ETESP

Earthquake & Tsunami Emergency Support Project

Soil Acidity and Aluminium

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1. INTRODUCTION

Simple acidification of the soil occurs as a result of rainfall. The basic principle is that rain is acid due to the presence of dissolved carbon dioxide. This, plus water, gives carbonic acid (H_2CO_3) :

 $H_2O + CO_2 = H_2CO_3$

The carbonic acid reacts with / dissolves metals found within the soil along the lines of:

 $M^+ + H_2CO_3 = MHCO_3 + H_2O$ - where M^+ is a Monovalent metal (cation) such as sodium (Na⁺) or potassium (K⁺) - and in an acid system this undergoes further transformation or hydrolysis:

 $2MHCO_3 + H_2O + CO_2 = M_2CO_3 + H_2CO_3 + 2H^+$

Of course one can have divalent and trivalent metals such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminium (Al^{3+}). The reaction would be, in the case of a divalent cation;

 $M^{++} + H_2CO_3 = MCO_3 + 2H^+$

Note that in both cases you have a surplus of hydrogen ions (H⁺).

Soil pH expresses the effective concentration of H^+ (Hydrogen) ions in the soil solution. Soil reaction or acidity level, measured by pH, is of considerable importance in all soils, and is one of the routine laboratory determinations done during a soil survey.

2. SOURCES OF METAL CATIONS

The source of the metal cations is either the existing exchange complex and / or the weathering of soil minerals. As leaching with 'acid' rainfall continues the exchange complex will release metal cations to buffer the hydrogen ions produced during the reactions above. That gives you an increasingly acid exchange complex and as the basic cations (Ca, Mg and K) become used up you get a hydrogen (H^+) enriched soil and pH falls

In the soil, the various anions and cations are held on the exchange complex, charged sites within the mineral fraction of the soil. The various anions and cations then pass to and fro between the exchange complex and the soil solution – water being the solvent for the soil solution.

The concentration of the soil solution is a function of the kinds and proportions of the exchangeable ions in the soil. The exchangeable ions found in the soil solution, where water is the solvent and the cations and anions the solute, normally comprise:

Cations (Positively charged)	Calcium Ca ²	Magnesium Mg ²⁺	Potassium K ⁺	Sodium Na ⁺	Hydrogen H ⁺	Ammonium NH₄ ⁺	Aluminium Al3 ⁺
Anions (Negatively charged)	Carbonate CO3 ²⁻	Oxygen O ²⁻	Bicarbonate HCO3 ⁻	Sulphate SO4 ²⁻	Chloride Cl ⁻	Hydroxyl OH ⁻	

Table 2.1 Cations and Anions found in soil

The various cations and anions are normally combined to form such compounds as:

Water	Calcium Carbonate	Sodium Chloride	Magnesium Chloride	Calcium Oxide
H2O	CaCO3	NaCl	MgCl ₂	CaO

3. SOIL ACIDITY and ALUMINIUM

Through natural selective uptake by plants, and solution and removal by the leaching action of rainfall, the more important, and more soluble and basic, cations are gradually removed from the exchange complex of the soil – notably the removal of calcium.

Aluminium is a component of many rocks and hence occurs naturally in most soils. Aluminium comes into the picture through mineral weathering and attack of the mineral surfaces of the alumino-silicates. Alumino-silicates cover clay minerals, feldspars, ferromagnesian minerals and, in particular, the micas. Hydrolysis of the mineral surface goes through several stages:

The mineral surface act as an alkali against acid and gives rise to species such as: [Al(H₂O)₃(OH)₂]

Increased leaching gives further hydrolysis, and the aluminium species behave as anions (negatively charged), and you get this: $[Al(H_2O)_2OH_3]^-$

This continues through a sequence of ionic forms of Al as the pH gradually decreases as explained above in Section 1. Finally you get things like: $Al(H2O)_n^{y+}$, where *n* can be 6 and *y* can be 3.

Note that these ions are positively charged because the pH is now acid.

These complex Al ions can form part of the exchange complex so you can have an acid, Al soil, and some of the Al will remain in solution, which is why you get toxicity to plants. The precise pH at which these changes occur depends a bit on the system, but some release of Al begins at around pH5.5, is quite noticeable around pH5, and becomes a distinct problem from about pH4.5 downwards.

