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# A discussion of acid sulfate soils mapping methodology as applied in Cairns, Far North Queensland

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## Abstract

This paper discusses the current methodology used by the Queensland Acid Sulfate Soils Investigation Team (QASSIT) within the QLD Department of Environment and Resource Management (DERM) to map acid sulfate soils in Queensland in a manner capable of assisting regional and local authorities to carry out land use planning, development application assessment, and similar tasks. A recently-completed mapping project in Cairns, Far North Queensland, provides an opportunity to discuss the details of the methodology, its costs and its benefits as compared with other mapping methodologies used in Australia.

## Key Words

Acid sulfate soils, mapping, sampling, methodology.

## Introduction

Coastal acid sulfate soils (ASS) are soils or sediments containing iron sulfides, primarily in the form of pyrite ($FeS_2$). They commonly form in coastal environments where a supply of iron, sulfate, and organic matter are available to bacteria in an anaerobic environment. ASS have been forming for many thousands of years and can be encountered in at least 23,000 $km^2$ of the Queensland coast, both at the surface and buried beneath newer soil layers (National Working Party on Acid Sulfate Soils 2000). ASS are relatively benign in their natural (wet or buried) environment but can be hazardous when disturbed, having the potential to cause widespread environmental damage via the release of acid and metals from the soil. As such they have become an issue of concern for environmental and planning authorities. QLD government State Planning Policy 2/02 (Government of Queensland 2002) makes ASS mapping a priority, and mapping projects are ongoing along the extensive QLD coastline.

## Spatial Representations of Acid Sulfate Soils

Acid Sulfate Soils mapping has been undertaken in a number of Australian jurisdictions within the last 15 years. Approaches have varied in their details, but have mostly focused on representing the risk or hazard of encountering ASS at a particular point in the landscape using methods similar to the 'integrated survey' approach (Hewitt *et al.* 2008). This approach has allowed for relatively rapid identification of coastal landscapes containing ASS, since it is largely based on geology data and/or aerial photo interpretation (API) accompanied by minimal confirmatory fieldwork (Naylor *et al.* 1998; Rampant *et al.* 2003; West Australian DEC 2007). Maps produced from such programs have been reasonably successful in assisting planners with ASS avoidance and management, but are not without problems. There is some suggestion that the extent of ASS has been underestimated in some landscapes (for example, compare ASS extent estimates in Rampant *et al.* 2003 and Victorian Department of Sustainability and the Environment 2009). Additionally, the concepts of risk and hazard themselves are frequently poorly understood and communicated, leading to map misinterpretation and poor decision making (Covello and Sandman 2001).

Other programs have employed more conventional fieldwork-heavy approaches which aim to map the occurrence of and depth to ASS, using remotely sensed and other data as assistants to mapping rather than primary information sources (Hill and Edmeades 2008; Malcolm *et al.* 2002). The 'free survey' technique (Reid 1988) has not recently been favoured in Australia but may be more appropriate for ASS maps, given the heterogeneity and unpredictability of low coastal plain deposits. Mapping in Queensland presently takes this approach, using field and laboratory data to delineate land units of a relatively homogeneous 'depth to ASS' as well as highlighting particular ASS features such as degree of oxidation (QASSIT 2002). However, free survey has its own problems, in particular the expense of field operations and laboratory analyses and the slower production pace. QLD ASS mapping is considered to be highly accurate at the scale at which it is produced (usually 1:50,000 or 1:25,000), but only limited areas of the state's coastline have been mapped at present and workers in many jurisdictions remain reliant on secondary mapping sources to estimate the extent of ASS.

## Planning to Map: Data Sources and Sample Site Selection

QLD ASS mapping project planning starts with a general literature search focusing on relevant landscape processes. An understanding of how landscape processes operate in the project area is essential to successfully applying the free survey technique, as sites are chosen in part to represent particular geomorphic and soil-forming environments. Of particular relevance to ASS survey are articles on estuarine formation processes (Dalrymple *et al.* 1992; Roy 1984) and Quaternary sea-level change (Pickett *et al.* 1985; Bloom *et al.* 1974), along with standard references on soil survey and laboratory methods (Ahern *et al.* 2004; Ahern *et al.* 1998; McDonald *et al.* 1990). Locally-specific information enhances understanding of the project area. In Cairns, some geological studies were available from the Geological Survey of Queensland (Jones 1985) and the QLD Department of Mines (Willmott and Stephenson 1989). Discussion of local coastal fringe geomorphology was available in Bird (1972) and Beach Protection Authority (1984).

Site selection is further guided by a combination of aerial photography and high-resolution elevation data, which together are capable of revealing landform and vegetation patterns indicative of ASS-forming environments. High-resolution aerial photography of the Cairns area was sourced from DERM archives, with the most recent rectified mosaic produced in 2006. The oldest full-coverage aerial photography from 1952 was used for comparison purposes, as development activity in the intervening decades has obscured or removed many landform and vegetation patterns.

A recurrent problem in ASS mapping is a lack of access to high-quality elevation data. Since the QLD mapping centres on detecting depth to ASS, accurate elevations are essential for normalising data across sample sites. In addition, small changes in elevation can signify changes in the depositional environment (for instance the existence of prior stream channels and swamp basins) which often imply a change in the depth to ASS and other soil characteristics. Elevation data therefore has a role in both sample site selection and map unit boundary delineation. Coastal ASS mapping project areas in QLD are naturally low-relief and low-elevation (<10m AHD), and so contour intervals >2m have limited utility. For the Cairns mapping project, Cairns City Council provided high-resolution Light Detection and Ranging (LiDAR) elevation information, allowing production of contour lines at up to 0.25m intervals. 0.5m and 1.0m contours proved most useful during field activities, revealing useful information without adding excessive and confusing detail.

Sample site densities required to produce maps of a given scale are discussed in McKenzie *et al.* (2008). The suggested rate of 1-5 sites per km$^2$ for 1:50,000 scale maps was met or exceeded by the survey team in 65% of the Cairns project area, using a standard target of 4 sites per km$^2$. While many sample sites are located on public land, site access is still often governed by landholder permission, geography, and safety. Site density in QLD ASS mapping is generally low in highly urbanised areas, national park and similar reserves, and in areas of low-lying mangrove flats. This is not necessarily problematic when producing a planning map, although it does mean that mapping data may not be well-suited to spatial statistical analysis. Urbanised areas are already disturbed significantly by excavation and filling activities and may also have undergone neutralisation treatment in places, and so a) mapping information isn't needed as much and b) sample sites within them cannot be extrapolated from spatially in the way that 'natural' sites can be, and therefore aren't very useful. Areas of marine plants (e.g. mangroves), parks and reserves, other areas are protected by several QLD laws (e.g. the *Fisheries Act 1994*) and are therefore not under significant development pressure. Mangrove areas can also safely be assumed to contain significant ASS from the surface downwards as a natural consequence of the interaction of ASS-forming factors. The maps therefore remain useful for decision-making in a planning context despite their variable sampling intensity.

## Soil Description, Field Testing and Sampling

Sampling equipment for ASS needs to extract a minimally disturbed/contaminated core large enough to describe and sample, and needs to be able to consistently reach the depth of ASS across the project area. This can be difficult to accomplish in the saturated, variable-textured sediments common to low coastal plains, but a variety of suitable machines and hand-operated samplers are available. In the case of the Cairns project, most mechanical sampling was undertaken with a GeoProbe™ model 54DT coring machine or a trailer-mounted vacuum vibro-corer. Hand sampling in difficult to access areas was undertaken using soil, sand, and tapered gouge augers. Augers were constructed to order from stainless steel, as equipment corrosion is a significant issue in ASS survey. Corrosion and sample cross-contamination is kept to a minimum by thorough cleaning at each site, using a high-pressure water sprayer. Based on QASSIT's field experience, sample site depths need to reach at least -1.0m AHD.

ASS sample site profiles are described according to MacDonald *et al.* (1990) with soil colours identified using the Munsell™ soil colour charts. This system identifies soil features in a manner consistent with other soil surveys carried out in Australia, and allows emphasis to be placed on soil diagnostic features particular to ASS (distinctive colours and mottle patterns, presence of shells and/or organic material, etc). Field tests of pH in water and pH after reaction with concentrated hydrogen peroxide are conducted according to Ahern *et al.* (1998) at 0.25m intervals down the soil profile (including at least one sample per horizon). Samples are collected at standard depths of 0.0-0.1m, 0.2-0.3m, 0.5-0.6m, 0.8-1.0m, 1.3-1.5m and every half-metre thereafter. Sample depths are adjusted when intersected by horizon boundaries, and a minimum of one sample per horizon is taken. Larger sample volumes are taken when the soil contains a high proportion of particles >2mm, since these coarse particles are discarded in the laboratory prior to grinding and analysis. Samples are stored in airtight plastic bags, accompanied by a waterproof identification tag. Bags are immediately stored in a portable fridge/freezer to minimise oxidation. In Cairns, samples were transferred to a deep-freeze unit at the end of each working day, and transported by refrigerated courier to the DERM soils laboratory in Brisbane in larger batches at the end of each sampling trip. Samples were kept frozen for no longer than three weeks before processing, although frozen storage for up to several months is possible with minimal oxidation.

## Data and Laboratory Analysis, Map Construction

All samples are thawed and air-dried at 85°C for a minimum of 48 hours, which minimises oxidation during drying, before fine-grinding to 0.5mm. ASS laboratory analysis is carried out according to Ahern *et al.* (2004; now Australian Standard 4969), with soil descriptions and field pH test results being used to guide sample analysis. Soil descriptions are entered into an electronic database and used to produce a GIS-ready dataset containing key soil and site features, lab results, and location information. Sample sites are assigned map unit codes according to the protocol described in QASSIT (2002) and then overlaid on elevation and air photo data. Units of homogeneous landform, depth-to ASS, and type of ASS are delineated by hand according to the managing project officer's best judgement and geomorphological understanding of the area. Since the map units produced by this method contain a variable number of sample sites (and because of the variations in sampling intensity discussed earlier) an intensity diagram detailing the effective scale of each map unit is prepared to accompany the ASS map itself. The final mapping product for Cairns was released mid-2009 at an overall scale of 1:50,000, and is accompanied by a detailed report on the project's findings.

## Towards a better ASS map?

The approach to mapping described above is considered capable of providing high-quality information well-suited to making planning decisions. Confidence in QLD's ASS mapping remains unquantified, however, due to an unfortunately persistent lack of funding for validation testing. Additionally, there have been few attempts to model or predict ASS landscapes (Hayne *et al.* 1996) in QLD, partly due to lack of funding and partly due to the difficulty of accurately modelling the extremely variable subsurface conditions common to low coastal plains. At best, one can comment that this kind of work does not appear to be standard practice anywhere else. It is possible that the accuracy of new integrated survey projects may improve somewhat (despite the lack of adequate correlative landscape models for coastal plains) thanks to availability of better-quality remotely-sensed data and improved laboratory procedures. However, no known attempts have been made to directly compare the accuracy of the free survey and integrated survey approaches to ASS mapping.
Separate to the debate about survey technique is the issue of how much and what type of information to include on ASS maps. For instance, mapping in some jurisdictions classifies ASS by the depositional environment in which it occurs before referring to other characteristics like depth to ASS. While such information is useful to soil scientists, it is debateable whether such information assists those who depend on the mapping most: planning staff, who generally have little knowledge of coastal geomorphology. At the 'regional' (~1:50,000) scales at which these maps are produced, the information may also be of little practical help to ASS management professionals. Similarly, information on ASS neutralising capacity may introduce a false sense of security when the prospect of disturbing 'self-neutralising' ASS arises, especially given the uneven spatial distribution of neutralising materials and the lower reliability of neutralising capacity analyses in the lab. Information to be included in ASS mapping products should be chosen based on ease of understanding and ability to improve management of ASS environments.
The rapid development of ASS mapping protocols in Australia in recent years raises the possibility of developing consistent national mapping standards. Issues of field and laboratory methodology, data analysis, and information representation such as those outlined in this paper will become significant points of discussion if such protocols are to be established.

## References

Ahern CR, Ahern MR, Powell B (1998) 'Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland'.(Department of Natural Resources, Indooroopilly, Queensland, Australia).
Ahern CR, McElnea AE, Sullivan LA (2004) 'Acid Sulfate Soils Laboratory Methods Guidelines'. (Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia).
Beach Protection Authority (1984) 'Mulgrave Shire northern beaches: a detailed study of coastline behaviour in north Queensland'.(Queensland Environmental Protection Agency, Brisbane).

Bird EC (1972) The beach-ridge plain at Cairns. *North Queensland Naturalist* **40**, 4-8.

Bloom AL, Broecker WS, Chappell JMA, Mathews RK, Mesolella KJ (1974) Quaternary sea level fluctuations on a tectonic coast. New $^{230}$Th/$^{234}$U dates from the Huon Peninsula, New Guinea. *Quaternary Research* **4**, 185-205.

Covello V, Sandman PM (2001) Risk Communication: Evolution and Revolution. In 'Solutions to an Environment in Peril (Ed. A Wolbarst), pp. 164-178 (Johns Hopkins University Press: Baltimore).

Dalrymple RW, Zaitlin BA, Boyd R (1992) Estuarine Facies Models: Conceptual basis and stratigraphic implications. *Journal of Sedimentary Petrology* **62**(6), 1130-1146.

Government of the State of Queensland (2002) State Planning Policy 2/02 Planning and Managing Development Involving Acid Sulfate Soils.

Government of the State of Queensland (1994) *Fisheries Act 1994.*

Hayne M, Graham T, Bierwirth P (1996) Development of acid-sulphate soils maps for the Australian Coastal Atlas. Australian Geological Survey Organisation.

Hewitt AE, McKenzie NJ, Grundy MJ, Slater BK (2008). Qualitative Survey. In 'Guidelines for Surveying Soil and Land Resources, 2nd Edition (Eds NJ McKenzie, MJ Grundy, R Webster, AJ Ringrose-Voase) pp. 285-306. (CSIRO Publishing: Melbourne)

Hill J, Edmeades BFJ (2008) Acid Sulfate Soils of the Darwin Region. Technical Report No. 09/2008D, Department of Natural Resources, Environment and Arts and Sport, Government of the Northern Territory.

Jones MR (1985) Quaternary geology and coastline evolution of Trinity Bay, North Queensland. Geological Survey of Queensland Publication 386.

Malcolm DT, Hall IR, Barry EV, Ahern CR (2002) Maroochy Caloundra Acid Sulfate Soil Sustainable Land Management Project Volume 1: Report on Acid Sulfate Soil Mapping. Department of Natural Resources and Mines, Report QNRM02230, Brisbane.

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS (1990) 'Australian Soil and Land Survey Field Handbook', 2nd Edition (Inkata Press: Melbourne)

McKenzie NJ, Grundy MJ, Webster R & Ringrose-Voase AJ (2008) 'Guidelines for Surveying Soil and Land Resources', 2nd Edition (CSIRO Publishing: Melbourne)

National Working Party on Acid Sulfate Soils (2000). National Strategy for the Management of Coastal Acid Sulfate Soils (New South Wales Agriculture: Wollongbar).

Naylor SD, Chapman GA, Atkinson G, Murphy CL, Tulau MJ, Flewin TC, Milford HB, Morand DT (1998) Guidelines for the Use of Acid Sulfate Soil Risk Maps, 2nd Edition. Department of Land and Water Conservation, Sydney.

Pickett JW, Thompson CH, Kelley RA and Roman D (1985) Evidence of high sea level during isotope stage 5c in Queensland, Australia. *Quaternary Research* **24**, 103–114.

QASSIT (Queensland Acid Sulfate Soils Investigation Team) (2002) Interpretation and Use of NR&W Acid Sulfate Soils Maps. Queensland Department of Environment and Resource Management, State Government of Queensland, Brisbane.

Rampant P, Brown A, Croatto G (2003) Acid Sulfate Soil hazard maps: guidelines for coastal Victoria. State Government of Victoria, Department of Primary Industries, Melbourne.

Reid RE (1988). Soil survey specifications. In 'Australian soil and land survey handbook: Guidelines for conducting surveys' (Eds RH Gunn, JA Beattie, RE Reid, van de Graaf, RHM) pp. 60-72. (Inkata Press: Melbourne)

Roy PS (1984) New South Wales estuaries: their origin and evolution. In 'Coastal Geomorphology in Australia' (ed. BG Thom) pp 99–121. (Academic Press: Australia)

Victorian Department of Sustainability and Environment (2009) Victorian Coastal Acid Sulfate Soils Strategy. State Government of Victoria, Melbourne.

West Australian DEC (Department of Environment and Conservation) (2007) Acid Sulfate Soil risk maps. Acid Sulfate Soils Fact Sheet #3. State of Western Australia, Perth.

Willmott WF, Stephenson PJ (1989) 'Rocks and Landscapes of the Cairns District' (Queensland Department of Mines: Brisbane)

# A national demonstration site for acid sulfate soil remediation in the Australian tropics – an overview of the East Trinity environmental success story

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## Abstract

Cooperation between Queensland Government scientists and CRC CARE scientists from Southern Cross University has led to a successful National Demonstration Site for the Remediation of Acid Sulfate Soils in tropical northern Australia. This 775 ha site became highly degraded and acidified (pH's <3 were common), following the construction of a large dyke through mangroves, installation of one-way floodgates, and an extensive drainage network to remove salt and grow sugar cane. The resulting and ongoing oxidation of acid sulfate soils caused severe soil and water acidification, failure of the agricultural enterprise, acid and metal discharges, and chronic fish kills in the adjacent Trinity Inlet. Conventional remediation by complete mixing of agricultural lime ($CaCO_3$) with the acid sulfate soil was estimated to cost >A$300 million. Instead, a much lower-cost, controlled, lime-assisted tidal exchange technique was trialled and is largely managing and remediating the acid sulfate soils, as well as transforming the once degraded and acidified trial area into a flourishing tidal wetland system. The remaining areas are being similarly treated and detailed measurements are being conducted. The resulting science is increasing the understanding of the complex acid, iron and sulfur chemical hysteresis involved in trying to reverse the site's extreme acidification.

## Key Words

Acid sulfate soil, environmental remediation, lime-assisted tidal exchange, wetland.

## Site and background

**Figure 1. Location of East Trinity site (lighter area across the inlet from Cairns CBD) (**Google image)

The East Trinity site is located on >700 ha of low lying coastal plain less than 1 km across the Trinity Inlet from Cairns CBD between the Wet Tropics and Great Barrier Reef World Heritage areas (Figure 1). Rainfall is strongly summer-dominant and East Trinity receives higher annual rainfall than the Cairns mean of 2220 mm due to orographic effects. Up to 4000 mm average annual rainfall drains through the site from the mountains close behind the site. Approximately 90% of the floodplain area is below the +2 m AHD contour (Australian Height Datum or mean sea level). Prior to disturbance, East Trinity was an ecologically diverse area of estuarine floodplain with mangrove communities below the 1 m AHD surface contour, and samphire communities on supratidal flats between 1–2 m AHD (Smith *et al.* 2003). The site experienced a maximum tidal range of up to 3.6 m, with highest tides to 1.9 m AHD.

In the 1970's a large earth sea wall or dyke was constructed across creeks and drainage lines, with one-way floodgates or tidal gates systems installed across the two main creek outfalls—effectively cutting off the tidal influence of Trinity Inlet. More that 27 km of drains were constructed and the land surface was laser levelled in order to reduce water-logging and leach salt out to enable sugar cane production. The lowering of the natural watertable exposed the framboidal pyrite ($FeS_2$) in the potential acid sulfate soils to air, causing oxidation and the production of sulfuric acid, creating a highly acidified landscape and releasing acid and toxic levels of iron, aluminium and other heavy metals from the soil into the waterways. This resulted in episodic fish kills both within the site and in Trinity Inlet which flows into the Great Barrier Reef Marine Park World Heritage Area. The drainage, removal of tidal influence, resulting in an acidified iron-rich landscape, together with clearing, resulted in loss of on-site mangroves (Figure 2). The alteration of hydrology and the acidification also affected adjacent wetlands outside the dyke, as evidenced by the death of mangroves (see Figure 2). In much of the drained areas, dense communities of *Melaleuca sp*. gradually colonised the highly acidified soils (commonly pH <3). In the first 25 years following disturbance, Hicks *et al.* (1999) estimated that the East Trinity site exported 72 000 tonnes of sulfuric acid (i.e. $1.5 \times 10^9$ mol $H^+$). More recent soil surveys (Smith *et al.* 2003) confirms that much of the potential acidity in the partially oxidised upper metre has been converted to existing acidity (up to 690 mol $H^+$ $tonne^{-1}$), with substantial amounts of retained acidity due to jarosite and other relatively insoluble, acidic hydroxy-sulfate minerals also present. Below the oxidised layer potential acidity of up to 4100 mol $H^+$ $tonne^{-1}$ (6.6 % oxidisable sulfur) was recorded.

**Acid sulfate soil management approach**

Conventional remediation by complete mixing of agricultural lime ($CaCO_3$) with the acid sulfate soil was estimated to cost >A$300 million—far exceeding any potential budget. Therefore the remediation goal for East Trinity was to treat and ultimately prevent the acidic (pH <3) and metallic discharges off-site and to have water of acceptable quality (pH >6) exiting the site on a consistent basis, in all seasonal conditions. Ideally, the selected management system would ultimately not need costly active ongoing treatment. In order to achieve this, a significant decrease in the acid and metal production from acid sulfate soils (ASS) on the site is required, together with prevention of further oxidation of the large store of pyrite still within the soils, particularly below the surface layers.

Lime-assisted tidal exchange was trialled as the principal acid sulfate soil management strategy for the East Trinity site. It involves the progressive and partial re-introduction of tidal waters through adjustable tidal gates, allowing both ingress and exit on each tide, together with the strategic addition of hydrated lime ($Ca(OH)_2$) to buffer incoming tidal water (and outgoing tidal water as necessary) to ensure that off-site acid and metal discharges were minimised and eventually halted. To make sure that treatment was timely and appropriate, and met 'environmental duty of care' an automated water monitoring network (downloading via mobile telephony) was established across the site, with soil and groundwater baselines also sampled at key locations. The lime-assisted tidal exchange was expected to:

neutralise existing acidity in the water column prior to discharge off-site;

neutralise existing acidity in the upper oxidised soil layers;

hydraulically push some of the existing surface soil acidity deeper into the profile where discharge into drains becomes unlikely and reduction reactions can neutralise some acidity;

precipitate iron, aluminium and heavy metals on the site as pH rises, rather than discharge off-site; and

limit further acid production and metal generation from potential ASS layers (still with huge pyrite reserves), through limiting oxygen to those layers by keeping them wet with regular tidal inundation.

**Figure 2. Acidified and iron-stained Firewood Creek, 1980's. Note iron staining from actual acid sulfate soils inside the dyke (left) and dead mangroves from acid and hydrological changes outside of the dyke (right).**

## Overview of results

In the areas which have been receiving regular tidal inundation for some years, substantial increases in soil pH (e.g. pH increases from 3 to 6; Ahern *et al.* 2008) and decreases in titratable acidity provide evidence for the neutralisation and hydraulic suppression of existing soil acidity. Trends in soil field pH and Titratable Actual Acidity (TAA) (Ahern *et al*. 2008) are showing substantial improvements as a result of lime-assisted tidal exchange for the trial Hills Creek catchment at the East Trinity site. Decreases in soil redox potential also show a change from oxidising and acid producing conditions to a more reducing state where pyrite oxidation formation and the production of alkalinity are favoured. The significant improvements in soil and water quality monitoring data is reflected in the environment, with vegetation and a variety of mangrove species (up to 4 m tall) returning to former degraded areas (see Figure 3). Importantly, the pH of water exiting the site has consistently been above pH 6 (Johnston *et al.* 2008, 2009), despite some area of persistent acidic drainage in the upper catchment areas. Levels of dissolved metals measured at discharge points have also dramatically improved under the lime-assisted tidal exchange regime and now meet ANZECC and ARMCANZ (2000) water quality guidelines. Surveys conducted by Queensland DPI Fisheries officers confirm that the previously sterile creeks that were impacted by acid and metals now support healthy populations of fish and crustaceans (Russell 2006).

## Conclusion

In the process of remediating the acid sulfate soils, the degraded and acidified soils and contaminated drains and streams in the trial area are being transformed into a flourishing tidal wetland system. While great success is being achieved, this is only a permanent solution to the acid sulfate soil problem if the site is kept regularly wet perpetually (using tidal exchange). Any reversion to former drained conditions without regular tidal inundation would allow oxidation of the reformed sulfides and would reverse the gains, allowing re-creation of an environmental hazard.

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**Figure 3. Lime-assisted tidal exchange has transformed this formerly acidified area (left photo 2003) of the East Trinity site with mangroves up to 4 m high (right photo 2008)**

## References

Ahern CR, Smith CD, McElnea AE, Finch N (2008) Lime-assisted tidal exchange reduces acidity of dyked acid sulfate soil at East Trinity, northern Australia. In Proceedings of 6ASSARD Conference, 16–20 September 2008, Guangzhou, China. ISBN 978-7-5359-4714-7.

ANZECC and ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. Canberra, Australia.

Hicks WS, Bowman GM, Fitzpatrick RW (1999). East Trinity acid sulfate soils. Part 1: Environmental hazards. CSIRO Land and Water Technical Report. 14/99. Available from http://www.clw.csiro.au/publications/technical99/tr14-99.pdf.

Johnston SG, Bush RT, Sullivan LA, Burton ED, Smith, CD, Martens MA, McElnea AE, Ahern CR, Powell B, Stephens LP, Wilbraham ST, van Heel S (2009). Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coastal and Shelf Science* **81**, 257–266.

Johnston SG, Bush RT, Sullivan LA, Smith CD, Martens MA, McElnea AE, Ahern CR, Powell B, Stephens LP, Wilbraham ST (2008) Assessing the effects of restoring tidal exchange upon water quality in two diked and drained estuarine creeks in northern Australia. In Proceedings of 6ASSARD Conference, 16–20 September 2008, Guangzhou, China. ISBN 978-7-5359-4714-7.

Russell DJ (2006) Remediation of acid sulfate soils at East Trinity, north Queensland: effects on Fisheries and water quality. In: Proceedings 'Catchments to Coast': The Society of Wetland Scientists 27th International Conference and the Australian Marine Sciences Association 44th Annual Meeting, 9–14 July 2006, Cairns.

Smith CD, Graham TL, Barry EV, Adams JJ, Ahern CR (2003) Acid sulfate soil and stratigraphic assessment. In 'Demonstration of Management and Rehabilitation of Acid Sulfate Soils at East Trinity' (Eds CD Smith, MA Martens, CR Ahern, VJ Eldershaw, B Powell, EV Barry, GL Hopgood, KM Watling) (Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia)., ISBN0734524668, QNRM03062.

# A systematic analysis procedure incorporating the chip-tray incubation method for the hazard assessment of Acid Sulfate Soils in the Murray-Darling Basin

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## Abstract

During a Murray-Darling Basin wide assessment of Acid Sulfate Soils (ASS), soil samples from over 3500 soil profiles were collected by staff from state and regional Natural Resource Management (NRM) agencies and submitted for pH incubation analysis. The large number of soil samples triggered the requirement for a new systematic analysis procedure to be developed. A reliable and systematic analysis procedure using chip trays was successfully developed and tested, which allowed: (i) a rapid and convenient means to incubate the soils in order to assess the hazards of soil acidification on all samples based mainly on pH incubation measurements and (ii) streamlined data acquisition for a wide range of ASS subtypes covering over 8,000 soil samples.

## Key Words

pH, incubation, Acid Sulfate Soils, wetland, Murray-Darling basin, chip-tray.

## Introduction

Acid Sulfate Soils (ASS) is the name given to those soils containing soil materials affected by iron sulfide minerals. These soils either contain sulfuric materials or have the potential to generate sulfuric materials in amounts that have an effect on soil pH. The Murray-Darling Basin (MDB) is currently experiencing the worst drought conditions in recent history. Declining water levels have caused non-acidic soils with previously accumulated sulfide minerals in wetlands, creeks, and lakes to be exposed to the atmosphere and undergo oxidation reactions, which generate sulfuric material and can turn these soil material acidic (pH < 4). Following their oxidation, ASS can cause detrimental impacts on the surrounding ecosystem in a variety of ways. The release of sulfuric acid and toxic elements can lead to the acidification of water bodies and toxic impacts of wetland ecosystems, aquatic biota and human health. Additionally, the disturbance of monosulfidic material can cause the surface waters to become rapidly deoxygenated.

The MDB ASS Risk Assessment Project, initiated by the Murray-Darling Basin Authority (MDBA), aims to assess the spatial extent of, and risks posed by these hazards in wetlands of environmental significance, as well as those that could pose a risk to surrounding waters. These wetlands were subjected to a tiered assessment process, whereby wetlands were screened through a desktop assessment stage, followed by a rapid on-ground appraisal (RAP), and then detailed on-ground assessment if results of previous stages indicate an increased likelihood of occurrence of ASS. More than 19,000 wetlands underwent desktop assessment, and this identified approximately 1,450 wetlands considered to have a higher likelihood of ASS occurrence which required further assessment. The RAPs were performed by state and regional NRM agency staff that had completed one of the six ASS rapid assessment training courses.

During the RAP, wetland soil samples were collected from up to 3 different soil profiles within a wetland representing a toposequence. As part of the RAP these soil samples were then submitted for incubation analysis. pH incubation is a method whereby ASS are kept in a moist state and exposed to the atmosphere allowing them to undergo oxidation reactions in an attempt to simulate the natural acidification behaviour of the soil. If the soil in question is hypersulfidic the pH will reduce substantially during incubation to a pH < 4, as a result of sulphide oxidation and hence pose an acidity hazard (Sullivan *et al.* 2009a,b). The use of pH incubation for classification is often considered preferable to other methods, such as peroxide addition, because the result of the experiment is arguably more representative of what would be expected to occur in the field (Dent 1986).

A total of 1,329 wetlands from South Australia (SA), New South Wales (NSW), Victoria and Queensland (QLD) were assessed resulting in over 8,000 soil samples being submitted for pH incubation analysis. The large number of samples triggered the requirement for, and allowed the testing of, a new systematic analysis procedure.

## Methods

The analysis procedure and associated pH incubation method using plastic chip-trays (Fitzpatrick *et al.* 2010) for the analyses of MDB soil samples is illustrated in the flow chart outlined in Figure 1. It illustrates the systematic order in which observations and analyses were conducted. Sections of the flow chart are examined further under subheadings below.

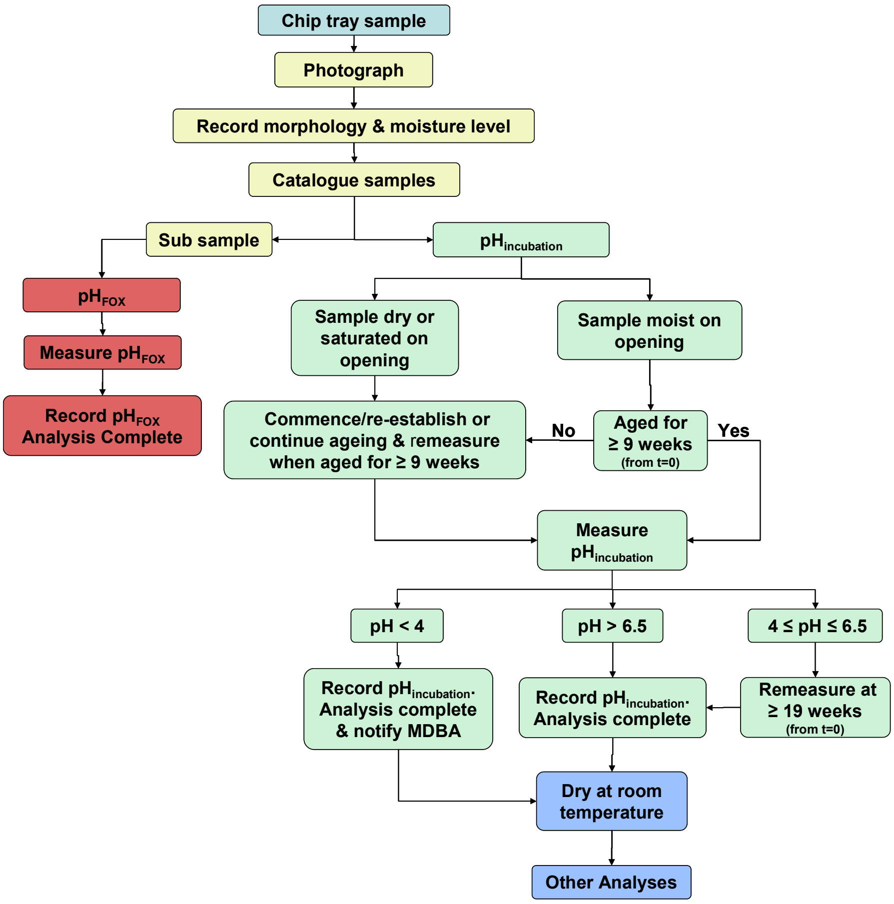


**Figure 1. Flow chart of the analysis procedure and pH incubation method of chip-tray samples.**

*Sample collection and preparation*

Approximately 50g of soil was collected at up to 3 depths (0-5cm, 5-30cm, and >30cm), designated as top, middle and bottom and placed into chip-trays (Figure 2). This was repeated for up to three different profiles selected along a toposequence. The samples were then moistened if dry to initiate incubation before wrapping the chip-tray tightly in Gladwrap® to prevent desiccation and spillage during transport and posting to the laboratory. Thus, the incubation period start date is the date of collection in the field. The practical consequence of this is that all samples for a wetland can be analysed simultaneously without the need to consider, for example, which samples were moist in the field and which were dry and not moistened until a later stage.

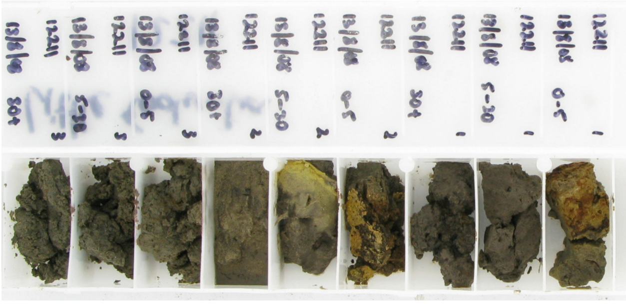


**Figure 2. Photograph of plastic chip-tray filled with soil from a wetland in South Australia.**

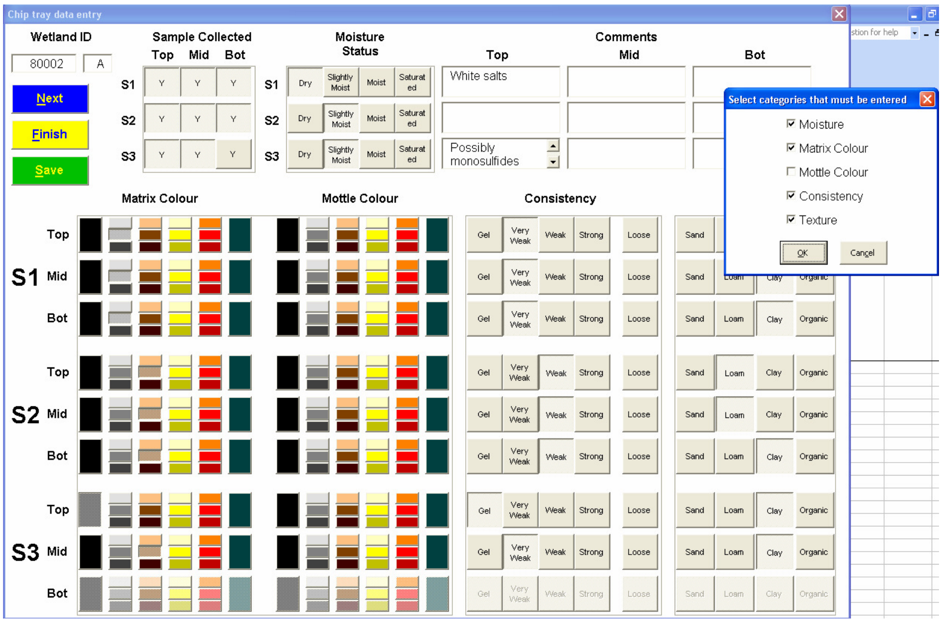
In previous studies, small squares of non-antibacterial sponge were placed in chip-trays over the soil samples to help reduce desiccation. This was later revised when many sponges were found to be decomposed upon opening in the laboratory. The addition of organic matter from the decomposition of the sponge had the potential to adversely affect results. The sponges were also found to remove the permanent marker labelling. Due to this the use of sponges was discontinued. Also in support of this move, it was later realised that the chip-tray construction was ideally suited to prevent excessive desiccation, whereby a slightly moistened sample has been found to remain at or slightly below field capacity for periods up to 9 weeks without attention.

*Photography*

Photographs of chip-tray samples from each wetland were obtained for reference purposes. Each photograph was acquired using an Ortary Photosmile$^{TM}$ light box, which provided consistent lighting for natural white-balanced and shadow-free photographs.

*Basic morphology and moisture level*

A simplified soil morphology description was collected for each sample. Descriptors were chosen on the added usefulness of the information they provide in relation to ASS hazard. Chosen descriptors include moisture status, colour, consistence, texture, and any other comments. Because a high sample throughput was essential for this project each morphology descriptor was refined to a limited number of choices. These are shown in Figure 3. To further assist with sample throughput, a virtual tick sheet was created in Visual Basic for Applications (VBA), which allowed the user to rapidly input morphology data by simply clicking on the appropriate buttons. When completed the virtual tick sheet would then insert the recorded information into an Excel® spreadsheet in the required format. Albeit limited, the simplified soil morphology description allowed the capture of key morphology information that otherwise would not have been collected.



