

$$\text{ECEC} = \text{sum of cations(pH 7 leachate)} + \text{KCl Al}$$

and

$$\text{Al saturation (\%)} = \text{KCl Al} \times 100 / \text{ECEC}$$

These two values are used mainly for acid soils, and for some soils ECEC is thought to be a better measure of exchange capacity than that obtained by distilling ammonia sorbed by soil during the ammonium acetate pH 7 leaching. Where aluminium saturation is greater than 60% aluminium toxicity is probable. There is doubt, however, whether either method gives a reasonable measure of CEC in variable charge soils derived from volcanic ash which are very common in Papua New Guinea. There is also doubt about the relevance of potassium chloride aluminium as a measure of aluminium in these soils, exchangeable aluminium is not a particularly good indicator of soil solution concentration (Radcliffe, 1984) and has had limited success as a toxicity

index (Webber et al, 1982).

Several authors have found that aluminium determined by extraction of the soil with 1M ammonium acetate at pH 4.8 is a better measure of aluminium on volcanic ash soils (Fassbender, 1969; Kamprath, 1973; Macfarlane, 1974, 1977). Aluminium extracted by ammonium acetate at pH 4.8 has been described as "extractable" by McLean (1965) and his method is reported to extract exchangeable aluminium plus soluble aluminium hydroxide (Pratt and Bair, 1961) and probably some hydroxyaluminium monomers or polymers which may be strongly adsorbed by the colloid. (Thomas, 1961). All the "extractable" aluminium fraction is thought to react with limestone when added to the soil.

Ammonium acetate extractable aluminium increases with the degree of weathering of the soil and also with the concentration of the extractant (Ayers et al, 1965). The method of McLean (1965) uses ammonium acetate quoted as 1M i.e. 1M in acetate and 0.5M in ammonium ions. The extractant used here is that used in the West Indies by Macfarlane and Walmsley (1977) which is 1M in ammonium acetate and adjusted to pH 4.8 with glacial acetic acid and is approximately 2M in acetate, i.e. double the strength of McLean's extractant.

Aluminium extracted by this solution has been found to be related to phosphate requirements for Volcanic Ash soils in the Eastern Caribbean (Macfarlane and Walmsley, 1977) and has been shown to be a better measure than potassium chloride extractable aluminium or McLean's ammonium acetate extractable aluminium for tropical peat soils with ash influence, with and without added lime, in Papua New Guinea (Macfarlane and Quin, in preparation).

Fassbender (1969), Alamos et al (1967), Kamprath, (1973), Gutnick et al (1967), and Alcayaga (1965) found similar relationships with ammonium acetate aluminium for Volcanic Ash soils. Pino (1982) citing Hernandez (1968)

states that there exists in these soils a possibility of aluminium toxicity especially on less resistant crops, aluminium accumulating in the roots and preventing P uptake. This agrees with the work of McCormick and Yates-Borden (1973) who showed that aluminium phosphate can precipitate at the root tips, blocking phosphorus transport pathways and that high external levels of aluminium can even extract phosphorus from the plant roots to produce such precipitation. Aluminium toxicity was also proposed as the reason for poor growth at low phosphorus concentrations in West Indian volcanic ash soils (Macfarlane, 1974) and in P.N.G. peat soils with volcanic ash influence (Macfarlane and Quin, in preparation).

The object of this investigation was to compare methods for measuring soil aluminium, to determine the soil factors which influence it, and to propose clear criteria which would separate soils with significant amounts of aluminium.

MATERIALS AND METHODS

Soils

The soils used in this investigation were normal routine samples that were submitted for analysis between 1983 and 1986. Not all the earlier soils were included in all the comparisons because they have been discarded since the original analyses. Table 1 shows the range and mean values of the soil test values determined.

Laboratory Methods

pH

pH of the soil was determined on a 1:5 soil solution suspension, after shaking for one hour.

Available phosphorus

Available phosphorus was determined on a 1:20 soil solution 0.5M sodium hydrogen carbonate extract after shaking for thirty minutes according to the method of Olsen et al (1954), modified by Banderis et al (1976).

Phosphate in solution was determined by the method of Murphy and Riley (1963).

Organic carbon

The Walkley-Black method was used.

