

# SOIL ACIDITY AND ITS AGRONOMIC IMPLICATIONS\*

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## Introduction

Soil acidity has been studied by soil scientists for over 50 years, during which time explanations advanced to explain its observed patterns and behaviour have almost completed an entire cycle. This point is clearly made in an excellent review paper by Jenny (1961). It is apparent that the so-called exchangeable  $H_3O^+$  ion does not represent all the acidity in the soil. A considerable quantity of  $H_3O^+$  ions are produced as a result of hydrolysis and association of various groups in the soil. These  $H_3O^+$  ions are not normally present as such, but come into being in an attempt by the soil to resist changes in pH. Following a tendency in the literature it is proposed to distinguish between exchangeable  $H_3O^+$  ions and titrateable acidity, the latter being the  $H_3O^+$  ions produced by the buffer groups on titration with base or otherwise raising the pH of the soil.

Soil acidity can be described in terms of quantity and intensity parameters. The intensity parameter most often used is the pH of the soil which represents the concentration of  $H_3O^+$  ions in the soil solution, while the quantity parameter expresses the amount of exchangeable or titrateable acidity. In the discussion to follow both aspects will be given attention in an attempt to present as clear a picture of the nature of soil acidity as possible. In addition, both the quantity and intensity aspects of soil acidity will be discussed in relation to their agronomic implications.

## Soil pH and its agronomic significance

The measurement of pH in pure electrolyte solutions can be carried out with far greater precision than is true of soil solutions and suspensions. In the case of pure electrolyte solutions, the major factor precluding a more precise measurement is the uncertainty of liquid junction potentials across the salt bridge. However, in the measurement of pH in soil solutions and suspensions, there are many more factors which can have a profound effect on the value measured. Some of these will now be very briefly discussed in order to illustrate the limitations which would govern the interpretation of soil pH values.

## The suspension effect

The fact that the pH measured in soil water systems depends on the position of the KCl salt bridge is well known. In general if the KCl bridge is placed in the suspension the pH is lower than when the bridge is in the supernatant liquid. The magnitude of this difference can often be as great as two pH units, depending on the concentration of clay in suspension (Figure 1). The position of the glass electrode is immaterial since if the system is in equilibrium, it would be contrary to the second law of thermodynamics

to obtain work from it. The suspension effect would therefore render pH measurements in soils and clay suspensions meaningless if there were no ways of avoiding the problem. Measurement of pH with the KCl salt bridge in the supernatant liquid is an obvious way of avoiding the problem. But other ways have been suggested (Coleman, Williams, Nielson & Jenny, 1950).

## The salt effect

This is the result of an exchange of either hydroxyl or hydronium ions on the soil colloids by neutral salts. A salt such as KCl or  $CaCl_2$  will usually reduce the soil pH by displacing the  $H_3O^+$  and  $Al_3^+$  ions from the soil colloids into the solution, thus effectively increasing the  $H_3O^+$  ion concentration in the supernatant liquid. The  $Cl^-$  ion is usually very weakly adsorbed by soils and any anion exchange effect with  $OH^-$  ions is usually masked by the exchange of  $H_3O^+$  and  $Al_3^+$  by the cation. The effect of increasing  $CaCl_2$  concentration on the pH measured in the supernatant liquid of four acid Natal soils is illustrated in Table 1.

From this table it is clear that fairly small dressings of fertilizer can produce a significant effect on soil pH. For example a KCl dressing of 100 kg/ha could result in the concentration of the soil solution increasing by approximately 0,002 moles/litre in a loam to clay loam soil at field capacity. In soils having very dilute soil solutions, such relatively small fertilizer applications could result in a pH decrease of up to 0,5 pH units.