Chip tray data entry

Wetland ID: 80002 A

Sample Collected (Top / Mid / Bot): S1 Y Y Y; S2 Y Y Y; S3 Y Y Y

Comments, Top: S1 White salts; S3 Possibly monosulfides

Select categories that must be entered

☑ Moisture
☑ Matrix Colour
☐ Mottle Colour
☑ Consistency
☑ Texture

**Figure 3. Screen capture of virtual tick sheet with details filled out for wetland ID 80002.**

The moisture status of each sample was recorded on a scale of 1 to 4. This was done each time the chip-tray was opened. During the incubation period moisture is required for the oxidation reactions to occur. Hence, this observation was used to determine whether or not a sample had been aging between the time of collection in the field and first opening in the laboratory or any subsequent openings.

*pH peroxide (pH$_{FOX}$)*

As part of the analysis procedure soils were subjected to the peroxide field oxidation method (pH$_{FOX}$). The method involves measuring the soil pH after the rapid oxygenation of reduced inorganic sulfur materials caused by the addition of hydrogen peroxide. pH$_{FOX}$ provides another means of assessing the acidity hazard.

*pH incubation*

All soil samples, except for soil surface efflorescences, were submitted for pH incubation analysis. The soil sample was homogenised by mixing with a glass rod while deionised water was added until an approximate soil-to-solution ratio of 1:1 was achieved. These steps and the pH measurement take place in the chip-tray. All pH measurements were obtained using an Ionode$^{TM}$ intermediate junction electrode that was calibrated at pH 4 and 7 at the beginning and end of each sample batch. The electrode was connected to a WP-81 TPS$^{TM}$ pH meter and referenced against temperature with a Pt sensor.

If a sample was found to have a moisture status of 2 or 3 (slightly moist or moist) on receipt it was stored and allowed to undergo incubation for ≥ 9 weeks starting from the date of collection. If a sample was found to be dry or saturated (moisture status 1 or 4) the appropriate amount of water was added or subtracted before incubating the sample for ≥ 9 weeks starting from that days date.

If a soil sample was found to acidify to a pH < 4 after an incubation period of 9 weeks or more, that sample was classified as hypersulfidic material and analysis for that sample was considered complete. Additionally, if a soil sample did not acidify over the same period to a pH below 6.5 analysis was also considered complete. In the case that the pH of a sample lies between a pH of 4 and 6.5 ($4 \leq pH \leq 6.5$) incubation is continued for a further ≥ 10 week period (i.e. total incubation period ≥19 weeks) before pH re-measurement. For these samples, analysis was considered complete after this second incubation period.

Samples were discriminated this way because it was reasoned that if after ≥ 9 weeks of incubation the pH of a sample did not drop below a pH of 6.5 the sample will not age to a pH < 4 given more time. This assumption was based on the fact that if a sample has a pH of > 6.5 it still contains an amount of acid neutralising capacity (ANC) and, hence, has ability to buffer acidity and resist changes in pH.

Ideally sample analysis would continue until a stable pH was obtained as suggested in recent literature (Sullivan *et al.* 2009b). However, when the scope of the project does not allow for this it is suggested that this method of sample discrimination is adopted as a suitable alternative.

## Results and Discussion

The systematic analysis procedure has functioned successfully throughout the project allowing the large number of samples to be managed and analysed efficiently and accurately. The analysis procedure has so far been used in the identification of over 400 wetlands containing hypersulfidic soils. Conversely, the analysis procedure has identified approximately 930 wetlands that are unlikely to contain ASS with hypersulfidic materials, a potentially greater achievement when considering the necessity for economical assignment of finite funds and time.

## Conclusion

The use of the chip-tray pH incubation method like other incubation methods is considered favourable over other methods for classification of hypersulfidic materials because it is a direct measurement and produces a more realistic result for testing of hypersulfidic soil materials in ASS by allowing the soil to "speak for itself" (Dent 1986). However, incubation methods are also very time exhaustive in that in some instances it can require > 19 weeks to give a conclusive determination and that soil samples must be periodically monitored for moisture status during the incubation. The systematic analysis procedure presented here provides a tested means that streamlines data acquisition, assures correct hazard identification, and is able to handle these and other problems even with very large sample numbers.

## References

Dent DL (1986) 'Acid Sulphate Soils: A Baseline for Research and Development'. I.RI Pub. No. 39. (International Institute for Land Reclamation and Improvement: Wageningen).

Fitzpatrick R, Grealish G, Shand P, Merry R, Creeper N, Thomas M, Baker A, Thomas B, Hicks W, Jayalath N (2010) Chip-tray incubation – a new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication. In '19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia'. Published on CDROM (In press).

Sullivan LA, Fitzpatrick RW, Bush, RT, Burton ED, Shand P, Ward NJ (2009a) 'Modifications to the classification of acid sulfate soil materials'. Southern Cross GeoScience Tech Report 309.

Sullivan LA, Ward NJ, Bush RT, Burton ED (2009b) Improved identification of sulfidic soil materials by a modified incubation method. *Geoderma* **149,** 33 – 38.

# Acid sulfate soil remediation: Drainage water quality as influenced by tidal forcing

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## Abstract

The aim of this study was the assessment of water quality at the landward periphery in a broadacre coastal acid sulfate soil area in tropical Queensland, Australia, as influenced by remediation by lime assisted re-introduction of tidal exchange. Focus lay on characterising alkalinity import to and acidity release from individual drains on the investigation site. The parameters determined were water level, pH, electrical conductivity, measured net alkalinity/net acidity, ferrous ion and total dissolved iron, aluminium and manganese. The parameters displayed gradients which could largely be attributed to the tidal influence. With increasing distance from the ocean, water level fluctuations in the drains became less pronounced, and the onset of the turning of the tides occurred later, as did the saline or brackish water influence. Net acidity and the metal concentrations decreased with increasing water levels during flood tide and then increased with decreasing water levels during ebb tide. Net alkalinity behaved in the opposite manner. While water quality in the lower to middle reaches of a drain clearly responded to the incoming water *via* neutralization, dilution, or flocculation, the water in the upper reaches was merely pushed back and forth by the tidally induced water level changes.

## Key Words

Reclamation, tidal exchange, neutralization, net alkalinity, net acidity, titratable acidity

## Introduction

A rigorous management program is crucial to alleviate acid sulfate soils' (ASS) impacts if disturbance has occurred or must be undertaken. A special challenge is presented by broadacre degraded coastal wetlands that have not been under any use for sometimes decades since bunding and drainage, but still continue to produce sulfuric acid and the notorious ASS impacts. Such areas suffer most from restricted access and hence limited applicability of basic agricultural management principles (particularly the incorporation of neutralizing agent into the soil). An option to manage them is the re-introduction of tidal influence. It provides means to treat the acidified soils and waters across such sites by inundating the soils (which slows down or halts continued pyrite oxidation) and by using the inherent buffering capacity of seawater (which neutralizes existing acidity). The extent to which this management can be successful is largely determined by the propagation of seawater up the waterways and into the area of acidified ASS, where its buffering capacity will decrease due to fresh water dilution and neutralizing of acid discharges in the catchment. Hence it is these dynamic aspects of the contained neutralization potential of water in the upper sections of waterways that are crucial to ASS remediation. In this study, the dynamic aspects of water quality along the upper section of a creek and its tributary drains were investigated in a tropical ASS area managed by lime-assisted tidal exchange. The aim was to assess the incoming water regarding its potential to neutralize acidity and to observe patterns of acidity release from individual drains during ebb tide.

## Material and Methods

### *Investigation site*

The investigation site – Hills Peat with its adjacent grassland – of this study lies on the eastern periphery of the East Trinity site. East Trinity lies less than 1 km across the Trinity Inlet from the Cairns Central Business District (145°46'E, 16°56'S) in North Queensland, Australia (Figure 1) and comprises two floodplains (Hills Creek and Firewood Creek) with >700 ha of ASS. East Trinity was bunded and drained in the early 1970s as a first step of a major drainage scheme to facilitate agricultural development. Severe actual ASS development with the typical adverse on- and off-site effects had taken place until tidal exchange had been re-introduced and assisted by hydrated lime application in the year 2002 (refer to Smith *et al.* 2003 and

Ahern *et al.* 2010 for a detailed description of the East Trinity site and the remediation actions). A level of 0.5 m AHD (Australian Height Datum) was selected as the upper limit of tidal exchange (the tidal amplitudes external to the bund wall typically range from about –1.6 to 1.8 m AHD) as a low risk strategy capable of preventing saline encroachment to neighbouring properties where agricultural crops are grown. However, the majority of actual ASS on the investigation site can be found below 1 m AHD so that a continued acidity production can take place in those soils. Little was known on the propagation of seawater more than three kilometres up Hills Creek into the 35 ha investigation site with its numerous man-made ditch drains. Thus, the aim of this study was to investigate the patterns of alkalinity import into the drains and of acidity export from the drains along upper Hills Creek.

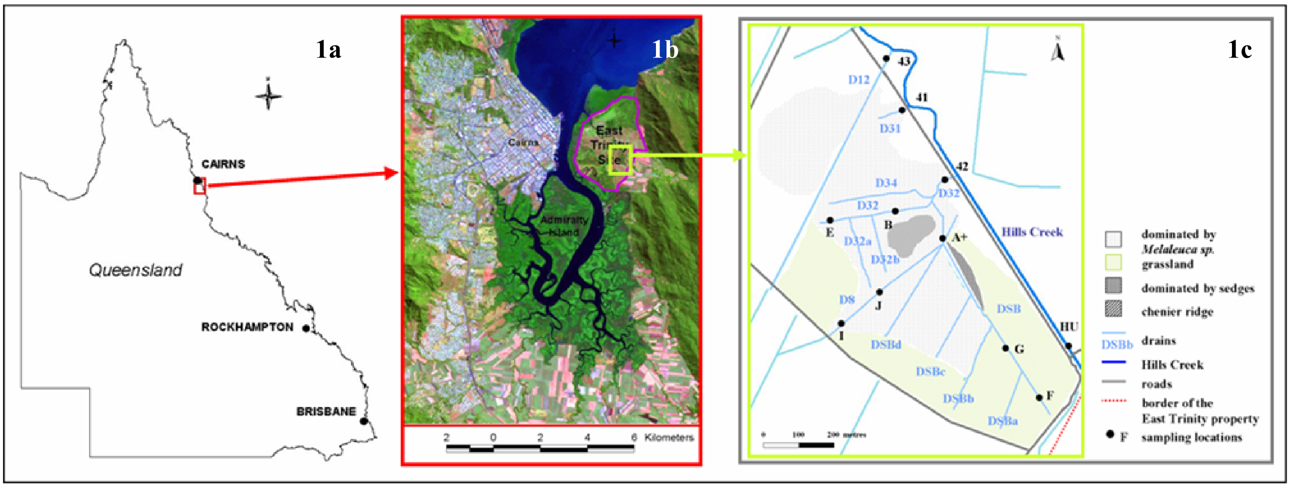

**Figure 1. Location of the East Trinity site in relation to Queensland, Australia (1a) and to Cairns and Trinity Inlet (1b) (by courtesy of CD Smith) and location of the investigation site with the sampling locations and vegetation units during the investigation period between December 2003 and May 2004 (1c).**

### *Sampling*

During the investigation period between December 2003 and May 2004, several sampling days were conducted that covered a full tidal cycle (i.e. 12 hours). One of them was the 15th of April 2004 and it serves as an example. Sampling and on-site determination of the parameters water level, pH value and electrical conductivity (EC) took place of 11 locations across the investigation site. The water quality monitoring and sampling depth was between 10 and 20 cm below the water surface. Water level readings and samples were taken at intervals of 20 to 60 minutes. Water samples were divided into a maximum of three sub-samples: one was frozen for later analysis of net alkalinity/net acidity, another was immediately filtered and put into pre-filled Ferrozine test tubes for the determination of ferrous ion ($Fe^{2+}$), another one was filtered and acidified for the determination of total dissolved iron (Fe), aluminium (Al), and Manganese (Mn).

### *Net alkalinity/net acidity*

Net acidity was essentially determined by following the APHA (1998) standard method, including the peroxide oxidation step. The method was modified by defining a stability criterion for the pH values because experience with the titration of the acid sulfate water samples from East Trinity showed a tendency of the samples to shift strongly in pH upon adding either the acid or the base. A pH was defined to be stable after not having changed for 20 seconds. Furthermore, an additional pH-endpoint was included into the titration schedule at pH 6.5 to make results from the titratable actual acidity (TAA) applied for soil material from ASS directly comparable to water acidities.

The APHA standard titration procedure directly delivers a value for net acidity (Kirby and Cravotta 2005a; 2005b). Net acidity is equal to negative net alkalinity. Net alkalinity is a practical and direct means of expressing the requirement of a water of neutralization, with a negative value indicating that it lacks alkalinity (or has excess acidity) with respect to the reference pH.

### *$Fe^{2+}$ and total dissolved metals*

The semi-quantitative Ferrozine test is used for the photometric determination of aqueous ferrous ion ($Fe^{2+}$). The sub-sample was sucked up into a 60 mL Terumo plastic syringe and filtered with a syringe filter with 0.45 µm pore diameter (Sartorius minisart syringe filters or Pall Life Sciences Acrodisc syringe filters).

Sample was added to the Ferrozine test solution until a weak violet colour developed, or if no recognizable colour developed, up to approximately 9 mL of sample was added and analysed within four weeks in a GBC UV-VIS spectrophotometer with a 10 mm flow-through cell and autosampler at 562 nm wavelength. The same filter and syringe were used for preparing an acidified sub-sample for the dissolved metals analysis. 50 mL of sample were filtered into a 60 mL centrifuge tube containing pre-measured 0.5 mL of 1 N nitric acid. ICP-AES analyses for the total content of dissolved aluminium, iron, and manganese were done with a Thermo Jarrell Ash "Iris Duo" ICP being operated at 1150 W.

## Results and Discussion

Figure 2 shows the variations in water level, net alkalinity to pH 6.5, $Fe^{2+}$ and total dissolved Al on 15th April 2004 for the sampling locations along the drain DSB. Similar observations were made along other drains on site as well as on other full or partial tidal cycle sampling days. DSB is fed with water from Hills Creek during high tide *via* location 42 (Figure 1c). The water levels in the drain fluctuated clearly with the tidal cycles. The water levels at location A+ in the lower reaches of DSB were lower throughout the full tidal cycle than those at locations G and F in the upper reaches of DSB.

Although it is common in the ASS context to report net acidities rather than net alkalinities, the net alkalinity approach (Kirby and Cravotta 2005a; 2005b) is used in this study for its practicability because it directly indicates whether a sample lacks alkalinity (negative net alkalinity) or has excess alkalinity and hence neutralizing capacity (positive net alkalinity) with respect to the reference pH. The reference point selected for net alkalinity was pH 6.5, which approximates the discharge aim of water which exits the East Trinity site (according to the marine guideline levels, ANZECC and ARMCANZ 2000). Most locations across the investigation site displayed negative net alkalinities in most of the samples throughout the sampling day. Hence they required the addition of neutralizing agent. The 'tidal' gradient that was observed for net alkalinity at most locations corresponded clearly to the water level changes. Values were highest in the two hours around high tide, then more or less steadily decreased to pre-high tide levels. All locations displayed this behaviour with the exception of the end-locations in all drains (location F in Figure 2).

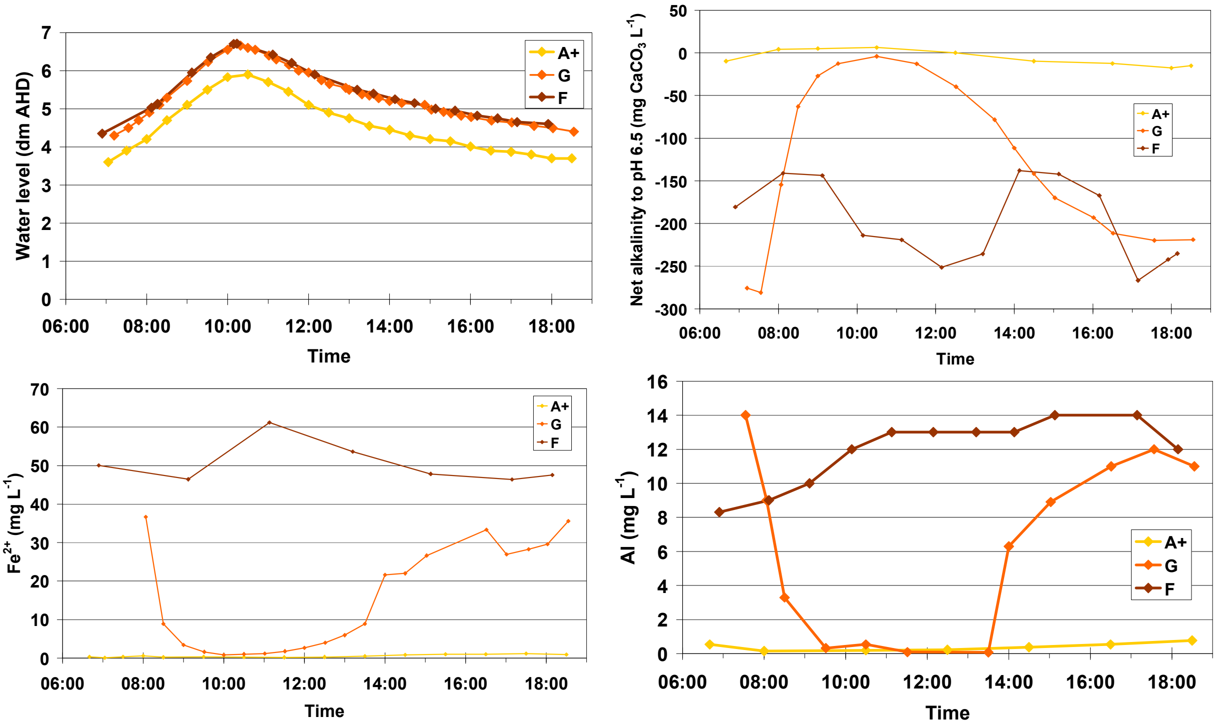

**Figure 2. Water levels, net alkalinities to pH 6.5, $Fe^{2+}$ concentrations and total dissolved Al concentrations as determined for the sampling locations along DSB during a full tidal cycle sampling day on 15th April 2004.**

The increased net alkalinities which were observed at most locations around high tide can be attributed to two main mechanisms, which are neutralization and dilution. Seawater possesses an inherent buffering capacity of 2.4 mol $H^+$ $m^{-3}$ (equalling 120.1 mg $L^{-1}$ $CaCO_3$ equivalents) (Dent and Bowman 1996) which is conferred largely by bicarbonate ions. Water some distance up a river or creek may have little bicarbonate left, particularly if there are acid discharges in the catchment and fresh water contributions from further up the catchment (Ahern *et al.* 2000). The latter corresponds to the fact that seawater buffering capacity by far exceeds that of fresh water (e.g. Dent 1986).

The decreasing net alkalinities with decreasing water levels correspond well with the idea that the share of soil pore water increases with decreasing drain water level, because soil drainage increases. Thus, the solutes (including largely acidic components) that are presumably transported with this soil drainage water and the reactions of these solutes with the water in the drain will decrease the net alkalinity. From the results of the $Fe^{2+}$ and the total dissolved metals it is clear that in fact there were increasingly more solutes at decreasing water levels, often particularly in the second phase of ebb tide. A third mechanism which plays a role with respect to solutes concentrations is flocculation due to changing conditions (e.g. pH, redox potential, dissolved oxygen). This is supposed to occur largely at the onset of salt water influence or where two other different water bodies meet.

## Conclusion

The parameters displayed gradients which could largely be attributed to the tidal influence. While water quality in the lower to middle reaches of a drain clearly responded to the incoming water *via* neutralization, dilution, or flocculation, the water in the upper reaches was apparently merely pushed back and forth by the tidally induced water level changes. Hence, it is recommended that a direct application of hydrated lime into the upper sections of the drains along the upper Hills Creek is carried out to further improve water and soil quality on the investigation site. However, quantifications of water flow rates as opposed to mere concentrations are imperative to estimate the hazard that is contained in specific drainage waters, and to calculate appropriate application volumes of hydrated lime.

## Acknowledgements

The authors gratefully acknowledge the German Academic Exchange Service (DAAD) for the financial funding of Sylvia Warnecke's stay with QASSIT and CSIRO Land and Water as part of DAAD's Master Thesis program. The authors also thank everybody who helped preparing and conducting the full tidal cycle sampling days and who assisted with helpful observations and comments in understanding Hills Peat.

## References

Ahern CR, Eldershaw VJ, Watling KM (2000) Principles of management: mitigation options requiring greater caution. In 'Acid Sulfate Soils: Environmental Issues, Assessment and Management, Technical Papers'. (Eds Ahern CR, Hey KM, Watling KM, Eldershaw VJ), Brisbane, 20–22 June, 2000. Department of Natural Resources, Indooroopilly, Queensland, Australia.

Ahern CR, Smith CD, McElnea AE, Bush R, Johnston S, Wilbraham S, Van Heel S, Powell B, Malone B (2010) A national demonstration site for acid sulfate soil remediation in the Australian tropics – an overview of the East Trinity success story. These Proceedings.

ANZECC and ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. Canberra, Australia.

APHA (1998) Acidity (2310)/Titration method. In 'Standard Methods for the Examination of Water and Wastewater', 20th edition (American Public Health Association: Washington, DC).

Cook FJ, Hicks W, Gardner EA, Carlin GD and Froggatt DW (2000) Export of Acidity in Drainage Water from Acid Sulphate Soils. *Marine Pollution Bulletin* **41 (7-12)**, 319-326.

Dent DL, Bowman G (1996) Quick, quantitative assessment of the acid sulphate hazard. CSIRO Division of Soils, Divisional Report No. 128.

Dent DL (1986) Acid sulphate soils: A baseline for research and development. (ILRI: Wageningen, The Netherlands).

Kirby CS, Cravotta III CA (2005a) Net alkalinity and net acidity 1: Theoretical considerations. *Applied Geochemistry* **20 (10)**, 1920-1940.

Kirby CS, Cravotta III CA (2005b) Net alkalinity and net acidity 2: Practical considerations. *Applied Geochemistry* **20 (10)**, 1941-1964.

Smith CD, Martens MA, Ahern CR, Eldershaw VJ, Powell B, Barry EV, Hopgood GL (2003) Demonstration of Management and Rehabilitation of Acid Sulfate Soils at East Trinity: Technical Report. Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia. ISBN 0 7345 2466 8.

# Acid Sulfate Soil Toposequences in Wetlands of the Lower River Murray

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## Abstract

Water levels have fallen dramatically in wetlands along a 250 kilometre length of the lower River Murray between Blanchetown (Lock 1) and Wellington, South Australia, in many cases exposing acid sulfate soil materials. The objective of this study was to provide critical baseline information to support management decisions for the soils and wetlands to minimise impact of these inland region acid sulfate soils. This paper: 1) presents an overview of the acid sulfate soil characteristics, 2) demonstrates the utility of toposequence models to provide an understanding of soil variation, and 3) describes how the information is used to support planning of management options.

For 62 wetlands, a total of 198 sites were investigated. Acid base accounting data identified 534 out of 653 samples (82%) as having a positive net acidity. Classification of soil material based on pH and chromium reducible sulfur values identified acid sulfate soil material in 270 out of 638 samples (43%). Forty-seven of the sixty-two wetlands (71%) have an acid sulfate soil extent within the wetland that is of concern. Conceptual toposequence models were developed which identified a recurring pattern of soil variation and provided a useful means to communicate information to decision makers and managers.

## Key Words

Acid sulfate soils, toposequences, wetlands, River Murray.

## Introduction

Wetlands along a 250 kilometre length of the lower River Murray between Blanchetown (Lock 1) and Wellington, South Australia (Figure 1) provide essential ecosystem services that include maintaining water quality in the river channel, providing habitats for native fish, frogs and other fauna, and recreational areas as well as for town supply and agriculture. Unprecedented drought during the past decade has recently led to significantly lowered river weir-pool levels, previously from about +0.75m AHD, down to -0.5m AHD, causing disconnections between numerous wetlands and the river channel. Nearly all of the 77 wetlands in this region are now dry, exposing acid sulfate soil materials that were previously covered with water. There is concern that these soils will be a hazard to ecosystem function and river water quality through acidification, release of toxic metals and de-oxygenation of water and environmental degradation of landscapes due to: (i) acidic soil, (ii) air borne dust, (iii) transport of acidity and metals once water levels rise, and (iv) acidic pulses during and following rainfall events.

Previous work by CSIRO Land and Water and others in subaqueous soil (lakes and rivers) and wetland environments in this region have identified various occurrences of sulfidic, sulfuric and monosulfidic black ooze materials in acid sulfate soils (see recent review paper and key references in Fitzpatrick *et al*. 2009). Occurrences of these acid sulfate soil materials can have serious environmental consequences relating to soil and water acidification, de-oxygenation of water, emission of foul smelling gases ($H_2S$, organo-S compounds) and release of heavy and trace metals (Simpson *et al.* 2008). However, apart from the preliminary work of Fitzpatrick *et al*. (2008) there is very limited information on the distribution, characteristics and processes of acid sulfate soils in this region to assist in the detailed understanding of such complex landscapes to support management decisions for the soils and wetlands to minimise impact. Consequently, the objective of this study was to provide the following critical baseline information to underpin and support planning of management options to mitigate harm to essential ecosystem services: 1) an overview of the acid sulfate soil distribution characteristics, 2) toposequence models to provide an understanding of soil processes and 3) local and regional variability in 62 of the 77 wetlands between Blanchetown and Wellington (Figure 1).

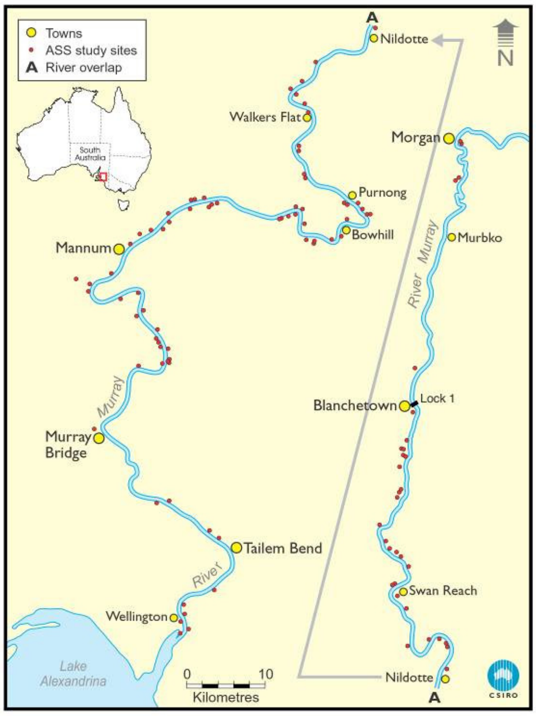

**Figure 1. Wetland locations and sample sites along the lower River Murray from Blanchetown to Wellington.**

## Methods

### *Field assessment*

Between August and October 2008, 198 soil profiles in 62 wetlands were studied, from which 687 soil layers were described and 653 soil samples were collected. The sample site location and number of sample sites placed within a wetland were determined by the type and size of the wetland. A number of factors were taken into consideration, and in general, 3 to 4 sites were located to represent a topographic transect within the wetland. Sampling locations were typically selected at the centre (low), edge (high), and intermediate points (mid) of each wetland. For wetlands that covered a larger surface area, extra transects were added to provide a better spatial distribution of sites.

Four to six layers were typically sampled per soil profile and generally the layers consisted of a surface (about 0 to 5 centimetres), subsurface (5 to 20 centimetres), subsoil (about 20 to 50 centimetres), deep subsoil (50 to 100 centimetres), occasionally subdivisions of the above intervals, and a deeper layer below if extracted. Samples were described according to standard methodology (McDonald *et al*. 1998; Schoeneberger *et al.* 2002). Layer depth ranges were recorded and for each layer the morphology and physical properties were described including: colour (matrix and mottles), texture, structure, consistency, and where present, features such as surface mineral efflorescences, plant material, and odour. Soil samples corresponding to the described layers were collected in sample jars for laboratory analysis and in chip-trays for archive storage and ageing experiments.

### *Laboratory analysis*

Laboratory analyses included $pH_{water}$, $pH_{peroxide}$, $pH_{incubation}$, and acid base accounting parameters ($S_{CR}$ (sulfide % S), $pH_{KCl}$, Titratable Actual Acidity (TAA), Acid Neutralising Capacity (ANC) and water-extractable $SO_4$ (1:5 soil:water suspension). Methods are described in Fitzpatrick *et al*. (2008).

## Results

The 62 wetlands ranged in size from < 1 to 250 hectares, and while each wetland had unique characteristics, there were a number of similarities with regard to soil morphology and distribution. The soils were often sampled as dry or moist, as surface water was not present at the majority of sites (only 5 sites had surface water), and the water table was occasionally encountered within 1 metre of the soil surface. Soil textures within the wetlands were dominated by clays that had cracks forming columnar structure with a firm to hard consistency. In some areas, the cracks were partially in-filled with windblown material or crumbling of the surface peds (Figure 2). Sandy soils occurred more frequently on the higher wetland margins and typically had no structure with a loose consistency. Medium textured or loamy soils were minor in occurrence.

Key laboratory measurements are summarised and presented in Table 1. Net acidity was positive in 534 out of 653 samples (82% of samples). These positive net acidity results occurred at all wetlands sampled along the 250 km of River Murray and at different depths indicating the widespread occurrence of acid sulfate soil materials.

Classification of soil material based on $pH_{water}$ and the pH change between $pH_{water}$ and $pH_{incubation}$ (Sullivan *et al.* 2008) identified sulfuric soil material in 55 out of 638 samples (9%), hypersulfidic soil material in 32 samples (5%), hyposulfidic soil material in 183 samples (29%). Sulfuric soil materials tended to occur in sandy surface soil layers where oxidation had occurred, while hypersulfidic and hyposulfidic soil materials occurred in the clay surface and subsurface layers. The distribution of these classified soil materials is still under investigation, but initial findings indicate that they are more likely to occur in the mid to down-river wetlands and unlikely to be identified in the wetlands near the up-river Blanchetown end.

Resource and time constraints meant that a limited number of sites were available to understand soil distribution. Conceptual toposequence models were developed for the wetlands showing soil material distribution and processes occurring to aid the interpretation of landscape patterns. These models allowed us to identify any recurrent patterns of soil variation. An example is presented in Figure 2. Describing acid sulfate soils in this way also provided an effective means to communicate information to decision makers and managers.

Based on the understanding of soil material distribution identified by the conceptual toposequence models and evaluation of the soil material classification and net acidity data, 47 out of the 62 assessed wetlands (71%) were identified as having an acid sulfate soil condition and extent within the wetland that is of concern.

**Table 1. Summary data for laboratory measurements of soil pH and net acidity for sampled layers**

| | $pH_{water}$ | $pH_{peroxide}$ | $pH_{incubation}$ | Chromium Reducible Sulfur ($\%S_{CR}$) | Net Acidity (mol $H^+$ $t^{-1}$) |
|---|---|---|---|---|---|
| Number | 638 | 638 | 632 | 653 | 653 |
| Mean | 5.89 | 3.58 | 5.27 | 0.06 | -5.03 |
| Median | 5.88 | 2.91 | 5.11 | 0.01 | 18.36 |
| Minimum | 2.43 | 1.20 | 1.68 | 0.00 | -3128.82 |
| Maximum | 9.08 | 8.76 | 8.45 | 2.21 | 1402.39 |

## Conclusions

This study has provided quantitative information identifying the widespread distribution of inland acid sulfate soil materials occurring in wetlands adjacent to the River Murray. A large, consistent and comprehensive data set of field, laboratory, photographic and map information has been collected and is currently under detailed evaluation and assessment. The data summarised in this paper provides an initial overview of key findings.

The data collected has already been used extensively by several Murray-Darling Basin agencies to:

- Determine impacts (both positive and negative) of the drought on wetlands.
- Identify those wetlands at high risk from acid sulfate soil hazards.
- Identify management options to reduce risks due to the current dry wetlands on the surrounding landscape.
- Guide selection of management options for when water reconnection occurs,
- Identify risks/outcomes associated with long-term disconnection as well as reconnection.
- Inform decisions regarding reconnection of wetlands upon return of normal river weirpool levels.
- Inform future potential hydrological management of wetlands and associated on-going monitoring needs.

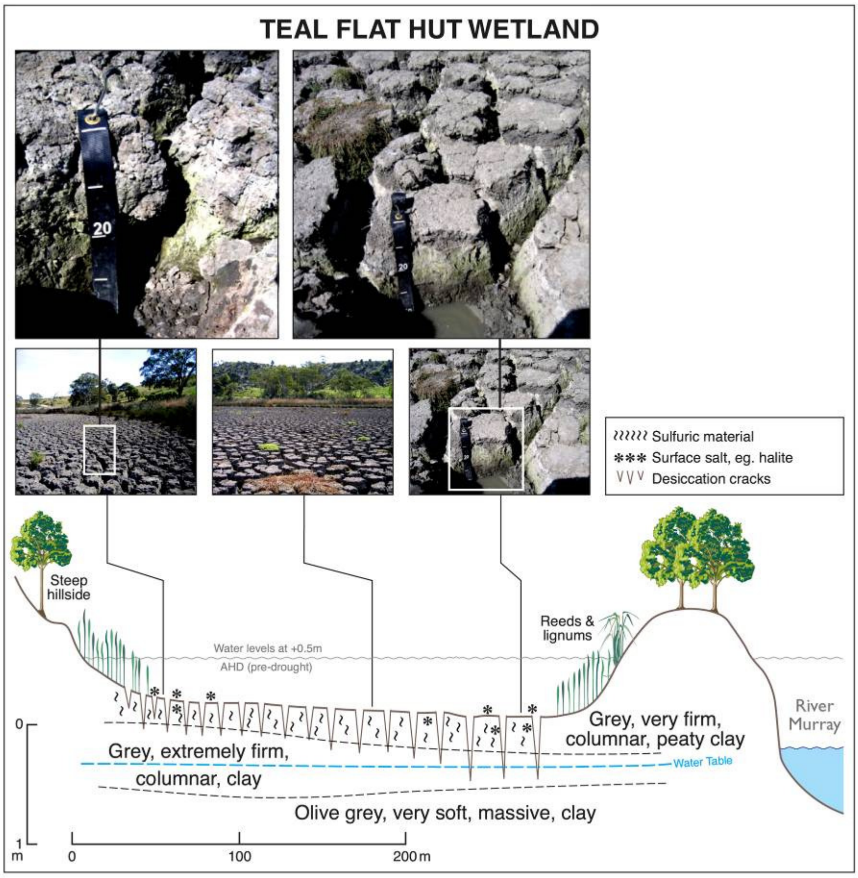

**Figure 2. Conceptual toposequence cross-section of Teal Flat Hut wetland, showing the distribution of various acid sulfate soil materials (for 2008 conditions) and other key soil features together with photographs**

## Acknowledgements

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## References

Fitzpatrick RW, Marvanek S, Shand P, Merry RH, Thomas M, Raven M (2008) Acid Sulfate Soil Maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre- drought and current drought conditions. CSIRO Land and Water Science Report 12/08. CSIRO, Adelaide. 16 pp. http://www.clw.csiro.au/publications/science/2008/sr12-08_withmaps.pdf.

Fitzpatrick RW, Shand P, Merry RH (2009) Acid Sulfate Soils. In 'Natural History of the Riverland and Murraylands'. (Ed JT Jennings) pp. 65-111. (Royal Society of South Australia (Inc.) Adelaide, South Australia).

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS (1990) 'Australian Soil and Land Survey Field Handbook', 2nd Edition, Inkata Press, Melbourne. pp. 87 - 183.

Schoeneberger PJ, Wysocki DA, Benham EC, Broderson WD (2002) 'Fieldbook for describing and sampling soils.' Natural Resources Conservation Service, National Soil Survey Center: Lincoln, NE., USA.

Simpson S, Angel B, Fitzpatrick R, Shand P, Merry R, Thomas M (2008) Acid, metal and nutrient mobilisation following rewetting of acid sulphate soils in the Lower Murray. CSIRO Land and Water Report 27/08, 148 pp.

Sullivan LA, Fitzpatrick RW, Burton ED, Bush RT, Shand P (2008) Assessing environmental hazards posed by acid sulfate soil materials and other inorganic sulfide-containing soil materials: classification issues. Plenary Paper, Joint Conference of the 6th International Symposium in Acid Sulfate Soils and the Acid Rock Drainage Symposium. Guangzhou, China, 16-20 September 2008.

# Acid sulfate soils in the Perth metropolitan area of Western Australia

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## Abstract

Acid sulfate soils (ASS) occur widely in the Perth metropolitan area of Western Australia. Projects likely to disturb ground or groundwater level are required to develop an ASS management plan if the sulfur content at the site is above 0.03%. In this context, a broad scale investigation was conducted to refine the ASS risk map and better manage the development activity in Perth metropolitan area. Soil cores for depths up to 6 metres were extracted from 162 sites. The cores were logged and analysed in the field for pH in water ($pH_F$) and 30% hydrogen peroxide ($pH_{FOX}$) at 0.25 m depth intervals. Samples for laboratory based sulfur analysis were taken where field $pH_{FOX}$ data (<3.0) indicated occurrence of ASS.

Highly leached Bassendean Dune System is one of the major surface geological formation in Perth region of the Swan Coastal Plain. In the topographic lows of the Bassendean formation, humus podzol soils with a strongly cemented dark brown, organic B horizon (coffee rock) are common. In the topographic mid slopes and crests, iron-humus podzol and iron podzol respectively occur. All these soils are sandy, highly leached and consequently poorly buffered. Evidence of ASS materials was found in over 80% of the investigated sites. Up to 11% sites contain chromium reducible sulphur ($S_{Cr}$) above the current ASS action criteria (0.03% ) in the top 2 m soil horizon. These sites are mostly in the estuarine sediments near the lakes and rivers. Forty five sites (27%) contain $S_{Cr}$ >0.03% at depths between 2-6 m. About 43% of the sites show zones of $pH_{FOX}$ lower than action criteria (<3.0) but their $S_{Cr}$ content are below 0.03% s. Rest of the sites, about 20%, have $pH_{FOX}$ >3.0. These sites are either clay-rich flood plains along the river or occasional old land-fill sites.