Extractable cations

The soil was leached with a 1M solution of ammonium acetate, with a 1:20 soil solution ratio (Metson, 1961). Sodium and potassium were determined by flame photometer. Calcium and magnesium were determined on a Varian atomic absorption spectrophotometer.

Cation exchange capacity (CEC)

Ammonium ions sorbed from the ammonium acetate leached, alcohol washed, soils were distilled from the soil into 1% boric acid solution using magnesium oxide and titrated against standard 0.1M hydrochloric acid.

Cation Exchange Capacity ECEC

Calculated from the sum of extractable cations + KCl extractable Al (1)
(see below)

pH in NaF

One gram of soil was shaken with 50 mL saturated sodium fluoride solution, according to the procedure of Fieldes and Perrott (1966).

Phosphate Retention

Saunders method (1965) was used.

Extractable Aluminium (1) AlK (McLean, 1965)

Air dry soil (10g) was leached with 100mL M potassium chloride solution. The leachate was made up to 100mL and aluminium concentration determined by atomic absorption spectrophotometer.

Extractable Aluminium (2), AlF, and Hydrogen (Thomas, 1982)

Reagents

1. M potassium chloride
2. M potassium fluoride titrated to a phenol phthalein end-point with 0.02M sodium hydroxide
3. Standard 0.02M sodium hydroxide
4. Standard 0.02M hydrochloric acid
5. Phenol phthalein indicator 1% in ethanol

Procedure

Potassium chloride (25mL) was added to 5g air dry soil, mixed and allowed to stand for 30 min. The suspension was filtered under vacuum by transferring to a Buchner funnel fitted with a filter paper and mounted on a 250mL vacuum flask. The soil was further washed with 5 x 25mL aliquots of potassium chloride solution. Phenol phthalein (5 drops) was added to the filtrate, which was titrated with 0.02M sodium hydroxide to the first permanent pale pink end point. M potassium fluoride solution (10mL) was added to the solution and titrated with 0.02M hydrochloric acid to a clear end point. After standing for 20 mins further hydrochloric acid was added to the clear end point. A blank titration using 150mL potassium chloride was also carried out.

The results were calculated as follows:

$$\text{meKCl acidity} = 100(\text{NaOH titre \{sample - blank\}}) \times M(\text{NaOH})/\text{wt of sample}$$

$$= \text{KClH}$$

$$\text{me KCl exchangeable Al} = 100(M \times \text{titre})\text{HCl}/\text{wt of sample}$$

$$= \text{AlF}$$

$$\text{me H} = \text{KCl acidity} - \text{KCl exchangeable Al}$$

$$= \text{H}$$

Extractable Aluminium (3) (AlA)

Reagents

Ammonium acetate solution pH 4.8. Ammonium acetate (77 g.L⁻¹) adjusted to pH 4.8 with glacial acetic acid (~M NH₄⁺ and ~2M OAc⁻).

Procedure

10g air dry soil was shaken on a reciprocating shaker with 50mL ammonium acetate solution in a centrifuge tube for 15 min. The suspension was centrifuged and the supernatant decanted into a 100mL volumetric flask. The shaking was repeated with a further 50mL of ammonium acetate and the second supernatant added to the first. The solution was made up to 100mL and the aluminium concentration determined by atomic absorption.

RESULTS AND DISCUSSION

Table 1 gives the range and mean of all the soil test values determined.

Correlation coefficients for the three aluminium methods with soil test values are shown in Table 2.

Potassium Chloride Aluminium, AlK, AlF

Exchangeable aluminium determined by the routine potassium chloride method (AlK) was very highly significantly correlated with aluminium determined by the new potassium chloride method, AlF ($r = 0.94^{***}$). This is to be expected since the soils use the same extractant and there are only minor differences in the extraction method. The method of determining the final aluminium concentration differs, as does the final soil solution ratio but the high correlation coefficient implies that there is little difference in the results obtained by the two methods.

Aluminium extracted by both potassium chloride methods was found to be negatively correlated with pH (AlK, $r = -0.46^{***}$, AlF, $r = -0.42^{***}$) and positively correlated with KCl acidity. ($r = 0.96^{***}$, for method (1) and $r = 0.98^{***}$ for method (2)). This is to be expected as aluminium will be more soluble at lower pHs where the hydrogen concentration is greater.

