Acidity, metals and acid sulfate soils

Bennett C.T. Macdonald[1], Ian White[1], Annabelle Keene[2], Mike D. Melville[3] and Jason Reynolds[3]

[1]Centre for Resource and Environmental Studies, Institute of Advanced Studies, Australian National University, Canberra, ACT, 0200, Australia. Email: ben.macdonald@anu.edu.au
[1]Centre for Resource and Environmental Studies, Institute of Advanced Studies, Australian National University, Canberra, ACT, 0200, Australia Email: ian.white@anu.edu.au
[2]Environmental Science and Management, Southern Cross University, Lismore, NSW, 2480, Australia Email: akeene@scu.edu.au
[3]School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW, 2052, Australia Email: m.melville@unsw.edu.au
[3]School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW, 2052, Australia Email: j.reynolds@student.unsw.edu.au

Abstract

Despite the generally uniform appearance of acid sulfate soils, there is considerable variation in the amount of existing acidity, pyritic weathering, and the amount of soluble and exchangeable ionic species within 5 Tweed River subcatchments. The levees contain more total potential acidity than the back-swamps (approximately >100 tonnes H_2SO_4/hectare) within the 5 studied catchments. There was also an association between texture and potential acidity within the studied subcatchment soils. The similar geomorphic units at each sites had similar metal and acidity contents. However, the discharge waters from 3 of the catchments were not similar: Blacks Drain was characterised by elevated levels of dissolved iron, aluminium and silica relative to Mcleod's Creek-Durranbah swamp and the Dulguigan Catchment drains

Keywords

Total potential acidity, total actual acidity, metals, water quality

Introduction

Acid sulfate soils (ASS) are a ubiquitous threat to the Australian lowland coastal landscape and early warnings of the risk these soils posed were ignored. In fact, Walker (1972) was quite emphatic, stating that "artificial drainage undertaken without regard to details of stratigraphy could lead to severe acidity and salinity conditions which, in back swamp soils, could be ameliorated only over a long period". Today, there has been extensive drainage of nearly all of the lowland catchments in New South Wales, including the Tweed River floodplain and Cudgen Lake catchment, which has greatly impacted on the water quality, aquatic life and overall productivity within both systems (Tulau 1999; White *et al.* 1996a). As predicted by Walker (1972), through natural pedogenesis and artificial drainage, the floodplains have been transformed from a store to a source of sulfur and metals which causes the pollution of downstream environments (Åström 2001; Macdonald *et al.* 2004b) and enhanced acidification and salinisation of these soils (Fanning 1993). The actual ASS contain large amounts of sulfuric acidity, and iron and aluminium oxy-hydroxides, and therefore, significant amounts of stored acidity. The management of total actual acidity (TAA) is critical in ASS management, however, it is hypothesised that the total potential mineral acidity (TPA), within the actual acid sulfate soil horizon is as equally important. The aim of this paper is to investigate the of Fe, Al, Cr, Mn, total actual acidity and total potential acidity content of the actual ASS of 5 catchments and the differences in water quality between 3 of the catchments.

Mineral acidity and total potential mineral acidity

There are essentially two acid pools within soil and water systems, mineral acidity and total potential mineral acidity. TAA, which is analogous to mineral-acidity, is defined by Konsten *et al.* (1988) as the total amount of freely available soil acidity. This TAA is comprised of soluble acidity, exchangeable acidity, acidity from protonated variably charged particles, and acidity carried by basic sulfate compounds (Lin *et al.* 2000). In ASS systems, the major mineral acid is sulfuric acid (H^+ in equation 1) generated from pyrite oxidation and is measured by total actual acidity method (McElnea *et al.* 2002b) and TAA has been defined by Stumm and Morgan (1996) as:
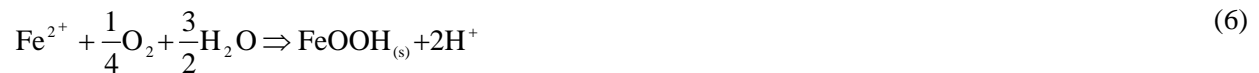
$$\text{Mineral acidity or TAA} = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \tag{1}$$

The total potential mineral acidity (TPA), is the second acid pool of waters and soils is composed of dissolved metal and organic acid species and H^+ and is defined by (Morel and Hering 1993; Stumm and Morgan 1996) as

$[TPA]= 2[Fe^{2+}] + 3[Fe^{3+}] + [Fe(OH)_2^+] + 2[FeOH^{2+}] - [Fe(OH)_4^-] + 3[FeSO_4]+3[Al^{3+}] - [Al(OH)_4^-] +$
$2[Al(OH)^{2+}] + [Al(OH)_2^+]+3[AlSO_4^+]+ 2[Mn^{2+}] +[HSO_4^-]-[HCO_3^-]-2[CO_3^{2-}]-[OH^-]+ [H^+] +[HA]$ (2)

[HA] represents organic acids.