About 33% of the investigated sites show $pH_{FOX}$ values well below 3.0 while their sulphur content is below the current action trigger level (0.03%s). The host soil material for these sites is extremely poorly buffered Bassendean sand. It appears that current action trigger level for these sandy soils in SCP may need to be reviewed.

## Key Words

Acid sulfate soils, Swan Coastal Plain, Groundwater acidity

## Introduction

Activities likely to disturb ASS, either directly or by lowering the water table, are managed appropriately in Western Australia by planning guidelines for urban and industrial land development projects (Western Australian Planning Commission 2003). Inappropriate excavation or dewatering of ASS materials is avoided and where necessary for economic or social reasons, An ASS management plan is developed and executed according to state guidelines (Department of Environment and Conservation 2004). These management processes currently utilise predictive ASS maps that are based on geological and soils maps (Degens 2006). The aim of this study was to estimate the actual extent and severity of ASS and refine the ASS boundary for Perth metropolitan area.

## Methods and Materials

Perth city extends about 25 km north, 20 km south and 20 km east from its city business centre on the bank of Swan River. Swan Coastal Plain (SCP), a Quaternary surface of the Perth Basin has a subdued topography developed by aeolian and alluvial processes (Davidson 1995). Extensive leaching on topographic highs, seawater invasion and deposition of fresh alluvial materials has shaped the nature of soil materials in the area. Prominent landform in SCP is a series of coastal dunes systems that are roughly parallel to the present coastline (McArthur 1991). The most easterly dune system covering most of the present study area is the highly leached Bassendean Dune System. Next towards the west respectively are, relatively younger and carbonate rich, Spearwood Dune System and Quindalup Dune System. The study particularly focussed on lower part of the Bassendean Dune System where groundwater table depth is less than 3 m.

Sample sites were generally located along rivers and paleodrainages marked by chains of wetlands (Semeniuk and Semenuik 2005). In areas of high risk such as sumplands and damplands, sites were selected at about 1 km distance. Soil cores were typically obtained from 6 m depths and logged for texture, colour, mottles, organic materials and any concretions. Field pH in water ($pH_F$) and 30% hydrogen peroxide ($pH_{FOX}$) was analysed at 0.25 m depth intervals. Sampling for laboratory based SPOCAS suites of analyses was based on $pH_F$ and $pH_{FOX}$ profiles. Generally, a representative sample was taken from a zone where $pH_{FOX}$ dropped below 3.0. The samples were placed in air-tight zip lock bags and maximum possible air was excluded before closing the zip locks. The sample bags were kept in field refrigerators for transport to laboratory. Potential acidity in un-oxidised sulfides was estimated by the chromium reducible sulfur method (QASSIT method 22B; Ahern *et al.* 2004).

## Results and Discussion

Most of the 162 sites sampled were located on sumpland and damplands in the Bassendean Dune System. The groundwater table in these areas is within 2m metres and soils are extremely sandy with minimum capacity to resist changes in pH.

### *Field soil pH measurements*

As a general rule soil $pH_{FOX}$ is expected to lower than $pH_F$ by 2-3 units due to oxidation some oxidisable soil components. A significantly lower $pH_{FOX}$ value (<3.0 and < $pH_F$ by 2 at least units) is considered indicative of ASS occurrence in form of sulfides. A total of 133 sites showed such soil pH profiles. About 18 % sites showed pH profiles where $pH_{FOX}$ did not significantly vary from $pH_F$. No samples were taken from these sites for laboratory analysis. In several instances $pH_{FOX}$ showed significant departure from $pH_F$ even in the aerobic surface horizons where sulfides are not generally expected to persist. Lower $pH_{FOX}$ in these cases are partly attributed to oxidation of certain organic species and poorly crystalline and readily hydrolysable Fe and Mn oxides.

### *SPOCAS and total titratable acidity analysis.*

A total of 423 samples from 133 sites were analysed for SPOCAS and total titrateable acidity. As discussed above, these samples were taken on the basis of field $pH_F$ and $pH_{FOX}$. More than 40% of these are derived from white to gray sands that occur below the B horizon which often consists of loose brown sands (incipient coffee rock) to indurated brown sand (coffee rock ) material. These sands are often below the groundwater table. About 40% of the samples fall in the category of coffee rock. Less than 15% of the samples were derived from estuarine sediments that include peats and clay and organic matter rich sediments.
Estuarine sediments showed the highest $S_{Cr}$ content with a median of 0.14. The median $S_{Cr}$ content for sandy materials was 0.02, which is same as the detection limit for $S_{Cr}$. Clearly, the $S_{Cr}$ content of sandy soil materials, which make up bulk of the samples, is very low. These soils however show $pH_{FOX}$ values well below 3.

### *PASS characteristics and distribution*

Evidence of PASS materials was found in over 80% of the investigated 162 sites. Up to 11% contained $S_{Cr}$ >0.03% in the top 2 m soil horizon. These were classified Class 1a. These sites were mostly in the estuarine sediments near the lakes and rivers. Forty five sites (27%) contained $S_{Cr}$ >0.03% at depth between 2-6 meters and were given risk Class 1b.

About 43% of the investigated sites had zones of low $pH_{FOX}$ (<3.0) but their $S_{Cr}$ content were either below 0.03% or below the detection limit of the laboratory used for this study. All of these were given moderate risk Class 2. Some of these however showed high TAA levels (>0.03%) and were furthered divided into Class 2a. Rest of the sites had neither high $S_{Cr}$ or TAA. These were put into Class 2b. Rest of the investigated sites, about 20%, did not have low $pH_{FOX}$ and therefore were given Class 3. These sites were either clay-rich flood plains along the river or occasional old land-fill sites.
Majority of the investigated contained PASS materials within 3 metre depth. Often, the PASS material was hosted by extremely sandy soils that are poorly buffered and highly porous. These sandy soils are likely to be readily drained with movement in groundwater table or their excavation.

## Conclusions

Soils containing PASS materials occur widely within Perth metropolitan area. The occurrence is most common in sumplands near the lake environments and along the Swan and Canning river systems. However they also widely occur in damplands and higher positions in the topography. The Bassendean sands that host the PASS materials are extremely poorly buffered.

A large number of sites (33%) with $pH_{FOX} < 3.0$ contained below 0.03%S or undetectable amount of $S_{CR}$. It is surprising that these soils with undetectable amount of $S_{CR}$ would have such a low $pH_{FOX}$. It appears that current acidity trigger value (0.03%S) is too high for poorly buffered soils of Swan Coastal Plain. Current trigger value has been solely based on coastal landscapes of eastern seaboard where clay rich sediments and silt are common. This ASS mapping program has highlighted an urgent need to resolve the net acidity trigger value (0.03%S) for sandy upland soils of WA.

**References**

Ahern CR, Sullivan LA, McElnea AE (2004) Laboratory Methods Guidelines 2004 – Acid Sulfate Soils. In: 'Queensland Acid Sulfate Soil Technical Manual'. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia. http://www.derm.qld.gov.au/land/ass/pdfs/lmg_a.pdf

Davidson WA (1995) Hydrogeology and groundwater resources of the Perth Region, Western Australia. *Western Australia Geological Survey Bulletin* 142.

Degens B (2006) Metadata Statement for the Acid Sulfate Soil Risk Map, Swan Coastal Plain, Western Australia. Department of Enviroment and Conservation, Western Australia.

Department of Environment (2004) Acid Sulfate Soils Guideline Series: Identification and investigation of acid sulfate soils. October 2004. http:\\acidsulfatesoils.environment.wa.gov.au

McArthur WM (1991) Reference soils of south-western Australia. Australian Society of Soil Science (WA Branch Inc. Perth Western Australia).

Semeniuk V, Semenuik C (2005) Wetland sediments and soils on the Swan Coastal Plain, Southwestern Australia: Types, distribution, susceptibility to combustion, and implications for fire management. *Journal of the Royal Society of Western* **88**, 91-120.

Western Australian Planning Commission (2003) Planning Bulletin 64. Acid Sulfate Soils. ISSN 1324-9142.

# Atlas of Australian Acid Sulfate Soils: Recent developments and future priorities

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## Abstract

The Atlas of Australian Acid Sulfate Soils (AAASS) is a web-based hazard assessment tool with a nationally consistent legend, which provides information about the distribution and properties of acid sulfate soils (ASS) across Australia. This tool is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au) and every polygon or mapping unit is attributed with information pertaining to: (i) 4 classes of “probability of occurrence”, (ii) 4 levels of confidence relating to the quality of data source, and (iii) 10 additional descriptors such as desiccation cracks. In Australia, ASS occupy an estimated 215,000 km$^2$ of which 58,000 km$^2$ is coastal ASS and 157,000 km$^2$ is inland ASS (Fitzpatrick *et al*. 2008a). In the coastal zone, 41,000 km$^2$ are exposed at some point during the tidal cycle, with the remaining 17,000 km$^2$ being permanently subaqueous. More than 126 km$^2$ of coastal ASS with sulfuric material have been mapped, however this is a significant underestimate, which will be modified with future work. Being web-based the Atlas is a constantly evolving national map of available ASS information, which also includes priority case studies at a range of localities across Australia. With ongoing recent field investigations and acquisition of more detailed local spatial data sets, especially in the Lower Lakes region in South Australia, resolution and accuracy of the inland ASS component are being continually improved from its current, first cut “broad brush” depiction.

Future priorities are to constantly integrate ASS data from any new regional ASS investigations to enhance, update and refine the AAASS and new case studies.

## Key Words

Acid Sulfate Soils, mapping, soil classification, pH, wetlands, ASRIS.

## Introduction

The Atlas of Australian ASS project was developed under the auspices of the National Committee for Acid Sulfate Soils (NatCASS) and completed by CSIRO Land and Water with assistance from staff in all states throughout Australia. The ASS mapping was inferred from a mix of state and territory ASS mapping and surrogate datasets. The ASS Atlas was put together in two parts using two different methodologies and classification paths. First, the Atlas of “Coastal” ASS was compiled using existing state ASS mapping (e.g. DIPNR 1997; QDEX 2008) and other datasets that mapped landscape indicators of ASS environments, e.g. coastal vegetation mapping. At a later stage, the interior of the Australian continent was back-filled with “Inland” ASS mapping, inferred from broader and coarser scale national soil and hydrography mapping. The results of these two exercises were combined to form the current Australian ASS Atlas (Fitzpatrick *et al.* 2008a), which is available on ASRIS (Australian Soil Resource Information System: www.asris.gov.au). ASRIS receives nearly 2000 visits per month with over half being new visitors. Copies or extracts of the AAASS are regularly sought by several government agencies, engineering firms and environmental consultants. But also farmers and land managers with internet access can readily see what the indicative ASS assessment is for their area of interest. The objective of this paper is to summarise recent developments and describe planned improvements.

## Results and Discussion

The seamless, systematic and uniform Atlas of Australian Acid Sulfate Soils (AAASS), represents the most extensive depiction of ASS across the nation, to date and is the product of contributions from all states in Australia. The ASS map is largely modelled from small scale surrogate data but combines explicit ASS survey mapping where it exists.

### *The “Coastal” ASS component*

Existing Coastal Acid Sulfate Soil mapping from states was re-interpreted to conform to the Atlas of Australian ASS legend classification (Fitzpatrick *et al.* 2008a). Classification of state mapping polygons to the Atlas legend was as follows: in the case of South Australia, New South Wales, Queensland and Western

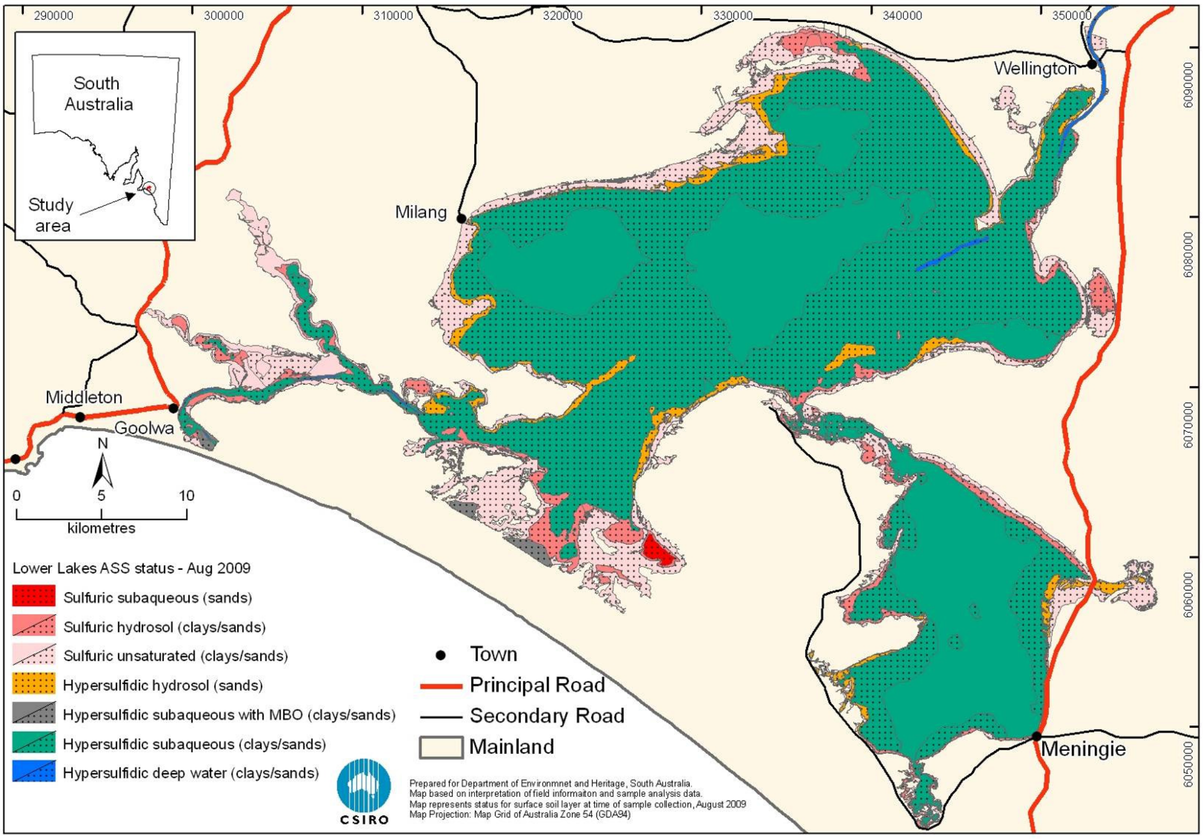
Australia the original state ASS classifications were directly translated to the Atlas legend classification. These translations were undertaken by the creators of the state data and other experts within the respective states. Due to the more broad classifications of the original Victoria and Tasmania ASS mapping, polygons for these two states were initially translated to a broad Atlas legend grouping (e.g. Tidal, Non-tidal) by the data custodians then subsequently differentiated further through intersecting with other layers. These included the 3 second Shuttle Radar Topography Mission (SRTM), digital elevation mode (DEM) and North Coast Mangrove mapping geographic information system (GIS) datasets. The former being used to differentiate within the Non-Tidal zones (i.e. classes Ae-j and Be-j) and the latter was used to differentiate the Tidal zones (i.e. Ab-d, Bb-d). Mapping of the Tidal-Zone classes was augmented for all states except South Australia and New South Wales with 1:100K Coastal Waterways Geomorphic Habitat Mapping by Geoscience Australia. This dataset was used to infer additional areas of subaqueous soils in subtidal wetlands (class Aa & Ba) and Intertidal Flats (class Ab & Bb).

*The "Inland" ASS component*
Provisional inland ASS classifications were derived from National and Tasmanian state soil classification coverages combined with 1:250K series 3 Hydrography and Multi-resolution Valley Bottom Floor Index (MrVBF; Gallant and Dowling 2003). A matrix was devised to translate combinations of Soil Order (Isbell 1996) and landscape "wetness" to the Atlas legend. The basis for constructing the inland ASS Atlas component is very coarse because it is underpinned by the Atlas of Australian Soils (1:2M scale) with "wetness" inferred from 1:250K topographic hydrography (Appendix 2 in Fitzpatrick *et al.* 2008a). A principle feature of the ASS Atlas is that every polygon is attributed with information pertaining to quality of its source, confidence in the ASS legend classification code and scale of mapping (Fitzpatrick *et al.* 2008a). Hence, every polygon or mapping unit is attributed with information pertaining to: (i) classes of "probability of occurrence", (ii) levels of confidence relating to the quality of data source, and (iii) additional descriptors such as: desiccation cracks, hypersaline or gypseous horizons; fill, organic, sandy or clayey materials.

*Nation wide estimates of the areas of various types of Acid Sulfate Soils*
The Atlas has enabled estimates of the area of ASS extent to be calculated across Australia. With the area scaling factors applied, there is estimated to be 154,269 km$^2$ of high probability ASS areas and 65,771 km$^2$ of low probability ASS areas. In Australia, ASS occupies an estimated 215,000 km$^2$ of which 58,000 km$^2$ is coastal ASS and 157,000 km$^2$ is inland ASS (Fitzpatrick *et al*. 2008a). In the coastal zone, 41,000 km$^2$ are exposed at some point during the tidal cycle, with the remaining 17,000 km$^2$ being permanently subaqueous. More than 126 km$^2$ of coastal ASS with sulfuric material have been mapped.

**Application of ASS Atlas legend to the mapping of ASS in Lower Lakes**
With ongoing field investigations and acquisition of more detailed local spatial data sets, the resolution and accuracy of the inland ASS component is being continually improved from its current, first cut "broad brush" depiction. For example, the current extreme drought in South-eastern Australia has had a major impact on the availability of water resources in the Murray Darling Basin (MDB). Nowhere can this be more clearly seen than in the lower reaches of the River Murray, especially below Lock 1 (Blanchetown) in Lakes Alexandrina and Albert (Figure 1) where water levels are at an unprecedented low (below sea level). The low water levels have caused a number of impacts related to inland acid sulfate soils (ASS) to be realised for the first time (Fitzpatrick *et al*. 2008b, 2009a,b). The Australian Soil Classification (ASC; Isbell 1996) has proved tremendously useful for soil classification and advancing understanding of soils across Australia. However, because the ASC and other internationally recognised classification systems such as Soil Taxonomy (Soil Survey Staff 2003) are generalised schemes, there is still the need for additional and complementary systems specifically tailored to particular environmental problems (e.g. ASS), land uses or regions (Fitzpatrick *et al.* 2003). These general classification systems do not yet incorporate the following new terminologies: subaqueous soils (Fitzpatrick *et al*. 2008a), monosulfidic, hypersulfidic and hyposulfidic materials (Sullivan *et al*. 2009). Therefore, the simplified Soil Identification Key was specifically developed and designed for inland acid sulfate soils, initially for ASS in the River Murray and Lower Lakes systems to identify and classify the various types and subtypes of acid sulfate soils and non-acid sulfate soils (Fitzpatrick *et al.* 2008a,b; 2009a,b; Grealish *et al*. 2010). The Soil Identification Key was used as the basis in Lower Lakes soil map legend showing ASS classes that allowed integration and incorporation of the following additional information: (i) soil characteristics with depth, (ii) water depth, (iii) soil water saturation through the use of bathymetry, (iv) occurrence of monosulfidic material, (v) soil texture, (vi) location of calcrete and granite rock outcrops (Grealish *et al*. 2010). This map consolidates many sources of

information and provides a generalised overview of ASS variation that occurred when the survey was conducted in August 2009. Each map unit or polygon in Figure 1 bears a colour and stippling pattern, which shows its map unit that relates to the AAASS legend (Fitzpatrick *et al*. 2008a). The ASS map shown in Figure 1 identifies the following areas classified as: (i) Hypersulfidic deep water clays, which comprise 438 ha; (ii) Hypersulfidic subaqueous soils (sands & clays), which comprise 66,781 ha (covering 80% of 89,145 ha.).



Prepared for Department of Environmnet and Heritage, South Australia.
Map based on interpretation of field informaiton and sample analysis data.
Map represents status for surface soil layer at time of sample collection, August 2009
Map Projection: Map Grid of Australia Zone 54 (GDA94)

**Figure 1. Acid Sulfate Soil map of Lake Alexandrina and Lake Albert (from Grealish *et al.* 2010).**

The ASS map shown in Figure 1 identifies the following areas classified as: (i) Hypersulfidic deep water clays, which comprise 438 ha; (ii) Hypersulfidic subaqueous soils (sands & clays), which comprise 66,781 ha (covering 80% of 89,145 ha.). (iii) Hypersulfidic hydrosol sands and clays, which comprise 3,303 ha; (iv) Sulfuric subaqueous soils (sand and clays), which comprise 250 ha and (v) Sulfuric soils and Sulfuric hydrosols, which comprise 18,685 ha (covering 20% of 89,145 ha). The ASS map also provides a baseline for predicting by identification of ‘hotspot’ areas where potential problems will occur, requiring future management scenarios such as: (i) continual lowering of water levels, (ii) minimise oxidation by guiding installation of containment or rewetting infrastructures (irrigation, regulators, pumping) and (iii) neutralisation of sulfuric material with limestone (e.g. examples summarised in Fitzpatrick *et al*. 2009b).

## Future priorities of AAASS and ASS Database

Future priorities are to constantly integrate ASS data from new regional ASS investigations such as priority case studies currently being conducted in the MDB (e.g. Lower Lakes region shown in Figure 1) to enhance, update and refine the AAASS. Such key studies are being incorporated in the constantly evolving national ASS map of available ASS information and especially also include a range of new localities across Australia (e.g. Tasmania, part of the Queensland wet tropics, Northern Territory and Western Australia Wheat Belt).

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## References

DIPNR (Department of Infrastructure, Planning and Natural Resources) (1997). Acid Sulfate Soils Risk Mapping. 128 map sheets at a scale of 1:25 000. This project was co-funded by the Natural Resources Audit Council (NRAC), and revised in 1997. ANZLIC unique identifier: ANZNS0359000004.

Fitzpatrick RW, Grealish G, Shand P, Simpson SL, Merry RH, Raven MD (2009a) Acid Sulfate Soil Assessment in Finniss River, Currency Creek, Black Swamp and Goolwa Channel, South Australia. CSIRO Land and Water Science Report 26/09. CSIRO, Adelaide, 213 pp.

Fitzpatrick RW, Powell B, McKenzie NJ, Maschmedt DJ, Schoknecht N, Jacquier DW (2003) Demands on Soil Classification in Australia. In 'Soil Classification: A Global Desk Reference'. (Eds H Eswaran, T Rice, R Ahrens, BA Stewart) pp. 77–100. (CRC Press LLC Boco Raton. FL).

Fitzpatrick RW, Powell B, Marvanek S (2008a) Atlas of Australian Acid Sulfate Soils. In 'Inland Acid Sulfate Soil Systems Across Australia'. (Eds RW Fitzpatrick, P Shand) pp. 90–97. CRC LEME Open File Report No. 249. (Thematic Volume) (CRC LEME, Perth, Australia).

Fitzpatrick RW, Shand P, Merry RH (2009b) Acid Sulfate Soils. In 'Natural History of the Riverland and Murraylands'. (Ed JT Jennings). pp. 65-111 (Royal Society of SA Inc. Adelaide, South Australia).

Fitzpatrick RW, Shand P, Marvanek S, Merry RH, Thomas M, Simpson SL, Raven MD, McClure S (2008b) Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. Prepared for Department of Environment and Heritage, SA. *CSIRO Land and Water Science Report 46/08.* CSIRO, Adelaide, 167. pp.

Grealish G, Fitzpatrick RW, Chappell A, Marvanek S (2010) Spatial variability of subaqueous and terrestrial Acid Sulfate Soils and their properties, for the Lower Lakes, South Australia. Project Report for Murray Futures Lower Lakes & Coorong Recovery Acid Sulfate Soils Program. Prepared for: Department of Environment and Heritage, South Australia and Department of the Environment, Water, Heritage and Arts. Client Report: CSIRO Sustainable Agriculture National Research Flagship 143 pp. http://www.clw.csiro.au/publications/science/2010.pdf

Gallant JC, Dowling TI (2003) A multiresolution index of valley bottom flatness for mapping depositional areas. *Water Resources Research* **39,** 1347.

Isbell RF (1996) The Australian soil classification system. CSIRO, Publishing, Melbourne.

Soil Survey Staff (2003) Keys to Soil Taxonomy. Ninth Edition. U.S. Dept. Agr. Nat. Res. Cons. Service, Washington D.C.

Sullivan LA, Fitzpatrick RW, Bush, RT Burton ED, Shand P, Ward NJ (2009) Modifications to the classification of acid sulfate soil materials. Southern Cross GeoScience Tech Report 309. pp. 11.

QDEX (Queensland Digital Exploration Reports System) (2008) Hardcopy ASS maps, GIS coverages, sample site descriptions and laboratory data may be purchased from (NRScDataCoordinator@derm.qld.gov.au)

# Chip-tray incubation: A new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication

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## Abstract

Chip-trays are plastic containers that are 50.5 cm long by 5.5 cm wide by 3.5 cm deep, and contain 20 compartments - or cells - that can be closed with a snap lock lid. Traditionally used by geologists (e.g. to store drill core fragments), for the past 5 years we have routinely used chip trays in a range of soil applications including soil survey, forensic investigations and mineralogical studies. This paper, however, focuses on recent adaptations to acid sulfate soil (ASS) protocols that rely on the use of chip-trays, which offer significant improvements to field sampling and soil storage, and provide the means for a new laboratory incubation method of ASS materials to better characterise and classify ASS types, including hypersulfidic, hyposulfidic and sulfuric materials. The chip tray-based improvements to ASS protocols have found use in a wide range of projects in diverse Australian ASS landscapes (e.g. coastal, and inland upland, wetland and riverine environments). For example, characterising hydro-toposequences, constructing ASS processes models and use in ASS risk assessment protocols.

## Key Words

Acid sulfate Soils, incubation, pH, plastic chip-trays, wetlands.

## Introduction

The Acid Sulfate Soil Working Group of the International Union of Soil Sciences has recently accepted in principle (see Sullivan *et al*. 2009b) the following changes to the classification of sulfide-containing materials: (i) revision of the concept underlying the existing term of “sulfidic” to “soil material containing detectable inorganic sulfides” and defined as “soil material containing ≥ 0.01% sulfidic S”; (ii) hypersulfidic material, to describe sulfidic materials that are capable of severe acidification ($pH < 4$) by sulfide oxidation (this is essentially the same concept underlying the ‘sulfidic’ term as used previously by Isbell 1996 and Soil Survey Staff 2003), (iii) hyposulfidic material, to describe sulfidic soil materials that are not capable of severe acidification from oxidation ($pH > 4$ after full oxidation), and (iv) monosulfidic material, to describe soil materials containing detectable monosulfides. In addition, Sullivan *et al.* (2009a) recently reviewed and proposed several improvements to the incubation method that underpins identification of ASS materials. The recommended improved incubation procedure is a modification of the duration of incubation from the fixed 8-week period in the Australian Soil Classification (Isbell 1996) and Soil Taxonomy (Soil Survey Staff 2003) definitions, to that proposed by Sullivan *et al*. (2009b), i.e. until a stable pH is reached after at least 8 weeks of incubation. Sulfuric material is defined by Isbell (1996) as having a $pH < 4$, whereas Survey Staff (2003) has defined a sulfuric horizon as having a $pH < 3.5$.

The objective of this paper is to describe improvements in field sampling, storage and incubation methods to help better characterise and classify hypersulfidic, hyposulfidic, sulfuric and monosulfidic materials in a wide range of landscapes in Australia. The improvements described include field collection and storage of moist soil samples in chip-trays, which offer standardised and improved incubation conditions to those previously used. This new approach has been extensively tested and refined since 2007 during several ASS investigations (e.g. Fitzpatrick *et al*. 2008a,b,c; 2009 a,b; Shand *et al*. 2008 a,b; 2009), and has been adopted by the Scientific Reference Panel of the Murray-Darling Basin (MDB) Acid Sulfate Soil Risk Assessment Group for use in the rapid and detailed assessment of acid sulfate soil materials in the MDB (MDBA 2010).

## Methods

### *Use of chip trays for sample collection and preparation*

Chip-trays (Figure 1) are plastic containers that are 50.5 cm long by 5.5 cm wide by 3.5 cm deep, and contain 20 compartments - or cells - that can be closed with a snap lock lid (i.e. partly air-tight). Our adapted ASS field protocol involves soil layer sub-samples to be placed in two separate plastic chip-trays [i.e. protocol routinely used by MDBA (2010) and CSIRO Land and Water Acid Sulfate Soils team in Adelaide see Fitzpatrick *et al*. (2008a,b,c; 2009a,b); Shand *et al*. (2008 a,b; 2009)]. The first chip-tray is used to display morphologically representative aggregates for each of the sampled layers (compartments filled to ¾ full with representative, intact aggregates or peds) for later-date visual reference (e.g. during report writing), and subsequently placed in the CSIRO Land and Water Acid Sulfate Soil archival system. If present, samples of salt efflorescences and/or coatings observed in the field should also be carefully collected and placed in soil morphology chip-tray for further mineralogical analysis. The second chip-tray (Figure 1) is used for ASS incubation testing ($pH_{INC}$) in the laboratory. Compartments are filled to approximately ⅓ full (Figure 1) by representative layer samples that are then moistened (not saturated) when necessary with deionised water. After at least 8-weeks of laboratory ageing (or in some cases more than 8 weeks) at approximately 25 °C, the soil samples are visually checked for formation of minerals (e.g. jarosite) that indicate significant acidification. Since the solution in contact with the soil in the chip-tray compartments is likely to be in equilibrium with the soil, the ageing pH of the whole soil in the tray can be measured using a calibrated pH meter or Merck pH indicator strips (Merck item numbers: pH 2.5–4.5: 1.09541.0001; pH 4.0–7.0: 1.09541.0002; pH 6.5–10.0: 1.09543.0001). A pH value of 4 or less measured in the chip-tray sample after at least 8-weeks confirms that the sample, which had a pH > 4 when measured in the field, is likely to develop sulfuric material on drying (i.e. is hypersulfidic). Soil treated with peroxide and then tested for pH is considered the extreme for oxidising soils and is used as an indicator to characterise ASS when the $pH_{OX}$ [laboratory equivalent to the field pH after treatment with hydrogen peroxide $pH_{FOX}$ (Ahern *et al*. 2004)] value is compared with the pre-treatment pH value. Therefore, we routinely compare the incubated pH values with $pH_{FOX}$ as a test for identification of acid sulfate soils.

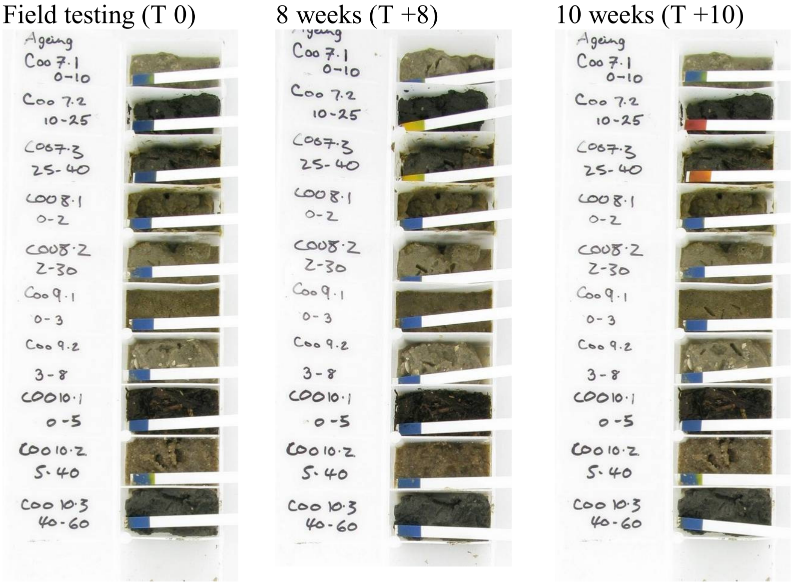
Field testing (T 0)
8 weeks (T +8)
10 weeks (T +10)

**Figure 1. Time sequence (T 0, T +8, T +10) for a chip-tray of soils from the Coorong in South Australia undergoing incubation. Each photograph shows soil pH as indicated by Merck pH strip colours at: (i) T 0, at sampling in the field, (ii) at T +8, after incubation for 8 weeks and (iii) at T +10, at 10 weeks. Here pH indicator strip colours indicate that most samples remain alkaline or neutral (blue colour >pH 7) with only two becoming acid after incubation for 10 weeks (red or pink colour - pH 3.9 to 4). (Fitzpatrick *et al*. 2008c).**

## Results and Discussion

The following five case studies describe the versatile use of the chip-trays for storing and incubating soil samples to determine ASS characteristics.

*Case study 1 – Lower Lakes (SA) samples showing close relationship between $pH_{INC}$ and $pH_{FOX}$*

Eighty five soils from Lower Lakes and adjacent wetlands in South Australia were assessed by Fitzpatrick *et al* (2008c) for ASS using $pH_{INC}$, $pH_{OX}$ and net acid generating potential (NAGP; see Ahern *et al*. 2004) measurements. There is good agreement between $pH_{OX}$ and NAGP (see Fitzpatrick *et al* 2008c). The $pH_{INC}$ (8 weeks) also generally correlates well with $pH_{OX}$, although pH values were not usually as low as those measured after peroxide treatment (usually 0.5 to 1.5 units greater). Some incubated samples from the

Lower Lakes do not proceed to full oxidation within 8 weeks, especially when the soil sample is kept either too moist or too dry.

*Case Study 2 – large data set comparison of* $pH_{INC}$ *with* $pH_{OX}$*, and identification of acid sulfate soil materials, River Murray and Lower Lakes, SA*
Data from three separate surveys conducted in the lower River Murray and Lower Lakes region were combined and evaluated (Grealish *et al*. 2009; Fitzpatrick *et al*. 2009a). This comprised a total of 1,452 samples and of these, 996 classified as either sulfuric or hypersulfidic. Of the 996 classified samples, 832 classified as hypersulfidic using $pH_{INC}$ (8 weeks). The following results were obtained when comparing $pH_{INC}$ (8 weeks - for hypersulfidic materials) and $pH_{OX}$ (i.e. $pH_{OX}$ of <2.5):

- 69% of samples classify as hypersulfidic using $pH_{INC}$ and have $pH_{OX}$ values of <2.5.
- 2% of samples classify as hypersulfidic using $pH_{INC}$ and do not have $pH_{OX}$ values of <2.5.
- 29% of samples were not classified as hypersulfidic using $pH_{INC}$ but have $pH_{OX}$ values of <2.5.

Therefore $pH_{INC}$ (8 weeks) in general compares favourably with $pH_{OX}$. However, about one third of samples do not classify as hypersulfidic using $pH_{INC}$ (8 weeks) but do have $pH_{OX}$ values <2.5. Hence, $pH_{INC}$ (19 weeks) will be determined on these samples and compared with $pH_{OX}$ values <2.5 to establish if this subset of samples will classify as either hypersulfidic or hyposulfidic materials.

*Case Study 3 - to identify acid sulfate soil risk areas requiring further investigation, Murray-Darling Basin*
For the MDB ASS risk assessment project, initiated by the Murray-Darling Basin Authority, a total of 1,329 wetlands from SA, NSW, Vic, and QLD were assessed by wetland officers resulting in over 8,000 soil samples being submitted for incubation analysis (Creeper *et al.* 2010). The large number of samples collected in chip-trays allowed for comprehensive testing of this combined field sampling procedure and incubation method across the MDB. The data obtained using this method triggered the requirement for further detailed ASS investigations to be conducted. The chip-tray approach both streamlines data acquisition and enhances correct hazard identification.

*Case Study 4 – community volunteer ASS monitoring, Lower Lakes (SA)*
An ASS field guide was developed for easy use by community volunteers to monitor ASS at fixed sites over a quarterly interval as the water levels in the Lower Lakes and tributaries fall (drought conditions) or rise (from reflooding). The field guide outlined a systematic protocol for site selection, soil description and sampling methodology using the chip-tray approach. The chip trays provided an ideal system for the community volunteers to closely observe and discuss the samples they had taken for description, and also provided an easy way to transport soil samples to the CSIRO laboratories for pH incubation measurements. The chip-trays served as easy-to-use storage media for soil samples for the moderately experienced soil surveyors. The community survey results for the ASS samples are collated and presented via a Google Earth interface, which shows the pH data and down-profile trends for scientific and community monitoring.

*Case Study 5 – seasonal evaluation of nine wetlands, River Murray (SA)*
Nine wetlands adjoining the River Murray were assessed for ASS by Shand *et al.* (2009) using $pH_{INC}$, $pH_{OX}$ and net acid generating potential (NAGP; see Ahern *et al*. 2004) measurements on four occasions over a 12 month period. Although NAGP predicted a greater incidence of net acidification, $pH_{INC}$ (using chip trays) and $pH_{OX}$ in most cases suggested similar outcomes. Spatial variation, which can be considerable in ASS, becomes a factor with sequential sampling. For those wetlands that dried over time, the clayey wetlands, which developed strong polygonal cracking tended to neutralise by mixing as the soil columns degraded and winter rainfall moved solutes. It is also probable that very slow reactions may become a factor affecting the soil materials over the extended periods of sampling.

