

## VARIABILITY OF ACID SULFATE SOIL CHEMISTRY AT EAST TRINITY REMEDIATION SITE, FAR NORTH QUEENSLAND, AUSTRALIA

A.E. McElnea, C.R. Ahern, J.A. Manders and C.D. Smith

Department of Natural Resources Mines and Energy, Brisbane, Australia.

### Abstract

A comprehensive acid sulfate soil investigation was undertaken at a 940 ha site at East Trinity, Cairns as part of a larger remediation project designed to mitigate the environmental harm being caused by this degraded coastal lowland area. The investigation found an extremely chemically diverse terrain with soil properties highly variable across the site. There were substantial areas with high levels of existing acid (including acidic peats), frequently underlain (often to great depths) with highly sulfidic sediments. Paradoxically, some of the sulfidic material contained large quantities of acid neutralising capacity in the form of marine micro-fauna *foraminifera*. The range in the values of the chemical parameters determined throughout the site were illustrated using selected soil profiles and were contrasted with that of a hydrologically undisturbed soil profile. The study showed the importance of quantifying all the acid-producing as well as the acid-neutralising components in the soil and led to improvement to the chemical methodology used to assess the net acidity in acid sulfate soils.

Additional Keywords: existing acidity, self-neutralising soil, *foraminifera*, potential acidity

### Introduction

The 940 ha East Trinity site adjacent to Cairns city in North Queensland is a degraded coastal lowland area, a legacy of inappropriate development and management over more than three decades. This mismanagement stemmed principally from a general lack of knowledge of the site, and specifically an ignorance of the occurrence of acid sulfate soils and the potential consequences of disturbing them. Acid sulfate soils naturally contain sedimentary pyrite (FeS<sub>2</sub>) and remain environmentally benign if maintained in a saturated state under reducing conditions. If disturbed and allowed to oxidise they produce sulfuric acid, which can solubilise large concentrations of toxic metals—a situation that has transpired at the East Trinity site. In May 2000 the Queensland Government purchased the East Trinity site (which is adjacent to the Wet Tropics World Heritage Area) with the intention to preserve Cairns' green outlook. They also started planning to remediate it, putting a stop to the leaching of a toxic brew of acid and metals into the nearby Trinity Inlet.

To formulate appropriate management strategies for the site it was necessary to carry out a detailed site investigation (comprising geomorphological, soil, vegetation, groundwater and stream water-quality components). Of these components, the soil investigation was of major importance, as it was this information that was needed to assess and quantify the acidity that was already present at the site, as well as the potential acidity that remained and that could be released in the future (were the then current inappropriate management to continue).

What the soil investigation found was an extremely chemically diverse terrain with soil properties highly variable across the site. There were substantial areas with high levels of existing acid (including acidic peats), frequently underlain (often to great depths) with highly sulfidic sediments. Paradoxically, some of the sulfidic material contained large quantities of acid neutralising capacity (ANC) in the form of marine micro-fauna *foraminifera*. Critical to this investigation was the development and selection of appropriate and specific chemical methodology to accurately assess the acidity (be that existing or potential) contained in these soils.

### Materials and Methods

#### *Soil sampling and treatment*

The soil sampling protocol involved the drilling of 85 boreholes on the site, principally along 4 parallel transects separated by 200 m, orientated perpendicular to the shoreline (63 boreholes), with the remainder strategically drilled to investigate particular stratigraphic aspects. Holes were drilled to an average depth of 7.8 m (but to as deep as 22 m) using a rapid hammer percussion coring apparatus (Geoprobe™) mounted on a tracked all-terrain vehicle, overcoming problems of poor site trafficability in this area of low elevation.

Soil cores were described on site by Qld Dept. of Natural Resources, Mines and Energy (NRM&E) staff using the Australian Soil and Land Survey Handbook (McDonald *et al.*, 1998) as a basis and classified according to the Australian Soil Classification (Isbell, 1996). Field pH of soil was measured before and after treatment with 30%

H<sub>2</sub>O<sub>2</sub> at 0.25 m intervals down the soil profile using a spear-point pH electrode attached to a portable pH meter. The vigour of the soil reaction with H<sub>2</sub>O<sub>2</sub> was assessed and recorded. Soil samples were taken, then refrigerated prior to laboratory analysis.