Multiple regression analysis using a linear model with all data shows that hydrogen ion concentration (H), pH, NaF pH and C account for 46.0% of the variation in AlK. H alone accounts for 34.5% of the variation.

The regression equation is:

$$\text{AlK} = 6.32 + 2.22\text{H} - 0.76\text{pH} - 0.19\text{NaFpH} - 0.08\text{C}$$

TABLE 1, MEAN AND RANGE OF TEST VALUES

Soil Test	Mean	Range
KCl Al (1) me%	0.52	0 - 12.1
KCl Al (2) me%	0.45	0 - 11.76
NH ₄ OAc Al (3) me%	4.72	0 - 29.6
pH	5.66	3.8 - 7.9
P (Olsen) mgkg ⁻¹	16.90	0 - 476
C %	3.28	0 - 18.6
Ca me%	10.45	0 - 194.7
P retention %	60.6	0 - 99
NaF pH	9.2	7.2 - 12.1
Sum cations me%	12.98	0 - 205.8
C.E.C. me%	18.6	1.0 - 116.0
E.C.E.C. (1) me%	13.5	0.07 - 205.8
E.C.E.C. (2) me%	6.94	0.15 - 45.02
Al saturation (1) %	10.2	0 - 100
Al saturation (2) %	12.6	0 - 100
H me%	0.13	0 - 3.08
KCl acidity me%	0.56	0 - 12.8

TABLE 2. CORRELATION COEFFICIENTS ALUMINIUM METHODS WITH SOIL TEST VALUES

Soil Test	KCl (1) (AlK)	KCl (2) (AlF)	NH ₄ OAc (3) (AlA)	Aluminium saturation (1)	Aluminium saturation (2)
KCl (1)	1.00				
KCl (2)	0.94***	1.00			
NH ₄ OAc (3)	0.18	0.14	1.00		
Al saturation (1)	0.70***	0.63***	0.23*	1.00	
Al saturation (2)	0.55***	0.58***	0.17	0.86***	1.00
pH	-0.46***	-0.43***	-0.41***	-0.54***	-0.49***
P (Olsen)	-0.09	-0.08	-0.14	-0.09	-0.08
C	-0.06	0.08	0.45***	-0.07	-0.14
Ca	-0.10	-0.11	-0.22*	-0.34***	-0.49***
Sum cations	-0.10	-0.11	-0.25**	-0.34***	-0.42***
C.E.C.	-0.01	-0.03	0.00	-0.06	-0.09
P retention	-0.02	-0.04	0.60***	0.05	0.04
NaF pH	-0.16	-0.15	0.52***	-0.02	0.07
H	0.59***	0.43***	0.19*	0.40***	0.27**
KCl H	0.96***	0.98***	0.17	0.64***	0.57***
E.C.E.C. (1)	0.11	-0.09	-0.21*	-0.19*	-0.30**
E.C.E.C. (2)	0.08	-0.08	-0.22*	-0.22*	-0.31**

Addition of C, P and CEC accounts for only a further 1.4% of the variation which is not significant.

Table 3 shows correlation coefficients between the three measures of aluminium and other soil properties for soils with pH < 5.5, i.e. those more likely to have aluminium problems. Some of the correlation coefficients are greater than those using all data, i.e. AlK with pH $r = -0.65^{***}$, with NaF pH $r = -0.31^{**}$, with ECEC (1) $r = 0.36^{***}$; AlF with pH, $r = -0.63^{**}$, with NaF pH $r = -0.29^{**}$, and with ECEC (2) $r = 0.31^{***}$.

Multiple regression of AlK with pH, H and CEC accounts for 62.5% of the variation in AlK. pH is the most important factor accounting for 42.6% of the variation.

The regression equation is:

$$\text{AlK} = 19.60 - 2.84\text{pH} + 1.93\text{H} + 0.45\text{NaFpH} - 0.043\text{CEC}$$

Addition of P, C and P retention to the regression accounts for only a further non-significant 1.8% of the variation in AlK. Thus AlK is dependent on soil acidity, i.e. pH, and the hydrogen ion content of the soil, and NaF pH which is a measure of allophane aluminium present in the soil.