## Conclusions

In summary, the chip tray field sampling incubation method is considered to represent a "realistic tool" for ASS testing based on allowing the soil to "speak for itself" (Dent 1986). A number of specific techniques are employed, but incubation tests are based on keeping the sample moist for a specified period (number of weeks). Recent recommendations by Sullivan *et al* (2009a) have increased the period from 8 weeks "until a stable pH is reached after at least 19 weeks of incubation", which allows slow oxidation of sulfide minerals to occur. Although chip tray incubation may mimic nature more closely than the extreme hydrogen peroxide oxidation because chip tray incubation conditions do not force acidification reactions to occur in totality, it can be argued that the complex processes occurring in the field are not adequately reproduced during laboratory ageing in chip-trays, e.g. complex landscape processes, which may include exchange with sub-surface waters (containing Acid Neutralizing Capacity) or biogeochemical reactions. These complex processes should also be taken into consideration wherever possible with interpretation of acid sulfate soil findings, which will often require a thorough understanding of water movement that is often site and scenario specific. The use of chip-trays as a valuable tool for characterising ASS has also proved remarkably useful for community volunteers to collect, discuss, describe and test samples to identify ASS materials.

## Acknowledgements

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## References

Ahern CR, McElnea AE, Sullivan LA (2004) ‘Queensland Acid Sulfate Soils Manual 2004’. (Department of Natural Resources, Mines and Energy, Indooroopilly: Queensland, Australia).

Creeper Nathan, Rob Fitzpatrick, Paul Shand Peter Self, Rob Kingham (2010) A systematic analyses procedure incorporating the chip-tray incubation method for the hazard assessment of Acid Sulfate Soils in the Murray Darling Basin. In ‘World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia’. (Published on CDROM (Submitted)).

Dent DL (1986) ‘Acid Sulphate Soils: a Baseline for Research and Development. I.RI Pub. No. 39’. (International Institute for Land Reclamation and Improvement: Wageningen).

Grealish G, Fitzpatrick RW, Chappell A, Marvanek S (2009) ‘Soil properties and distribution of Acid Sulfate Soils in the Lower Lakes, South Australia. Prepared for: Department of Environment and Heritage, South Australia and Department of Water, Environment, Heritage and Arts. CSIRO Land and Water Science Report 49/09’. (CSIRO: Adelaide).

Fitzpatrick RW, Grealish G, Shand P, Simpson SL, Merry RH, Raven MD (2009a) ‘Acid Sulfate Soil Assessment in Finniss River, Currency Creek, Black Swamp and Goolwa Channel, South Australia. CSIRO Land and Water Science Report 26/09’. (CSIRO, Adelaide).

Fitzpatrick RW, Shand P, Merry RH, (2009b) Acid Sulfate Soils. In ‘Natural History of the Riverland and Murraylands’. (Ed JT Jennings) pp. 65-111 (Royal Society of South Australia Inc.: Adelaide, South Australia).

Fitzpatrick RW, Shand P, Marvanek S, Merry RH, Thomas M, Simpson SL, Raven MD, McClure S (2008a) ‘Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. Prepared for Department of Environment and Heritage, SA. CSIRO Land and Water Science Report 46/08’. (CSIRO: Adelaide, 167).

Fitzpatrick RW, Shand P, Thomas M, Merry RH, Raven MD, Simpson SL (2008b) ‘Acid sulfate soils in subaqueous, waterlogged and drained soil environments of nine wetlands below Blanchetown (Lock 1), South Australia: properties, genesis, risks and management. Prepared for South Australian Murray-Darling Basin Natural Resources Management Board. CSIRO Land and Water Science Report 42/08’. (CSIRO: Adelaide).

Fitzpatrick RW, Shand P, Merry RH, Thomas B, Marvanek S, Creeper N, Thomas M, Raven MD, Simpson, SL, McClure S, Jayalath N (2008c) ‘Acid sulfate soils in the Coorong, Lake Alexandrina and Lake Albert: properties, distribution, genesis, risks and management of subaqueous, waterlogged and drained soil environments. Prepared for Department of Water, Environment, Heritage and Arts. CSIRO Land and Water Science Report 52/08’. (CSIRO: Adelaide).

Isbell RF (1996) ‘The Australian Soil Classification System’. (CSIRO Publishing: Melbourne).

MDBA (Murray–Darling Basin Authority) (2010) ‘Detailed Assessment of Acid Sulfate Soils in the Murray-Darling Basin: Protocols for Sampling, Field Characterisation, Laboratory Analysis and Data Presentation’. (MDBA Publication 57/10).

Shand P, Merry RH, Fitzpatrick RW (2008a) ‘Acid sulfate soil assessment of Lock 8 and Lock 9 Weir Pools. CSIRO Land and Water Science Report 40/08’.

Shand P, Merry RH, Fitzpatrick RW (2008b) ‘Acid sulfate soil assessment of the Noora Basin, SA. CSIRO Land and Water Science Report 41/08’.

Shand P, Merry RH, Fitzpatrick, RW, Thomas M (2009) ‘Acid sulfate soil assessment of disconnected wetlands between Lock 1 and Lock 5, River Murray, South Australia’. (CSIRO: Water for a Healthy Country National Research Flagship).

Soil Survey Staff (2003) ‘Keys to Soil Taxonomy. 9th Ed’. (USDA–Natural Resources Conservation Service: Washington, DC).

Sullivan LA, Ward NJ, Bush RT, Burton ED (2009a) Improved identification of sulfidic soil materials by a modified incubation method. *Geoderma* **149,** 33 – 38.

Sullivan LA, Fitzpatrick RW, Bush, RT, Burton ED, Shand P, Ward NJ (2009b) ‘Modifications to the Classification of Acid Sulfate Soil Materials. Southern Cross GeoScience Tech Report 309’.

# Climate change: a frontier for acid sulfate soil research

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## Abstract

Sea-level is predicted to continue to rise this century, threatening the integrity of coastal floodplains throughout the world. The low-lying elevation of much of the 17 million ha of acid-sulfate soils that occur worldwide, renders these landscapes particularly vulnerable to the impacts of climate change. Acid sulfate soils landscapes are regulated by redox driven biogeochemical processes that are sensitive to watertable dynamics, tidal exchange and temperature. The increased likelihood of extreme weather events such as drought and floods and rising global temperatures are directly relevant to the redox and hydrological processes that influence acid sulfate soil behaviour and their impact on the environment. This paper examines aspects of climate change and highlights some of the key challenges for acid sulfate soil research.

## Keywords

Pyrite; iron sulfides; monosulfides; wetlands; sulfuric.

## Introduction

Dealing with global warming, climate change and rising sea-levels has been described by international leaders as possibly the largest moral and environmental dilemma of our time. The low-lying elevation of much of the 17 million ha of coastal acid sulfate soils (CASS), render these landscapes particularly vulnerable to rising sea-levels. Being landscape systems dominated by redox processes that are sensitive to watertable dynamics, the increasing likelihood of extreme weather events such as drought and floods as predicted by climate scientist (IPCC 2007) will also affect how CASS behave and impact the environment. Major shifts in fundamental coastal acid sulfate soil biogeochemistry and hydrology are anticipated, yet the consequences of global climate change to soil and water quality in these landscapes are largely unexplored.

Climate change is dependent on a complexity of regional factors and its impacts will vary across the globe (IPCC 2007). Even within continents the predicted impacts on weather patterns and sea-level are diverse. It is anticipated that tropical regions will experience increasing rainfall and more frequent cyclones. Other areas will become increasingly prone to extreme droughts. Understanding these potential impacts of climate change on CASS landscapes is particularly important, given the utility of these areas for agriculture and urban communities, their unique capacity to cause extreme environmental degradation, and their sensitivity to climatic factors such as temperature and hydrology and susceptibility to sea-level inundation. There is a strong and expanding fundamental knowledge of processes in CASS landscapes, but limited studies to date that consider the impacts of climate change. This paper examines some of the key issues of climate change of relevance to ASS.

## Climate change

The predicted impacts of climate change are warmer conditions, an increasing proportion of rainfall to occur from heavy falls, increasing occurrence of drought in many regions, increasing frequency of intense tropical cyclones, and incidents of extreme high seas (e.g. tsunamis, storm surges) (IPCC 2007). All of these predicted impacts of climate change have direct relevance to CASS landscapes, through either exacerbating oxidation by drought, re-instating reductive geochemical processes or changing the export and mobilisation of contaminants. The potential impacts of climate change vary between regions (IPCC 2007), and for CASS, the relative importance of any one of these issues will vary depending on landscape elevation and latitude. Specific land management factors such as man-made drainage will also affect how climate change impacts CASS. These issues are discussed in the following sections.

### *Sea-level rise*

Tidal inundation of CASS is capable of shifting the geochemical regime from oxidising and acidifying, to reductive and neutralising system. This has been examined experimentally and recently demonstrated on a field scale by our research group at East Trinity, north-eastern Australia (Johnston *et al*. 2009). The CASS at

East Trinity oxidised and acidified in the 1970s, when developers installed a 7 km long seawall, tidal gates, drained and cleared 740 ha of tidal wetland to grow sugarcane. This dewatered underlying sulfidic soils, exposing and oxidising iron sulfide minerals, resulting in slugs of highly acidic water as low as pH 2.5, crop failure, fish kills and major impacts on neighbouring wetlands (Johnston *et al*. 2009). Tidal inundation of this site commenced incrementally in 2001–02, and now most of the formerly acidified areas across the site are regularly inundated by tidal waters.

Microbial driven reductive geochemical processes have established quickly at East Trinity, much of the acidity has been naturalised in the soil profile (Figure 1), dramatically improving surface and groundwater water quality (Johnston *et al*. 2009). The site has reverted from a once chronic and severely acidic condition to a situation where acidic discharges are now very rare (Johnston *et al*. 2009). The geochemical transition at the East Trinity site caused by seawater inundation has initiated extensive reductive dissolution of Fe (III) oxide minerals, resulting in very high concentrations of pore water $Fe^{2+}$ (>2000 mg L-1) in the former sulfuric horizons and thick accumulations of reactive Fe (III)-oxide minerals at the ground surface (Figure 2). Iron reduction at this scale has a range of geochemical consequences, such as the mobilisation of arsenic and other contaminant metals (Burton *et al*. 2008). The longer term consequences of tidal inundation are the focus of current research at the East Trinity study site.

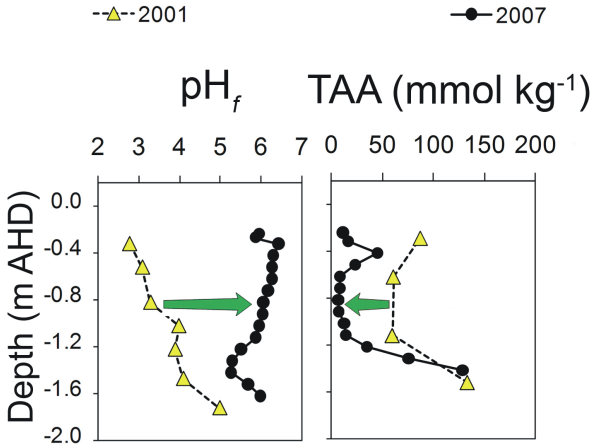

**Figure 1. Changes in soil pH and Total Actual Acidity (TAA), for a former sulfuric soil horizon at the East Trinity Wetland, Cairns, Eastern Australia, showing a dramatic increase in soil pH and decrease in TAA after 6 years of permanent tidal inundation (adapted from Johnston *et al.* 2009).**

**Figure 2. Photos illustrating the abundance of iron in the shallow groundwater and as surface precipitate accumulations at East Trinity, resulting from tidal inundation triggered microbial reduction of iron minerals within the deeper, former sulfuric soil layers.**

Tidal inundation at East Trinity has also triggered a succession of floodplain vegetation communities towards more salt tolerant species. Vegetation types vary in their supply of labile organic carbon for reductive iron-sulfur cycling. Distinctive relationships are known to occur between vegetation types and liability of organic carbon (Blodau and Peiffer 2003; Johnston *et al.* 2003). The magnitude of vegetation change and indirect effects on CASS are still largely unquantified.

*Periodic sea-water inundation*
CASS are prone to pulse events of saline water intrusion, due to extreme tides, storm surge and tsunamis.

These events are generally short-lived and do not shift systems from oxidative to reductive geochemical condition. The inundation of acidic soils with saline water has a number of important possible direct effects that include: 1) Enhancing the release of acidity as $Al^{3+}$ via cation exchange processes, which may then acidify surface or downstream waters (Wright *et al.* 1988); 2) Enhancing the release of Fe (Portnoy and Giblin 1997). Cyclic redox transformations of Fe greatly influence the acidity, chemistry and oxygenation status of overlying waters (Burton *et al.* 2006); 3) Enhancing the release of nutrients into pore waters, particularly $NH_4$ (Portnoy and Giblin 1997).

Recent research by our group at Southern Cross University has examined the response of a range of CASS to short-term saline water inundation. The results of this research are being presented in detail at the 19th World Congress on Soil Science (Wong *et al*. submitted). Saline water generally causes a rapid displacement of acidic metal cations and metal contaminants, resulting in lower pH and increased metal contents in surface waters. The potential for greater release of acidity and contaminants by periodic saline water ingress will be enhanced under the currently predicted changing climate scenario of increasing storm surges and extreme high tides.

*Increasing frequency of extreme weather events: droughts and floods*

*Drought*

The effects of prolonged drought on the further oxidation and acidification of CASS have been examined for agricultural areas (e.g. Wilson *et al*. 1999). Drought can exert its greatest impact on already drained and therefore, hydrologically stressed CASS landscapes. Interestingly, Wilson *et al*. (1999) found that in periods of drought, water quality in agricultural field drains improved. This was attributed to an inversion of the hydraulic gradients caused by crop water use, lowering the groundwater to below the drainage system and effectively preventing seepage. However, when rainfall does return and droughts break, extremely poor quality can result. It is well known that 'first-flush' flood events in CASS cause the greatest impact (Sammut *et al*. 1996).

Exposure of unoxidised sulfidic soils by extreme drought is an emerging concern in drought prone regions. In their natural state, CASS landscapes are characteristically waterlogged, and drought has rarely been considered a significant threat. However, water capture and irrigation have reduced the discharge of most major catchments throughout the world, particularly at critically dry periods. Demand for secure water in developing nations is increasing and regulation of river flows is continuing (e.g. the Mekong). The vulnerability of drying out water bodies that currently prevent subaqueous sulfidic soil materials from oxidising is largely unknown. With higher temperatures, increasing evaporative losses, less rainfall and greater demand on water resources under a changing climate, subaqueous sulfidic areas that are currently protected by natural water bodies will become increasingly susceptible to exposure by drought. An insight to the potential scale of drought triggered CASS impacts is currently provided in the Murray-Darling river basin of Australia, arguably one of the most highly regulated and stressed major river systems. An extreme drought period that has dominated the catchment since the year 2000, has lowered lake water levels, exposing thousands of hectares of sulfidic shoreline and lake-bed sediments (Fitzpatrick *et al*. 2008). These sediments are beginning to oxidise and acidify, and predictions indicate that water levels will continue to drop for the next couple of years. Climate change predicts a greater occurrence of drought, the vulnerability of subaqueous ASS and potential consequences to water quality have not been systematically assessed.

*Floods*

Biogeochemical processes occurring in CASS landscapes exert a controlling influence on drainage water quality (Burton *et al.* 2006). Catastrophic fish kills as a result of extreme deoxygenation and/or acidification can result from large flood events (Bush *et al*. 2004; Sammut *et al.* 1996; Johnston *et al*. 2004). In isolation, it would seem reasonable to expect that an increase the frequency of flood events will increase the environmental and agronomic impact from CASS. However, there is a range other factors that may contribute to the magnitude of floodwater impacts, such as the abundance of monosulfidic black ooze (MBO) in drains and seasonality. Deoxygenation is known to be far more intense during summer floods due to the more rapid decomposition of floodplain vegetation (Johnston *et al*. 2004). A consideration of how contaminants accumulate in the soil profile and how MBO materials accumulate in drains between floods, and the influence of seasonality is required to begin to understand how future climate change may affect flood induced impacts in CASS landscapes.

## Conclusions

Climate change is predicted to causes many environmental impacts that have direct relevance to CASS. Our scientific understanding of the chemical, biological and hydrological processes in CASS indicates that climate change will have an impact on these soils and CASS landscapes. However, advancing our understanding of these impacts will require new science that integrates the key areas of understanding the influence of climate change on the parameters which govern them. This is a critical and emerging frontier for acid sulfate soil research.

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## References

Blodau C, Peiffer S (2003) Thermodynamics and organic matter: constraints on neutralisation processes in sediments of highly acidic waters. *Applied Geochemistry* **18**, 25-36.

Burton ED, Bush RT, Sullivan LA (2006) Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica Acta* **70**, 5455-5468.

Burton ED, Bush RT, Sullivan LA, Johnston SG, Hocking RK (2008) Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chemical Geology 253, 64-73.

Bush RT, Sullivan LA Fyfe D (2004) Redistribution of monosulfidic black oozes by floodwaters in a coastal acid sulfate soil floodplain. *Australian Journal of Soil Research* **42**, 603-608.

Dent D (1986) ‘Acid Sulphate Soils: a Baseline for Research and Development.’ ILRI Publication No. 39. (International Institute for Land Reclamation and Improvement: Wageningen, Netherlands)

Fitzpatrick R, Marvanek S, Shand P, Merry R, Thomas M (2008). Acid sulfate soil maps of the River Murray below Blanch town (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre drought and current drought conditions. (CSIRO Land and Water, Glen Osmond, SA.)

IPCC (2007) Climate Change 2007: The physical science basis, summary for policy makers. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC Secretariat, Switzerland pp 1-18.

Johnston SG, Slavich PG, Hirst P (2003) Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to Melaleuca quinquenervia encroachment. *Australian Journal of Soil Research* **41**, 1343-1367.

Johnston SG, Slavich PG, Hirst P (2004) The acid flux dynamics of two artificial drains in acid sulfate soil backswamps on the Clarence River floodplain, Australia. *Australian Journal of Soil Research* **42 (5)**, 623-637.

Johnston SJ [editor’s comment: don’t use et al; give all author’s names] (2009) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335-346.

Portnoy JW, Giblin AE (1997) Biogeochemical effects of seawater restoration to diked salt marshes. *Ecological Applications* **7**, 1054-1063.

Sammut J, White I, Melville MD (1996) Acidification of an estuarine tributary in Eastern Australia due to drainage of acid sulfate soils. *Marine and Freshwater Research* **47** 669-684.

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

Wright RF, Norton SA, Brakke DF, Frogner T (1988) Experimental verification of episodic acidification of freshwaters by sea salts. *Nature* **334**, 422-424.

# Dissolution of phyllosilicates under saline acidic conditions

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## Abstract

The effect of saline acidic conditions on the dissolution rates of kaolinite, illite and montmorillonite was investigated. The dissolution experiments were carried out at pH 1 and 2 at 25°C under far from equilibrium conditions using stirred flow-through reactors. The dissolution rates were calculated on the basis of steady state Al and Si concentrations, except for illite dissolution experiment at pH 2, where the rate was calculated from Al release rate. There is a good agreement between the estimates obtained from Al and Si values for the dissolution rates of studied minerals. An initial rapid and incongruent release of elements was followed by a slow and congruent release rate at the steady state. Preferential release of Al at the initial stages was observed for kaolinite and illite in all the experiments while no such trend was observed for smectite. The calculated (log Al) dissolution rates at pH 1.0 and 2.06 are -12.61 and -13.30 for kaolinite, -12.79 and -12.86 for illite and -12.64 and -12.92 for smectite, respectively. Our results showed higher dissolution rates of kaolinite under saline acidic conditions as compared to the non-saline acidic conditions.

## Key Words

Steady state, acidity, clay minerals, pyrite, acid sulfate soils, aluminosilicates.

## Introduction

Pyrite is the most commonly occurring iron sulfide mineral in soils and it forms in anaerobic soil materials. Oxidation of pyrite due to natural and anthropogenic activities leads to the release of copious amounts of sulfuric acid in soil and water environments, and formation of acid sulfate soils (ASS). In Australia, many different types of ASS have been found because of diversified hydrology and biogeochemistry in different areas of the continent. The two main types include coastal and inland ASS. Coastal ASS cover an area of 95,000 km$^2$ in Australia. Most of these soils lie beneath coastal estuaries and tidal basins and many are very close to significantly populated centres. Inland ASS were not given much attention until the identification of sulfidic sediments in inland non-tidal seepage area of Mt. Lofty Ranges, South Australia (Fitzpatrick *et al.* 1996), wetlands of Murray Darling Basin (Lamontagne *et al.* 2004) and the sediments of Bottle Bend Lagoon (McCarthy *et al.* 2006).

A soil becomes acidic when acid neutralizing processes in the soil consume less $H^+$ than is being produced by the acid producing processes. The components of the soil with a capacity to neutralize acidity generated by various processes include soil solution, exchange complex and minerals. Mineral dissolution becomes the major acid consuming process in highly acidic systems with pH ≤ 4. Phyllosilicates in soils have the largest capacity to consume acidity generated by various processes because of their presence in soil in large quantities. Although the dissolution of phyllosilicates occurs over the whole pH range, the rate of dissolution increases as the pH decreases in the acidic pH range (Rozalen *et al.* 2008). The acid neutralization from phyllosilicates dissolution is strongly dependent on their respective dissolution rates. In the past few decades many studies were conducted to determine the dissolution rates of kaolinite (Cama and Ganor 2006; Cama *et al.* 2002; Huertas *et al.* 1999; Nagy *et al.* 1991; Yang and Steefel 2008) while only a few studies have measured dissolution of illite (Kohler *et al.* 2003) and montmorillonite (Amram and Ganor 2005; Golubev *et al.* 2006; Huertas *et al.* 2001; Rozalen *et al.* 2008) under different solution conditions. These past studies were conducted under different temperatures and input solution compositions, however, none of them measured the dissolution of phyllosilicates in saline acidic environments. The aims of the present study were to determine the dissolution rates of most commonly occurring phyllosilicates in Australia, i.e. kaolinite, illite and montmorillonite, in saline acidic input solutions, and to determine the effects of pH and ionic strength on mineral dissolution rates.

## Methods

*Pre-treatment and characterization*

Kaolinite (KGa-2), illite (IMt-2) and montmorillonite (SWy-2) samples were obtained from the Source Clay Repository of the Clay Minerals Society. After separating the clay fraction (<2 μm), the mineral samples were saturated with $Na^+$ and washed repeatedly to remove excess salts before freeze drying. Mineralogical characterization of the pre-treated samples was done by X-ray diffraction (XRD). Minor amounts of quartz were found in both montmorillonite and illite samples, and rutile was observed in kaolinite. The bulk chemical composition of the clay samples was determined using X-ray fluorescence (XRF) and Fe(II) in the mineral samples was determined by the 1, 10 phenanthroline method (Amonette and Templeton 1998). The structural formulae of minerals was calculated from the XRF and Fe(II) data (Cicel and Komadel 1994). The corresponding Al/Si ratios obtained from structural formulae of kaolinite, illite and montmorillonite are 1.03, 0.55 and 0.40, respectively. The specific surface area of the Na-saturated clay samples was measured by five point $N_2$ adsorption using Brunauer-Emmett-Teller method, and the values were 21, 42 and 37 $m^2/g$ for kaolinite, illite and montmorillonite, respectively.

*Experimental settings*

Dissolution experiments were carried out using stirred flow-through reactors (46 mL volume). The experiments were conducted at 25±1°C by immersing the reactors in a thermostatic water bath held at the desired temperature. A constant flow rate of the input solution was maintained by a Gilson peristaltic pump. Flow rate range of 0.02-0.05 mL/min was used in different experiments. The flow rate and input solution composition were kept constant for long enough time to reach the steady state. The input solutions at specific pH were prepared by diluting concentrated $H_2SO_4$ with E-pure water and NaCl was used to maintain a constant ionic strength of the solution. The effluent solution was collected every day and the total concentrations of Al and Si were determined colorimetrically by Catechol violet (Dougan and Wilson 1974) and Molybdate blue method (Koroleff 1976), respectively. The concentrations of Ca, Fe, K, Mg and Na were determined by inductively coupled plasma atomic emission spectroscopy. The variations in the output Al and Si concentrations and pH were monitored throughout the duration of each experiment while the amounts of Fe, K, Mg and Na were determined for only selected samples when steady state was reached for Al and Si. The experimental conditions for all experiments and the concentrations of Al and Si at steady state are presented in Table 1.

*Kinetics calculations*

The dissolution reactions of kaolinite, illite and montmorillonite in acidic conditions can be expressed as:

$$(Si_{3.85}Al_{0.15})[Al_{3.81}Ti_{0.13}Fe^{3+}{}_{0.06}Fe^{2+}{}_{0.02}]O_{10}(OH)_8+11.6H^+\rightarrow 3.85H_4SiO_4+3.96Al^{3+}+0.13Ti^{4+}+0.06Fe^{3+}+0.02Fe^{2+}+2.6H_2O \tag{1}$$

$$K_{1.38}Na_{0.05}(Si_{7.02}Al_{0.98})[Al_{2.87}Mg_{0.46}Fe^{3+}{}_{0.39}Fe^{2+}{}_{0.28}Ti_{0.07}]O_{20}(OH)_4+17.92H^++3.08H_2O\rightarrow 1.38K^++0.05Na^++7.02H_4SiO_4+3.85Al^{3+}+0.46Mg^{2+}+0.39Fe^{3+}+0.28Fe^{2+}+0.07Ti^{4+} \tag{2}$$

$$K_{0.01}Na_{0.56}(Si_{7.98}Al_{0.02})[Al_{3.13}Mg_{0.45}Fe^{3+}{}_{0.32}Fe^{2+}{}_{0.06}Ti_{0.01}]O_{20}(OH)_4+13.1H^++6.9H_2O\rightarrow 0.01K^++0.56Na^++7.98H_4SiO_4+3.15Al^{3+}+0.45Mg^{2+}+0.32Fe^{3+}+0.06Fe^{2+}+0.01Ti^{4+} \tag{3}$$

The equilibrium constants for the dissolution reactions of illite and montmorillonite were computed from equations and parameters reported by Vieillard (2000). For kaolinite dissolution reaction a log $K_{eq}$ value of 8.95 reported in earlier studies (Nagy *et al.* 1991) was used.

The dissolution rate ($mol/m^2s$) in a stirred flow-through reactor was calculated from the release rate of Al or Si at the steady state by using the following equation (Cama *et al.* 2000):

$$Rate_j = -\frac{1}{V_j}\frac{q}{SM}\left(C_j\right) \tag{4}$$

where $C_j$ is the concentration of component $j$ (Al or Si) in the output solution (mole/L), q is the fluid volume flow through the reactor (L/s), S is the specific surface area ($m^2$), M represents the mineral mass (g) and $V_j$ is the stoichiometric coefficient of component $j$ in the dissolution reaction.

The saturation state of the solution with respect to mineral (kaolinite, illite or montmorillonite) dissolution was calculated in terms of Gibbs free energy of reaction $\Delta G_r$:

$$\Delta G_r = RT\ln\left(\frac{IAP}{K_{eq}}\right) \tag{5}$$

where IAP is the ion activity product, $K_{eq}$ is the equilibrium constant, T represents the absolute temperature and R is the gas constant. Activities of various ions in the solution were calculated using *Visual MINTEQ* V 2.61 geochemical model.

## Results

The dissolution was very fast at the start of each experiment with rapid, incongruent release of Al, and Si which became slower after first 200 hours of the experiment as shown in Figure 1. In kaolinite and illite experiments, initially Al was released at a much faster rate than Si and continuously decreased before reaching the steady state. In case of montmorillonite dissolution, there was not much difference in the initial release rate of Al and Si. The steady state concentrations of Al and Si for kaolinite and illite showed a congruent dissolution of these minerals at the studied experimental conditions while a higher Al release was observed for montmorillonite under saline acidic conditions.

**Table 1. Dissolution rates for kaolinite, illite and montmorillonite at pH 1 and 2 in 0.25 M NaCl solution at 25°C**

| Mineral | Initial mass (g) | pH input | Flow rate (mL/min) | Duration (h) | C Si out (µmol/L) | C Al out (µmol/L) | Al/Si | log Rate Si (mol/m$^2$s) | log Rate Al (mol/m$^2$s) |
|---|---|---|---|---|---|---|---|---|---|
| KGa-2 | 0.4014 | 1.00 | 0.0477 | 1803 | 10.1 | 10.2 | 1.01 | -12.61 | -12.61 |
| KGa-2 | 0.3885 | 2.06 | 0.0377 | 2170 | 2.63 | 2.62 | 1.00 | -13.28 | -13.3 |
| IMt-2 | 0.1163 | 1.00 | 0.0431 | 1890 | 8.48 | 4.16 | 0.49 | -12.75 | -12.79 |
| IMt-2 | 0.1164 | 2.06 | 0.0545 | 1677 | 3.1 | 2.84 | 0.96 | - | -12.86 |
| SWy-2 | 0.1221 | 1.00 | 0.0428 | 1731 | 9.11 | 4.61 | 0.51 | -12.74 | -12.64 |
| SWy-2 | 0.1226 | 2.06 | 0.0357 | 1942 | 5.47 | 2.87 | 0.52 | -13.05 | -12.92 |

Our results for kaolinite dissolution experiment at pH 1 and 2 and 0.25 ionic strength showed a significant increase in the mineral dissolution rate (Table 1) as compared to the previous studies conducted at lower ionic strengths. Cama *et al*. (2002) reported a dissolution rate of -12.96 and -13.47 for kaolinite (KGa-2) at pH 1 and 2 and ionic strength of 0.12 and 0.011, respectively. Zysset and Schindler (1996) also reported a higher dissolution rate for K-montmorillonite in 1 and 0.1 M KCl solutions than in 0.03 M KCl solution. To evaluate the effect of ionic strength on the dissolution of illite and montmorillonite, we are conducting further experiments.

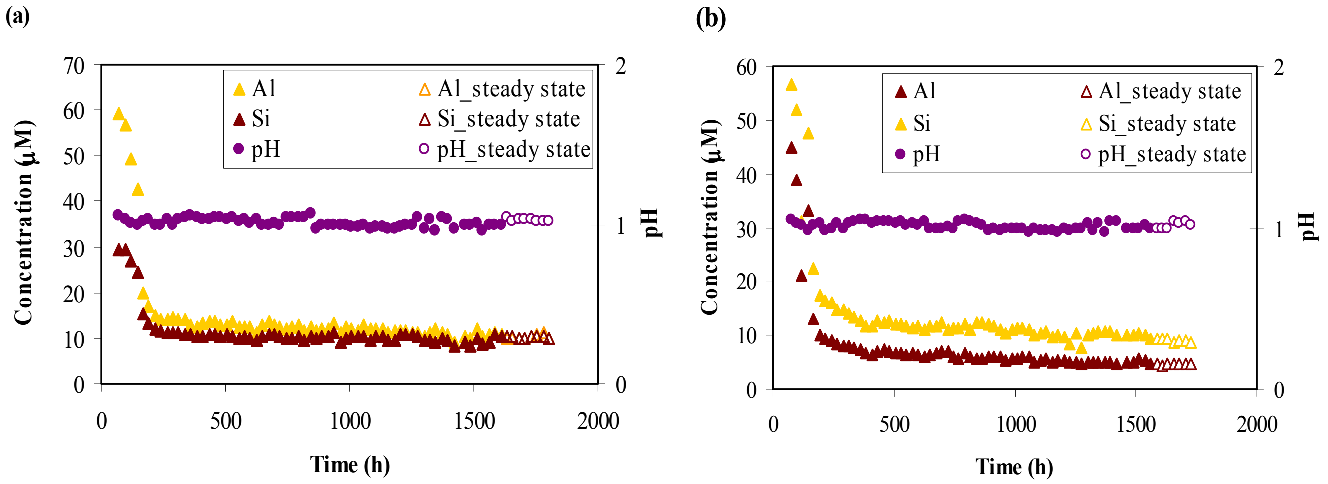

**Figure 1. Variation in Al and Si concentrations and pH as a function of time in two representative flow-through dissolution experiments conducted at pH 1.0 (a) kaolinite and (b) smectite**

## Conclusion

The preliminary results suggest that the effect of pH on the dissolution rates of the kaolinite, illite and montmorillonite is similar, indicating a common rate limiting step in the dissolution of phyllosilicates. The dissolution rate of kaolinite appears to have increased with increasing ionic strength of the solution. However, further experiments are needed to confirm these results for all three minerals.

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## References

Amonette JE, Templeton JC (1998) Improvement to the quantitative assay of nonrefractory minerals for Fe (II) and total Fe using 1, 10 phenanthroline. *Clays and Clay Minerals* **46**, 51-62.

Amram K, Ganor J (2005) The combined effect of pH and temperature on smectite dissolution rate under acidic conditions. *Geochimica et Cosmochimica Acta* **69**, 2535-2546.

Cama J, Ganor J (2006) The effects of organic acids on the dissolution of silicate minerals: A case study of oxalate catalysis of kaolinite dissolution. *Geochimica et Cosmochimica Acta* **70**, 2191-2209.

Cama J, Ganor J, Ayora C, Lasaga CA (2000) Smectite dissolution kinetics at 80 degrees C and pH 8.8. *Geochimica et Cosmochimica Acta* **64**, 2701-2717.

Cama J, Metz V, Ganor J (2002) The effect of pH and temperature on kaolinite dissolution rate under acidic conditions. *Geochimica et Cosmochimica Acta* **66**, 3913-3926.

Cicel B, Komadel P (1994) Structural formulae of layer silicates. In 'Quantitative methods in soil mineralogy'. (Eds JE Amonette, LW Zelazny) pp. 114-136 (Madison, WI).

Dougan WK, Wilson AL (1974) Absorbtiometric determination of aluminium in water-comparison of some chromogenic reagents and development of an improved method. *Analyst* **99**, 413-430.

Fitzpatrick RW, Fritsch E, Self PG (1996) Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* **69**, 1-29.

Golubev SV, Bauer A, Pokrovsky OS (2006) Effect of pH and organic ligands on the kinetics of smectite dissolution at 25°C. *Geochimica et Cosmochimica Acta* **70**, 4436-4451.

Huertas FJ, Caballero E, de Cisneros CJ, Huertas F, Linares J (2001) Kinetics of montmorillonite dissolution in granitic solutions. *Applied Geochemistry* **16**, 397-407.

Huertas FJ, Chou L, Wollast R (1999) Mechanism of kaolinite dissolution at room temperature and pressure Part II: Kinetic study. *Geochimica et Cosmochimica Acta* **63**, 3261-3275.

Kohler SJ, Dufaud F, Oelkers EH (2003) An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50 degrees C. *Geochimica et Cosmochimica Acta* **67**, 3583-3594.

Koroleff F (1976) Determination of silicon. In 'Methods of sea water analysis'. (Eds K Grasshoff, M Ehrhardt, K Kremling) pp. 149-158. (Verlag Chemie USA: Weinheim; Deerfield Beach, Florida).

Lamontagne S, Hicks WS, Fitzpatrick RW (2004) Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: implications for floodplain salinity management Technical Report 28/04. CSIRO Land and Water, Adelaide.

McCarthy B, Conallin A, D'Santos P, Baldwin DS (2006) Acidification, salinisation and fish kills at an inland wetland in south-eastern Australia following partial drying. *Ecological Management and Restoration* **7**, 218-223.

Nagy KL, Blum AE, Lasaga AC (1991) Dissolution and precipitation kinetics of kaolinite at 80°C and pH 3: The dependence on solution saturation state. *Ameican Journal of Science* **291**, 649-686.

Rozalen ML, Huertas FJ, Brady PV, Cama J, Garcia-Palma S, Linares J (2008) Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25 degrees C. *Geochimica et Cosmochimica Acta* **72**, 4224-4253.

Vieillard P (2000) A new method for the prediction of Gibbs free energies of formation of hydrated clay minerals based on the electronegativity scale. *Clays and Clay Minerals* **48**, 459-473.

Yang L, Steefel CI (2008) Kaolinite dissolution and precipitation kinetics at 22 °C and pH 4. *Geochimica et Cosmochimica Acta* **72**, 99-116.

Zysset M, Schindler PW (1996) The proton promoted dissolution kinetics K-montmorillonite. *Geochimica et Cosmochimica Acta* **60**, 921-931.

# Dissolved inorganic carbon in coastal acid sulfate landscapes

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## Abstract

An acid sulfate soil landscape was investigated to understand the pattern of dissolved inorganic carbon (DIC). Drainage water was measure in situ for DIC using a novel conversion methodology. Sediments and soils were collected and used in an incubation experiment to induce oxidation. Temporal and spatial variations in DIC and stable isotope ($^{13}C_{DIC}$) concentration were found to exist between the groundwater and surface water. This demonstrated a hydrologic boundary between the surface water located in the drainage system and the underlying groundwater. Lab-based atmospheric equilibration studies of groundwater showed temporal decreases in pH, Fe(II), alkalinity, and, DIC with an associated increase in $^{13}C_{DIC}$ when compared to non-acid sulfate impacted waterbodies. The loss of DIC was demonstrated to follow first-order kinetics.

## Key Words

Dissolved inorganic carbon, acid sulfate soil, carbon efflux

## Introduction

Understanding the control of carbon fluxes from terrestrial ecosystems is of interest due to their contribution to the global carbon cycle. Several important studies have focused on the transfer of $CO_2$ between the atmosphere, soils, and vegetation. However, there is limited information on the links between hydrology and the biogeochemical processes that may regulate $CO_2$ fluxes. The overall contribution of the outgassing of $CO_2$ from surface waters is recognised as a significant component of the terrestrial carbon efflux. Drainage waters from coastal acid sulfate landscapes have elevated metal concentrations, which upon hydrolysis generates additional acidity (Green *et al.* 2006). We have previously shown that variable flow events in drainage systems of acid sulfate landscapes results in variable discharge of metals (Macdonald *et al.* 2007). Studies on gaseous emissions from terrestrial acid sulfate landscapes have provided a detailed understanding of gaseous emissions (Macdonald *et al.* 2004a; Kinsela *et al.* 2007) and shown the importance of acid sulfate soils as carbon emitters (Denmead *et al.* 2008). At the same instance, metal oxidation and hydrolysis in acid sulfate waters are increasingly well understood, however, the relationship between metal oxidation, hydrolysis and carbon flux has yet to be determined.