However, these reactions do not normally occur unless the soil is already acidic with a pH of 5.5 or less. The natural acidification through rainfall, removal of calcium and its replacement by hydrogen in the exchange complex can reduce pH values to this level of 5.5.

4. Soil Acidity Classes and Relationships with Aluminium

Table 4.1 Soil Acidity / Reaction Classes

Acidity / Reaction pH (water)	>7.6	7.5 - 6.6	6.5 – 5.6	5.5 – 4.6	< 4.5
Soil Reaction Class	alkaline	neutral	slightly acid	very acid	extremely acid

A recent literature search indicates that in upland or dryland soils in the Aceh provinces there is a soil acidity problem and aluminium is involved. Further, experience in other areas have shown that the aluminium saturation percent (ASP = Exchangeable aluminium/ Cation Exchange capacity x 100) increases quite dramatically once soil pH reaches a level of 6.0 and less – and in future all samples with pH (water) of 6.0 or less should have exchangeable aluminium measured. This is to ensure that, if there are erroneous pH values being quoted by the laboratory, soils that might be more acid than it appears are checked for aluminium.

This increase in ASP with falling pH is illustrated for topsoil data in Figure 1 below and for subsoil data in Figure 2. Note that there are relatively few data included in these figures but the pattern is extremely clear and that these data are NOT from Aceh but elsewhere but are used for illustrative purposes.





Figure 4.2 Aluminium Saturation Percent Against pH Water for Subsoils



The standard amelioration procedure required for acidic soils is the application of liming material. Liming material is basically any soluble or partially soluble form of calcium and includes such materials as ground limestone, slaked lime, burned lime etc.

5. LIMING of ACIDIC SOILS for DRYLAND CULTIVATION

5.1. Generalised Calculation

The following liming rates are suggested from interpretation of data suggested by Hausenbuiller (1978). These suggested rates would, however, require testing via field trials and soil sampling.

			Tons / Ha	
Climatic Region	Particle Size Class	pH 3.5 to 4.5	pH 4.5 to 5.5	pH 5.5 to 6.5
Warm temperate to tropical	L – sandy	0.7	0.7	0.9
	M – coarse-loamy	0.9	1.1	1.5
	Mz and Hz	1.5	1.9	2.5
	H – fine-loamy	2.1	2.8	3.5
	V - clayey	2.5	3.1	4.0

Table 5.1 Lime Requirement Based on Texture

Note: The above code letters, L, M, Mz, etc are standard USDA PSC codes.

The liming material used in the Hausenbuiller publication was limestone but studies in Sudan (LIMING OF QOZ SOILS Land Use Planning Note AAH/1/88, WSDC, 1988) suggested that the form of liming material is not that important. In the Sudanese trials limestone, burnt lime and slaked lime were all used with measures of success. [Note AAH/a/88 can be studied at WWW.geocities.com/austin-supermi/].

5.2 Lime Requirement Calculated from Laboratory Data

Formulae do exist for calculating the lime requirement of acidic soils, and some of these do make use of known aluminium saturation percentage (ASP) figures. However, in some cases blanket usage of such calculated liming rates have led to over liming and a cautious approach to liming is required.

The formula of Cochrane et al (1980) is based on known exchangeable cations in the soil in question and is presented below.

Table 5.2 Formula for Lime Requirement Based on ASP

Lime Requirement		
Tonnes / Hectare CaCO ₃ equivalent	=	1.8 X {AI – RAS X (AI + Ca + Mg) / 100}

Where:

RAS	Required Aluminium Percentage (ASP)	Refer to crop tolerances to ASP
ASP	Aluminium Saturation Percentage	Exchangeable AI / Cation Exchange Capacity X 100
AI	Exchangeable AI as me / 100g	From laboratory data
Ca	Exchangeable Ca as me / 100g	From laboratory data
Mg	Exchangeable Mg as me / 100g	From laboratory data

A worked example of the above formula is given below.