On the other hand, other salts whose anions are relatively strongly absorbed either electrostatically or by ligand exchange on to soil surfaces (e.g.  $SO_4^{2-}$ ,  $H_2PO_4^-$ ) can cause an increase in pH over that in water as the result of an excess exchange of  $OH^-$  ions over  $H_3O^+$  and  $Al_3^+$  ions. This type of reaction is likely to be limited to soils falling

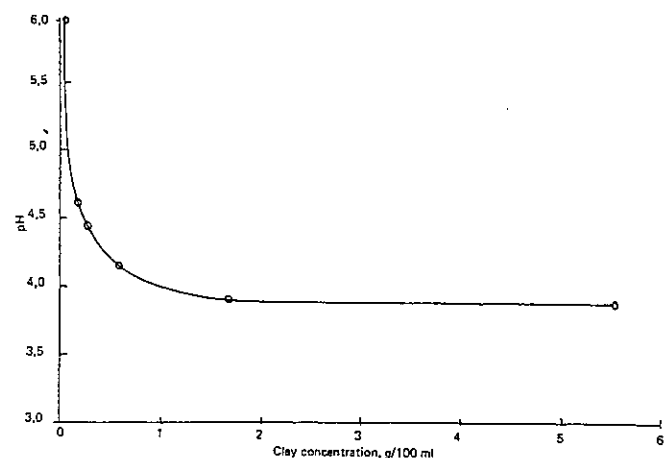


FIG 1 Effect of clay suspension concentration on pH (van Olphen, 1963)

\*Paper read at FSSA symposium on Lime in Agriculture, Pietermaritzburg, 13/3/75.

TABLE 1 pH values of four soils determined in CaCl<sub>2</sub> solutions of varying concentration at a soil: solution ratio of 1:5 (Reeve, 1968)

CaCl <sub>2</sub> conc M/l	pH			
	Farningham	Clovelly	Balmoral	Avalon
0,02	4,09	4,17	4,60	5,25
0,01	4,21	4,30	4,69	5,37
0,004	4,34	4,48	4,98	5,59
0,002	4,45	4,66	5,04	5,63
0,001	4,50	4,83	5,47	6,01
0,0002	5,02	5,26	5,61	6,03

into the highly weathered group containing large quantities of sesquioxenic material.

However, in general neutral salts tend to decrease the measured pH of most soils and therefore care should be taken to circumvent variation in pH values as a result of the salt effect. This is usually achieved by measuring the pH in a strong salt solution, which is of sufficient strength to eliminate any minor effects of salt originally present in the soil.

#### Soil-solution ratios

Ideally one would wish to measure soil pH at field capacity or at some other moisture tension that is closely related to field conditions. However, as contact between the glass electrode and the soil solution at these moisture tensions is often very poor, it is difficult to obtain a satisfactory measurement. One has therefore to add water or some other solution in order to obtain satisfactory contact.

If water is used for this purpose the soil solution is diluted bringing into play the salt effect which we have discussed above. In general, the addition of water to a soil prior to pH measurement has the effect of increasing the pH at

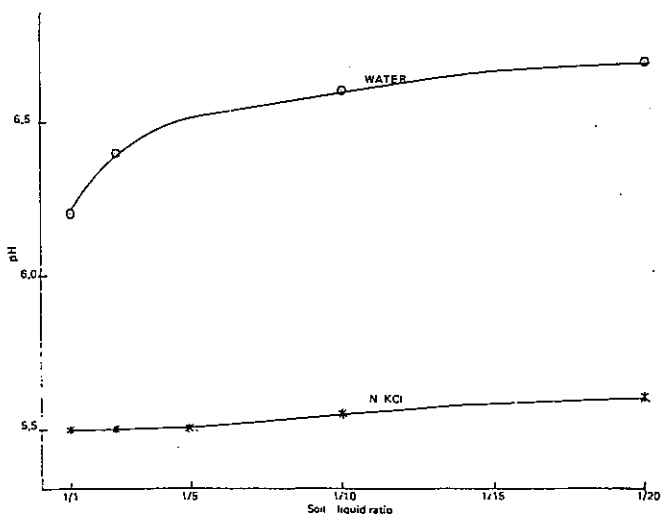


FIG 2 Effect of soil: liquid ratio on soil pH measured in water and N KCl

high over low dilutions. Thus, pH determined in water can be very sensitive to the soil-water ratio used as is illustrated in Figure 2.