The acidification of drainage water should result in a drive of equilibria to $CO_2$* ($CO_{2(aq)+}H_2CO_3$). The degassing of the $CO_2$ component should be accompanied by an enrichment in $^{13}C$ as $^{12}C$ is preferentially lost. It is not known precisely how these processes operate under different hydrologic regimes and varying sediment/soil geochemistry in acid sulfate landscapes. It is the aim of this work to produce an accurate in situ measurement technique for the quantification of DIC and measure diurnal flux between soils and sediments and the overlying waters. By investigating biogeochemical processes in situ and under laboratory controlled conditions, an understanding of the interrelationship between metals, acidity and carbon was established.

## Methods

### *Study Site*

The study area is Black's Drain a subcatchment (520 ha) of the Tweed River, in northern New South Wales (28°18'S, 153°31'E), eastern Australia. Originally, the subcatchment was a poorly drained backswamp, but today is extensively drained and the predominant floodplain landuse is currently sugarcane production. The climate of the Tweed Valley is humid and subtropical with a summer-dominant (November-March) average annual rainfall at neighbouring Murwillumbah is 1682 mm. The site is characterised by acid sulfate soils which dominate the floodplain (at 325 ha or 93%), and produce acidic, metal-rich discharge (see Macdonald *et al.* 2007). The soils are characterised by an A1 horizon that is an organic clay loam with 5% organic C, pH ~4-6, and 65% porosity. The A2 horizon is strongly acidic (pH <4), while the reduced subsoil B horizon is 85% clay, pH ~6.5.On average, acid sulfate soil within the region contains the equivalent of 50-70 tonnes of soluble $H_2SO_4$/ha within the sulfuric horizon (Macdonald *et al.* 2004b).

One drain sampling point at upstream and downstream locations of Black's Drain was selected based on the findings of Macdonald *et al.* (2007) for water quality and Collins *et al.* (2009) on iron oxide composition. The upstream site is dominated by discharge from acid sulfate soil, whilst the downstream site is a mix of acid sulfate discharge and tidal water from the adjoining Tweed River.

*DIC analysis*

An $CO_2/H_2O$ infra-red gas analyser (LI-840, LI-COR Biosciences) was modified to measure DIC concentration in situ following conversion of aqueous DIC to $CO_{2(g)}$. The procedure involved the uptake of 10 ml of drainage water by peristaltic pump and addition of perchloric acid (0.5 ml) in a sealed line for conversion of DIC to $CO_{2(g)}$. The evolved $CO_{2(g)}$ passes through a hydrophobic membrane into a gas line and is analysed by infra-red. The $CO_{2(g)}$after passing through the infra-red is trapped in a molecular sieve which is preserved for 13C analysis and transported back to the lab. $^{13}C$ and $^{12}C$ isotopes were measured using a GV Instruments Isoprime ratio mass spectrometer. Samples were collected every 6 hours for a 72 hour period. For each DIC sample a corresponding sample was taken for field pH, Fe(II)/Fe(III), EC, DO, and a sample preserved with $HNO_3$ for determination of metals (ICP-OES and ICP-MS).

*Sediment/Soil dispersion and incubation*

Soils and sediments were collected from the drain bottom at depth of 0.5 m AHD (monosulfide enriched), and from drain edges (at 1.2 m AHD and above drain water height on the drain bank) adjacent to the DIC measurement locations. Samples of unoxidised sediment (potential acid sulfate soil) and groundwater were sampled (at a depth of 1.2 AHD metres (2.5 metres depth the ground surface) and 15 metres perpendicular from the drain) and sealed in airtight containers. Additional to this, an organic rich surface soil was collected from the sugar cane cropping zone to investigate organic additions. All samples were chilled to 3ºC. Triplicate 50 g samples were homogenised in 200 ml of MQ water and allowed to oxidise under a controlled environment in a sealed incubation chamber for a period of 72 hours. The incubation chamber included comprised a sealed vessel, inlet and outlet for pressurised high-purity oxygen to pass and a magnetised stirring bar to allow for continual mixing. At 4-hour intervals a sample was withdrawn via syringe and analysed for DIC and metal concentrations (as above). A 5 L sample of Tweed River water was collected from 5 km upstream of the Tweed River, beyond the extent of acid sulfate soil presence and used as a non-acid sulfate impacted water body control sample.

## Results

The characteristics of the drainage water from upstream (acid sulfate impacted) and downstream (tidal Tweed River impacted) are presented in Table 1. Evident are an increase in concentration of DIC and Eh in the downstream water as a result on estuarine Tweed River water entering the drainage system. Upstream beyond the limits of tidal reach, alkalinity and DIC are depleted. The loss of DIC in the upstream waters as $CO_{2(g)}$ is driven by the oxidation and hydrolysis of metals derived from the surrounding acid sulfate soils. A time-series plot of the soil and sediment suspension data (Figure 2) shows an exponential decline. The same trend in decline also applied to the sampled 'groundwater', which followed a pattern similar to the unoxidised potential acid sulfate soil over the 72-hour experiment. The reaction mechanism for exponential decreases in DIC concentration over time is governed by first order kinetics:

$$\mathrm{Ln}f = \ln(C_t / C_o) = -kt \qquad (1)$$

where $f$ is the fraction of residual DIC since the start of the DIC transformation, $C_t$ is the residual concentration of DIC at time $t$, $C_o$ is the concentration of DIC at the start to the experiment and $k$ is the rate constant. A decrease in Fe(II), alkalinity and pH have been reported in studies conducted on drain sediments collected at this location same (Burton *et al.* 2006). However, this is the first instance where DIC has been measured and shown to decrease.

**Table 1. Characterisation of drainage waters from acid sulfate soils (BD = Below Detection Limit).**

| | pH | EC (dS/m) | Alk ($CaCO_3$ mg/L) | DO (mg/L) | Eh (mV) | $SO_4^{2-}$ (mg/L) | Fe(II) (mg/L) | $^{13}C$ (‰) | DIC (mM C/L) |
|---|---|---|---|---|---|---|---|---|---|
| Upstream | 2.8 – 4.8 | 4.5 – 5.2 | 0 – 0.8 | 4.0 - 5.7 | 280 - 360 | 20 - 32 | 1.2 – 4.3 | BDL - 0.1 | 0 – 0.6 |
| Downstream | 5.5 - 6.6 | 0.7 – 1.6 | 28 – 37 | 5.2 – 7.3 | 410 - 430 | 360 - 390 | 0.1 - 1.7 | -1 - 1 | 0.8 - 1.2 |

The $^{13}C_{DIC}$ in the drainage water as with the DIC concentration was dependant upon the acidity generated via the hydrolysis of metals from the acid sulfate soil. The same result could be repeated in the monosulfide incubation experiment where $^{13}C_{DIC}$ decreased over the 72-hour incubation time. The unoxidised potential acid sulfate soil had an increase in $^{13}C_{DIC}$ over the incubation period. This was due to buffering capacity of the small amount of carbonate present in the estuarine deposited material. Overall the shift in $^{13}C_{DIC}$ is controlled by the isotopic fractionation, which is dependent upon whether DIC transformation and potential loss occurs by equilibration or kinetic processes. A discontinuity existed between the drainage water and the underlying groundwater that appears to confirm the assumption that hydraulic conductivity is exceedingly low in these landscapes.

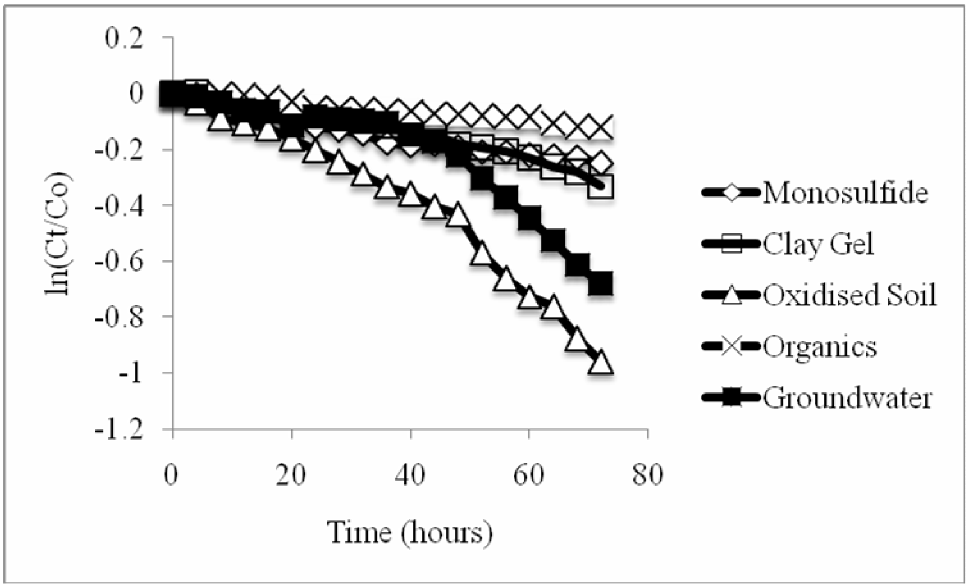

**Figure 1. Results from the oxidation experiment presented as a actual to initial DIC concentration.**

At the pH and alkalinity levels of the upstream acid sulfate waters it can be assumed the all DIC exists as $CO_2$*. However, the tidal water which enters the drainage system has a higher pH and DIC will be dominated by $HCO_3^-$ and as expected has an enrichment of $^{13}C_{DIC}$. It can be suggested that the continuous loss of DIC associated with the mixing of estuarine tidal waters and acid sulfate soil discharge water, is subject to kinetic isotopic fractionation effects. In these acid sulfate discharge waters, the extent of $HCO_3^-$ dehydration to $CO_{2(aq)}$ is controlled by the $HCO_3^-$ concentration relative to the concentration of protons produced by Fe(III) hydrolysis. It is likely that subjected to repeated cyclic precipitation and dissolution of Fe(III)/Fe(II) will typically exhaust the pool of DIC in drainage systems. Such a cyclic nature at this same site has been considered by Collins *et al.* (2009).

## Conclusion

Monosulfide sediments and groundwaters exposed to atmospheric conditions had high rates of $CO_2$ loss. Such loss may explain the depleted nature of DIC in discharge waters from acid sulfate landscapes. The hydrolysis of metals during the oxidation of sulfidic sediments generates a loss of DIC which can be modelled to follow first order kinetics. It is more difficult to understand $^{13}C_{DIC}$ processes in acid sulfate discharge waters; however an enrichment process does occur in the studied samples and may follow a kinetic loss mechanism.

**References**

Burton ED, Bush, RT, Sullivan LA (2006) Acid-volatile sulfide oxidation in coastal flood plain drains: Iron-sulfur cycling and effects on water quality. *Environmental Science & Technology* **40**, 1217-1222.

Collins RN, Waite TD (2009) Isotopically exchangeable concentrations of elements having multiple oxidation states: The case of Fe(II)/Fe(III) isotope self-exchange in coastal lowland acid sulfate soils. *Environmental Science and Technology* **43**, 5365-5370.

Denmead OT, Macdonald BCT, White I, Griffith DWT, Bryant G, Naylor T, Wilson S, Salter B, Stainlay W, Robke H (2008) Water, carbon and nitrogen fluxes from a tropical crop sugarcane. 28th American Meteorological Society Conference on Agricultural and Forest Meteorology, April 28- May 2, 2008, Orlando, FL.,USA.

Green R, Waite TD, Melville MD, Macdonald BCT (2006) Characteristics of the acidity in acid sulfate soil drainage waters, McLeods Creek, Northeastern NSW, Australia. *Environmental Chemistry* **3**, 225-232.

Kinsela AS, Reynolds JK, Melville MD (2007) Agricultural acid sulfate soils: A potential source of volatile sulfur compounds? *Environmental Chemistry* **4**, 18-25.

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

Macdonald BCT, Smith J, Keene AF, Tunks M, and Kinsela A (2004b) The chemical properties of sediments in a coastal estuarine lake affected by runoff from sulfuric soils. *Science of the Total Environment* **329**, 115-130.

Macdonald BCT, White I, Astrom ME, Keene AF, Melville MD, Reynolds JK (2007) Discharge of weathering products from acid sulfate soils after a rainfall event, Tweed River, Eastern Australia. *Applied Geochemistry* **22**(12), 2695-2705.

# Do acid sulfate soils need to be ring-mill ground to ensure an accurate Acid Base Account?

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## Abstract

Australian Standard acid sulfate soil methods require the grinding of soil to <0.075 mm. This necessitates the use of a ring-mill or similar apparatus, which is expensive and time-consuming. We investigate whether ring-mill grinding is needed for accurate and reproducible acid-base accounting, or if conventional fine-grinding (i.e. <0.5 mm) is sufficient to obtain acceptable results. Preliminary unreplicated experiments provided valuable information used to formulate the final experimental work. Following these initial experiments, five soils from an ASS survey in coastal central Queensland were selected for further investigation. These soils were chosen to reflect the range of chemical properties found in acid sulfate soils. Soils from the two treatments were analysed in quintuplicate by Chromium and SPOCAS suite analyses (Ahern *et al.* 2004). While individual analytes did show significant differences between treatments in some soils, there was no significant difference in the net acidity between ring-mill grinding and conventional grinding for soils without acid neutralising capacity (ANC). For the self-neutralising soils, conventional grinding gave significantly lower ANC results compared to the ring mill. It is uncertain whether ring-mill grinding gives a true reflection of the ANC available in the natural environment, as commercially-available agricultural lime ($CaCO_3$) is usually >0.075 mm diameter.

## Key Words

Acid sulfate soils, analysis, soil grinding, ring-mill, acid-base account.

## Introduction

With rising world population and with that growing coastal development, increasingly 'the nastiest soils in the world' (Dent 1986) are being disturbed. Without proper management, these acid-producing soils have the potential to cause serious/severe environmental harm, degrade expensive infrastructure (bridges, roads, pipelines) as well as impact upon human health. With the advent of a regulatory and best-practice management framework for acid sulfate soils in many Australian states, the disturbance and subsequent development of often environmentally sensitive coastal areas are now subject to much greater scrutiny. In Queensland, the State Planning Policy SPP2/02 (supplemented by the Queensland ASS Technical Manual) compels developers and Councils to follow set protocols for the sampling, chemical analysis, confirmation testing and management of acid sulfate soils (ASS). Consequently, soil testing laboratories that traditionally had an agricultural focus, along with new testing facilities, are now gearing up for ASS testing.

The chemistry of ASS is complex, as can be the chemical analysis and interpretation of test results. As with all soil analysis, appropriate sample preparation is fundamental to obtaining accurate, precise and representative results. Protocols must be such that a suitably ground, well-mixed sub-sample is produced that is representative of the soil collected in the field. Guidelines for the analysis of ASS (Ahern *et al.* 2004) and a recent Australian Standard (AS4969.1—2008 Analysis of acid sulfate soil—Dried samples—Methods of test, Method 1: Pre-treatment of samples) call for grinding of soils to less than 0.075 mm to ensure sample homogeneity and greater reactivity. Maher *et al.* (2004) used 4 soils to compare the chromium reducible sulfur ($S_{CR}$) and water soluble sulfate results obtained following 2 grinding treatments, 1) gently hand grinding to pass a 1 mm sieve and 2) ring-mill grinding for various grinding times from 1–30 minutes. The authors reported higher levels of $S_{CR}$ for the ring mill ground soil compared to the hand-ground sample and only minor differences for water soluble sulfate between the 2 grinding treatments. Higher recovery of $S_{CR}$ was attributed to abrading coatings of pyrite grains as a result of more aggressive grinding.

Gently hand grinding before sieving is not a recommended procedure in the Australian soil testing industry. It is unlikely that a representative sub-sample could be achieved for samples dominated by coarse sand and organic matter. In the Australian Laboratory handbook of Soil and Water Chemical Methods (Rayment and Higginson 1992) and its soon to be released revision (Rayment and Lyons, In Press), three soil grinding specifications are recommended. Coarse grinding to pass a 2 mm sieve is recommended for ‘plant available’ soil tests. For organic carbon and total nitrogen, generally smaller sample weights are required and fine grinding to pass a 0.5 mm sieve is recommended for homogeneity. The third specification <0.05 mm (ultra-fine grinding) involves the use of ring-mill systems. However such ultra-fine grinding is only recommended for XRF spectroscopy to avoid random scattering of fluorescent light from the surface of the sample pellet.

To date, no systematic comparison between regular fine grinding (<0.5 mm) and ring-mill grinding has been reported for ASS. This study compares five soils prepared by fine grinding to <0.5 mm (hereafter called ‘conventional fine grinding vs ring mill grinding for the ASS tests comprising the Chromium and SPOCAS suites.

## Methods

*Soil grinding mills*

After fan-forced drying of soil at 85ºC, the entire sample was ground to pass a 2 mm sieve. Those soils high in clay content that set hard were first fractured using a wooden mallet as shown in Figure 1. The coarse-ground sample was thoroughly mixed before the entire sample was finely ground to pass a 0.5 mm sieve (Figure 2). After this fine grinding samples were thoroughly mixed. Figure 2 shows the ring mill system used to grind a 30–50 g sub-sample of fine ground soil, for 2–3 minutes grinding time using the steel rings shown.

**Figure 1. Soil preparation equipment and coarse grinder (<2 mm) used in this study. Fine textured soils can dry very hard and need to be disaggregated up using either a mallet or device such as a vice before coarse grinding.**

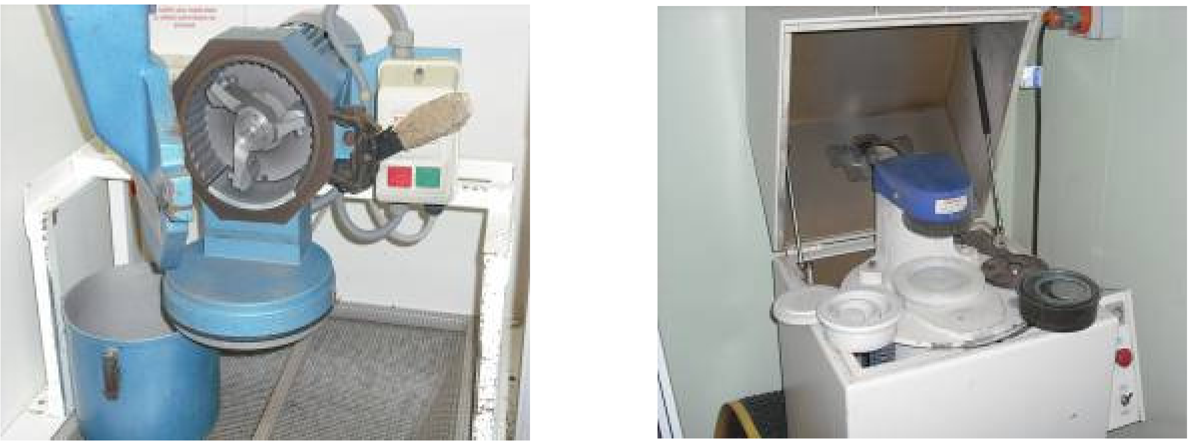

**Figure 2. Soil grinding equipment used for fine grinding to <0.5 mm (left) or <0.05 mm using a ring mill grinder (right). Both fuzed zirconia rings and steel rings are shown.**

*Chemical analysis*

The five soil samples were analysed in quintuplicate following the methods described in Laboratory Methods Guidelines (Ahern *et al*. 2004). These tests include: $S_{CR}$ (chromium reducible sulfur – Sullivan *et al*. 2000), $S_P$ (peroxide sulfur), $S_{KCl}$ (KCl-extractable S), $S_{RAS}$ (residual acid-soluble sulfur), TAA (titratable actual acidity), TPA (titratable peroxide acidity), $ANC_E$ (excess ANC), $pH_{KCl}$ (pH of suspension 1:40 1M KCl extract) and $pH_{OX}$ (pH of 1M KCl suspension after initial peroxide digestion). Calculations derived from tests including $S_{POS}$ (peroxide oxidisable sulfur) are also compared for the two grinding treatments.

## Results and Findings

Data in Figure 3 and Table 1 indicate that fine-grinding of soils is just as effective as ring-mill grinding in recovering chromium reducible sulfur ($S_{CR}$) for acid sulfate soils. Whilst the average standard deviation of results for ring-mill grinding is slightly less than for fine-grinding, on average fine-grinding produces a slightly higher result than ring-milling. Maher *et al*. (2004) surmised that grinding (they only looked at ring-mil ground soil) was necessary to abrade coatings on sulfide grains to maximise recovery, but for the 5 soils studied here it appears that conventional fine-grinding is also capable of ensuring adequate sulfide recovery.

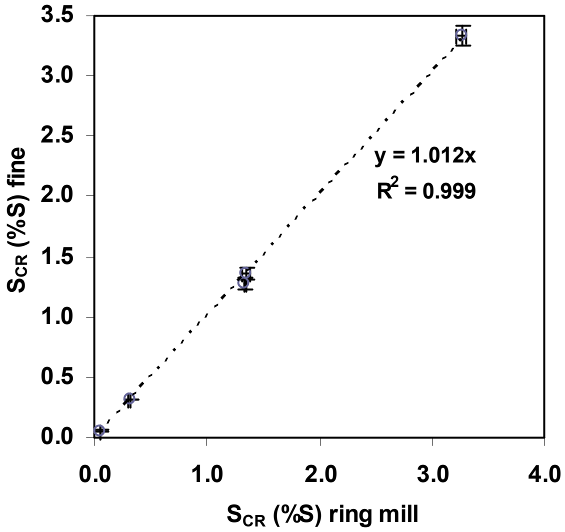

**Figure 3. Effect of grinding treatment on chromium reducible sulfur ($S_{CR}$). (Means shown, error bars represent ±1 s.d. for 5 replicates).**

For environmental management/risk assessment purposes the quantity 'net acidity' is of principal importance, as it represents a worst-case scenario of the amount of acidity that a soil may generate if it is allowed to fully oxidise and release its entire store of acidity. In the acid-base accounting (ABA) equation, the net acidity represents the sum of the potential sulfidic acidity (i.e. $S_{CR}$ or $S_{POS}$), actual acidity (TAA) and retained acidity ($S_{RAS}$ or $S_{NAS}$), minus soil ANC (moderated by an empirical fineness factor, to allow for the surface area of carbonates in the sample). It is apparent for the three soils (in Figure 4 and Table 1) not containing ANC, that there is no statistical difference in net acidity calculated from the SPOCAS suite between fine-grinding and ring-mill grinding treatments.

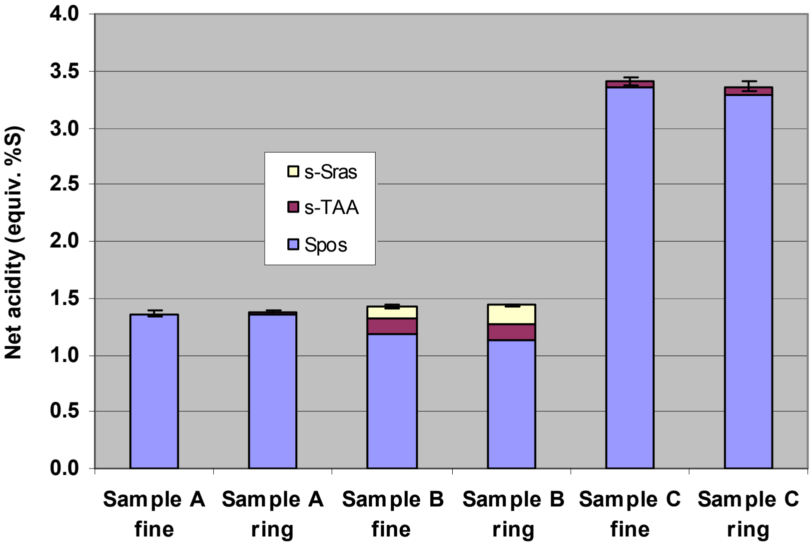

**Figure 4. Effect of grinding treatment on net acidity by the SPOCAS suite for 3 soils without ANC (Means shown, error bars represent ±1 s.d. for 5 replicates).**

However, individual analytes do show differences for some soils. For instance, $S_{KCl}$ shows a general trend to increasing values for the more vigorous ring mill grinding. This could represent oxidation of sulfide and its conversion to sulfate during the grinding process, or simply greater exposure of soil mineral surfaces hence more effective extraction of sulfate by 1M KCl. If the former were the case, then a commensurate increase in TAA might be expected, compensated by a proportionate decrease in $S_{POS}$. This appears to be the case for samples B and C (Table 1), though the increase in TAA does not exactly tally with the decrease in $S_{POS}$. For sample A there is little discernible effect. The increase in the TAA may simply be a consequence of the increased surface area and exposure of fresh mineral surfaces for titration. Conventional fine grinding did however yield substantially lower (i.e. 15–18%) $ANC_E$ results compared to ring-milling. This is not unexpected, since the determination involved a slow titration with dilute acid whose kinetics are controlled by surface area. The neutralisation reactions are also surface-controlled in the field. The ring mill grinding of shells and other carbonates that contribute to the lab ANC may be an overestimate of field ANC. It is uncertain whether ring-mill grinding gives a true reflection of the ANC available in the natural environment, or for lime-treated ASS, as shells and commercially-available agricultural lime ($CaCO_3$) are usually >0.075 mm in diameter.

**Table 1. Comparison between fine grinding and ring mill grinding for a range of ASS analytes (Means shown, italicised data represents the s.d. of 5 replicates of the preceding analyte. A fineness factor of 1.5 for ANC was used in net acidity calculations).**

| **Soil** | **A** | | **B** | | **C** | | **D** | | **E** | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Analyte** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** |
| **$S_{CR}$** | 1.366 | 1.352 | 1.282 | 1.340 | 3.336 | 3.266 | 0.058 | 0.056 | 0.318 | 0.314 |
| ***(%S)*** | *0.048* | *0.028* | *0.049* | *0.012* | *0.080* | *0.049* | *0.0044* | *0.005* | *0.004* | *0.009* |
| **$S_{POS}$** | 1.353 | 1.357 | 1.180 | 1.124 | 3.354 | 3.291 | 0.067 | 0.042 | 0.319 | 0.280 |
| ***(%S)*** | *0.029* | *0.013* | *0.018* | *0.011* | *0.030* | *0.046* | *0.004* | *0.002* | *0.005* | *0.008* |
| **$pH_{KCl}$** | 5.10 | 5.42 | 3.60 | 4.10 | 5.22 | 5.30 | 9.20 | 9.26 | 8.80 | 8.88 |
| | *0.00* | *0.04* | *0.00* | *0.00* | *0.04* | *0.00* | *0.04* | *0.05* | *0.00* | *0.04* |
| **s-TAA** | 0.012 | 0.016 | 0.134 | 0.146 | 0.052 | 0.073 | n/a | n/a | n/a | n/a |
| ***(%S)*** | *0.001* | *0.000* | *0.003* | *0.003* | *0.001* | *0.001* | *n/a* | *n/a* | *n/a* | *n/a* |
| **$pH_{OX}$** | 2.16 | 2.15 | 2.10 | 2.08 | 1.88 | 1.90 | 7.08 | 7.40 | 6.98 | 6.98 |
| | *0.05* | *0.06* | *0.00* | *0.04* | *0.04* | *0.00* | *0.04* | *0.07* | *0.04* | *0.04* |
| **s-TPA** | 1.343 | 1.342 | 1.337 | 1.278 | 3.872 | 3.808 | n/a | n/a | n/a | n/a |
| ***(%S)*** | *0.015* | *0.010* | *0.018* | *0.017* | *0.021* | *0.054* | - | - | - | - |
| **$ANC_E$** | n/a | n/a | n/a | n/a | n/a | n/a | 9.88 | 11.64 | 5.26 | 6.42 |
| ***(%CaCO$_3$)*** | - | - | - | - | - | - | *0.33* | *0.11* | *0.11* | *0.04* |
| **$S_{KCl}$** | 0.151 | 0.161 | 0.288 | 0.286 | 0.394 | 0.411 | 0.012 | 0.037 | 0.038 | 0.077 |
| ***(%S)*** | *0.001* | *0.002* | *0.005* | *0.006* | *0.012* | *0.010* | *0.000* | *0.002* | *0.000* | *0.006* |
| **$S_{RAS}$** | n/a | n/a | 0.154 | 0.222 | n/a | n/a | n/a | n/a | n/a | n/a |
| ***(%S)*** | - | - | *0.012* | *0.011* | - | - | - | - | - | - |
| **Net acidity** | 1.365 | 1.373 | 1.430 | 1.436 | 3.406 | 3.364 | -2.088 | -2.472 | -1.017 | -1.278 |
| **SPOCAS** | *0.029* | *0.015* | *0.021* | *0.014* | *0.030* | *0.046* | *0.07* | *0.025* | *0.025* | *0.013* |

## References

Ahern CR, McElnea AE, Sullivan LA (2004) *Acid Sulfate Soils Laboratory Methods Guidelines.* Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

AS4969.1 (2008) Analysis of acid sulfate soil-Dried samples-Pre-treatment of samples.

Dent D (1986) 'Acid sulphate soils: A baseline for research and development.' (ILRI: The Netherlands)

Maher CA, Sullivan LA, Ward NJ (2004) Sample pre-treatment and the determination of some chemical properties of acid sulfate soil materials. *Australian Journal of Soil Research*, **42**, 667–670.

Rayment GE, Lyons D (In press) 'Soil chemical methods—Australasia.' (CSIRO Publishing)

Rayment GE, Higginson FR (1992) 'Australian laboratory handbook of soil and water chemical methods.' Inkata Press.

Sullivan LA, Bush RT, McConchie DM (2000) A modified chromium reducible method for reduced inorganic sulfur: optimum reaction time for acid sulfate soil. *Australian Journal of Soil Research* **38**, 729–734.

# Effectiveness of Lime Particle Size in the Neutralisation of Sulfidic Acid Sulfate Soil Materials

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## Abstract

The effectiveness of the acid neutralising capacity of a range of lime particle sizes in alkaline and acidic sulfidic acid sulfate soils has been determined by an incubation method. The criterion for acceptable acid neutralising capacity was the ability of the neutralising material (e.g. lime) to maintain the soil materials' pH at greater than or equal to 6.5. In incubated alkaline sulfidic soil materials this criterion was satisfied by lime particle sizes below 1 mm; while in incubated acidic sulfidic soil materials, a particle size of below 0.5 mm was required. This experiment has demonstrated, for the first time, the lime particle sizes required for the optimum treatment and remediation of sulfidic acid sulfate soil materials.

## Key Words

Lime, acid sulfate soil, particle size, neutralisation, remediation

## Introduction

Prior to this study, the appropriate particle size range of carbonate liming materials that can effectively neutralise existing and/or potential acidity within acid sulfate soils had not been determined directly. The effectiveness of agricultural lime (i.e. ground geological limestone) has been accepted on the basis of particle size to be: 100% effective for particles <0.300 mm; 60% effective between 0.300 mm to 0.850 mm and; 0.10% effective for particles >0.850 mm (Stone *et al.* 1998). These values have apparently been derived from liming studies of agricultural soils, which are usually very different in behaviour from acid sulfate soils and, accordingly, managers use these assumptions with less-than-total confidence. A demonstration of uncertainly regarding particle size effectiveness in acid sulfate soil management is the recent liming of acid sulfate soils in South Australia at Currency Creek on the Lower Lakes of the River Murray with ultra-fine lime to ensure effective treatment (SA DEH 2009). Superfine (<0.45 μm) lime is generally supplied for enrichment of calcium-depleted alkaline or circumneutral soils and has a considerably higher cost due to the requirement for further processing by ball mill after the initial crushing stage (Whear 2009). Here we use direct incubation/remediation trials using representative acid sulfate soil materials and a range of particle size fractions of agricultural lime to provide the first data on liming efficacy in acid sulfate soil materials in relation to the particle size of agricultural lime. Further studies are currently being undertaken in order to develop a comprehensive assessment of lime particle size efficiency in a wider range of acid sulfate soil materials.

## Method

Mined geological limestone (calcite, $CaCO_3$), representative of the liming material generally used for remediation and treatment of acid sulfate soil materials was characterised by a variety of techniques and used to determine the effect, over time, of the various particle sizes on the pH of incubated acid sulfate soil samples. The mineralogy and crystal structure of the lime was determined by X-ray Diffraction (XRD) and the morphology of the lime before and after incubation was characterised by Analytical Scanning Electron Microscopy (ASEM). Chemical composition of the lime was confirmed by Energy Dispersive X-ray analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS) before and after incubation.

## Experimental

Lime was sourced from South Queensland Lime Pty Ltd in various grades and sieved to make fractions of 1 - 2 mm, 0.5 - 1 mm, 250 - 500 μm, 180 - 250 μm, 125 - 180 μm, 90 - 125 μm, 63 - 90 μm. Particles below 63 μm were gravity separated to 20 - 63 μm and < 20 μm fractions. The alkaline sulfidic acid sulfate materials used for this study were collected from the Tuckean Nature Reserve, NSW; with acidic sulfidic materials collected from Yamba, NSW. The extracted soils were transported and stored under thermally isolated conditions and with zero headspace in order to minimise air ingress. Sulfide content was determined by the Chromium Reducible Sulfur ($S_{CR}$) method 22B; and Titratable Actual Acidity (TAA) by method 23F of the Acid Sulfate Soils Laboratory Methods Guidelines (Ahern *et al.* 2004). The liming rate was calculated using the liming conventions of the Acid Sulfate Soils Laboratory Methods Guidelines (Ahern *et al.* 2004), using the net acidity (assuming negligible existing ANC based on past experience with these soils), a safety factor of 1.5 and a lime purity of 96% of pure $CaCO_3$ as per supplier specifications. The entire range of lime particle sizes was examined in the alkaline sulfidic soil, while the fractions examined in the acidic sulfidic soils ranged from 1 - 2 mm to 125 - 180 µm. A lower limit of 125 - 180 µm was used in the acidic sulfidic study as preliminary assessment had determined the effectiveness of lime of this particle size for sulfidic soil. The acid sulfate soil materials were mixed with agricultural lime fractions at the required liming rate for each soil and incubated as 10 cm x 12 cm blocks of 2 mm in height (Sullivan *et al.* 2009). Incubations were kept moist by covering with sponge moistened by spraying with ultrapure water. Sampling was initially undertaken at weekly intervals, and with decreasing frequency after the first four weeks. Determination of pH was undertaken on strips of soil cut from the incubation slabs and mixed 1:1 by weight with ultrapure water. The pH was measured using an Orion 420A+ pH meter and Thermo 910600 temperature-compensated combination pH probe. The instrument was calibrated daily with fresh pH 4 & 9 buffers and referenced to a check buffer at pH 7.

XPS studies of the lime particles before and after incubation were undertaken on a Kratos AXIS Ultra HSA X-ray Photoelectron Spectrometer using monochromated 1486.6 eV Al $K_\alpha$ irradiation generated by a voltage of 15 kV and with a current of 10 mA. A hybrid (magnetic/electrostatic) lens was used to collect the ejected electrons. A pass energy of 160 eV, 1 eV step and 100 ms dwell time was applied for survey scans, with detail scans run at pass energy of 20 eV, 0.05 eV step and 250 ms dwell time. Charge was neutralized using an electron flood gun and binding energies were referenced to adventitious carbon at 285 eV. Particles were removed from incubated samples at 16 weeks for XPS study and were rinsed repeatedly with ultrapure water with gentle agitation prior to drying under desiccation for XPS analysis. SEM images and elemental analyses were obtained using a Leica 440 ASEM, using carbon coated particles of agricultural lime including untreated, incubated and incubated particles $Na_2CO_3$ treated. XRD studies were performed on a Bruker Endeavour D4 X-ray diffractometer using a particle size of <20 µm.

## Results

Figure 1 shows the pH incubation data for the unoxidised, initially alkaline sulfidic Tuckean soil. With the exception the 1 - 2 mm grade of agricultural lime, the pH of all limed incubating soil materials showed adequate neutralisation resulting in maintenance of pH >6.5 over the duration of the experiment.

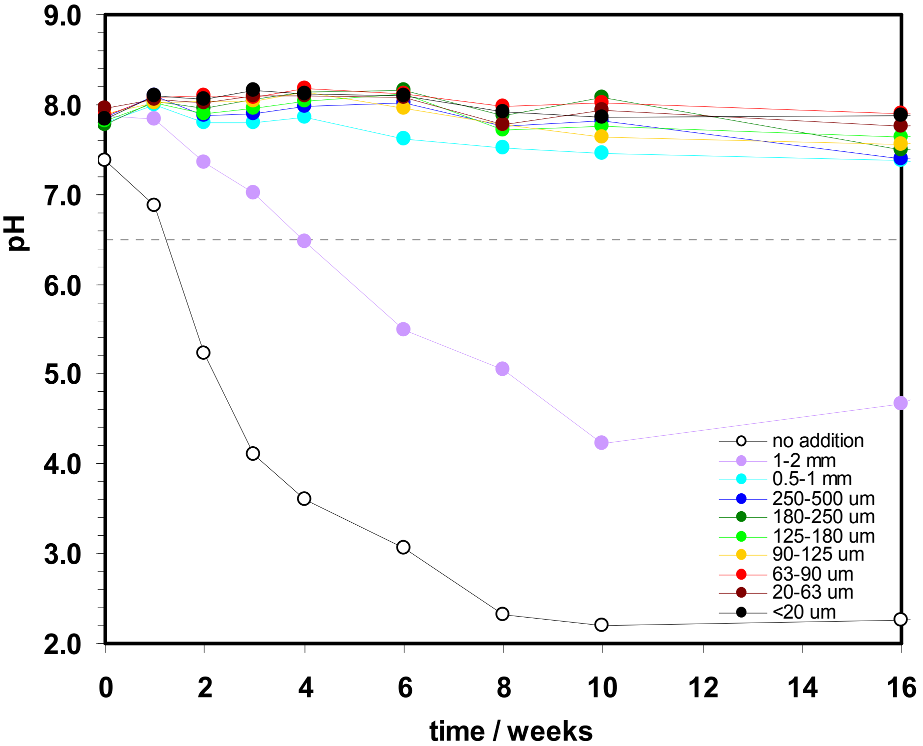

**Figure 1. Incubating alkaline sulfidic soil pH data when treated with a range of agricultural lime particle sizes. Each data point represents a duplicate mean.**

It can be inferred from these data that, for neutral or alkaline sulfidic material that is subject to oxidation, liming materials need to be <1.0 mm in size in order to effect remediation upon exposure of the soil to oxygen. Of course, this inference needs to be verified for other neutral or alkaline sulfidic materials.