Table 5.3 Data for Lime Requirement Calculation

Site	Depth	PH Water	Ca	Mg	AI	CEC	ASP
PH076	0 – 10cm	5.0	4.40	0.60	3.80	9.60	40

Aim: To reduce the ASP from 40% to 20%, a level which would be tolerated by field beans or soybean.

A worked example of using the formula in Table 5.2 is given below.

As with the rates suggested in the "Generalised Calculation" presented previously the amounts of liming material are quite considerable at something over 3 tonnes per hectare. The advantage of the Cochrane formula is that it is based on known data, but field trials would have to be conducted to verify the effectiveness of such an application of liming material.

Table 5.4 Worked Example of Lime Requirement Based on ASP

Lime Requirement Tonnes / Hectare CaCO ₃ equivalent	=	1.8 X {3.80 - 20(3.80 + 4.40 + 0.60) / 100}
	=	1.8 X {3.80 - 1.76}
	=	1.8 X 2.04
	=	3.67 tonnes / ha

6. ALTERNATIVE AMELIORATION

On a practical side, the scattered distribution of farms and the cost plus difficulty of transport to anywhere more than 0.5km from a roadside means that it is totally impracticable to recommend lime applications running into tonnes / hectare.

The standard procedure of application of farmyard manure (FYM) may already be helping ameliorate the aluminium problem. Organic matter does have the ability to form complexes with aluminium and basically take it out of play in the soil. Application of large amounts of FYM have recently been shown to significantly effect the properties of soils used for strawberry cultivation - by increasing the electrical conductivity of the soil and altering nutrient balances. Hence, there is every possibility that significant applications of FYM could have a desired (ameliorative) effect on acidic arable soils in that it might:

Increase the basic nutrients – NPK; Improve soil structure, and Form complexes with aluminium and help reduce possible aluminium toxicity and acidity.

Some studies investigating the interactions between pH, aluminium and organic matter could well be beneficial to arable agriculture in Aceh.

7. ALUMINIUM TOLERANCES

There is not a great deal of data published on the tolerance of various crops to aluminium. The following are what data have been located:

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Table 7.1 Aluminium Tolerances

Source	Publication	ASP Range %	Tolerant Crops (Suitable Varieties)
Sanchez P.A. 1976	Properties and Management of Soils in the Tropics, Wiley and Sons	10 - 20 20 - 40 40 - 60 60 - 80	Alfalfa, Sorghum Soybean, field beans Maize, cowpea Upland rice, pigeon pea, coffee, mango, cashew, citrus, pineapple
Source	Publication	Exch-Al	Statement

Source	Publication	Exch-Al Me / 100g	Statement
FAO, 1979	Soils Bulletin No 42, FAO, Rome	>2.00	If all other factors are favourable for plant growth then this level of Al in the exchange complex considered toxic for plant growth.

8. WETLAND SOILS

When acidic soils are flooded or puddled, such as for wetland rice cultivation, the pH will rise, in time, to near neutral – around 6.5. The reactions are very complicated but, in general, there are reactions in flooded soils which consume protons (hydrogen ions - H^+) and so the pH rises.

The most common chemical reaction is reduction and the most normally quoted reaction is the one involving the reduction of ferric iron to ferrous forms:

 $Fe(OH)_3 + H^+ = Fe(OH)_2 + H_2 O$

Hence, in this case, some of the hydrogen ions, or protons, H+ are used up and the soil pH rises. In addition, with increasing hydrolysis the aluminium hydroxy compounds formed are not exchangeable and hence the aluminium falls out of play as far as acidity is concerned

However, as soon as wetland soils start to dry out, such as when left un-irrigated for fallow, they rapidly re-acidify. Sulphur is also very involved in the acidification process of wetland soils when they dry out but, to date, the presence of sulphurous compounds in soils in Aceh is known and this could be an additional problem that may need to be addressed.

The pH of sawah top-soils can be influenced by the quality of the irrigation water applied. Most data seen on water quality suggest that there is unlikely to be a problem from this source in Aceh.