However, when the pH is measured in a salt solution, one usually adds sufficient solution at a sufficiently high concentration in order to effectively mask any effect of the natural salt in the soil. Under these conditions the measurement of pH is very much less sensitive to soil solution ratios.

#### Practical implications of pH measurement

One should avoid, if it is at all possible, the measurement of pH in a soil suspension, because of the problems associated with the suspension effect. However, this effect can be reduced to a considerable extent by the use of strong salt solutions, but the use of these in turn does not always approximate well to field conditions. As a general rule, therefore, one should ensure that the calomel electrode is always situated in the supernatant liquid.

The most serious objection to measuring pH in soil-water mixtures is the large pH variation that is caused by the salt effect and by various dilution ratios. Natural salt differences occur between soil types, whilst fertilization practices vary on the same soil. It is impossible therefore to attribute any intrinsic value to pH measurements that have not in some way made allowance for the salt effect. In addition, widely differing salt concentrations present in soils may also lead to liquid junction potential problems. The measurement of pH in some standard salt solution would appear therefore to be the method most suited for use as a routine standard method.

There are two schools of thought on what type of salt should be used when measuring the pH in salt solutions. One group favours the use of N KCl, whereas the other favours the use of 0,01 M CaCl<sub>2</sub>. However, this problem will not be dealt with here, as the results obtained by the two methods are very closely correlated and the differences are of an academic nature.

#### Sources of soil acidity

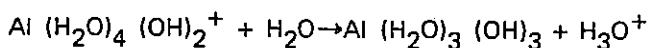
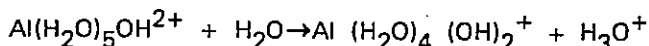
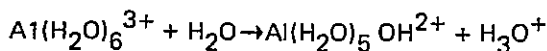
Various groups in the soil are considered responsible for the production of tritratable acidity and according to Jackson (1963) they are as follows:

- (i) strong acids, soil pH below 4,2:
  - (a) mineral colloidal electrolytes
  - (b) free H<sub>2</sub>SO<sub>4</sub> from FeS<sub>2</sub> or S
- (ii) weak acids, soil pH below 5,2:
  - (a) aluminohydronium ions
  - (b) possibly some humus carboxyl

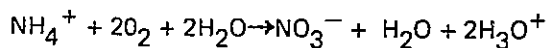
- (iii) very weak acids, soil pH 5,2 – 6 or 7:
  - (a) humus carboxyl
  - (b) polyaluminio edge  $\text{OH}_2^{0,5+}$
  - (c)  $\text{H}_2\text{CO}_3$ , basic aluminium sulphate
- (iv) very, very weak acids, soil pH 6,5 or 7 to 9,5:
  - (a) humus phenolic
  - (b) polyaluminumhydroonium edge pairs  $\text{OH}_2^{0,5+}$   
... $\text{OH}_2^{0,5-}$
  - (c)  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{NaHCO}_3$
- (v) extremely weak acids: soil pH > 9,5:
  - (a) humus alcoholic hydroxyl
  - (b) silicic acid  $-\text{OH}$
  - (c) gibbitic  $-\text{OH}$

Fundamentally all five acidity groups depend on proton association, but differ only in acid strength of the functional groups. Group (i) derives from the presence of exchangeable  $\text{H}_3\text{O}^+$  ions, while groups (ii) and (iii) are of most concern in practice as sources of acidity which have significance from the agronomic point of view. As aluminohydroonium ions are by far the most important contributors to these two categories, the ensuing discussion will be confined to aluminium as a source of acidity.

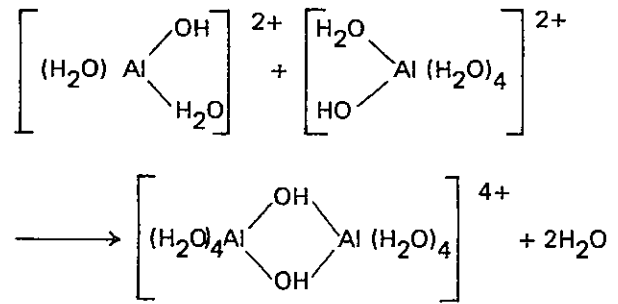
In solution aluminium ions are hydrated and readily lose protons forming hydroxo complexes in the following manner:



