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## **EFFECT OF GROUNDWATER TABLE ON THE FORMATION OF ACID SULPHATE SOILS**

by

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### **ABSTRACT**

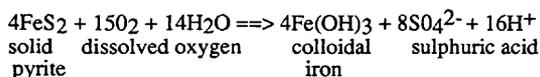
Acid sulphate soils are formed when pyrite within a soil layer is oxidised, generating sulphuric acid. The oxidation of pyrite often results in yellow mottles of jarosite. The pH levels in greatly affected areas are often less than 4.0, and the associated environmental impacts include fish kills, retarded growth of crops and changes in water chemistry. Certain regions of acid sulphate soils along the South Coast of NSW are of much concern, because of limited land available for food production and cash crops. This study quantifies the effect of changes of the groundwater table on the acidity of the coastal flood plain in Berry, located on the Illawarra coastline, New South Wales. Based on several boreholes and drain sites, the existence of jarosite was verified, characterising the study area as a potential acid-sulphate soil region. The field investigation of the study area included the monitoring of groundwater and drain water quality, including the pH and aluminium levels. The study shows convincingly that the increase in groundwater level is effective in preventing adverse pH and aluminium levels.

### **INTRODUCTION**

Acid sulphate soils develop where the production of acid from the oxidation of pyrite exceeds the neutralising capacity of the parent material, and often, the pH levels drop below four (Naylor, 1993). In coastal regions, acid sulphate soils are mainly encountered where tidal estuaries debouch into low-lying or backswamp areas. The consequences of acidsulphate soils and acidic drain waters have adverse environmental effects on vegetation and aquatic life in terms of fish kills, reduced crop harvest and changes in water chemistry. In particular, coastal plains of some countries including Australia, Thailand, Indonesia, Malaysia, New Zealand and Netherlands have been affected. The geological stratigraphy in most coastal flood plains of New South Wales comprises a thin to moderately thick layer of alluvium overlying relatively thick estuarine and lagoonal sediments deposited since the

Pleistocene era. In the Southern Illawarra Coast, the occurrence of pedogenesis has been a predominant function of the oxidation products of pyritic estuarine substrata, seasonal groundwater fluctuations, and the properties and thickness of the alluvium veneer (Willett & Walker, 1982).

Chapman (1994) determined the groundwater pH to be as low as 3.1 on low lying farming land in Berry. Significant sulphidic contents (% by weight of FeS<sub>2</sub>) have been measured in soil samples recovered from the Berry-Nowra region, and in certain sites, the pyrite contents exceed 1.5-2.0%. The production of acid from pyrite is only possible once these sulphidic materials are exposed to oxygen in the atmosphere. In the Berry flood plains, the installation of deep trenches and drains for agricultural purposes has caused significant lowering of the water table, thereby exposing the pyrites to react with atmospheric oxygen. The subsequent oxidation reaction is given by the following equations where the concentration of H<sup>+</sup> ions represents the measured pH levels.



During this oxidation phase, the complex by-product jarosite, KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH), is also formed as yellow mottles in the soil. Very low lying deposits containing pyrite usually remain in a waterlogged environment or swamps. They can be considered as potential acid sulphate soils (Fig.1a) because they have no adverse effects on the environment, until such time they are sufficiently drained for possible oxidation (Fig. 1b). Subsequent heavy rainfall may flood the low lying land areas, bringing significant levels of Al and Fe ions to the surface (Fig. 1c).

### IDENTIFICATION OF ACID SULPHATE SOILS

While there is no conventional test to determine the presence of acid sulphate soils (ASS), there are a number of indicators which may be used to identify both acid sulphate and potential acid sulphate soils. The three common ways in which acid sulphate soils are identified include site inspection, subsurface inspection and using groundwater quality as an indicator. In the Berry area, the following indicators confirm the existence of ASS: (a) low pH levels and iron-stained drainwater, (b) acidic soils with increasing acidity towards the drains (pH<5), where the lowering of the phreatic surface is a maximum and (c) the existence of clear iron stains on drain surfaces. A subsurface inspection often facilitates the identification of jarosite, a visual indicator of potential acid sulphate soils. Samples augured in such sites usually expose these yellow mottles of jarosite within the soil profile.

