

EFFECT OF SOIL pH AND ORGANIC MATTER ON LABILE ALUMINIUM IN SOILS UNDER PERMANENT GRASS

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Summary

The rates of extraction of Na, K, Mg, Ca, and Al with 1M NH_4NO_3 from the mineral- and organic-rich layers of some Park Grass (Rothamsted) soils were measured at the pH of the soil. Below pH 3.7 exchangeable Al, derived from the kinetics curve, increases with decreasing soil pH and is less in the organic-rich layer. The sum of the basic exchangeable cations, $\Sigma(\text{Na} + \text{K} + \text{Mg} + \text{Ca})$, increases with increasing soil pH and is more in the organic-rich layer.

The extraction of exchangeable Al obeys first order kinetics, the rate constant being similar for all the soils (mean value $36 \pm 7 \times 10^{-6} \text{ s}^{-1}$), which implies that exchangeable Al is released from surfaces with similar properties for the adsorption of Al, and that the rate is not affected by soil pH and organic matter. The rate of extraction of non-exchangeable Al is the same in the mineral- and organic-rich layers of each soil, and is maximal at about pH 3.7, decreasing sharply at more and less acid pH values.

Introduction

THE association of large amounts of Al, non-exchangeable to 1M NH_4Cl and 1M KCl , with organic matter has been observed by several workers. McLean, Reicosky, and Lakshmanan (1965) found that the cation-exchange capacity (KCl-CEC), determined by leaching or centrifugal extraction of several acid soils with unbuffered 1M KCl solution, increased with liming, particularly when they contained much organic matter. Destruction of organic matter decreased the 'KCl-CEC' only when the soil had been limed, and the amount of the decrease was proportional to the organic matter content. Pionke and Corey (1967) found that 'non-exchangeable acidic' Al (the difference between Al extracted with 1M NH_4OAc , pH 4.8, and neutral M KCl) correlated significantly with pH, organic matter and clay content, the correlation with organic matter being most significant, thus implying the existence of Al-organic matter complexes in soils. Reeve and Sumner (1971) obtained similar correlations for Al and organic matter in surface soils but not in subsoils.

Exchangeable Al is less in surface than in subsurface soils from Virginia (Coleman and Thomas, 1967) possibly because of differences in their organic matter contents. Thomas (1975) found that, from soil treated with different amounts of HNO_3 , Al extracted by 1M KCl was less as organic matter content increased at any given pH level.

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These observations explain why acid soils containing much organic matter give low Al concentrations in the soil solution and produce good yields of corn and soybeans (Evans and Kamprath, 1970). Similarly Silva Rodriguez and Schaefer (1971) observed in the Nadi soils of Chile (volcanic ash soils) that high Al content is not harmful to natural vegetation because of organic matter accumulation, and that fulvic acid in such soils chelated about 300 mg of Al per g of C (0.133 atoms Al/atom C \equiv approximately 8 atoms C/atom Al).

Recently organic compounds have been used to prevent the dissolution of Al in acid soils instead of liming them. Hoyt and Turner (1975) reported that adding alfalfameal, sucrose, and peat moss to very acid soils (pH 4 to 5.5), decreased toxic quantities of exchangeable Al, especially with alfalfameal. This was attributed primarily to the complexing of exchangeable Al by organic matter.

In our work, Al-organic matter relationships in acid surface and subsurface soils of the Park Grass experiment at Rothamsted were examined using the method of extracting exchangeable Al devised earlier by Sivasubramaniam and Talibudeen (1972) in which the kinetics of Al extraction from the soil were analysed to differentiate between exchangeable and non-exchangeable Al. Organic matter Ca and Mg relationships and the possible interrelationships of the basic cations with Al through soil organic matter were also studied.

Materials and methods

Soils

Soils from the Park Grass experiment were selected (Table 1) which after continuous manuring since 1856 have attained stable pH values. The organic-rich (0 to 7.6 cm) and mineral-rich (7.6 to 22.9 cm) layers were sampled from the acid section of the plots, taking 1.27 cm cores from about 25 evenly spaced points on each plot.

The soil samples were air-dried and the coarser fractions ground in stages to <60 mesh in a ball mill thus minimising the effect of ball-milling on the finer fractions. Soil pH values were measured in 1M KCl at a 1:2.5 ratio. Organic carbon was determined by the Walkley-Black method using a recovery factor of 1.3.