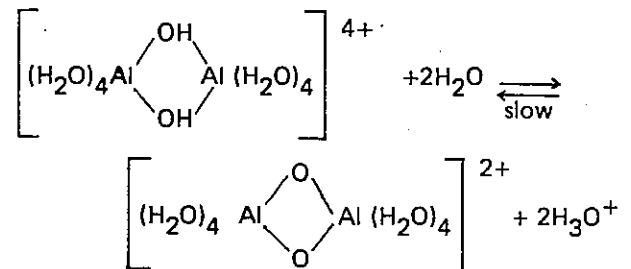
From these equations it can be seen that as hydroxo complexes are formed, hydronium ions are released, which contribute to acidity. On the other hand, if the soil is acidified by the application of nitrogenous fertilizers which give rise to acidity in accordance with the following equation:



then the hydronium ions produced in the oxidation of the ammonium forms of nitrogen will cause the above three reactions to be reversed, so that aluminium compounds will be dissolved giving rise to  $\text{Al}^{3+}$  in solution. The hydroxo groups have strong co-ordinating tendencies and act as bridging groups between two metallic cations; thus when two or more such hydroxo complexes polymerize the process is known as olation and the bridging OH groups are called OL groups, as indicated in the following equation:



Olation may be followed by oxolation whereby OH groups are converted to OXO groups by the loss of a proton. In pure aluminium solutions this can readily be effected by heating which causes the pH of the solution to become more acidic. On cooling this reaction is slowly reversible as indicated in the following equation:



These reactions show how aluminium hydrolysis can give rise to acidity. Similar reactions are believed to take place in the soil except that it appears that hydrolysis proceeds slightly further in the presence of soil or clay than in pure solution:

### Agronomic implications of soil acidity

#### Effect of pH on cation exchange capacity

In soils which have a high pH dependent cation exchange capacity (confined mainly to the ferrallitic soils) pH can have a profound effect on the value of the cation exchange capacity determined, as illustrated in Figure 3. This in turn

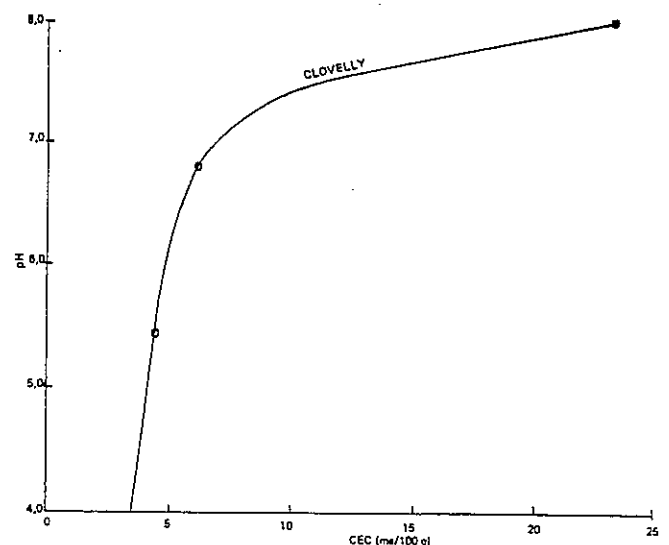


FIG 3 Effect of pH on cation exchange capacity of a Clovelly soil

affects the method by which lime requirement is determined. Most methods of lime requirement which have been developed in temperate latitudes involve a buffer technique and the lime requirement so determined is a function of the amount of base required to bring the soil to a near neutral pH value. When such buffer techniques are applied to highly leached soils in South Africa, one obtains lime requirements which are exceedingly high; consequently Reeve and Sumner (1970) developed a method based on exchangeable aluminium for determining the lime requirement which seemed to be more suited to these soils. An indication of the different amounts of lime required by these two types of method, together with estimates based on field response by plants are presented in Table 2.