### Analysis

Refrigerated or frozen soil samples were dried at 80–85 °C in a fan-forced air-extracting oven for 48 h, then ground to <0.5 mm in a hammer mill. A total of 989 soil samples were analysed at the Natural Resource Sciences Laboratories, NRM&E in Brisbane. A range of analyses were undertaken to characterise the soils in terms of their existing acidity (i.e. *actual acidity* in the form of soluble and exchangeable acidity, and *retained acidity* held in sparingly soluble hydroxy-sulfate minerals such as jarosite), potential acidity (in the form of sulfides, principally sedimentary pyrite, FeS<sub>2</sub>) and acid neutralising capacity (e.g. in the form of carbonates). Chemical methods used included those contained in the *Acid Sulfate Soils Laboratory Methods Guidelines* (Ahern *et al.*, 1998), as well as the improved suspension peroxide oxidation combined acidity and sulfate method (McElnea *et al.*, 2002).

### Results and Discussion

Before being banded and cleared for cane farming over 30 years ago, the East Trinity site (see Graham *et al.* 2004, these proceedings) was a natural, tidally-influenced floodplain, largely covered by mangrove and saltmarsh vegetation. The pre-disturbance situation is approximated by the profile described by Borehole #45, situated on the inlet side of the bund wall that presently hydrologically constrains the site. Prior to disturbance the soils on the site were largely maintained in a saturated state, with sulfides remaining unoxidised and little existing acidity present in the system. This is illustrated by Figure 1, which shows the distribution of actual acidity, retained acidity, potential and acid neutralising capacity throughout the soil profile. The pH of the soil is near neutral throughout the entire depth of the profile, resulting in there being no actual or retained acidity present. The soil net acidity is simply comprised of potential acidity hidden in the unoxidised sulfides. At the surface, sulfide levels are low, but quickly increase to high levels (equivalent to more than 2% pyrite sulfur) which is maintained throughout the core sampled (2 m depth). These sulfide levels are typical of those occurring at depth throughout the site, although the maximum sulfide content ranges up to 6.6 %S.

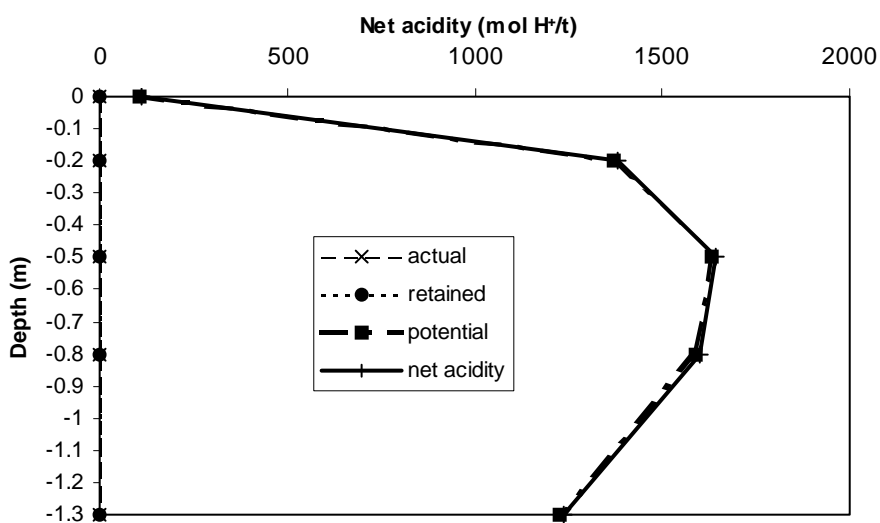
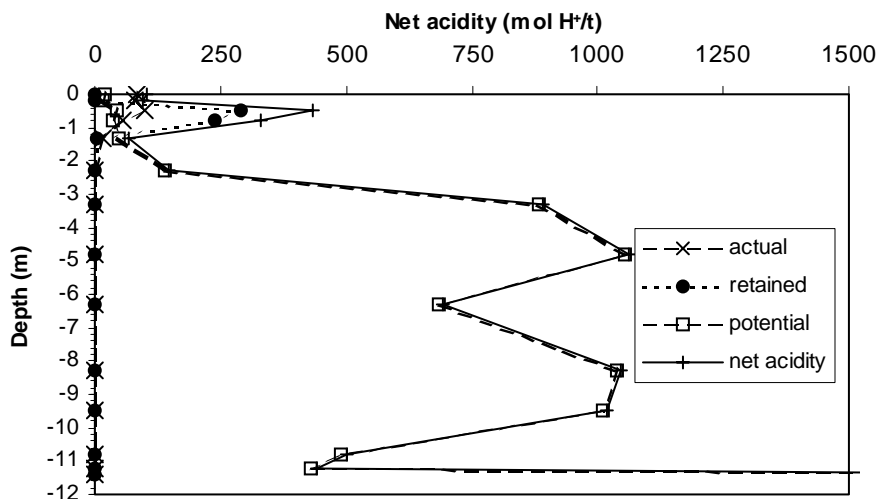