Extraction of Al, Na, K, Mg, and Ca

Aluminium and other more basic cations were extracted by leaching 1 g soil on a porosity 1 sintered glass crucible with 1M NH_4NO_3 , adjusted to the pH of each soil, for 48 h at approximately 5 ml h^{-1} using peristaltic pumps and a modified LKB fraction collector. Up to three samples were thus examined simultaneously. Each soil was extracted in quadruplicate. Sivasubramaniam and Talibudeen (1972), using acid soils from long-term experiments of the Tea Research Institute, Sri Lanka, had established that the soil and 1M NH_4Cl

TABLE 1
Description of soils

Soils	Treatment ¹	pH in 1M KCl (1:2.5)	% C (Walkley-Black)
3U/O	Nil	4.24	5.25
2 + 3U	Nil	4.23	2.37
7U/O	PKNaMg	3.78	3.78
7U	PKNaMg	3.90	1.95
8U/O	P NaMg	4.08	3.67
8U	P NaMg	4.18	2.02
11U/O	N ₃ PKNaMg	2.88	11.02
11U	N ₃ PKNaMg	2.98	2.95
11L/O	N ₃ PKNaMg	3.54	9.30
11L	N ₃ PKNaMg	3.38	3.20
14U/O	N ₂ *PKNaMg	5.05	4.19
14U	N ₂ *PKNaMg	5.02	2.02
15U/O	PKNaMg	3.87	3.58
15U	PKNaMg	3.97	2.12

U = unlimed; L = limed; O = organic-rich layer

¹ For details of manuring see Warren and Johnston (1964)

*N as NaNO₃.

solution were in equilibrium when the leaching rate was between 5 and 8 ml h⁻¹. Fractions of leachate were collected at 3 h intervals up to 48 h. The cumulative Al extracted, plotted against time, became approximately linear after 24 h. Exchangeable Al, Al_x, was obtained by extrapolating the linear part of the curve to 'zero time' (Sivasubramaniam and Talibudeen, 1972).

This relationship represents two simultaneous processes, the extraction of exchangeable Al, Al_x, and non-exchangeable Al, Al_{n_x}. The rate of extraction of Al_{n_x} is constant, represented by a linear relationship. The extraction of Al_x is a first order process, the rate being proportional to the amount of Al_x on exchange sites at any time (Sivasubramaniam and Talibudeen, 1972).

The effluent pH was always greater than the influent pH because the hydrolysed forms of adsorbed Al ions are more basic than those in solution (Lim and Talibudeen, 1975; Pyman, Posner, and Talibudeen, 1976). However, the effluent pH decreased gradually to a constant value when the extraction rate became constant (Fig. 1).

The amounts of Na, K, Mg, and Ca extracted in the first fraction were taken as exchangeable basic cations because the amounts extracted later were negligible.

Analytical

Aluminium in the leachate was determined by the Aluminon method (Chenery, 1948), Ca (by emission, with 500 parts 10⁻⁶ La and radiation buffer added), Mg (by atomic absorption, with 500 parts

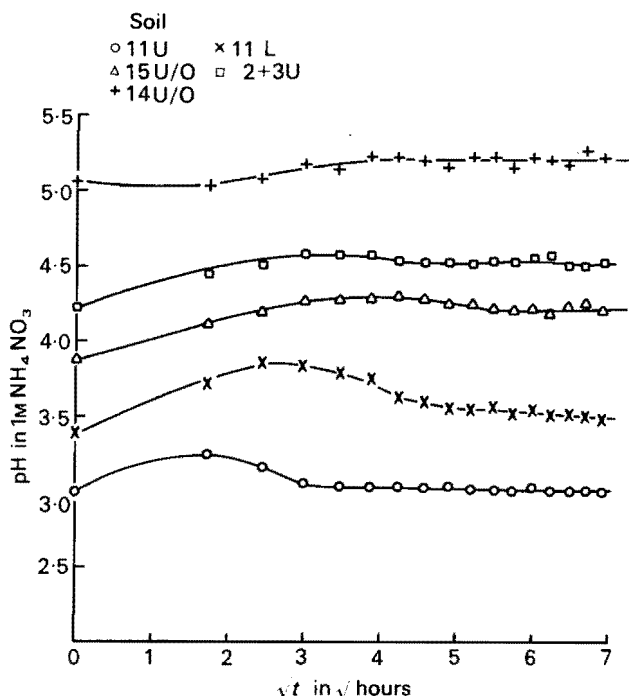


FIG. 1. Progressive change of 1M NH_4NO_3 leachate pH for five Park Grass soils.