### Physiological effects of soil acidity

Many crops grow successfully in nutrient solutions with pH values of 4 to 8 when precautions are taken to eliminate harmful side effects. Roots are injured when the pH lies below 3 and at pH values above 9 they are unable to adsorb phosphates. In the pH range 4 to 8, which embraces most agricultural soils, the concentration of hydronium ions as such is therefore not important; rather the conditions associated with low pH are far more important. The major side effect of soil acidity is the presence of labile aluminium in soils in ionic form which can readily be taken up by many plants. Aluminium is toxic to most plants which differ widely in their tolerance and ability to take it up. In general the tolerance of plant species to acid soils corresponds well with their tolerance to aluminium in nutrient solution. The nature of this differential aluminium tolerance has not been clarified, very likely because the mechanism of aluminium toxicity is still under question. However, aluminium injury has

TABLE 2 Lime requirements of eight Natal Oxisols according to different criteria (metric ton  $\text{CaCO}_3$  /ha) (Reeve and Sumner, 1970)

Soil	Criterion			
	Max yield of trudan	Exch Al 0,2 meq/100g	pH 6,0* SMP	pH 6,5* SMP
Griffin	4,0	4,0	13,0	19,5
Clovelly	3,0	2,8	10,0	15,0
Lidgetton	3,0	3,0	10,0	15,0
Farmhill	1,0	0,8	9,0	13,5
Hutton	4,0	4,6	10,0	15,0
Farningham A	3,0	2,8	8,0	12,0
Farningham B	0,0	0,0	9,0	13,5
Balmoral	1,0	1,0	6,0	9,0
Means	2,4	2,4	9,4	14,1

\*SMP = Shoemaker, McLean & Pratt (1961)

TABLE 3 Differential tolerance of various species to Al in solution

Plant	Al added	
	ppm	%
Maize	0,0	100
	1,5	87
	6,0	45
Barley	0,0	100
	1,5	41
	6,0	22
Oats	0,0	100
	1,5	75
	6,0	75

been associated with a decrease in the uptake of phosphate and calcium as well as with decrease in overall permeability of plant roots. In most crop plants aluminium usually accumulates in the roots with relatively little transport to the tops. Certain species have a tendency to accumulate large quantities of aluminium in their above ground parts and this seems to be associated with the rather acid cell saps. There is also some evidence to show that some roots have the capacity to mobilise relatively insoluble aluminium in surrounding soil. The differential tolerance of various plant species to aluminium in nutrient solution is shown in Table 3.

### Effect of soil acidity on the availability of nutrients

In acid soils the development of the roots of various crops is often rather restricted, which can lead to a plant not being able to obtain sufficient mineral elements. In most cases the acidity *per se* has relatively little effect on the availability of many of the nutrient elements. However, there is a tendency for P availability to be depressed under conditions of high acidity as a result of precipitation of  $\text{H}_2\text{PO}_4^-$  ions by Al and Fe compounds. Furthermore, there is evidence to show that under such conditions P may also become immobilised within the root or conducting tissue of the plant. In the case of molybdenum, deficiency often results under acid conditions as a result of the immobilisation of  $\text{MoO}_4$  anions on sesquioxides material. Under acid conditions trace elements such as Fe, Mn, Cu and Zn are more soluble and therefore more easily available to the plant.

Symbiotic nitrogen fixation is often drastically reduced under acid conditions. In the case of a large number of Rhizobia strains the direct effect of hydronium ion concentration appears to be more crucial than it is for higher plants. It is not clear whether poor nodulation in acid soils is due to a direct effect of acidity on the infection of the host and the subsequent nodulation process, or whether it results from the lack of viable organisms in the soil. The evidence suggests that calcium is specifically

required either for inoculation or for nodule development. Once root nodules are formed, their nitrogen fixing function is especially sensitive to acidity and to deficiencies of calcium and molybdenum.

As soil becomes progressively more acid, the dominant microbial population shifts from bacteria to the actinomycetes and fungi, although individual species of each may vary widely in acid tolerance. Mineralisation of N, P and S from organic matter, immobilisation and transformations of these nutrients, etc are affected by soil acidity. In general the rates of mineralisation increase with increasing pH, but the reactions are possible under acid conditions. Nitrification is very sensitive to pH and all but ceases under acid conditions.

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