Aluminium saturation

Correlations using aluminium saturation Al% (1) $\{\text{Al}\% = 100 \cdot \text{AlK} / \text{ECEC}(1)\}$ are shown in Table 2. Correlations with pH, P, Ca, SC, P retention, ECEC (1) and (2) are higher than those using AlK or AlF, showing that Al saturation is more closely related to these soil properties than the aluminium concentration per se. Grouping the data using only samples with pH < 5.5 (Table 3) improves only the correlation with C, $r = -0.22^*$ for Al % (1), $r = -0.31^{**}$ for Al % (2).

TABLE 3 CORRELATION COEFFICIENTS ALUMINIUM METHODS WITH SOIL TEST VALUES pH < 5.5

Soil Test	KCl (1) ALK	KCl (2) AlF	AlA	NH ₄ OAc (3)	Aluminium saturation (1)	Aluminium saturation (2)
KCl (1) ALK	1.00					
KCl (2) AlF	0.94***	1.00				
NH ₄ OAc(3) AlA	0.09	0.06	1.00			
Al saturation (1)	0.68***	0.62***	0.05	1.00		
Al saturation (2)	0.53***	0.57***	-0.18	0.86***	1.00	
pH	-0.65***	-0.63***	0.17	0.56***	0.41***	1.00
P (Olsen)	-0.11	-0.11	-0.13	-0.08	0.07	
C	-0.16	-0.19	0.47***	-0.22*	0.31**	
Ca	-0.04	-0.07	-0.14	-0.31**	-0.40***	
Sum cations	-0.02	-0.05	-0.15	-0.32**	-0.42***	
C.E.C.	-0.04	0.00	0.23*	-0.05	-0.18	
P retention	-0.17	-0.18	0.59***	-0.14	-0.11	
NaF pH	-0.31**	-0.29**	0.52***	-0.17	0.03	
H	0.58***	0.42***	0.13	0.36***	0.21*	
KCl H	0.96***	0.98***	0.08	0.63***	0.54***	
E.C.E.C. (1)	0.36***	0.31**	-0.10	-0.04	0.19*	
E.C.E.C. (2)	0.31**	0.31**	-0.12	-0.09	0.20*	

Multiple regression analysis on all samples using Al % (1) reveals that Al % (1) is most dependent on pH which accounts for 28.3% of the variation in Al % (1). Adding the variables H and C accounts for 37.7% of the variation in Al % (1).

The regression equation is:

$$\text{Al}\%(1) = 99.2 - 15.7\text{pH} - 14.3\text{H} - 1.81\text{C}$$

Using only data from samples with pH < 5.5, the picture is changed slightly, H and C do not appear in the equation. pH alone accounts for 30.4% of the variation in Al%(1). Addition of ECEC(1), SC and Ca increases the variation accounted for to 60.4%.

The regression equation is:

$$\text{Al}\%(1) = 113.5 - 18.2\text{pH} - 14.5\text{SC} + 6.7\text{ECEC}(1) + 7.8\text{Ca}$$

Ammonium Acetate aluminium, AlA

Ammonium acetate extractable aluminium was poorly correlated with either of the potassium chloride measures (Table 3), this is in agreement with Lin and Coleman (1960), although McLean et al (1959) have found that neutral potassium chloride and ammonium acetate at pH 4.8 extract similar quantities of aluminium. Ayres et al (1965) concluded that ammonium acetate aluminium is a better indicator of soil weathering than potassium chloride aluminium.

While ammonium acetate has been found to be a poor extractant of organic bound aluminium in muck soils (Hargrove and Thomas, 1984) it is generally found that in well developed Andisols that part of the non-exchangeable aluminium extracted by ammonium acetate at pH 4.8 is from the organically complexed forms, while in more weathered soils the inorganic forms of aluminium seem to be the main source of non-exchangeable aluminium fractions (Igue and Fuentes, 1972).

Aluminium extracted by pH 4.8 ammonium acetate was found to be correlated with pH ($r = -0.49^{***}$), organic carbon ($r = 0.45^{***}$) and also with NaF pH ($r = 0.51^{***}$), and phosphate retention ($r = 0.60^{***}$). A high proportion of the soils used here are derived from volcanic ash and these relationships are to be expected since NaF pH is related to allophane derived aluminium, which is complexed to the organic matter and is largely responsible for the high phosphate retention of these soils.

Multiple regression using AlA shows, as expected, that a different relationship exists between AlA and soil properties than that with AlK and Al%(1). Regression of AlA with P retention accounts for 36.1% of the variation in AlA. Addition of pH, NaF pH, C and Ca to the regression increase the variation accounted for to 55.2%.