White and Melville (1993), Naylor (1993) and Mulvey (1993) recommend the chemical analysis of groundwater to determine the concentrations of soluble chloride [Cl<sup>-</sup>] and soluble sulphate [SO<sub>4</sub><sup>2-</sup>]. The chloride to sulphate ratio (Cl:SO<sub>4</sub>) gives an initial indication of sulphidic material present. For example, seawater with an average Cl:SO<sub>4</sub> of 7.2, for [SO<sub>4</sub>] = 2,700 mg/l and [Cl<sup>-</sup>] = 19,400 mg/l, provides a reference for the evaluation of sulphidic material in a soil. A soluble chloride:sulphate ratio of less than four and approaching two is a strong indication of other sources of sulphate, a major part of which possibly originating from pyrite oxidation (Mulvey, 1993). Naylor (1993) describes the general morphology of potential acid sulphate soils as waterlogged, grey to dark greenish grey in colour and having the consistency of a soft clay. This description is quite applicable to the Berry region under investigation, where silty clay samples are generally mid to dark greenish grey. A field test for the evaluation of potential acid sulphate soils was proposed by Dent (1986) which involves adding hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to the soil. After the reaction is complete the soil pH is

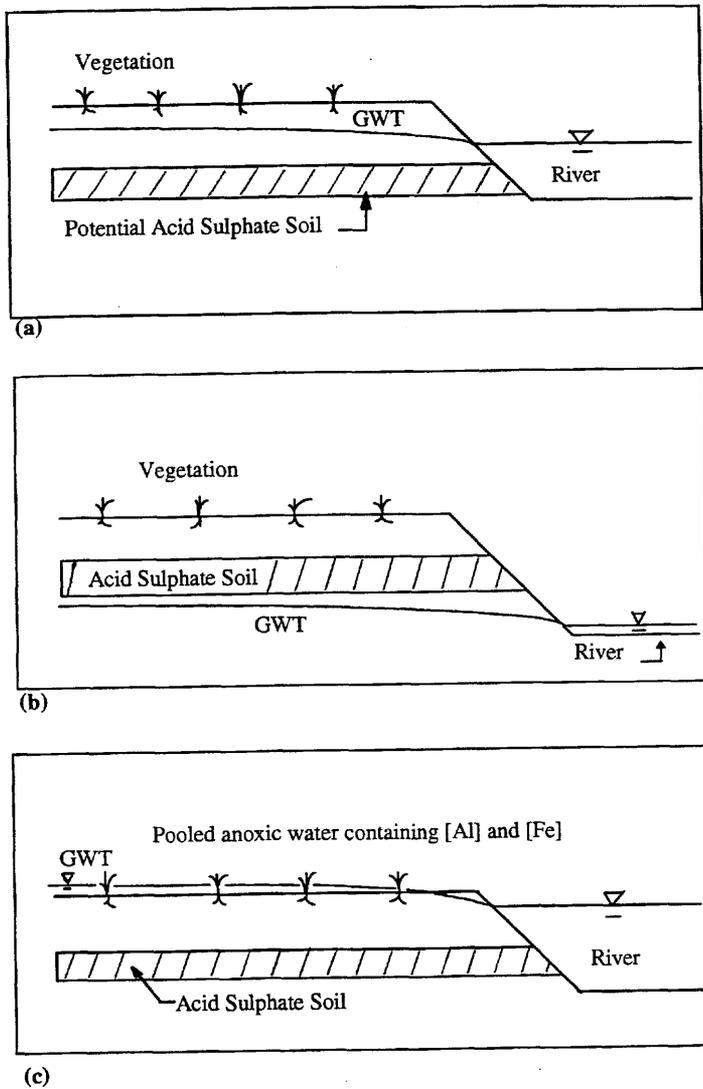


Figure 1. (a) Potential acidic sulphate soil; (b) formation of acidic sulphate soil and leaching of acid into waterways; (c) acid and dissolved metals are discharged to waterways following rain.

recorded and if it is less than 2.5, the soil is deemed to be pyritic and will oxidise once exposed to oxygen.

**Environmental and agronomic impacts**

The environmental and agronomic impacts of acid sulphate soils include those on human life, plants and animals. The effect of acid sulphate soils on plant life is documented through various literature devoted to optimum growth conditions for plants. High acidity (low pH) will impair plant root development and affect nutrient and water uptake, resulting in withering and dying of mainly young plants. High aluminium and iron have direct and indirect adverse effects on plant life. Moreover, the adverse structural effects of sulphate attack on concrete foundations and the corrosion of metal pipes are of concern. For instance, significant fish and crustacea kills along a 23 km stretch of river due to acid drainage (Green, 1993) have been reported. Aluminium and iron which are mobilised (released) from soil at pH values less than 5 present another threat. A phenomenon known as *epizootic ulcerative syndrome (EUS)* or 'red spot disease' is a direct result of aluminium and iron depositing on the gills of fish (Dent, 1986).