Figure 2 shows the pH incubation data for the partially-oxidised acidic sulfidic Yamba soil. The pH of all limed incubating soil materials with the exception of those where lime in the 1 - 2 mm and 0.5 – 1 mm grades show adequate neutralisation resulting in maintenance of pH >6.5 within 1 week of lime addition. It can be inferred from these data that, for oxidised acidic material with some remaining sulfidic component, liming materials need to be <0.5 mm in size in order to effect remediation. Again, this inference needs to be verified for other acidic sulfidic materials

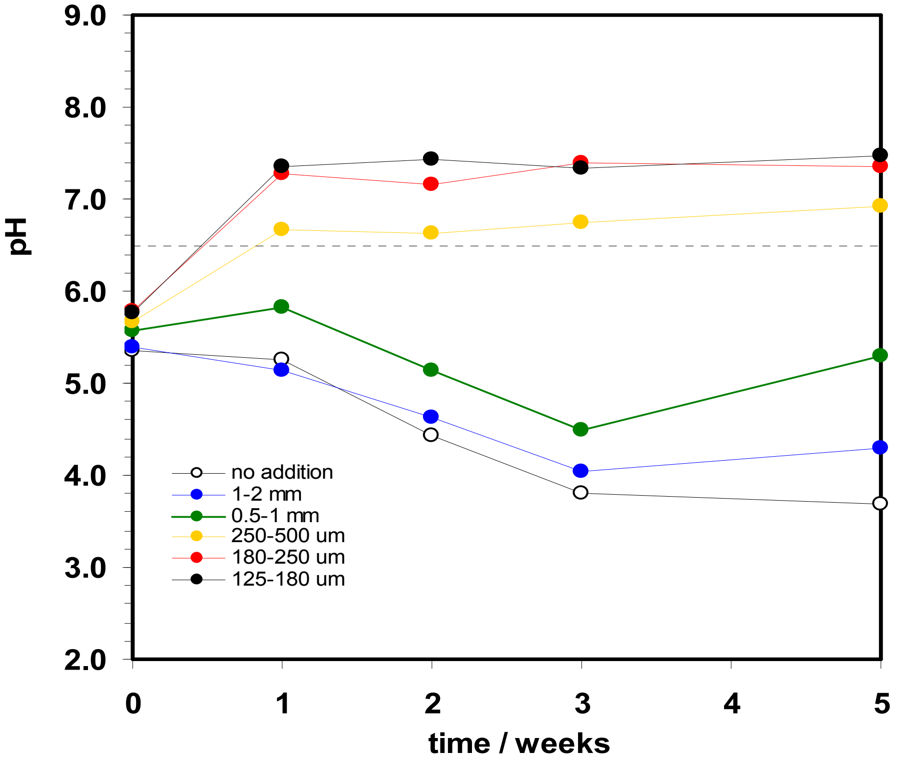

**Figure 2. Incubating acidic sulfidic soil pH data when treated with a range of agricultural lime particle sizes. Each data point represents a duplicate mean.**

XRD studies of lime powdered to <20 µm showed the mineralogy of the lime to be calcite. Figure 3 presents SEM images of a ball-milled agricultural lime particle and a particle after incubation in an acidic sulfidic soil for 16 weeks. Fine lime particles can be seen adhering to the 1 - 2 mm particle after grinding, but these are removed, presumably by dissolution, after prolonged incubation.

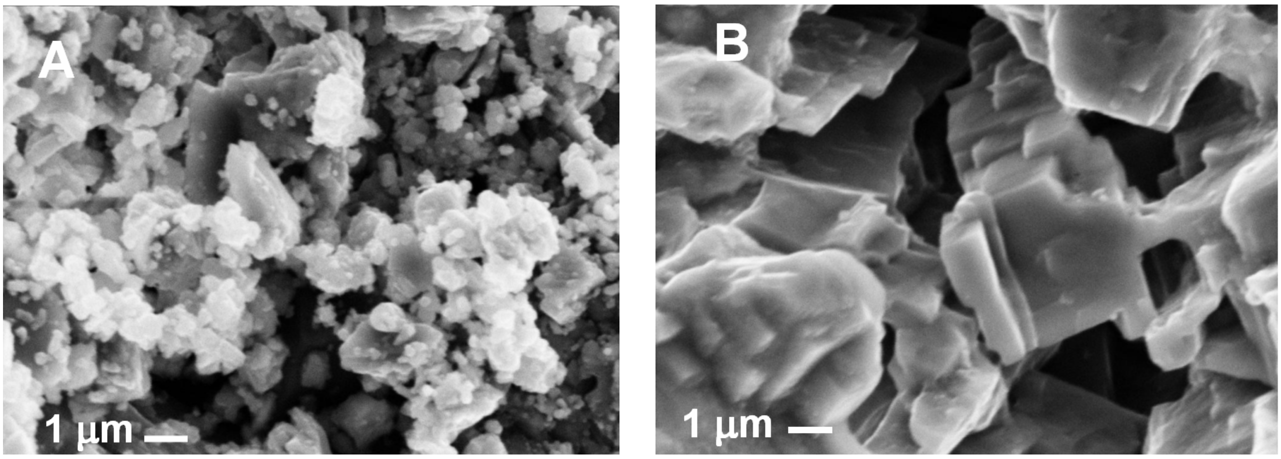

**Figure 3. A) SEM image of surface of a sieved 2 mm lime particle showing adherent microparticles; B) surface of effective lime particle after incubation in acid sulfate soil for 16 weeks.**

Etching of the calcite is clearly observed as a consequence of incubation in Figure 3B, exposing an internal structure with an apparent rhombohedral habit. The formation of channels within the structure can also be observed.

Lime particles were examined by XPS in order to determine if a passivating surfical layer, e.g. ferric or gypsic precipitate (Soler *et al.* 2008) had formed, which may have prevent further dissolution from the lime particles. A lime particle was selected as a standard from particles subjected to ball mill grinding and sieved to 1 - 2 mm. The sample showed predominantly Ca, C and O with an impurity from Si and Al below the instrumental limit of detection of 1 atom %. Carbonate samples incubated in the sulfidic Tuckean soil were removed after 16 weeks, by which time samples limed with 1 - 2 mm particles had reached a pH of 4.7. This lime grade was considered ineffective as it was unable to neutralise the acidity of the surrounding soil material by raising the pH above 6.5. The soil material limed with 0.5 - 1 mm particles had a pH of 7.4 by 16 weeks and these lime particles were considered effective. Both the effective and ineffective lime particles show similar surface characteristics when observed by XPS. Peaks due to Si, Al and Fe were observed, with a trace of Mg below the quantifiable limit. The presence of surface contamination by nanoparticulate clays was observed during ASEM analysis of the incubated particles. Interference by adherent clay particles would obscure any differences due to the surface coating of the effective and ineffective lime particles as determinable by XPS. In an attempt to overcome clay contamination, incubated samples of effective and ineffective incubated lime particles were further treated with 0.01 M $Na_2CO_3$ in an attempt to disperse and remove clay particles from the surface. XPS of these samples showed a relative decrease of Si, Al and Fe, while SEM imaging showed an apparent restructuring of the surface. The combination of clay contamination in untreated samples; significant risk of surface layer disruption during restructuring and carbonate precipitation in samples treated with dispersant; and the roughness of the surfaces of the incubated lime particles prevented the unambiguous determination of the presence of a passivation layer on incubated lime materials using XPS. Studies using transmission electron microscopy (TEM) may be of greater benefit.

## Conclusion

The data indicates *inter alia* that if acidic sulfidic soil materials require liming, then agricultural lime with particles sized below 0.5 mm can be relied upon to neutralise the acidity that exists and may develop over time scales appropriate to management (i.e. ~1 week). In the case of the treatment of neutral/alkaline sulfidic materials to prevent acidification, the data indicates that agricultural lime below 1.0 mm in particle size would be effective. Verification of this liming behaviour for other sulfidic materials is currently in progress.

## Acknowledgements

A supplier of geological lime, South Queensland Lime Pty. Ltd., Gore, Qld, has been involved in this project by supplying geological lime of varying particle size fractions and providing industry viewpoints on the nature of liming practices being used for acid sulfate soil management. The funding for this project was provided under CRC CARE project 2-4-01-05/06 ‘Developing a hydrogeochemical model for predicting contaminant production, consumption and export from acid sulfate soil (ASS)’. The authors would like to thank and acknowledge Dr Barry Wood of the University of Queensland’s Centre for Microscopy and Microanalysis (CMM) for valued discussions and XPS acquisition.

## References

Ahern CR, McElnea AE, Sullivan LA (2004) Acid Sulfate Soils Laboratory Methods Guidelines. (Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland).

Department for Environment and Heritage, Government of South Australia (2009) Fact Sheet: Limestone trials in Currency Creek and Finniss River. http://www.environment.sa.gov.au/cllmm/fact-sheets-limestone-trials.html. (Accessed: November 24th 2009)

Soler JM, Boi M, Mogollon JL, Cama J, Ayora C, Nico PS, Tamura N, Kunz M (2008) The passivation of calcite by acid mine water. Column experiments with ferric sulfate and ferric chloride solutions at pH 2. *Applied Geochemistry* **23**, 3579-3588.

Stone Y, Ahern CR, Blunden B (1998) Acid Sulfate Soils Manual 1998. (Acid Sulfate Soils Management Advisory Committee; Wollongbar, NSW).

Sullivan LA, Ward N, Bush RT, Burton ED (2009) Improved identification of sulfidic soil materials by a modified incubation method. *Geoderma* **149**, 33-38.

Whear R (2009) Advice on current costs and practices in industrial applications of lime. (South Queensland Lime, Pty. Ltd.: Gore, Qld.) Personal Communication.

# Effects of compost and lime amendment on soil acidity and N availability in acid sulfate soil

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## Abstract

The aims of this study were to investigate changes in soil acidity, exchangeable and dissolved aluminum (Al) and N availability after application of lime and/or compost. In the Mekong delta, field experiments were established on severely acid sulfate soil recently cultivated with *Momordica cochichiensi.* Before planting, soil samples were taken at 0-20 cm depth for incubation experiments. The results from our field experiments showed that applying 5 kg compost per plant in addition to a basal application of 37.5 g N, 220 g $P_2O_5$ and 85 g $K_2O$ per plant led to an increase in soil pH and a decrease soil exchangeable $Al^{3+}$ ($P < 0.05$). In incubation experiments, lime ($CaCO_3$) was added at rates of 80 and 202.5 mg/20 g soil, based on the results from lime requirement tests to reach desired pH values. In addition, compost was added solely or in combination with lime at an amount of 1.25 g. The results showed that application of lime at a rate of 80 mg $CaCO_3$/20 g soil in combination with 1.25 g compost increased soil pH from 3.13 to 6.07. This combination also significantly decreased soil exchangeable and dissolved Al and increased soil content of $NH_4^+$-N. Application of compost alone or in combination of liming enriched soil with both $NH_4^+$-N and $NO_3^-$-N. A significant increase in soil $NO_3^-$-N after amending acid sulfate soil with compost only, may suggest that compost may be a source of nitrifying microorganisms.

## Key words

Acid sulfate soils, liming, compost, dissolved aluminum, nitrogen availability.

## Introduction

In an attempt to introduce various beneficial plant species for agricultural production on acid sulfate soils, the growth of *Momordica cochichiensis* has been tested. This species is considered as a high value fruit crop but has not been planted on acid sulfate soils in the Mekong delta. Besides testing the adaptive ability of *Momordica* plant, this study also aimed at establishing a practical recommendation regarding amendments of compost and lime to counteract soil acidity and potentially toxic levels of dissolved aluminum. In parallel with *in situ* experiments, incubation experiments were carried out to investigate changes in soil acidity and dissolved Al combined with addition of N-containing compost affected soil N mineralization.

## Methodology

A field experiment was established in Tri Ton district, An Giang province, which is one of the main areas of severely acid sulfate soils in the Mekong delta. The soil is classified as a *Typic Sulfaquepts* (USDA). All plots were fertilized with a basal dressing consisting of 37.5 g N, 220 g $P_2O_5$ and 85 g $K_2O$/plant. Before planting, lime ($CaCO_3$) was added to all plots at a rate of 2 tons/ha to counteract acidity and moderate dissolved Al and Fe toxicity. To investigate the effects of compost on soil pH and Al, there were two treatments set up with four replicates each: (1) the control without compost, and (2) sugar-cane filter cake compost added at 5 kg/plant. After planting *Momordica*, soil sampling was carried out at day 48 and at day 82 to monitor changes in soil pH and exchangeable Al content under liming and compost application.
For the incubation experiment, soil was sampled before applying lime and compost. Lime and compost were then added in the laboratory solely or in combination in six following treatments:

(1) Control (without lime and compost)
(2) + 1.25 g compost
(3) + 80 mg $CaCO_3$
(4) + 80 mg $CaCO_3$ and 1.25 g compost
(5) + 202.5 mg $CaCO_3$
(6) + 202.5 mg $CaCO_3$ and 1.25 g compost

The experiment was carried out in completely random design with four replicates for each treatment. Soil sampling was carried out at day 0 and day 28 during the course of incubation. At each sampling date, the pH, titratable acidity, exchangeable $Al^{3+}$, total dissolved Al as well as the amounts of accumulated mineral N were analyzed.

## Results

*In situ experiment:*

Applying 5 kg compost on a basal application of 2 tons $CaCO_3$/ha per plant reduced soil exchangeable $Al^{3+}$ during 82 days after planting (Figure 1). Soil pH remained at a low level revealing that much more lime needed to be applied.

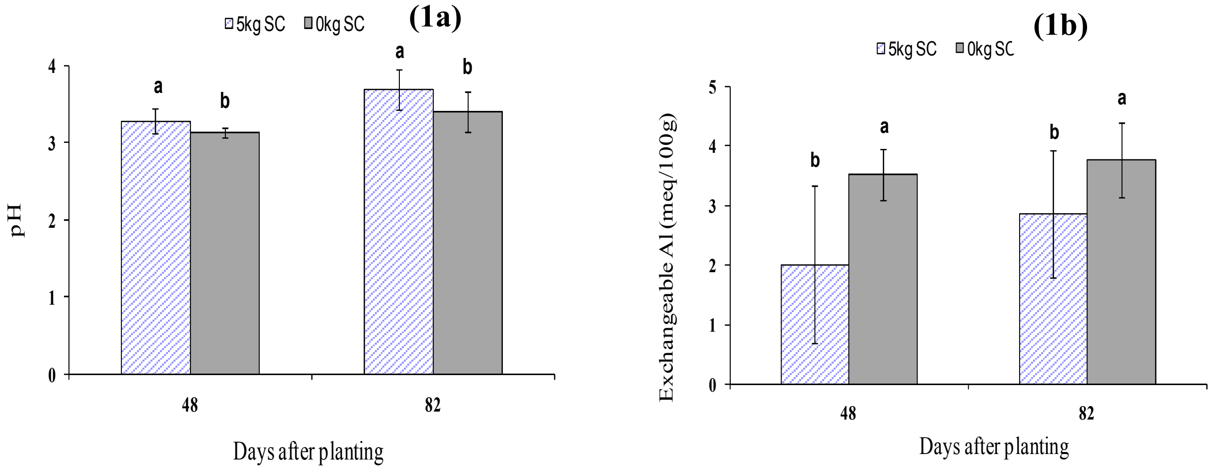

**Figure 1. Effects of compost amendment on soil pH (1a) and the contents of exchangeable $Al^{3+}$ (1b). Vertical bars on the columns are standard deviations of mean values (n = 4), "SC" is an abbreviation of sugar cane filter cake compost**

*Incubation experiment:*

Applying lime solely or in combination with compost significantly increased soil pH. Similarly, the contents of titratable acidity, exchangeable $Al^{3+}$ and dissolved Al decreased dramatically with increasing the amounts of amended lime and/or compost. In the treatment where lime was applied at a level of about 200 mg $CaCO_3$/20 g soil, soil acidity was completely neutralized (Table 1 and 2). Applying only compost could either moderate soil acidity or reduce the contents of exchangeable $Al^{3+}$ and dissolved Al. The observed reduction in Al solubility that occurred when compost was applied, may have resulted from chemical reactions between anionic functional groups of organic molecules and solution cation: polyvalent Al can link negatively charged functional groups of organic molecules together and, hence, reduce their solubility by flocculation or binding them to negatively charged exchange sites (Tipping and Woof 1991; Guggenberger *et al.* 1994b).

Net N mineralization was enhanced significantly as lime and compost was applied either solely or in combination. Effects of liming on net N mineralization has attributed to a reduction of Al toxicity and an increase in soil pH that can both result in an increase of total microbial activity (Andersson *et al.* 1994; Ivarson 1997) and a release of labile organic matter (Curtin *et al.* 1998; Andersson 1999). On the other hand, applying only compost (total N content 2.7%) enhanced both $NH_4^+$-N and $NO_3^-$-N accumulation during the course of the incubation (Figures 2a & 2b). This study indicated that compost might also be a source of soil nitrifiers. Nitrification could be disadvantageous since it increases N losses via leaching and run-off and promotes soil acidity by producing $H^+$ ions via enzymatically oxidative processes involving $NH_4^+$ ions. However, this study showed that compost in itself caused an increase in soil pH despite the proton production associated with the formation of nitrate (Table 1; Figure 2b).

**Table 1. Changes in pH and titratable acidity in the soil amended with lime and compost during 28-day aerobic incubation. (±) values are standard deviation (n = 3). The mean values followed by the same letter in the same column are not statistically significant. Values of differences followed by superscript **, * and $^{ns}$ show the differences between the initial and final observed values at 0.001, 0.05 significant levels and no significance, respectively.**

| Treatments | Initial pH | Final pH | Differences[a] | Initial titratable acidity (meq $H^+$/100 g) | Final titratable acidity (meq $H^+$/100 g) | Differences |
|---|---|---|---|---|---|---|
| Control (20 g soil) | 3.13 f | 3.19 f | -0.057* | 13.20 (± 0.07) f | 9.93 (± 1.412) e | -3.28** |
| + 1.25 g compost | 3.85 e | 4.16 e | -0.310* | 7.55 (± 0.11) e | 1.28 (± 0.000) c | -6.28** |
| + 80 mg $CaCO_3$ | 4.94 d | 4.51 d | 0.433* | 3.18 (± 0.26) d | 2.70 (± 0.075) d | -0.48$^{ns}$ |
| + 80 mg $CaCO_3$ and 1.25 g compost | 6.07 c | 5.02 c | 1.047** | 0.28 (± 0.04) c | 0.15 (± 0.075) b | -0.13$^{ns}$ |
| + 202.5 mg $CaCO_3$ | 7.33 b | 6.10 b | 1.227** | 0.18 (± 0.04) b | 0.03 (±0.043) a | -0.15$^{ns}$ |
| + 202.5 mg $CaCO_3$ + 1.25 g compost | 7.55 a | 6.42 a | 1.130** | 0.03 (± 0.04) a | 0.03 (± 0.043) a | 0.00$^{ns}$ |

(a) Differences between the values of pH and titratable acidity obtained at day 28 and those at day 0 (after amendments) in incubation experiment. (-) values indicate a decrease in the observed parameters during 28-d incubation and vice versa.

**Table 2. Changes in the contents of exchangeable Al and dissolved Al at day 28 after amending $CaCO_3$ and compost. (±) values are standard deviation (n = 3). The mean values followed by the same letter in the same column are not statistically significant. Values of differences followed by superscript **, * and $^{ns}$ show the differences between the initial and final observed values at 0.001, 0.05 significant levels and no significance, respectively.**

| Treatments | Initial exch. $Al^{3+}$ (meq/100 g) | Final exch. $Al^{3+}$ (meq/100 g) | Differences | Initial dissolved Al (mg/l) | Final dissolved Al (mg/l) | Differences |
|---|---|---|---|---|---|---|
| Control (20 g soil) | 10.48 (± 0.04) c | 8.68 (± 1.20) c | -1.80* | 2.25 (± 0.09) b | 2.34 (± 0.42) | 0.09$^{ns}$ |
| + 1.25 g compost | 4.58 (± 0.27) b | 0.50 (± 0.11) a | -4.08** | 0.46 (± 0.16) a | nd | nd |
| + 80 mg $CaCO_3$ | 0.93 (± 0.35) a | 2.30 (± 0.11) b | 1.38* | nd | nd | nd |
| + 80 mg $CaCO_3$ + 1.25 g compost | nd | nd | nd | nd | nd | nd |
| + 202.5 mg $CaCO_3$ | nd | nd | nd | nd | nd | nd |
| + 202.5 mg $CaCO_3$ + 1.25 g compost | nd | nd | nd | nd | nd | nd |

nd: below detection limit

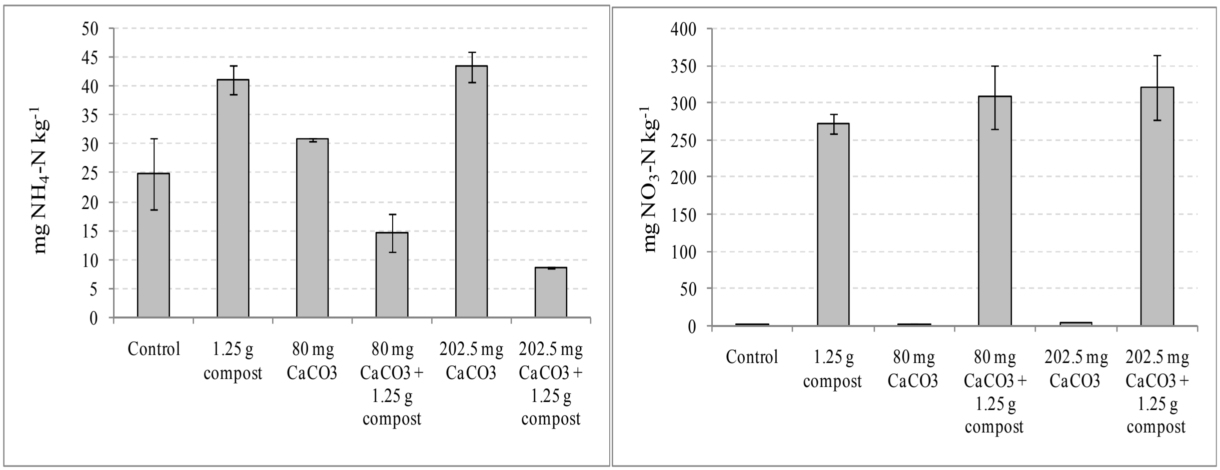

**Figure 2. Mineral $NH_4^+$-N and $NO_3^-$-N released at day 28 over the course of incubation at different rates of liming and compost application**

## Conclusion

The incubation experiment from this study demonstrated that the application of compost and lime could mitigate soil acidity and Al toxicity as well as improve N availability in the studied acid sulfate soils. Applying lime solely could improve soil pH and N availability. However, amending compost is recommended to be used to further improve soil fertility and soil biological properties.

In a field experiment, the addition of sugar-cane filter cake compost and lime significantly increased soil pH and reduced exchangeable Al. However, changes in soil pH were minor indicating that much more lime needed to be applied to completely counteract acidity in this soil. It is also suggested that the effects from applying lime and compost on soil chemical and biological properties should be taken into long-term consideration.

## References

Andersson S, Valeur I, Nilsson I (1994) Influence of lime on soil respiration, leaching of DOC, and C/S relationships in the mor humus of haplic podsol. *Environmental International* **20**, 81-88.

Andersson S (1999) Influence of liming substances and temperature on microbial activity and leaching of soil organic matter in coniferous forest ecosystem. Doctoral thesis. Swedish University of Agricultural Sciences.

Curtin DC, Campbell A, Jalil A (1998) Effects of acidity on mineralization: pH-dependence of organic matter mineralization in weakly acidic soils. *Soil Biol. Biochem*. **30**, 57-64.

Guggenberger G, Glaser B, Zech W (1994b) Heavy metal binding by hydrophobic and hydrophilic dissolved organic carbon fractions in a spodosol A and B horizon. *Water Air Soil Pollut*. **72**, 111-127.

Ivarson KC (1977) Changes in decomposition rate, microbial population and carbohydrate content of an acid peat bog after liming and reclamation. *Canad. J. Soil Sci*. **57**, 129-137.

Tipping E, Woof C (1991) The distribution of humic substances between the solid and aqueous phases of acid organic soils: A description based on heterogeneity and charge-dependent sorption equilibria. *J. Soil Sci*. **42**, 437-448.

# Hydric halitic sulfuric soils in secondary salinised landscapes of Southwest Western Australia

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## Abstract

Rising water-tables due to clearing of native vegetation in the south-west of Western Australia have been recognised as causing secondary salinisation of landscapes with impacts mostly considered to be due to increased salt accumulation and water-logging. Much of the shallow saline groundwater rising to the surface has recently been recognised as being acidic ($pH<4.5$) posing an additional threat. We report on the first broad survey to characterise lake sediments under the influence of increased regional acidic saline groundwater discharge in the agricultural zone of Western Australia (spanning an area 300 x 100 km). This found that $pH<4$ in shallow horizons (<15 cm) of most profiles along with total titratable acidity marginally less than those in actual Acid Sulfate Soils. Deeper horizons tended to have higher pH, with less total titratable acidity, but with sometimes significant occurrences of alunite, although few indications of secondary minerals characteristic of actual ASS such as jarosite and schwertmannite. Most contained only minor evidence of potential acidity being present within the profiles and this generally overlaid the horizons containing alunite minerals. We suggest that discharge of acidic groundwater via water-table rise or deep drains to lakes and floodplains has led to the formation of sediments that have similar chemistry to those of inland Acid Sulfate Soils rather than acidity having been generated within the profiles.

## Key Words

Saline acidic sediments, inland acid sulfate conditions, alunite, salinised soils.

## Introduction

Rising water-tables due to clearing of native vegetation in the south-west of Western Australia have long been recognised to be the cause of widespread secondary salinisation of landscapes (Hatton *et al.* 2003). The effects of rising saline water-tables are recognised as being primarily due to increased accumulation and mobility of salts in surface soil profiles and increased waterlogging (Hatton *et al.* 2003). Much of the shallow saline groundwater in salinised valley floors in the south-west of Western Australia has been recently recognised as being acidic ($pH<4.5$) posing an additional threat to these landscapes (Shand and Degens 2008). The effects of this groundwater discharge on hydric soils in playas and claypans is not certain and may lead to the formation of conditions similar to those of acid sulphate soils (ASS). Potential ASS materials may also have formed in previous decades of waterlogging under saline conditions (Fitzpatrick and Shand 2008). These carry implications for the management of such waters, particularly since there is the risk of impacts of acidity on aquatic ecosystems compounding the existing impacts of salinisation (Shand and Degens 2008, Steward *et al.* 2009). We report on results of the first broad scale survey of these secondary salinised hydric halitic soils (Fitzpatrick and Shand 2008) under the influence of acidic saline groundwaters in low lying landscapes spanning an area of over 50,000 km$^2$.

## Methods

A broad survey of shallow soil profiles in secondary salinised lakes containing acidic ($pH<4$) drying phase waters (identified in Shand and Degens 2008) was conducted across the central part of the Western Australian agricultural zone (Figure 1). Representative pits were dug in twelve lakes and shallow (<30 cm) horizons, colours, textures, mottling, major inclusions were described. Sampling depth was constrained by shallow water-tables, silcretes and the focus on horizons most likely to influence overlying water quality. Samples were collected from each horizon, sealed in ziplock bags and frozen on-site for transport to the laboratory. Sediments were analysed for basic soil properties ($pH_{1:5\ water}$, electrical conductivity or $EC_{1:5\ water}$, organic C and carbonate C), major and minor elements by XRF, mineralogy by quantitative XRD (PANalytical X'Pert Pro Multi-purpose Diffractometer) and ASS properties. The latter analyses included analysis of sulphide-S using the chromium reducible S method (Australian standard acid sulfate soil method 22B Ahern *et al.* 2004) and total titratable acidity determined by titration to pH 6.5 (Australian standard acid sulfate soil analysis method 23F; Ahern *et al.* 2004). Only selected results are presented here.

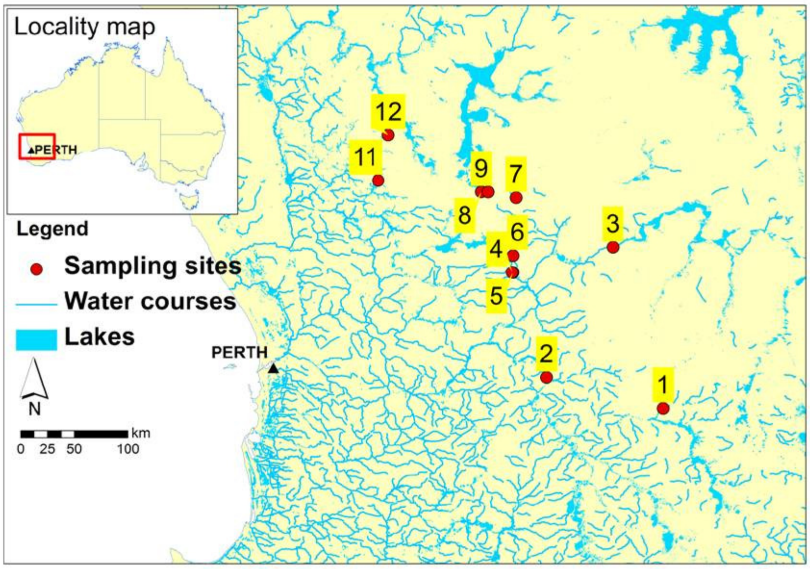

**Figure 1. Location of playas and clay pans sampled across secondary salinised landscapes in the Western Australian agricultural zone**

## Results

Most profiles exhibited horizons with pH<4.5 with some as low as 3.6 and all were hypersaline with EC generally exceeding 800 mS/m (Table 1). Total titratable acidity could be as much as 109 moles $H^+$/tonne, although most were less than 45 moles $H^+$/tonne (Table 1). Shallow horizons were frequently halitic crusts commonly overlying soft silts with deeper horizons consisting of consolidated red or grey clays (Figure 2).

All soil profiles were dominated by kaolin clays and contained at least one horizon with alunite (>9%; Table 1). Some sites contained horizons with up to 68% alunite. Most profiles did not contain detectable schwertmannite or jarosite with only one profile (site 8) containing jarosite (up to 7%). Significant concentrations of salts such as halite, gypsum and bassanite (suspected to be formed during oven drying for sample analysis) also occurred in all profiles. There were no carbonate minerals in any of the profiles.

Sulfidic horizons occurred mostly in near surface layers in some lakes, although only some contained evidence of pyrite of any significance. Pyrite, evident by analysis of chromium reducible S ($S_{Cr}$), was generally not detected (<0.005%S) or less than 0.01% in the profiles at most sites. Where present at >0.01%S, pyrite was evident in either thin (<2 cm) surface or near surface horizons (<5 cm) at up to 0.6%S, although most occurrences were 0.01 to 0.04%S. These horizons also tended to contain the greatest concentrations of organic C within the profile and were prominent in formerly vegetated or lakes sited within the main flow path of floodways.

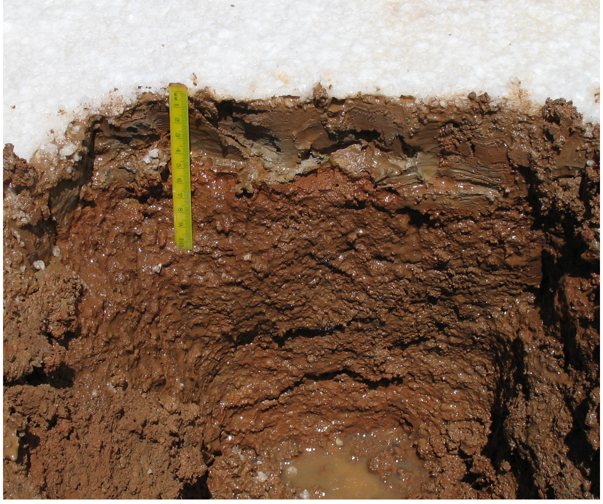

**Figure 2. A typical hydric halitic sulfuric profile (Site 3)**

**Table 1. Selected profiles illustrating common acidic soil chemistry and mineralogy of secondary salinised soils in playas and claypans (indicated in Figure 1).**

| Site | Hydrology & vegetation | Depth (cm) | Soil horizon description | pH[1] | EC[1] (mS/m) | %$S_{Cr}$[2] | TAA[3] (mole $H^+$/tonne) | Alunite[4] (%) |
|---|---|---|---|---|---|---|---|---|
| 3 | Flow through non-vegetated playa | 0-1 | Halitic crust | 3.8 | 14040 | <0.01 | 3 | <1 |
| | | 1-5 | Grey-brown clay, black mottles | 4.7 | 5000 | <0.01 | 27 | 3 |
| | | 5-8 | Red clay | 4.2 | 3004 | <0.01 | 36 | 12 |
| | | 8-30 | Dark red clay | 4.1 | 2745 | <0.01 | 38 | 44 |
| 4 | Terminal formerly non-vegetated playa | 0-1 | Halitic crust | 4.4 | 12690 | <0.01 | 0 | 5 |
| | | 1-1.5 | Red-brown gypsic silt | 4.0 | 7270 | <0.01 | 38 | 7 |
| | | 1.5-3 | Dark brown clay | 3.8 | 4740 | <0.01 | 66 | 20 |
| | | 3-15 | Grey clay | 3.8 | 2336 | <0.01 | 35 | 68 |
| | | 15-20 | Light grey clay | 3.8 | 2155 | <0.01 | 35 | 60 |
| 6 | Flow through non-vegetated playa | 0-3 | Gypsic sand | 4.7 | 2013 | <0.01 | 23 | <1 |
| | | 3-6 | Greenish grey silt | 4.3 | 2680 | 0.02 | 53 | <1 |
| | | 6-7 | Gypsic pan | *3.2* | N/A | N/A | N/A | <1 |
| | | 7-13 | Grey silt (soft) | 4.4 | 1400 | 0.04 | 32 | 3 |
| | | 13-17 | Red-brown clayey silt | 4.1 | 1346 | <0.01 | 44 | 16 |
| | | 17-21 | Olive yellow sand | 4.7 | 928 | 0.01 | 24 | 6 |
| | | 21-36 | Grey silty clay | 4.2 | 1645 | 0.03 | 45 | 26 |
| 7 | Terminal formerly vegetated clay pan | 0-12 | Halitic crust | *1.9* | N/A | N/A | N/A | <1 |
| | | 12-15 | Brown gypsic silt | 3.6 | 5300 | 0.01 | N/A | 5 |
| | | 15-15.5 | Light-brown sand | *1.9* | N/A | N/A | N/A | <1 |
| | | 15.5-19 | Grey brown sandy clay, y-r mottles | 4.7 | 2580 | 0.03 | 31 | 18 |
| | | 19-25 | Dark-grey brown sandy clay | 5.2 | 2000 | <0.01 | 16 | 28 |
| | | >25 | Indurated clay | N/A | N/A | N/A | N/A | N/A |
| 8 | Terminal formerly vegetated clay pan | 0-2 | Halitic crust | *2.4* | N/A | N/A | N/A | N/A |
| | | 2-3 | Yellow-brown black mottled gel | 3.8 | 63.2 | 0.06 | N/A | <1 |
| | | 3-7 | Soft black silt | 4.0 | 55.8 | <0.01 | 55 | <1 |
| | | 7-11 | Soft brown silt | 3.8 | 42.8 | <0.01 | 109 | 9 |
| | | 11-40 | Dark-grey brown sandy clay | 4.3 | 15.1 | <0.01 | 52 | 4 |
| | | 40-45 | Grey-brown sandy clay | 4.2 | 18.3 | <0.01 | 58 | 6 |
| 9 | Flow through non-vegetated playa | 0-1 | Gypsic yellow-brown silt | 3.9 | 45.0 | 0.27 | 96 | <1 |
| | | 1-3 | Very-soft dark-grey silt | 4.7 | 50.2 | 0.06 | 47 | <1 |
| | | 3-5 | Dark-grey clayey silt, black mottles | 5.1 | 28.2 | 0.01 | 26 | 2 |
| | | 5-9 | Soft grey silt | 5.1 | 24.7 | 0.02 | 24 | 12 |
| | | 9-15 | Red silty clay | 4.5 | 17.3 | <0.01 | 38 | 19 |
| 12 | Flow through formerly vegetated clay pan | 0-0.03 | Yellow-brown gel, grey mottles | 5.4 | 76.1 | <0.01 | 2 | <1 |
| | | 0.03-1 | Black silt | 5.6 | 57.8 | 0.08 | 0 | 3 |
| | | 1-5 | Black clayey silt | 5.6 | 34.6 | 0.61 | 0 | 5 |
| | | 5-15 | Firm grey sandy clay | 4.8 | 10.5 | <0.01 | 11 | 11 |
| 11 | Flow through formerly vegetated clay pan | 0-0.03 | Yellowish-red gel | 4.8 | 52.8 | <0.01 | 42 | 2 |
| | | 0.03-2 | Black silty clay with grey mottles | 5.7 | 25.0 | 0.04 | 0 | 4 |
| | | 2-5 | Grey clay with red mottles | 6.5 | 19.3 | <0.01 | 0 | 3 |
| | | 5-20 | Brownish grey clay , red-brown mottles | 6.1 | 19.4 | <0.01 | 0 | 8 |

[1] Soil pH and EC (electrical conductivity). Values in italics measured *in situ* using WTW spear point pH probe.
[2] $S_{Cr}$ = chromium reducible sulphur (Ahern *et al.* 2004).
[3] Titratable Actual Acidity (Ahern *et al.* 2004).
[4] Alunite as a proportion of identifiable minerals by quantitative XRD.