Sulfide oxidation supplies a significant source of Fe and H^+ to the soil profile, and further mineral weathering of aluminosilicates and oxide minerals releases other metals such as Al, Si, and Mn and heavy metals such as Cr (see Evangelou 1995). Minerals, such as jarosite, ferrihydrite, schwertmannite, goethite and hematite, and oxyhydroxides represent a significant store of acidity within the actual acid sulfate soils and until recently this store has been overlooked, but their importance is now being recognised and methods are being developed to quantify and examine these acid stores (McElnea *et al.* 2002a; 2002b). Essentially the potential mineral acidity or TPA, as defined by equation 2, is the acidity that is generated as a result of the oxidation and hydrolysis of dissolved metal ions and organic acids in water. During inundation of actual acid sulfate soil (AASS), Fe and Al minerals could be dissolved, and ions of these minerals are released into the soil solution. The dissolved metal species now existing in interstitial waters could be transported to the soil surface or to the adjacent drains where oxidation, hydrolysis and precipitation reactions will occur, generating acidity. Typical reactions are defined in equations 3-6

$$Mn^{2+} + \frac{1}{4}O_2+\frac{3}{2}H_2O \Rightarrow MnOOH_{(s)}+2H^+ \tag{3}$$

$$Al^{3+} + 3H_2O \Rightarrow Al(OH)_{3(s)}+3H^+ \tag{4}$$

$$Fe^{3+} + 3H_2O \Rightarrow FeOOH_{(s)}+3H^+ \tag{5}$$

$$Fe^{2+} + \frac{1}{4}O_2+\frac{3}{2}H_2O \Rightarrow FeOOH_{(s)}+2H^+ \tag{6}$$

Methods
Study Area
The Tweed River and Cudgen floodplains are drowned river valleys, formed following sea level rise since 20,000 yr BP, and which resulted in the landward movement of offshore marine sands and clays into the prior valleys and the formation of a sand barrier (Roy 1973; 1984). The mud basins behind these sand barriers progressively in-filled with estuarine material and today are relative mature floodplains, characterised by broad, low elevation (<1m AHD) backswamps which grade into well-developed fluvial levees. These estuarine sediments are rich in sulfide minerals and there are approximately 9700ha of high risk and 2000ha of low risk ASS within the Tweed and Cudgen catchments (Figure 1). The study areas, Mcleod's Creek-Durranbah Swamp (2146 ha), Dulguigan (597 ha) and Cudgen Lake (798 ha) catchments are "acid sulfate soil hotspots", and Blacks Drain (520 ha) and Tumbulgum-Terranora (610 ha) catchments are low risk ASS areas. These catchments represent the range of ASS conditions that are found within the Tweed River and Cudgen floodplains.

The study area has a sub-tropical climate. The average annual evaporation is 1275 mm and average annual precipitation is 1687 mm at Murwillumbah. 70% of this rainfall occurs between the months of December and May due to summer-time cyclonic weather patterns. Total average evaporation is 1215 $mmyr^{-1}$ at Murwillumbah, and 1.7 mm day^{-1} during winter and 5.3 mm day^{-1} during summer. During winter or drought periods the depth of the water table is controlled by evapo-transpiration, which may lower the water table sufficiently to expose the reduced sulfidic layer to oxidation (Wilson *et al.* 1999). Besides this natural oxidation, anthropogenic disturbance through drainage, peat burning and ploughing have also caused the oxidation of sulfidic soils and subsequent production of sulfuric acid. The drainage networks which have been haphazardly installed within coastal floodplains, such as the Tweed floodplain, are the conduit by which acid and metal rich drainage waters are moved from the land surface to the estuary (see White *et al.* 1996b).

Soils
(a) Soil sampling. During summer, 2002, 24 sediment profiles from four subcatcments of the Tweed River: Dulguigan, Tumbulgum-Terranora, and Blacks Drain, and 8 profiles from Mcleod's Creek-Durranbah swamp were sampled in 1999, and the Cudgen Lake catchment was sampled in 1998. These soils were sampled to examine the spatial distribution of existing and potential acidity (Figure 1). The sediment was extracted at 0.1 m intervals using a bucket auger and a soil gouge. Soil pH was measured

(Ionode Intermediate junction pH probe coupled to a TPS WP81 meter), soil profile descriptions were taken, and five bulked samples were selected from each profile to represent, the organic, acid sulfate, transition zone above the oxidation front, transition zone below the oxidation front and the potential acid sulfate horizons. The samples were sealed in plastic bags, frozen to minimise further oxidation and transported to the laboratory. At the laboratory, the pH of the samples were checked with the field pH, those which were oxidised were discarded (lab pH<field pH) were discarded. Wet samples were used in the experiments and the results corrected to oven-dried moisture content.