10^{-6} Sr), Na (by emission, with 25 parts 10^{-6} Li) on a Unicam flame photometer SP900A, and K (by emission) on an EEL flame photometer.

Standard solutions for all calibrations were prepared in 1M NH_4NO_3 .

Results and discussion

Exchangeable Al(Al_x)

Plotting Al_x (Table 2) against soil pH for the organic-rich and mineral-rich layers gives curves of similar shape, Al_x values increasing with decreasing pH. However, at soil pHs < 3.7 Al_x increases more with the mineral-rich soils than with the organic-rich soils. Above pH 3.7 the curves for both sets of soils are indistinguishable ($P = 0.05$, Fig. 2) tending to zero as the pH increases. This gradual decrease above pH 3.7 is caused by more basic cations, especially Ca, occupying exchange sites increasingly, and also by the progressive loss of soluble Al to form $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (gibbsite $pK_{sp} = 33$). Because the pH and texture (mineralogy and particles size distribution) of the surface- and subsurface-soil in each comparison are similar, their organic matter contents must account for the differences in the Al_x :pH curves.

Organic matter complexes Al ions in several ways, forming mono- or multi-dentate chelates, depending on the nature and distribution of

TABLE 2

Extraction of Al with 1M NH_4NO_3 ; exchangeable Al(Al_x), and rates of extraction of non-exchangeable Al($d(\text{Al}_{n_x})/dt$).

Soil	Al_x (me kg^{-1})	$d(\text{Al}_{n_x})/dt \times 10^6$ (me $\text{kg}^{-1} \text{ s}^{-1}$)
3U/O	4.8 ± 0.4	51.9 ± 1.7
2 + 3U	2.4 ± 0.8	47.5 ± 1.1
7U/O	15.8 ± 0.8	141.9 ± 21.1
7U	14.8 ± 2.3	155.0 ± 21.1
8U/O	8.9 ± 0.8	78.1 ± 7.5
8U	6.7 ± 1.3	53.9 ± 6.1
11U/O	45.8 ± 4.2	85.6 ± 18.1
11U	82.7 ± 1.7	73.3 ± 9.2
11L/O	22.6 ± 2.5	215.6 ± 46.7
11L	69.9 ± 2.6	148.6 ± 7.2
14U/O	3.8 ± 0.9	15.6 ± 3.1
14U	1.5 ± 0.2	19.2 ± 0.8
15U/O	21.4 ± 1.6	182.8 ± 21.9
15U	17.7 ± 1.1	138.1 ± 11.4

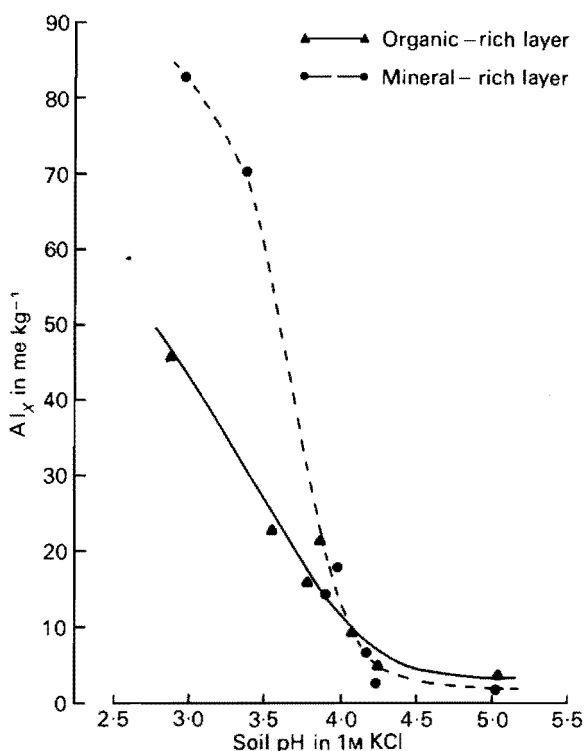


FIG. 2. The effect of soil pH on exchangeable Al(Al_x) in 1M NH_4NO_3 in 'organic'- and 'mineral'-rich layers.