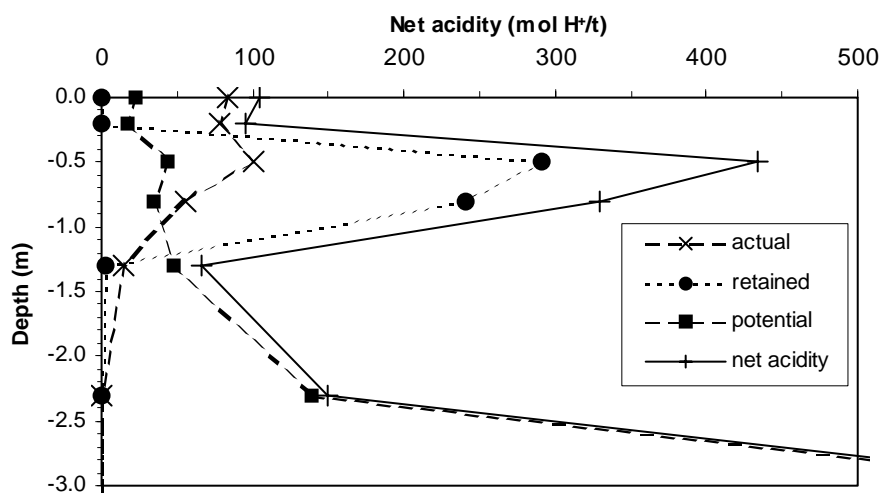
Figure 1. Distribution of actual, retained, potential and net acidity in East Trinity borehole #45

The chemical conditions in this profile contrasts with what is occurring on the site (inside the bund wall). Graham *et al.* (these proceedings) describe the character and the inferred depositional history of the geomorphological/sedimentological units they identified at the East Trinity site. In their paper they discuss this in terms of one of the sampling transects (Transect #4). The following two soil profiles examined here come from along this transect. The core taken at Borehole #52 extends to a depth of 11.5 m into a palaeochannel of the main stream (Hills Creek) that dissects the site. The draining of the site and concomitant lowering of the watertable has had profound effects on the distribution of the various forms of acidity throughout this particular soil profile. Below 2 m depth, the soil remained relatively unaffected by the site drainage. Sulfide content varied throughout the profile below 2 m, but was generally between 1 and 2 %S. The net acidity in this section of the profile again reflected the sulfide content of the soil (Figure 2a).



**Figure 2a. Distribution of actual, retained, potential and net acidity in East Trinity borehole #52**

In the upper part of the profile (i.e. above 2 m) the situation was quite different (Figure 2b). The potential acidity at the soil surface was low—sulfides that were present before site disturbance had largely been oxidised. The potential acidity represented only a small fraction of the net acidity in this part of the profile. Far more important was the actual and retained acidity. (This is collectively referred to as the existing acidity). The actual acidity reaches a maximum of 100 mol H<sup>+</sup>/t at around 0.5 m depth, gradually decreasing to 15 mol H<sup>+</sup>/t by 1.3 m. While this actual acidity is quite substantial and constitutes a large proportion of the net acidity in the first 0.2 m of the profile, between 0.5 and 1 m the retained acidity represents the major fraction of the soil's net acidity. This is a significant finding with important management implications. Often it is assumed that the retained acidity only represents a small proportion of the soil net acidity, and as a consequence it is not always requested to be measured when samples are submitted for laboratory analysis. It can be an especially important fraction in oxidised soil layers, where sulfides do not constitute the soil's principal acid risk. Unlike the actual acidity fraction, which is quite soluble and tends to be the acidity mobilised after a rainfall event (as water infiltrates through the drier oxidised part of the soil profile), the retained acidity may only be released slowly (over years or even decades), so it must be considered when formulating longer-term management strategies for acid sulfate soils.