(b) Titratable actual and potential acidity of the actual ASS. For each sample 1:5 sediment:water and 1:5 sediment:1M KCl extracts were prepared using 5 g of soil and 25 mL of either deionised water or 1M KCl. Aliquots of these extracts were used to measure pH, electrical conductivity (EC) and TAA. The method for determining TAA was adapted from Konsten *et al.* (1988) For the samples with pH<5.5, a 5 mL aliquot was titrated using 0.01M NaOH to an endpoint of pH 5.5, and the amount of total actual acidity present calculated in mol H^+ kg^{-1} for each horizon depth increment. TPA for each sample was determined using a method adapted from Konsten *et al.* (1988).1:5 sediment:KCl extracts were prepared, 20 mL of 30% H_2O_2 was added and the sample heated to accelerate the reaction. The sample was left to stand overnight and additional aliquots of 30% H_2O_2 were added until oxidation had ceased. The samples were heated to allow excess H_2O_2 to decompose. The sample was returned to room temperature, filtered and deionised water added to return the sample to the original 1:5 composition. An aliquot was titrated using 0.01M NaOH to an endpoint of pH 5.5, and the amount of total potential acidity present was calculated in mol H^+ kg^{-1} soil. In ASS research and management a pH value of 5.5 is often chosen to delineate between AASS and PASS (Konsten *et al.* 1988; Stone *et al.* 1998). This arbitrary boundary has been chosen because in systems where the pH<5.5 the acidity is dominated by sulfuric acidity generated by pyrite oxidation. This will under-represent the amount of acidity present in the TAA and TPA determinations because the acid end point is defined at pH=8.3, the bicarbonate equivalence point (Morel and Hering 1993).
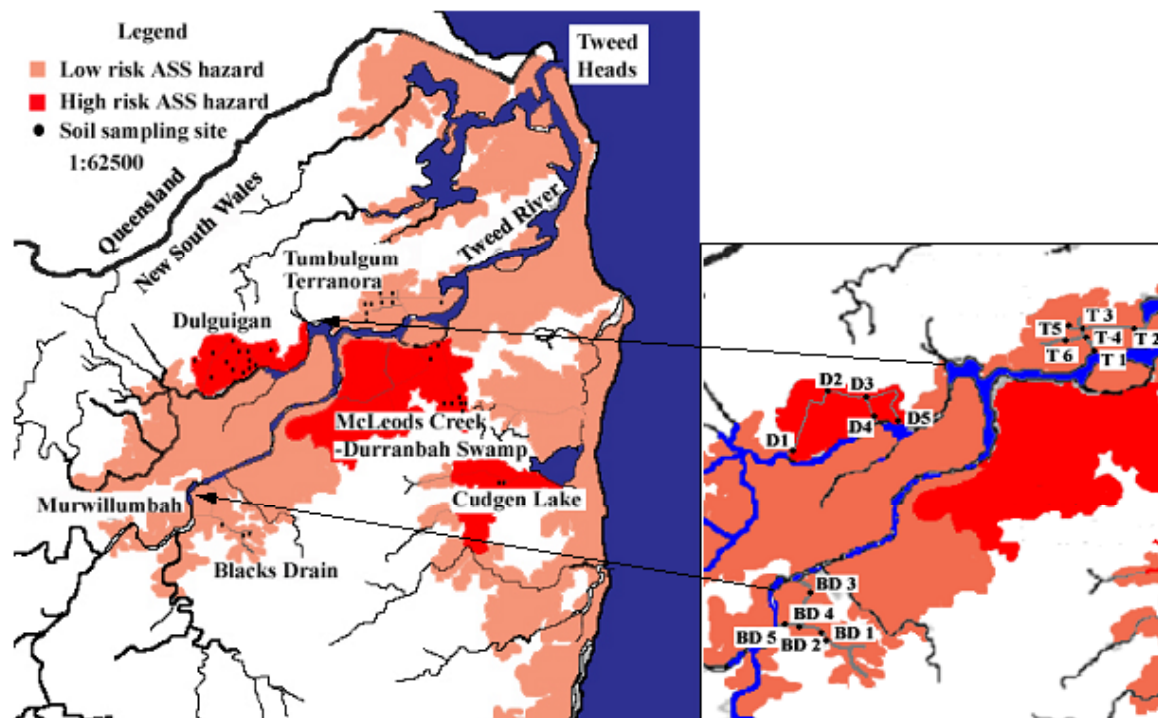

Figure 1. Location of study areas and soil sampling locations within the Tweed Shire Council, northern New South Wales. The blow-out shows the location of the water sampling points in the Blacks Drain, Dulguigan, Tumbulgum-Terranora drainage networks.

(c) Oxidisable cations Fe, Al, Si, Mn, and Cr of the actual ASS. (Terranora-Tumbulgum, Mcleod's Creek-Durranbah swamp, and Blacks drain only) After centrifuging, 5 min at 3500 rpm and filtering (Millipore 0.45 μm) Fe, Al, Si, Mn, and Cr from the TPA KCl-extracts were measured using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). These represent the

concentration of oxidisable, exchangeable and soluble cations in the soil porewaters, and variation in their concentrations can be used to indicate pyrite oxidation and pedogenic and weathering processes.

(d) Depth-weighted concentration. An overall TAA, TPA and cation value for each profile was calculated by summing the depth-weighted horizon values and converting to equivalent tonnes of H_2SO_4 per hectare, using measured bulk density (t m^{-3}). The depth-weighted concentrations only include the horizons above the oxidation front.