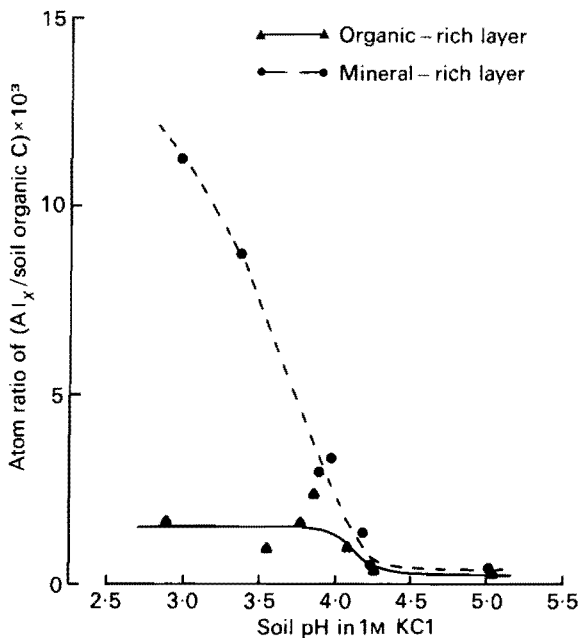


FIG. 3. The effect of soil pH on the atom ratio Al_x /soil organic C in 'organic'- and 'mineral'-rich layers.

chelating groups on organic matter surfaces. In general, Al_x can be displaced from mono-dentate complexes by solutions of NH_4^+ salts with strongly acidic anions, whereas non-exchangeable $Al_{n,x}$ in multi-dentate chelation can be displaced only by NH_4^+ salts with stronger chelating organic anions. Thus, Al_x determined in this way and displaced from mineral and organic surfaces by 1M NH_4NO_3 accounts for the Al_x of the soil.

From such results, it is not possible to derive separate values for surface densities of negative charge on the mineral and organic parts of the soil. One can only say that the much smaller Al_x values for the organic-rich layer denote that most of the Al dissolved by soil acidity is immobilised by increased multi-dentate links in the organic-rich layer and cannot be released by 1M NH_4NO_3 . Sivasubramaniam and Talibudeen (1972) showed earlier that 1M NH_4OAc released Al ions that could not be released by 1M NH_4Cl from soils containing similar amounts of organic carbon.

If exchangeable Al is related to total organic carbon, the atom ratio Al_x/C must reflect the Al-binding properties of the organic matter in the soil. Figure 3 shows that this ratio below pH 4.1 is approximately

constant ($1.53 \times 10^{-3} \pm 0.27 \times 10^{-3}$) for the organic-rich layer, but increases sharply with decreasing pH for the mineral-rich layer. The ratio corresponds to 650 C atoms per Al atom and, when compared with the 8 C atoms per Al atom for fulvic acid (Silva Rodriguez and Schaefer, 1971), suggests that only about one per cent of the carbon in these soils is similar in reactivity to fulvic acid. The organic-rich surface layer in these soils accumulates fresh plant residues each year but the mineral-rich layer only receives highly decomposed skeletal organic residues.

Non-exchangeable Al (Al_{n_x})

Non-exchangeable Al extracted in 48 h with 1M NH_4NO_3 , is the difference between the total Al extracted in 48 h and Al_x . It expresses the constant rate of extraction of Al_{n_x} and will be discussed later.

Exchangeable Na, K, Mg, and Ca

The sum of the basic cations extracted by 1M NH_4NO_3 from the soils increases with increasing pH, reflecting the decrease in Al_x . In all soils this sum is greater for the organic-rich than for the mineral-rich layer of the soil (Fig. 4), except for the pair of soils from Plot 15 in which this sum is the same and Al_x in the organic layer is more than predicted by the Al_x :pH relationship (Fig. 2). The sum of basic cations

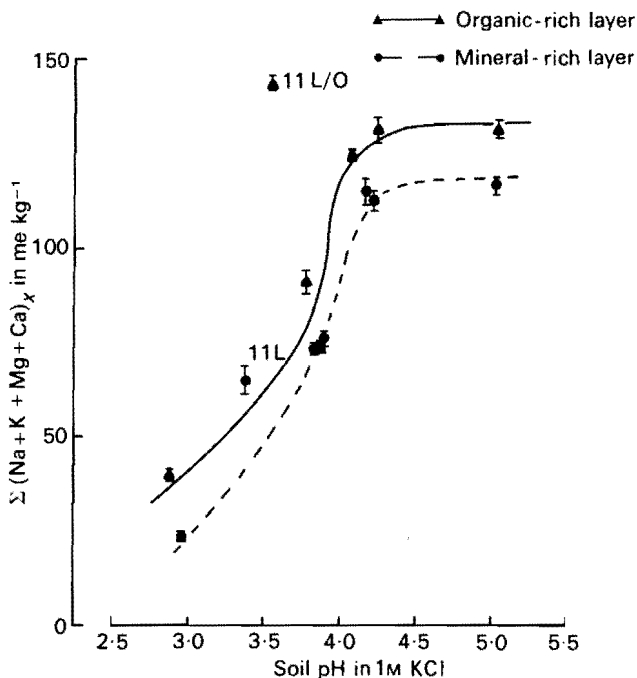


FIG. 4. The effect of soil pH on the sum of exchangeable Na, K, Mg, and Ca ($me\ kg^{-1}$) in 1M NH_4NO_3 for 'organic'- and 'mineral'-rich layers.