**Figure 2b. Distribution of actual, retained, potential and net acidity in East Trinity borehole #52 (truncated)**

The final soil profile (Borehole #49) is unusual in some aspects, at least in a Queensland acid sulfate soil context. As was the case for the previous profile, potential acidity (i.e. sulfide content) was relatively low in the upper section of the profile (see Figure 3), but increased rapidly at depth. Unlike the previous profile however, there was no actual or retained acid present at any interval throughout the profile. Presumably sulfides had been present closer to the surface (e.g. at 0.8 m) before disturbance and had subsequently been oxidised, so why had the soil not

become acidic? The profile interval between 0.2 and 1.5 m was found to contain substantial amounts of ANC (equivalent to as much as 5% CaCO<sub>3</sub> by weight in some samples). This ANC was not obvious visually in the field (e.g. in the form of appreciable amounts of shell or shell fragments) but was alluded to by vigorous reaction of the moist soil with dilute hydrochloric acid (1 M HCl). A subsequent palaeontological investigation (revealed the presence of a calcitic foraminiferal assemblage (dominated by the species *Ammonia breccarii*) (Graham *et al.*, these proceedings). In the upper part of the profile the ANC was well in excess of the potential acidity held in sulfide, resulting in a large negative net acidity. Such soils are termed ‘self-neutralising’. (In some soil horizons analysed from the site, ANC results exceeded the equivalent of 15% CaCO<sub>3</sub>). However, further down the profile, ANC values decreased as sulfide content increased, resulting in substantial net acidity values. Soils such as these indicate the potential folly of relying solely on the measurement of sulfide content as a basis for assessing the net acid risk represented by acid sulfate soils.

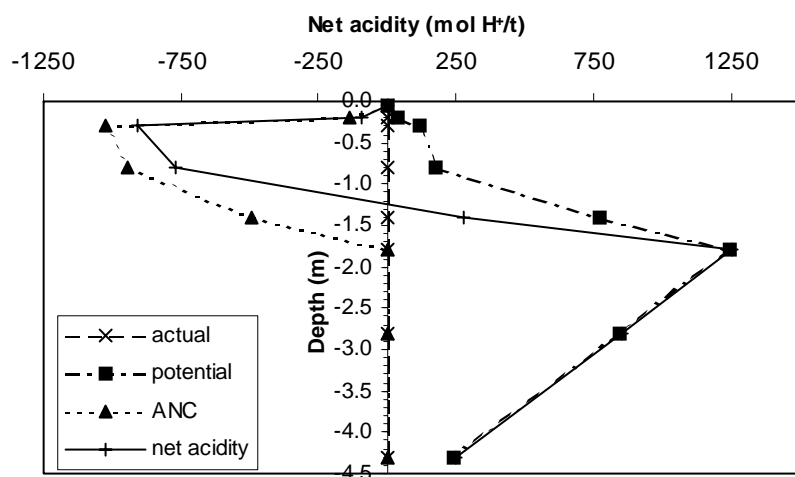


Figure 3. Distribution of ANC, actual, potential and net acidity in East Trinity borehole #49

Samples from this profile (and similar profile at this site) were instrumental in the development of improved chemical methodology for the analysis of ASS in this country. Substantial discrepancies were recorded between two parameters typically used to estimate potential acidity in ASS. Peroxide oxidisable sulfur (or S<sub>POS</sub>) values were found to be significantly lower than the chromium reducible sulfur (S<sub>CR</sub>) for self-neutralising soil samples. This represented an interference in the determination of S<sub>POS</sub>. This led to a method variation alteration to the peroxide digestion employed (including a titration with HCl to dissolve excess carbonate) that ensured complete oxidation and hence recovery of pyrite in the S<sub>POS</sub> result (Latham *et al.*, 2002).

## Conclusions

A detailed acid sulfate soil investigation conducted at the East Trinity site found a great degree of variability in the distribution and extent of actual, retained and potential acidity and of acid neutralising capacity. The study underlined the necessity to accurately and comprehensively characterise the various acid producing and acid neutralising components of these soils in order to sensibly assess possible management options as part of the wider remediation project. A fortuitous by-product of the investigation was the development of improved chemical methodology for determining the various soil components.

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