**FIELD INVESTIGATION**

***Presence of Acid Sulphate Soils in the Berry Test Site***

As there is no standard geological method of quantifying the existence of acid sulphate soil deposits, the presence of jarosite within the soil profile and the chloride:sulphate ratio were used as indicators to establish the acid sulphate soil location in the field.

**Table 1: Presence and depth of jarosite in study area**

Borehole #	Presence of Jarosite	Depth of Jarosite (mm)	Comments
1	yes	1000-1800	traces only
2	yes	1000-1800	jarosite on root paths
3	yes	1200-1700	a few prominent mottles
4	yes	1200-1600	more than borehole #3
5	yes	-	-
6	yes	1000-1600	many jarosite mottles
7	yes	1000-1700	some mottles (as in #4)
8	yes	1200-2000	less than borehole #7

Table 1 summarizes on the basis of core recovery from eight boreholes, showing the depth of jarosite below the ground surface. The locations of the boreholes are shown in Figure 2. Samples were augured and examined to detect yellow straw-like mottles of jarosite which are clearly visible if present in significant quantities. The chloride-sulphate ratio of the soil was also determined on a weekly basis for the observation wells 1, 2 and 5, and for the drain sites 1, 2 and 3 (Figure 2). The average ratios for the monitoring period from July to October 1994 are given in Table 2. The low Cl:SO<sub>4</sub> ratios (except observation well #5) together with the borehole information given in Table 1 verify without doubt that the study area in Berry is an acidsulphate zone.