in both layers of the only limed acid soil (11L/O:pH 3.54 and 11L:pH 3.38) is much greater than predicted by the curve for the unlimed soils (Fig. 4) demonstrating the accumulation of exchangeable Ca residues even at such low pH values, and suggesting that the $\Sigma(\text{Na} + \text{K} + \text{Mg} + \text{Ca})$:pH relationship for limed acid soils would be different than for unlimed acid soils.

The number of Mg + Ca atoms released per atom of C is always less in the organic- than in the mineral-rich layer of the soils. This difference between the mineral and organic layers is defined here by

$$\Delta \left[\frac{\text{Mg}_x + \text{Ca}_x}{\text{C}} \right] = \left[\frac{\text{Mg}_x + \text{Ca}_x}{\text{C}} \right]_{\text{mineral}} - \left[\frac{\text{Mg}_x + \text{Ca}_x}{\text{C}} \right]_{\text{organic}}$$

where atom ratios are used throughout. The corresponding symbol for exchangeable Al is $\Delta(\text{Al}_x/\text{C})$. The value of $\Delta[(\text{Mg}_x + \text{Ca}_x)/\text{C}]$ is always positive, even at pH values as low as 2.9, suggesting that the upper organic-rich layer is less active in such linkages than the lower mineral-rich layer.

$\Delta[(\text{Mg}_x + \text{Ca}_x)/\text{C}]$ increases with soil pH (Fig. 5) indicating that the organic matter accumulating progressively in the lower layers is more active in this respect at higher pHs. Also $\Delta[(\text{Mg}_x + \text{Ca}_x)/\text{C}]$ is inversely related to $\Delta[\text{Al}_x/\text{C}]$ (Fig. 6), reflecting the changeover in the chelating

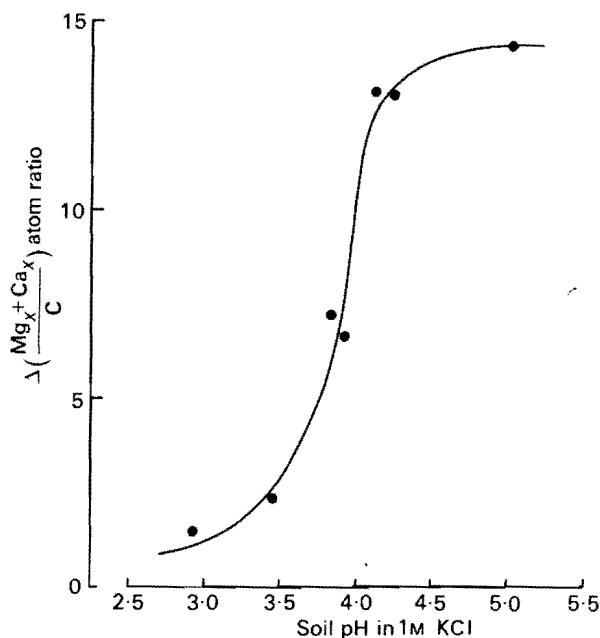


FIG. 5. The effect of soil pH on $\Delta[(\text{Mg}_x + \text{Ca}_x)/\text{C}]$.

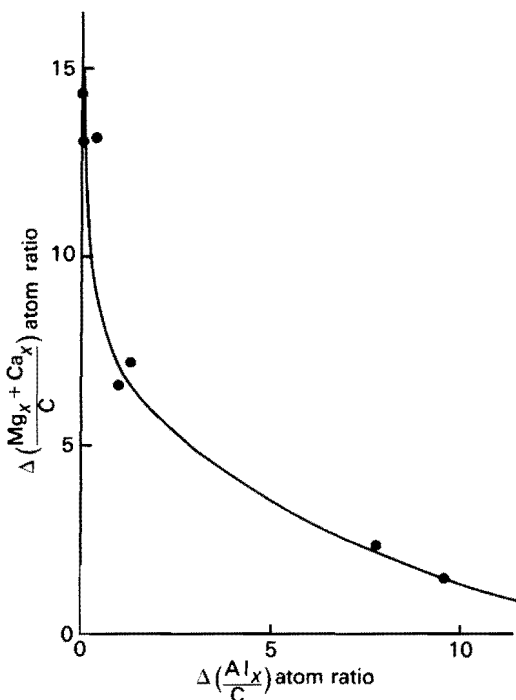


FIG. 6. Relationship between $\Delta[(Mg_x + Ca_x)/C]$ and $\Delta[Al_x/C]$ for some acid Park Grass soils.