Waters
(1) Quantification of drain water quality. Water quality sampling has been conducted monthly, (26/06/02-30/04/03) and daily during rainfall events (01/04/03-27/04/03), from selected drains in the Blacks and Dulguigan, and Terranorra-Tumbulgum catchments (Figure 1). Samples were collected approximately 0.2 m below the drain water surface in clean, air-tight, plastic bottles, on the outgoing (low) tide. Samples were collected, filtered (Millipore 0.45 μm) and acidified (HNO_3 pH<2) for the measurement of soluble cations. The concentration of all cations (Na, Ca, Mg, K, Fe, Mn, Al, and Cr) in mg/L was analysed in the samples by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES). Samples were also collected for the measurement of Cl and SO_4 anions, which were analysed by Ion Chromatography (IC). Water measurements were taken by water quality monitoring units (TPS 90-FLMV), for the parameters: electrical conductivity EC (dS/m), pH, dissolved oxygen DO (mg/L), redox potential (standard hydrogen electrode, SHE: Volt), and temperature (°C) during sample collection.

(2) Weathering Index. The weathering index based on soluble cation concentrations (mg/L) is defined as: $WI = (Al + Fe + Si)/(Na + Ca + Mg + K)$.

Results and Discussion
(1) Catchment and Soil Profile Description and Chemical Characteristics. The analysis of the soil properties has been grouped according to catchment, soil texture and geomorphic unit (Table 1). All of the soils have been drained and converted to sugarcane agriculture, except the Cudgen backswamp which is inundated for longer periods after rainfall.

Table 1. Soil textural class of the sampled soils, and geomorphic unit and landuse classes for the five subcatchments.

Catchment	Soil texture	Geomorphic Unit	Landuse
Dulguigan	Medium clay	River levee, backswamp	Sugarcane
Mcleod's Creek-Durranbah swamp	Medium clay	River levee, backswamp	Sugarcane
Terranorra-Tumbulgum	Medium sand, Medium clay	Drained backswamp	Sugarcane
Blacks Drain	Medium clay	Drained backswamp	Sugarcane
Cudgen	Medium clay	Drained backswamp	Swampland

The sampled backswamp soils, according to the Soil Survey Staff (1998), generally key as Typic Sulfaquepts but, if the pH is above 3.5, the sampled soils are better described as Humaquepts (see Macdonald *et al.* 2004a). All the profiles consists of four distinct layers (see pH profiles in Figure 2): an organic layer which is characterised by elevated carbon content, typically 3-4%; a sulfuric layer; a transition zone; and the unoxidised sulfidic layer (potential ASS = PASS). The extent of each layer varied slightly between each catchment. The transition zone between the AASS and the PASS has increasing alkalinity (reflected by pH characteristics) and nil TAA. The TAA of the transition zone is greater than the AASS and this may reflect oxidation of reduced transitional sulfur minerals during analysis. The PASS is characterised by light blue-grey coloured gel in contrast to the red and yellowed mottling of the structured AASS horizon (Calvert and Ford 1973; Macdonald *et al.* 2004a).
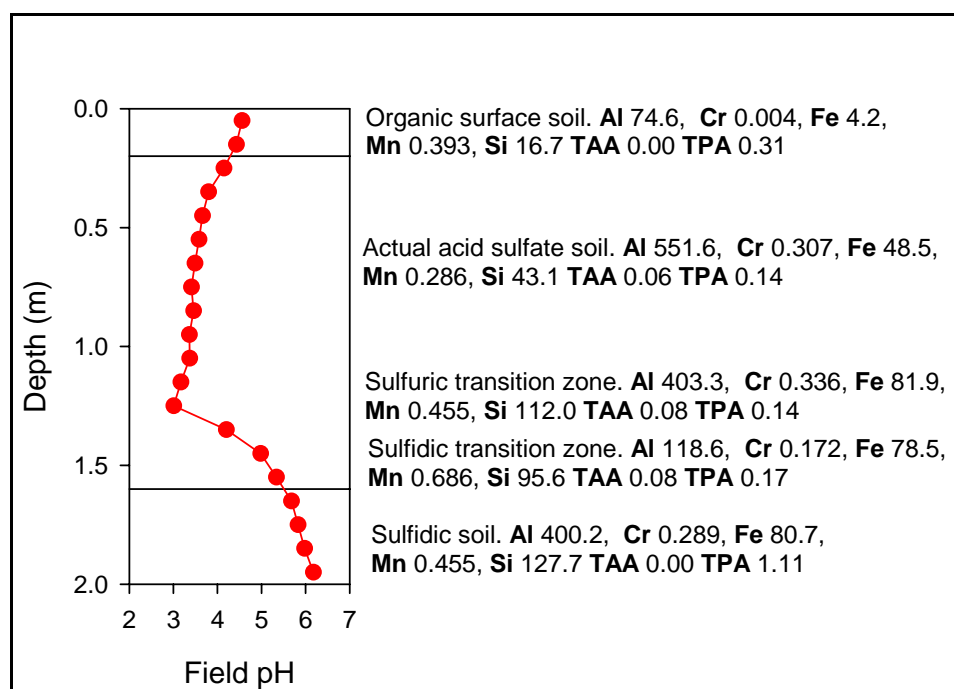
Figure 2. Soil field pH, horizon boundaries and oxidisable metal concentrations (mmol$_c$kg^{-1}) of a representative profile from the Dulguigan Catchment.