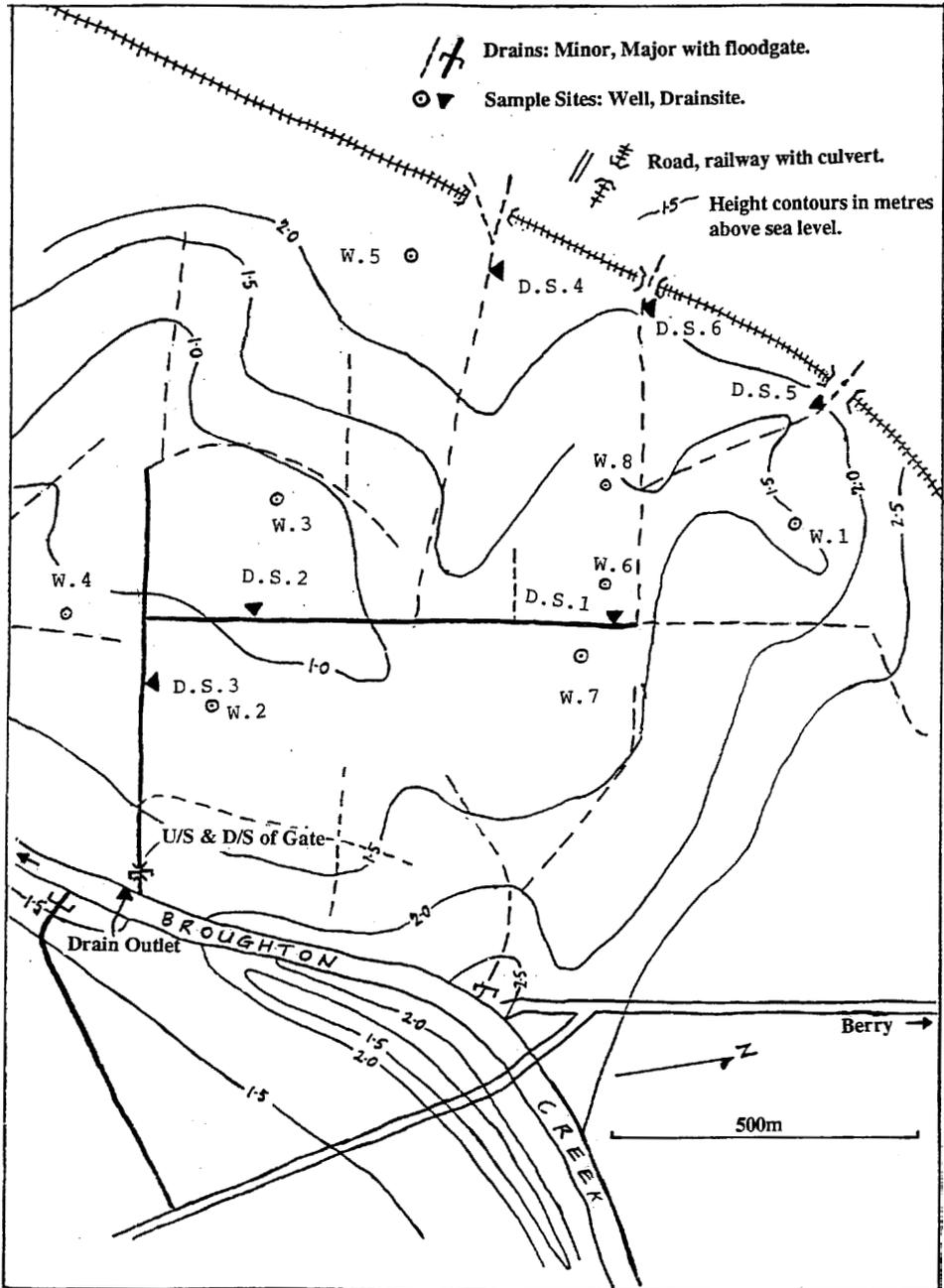


Figure 2 Site map showing topography with observation wells and drain sites  
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Table 2: Average chloride:sulphate ratios within the study area

Observation Point	Average Cl:SO <sub>4</sub> ratio
Well # 1	3.37
Well # 2	0.05
Well # 5	3.16
Drain Site # 1	0.79
Drain Site # 2	0.27
Drain Site # 3	0.20
Broughton Creek	6.37

Table 3: Average pH values for all sampling points

Observation Points	Mean pH	Drainage Sites	Mean pH
Well # 1	4.44	Drain # 1	4.18
Well # 2	3.78	Drain # 2	4.01
Well # 3	3.47	Drain # 3	3.42
Well # 4	3.48	Drain # 4	6.98
Well # 5	6.61	Drain # 5	7.19
Well # 6	3.45	Drain # 6	6.59
Well # 7	3.45	Floodgate (upstream)	3.39
Well # 8	3.55	Broughton Creek	6.76

Table 4: Variation of soil pH values with depth at observation wells

Sampling Point	Sub-surface Soil pH (depth = 200mm)	Sub-surface Soil pH (depth = 1000mm)
Well # 1	4.6	4.0
Well # 2	4.1	3.2
Well # 3	4.1	3.1
Well # 4	4.0	3.1
Well # 5	4.6	4.5
Well # 6	4.1	3.2
Well # 7	3.9	3.1

### ***Groundwater Acidity***

The groundwater samples obtained from each of the eight observation wells and the drain water sources around the site were tested for acidity on a weekly basis. Over the monitoring period, the average pH values measured are given in Table 3 for various sampling points. Excluding wells 1 and 5, the pH range for the observation wells is very low at 3.45 to 3.78. These values indicate that the  $[H^+]$  ion concentration of the groundwater is well over 1000 times greater than that of neutral water, verifying the production of acid by pyrite oxidation within the soil surrounding these observation wells. If not for the annual lime treatment of the area by dairy farmers, these pH values will be even smaller.

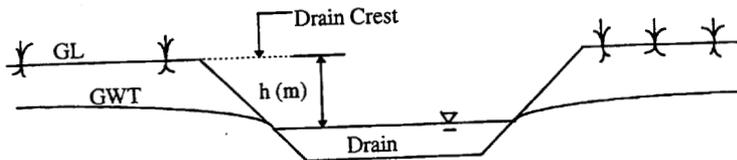
For observation well 5 which is less than 2m deep, the average pH value over the testing period was 6.61. It was found by subsequent boring that pyrite exists significantly below the bottom of well No.5, and therefore, any acid formation could not be detected from this particular well. It is relevant to note that the drain sites 1-3 carry acidic water, whereas drain sites 4-6 carry almost neutral water. This is because the drain sites 4, 5 and 6 (Figure 2) are charged with neutral (stream) water flowing into the study area from the higher elevations. In contrast, drains 1, 2 and 3 represent water flowing out of the test site into Broughton Creek at lower elevations. In other words, only the water in the latter drains represent the actual groundwater seepage conditions within the study area. Therefore, the water quality of drain sites 1-3 has been used as an indicator of acid-sulphate soil formation within the study area.