The regression equation is:

$$\text{AlA} = 2.20 + 0.6\text{Pret} - 1.7\text{pH} + 0.9\text{NaFpH} + 0.7\text{C} - 0.2\text{Ca}$$

Since ammonium acetate aluminium is suggested to be a better measure of aluminium for volcanic ash soils, the correlation analysis was repeated using only data from soils with NaF pH > 9.4 i.e. those soils containing allophane. Correlation coefficients (shown in Table 4) of AlA with pH ($r = -0.51^{***}$), C ($r = 0.33^{***}$), Ca ($r = -0.37^{***}$), SC ($r = -0.39^{***}$), CEC ($r = 0.21^*$), ECEC(1) ($r = -0.37^{***}$), ECEC(2) ($r = -0.31^{**}$) are all higher than those where all data are included.

Multiple regression of AlA for samples with NaF pH > 9.4 gives the following equation:

$$\text{AlA} = -5.22 + 0.13\text{Pret} + 0.24\text{pH} + 0.75\text{C} - 0.42\text{SC} + 0.18\text{CEC}$$

accounting for 50% of the variation in AlA.

**TABLE 4 CORRELATION COEFFICIENTS AMMONIUM
ACETATE ALUMINIUM WITH SOIL TEST VALUES
(NaF pH > 9.4)**

Soil Test	NH ₄ OAc (3)
Al saturation (1)	-0.10
Al saturation (2)	-0.08
pH	-0.51***
P (Olsen)	-0.06
C	0.33***
Ca	-0.37***
Sum cations	-0.39***
C.E.C.	0.21*
P retention	0.58***
NaF pH	0.38***
H	0.17
KCl H	0.22*
E.C.E.C. (1)	-0.37***
E.C.E.C. (2)	-0.30**

Phosphate retention and pH both control the supply of soil solution phosphorus. It would seem logical from the above relationship that AlA also affects soil solution phosphorus. Such a relationship has been found in soils of volcanic origin or influence in the West Indies (Macfarlane, 1974; Macfarlane and Walmsley, 1977) and in P.N.G. (Macfarlane and Quin, in preparation). Further work needs to be done to investigate this relationship in P.N.G. Volcanic Ash soils.

Criteria for separating soils containing significant quantities of aluminium

i. Potassium chloride aluminium

There are no soils with aluminium saturation greater than 30% which have pH > 5.5, in agreement with Thomas (1982).

Of the samples (15) which have aluminium saturation greater than 60%, where aluminium toxicity of most plant species is to be expected, none has a pH > 5.2, available phosphorus greater than 8.0 mg.kg⁻¹ (generally < 2.0 mg.kg⁻¹), calcium greater than 1.6 me% ECEC greater than 12.6 me%, SC greater than 4.36me% (generally less than 2.6me%, carbon greater than 2.45% (generally less than 1.25%) and BS greater than 42%. Only one of these soils has a P retention greater than 70%, (this soil has P retention of 93% and a NaF pH of 11.1) and is the only volcanic ash soil to appear in this category, implying that potassium chloride aluminium is not a good measure of soil solution aluminium for these soils, since it has often found that aluminium is a problem even where KCl aluminium is low.

Of the soils with Al% between 30 and 60% where aluminium toxicity is possible no soil has pH > 5.5, Ca > 9.0 me% (generally < 3.5me%) or carbon > 5.5, (except for peat soils). Available P is variable but is generally less than 10 mg.kg⁻¹. ECEC is generally less than 10 me%.

No soil with $\text{pH} < 5.5$ and $\text{Al}\% > 30\%$ has $\text{Ca} > 3.5\text{me}\%$ and $\text{C} > 5.5$ or $\text{P} > 10\text{mg.kg}^{-1}$.

No soil with $\text{pH} < 5.5$ and $\text{Al} > 30\%$ (apart from peat soils) have $\text{C} > 5.5\%$ and $\text{P} > 10 \text{ mg.kg}^{-1}$.

No soil of $\text{pH} < 5.5$ with $\text{Al} > 30\%$ has $\text{P} > 10 \text{ mg.kg}^{-1}$ and $\text{Ca} > 3.5\text{me}\%$ or $\text{C} > 5.5\%$.