Figure 2 shows a representative ASS profile from the Dulguigan catchment. Pyrite oxidation causes weathering of aluminosilicates host minerals which releases Al, Si, Mn and Fe into solution (Willett *et al.* 1992). These ions are mobilised by organic complexes, and low pH pore water (Hallsworth *et al.* 1953), and are transferred from the oxidation front to the AASS due to water table movements (Nordstrom 1982; Willett and Walker 1982) and capillary movement due to evapo-transpiration (Pellerin *et al.* 2002; Wilson *et al.* 1999). These metals are typically precipitated within AASS horizons, which is reflected by the elevated oxidisable Al content of the soils, which is effectively the B-horizon, due to changes in the pH and Eh conditions (Oades 1963). The oxidisable Fe, and Si concentration of the AASS are less than the transition and sulfidic horizons because they have been exported from the soil profile during the ground water discharge.

(2) Mass of metals, TAA and TPA within the different catchments. There is considerable difference between the TPA and TAA content of the soils and at all sites with the TPA values are greater than the TAA values (Table 2). This was unexpected because previous studies had shown that above the oxidation front, the caneland AASS was free of pyrite (Lin *et al.* 1995; van Oploo 2000; Wilson 1995). The process of pyrite diagenesis typically within AASS tends to be slow and limited by organic matter supply (Rabenhorst and Fanning 2002) during brief periods of inundation and the predominating oxidising conditions that exist in the drained profiles. However, studies exist (e.g. Rosicky *et al.* 2000) that show that pyrite can be present in the surface of acid sulfate soils scalds and flooded acid sulfate soils. Within this study, all of the soils are drained, except the poorly-drained Cudgen site, and drought occurred during the main sampling period (2002; lowest rainfall in 100 years) which would not have favoured the formation of pyrite and transitional sulfur species. It is therefore likely that the potential acidity present is these AASS and the sulfuric transition horizon, as reflected in the metal and TPA concentrations in Figure 2, is probably being generated from metal hydrolysis, however a minor portion may include organic acids. The sulfidic transition horizon will contain some transitional sulfur species and pyrite due to partial oxidation of the profile. Table 2 shows that within AASS horizons there is significant source of oxidisable metals, which will contribute to the total potential mineral acidity pool, whereas sulfuric acidity from pyrite is the dominant form of acidity at the oxidation front. The importance and significance of measuring metal acidity needs to be incorporated into current and future management options for ASS.

(3) Geomorphic relationship with spatial variation of oxidation products. The levees at Mcleod's Creek-Durranbah swamp and Dulguigan hotspot have TPA content approximately 100 tonnes H$_2$SO$_4$/hectare more than the backswamps (Table 2). Elevated TPA values for levee soils which decrease towards the backswamp have been described by Sylla *et al.* (1996) for a series of West African Rivers.

They gave no clear cause of the spatial variation of TPA, but suggested that the backswamps are better aerated and drained. This may be the case, but it does not explain the elevated TPA contents of the levees, especially since the levees are composed of fluvial, flood-deposited sediments which should not contain pyrite. TAA, Al, Fe, Cr, and Si content of the levee and the backswamp soils are similar. There appears to be a texture control on the measured parameters, the clay texture has a greater TPA, Fe, Al, and Cr content relative to the sandy texture.

Table 2. Mean and standard error of total potential acidity and total actual acidity (H^+ report as H_2SO_4 equivalents), oxidisable Fe, Si, Cr, Mn, and Al (tonnes/hectare) content of the actual acid sulfate soils at the 5 study areas.

|	TPA		TAA		Al		Fe		Si		Cr		Mn	
	mean	se	Mean	se	mean	se	mean	se	mean	se	mean	se	mean	se
Dulguigan: clay texture														
Levee	260	76	60	22	66	23	23	8	29	12	0.4	0.05	29	12
Backswamp	147	26	58	12	81	13	28	6	23	5	0.3	0.04	2.0	0.5
Mcleod's Creek-Durranbah swamp: clay texture														
Levee	150	73	30	18										
Backswamp	54	6	25	2										
Terranora-Tumbulgum Backswamp														
sandy texture	56	20	40	21	105	27	34	5	3.5	1.5	0.3	0.03	15	7
medium clay texture	96	16	50	13	107	13	40	15	0.3	0.04	2.7	1	12	5
Blacks Drain Backswamp														
clay texture	159	40	67	15	89	5	64	40	53	15	0.2	0.03	3.5	0.6
Cudgen Backswamp														
clay texture	54	6.8	5.3	1.5										