### ***Soil Acidity***

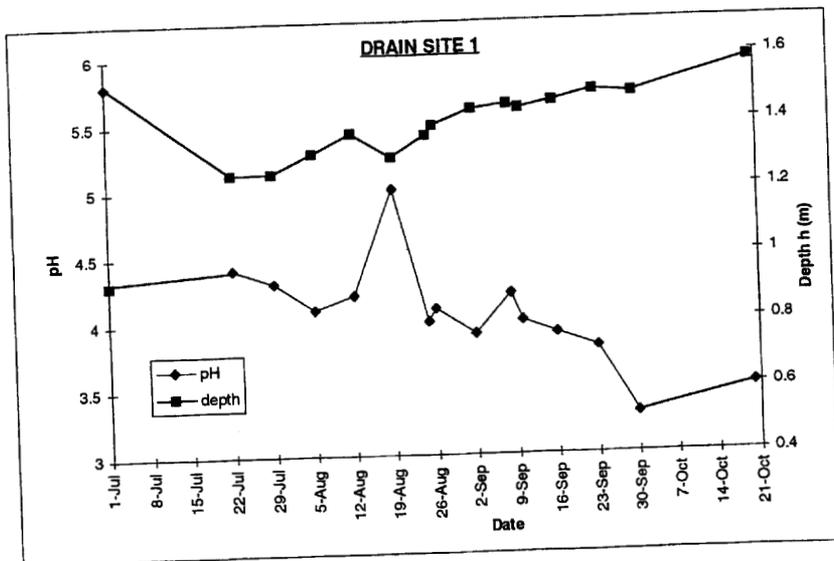
Table 4 indicates the difference in soil pH values at depths of 200mm and 1000mm below the ground surface, respectively (Sbeghen, 1995). There is no doubt that the soil acidity increases with depth below the ground surface (up to about 1.8m). This is not surprising because the first 200-300mm of the top soil consists of organic matter, and is often lime-treated. A soil pH as low as 3.1 at a depth of 1m below the surface verifies considerable oxidation of the pyrite layer, once the groundwater table falls below this depth. From the findings of the study, it may be concluded that there is an active acid sulphate soil layer between 1.0 and 2.5m below the ground surface on the Berry floodplain. Although the presence of some pyrites and jarosites could be identified at depths around 0.5m in certain areas, the measured pH values were affected by the use of organic fertilisers and lime-treatment.

### ***Groundwater Effects***

The variation of the groundwater depth in the observation wells and the drains is fundamental to the development of an acid sulphate soil management strategy. Table 5 summarises the groundwater depths in the observation wells and the water levels in the drains. From the recorded depths on the Berry site during the monitoring period, the level of the groundwater in the observation wells is greater than the surface water level in the drains. This implies that over this relatively dry monitoring period, groundwater was constantly feeding the drains. However, during heavy rainfall, it has been observed that the drain water levels would rise quickly above the observation well levels. Subsequently, the associated rise in phreatic surface would submerge the potential acid sulphate soil layer, thus preventing any pyrite oxidation, hence, acid formation. In other words, if the water levels of the drains can be maintained at high levels, the pH of both drainwater and groundwater should increase towards more favourable values.



(a)



(b)

Figure 3: (a) Definition of depth of water level, h and (b) relationship between h and pH over the monitoring period.

Table 5: Reduced level of groundwater table in comparison with drain water levels

Date (1994)	Reduced Water Level in Wells (m)							Reduced Drain Water Level (m)
	1	2	3	4	5	6	7	
1-Jul	9.29	8.43	8.75	8.59	11.37			8.34
22-Jul	8.86	8.26	8.43	8.37	10.40			8.01
29-Jul	8.86	8.24	8.43	8.38	10.27			8.01
5-Aug	8.83	8.20	8.32	8.32	10.04			7.95
12-Aug	8.74	8.15	8.26	8.31	9.87			7.89
19-Aug	8.69	8.13	8.27	8.32	9.81			7.98
25-Aug	8.67	8.11	8.21	8.28	9.72			7.91
26-Aug	8.61	8.13	8.21	8.31	9.63			7.87
2-Sep	8.62	8.12	8.20	8.26	9.73			7.82
8-Sep	8.58	8.07	8.13	8.23	9.70			7.81
16-Sep	8.55	8.06	8.09	8.19	9.69			7.80
23-Sep	8.46	8.04	8.07	8.14	9.57	8.03	7.03	7.77
30-Sep	8.38	7.99	8.05	8.10	9.24	7.99	7.82	7.78
20-Oct	8.15	7.93	7.97	8.05	9.25	8.01	7.72	7.68

Note: the reduced levels are in relation to the 10.000m bench mark at the Broughton Creek floodgate.