## Conclusions

The acidic saline lake sediments present characteristics similar to those of inland ASS however are more saline and commonly do not contain other iron hydroxyl sulphate minerals common in ASS or inland ASS such as jarosite or schwertmannite (Fitzpatrick and Shand 2008). This may reflect the acidity source being predominantly pH 3-4.5 saline groundwaters which can contain high concentrations of aluminium (Shand and Degens 2008). Iron can also occur in high concentrations (Shand and Degens 2008), which would be expected to precipitate as jarosite or schwertmannite (given groundwater pH; Long *et al.* 1992). Although traces of pyrite (as indicated by chromium reducible S) occur in surface and sub-surface sediments of some lakes, pyrite is not thought to the main source of acidity. Pyrite may have completely oxidised, however, drying or exposure of the sediments is unlikely given that the all of the lakes have not experienced drought and have been permanently waterlogged under the influence of rising groundwater over the past 50 – 100 years. Furthermore, the concentrations of alunite in some places (up to 68%) suggest significant potential acidity must have been present or that acidity had concentrated within the profiles by way of discharge of iron and aluminium rich groundwater over significant periods of time and all sites were not primary salt lakes. This may also explain the fate of iron in groundwater, which may have initially precipitated as jarosite or schwertmannite minerals that subsequently transformed to goethite.

The accumulations of significant concentrations of alunite in subsurface sediments may be residual from previous exposure of lake sediments to acidic conditions in previous climate regimes. This probably occurred under climate variations during the Quaternary geological period which caused periodic expansion and contraction of groundwater discharge areas in the landscape, of which the playas are regarded as remnants of this activity (George *et al.* 2008). Although alunite has been identified in a primary salinised lakes in Victoria (Long *et al* 1992) and southern WA (Bowen and Benison 2009), the present study indicates that these also occur in secondary salinised lakes. Evidence that some lakes were vegetated prior to secondary salinisation (Table 1) and accumulations of sulfides in shallow horizons indicate that recent alkaline conditions may have prevailed. These appear to be experiencing re-acidification.

## References

Ahern CR, Sullivan LA, McElnea AE (2004) Laboratory Methods Guidelines 2004 – Acid Sulfate Soils. In 'Queensland Acid Sulfate Soil Technical Manual'. Department of Natural Resources, Mines and Energy, Indooroopilly Queensland Australia.

Bowen BB, Benison KC (2009) Geochemical characteristics of naturally acidic and alkaline saline lakes in southern Western Australia. *Applied Geochemistry* **24**, 268–284.

Fitzpatrick R, Shand P (2008) Inland Acid Sulfate Soils: Overview and conceptual models. In 'Inland Acid Sulfate Soil Systems Across Australia'. (Eds. R. Fitzpatrick, P Shand) pp. 6-74. CRC LEME Open File Report No. 249 Thematic Volume. (CRC LEME: Perth, Australia).

George RG, Clarke J, English P (2008). Modern and paleogeographic trends in the salinisation of the Western Australian wheatbelt: a review. *Australian Journal of Soil Research* **46**, 751–767.

Hatton TJ, Ruprecht J, George RJ, (2003) Preclearing hydrology of the Western Australian wheatbelt: Target for the future. *Plant and Soil* **257**, 341–356.

Long DT, Fegan NE, McKee JD, Lyons WB, Hines ME, Macumber PG (1992) Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: Lake Tyrrell, Victoria, Australia. *Chemical Geology* **96**, 183–202.

Shand P, Degens B (2008) Avon catchment acid ground-water: geochemical risk assessment, CRC-LEME Open File Report 191, CSIRO Exploration and Mining, Bentley, WA. http://crcleme.org.au/Pubs/OPEN%20FILE%20REPORTS/OFR%20191/OFR%20191.pdf.

Stewart B, Strehlow K, Davis J (2009) Impacts of deep open drains on water quality and biodiversity of receiving waterways in the wheatbelt of Western Australia. *Hydrobiologia* **619**, 103–118.

# Identifying the Impact of Acid Sulfate Soils on a Humic Boreal Lake

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## Abstract

Many rivers and watercourses in western Finland have experienced several massive fish kills during the last decades caused by acidity and high metal levels. Naturally occurring humic acids make watercourses in this area acidic, but additional acidity is created by the artificial drainage of sulfide-bearing sediments. This has caused confusion and debate about the causes to the fish kills. This study identifies the sources of the acid and metal load on a humic boreal lake. Acid sulfate soils (a.s. soils) with a pH minimum of 3.2, high concentrations of sulfur and corresponding high titratable acidity were found in the drainage area of the lake. In stream waters, the concentrations of acidity and metals were high, and correlated well with sulfate (sulfide oxidation is the only potential source). A negative correlation between acidity and organic carbon (indicator of humic acids) was found. This confirms that the main reasons for acidity and related fish kills in the area are caused by a.s. soils, not humic acids from forest and/or peat areas.

## Key Words

Geochemical exploration.

## Introduction

Large areas on the Finnish coast are covered with fine-grained sulfide-bearing sediments. When these sediments are drained, sulfuric acid is created by oxidation of the sulfides. Soil minerals dissolve in this acidic environment (pH<4) releasing large quantities of metals. The acidic water flushes the potentially toxic metals to streams (Åström and Björklund 1995, 1996) causing ecological damage (Hudd *et al.* 1984).

In large parts of western Finland sulfide rich sediments developed in a shallow brackish sea hundreds to thousands of years ago. Due to a flat topography and a fast rate of land uplift (up to 8 mm per year), large areas of sea sediment has been lifted above sea water level. Today the sulfide rich sediments (0.2 to 2 % sulfur) occur in areas up to 90 m above current sea level (Erviö 1975). Even though these soils are located high above sea level, they have a high groundwater level in their natural state. This is due to the flat topography and a peat layer that protects it from drying. Some of these sediments also lie under shallow lakes. In general, the sulfide minerals in these soils remain inert if left in their natural state (Boman *et al.* 2008, Österholm and Åström 2004).

These fine-grained soils are, if drained and limed, easy to cultivate and very nutrient rich, and are therefore largely in agricultural use. The draining of these soils has occurred mainly during the last 50 years when the use of effective subsurface pipe drainage became common. Since then, many watercourses have become severely acidified. Because of the artificial draining, the oxidation depth in the a.s. soils extends down to 2.0 m. However, because of granitic bedrock and soil rich in humic acids, watercourses in northern Europe are naturally acidic (Laudon *et al.* 2000). It may therefore be difficult to distinguish acidity occurring naturally from acidity derived from reclamation of a.s. soils. To do this, water samples were taken during four occasions in 2007 from all the main ditches, small streams and the four rivers discharging into Larsmo and Öja Lake, an artificial freshwater reservoir. The analysis included pH, electric conductivity, acidity, total organic carbon, sulfate and metals. Soil samples from ten farmland sites in the catchment were also analysed for pH, acidity, metals and sulfur.

## Acidity in soil

Soil profiles were taken from farmlands located 0-25 m above sea level. Seven of the profiles can be regarded as acidic (pH < 4) a.s. soils, with a pH-minimum of 3.2. Three profiles can be regarded as semi-acidic a.s. soils, because despite a higher pH (minimum pH 4.1-4.5), they still have high concentrations of sulfur. The median oxidation depth is 1.9 m. The titratable peroxide acidity (Modified method after Ahern *et al.* (2004), Acid Sulfate Soils Laboratory Methods Guidelines version 2.1) in the oxidised and reduced zones in the profiles from the drainage area correlates well with sulfur content (Fig 1), which indicates that the severe acidity is caused by sulfide oxidation.

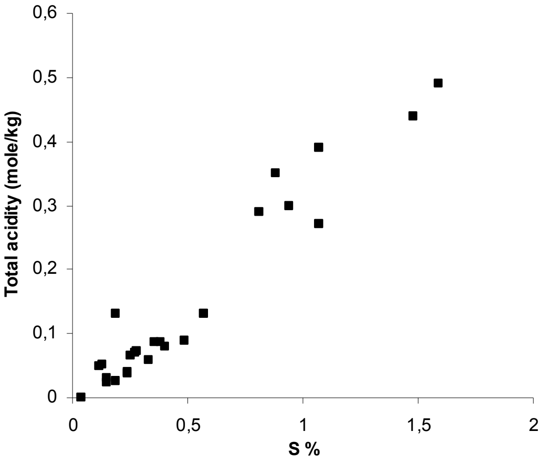

**Figure 1. Sulfur versus total acidity in soil.**

## Acidity and metals in water

The median pH of low-order streams and rivers that discharge into Larsmo and Öja Lake is 4.7 and 5.0 respectively. These low pH values could in principle be caused by organic acids. However, there was a negative correlation (p= -0.73) between total organic carbon (TOC) and acidity in the water samples (Fig 2). In contrast, pH had a negative correlation with sulphate, whereas acidity and a number of metals known to be associated with a.s. soils had a positive correlation with sulfate (Figure 3). According to numerous studies (Åström & Björklund 1997, Åström 1998, Nordmyr *et al.* 2008 and Österholm *et al.* 2005), Fe does not leach from a.s. soils in any great extent. However, in the current study area (Larsmo and Öja Lake), Fe is likely to be enriched by a.s. soils in some of the more severely affected watercourses (Figure 3).

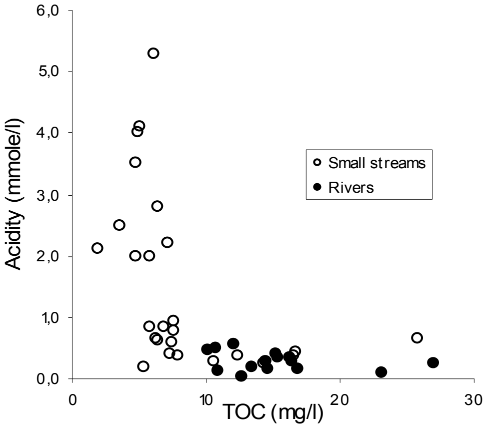

**Figure 2. Total organic carbon versus acidity of water.**

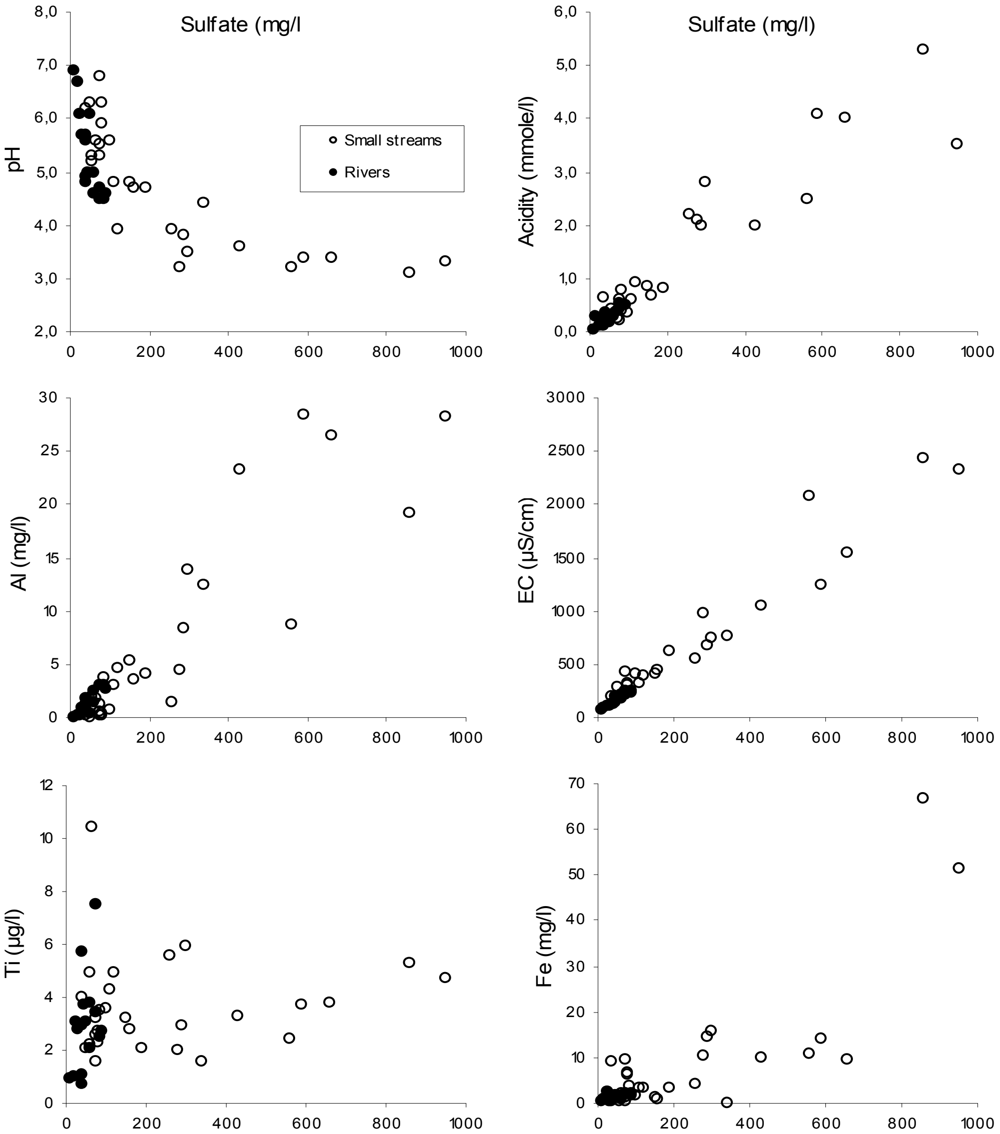

Figure 3. Sulfate versus pH, acidity, Al, EC, Ti and Fe of water in small streams and rivers.

## Conclusions

It is common that humic acids cause a low pH-level in boreal watercourses, potentially harmful for biota. In the study area, however, sulfur in the soil correlated positively with soil acidity, and sulfate in recipient water correlated negatively with pH and positively with acidity and potentially toxic metals. Concentrations of organic carbon (indicator of humic acids) showed an inverse trend to these variables. Thus, on the basis of these unambiguous trends, it could be concluded that the severe acidity associated with high metal concentrations that cause fish kills in the Larsmo and Öja Lake are mainly caused by sulfur oxidation in the sulfide-bearing sediments, not by soils discharging humic acids.

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## References

Ahern CR, McElnea AE, Sullivan LA (2004) ‘Acid Sulfate Soils Laboratory Methods Guidelines’. (Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia).

Åström M, Björklund A (1995) Impact of acid sulphate soils on stream water geochemistry in western Finland. *Journal of Geochemical Exploration* **55**, 163-170.

Åström M, Björklund A (1996) Hydrogeochemistry of a stream draining sulfide-bearing postglacial sediments in Finland. *Water, Air and Soil Pollution* **89**, 233-246.

Åström M, Björklund A (1997) Geochemistry and acidity of sulphide-bearing postglacial sediments of western Finland. *Environmental Geochemistry and Health* **19**, 155-164.

Åström M (1998) Partitioning of transition metals in oxidised and reduced zones of sulphide-bearing fine-grained sediments. *Applied Geochemistry* **13**, 607-617.

Boman A, Åström M, Fröjdö S (2008) Sulphur dynamics in boreal acid sulphate soils rich in metastable iron sulphide – The role of artificial drainage. *Chemical Geology* **255,** 68-77.

Erviö R (1975) Cultivated sulphate soils in the drainage basin of river Kyrönjoki. *Sci. Agric. Soc. Finl.* **47**, 550-561.

Hudd R, Hildén M, Urho L, Axell M-B, Jåfs L-A (1984) Fishery investigation (in 1980-1982) of the Kyrönjoki River estuary and its influence area in the northern Quark of the Baltic Sea. *Vesihallitus. Report 242B*, Helsinki, 277 pp.

Laudon H, Westling O, Bishop KH (2000) Cause of pH decline in stream water during spring melt runoff in northern Sweden. *Canadian Journal of Fisheries and Aquatic Sciences* **57**, 1888-1900.

Nordmyr L, Österholm P, Åström M (2008) Estuarine behaviour of metal loads leached from coastal lowland and acid sulphate soils. *Marine Environmental Research* **66**, 378-393.

Österholm P, Åström M (2004) Quantification of current and future leaching of sulphur and metals from Boreal acid sulphate soils, western Finland. *Australian Journal of Soil Research* **42**, 547-551.

Österholm P, Åström M, Sundstöm R (2005) Assessment of aquatic pollution, remedial measures and juridical obligations of an acid sulphate soil area in western Finland. *Agricultural and Food Science* **14** (1), 44-56.

# Isotopic variations of Fe and Zn in Finnish acid sulfate soils

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## Key words

Fe isotopes, Zn isotopes, acid sulfate soils, MC-ICP-MS.

## Abstract

The use of a Neptune high-resolution MC-ICP-MS (Thermo Fisher Scientific) in this study has enabled high precision measurements of Fe and Zn isotopic ratios in Finnish acid sulfate soils in one near shore area (Vassor) and one inland area (Rintala).

## Introduction

The development of precise instrumentation such as high resolution MC-ICP-MS and improved analytical methods has made it possible to obtain reliable analyses of Fe and Zn isotopes in a range of biological and geological samples (Malinovsky 2004). These stable isotopes have a wide range of applications and can for instance be used to fingerprint sources of Fe and Zn or to evaluate the biogeochemical reactions that impact their transport (Fernandez and Borrok 2009). Unlike Zn, Fe is a redox sensitive element and is fractionated by many biological and abiotic processes in soils and sediments, such as changes in redox state, complexation with soil organic matter, bacterial interactions, and during precipitation reactions and surface adsorptions (Borrok *et al*. 2009 and references therein). Non-redox fractionation of Zn isotopes have been measured during adsorption on oxides and hydroxides (e.g. Pokrovsky *et al*. 2005; Juillot *et al*. 2008) and complexation with organic matter (Jouvin *et al*. 2009).

In this study we focus on the isotopic variations of Fe and Zn in Finnish acid sulfate (AS) soils. Typical for Finnish AS soils is the abundance of metastable iron sulfide (approximate composition of $FeS_{1.1}$; up to c. 0.9% of the dry weight) and pyrite ($FeS_2$; commonly 1-2% of the dry weight) in the unoxidised parent material (Boman *et al*. 2008; 2010). Another characteristic feature for these soils is extensive leaching of acidity ($H_2SO_4$) and many potentially harmful elements, such as Zn and retention of Fe (Åström 1998). In Finland, which have the largest AS soil occurrences in Europe (Andriesse and van Mensvoort 2006), these soils cover an area of at least 43,000-130,000 ha (Yli-Halla *et al*. 1999). The total global area underlain by corresponding soils is estimated to c. 17 million ha (Andriesse and van Mensvoort 2006).

The use of a Neptune high-resolution MC-ICP-MS (Thermo Fisher Scientific) in this study has enabled high precision measurements of Fe and Zn isotopic ratios in Finnish AS soil materials. A better knowledge of the isotopic variations of Fe and Zn in these materials provides new insight into the mechanisms controlling the mobility of these metals.

## Methods

### *Study areas and sampling*

The study sites are located on typical Finnish AS soil areas in western Finland (Figure 1) and have been characterised by previous studies (e.g. Boman *et al*. 2008; 2010). One area, Vassor (63°9.484´N, 22°0.549´E), is located close to the present shore line and one area, Rintala (62°46.017´N, 22°36.822´E), is located some 100 km inland (Figure 1). One vertical core (300 cm) was collected from each site consisting of (1) the upper cultivated plough layer (0-40 cm), (2) the acidic horizon (pH <4), (3) the transition zone (pH >4.0 to 7.0) and (4) the sulfidic parent material (pH >7.0) (Boman *et al*. 2008; 2010). During sampling, the cores were sectioned into 5 cm (Vassor) and 10 cm (Rintala) increments. From these increments, using previous data in Boman *et al*. (2008; 2010) on sulfur speciation and isotopes and occurrence of *aqua regia* extractable Fe and Zn, a total of 29 samples (14 from Rintala and 15 from Vassor) were chosen for study.

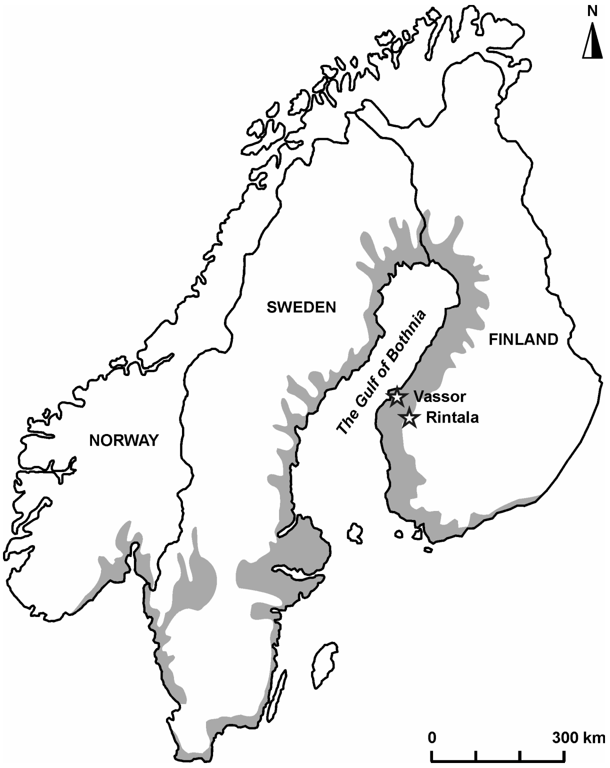

**Figure 1. Location of the study areas. The shaded area indicates the maximum extent of the former Litorina Sea and the area where AS soils can be expected.**

*Analyses*

The dried (50°C) samples were analysed for $^{56}Fe/^{54}Fe$ and $^{66}Zn/^{64}Zn$ ratios by high-resolution MC-ICP-MS using a Neptune (Thermo Fisher Scientific). The measured $^{56}Fe/^{54}Fe$ and $^{66}Zn/^{64}Zn$ ratios are reported as $\delta^{56}Fe$ and $\delta^{66}Zn$ values, respectively, in parts per mil deviation of the sample relative to the corresponding isotopic ratios of IRMM-014 and IRMM-3702 standards, respectively. The total concentrations of Fe and Zn were analysed by ICP-SFMS (Element2, Thermo Fisher Scientific) after digestion of about 2 g of dried material in $HCl:HNO_3:HF$ (3:1:1).

## Results and discussion

*Iron and Zn*

The total concentrations of Fe (percentage of dry weight) and Zn (mg/kg of dry weight) are presented in Figure 2. Generally, Fe is mostly retained in Finnish AS soils due to precipitation of various ferric minerals e.g. oxyhydroxides [e.g. $Fe(OH)_3$ and FeOOH] and jarosite [$KFe_3(SO_4)(OH)_6$] (e.g. Palko 1994; Åström 1998). The decrease of Fe in the upper meter at Rintala (Figure 2) is therefore most likely explained by heterogeneities of parent material (Österholm and Åström 2002).

In the sulfidic parent material at Rintala and Vassor, up to c. 28% of Fe, calculated from sulfur speciation data in Boman *et al.* (2008; 2010) and total Fe in this study (Figure 2), is associated with iron sulfides, while the rest is most likely associated with silicates (cf. Åström and Björklund 1997). In the acidic horizon and upwards, the corresponding iron sulfide associated Fe content is <1% (Boman *et al.* 2008; 2010), indicating the mobility of this metal within the soil column. The carrying phases of Zn in the studied materials are not fully known, but according to Åström and Björklund (1997), trace elements such as Zn in similar AS soil materials are largely associated with aluminosilicates.

The decrease of Zn in the acidic horizon at both locations (partial decrease at Rintala) as well as the concentration peak of this element in the transition zones (slightly elevated at Vassor) (Figure 2) is typical for Finnish AS soils (e.g. Åström 1998). Above c. 100 cm at Rintala, the Zn concentration was, however, increasing (Figure 2), which may be explained by heterogeneities of parent material (Österholm and Åström 2002). The reason for the increase of Zn (and other elements) in the transition zone is not fully understood but Åström (1998) suggested that it may be due to (1) downward migration of elements (Zn in this case) released in the acidic horizon followed by (2) reprecipitation/adsorption of the element in the transition zone.

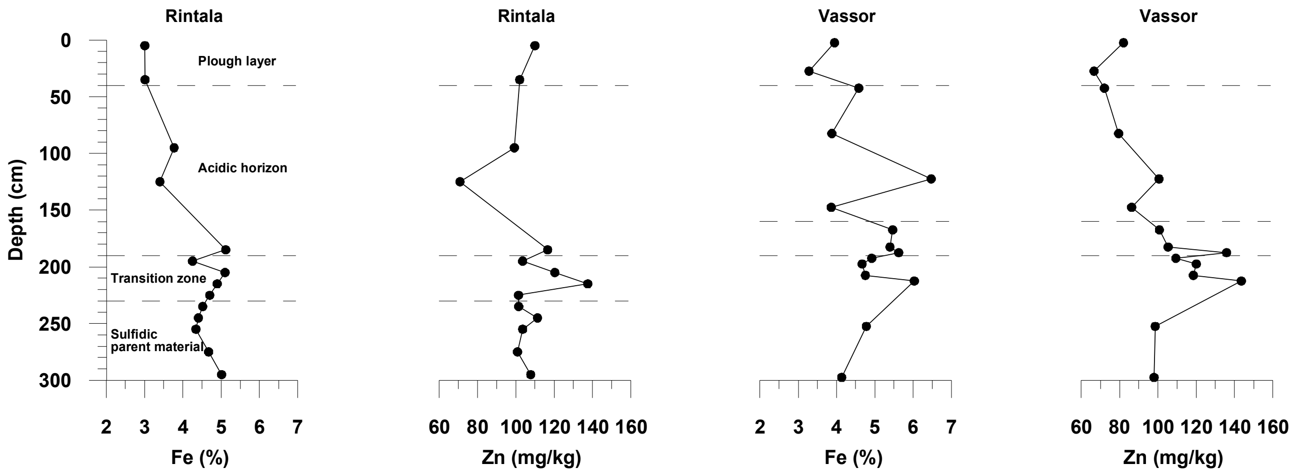

**Figure 2. Total concentrations of Fe (percentage of dry weight) and Zn (mg/kg of dry weight) at Rintala and Vassor.**

*Isotopic variations of Fe and Zn*

The isotopic variations of Fe are presented in Figure 3. The $\delta^{56}$Fe value varied slightly within the profiles and between the sites. The main difference between the sites was the general occurrence of positive $\delta^{56}$Fe values ($\pm 1\sigma$), ranging from $(-0.01 \pm 0.02)$‰ to $(0.31 \pm 0.03)$‰, in the parent material at Rintala compared to more negative $\delta^{56}$Fe values ($\pm 1\sigma$), ranging from $(-0.19 \pm 0.01)$‰ to $(0.16 \pm 0.01)$‰, at Vassor. This is believed to reflect different depositional conditions during the formation of these sediments (cf. Malinovsky 2004), with more oxidised conditions at Rintala and more reduced conditions at Vassor. This is also indicated in the ratio between metastable iron sulfide and pyrite which is consequently much lower at Rintala (c. 10/90) compared to Vassor (c. 50/50) (Boman *et al.* 2008; 2010). Approaching the lower border of the transition zone, both sites displayed similar features with a sudden dip towards more negative $\delta^{56}$Fe values (Figure 3). This may have several explanations but the main reason is most likely redox driven processes which have shown to produce the largest Fe isotope fractionations in nature (Johnson *et al.* 2008). The transition zone is subject to fluctuating redox conditions due to occasional changes in the groundwater level which will certainly contribute to changes (variations) in the isotopic composition. Above the transition zone at both sites, the $\delta^{56}$Fe values ($\pm 1\sigma$) were positive and ranged from $(0.01 \pm 0.04)$‰ to $(0.17 \pm 0.05)$‰ at Rintala and from $(0.05 \pm 0.01)$‰ to $(0.16 \pm 0.04)$‰ at Vassor (Figure 3). This slight increase of $\delta^{56}$Fe probably reflects precipitation of ferric minerals (Johnson *et al.* 2008) and possibly some loss of isotopically light Fe.

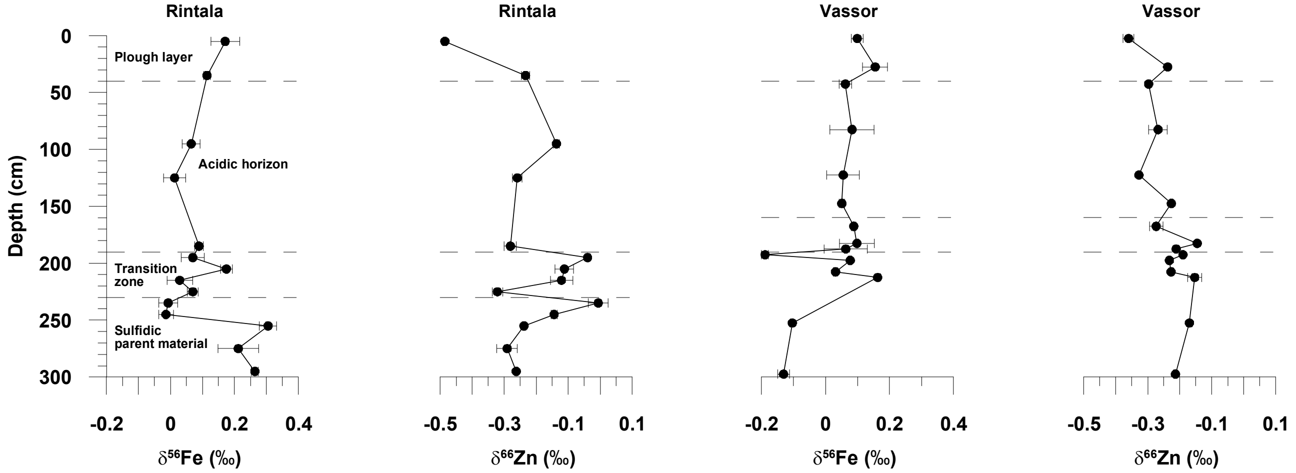

**Figure 3. Isotopic variations of Fe and Zn at Rintala and Vassor (error bars are one standard deviation).**

The isotopic variations of Zn are presented in Figure 3. At both sites, all measured $\delta^{66}$Zn values ($\pm 1\sigma$) were negative and ranged from (-0.49 ± 0.01)‰ to (-0.01 ± 0.03)‰ at Rintala and from (-0.36 ± 0.02)‰ to (-0.15 ± 0.02)‰ at Vassor. Generally, the $\delta^{66}Zn$ values were slightly decreasing upwards, implying enrichment of the heavier isotopes in the leached Zn fraction. However, we do not have any isotopic data to support this assumption. Possibly this isotopically heavy Zn has previously been adsorbed on oxides and hydroxides and is now released due to the acidic conditions (Pokrovsky *et al*. 2005).

## Conclusions

This study shows that the isotopic composition of Fe and Zn varies within the soil column of Finnish AS soils. There are indications of loss of isotopically heavy Zn during oxidation of AS soils, but the possible fractionation mechanism is not known. The isotopic variations of Fe are probably related to redox processes. More detailed studies on the partitioning, together with isotopic analyses, of Fe and Zn in Finnish AS soils are needed. Speciation of Fe and Zn will significantly contribute to the understanding of the isotopic variations in these profiles.

## References

Åström M (1998) Partitioning of transition metals in oxidised and reduced zones of sulphide-bearing fine-grained sediments. *Applied Geochemistry* **13**, 607-617.

Åström M, Björklund A (1997) Geochemistry and acidity of sulphide-bearing postglacial sediments of western Finland. *Environmental Geochemistry and Health* **19**, 155-164.

Boman A, Fröjdö S, Backlund K, Åström ME (2010) Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* **74**, 1268-1281.

Boman A, Åström M, Fröjdö S (2008) Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide - The role of artificial drainage. *Chemical Geology* **255**, 68-77.

Borrok DM, Wanty RB, Ridley WI, Lamothe PJ, Kimball BA, Verplanck PL, Runkel RL (2009) Application of iron and zinc isotopes to track the sources and mechanisms of metal loading in a mountain watershed. *Applied Geochemistry* **24**, 1270-1277.

Fernandez A, Borrok DM (2009) Fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks. *Chemical Geology* **264**, 1-12.

Johnson CM, Beard BL, Roden EE (2008) The Iron Isotope Fingerprints of Redox and Biogeochemical Cycling in Modern and Ancient Earth. *Annual Review of Earth and Planetary Sciences* **36**, 457-493.

Jouvin D, Louvat P, Juillot F, Maréchal CN, Benedetti MF (2009) Zinc Isotopic Fractionation: Why Organic Matters. *Environmental Science & Technology* **43**, 5747-5754.

Juillot F, Maréchal C, Ponthieu M, Cacaly S, Morin G, Benedetti M, Hazemann JL, Proux O, Guyot F (2008) Zn isotopic fractionation caused by sorption on goethite and 2-Lines ferrihydrite. *Geochimica et Cosmochimica Acta* **72**, 4886-4900.

Malinovsky D (2004) Fractionation of Fe and Zn isotopes: Methods and some applications in aqueous geochemistry. PhD Thesis, Luleå University of Technology, Sweden.

Österholm P, Åström M (2002) Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. *Applied Geochemistry* **17**, 1209-1218.

Palko J (1994) Acid sulphate soils and their agricultural and environmental problems in Finland. PhD Thesis, University of Oulu, Finland.

Pokrovsky OS, Viers J, Freydier R (2005) Zinc stable isotope fractionation during its adsorption on oxides and hydroxides. *Journal of Colloid and Interface Science* **291**, 192-200.

# Landform mapping for SOTER at scale 1:1 million using SRTM-DEM

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## Abstract

A digital soil mapping based procedure has been developed and tested to support the SOTER (SOil and TERrain) digital database development. This quantitative procedure was aimed to maintain the original mapping concept and create a database analogue to the “manually” created, existing SOTER databases. The SOTER mapping unit delineation is based on physiographic criteria, namely slope, relief intensity, hypsometry and dissection. These terrain features were derived from an SRTM digital elevation model. The SRTM data were processed to remove the forest-generated elevation distortion and to create an artefact-free SRTM-DEM. Several GIS techniques were employed to translate the SOTER mapping concept. The traditional – manual – delineations and the quantitative procedure results have been compared and evaluated, and found to be significantly dissimilar. In order to explain the differences, the traditional SOTER delineations were tested against the SRTM based terrain features, like slope percentage and relief intensity. These tests showed significant discrepancy between the corresponding terrain feature classes and the SRTM overlays. The results proved that the manual SOTER unit delineations often do not represent the corresponding terrain features in majority. Therefore, the traditional and the quantitative manners of soil unit delineations are by their nature not comparable.

## Key Words

Digital soil mapping, small scale databases, SOTER, SRTM, digital terrain modelling.

## Introduction

Until recently, only manual methods were used to delineate SOTER (SOil and TERrain Digital Database) Units (ISRIC 1993). The aim of the present study was to develop a quantitative method to derive terrain classes that maintain the SOTER mapping concept and test the feasibility of reproducing existing, manually created database using Digital Soil Mapping (DSM) tools and environmental covariates.

## Materials and methods

The procedure to generate the terrain units was developed by Dobos *et al.* (2007). This procedure was applied in this study with slight modifications. The aim was to develop a quantitative method to derive terrain classes corresponding to the SOTER concept (ISRIC 1993) using Shuttle Radar Topography Mission (SRTM) data. The SRTM data was pre-processed to remove the artefacts and the elevation distortion due to the forest cover using the procedures developed by Köthe and Bock (2009). According to the manual, four terrain attributes are used to define the SOTER Terrain Unit: hypsometry (elevation), slope percentage, relief intensity and dissection. The GIS layers of these attributes were derived from the SRTM digital elevation model by translating and reformatting the terrain class characteristics given by the SOTER manual. These four layers are combined to produce the complex landform classification. This combined layer was then vectorized, and finally generalized to achieve the polygon size limit appropriate for the 1:1 and 1:5 million scales of the database to be produced. The original procedure has been slightly modified. The PDD layers were calculated only for the areas with a relief intensity higher than 50 meters/ km$^2$.

The polygon system derived through the quantitative procedure has been compared with the existing, hand drawn SOTER polygon system of the SOVEUR database (Batjes 2000). However, no quality measure for the SOVEUR database was available. Therefore, the existing, traditional SOTER polygon system was tested against the SRTM derived terrain parameters. Two terrain parameters, the slope and the relief were chosen for the test and were derived from the SRTM DEM. The traditional SOTER unit system and the continuous slope and relief layers were overlaid, and descriptive statistics were calculated to characterize the area under the SOTER polygon having the same geomorphological classes.