Water Chemistry

Blacks Drain is characterised by poor water quality and reflects the recent drainage history of the site. This drain was deepened to 2 m below the ground surface along it's entire reach in the early 1980's, and at this depth the drain intercepts the PASS. The upper catchment drain is fed by seasonal springs that cease flowing during the dry season, which allows further oxidation within the drain. Oxidation products are flushed down the system during the next rainfall event and it is common for the entire reach of the drain to be discharging water that has a pH<3.0 for many days. The water quality of the upper reaches of Blacks Drain (BD1-4) are characterised by ASS discharge: a Cl:SO_4 ratio << 7, approaching 0; and a weathering index above 0.2. The water quality (Figure 3) of the lower reaches of Blacks Drain (BD5-6), are influenced by the Tweed River which lowers the weathering index due to inputs of tidal water rich in base cations but overall the Cl:SO_4 is less the7.1 (the value for sea water) which indicates that additional sulfur is being added to the system. The discharge waters at all sites are also characterised by elevated soluble iron, aluminium and silicon. These oxidation products are predominantly sourced from the soil adjacent to the drains, where acidic ground waters rich in weathered metals and acidity causes metal dissolution in the AASS horizon. The oxidation and weathering products are transported laterally through the organic topsoil layers to the adjacent drains or via overland flow if the water table broaches the ground surface. The Terranora-Tumbulgum backswamp and Dulguigan hotspot drainage network is different to the Blacks Drain system and are not fed by seasonal springs, but are tidally flushed by the Tweed River. The water quality in these systems is generally good because of the tidal flushing, but the Cl:SO_4 ratio is below 7.1, indicating that sulfur is being added to the drainage from pyrite oxidation. There appears to be little metal export at both sites and this is reflected in the iron, aluminium and silicon contents of the drainage waters. The differences between the water chemistry at Terranora-Tumbulgum and Dulguigan hotspots and Blacks Drain could be due to the following reasons

- The drain banks and the soil only 1-3m away from drain edges in these ASS catchments are the primary source of oxidation products (Cook *et al.* 2000; Kinsela and Melville 2004). It is possible that extensive weathering and export of the oxidation products from the drain banks has already occurred in these drainage networks compared to newer Blacks Drain banks.
- Sequential acid weathering of the soil profile has caused the release of iron within the Terranora-Tumbulgum and Dulguigan catchments relative to the Black's Drain catchment because of the longer oxidation. This phenomena has been observed in acidified soils in North America (Reinhardt *et al.* In

Press). This is reflected in the elevated iron concentrations in the discharge waters and oxidisable metal content of Blacks Drain relative to the other catchments.

- Terranora-Tumbulgum and Dulguigan catchments discharge waters are strongly influenced by tidal flushing. The buffering capacity of the sea water neutralises acidity in the drainage waters, which is reflected by the measured pH (Figure 3), and causes the precipitation of the dissolved Fe and Al. The water sampling method, i.e. filtering, does not measure this precipitated fraction and hence export may still be occurring.

- The seasonally dry drains in the Black's Drain catchment result in the oxidation of the drain banks and bottom, and large store of exportable metals and acidity in the wet season.
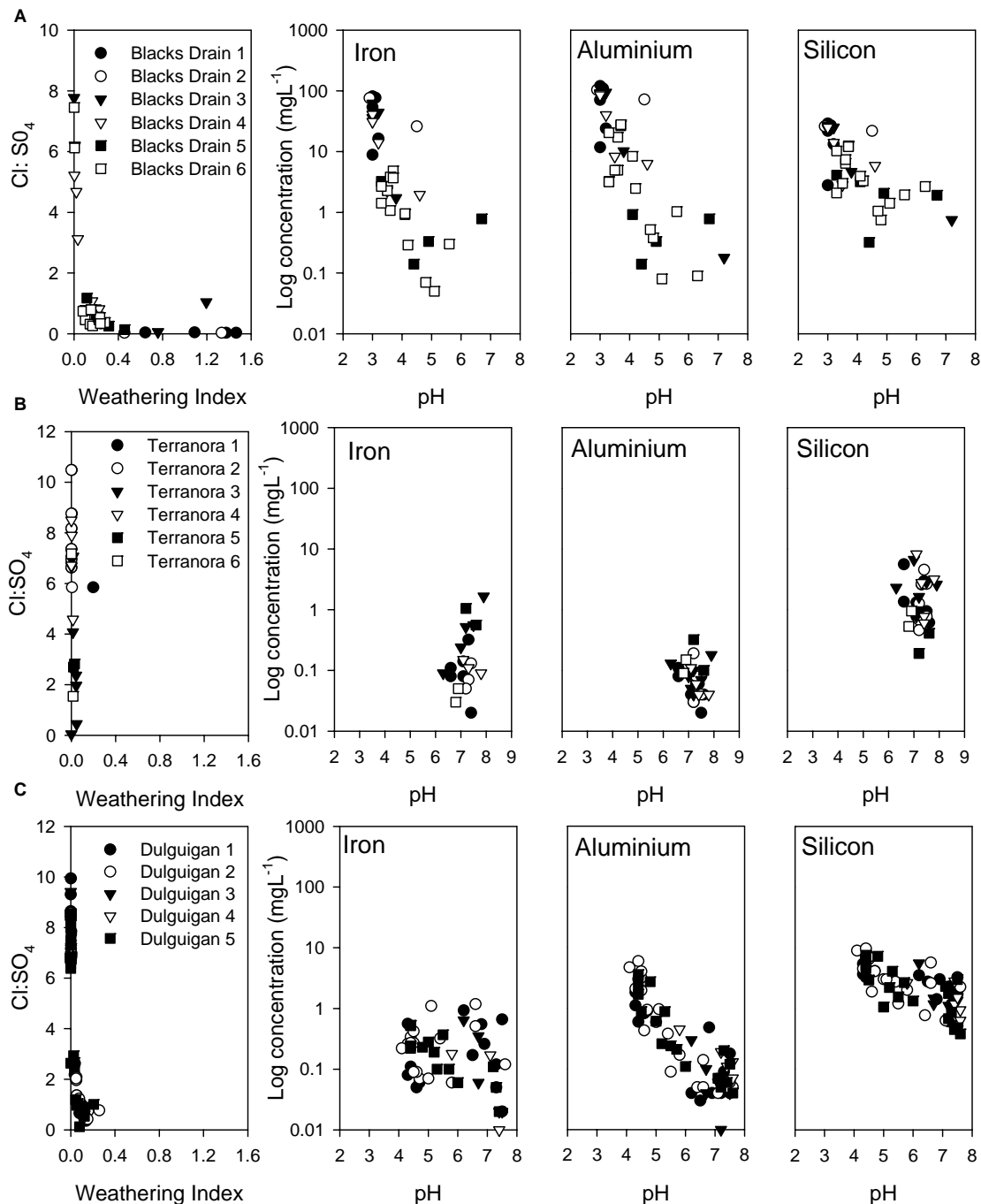
Figure 3. Water quality for sampling sites at the Blacks Drain (a) and Terranora-Tumblegum (b) backswamp and Dulguigan hotspot (c)