activity of soil organic matter for Al to (Mg + Ca) as soil pH increases, the point of inflexion being at about 3.9.

Rate of extraction of exchangeable Al(Al_x)

The relationship between Al-extracted and time represents the sum of the processes of extraction of Al_{n_x} and Al_x . This curve becomes linear after 24 h and the slope of the linear part is the constant rate of Al_{n_x} extraction. Subtracting Al_{n_x} at each time from the total Al extracted gives the progressive rate of extraction of Al_x which slows to zero after 24 h (Sivasubramaniam and Talibudeen, 1972). The NH_4^+ concentration in the influent solution is in considerable excess, hence the rate at which Al_x is extracted can be considered proportional to the concentration of Al on exchange sites and be expressed by a first order kinetic equation:

$$\frac{d(Al_t/Al_0)}{dt} = -k_x Al_t \quad (1)$$

where Al_0 and Al_t are the amounts of Al on exchange sites at zero time and at time t of extraction respectively, and k_x is the absolute velocity

constant of the reaction. Integrating equation (1) with the boundary conditions,

$$t = 0 \frac{Al_t}{Al_0} = 1; \quad t = \infty \frac{Al_t}{Al_0} = 0, \quad \text{gives} \quad \ln \left(\frac{Al_t}{Al_0} \right) = -k_x t.$$

If the rate of release of Al_x follows this equation, the relationship between $\ln(Al_t/Al_0)$ and t should be linear, with the negative regression coefficient, k_x , as the rate constant. Values of k_x obtained in this way were very similar for all the soils. In four soils k_x values were identical for the organic- and mineral-layers. This indicates that Al_x in both organic- and mineral-layers is released from surfaces with similar properties for the adsorption of Al which are not affected by the nature of the adsorbed organic matter. Thus soil pH and organic matter did not affect the rate constant for the release of Al_x significantly, the mean value for the 14 soils being $36 \pm 7 \times 10^{-6} \text{ s}^{-1}$.

Rate of extraction of non-exchangeable Al (Al_{n_x})

Figure 7 shows that the relationship between the rate of Al_{n_x} extraction $d(Al_{n_x})/dt$ (Table 2), and soil pH for organic- and mineral-layers is identical, exhibiting a maximum at about pH 3.7. Such a maximum was also observed by Pionke and Corey (1967) for Al_{n_x} , calculated from the difference between Al extracted with 1M NH_4 OAc at pH 4.8 and with 1M KCl. They suggested that this maximum was caused by the tendency of Al_{n_x} to change to Al_x at low pHs and for both kinds of Al to change eventually into $Al(OH)_3$ at high pH values. The Al_{n_x} extracted using 1M NH_4 OAc is largely that complexed by soil organic matter (cf. Sivasubramian and Talibudeen, 1972). The maximum observed at pH 3.7 suggests that at lower pH values, the organic matter- Al_{n_x} complex becomes increasingly unstable.

However, most of the Al_{n_x} extracted with 1M NH_4 NO_3 dissolves from the edge faces (constituting <20 per cent of the total surface area) of micaceous and kaolinitic minerals, as well as from hydrous oxides of Al in acid soils and hydrolysed interlayers in soil micas. The positive charge on these surfaces increases with decreasing pH and probably holds anionic groups on soil organic matter by coulombic attraction causing its reactive fraction to cover these surfaces uniformly. Similarly, proton-accepting groups (e.g. amino- and amido- groups) participating in proton-bridging between such groups and the $(-Al \text{ } \overset{O}{\underset{O}{\parallel}} \text{ } OH)$ sites at these octahedral edge faces could contribute also to a protective film. These factors probably contribute to the observation that Al_{n_x} from clay minerals extracted by 1M NH_4 NO_3 decreases with decreasing pH. At pH >3.7, however, hydrated aluminium oxides ($Al_2O_3 \cdot nH_2O$) are precipitated increasingly, causing a maximum to be obtained at this pH.

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