**Drain Water Depth and Acidity**

In order to evaluate the effect of raising the drain water level depth on the acidity of groundwater leaving the Berry site, weekly monitoring of drainwater depths and pH was conducted. For example, Figure 3 illustrates the relationship between the water depth below ground level (h) and the resulting pH as measured in drain site No.1. Figure 3 verifies that as the drain water level drops, the pH levels decrease. This also implies adverse consequences on aquatic biota in Broughton Creek, once acidic groundwater is discharged to the source. On the contrary, if the water level in the drains can be increased (ie. reduction of h in Figure 3a), the acidity will diminish thus improving water quality. The relationship between measured pH levels in the three drain sites 1, 2 and 3 and their water levels are plotted in Figure 4. Drain sites 1-3, as mentioned earlier, contain seepage water within the study area. Upper and lower bound relationships between pH values and the depth of groundwater table can be established for the measured data from the three drain sites. The resulting empirical equations are given below.

$$\begin{aligned}
 \text{pH} &= -1.43h + 6.22 && \text{(upper bound)} \\
 \text{pH} &= -1.80h + 5.86 && \text{(lower bound) -----(1)}
 \end{aligned}$$

The above relationships allow an estimate of the minimum depth of water in the drains (hmin) required to maintain an acceptable level of water quality. For example, to maintain a pH level of 5.5 in drains, by Eqn. 1 the distance from the drain crest to the water level must be about 500 mm by the upper bound, and 200 mm by the lower bound expression. In practical terms, this suggests that the water within the drains must be maintained at high levels (close to drain crest) in order to achieve acceptable pH values in excess of say 5.5. During the periods of little rain, this is only be possible by using temporary weirs, installed across selected drain locations. However, excessively high water tables would create problems for farmers in terms of trafficability of farm machinery as well as unfavorable effects on certain crops.

Therefore, it is anticipated that an optimum balance between the elevated water table and reduced lime treatment should be achieved.

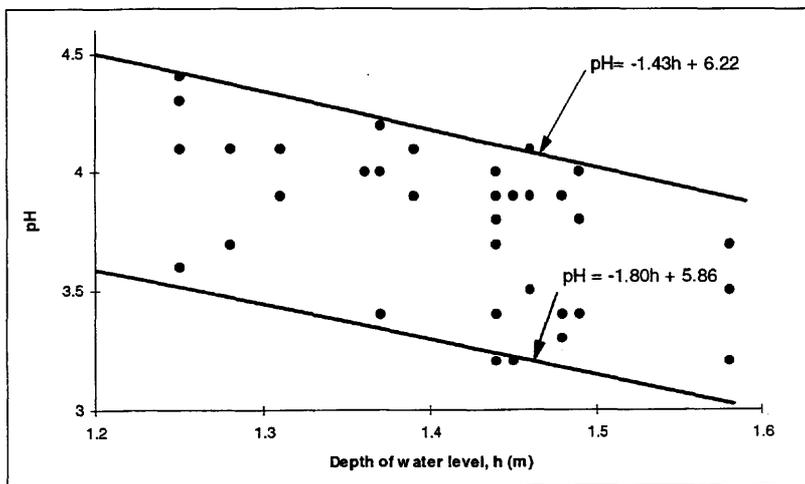


Figure 4 Relationship between drain level and pH for drain sites 1, 2 and 3.

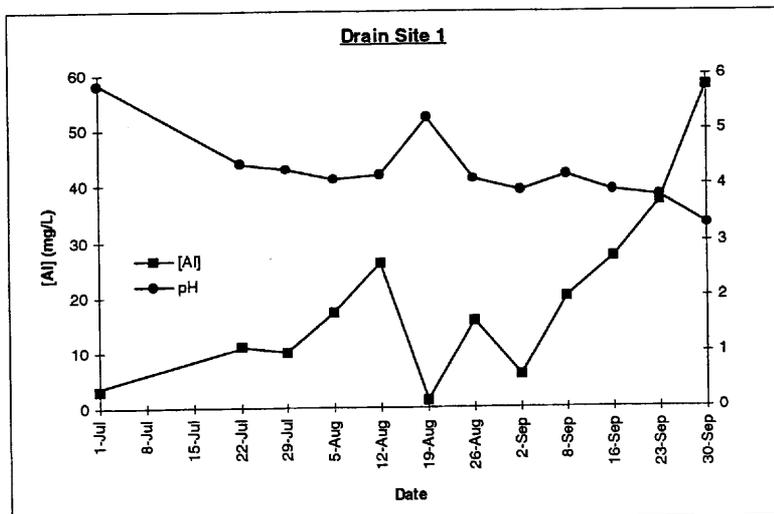
**Drain Water Depth and Aluminium Concentration**