Conclusions

The functioning of the acidity pool within the AASS layers is a more complex process than in the sulfidic layers, being composed of total potential mineral acidity (Equation 2) rather than just that stored in pyrite. The store of mineral acidity within ASS is an important component of the acidity pool within all of the sampled soils. The levee banks within the catchments have an elevated mineral acidity relative to the backswamp soils, but the drivers behind this are unclear. The clay textured ASS also have a larger total potential mineral acidity pool relative to the sandy texture ASS. The more recently-drained catchment, Black's Drain, has a larger total potential mineral acidity pool and the drainage water contain an elevated concentration of metals and acidity, relative to the other catchments. The water quality in this catchment is characterised by ASS discharge waters. The Terranora-Tumbulgum and Dulguigan catchments discharge waters are strongly controlled by sea water buffering but the Cl:SO$_4$ ratio shows that additional sulfur is being added to the system from the soils. The pH characteristics of these catchments will cause the precipitation of Fe and Al within the drainage waters, and due to the sampling methodology employed in this study, the export of Al and Fe from these catchments was effectively hidden. This has important implications to management and sampling:

1. In sea water buffered systems what is the quantity and fate of the dissolved metals from the ASS ground waters?

2. What is the most appropriate methodology to quantify metals that are being exported from ASS catchments?

It is clear from this study that further investigations on the mineral acidity and how this pool of acidity operates within AASS, especially during inundation and the links to water quality, are warranted.

Acknowledgements

References

Åström M (2001) The effect of acid soil leaching on trace element abundance in a medium-sized stream, W. Finland. *Applied Geochemistry* **16**, 387-396.

Calvert DV, Ford HW (1973) Chemical properties of acid sulphate soils recently reclaimed from Florida marshland. *Soil Science Society of America Proceedings* **37**, 367-371.

Cook FJ, Rassam DW, Gardner EA, Carlin GD, Millar GE (2000) Drained acid sulfate soils: pathways of acid export. In 'Acid Sulfate Soils: Environmental Issues, Assessment and Management, Technical Papers, Brisbane, 20-22 June, 2000'. (Eds CR Ahern, KM Hey, KM Watling and VJ Eldershaw). (Department of Natural Resources: Indooroopilly, Queensland, Australia)

Evangelou VP (1995) 'Pyrite oxidation and its control: solution chemistry, surface chemistry, acid mine drainage (AMD), molecular oxidation mechanisms, microbial role, kinetics control, ameliorates and limitations, microencapsulation.' (CRC Press: Florida)

Fanning DS (1993) Salinity problems in acid sulfate coastal soils. In 'Towards the rational use of high salinity tolerant plants'. (Eds H Lieth and AA Al-Masoom) pp. 491-500. (Kluwer Academic Publishers: Netherlands)

Hallsworth EG, Costin AB, Gibbons FR (1953) Studies in pedogenesis in New South Wales. VI. On the classification of soils showing features of podzol morphology. *Journal of Soil Science* **4**, 241-256.

Kinsela AK, Melville MD (2004) Leaching of soluble acidity within acid sulfate soils under sugarcane cropping. *Australian Journal of Soil Research*.

Konsten CJM, Brinkman R, Andriesse W (1988) A field laboratory method to determine total potential and actual acidity in acid sulphate soils. In 'Selected Papers of the Dakar Symposium on Acid Sulphate Soils'. (Ed. H Dost) pp. 106-134. (ILRI: Wageningen, The Netherlands)

Lin C, Melville MD, White I, Wilson BP (1995) Human and natural controls on the accumulation, acidification and drainage of pyritic sediments: Pearl River Delta, China and coastal New South Wales. *Australian Geographical Studies* **33**, 77-88.