9. CONCLUSIONS and RECOMMENDATIONS

- There is a soil acidity problem in parts of Aceh and this is associated with exchangeable aluminium.
- Some soils may be acidifying further due to the addition of sulphur compounds deposited by the tsunami.
- Before any new developments or expansion of existing dryland agriculture is implemented there should be a rapid assessment of the acidity of the soils to be used.
- During all future surveys and soil sampling exercises careful attention will be paid to soil acidity and possible aluminium effects.
- Field trials to test any calculated liming rates must be designed and installed in susceptible areas to establish accurate rates of liming.
- Field trials should be established to investigate the links and relationships between soil pH, aluminium and organic matter (FYM).
- Tolerances of local crop varieties to aluminium should be established.

ABBREVIATIONS and GLOSSARY

(Simple metric units and chemical element symbols not included)

AmOAc asl ASP AvP, AP AWC / AWHC	Ammonium acetate (extractant for exchangeable cations and for measuring CEC) Above sea level Aluminium Saturation Percentage Available Phosphate Available water capacity (amount of water held in soil at suctions low enough for root uptake, = MC% FC – MC% WP)
BS%	Base saturation percentage
C ca CEC CL cm	Clay (finest mineral particles in soils, < 2um in diameter, important store for some nutrients and water, make soils sticky & heavy to work) Approximately Cation exchange capacity Clay loam Centimetre
EBS% EC ECEC ET Evapotranspiration Exch Extr	Effective base saturation (= TEB/ECEC) Electrical conductivity Effective cation exchange capacity (=TEB + Extr Al + Extr H) Evapotranspiration Sum of evaporation from soil and other surfaces, and transpiration from leaves Exchangeable (for cations) Extractable (for soil nutrients)
FAO FC FeMn Freely drained FYM	Food & Agriculture Organisation, Framework for Land Evaluation Field capacity (MC% at suction of 0.1 atmospheres) Ferri-managaniferous, dark red - reddish brown - black stains and soft concretions with high contents of ferric iron and manganese in horizons with seasonally impeded drainage Soils in which most large pores drain their water soon after rain or irrigation at all times of the year. Identified by moist or dry feel, and warm brown, reddish or yellowish colours and absence or grey, rust or orange mottles Farmyard manure
GIS GPS	Geographical information system Global positioning system
ha HCl Horizon	Hectare Hydrochloric acid Soil layer
ID Imperfectly drained In situ	Imperfectly drained (soil) Soils in which most large pores drain their water soon after rain or irrigation for much of the year, but remain filled for long spells in summer Identified by moist or wet feel, and grey or brown colours and many grey, rust or orange mottles. In original position or place (Latin)
L	Loam (Mixed soil with substantial quantities of all three particle size classes, i.e. clay, silt
LS	and sand) Land Suitability
MD / MWD Munsell	Moderately well drained (soil) System of standard soil colour notation, operated by matching soil against standard charts. Colour described by 'hue' (Spectral composition, red, yellow, blue, green); 'value' (dilution with white), & 'chroma' (darkness)
NA ND	Not applicable / Not applied No data / Not Determined

NS	Not sampled (in soil profile descriptions)
OC	Organic carbon
OM	Organic matter
Р	Phosphate
PD	Poorly drained (soil)
PM	(Soil) Parent Material
Pptn	Precipitation, rainfall
pH	Measure of acidity - alkalinity
Si	Silt (intermediate sized mineral particles in soils, 2 - 50 um in diameter, important store for plant available water, make soils slippery & vulnerable to surface erosion and capping, aka Z, Zi)
SMR	Soil Moisture Regime, defined in Soil Taxonomy
SMU	Soil mapping unit
ST	Soil Taxonomy (USDA system of soil classification)
STR	Soil temperature regime, defined in Soil Taxonomy
Surface wash	Movement of individual surface soil particles by running surface water.
SWXD / SXD	Somewhat excessively well drained (soil)
Tr	Trace
TEB	Total exchangeable bases (= exchangeable $Ca + Mg + Na + K$)
Tot-N	Total nitrogen
USDA	United States Department of Agriculture
VPD	Very poorly drained (soil)
WD	Well drained (soil)
WT	Water table
XD / XWD	Excessively well drained (soil)
Z, Zi	Silt (intermediate sized mineral particles in soils, 2 - 50 um in diameter, important store for plant available water, make soils feel slippery & vulnerable to surface erosion and capping, aka Si)