The aluminum ion (soluble) concentration was also sampled on a weekly basis from several observation points. Once the soil pH is less than 5, aluminum is able to leach out from the soil with toxic consequences on flora and fauna. In March 1987, a two year drought in Northern NSW was followed by 0.5m of rain within a few days. It is reported that thousands of dead fish, crabs and prawns littered the river for many days. The flocculating effect of aluminium leached from the acid sulphate soil on the Tweed River banks and the acidic groundwater discharged with the onset of rain was directly responsible for the considerable fish and crustacea kills along a 15 km stretch of the Upper Tweed River (Buckley et al., 1993).

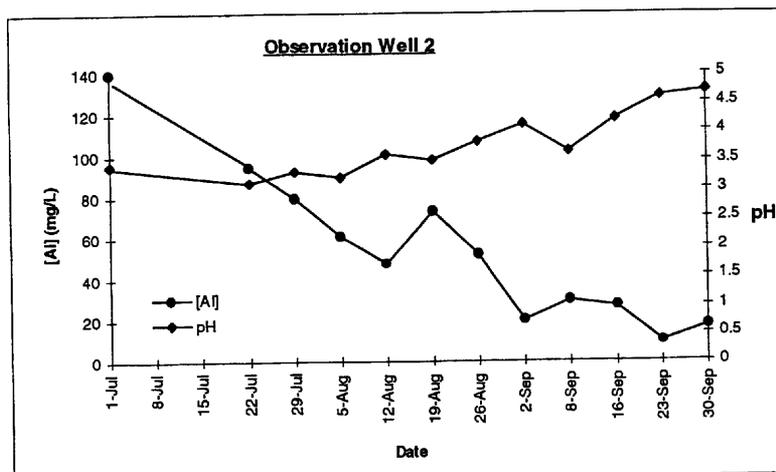
The relationships between soluble aluminium and pH for drain site 1 and observation well # 2 are shown in Figure 5. There is no doubt that the increase in pH levels are associated with a decrease in Al levels. In the Berry test site, increasing the water level, and thereby decreasing the acidity of drain water will reduce the extent of aluminium mobilised in the low-lying soil, resulting in less metal discharge to the nearby Broughton Creek. A statistical correlation between aluminium concentration [Al] and pH values was established for the drain sites and observation wells using a linear regression analysis (r2 = 0.91), as shown in Figure 6 and represented by Eqn. 2.

$$[Al] = -45.8 \text{ pH} + 220.4; \quad [Al] \text{ in mg/L} \text{ -----(2)}$$

For example, if the pH of the groundwater falls below 4.0, the aluminium concentration could be expected to exceed 35 mg/l, whereas under extreme acidic conditions



(a)



(b)

Figure 5; Variation of Aluminium with pH at (a) drain site #1 ; (b) observation well 2.

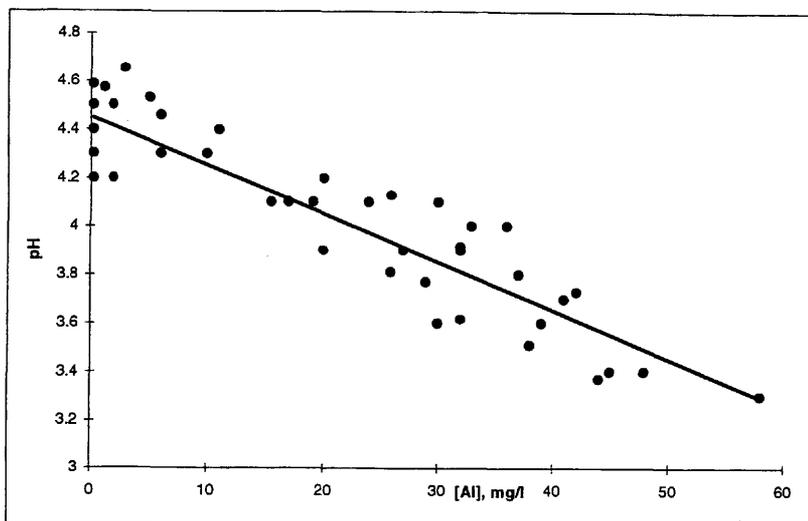


Figure 6 : Variation of Aluminium concentration with pH for measurements obtained at selected observation wells and drain sites.