Lin C, O'Brien K, Lancaster G, Sullivan LA, McConchie D (2000) An improved analytical procedure for determination of total actual acidity (TAA) in acid sulfate soils. *The Science of the total environment* **262**, 57-61.

Macdonald BCT, Denmead OT, White I, Melville MD (2004a) Natural sulfur dioxide emissions from sulfuric soils. *Atmospheric Environment* **38**, 1473-1480.

Macdonald BCT, Smith J, Keene AF, Tunks M, Kinsela A, White I (2004b) Impacts of runoff from sulfuric soils on sediment chemistry in an estuarine lake. *Science of the Total Environment* **329**, 115-130.

McElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soils. *Australian Journal of Soil Research* **40**, 1115-1132.

McElnea AE, Ahern CR, Menzies NW (2002b) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* **40**, 1133-1157.

Morel FMM, Hering JG (1993) 'Principles and applications of aquatic chemistry.' (John Wiley and Sons, Inc.: New York)

Nordstrom DK (1982) Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In 'Acid Sulfate Weathering'. (Eds JA Kittrick, DS Fanning and LR Hossner) pp. 37-56. (Soil Science Society of America: Madison, Wisconsin, USA)

Oades JM (1963) The nature and distribution of iron compounds in soils. *Soils and Fertilizers* **16**, 69-80.

Pellerin BA, Fernandez IJ, Norton SS, Kahl JS (2002) Soil aluminium distribution in the near-stream zone at the Bear Brook Watershed in Maine. *Water, Air, and Soil Pollution* **134**, 189-204.

Rabenhorst MC, Fanning DS (2002) Acid sulfate soils, problems. In 'Encyclopedia of Soil Science'. (Ed. R Lal) pp. 23-26. (Marcel Dekker, Inc.: New York)

Reinhardt RL, Norton SA, Handley M, Amirbahman A (In Press) Dynamics of P, Al, and Fe during high discharge episodic acidification at Bear Brook watershed in Maine, USA. *Water Air and Soil Pollution.*

Rosicky M, Slavich P, Sullivan L, Hughes M, Wood M (2000) Acid sulfate scalds on the NSW coast: Characterisation and potential revegetation techniques. In 'Proceedings of Workshop on Remediation and Assessment of Broadacre Acid Sulfate Soils, held at Southern Cross University, Lismore, 31 August - 2 September, 1999'. (Ed. PG Slavich) pp. 111-121. (ASSMAC: Australia)

Soil Survey Staff (1998) 'Keys to Soil Taxonomy.' (Poncahontas Press: Virginia)

Stone Y, Ahern CR, Blunden B (Eds) (1998) 'Acid Sulfate Soils Manual.' (Acid Sulfate Soil Management Advisory Committee: Wollongbar, NSW, Australia)

Stumm W, Morgan JJ (1996) 'Aquatic Chemistry: chemical equilibria and rates in natural waters.' (Wiley: New York)

Sylla M, Stein A, van Mensvoort MEF, van Breemen N (1996) Spatial variability of soil actual and potential acidity in the mangrove agrosystem of West Africa. *Soil Science Society of America Journal* **60**, 219-229.

Tulau MJ (1999) 'Acid sulfate soil management priority areas in the lower Tweed floodplains.' DLWC, Sydney, Australia.

van Oploo P (2000) Soil and pore-water relations of a coastal acid sulfate soil in northern New South Wales, Australia. PhD Thesis, University of New South Wales.

Walker PH (1972) Seasonal and stratigraphic controls in the coastal floodplain soils. *Australian Journal of Soil Research* **10**, 127-142.

White I, Melville MD, Sammut J, Wilson BP, Bowman GM (1996a) Downstream impacts from acid sulfate soils. In 'Downstream effects of Land Use'. (Eds HM Hunter, AG Eyles and GE Rayment) pp. 165-172: Department of Natural Resources, Queensland)

White I, Wilson BP, Melville MD, Sammut J, Lin C (1996b) Hydrology and drainage of acid sulfate soils. In 'Proceedings of the 2nd National Conference of Acid Sulfate Soils' pp. 103-107. (Robert J Smith and Associates and ASSMAC: Australia)

Willett IR, Crockford RH, Milnes AR (1992) Transformations of iron, manganese and aluminium during oxidation of sulphidic materials from an acid sulfate soil. *Biomineralization Processes of Iron and Manganese, Catena Supplement* **21**, 287-302.

Willett IR, Walker PH (1982) Soil morphology and distribution of iron and sulphate fractions in a coastal floodplain toposequence. *Australian Journal of Soil Research* **20**, 283-294.

Wilson BP (1995) Soil and hydrological relationships to drainage from sugarcane acid sulphate soils. PhD, University of New South Wales.

Wilson BP, White I, Melville MD (1999) Floodplain hydrology, acid discharge and change in water quality associated with a drained acid sulfate soil. *Marine and Freshwater Research* **50**, 149-157.