It would appear unlikely that a soil with $\text{pH} > 5.5$ contains toxic levels of potassium chloride extractable aluminium or aluminium saturation greater than 30%.

Soils with $\text{pH} < 5.5$ and any two of the following: $\text{P} > 10\text{mgkg}^{-1}$, $\text{Ca} > 3.5\text{me}\%$, $\text{C} > 5.5\%$ are also unlikely to contain levels of aluminium considered toxic as measured by extractable with potassium chloride.(i.e Al saturation $> 30\%$).

The only exceptions to the above appear to be peat soils, characterised by their very high organic matter levels and acidity.

ii. Ammonium acetate aluminium

Of the 241 samples tested 122 have $\text{AlA} > 4.0 \text{ me}\%$, and of these 90 have pH in $\text{NaF} > 9.4$, i.e. are allophane containing, 37 of these have a P retention $> 90\%$ and would be classified as andepts. Only two soils with $\text{pH} > 9.4$ and P retention $> 90\%$ have $\text{AlA} < 4.0 \text{ me}\%$. Aluminium extracted by ammonium acetate has been found to be related to phosphate availability in volcanic ash soils (Macfarlane 1974, Macfarlane and Walmsley, 1977). A tentative critical level of 350 to 400 mg.kg^{-1} (3.9 - 4.4 $\text{me}\%$) has been suggested by the same authors.

Considering all soils with $\text{AlA} > 4.0\text{me}\%$ and pH in $\text{NaF} > 9.4$ it can be seen that such soils have a wider range of properties than those with

Al%(1) > 30%. All are of acid reaction with pH from 3.9 to 6.8, in general pH < 5.6., carbon values can be higher as would be expected from the tendency of volcanic ash to accumulate organic matter. Carbon ranges from 0.1 to 14.6%, but most soils have C < 5.5%. P levels are as high as 32 mg.kg⁻¹ but most are less than 8mg.kg⁻¹. Calcium levels range from zero to 18 me% but are generally less than 10me%. SC range from 0.1 to 21 me%, CEC 2.2 to 35.8%, ECEC are generally less than 6me%. P retention ranges 39 to 98% but is generally greater than 85%.

It is more difficult to define criteria which would separate soils which may have toxic levels of ammonium acetate extractable aluminium. Certainly if NaF pH is greater than 9.4 and P retention > 90% aluminium levels can be expected to reduce yield. Where NaF pH > 9.4 and P retention < 90% soils with AlA > 4.0 me% generally but not always have pH < 5.5, low C, P, Ca and B.S. compared with the soils with AlA < 4.0 me% which have generally higher pHs, P and Ca levels. Only one of these soils has an Al % of more than 30%, this being a soil with very low KCl Al and ECEC.

SUMMARY AND CONCLUSIONS

The two potassium chloride methods used were highly correlated ($r = 0.94^{***}$) and either method is suitable for determining KCl extractable aluminium. The new method (AlF) is simpler and more easily operated by trained or trainee personnel. It does not involve aluminium determination by atomic absorption and is, therefore, in future to be used as routine by the Chemistry Section for determining KCl extractable aluminium.

Potassium chloride aluminium was found to be related to measures of acidity (H and pH) and NaF pH.

Aluminium saturation is also related to H and pH although H is less important below $\text{pH} < 5.5$.

No soil with pH greater than 5.5 has an aluminium saturation greater than 30%.

Soils with $\text{pH} < 5.5$ and $\text{Ca} > 3.5 \text{ me\%}$ and/or $\text{C} > 5.5\%$ and/or $\text{P} > 10 \text{ mg.kg}^{-1}$ are unlikely to have Al saturation greater than 30%, apart from peat soils, with very high O.M. and very low pHs.

Ammonium acetate aluminium (AlA) is generally higher than KCl aluminium but is poorly correlated with it. Although AlA, AlK and AlF are also correlated with pH and NaF pH, P retention accounts for a greater percentage of the variation in AlA than pH.

Ammonium acetate aluminium values imply that a greater proportion of soils have aluminium problems than do those from the potassium chloride determinations. Many of these samples are variable charge andisols derived from volcanic ash. Further work is needed on AlA in Volcanic Ash soils to validate the method as a measure for soil solution aluminium and to investigate its relationship with available (soil solution) phosphorus.

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