(pH<3.0), the aluminium concentration will exceed 80 mg/l. The above values are detrimental to most vegetation and aquatic life.

From a practical point of view, Equations 1 and 2 serve as a basis for an acid-sulphate soil management strategy. Given the acceptable levels of [Al] for a particular crop, the corresponding pH level can be estimated from Eqn. 2. Subsequently, the desirable groundwater level can be determined from Eqn. 1 for the site in question. A combined proposal between the Environmental Protection Authority, Shoalhaven City Council and the University of Wollongong has been initiated recently to install temporary weirs (eg. removable sand bags), and to modify the existing floodgates to carry out several field trials with elevated drain water levels.

### CONCLUSIONS

The production of acid from acid sulphate soils can have detrimental affects on flora and fauna within a close proximity to the acid sulphate zone. On the basis of this research study, empirical relationships between measured groundwater and drain water depths with pH values have been determined. For agricultural purposes, the effect of pH on Al concentration was also studied and quantified.

Based on the current field monitoring scheme, the following conclusions can be drawn: (i) The presence of jarosite, low chloride:sulphate ratios and low pH values measured at the Berry test site warrants its classification as a potential acid sulphate soil zone. The active acid sulphate soil layer lies between 1m and 2.5m below the ground surface. The drawdown of the groundwater table during dry periods promotes the oxidation of the exposed pyrite. The closer the pyrites to the ground surface, the greater the risk of acid-sulphate soil formation.

(ii) Al ions are mobilised significantly in the low-lying soil as pH values drop below 4.5. If the Al concentration in the soil exceeds 1 to 2 ppm (Dent, 1986), many crops can be adversely affected. Knowing the relationship between the mobilised [Al] levels and the corresponding pH values, the desirable groundwater level can be estimated for a given crop from Eqns. 1 and 2.

(iii) The empirical field relationship between groundwater depth and pH values serves as a basis for acid-sulphate soil management. For instance, raising the water level in the drains by using temporary weirs will cause a corresponding rise in the groundwater table to partially or fully submerge the potential acid-sulphate deposits.

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### REFERENCES

- [1] Buckley, D.R., Easton, C. & Tunks, M. (1993). Acid water fish kills in the Tweed Shire, Proc. of the 19th AIEH National Conference, Tweed Heads, Australia, pp. 15-17.
- [2] Chapman, S. J. (1994). Development of a strategy for the management of acid sulphate soils in Berry, NSW, BE Thesis, University of Wollongong, Australia, 87p.
- [3] Dent, D. (1986). Acid Sulphate Soils: A baseline for research and development. International Institute for Land Reclamation & Improvement, Netherlands, 130p.
- [4] Dent, D. and Pons, L. (1993). Acid and muddy thoughts. Bush, R. (Ed). Proc. of the First National Conference on Acid Sulphate Soils, pp.1-15.
- [5] Green, D. (1993). Rivers of death. *Fishing World*, April issue, Vol. 27, pp.38-41.
- [6] Naylor, S. (1993). Draft Environmental Guidelines for the Assessment and Management of Coastal Land Development in Areas of Acid Sulphate Soils, Environmental Protection Authority, Grafton, Australia, 78p.
- [7] Mulvey, P. (1993). Pollution, prevention and management of sulphidic clays and sands. Proceedings of the First National Conference on Acid Sulphate Soils, Coolangatta, Australia, pp. 116-128.
- [8] Sbeghen, B. (1994). Development of a strategy for the management of acid sulphate soils in Berry, NSW, MEnvSc Thesis, University of Wollongong, Australia, 95p.
- [9] White, I. and Melville, M. D. (1993). Treatment and containment of potential acid sulphate soils. Report No. 53, Centre for Environmental Mechanics, CSIRO, Canberra, 25p.
- [10] Willett, I.R. and Walker, P.H. (1982). Soil Morphology and distribution of iron and sulfur fractions in a coastal flood plain toposequence. *Australian J. of Soil Research*, Vol. 20, pp.283-294.