## Results and discussion

The polygon system derived by the procedure follows the main geomorphological trends, and identifies terrain units according to the scale (Figure 1). As a result of the rigorous, quantitative procedure, the polygons represent relatively homogeneous units as far as the four terrain parameters are considered. In order to test the resulting database a comparison with the traditional, manually delineated polygon system of the SOVEUR was performed. The overlay of the two datasets is shown in Figure 1. The SOVEUR database is compiled from manually delineated polygons, produced by the participating countries individually. Therefore, the national windows may have different approaches and interpretations of the SOTER manual and the national diversity of mapped physiographic and soil features. The quantitative SOTER is fully SRTM based, following the procedure described above, theoretically representing the SOTER concept. However, when the two polygon systems are overlaid, no clear similarity can be identified between them. The SRTM-based system has higher polygon density and a better match with the background SRTM image, from which it has been derived. It has to be noted here that the SOVEUR polygons already contain the parent material information as well, and the scale of that is also a little bit coarser, 1:2.5M, while the SRTM-derived one is 1:1M, which may explain some of the discrepancies.  Despite of these differences, the major lines should have some similarity, which is not the case here.  Based on this experience, we may conclude, that the digital procedure failed to reproduce the same database. However, the differences may have resulted from the non-rigorous application of the SOTER manual as well when it was used in a traditional way. Therefore, a quality check of the traditional database was performed using the SOVEUR database. Two terrain parameter layers, the slope and the relief intensity, were calculated from the SRTM database, classified into the SOTER classes and were used as ground truth information. The SOVEUR polygons classified into the same geomorphologic units – having defined slope and relief intensity classes - were selected and were used to overlay/mask the classified slope and relief images. In theory, the majority of the slope and relief layer pixels should match with the correlating polygon classes. The results of this test did not confirm this hypothesis.

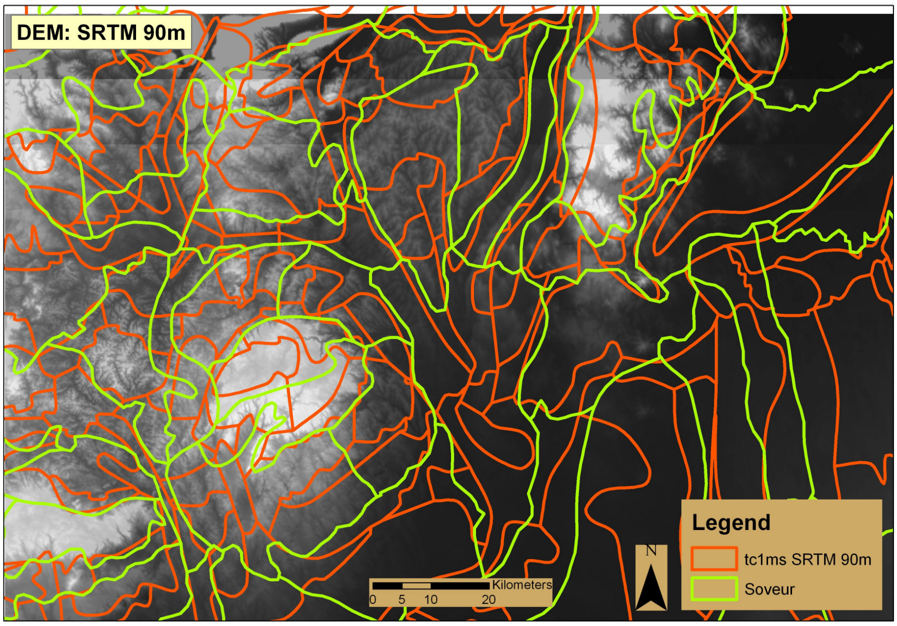

**Figure 1.  The overlay of the traditional (SOVEUR) and SRTM-derived (tcm1s SRTM 90 m) polygon systems.**

The databases of six countries (Hungary, Slovakia, Czech, Romania, Ukraine and Poland) were tested, but only the Hungarian results are presented here which shows the main trends of all databases (Tables 1 and 2). The results show very distinctive trends, namely the higher the relief and the slope the lower the match between the traditional SOTER and the SRTM-derived terrain parameters.  The traditional mappers tended to overestimate the slope and the relief classes when allocating the attribute information to the polygons. Therefore, the low relief classes lost some of their members while the remaining area showed a clear and pure membership of the corresponding class. However, the areas with overestimated relief and slope have only a small portion of the real members, complemented with the areas having lower values in reality, but being misclassified and shifted to the higher relief/slope areas. The differences are often shocking, like in the relief intensity class for medium gradient mountain case, where not even one pixel matches to the corresponding polygon. Only one-fourth of the area of the polygons having higher than 50m/km$^2$ relief intensity assigned to them matches to the corresponding SRTM pixel class (Table 2). The same trends occur in the higher slope classes as well (dissected plain, valley, medium gradient escarpment) (Table 1).

**Table 1. The validation of the slope classes of the SOVEUR database using the SRTM-derived data.**

| Landform classes of the SOVEUR with the corresponding slope class | Total number of SRTM pixels within the corresponding polygons | The number of SRTM pixels matching the polygon class | Percent of matching SRTM pixel classes |
|---|---|---|---|
| low-gradient foot slope, 0-8% | 874532 | 812925 | 92,9 |
| valley floor, 0-8% | 586637 | 550996 | 93,9 |
| plain, 0-8% | 9867338 | 9834630 | 99,7 |
| plateau, 0-8% | 149332 | 133084 | 89,1 |
| dissected plain, 8-30% | 851363 | 37907 | 4,4 |
| medium-gradient hill, 8-30% | 2527481 | 500463 | 19,8 |
| Ridges, 8-30% | 46944 | 9860 | 21,0 |
| valley, >8% | 490751 | 45657 | 9,3 |
| Narrow plateau, >8% | 287686 | 43245 | 15,0 |
| Medium-gradient mnt. 15-30% | 621468 | 97943 | 15,7 |
| medium-gradient escarpment zone 15-30% | 62838 | 3964 | 6,3 |

**Table 2. The validation of the relief intensity classes of the SOVEUR database using the SRTM-derived data.**

| Landform classes of the SOVEUR with the corresponding relief intensity class | Total number of SRTM pixels within the corresponding polygons | The number of SRTM pixels matching the polygon class | Percent of matching SRTM pixel classes |
|---|---|---|---|
| low-gradient foot slope, 0-100 m/km$^2$ | 875214 | 862084 | 98,50 |
| valley floor, 0-100 m/km$^2$ | 587187 | 579422 | 98,68 |
| plain, 0-100 m/km$^2$ | 9869464 | 9866850 | 99,97 |
| plateau, 0-100 m/km$^2$ | 149332 | 146632 | 98,19 |
| medium gradient escarpment zone, <600m/2km | 62838 | 62838 | 100,00 |
| dissected plain, <50m/slope unit | 853038 | 803471 | 94,19 |
| medium gradient hill, >50m/slope unit | 2529428 | 661159 | 26,14 |
| Ridges, >50m/slope unit | 46944 | 12930 | 27,54 |
| medium-gradient mnts >600 m/2km | 621468 | 0 | 0,00 |

## Conclusions

The original aim of this study was to develop a quantitative procedure to speed up the database development and make use of the emerging technology and digital data sources, such as Digital Elevation Models. The SOTER manual describing the database development procedure was published in 1993. Since then, a significant portion of the World has been covered with SOTER databases. In the last decade Digital Soil Mapping (DSM) techniques and the supporting digital databases have changed the way of mapping and database development. These techniques have been adapted by this group and a quantitative procedure was developed to replace the traditional methodology of SOTER development. A rigorous procedure to maintain the original mapping concept was introduced and tested here. The comparison of the traditional and the quantitative procedure showed major discrepancies, which were difficult to explain. Therefore, a quality check on the SOVEUR database was performed using SRTM-derived terrain parameters as ground truth information. The results demonstrated that the thematic content of the traditional databases do not always match with the corresponding/assigned information. The characteristics/quality of a database depends on the procedure, the input data sources and the interpreter of the procedure. Even having a more or less clearly defined procedure with quantitative classes, a manually made database often introduces much shift from the original content. Therefore, translating a manual procedure to a quantitative one to reproduce a map or a database raises some important questions among which the first is: how to maintain the original mapping concept and conform to the original methodology defined by the manual of mapping procedures? However, the traditional maps have a great portion of subjectivity which may result from different interpretations when the procedure is used by different experts. This factor also has a significant impact on the final product. The final dilemma that remains on the table is what to reproduce, the procedure or the map? The new environmental covariates and the new DSM tools represent a different developing environment, and that necessarily means different products. Maintaining the linkage between the traditional and the quantitative products is not always possible and not always necessary either.

## References

ISRIC (1993) Global and National Soils and Terrain Databases (SOTER): Procedures Manual. UNEP-ISSS-ISRIC-FAO, Int. Soil Reference and Information Centre, Wageningen, The Netherlands.

Dobos E, Daroussin J, Montanarella L (2007) A quantitative procedure for building physiographic units for the European SOTER database. In 'Digital Terrain Modelling. Development and Applications in a Policy Support Environment'. (Eds R Peckham, Gy Jordán.) pp.227-259. (European Commission, Springer), ISBN 978-3-540-36730-7.

Köthe R, Bock M (2009) Preprocessing of Digital Elevation Models – derived from Laser Scanning and Radar Interferometry – for Terrain Analysis in Geosciences – Proceedings of Geomorphometry 2009. Zurich

Batjes NH (2000) SOTER summary file for Central and Eastern Europe (ver. 1.0). Report 2000/06, ISRIC, Wageningen, pp. 11

# Low temperature transformation of schwertmannite to hematite with associated $CO_2$, SO and $SO_2$ evolution

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## Abstract

Schwertmannite forms surface accumulations on organic litter in coastal flood plain acid sulfate soil landscapes of eastern Australia that are subject to wildfire and prescribed burning events. Naturally occurring schwertmannite ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$), is a product of acid sulfate soil oxidation and severe acidification. We report experimental evidence that relatively low temperature fires, fueled by organic-matter admixed with schwertmannite surface accumulations will transform the mineralogy of schwertmannite whilst liberating the Greenhouse gases $CO_2$, SO and $SO_2$. Three schwertmannite samples were examined, 2 natural and 1 synthetic. Thermal gravimetric analysis of the natural samples measured simultaneous $CO_2$, SO and $SO_2$ evolution at ~200-400$^oC$. The natural schwertmannite, with organic matter, partially transformed to hematite in this temperature range. The synthetic schwertmannite, without organic matter, started to transform to hematite only at ≥600$^oC$. The evolution of these gases and the partial transformation to hematite clearly shows combustion of organic matter, in close association with schwertmannite, raises the immediate temperatures to ≥600 $^oC$. When heated to ≥800$^oC$ all samples were completely transformed to hematite. This study provides the first evidence that wildfire can transform the mineralogy of schwertmannite at relatively low temperatures and therefore presents an original and significant insight into the iron cycle in coastal flood plain acid sulfate soil landscapes.

## Key Words

Schwertmannite, acid sulfate soil, hematite, $CO_2$, SO, $SO_2$.

## Introduction

Schwertmannite, an oxyhydroxysulphate of iron is a, poorly crystalline, yellowish-brown mineral with a structure analogous to akaganéite (Loan *et al.* 2004). Schwertmannite forms in low pH waters (2.8 to 4.5) of both natural waterbodies and waterbodies the result of mining and artificial drainage (Acero *et al.* 2006). Schwertmannite is a labile source of iron, sulfate and acidity and has a major role in controlling the geochemistry of acidified waterbodies (Burton *et al.* 2006). Sulfidic subsoils, deposited during the Holocene, underlay approximately 3 million hectares of Australian coastal flood plain. Coastal flood plain acid sulfate soils, disturbed and drained over the last 100 years, pose a land and waterbody management challenge (Johnston 2003). Schwertmannite forms surface accumulations in coastal flood plain acid sulfate soil landscapes of eastern Australia (Henderson *et al.* 2007). These accumulations have been implicated in maintaining severely acidic surface waters in these landscapes (Sullivan and Bush 2004) as well as being a primary iron mineral responsible for the formation of the monosulfidic black oozes accumulations (Burton *et al.* 2007; Henderson *et al.* 2006). Wildfire and prescribed fire regimes to reduce wildfire hazard frequently occur across the Australian continent including coastal flood plain acid sulfate soil landscapes (Bradstock *et al.* 2006). Such burning events can induce changes in iron mineralogy. For example, Grogan *et al.* 2003, attributed the transformation of goethite to maghemite in a coastal flood plain acid sulfate soil landscape to heating by bushfires of temperatures >300$^oC$. An anomalous feature commonly observed in the wetland soils of these landscapes is the presence of abundant and thick (up to 5 cm) hematitic surficial layers, especially on soil profiles in areas affected by recent bushfires (Henderson *et al.* 2007). The presence or absence of reductants, including organic matter, elemental sulfur or sucrose, dictate the nature of the intermediate iron phases prior to complete conversion to hematite by heating (Loan *et al.* 2004). The transformation temperature is usually dependant on the crystallinity, and for iron minerals, the degree of aluminium substitution. The literature indicates that schwertmannite starts to transform to hematite at temperatures >600$^oC$ accompanied by evolution of $SO_3$ (Yu *et al.* 2002). Many of the studies into the behaviour of schwertmannite with heating were undertaken using purified or synthetic schwertmannite samples (Majzlan *et al.* 2004). The mineralogy including thermal behaviour of a purified schwertmannite sample from a naturally acidic stream has been reported to be essentially identical to that of synthetic samples (Schwertmann *et al.* 1995). However, natural schwertmannite accumulations in coastal flood plain acid sulfate soil landscapes are usually in intimate association with appreciable quantities of organic debris such as leaf litter (Henderson *et al.* 2008). These organic materials are capable of ignition at relatively low temperatures (< 400°C) (Dold *et al.* 2005) and accordingly may influence the thermal behaviour and subsequent mineralogy of natural schwertmannite accumulations from these landscapes. The objective of this study was to examine the influence of this closely associated organic matter on the thermal behaviour, mineralogy and evolution of gases during heating of natural schwertmannite accumulations from coastal flood plain acid sulfate soil landscapes.

## Materials and methods

Natural samples were collected from coastal flood plains of New South Wales as leaf litter coated by schwertmannite. Samples were air dried and sieved. Synthetic schwertmannite was manufactured after Regenspurg (Regenspurg 2002). Samples were ramp heated in a muffle oven at 50°C $h^{-1}$ to both 400°C and 800°C. Randomly orientated powdered samples were examined using a Phillips PW 1050/70 diffractometer. Samples for X-ray diffraction analysis were gently hand ground. Total sulfur and carbon were analysed by an Elementar® combustion oven. Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Evolved Gas Analysis (EGA) were performed in a Netszch STA 409C Simultaneous Thermal Analyser coupled to a Balzers Thermostar mass spectrometer.

## Results

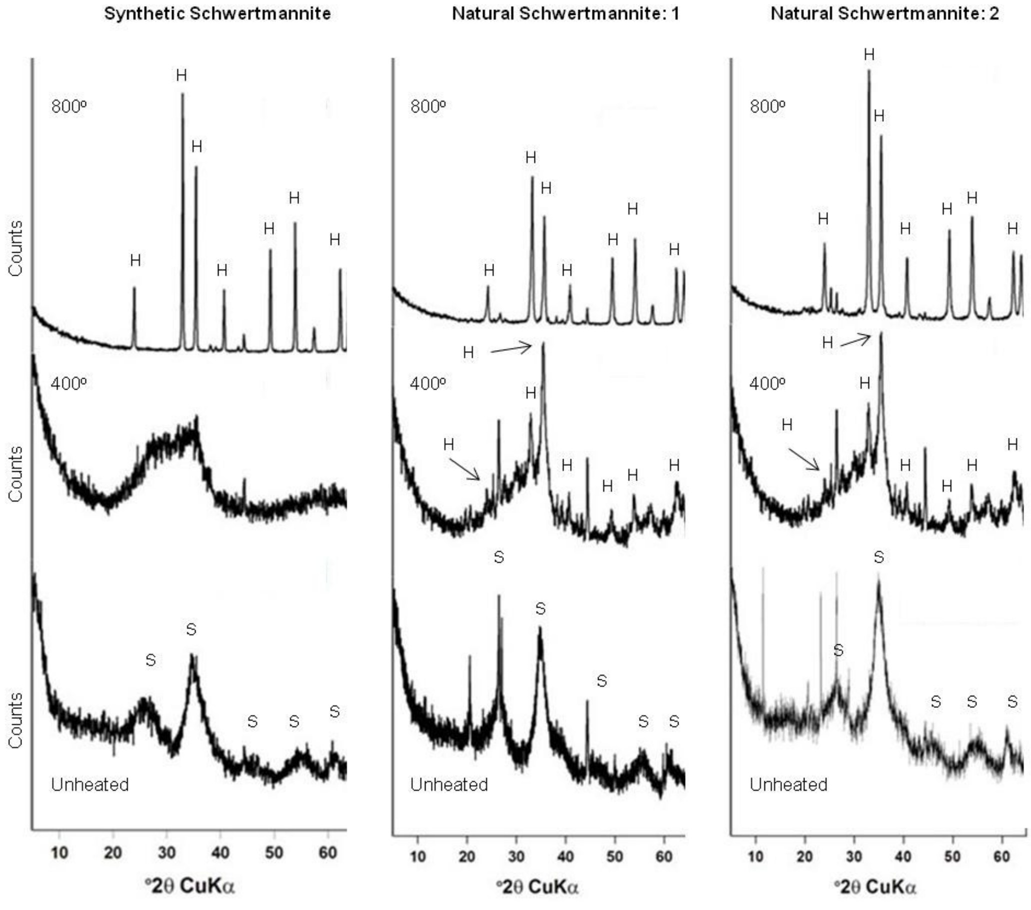

**Figure 1. S = Schwertmannite Peaks and H = Hematite Peaks.**
**In line with the literature, heating to 800°C caused complete transformation of both natural and synthetic schwertmannite to hematite. However, heating to only 400°C caused partial transformation of the schwertmannite to hematite in the natural schwertmannitic accumulations but not in the synthetic schwertmannite.**

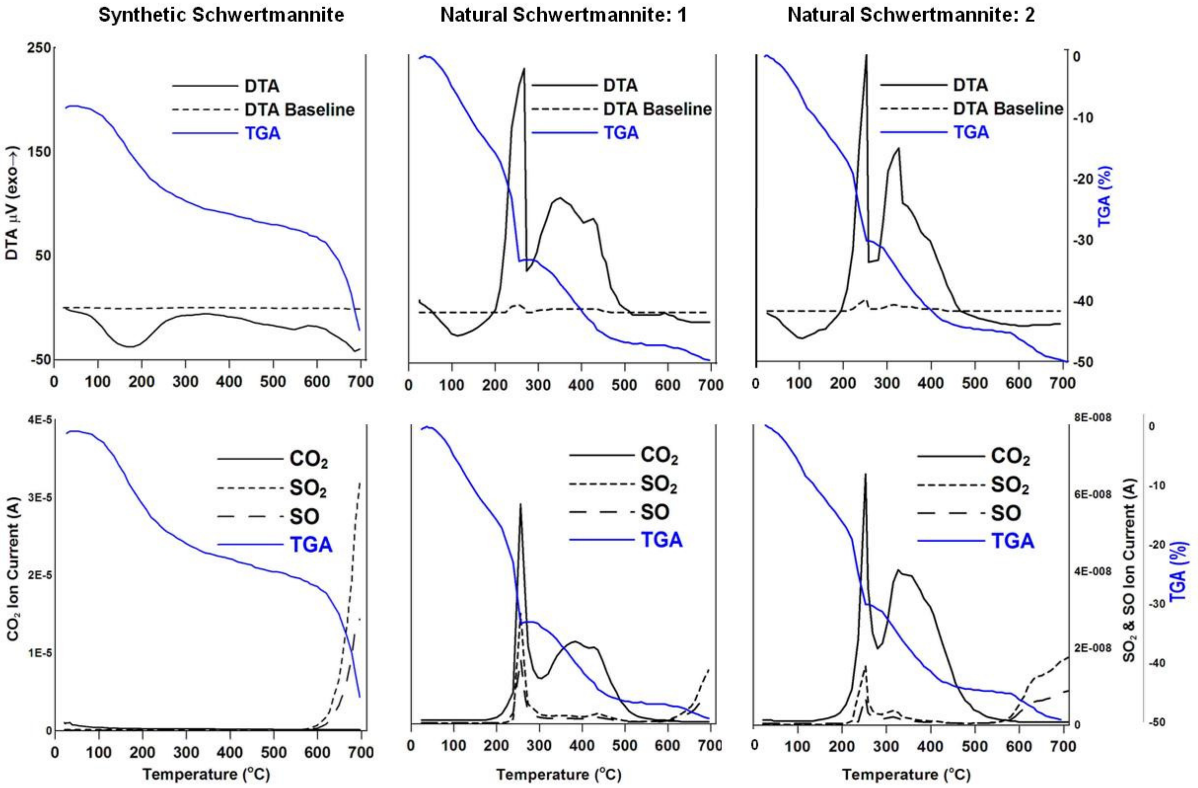

**Figure 2. As all samples were heated, water was lost endothermically to ~ 200°C. After 600°C, SO and $SO_2$ was evolved, endothermically, as the synthetic schwertmannite began to convert to hematite. However the intimately admixed organic matter in the natural schwertmannite accumulations acted as an accelerant reacting exothermically from ~ 200 °C to 500°C causing the production of both heat and $CO_2$ upon pyrolysis. Micro-scale hot spots were created (>600°C) as evidenced by the production of SO and $SO_2$ (in accord with heat and $CO_2$ production), and appearance of hematite peaks at 400°C in XRDs.**

**Table 1. Heating to 800°C removed much of the sulfur but not all of it. Heating to 800°C effectively removed carbon.**

| Sample | Treatment | Sulfur Content (%) | Carbon Content (%) |
|---|---|---|---|
| Natural Schwertmannite: 1 | Unheated | 2.90 | 10.08 |
| Natural Schwertmannite: 1 | 400°C | 2.82 | 0.05 |
| Natural Schwertmannite: 1 | 800°C | 1.82 | 0.02 |
| Natural Schwertmannite: 2 | Unheated | 3.17 | 12.91 |
| Natural Schwertmannite: 2 | 400°C | 3.05 | 0.05 |
| Natural Schwertmannite: 2 | 800°C | 0.72 | 0.02 |
| Synthetic Schwertmannite | Unheated | 7.41 | 0.06 |
| Synthetic Schwertmannite | 400°C | 7.91 | 0.02 |
| Synthetic Schwertmannite | 800°C | 0.02 | 0.01 |

## Conclusion

This study has shown that the hematitic surficial horizons common in the soils of coastal flood plain acid sulfate soils landscapes can be readily formed by bush fires during dry seasons by the burning of organic matter-rich schwertmannite accumulations. Even low temperature (as measured conventionally) bush fires (e.g. < 300°C) could convert schwertmannite accumulations to hematitic surficial horizons due to the intimate association of the schwertmannite minerals with organic matter that acts as an accelerant. Bushfires in these landscapes can produce SO and $SO_2$ (in addition to $CO_2$) to the atmosphere during bushfires by the pyrolytic oxidation of iron precipitate minerals.

## References

Acero P, Ayora C, Torrentó C, Nieto JM (2006) The behaviour of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. *Geochimica et Cosmochimica Acta* **70**, 4130-4139.

Bradstock RA, Bedward M, Cohn JS (2006) The modelling effect of differing fire management strategies on the conifer *Calltris verrucosa* within semi-arid mallee vegetation in Australia. *Jounal of applied ecology* **43**, 281-292.

Burton ED, Bush RT, Sullivan LA (2006) Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica. Acta* **70**, 5455-5468.

Burton ED, Bush RT, Sullivan LA, Mitchell DRG (2007) Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands. *Geochemical et Cosmochimica Acta* **71**, 4456-4473.

Dold J, Greenberg B, Weber R, Zinoviev A, Sivashinsky G (2005) A porous-medium model for vegetation in bushfires. In '5th Asia-Pacific Conference on Combustion' pp. 289-292Adelaide, Australia).

Henderson SP, Sullivan LA, Bush RT, Burton ED (2006) The influence of naturally occurring schwertmannite on sulfur biomineralisation in coastal acid sulfate soils landscapes In '18th World Congress of Soil Science'. Philadelphia, USA.

Henderson SP, Sullivan LA, Bush RT, Burton ED (2007) Schwertmannite transformation to hematite by heating: implications for pedogenesis, water quality and CO2/SO2 export in acid sulfate soil landscapes. In '17th Annual V.M. Goldschmidt Conference'. Koln, Germany (Geochemical Society, and European Society for Geochemistry).

Henderson SP, Sullivan LA, Bush RT, Burton ED (2008) Thermal transformation of schwertmannite to hematite: anomalous stored acidity. In '6th International Acid Sulfate Soils Conference and the Acid Rock Drainage Symposium'. Guangzhou, Peoples Republic of China.

Johnston SG, Slavich, P G, Hirst, P (2003) Alteration of groundwater and sediment geochemistry in a sulfidic backswamp due to *Melaleuca quinquenervia* encroachment. *Australian Journal of Soil Research* **41**, 1343-1367.

Loan M, Cowley JM, Hart R, Parkinson GM (2004) Evidence on the structure of synthetic schwertmannite. *American Mineralogist* **89**, 1735-1742.

Majzlan J, Navrotsky A, Schwertmann U (2004) Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite ($\sim Fe(OH)_3$), schwertmannite ($\sim FeO(OH)_{3/4}(SO_4)_{1/8}$) and $\varepsilon$-$Fe_2O_3$. *Geochemical et Cosmochimica Acta* **68**, 1049-1059.

Regenspurg S (2002) Characterisation of schwertmannite - geochemical interactions with arsenate and chromate and significance in sediments of lignite opencast lakes. University Bayreuth.

Schwertmann U, Bigham J, M, , Murad E (1995) The first occurence of schwertmannite in a natural stream environment. *European Journal of Mineralogy* **7**, 547-552.

Sullivan LA, Bush RT (2004) Iron precipitate accumulations associated with waterways in drained coastal acid sulfate landscapes of eastern Australia. *Marine and Freshwater research* **55**, 727-736.

Yu JY, Park M, Kim J (2002) Solubilities of synthetic schwertmannite and ferrihydrite. *Geochemical Journal* **36**, 119-132.

# Managing acidity movement in the coastal land with acid sulphate soils: a modeling approach

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## Abstract

A new acidity module has been developed and coupled successfully into an existing hydraulic and salinity model for simulating acidity movement in canals under the controlled marine water intake in the coastal land with acid sulphate soil (ASS). The model allied with the Camau peninsula, Mekong Delta, Vietnam indicates that the most suitable option for improving the acidity condition is to open main sluice gates one day every week when difference of tide amplitude of between the East and West seas is highest and to widen the canals connected to the West sea.

## Key Words

Modeling, acid sulphate soil, coastal, salinity, acidity.

## Introduction

The study area located in the Camau peninsula, Mekong delta, Vietnam (Figure 1) is a coastal land with a total area of 950,000 ha of which the acid sulphate soils (ASS) occupied 63%. Before 2000, the study area had been adversely affected by acidic pollution from ASS when it was protected from salinity by sluices along the East sea for rice production (Hoanh *et al.* 2003). However, land use changed to shrimp or shrimp-rice system that requires brackish water has reduced the acidity in the fields significantly. Powell and Martens (2005) explained that in the ASS area saline water creates the suppression of the hydrological transport of aqueous acidic products and supports the *in-situ* reformation of solid phase iron-sulfide minerals. Other studies (Indraratna *et al.* 2002; Johnston *et al.* 2005; Åström *et al.* 2007) also indicated the reduction of acidity impacts through the hydrological suppression, neutralisation or dilution of acidic products. A study on applying the inundation by marine water for a large ASS area was also carried out at East Trinity, New South Wales (Johnston *et al.* 2008). In the study area severe acidic pollution in the canal network usually occurs at the beginning of rainy season due to acidity leached out from the dredged acid soils deposited along canal bank. Therefore this study focused on simulation of acidity movement in canal network when saline water is intaken through sluices to find out the most suitable option for water quality management.

## Methodology

### *Developing a new acidity module*

The new acidity module was developed (Figure 2) and coupled into an existing hydraulic and salinity model, the Vietnam River Systems and Plains (VRSAP) model (Dong 2000). The acidity module (Figure 3) simulates the acidity transport in canals by flow, diffusion of lateral acidity input along canals and reaction between saline water and acidity. The two latter components were quantified from laboratory and field experiments (Phong 2009). The new acidity module was calibrated and verified by Phong (2009).

### *Delineating zones for model analysis*

Land uses in the study area vary from 2 shrimp crops in the southwest part (zones So to S3) where saline water is dominant to three rice/upland crops in the eastern part (zone F) where fresh water is dominant (Figure 1). Two rice crops or one shrimp crop in the dry season followed by one rice crop in the rainy season are cultivated in the zones with alternate brackish and fresh water (B1, B2 and S1, S2). To simplify the water quality requirement, salinity of 5 ppt is used as a threshold for rice crop. At Ninh Quoi (NQ), salinity should be less than 5 ppt throughout the year to allow 3 rice/upland crops in zone F.

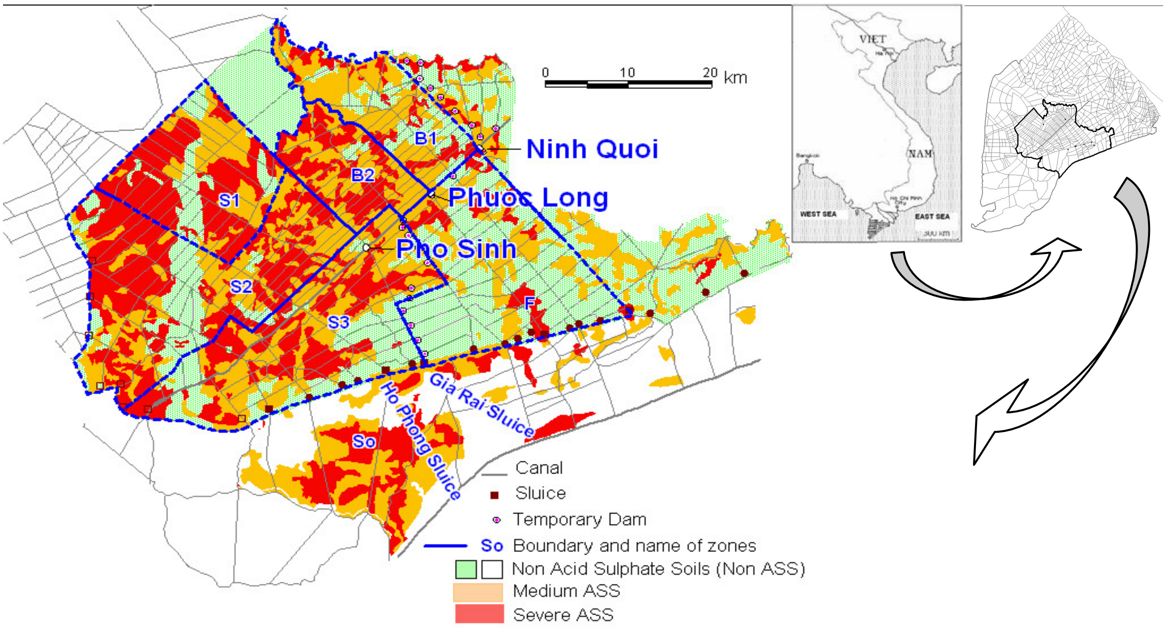


**Figure 1. Zoning for water management in ASS area.**

*Matching salinity with land use requirements while minimizing acidity impacts*
The model was applied to explore a suitable water management option for matching salinity requirement in different land use zones while minimizing acidity impacts in the study area. Model results were transferred to GIS for mapping the isohalines and the pH isolines to check the salinity and acidity movement in all land use zones.

Different sluice operation options were studied for managing salinity in the study area (Hoanh *et al.* 2003). In this study, acidity movement in the canal network is investigated in an option of operation of both Ho Phong (HP) and Gia Rai (GR) sluices combined with canal widening to allow easier saline water intake and improving acidity problem.

The expectation of water management is to push out acidity to the West sea direction where the land is still fallow or mainly covered by forest. Among the primary canals that links the East sea side to the West sea side, the Ninh Thanh Loi (NTL) and the Quan Lo-Chu Chi (QLCC), with a width from 10 m to 50 m, are the shortest (20-25 km) canals connected directly to the HP and GR sluices (Figure 4a).

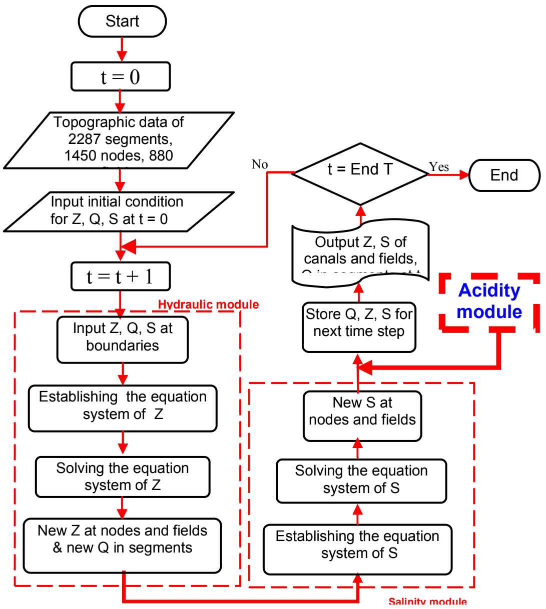
## Results and discussions

As a result of field experiment to quantify sources of acidity pollution along canals (Phong 2009), Table 1 shows the total amount of acidity in water leached out by water components (runoff, bypass, percolation and seepage) from canal embankments at the beginning of rainy season are strongly affected by both acid soil type and dredged years and it is extremely high at canal embankment with dredged severe acid soil deposited between 1-2 years (mid).

**Table 1. The total amount of acidity leached out from canal embankment (mol $H^+$ $m^{-2}$ of surface of canal embankment) during field experiment from 15/4 to 30/7/2005.**

| Age of deposit | Soil type | | |
|---|---|---|---|
| | Severe ASS | Medium ASS | non ASS |
| Old | 3.7 | 3.5 | 0.3 |
| Mid | 19.7 | 13.2 | |
| New | 1.9 | 2.5 | |

Note:
Soil type: Severe, medium ASS: Depth of sulphuric horizon are from 0-50 or and >50 cm, respectively.
Age: Old > = 3 years; Mid >1 to 2 years; New <= 1year.



Notes: Z, S are water level and salinity at nodes and fields, and Q is discharge in segments. t is current time step. End T is last time step.

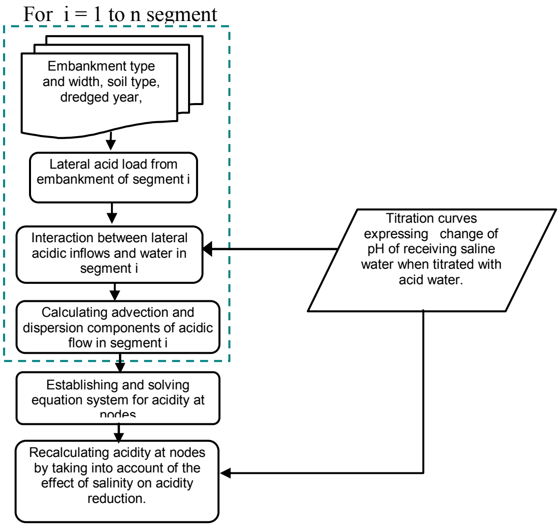
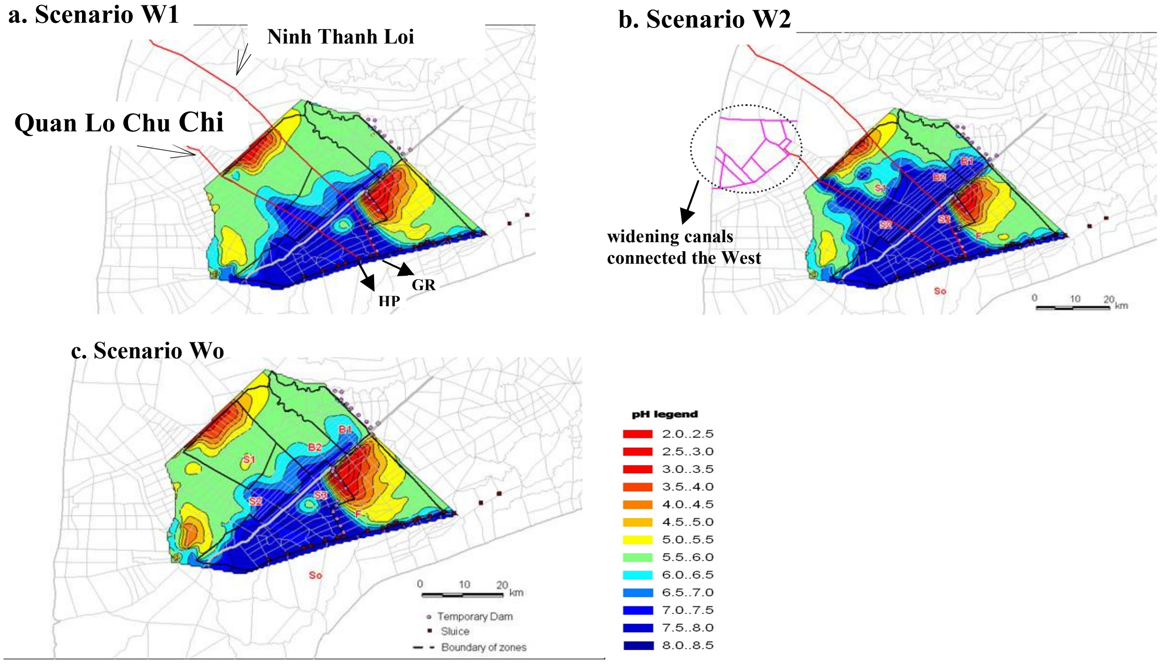


**Figure 2. The ACIDITY module in the VRSAP model.** **Figure 3: The ACIDITY module**


a. Scenario W1

b. Scenario W2

c. Scenario Wo

**Figure 4 Acidity propagation under scenarios a. W1: sluice operation and widening NTL and QLCC canals b. W2: sluice operation with widening more canals connected QLCC to West Sea; and c. Wo (control scenario) only sluice operation without canal widening.**

Two scenario groups of sluice operation and canal widening were analyzed by the model. In the scenario group 1, only sluice operation was considered by analyzing role of each sluice and different combinations of sluices. In the scenario group 2, both sluice operation and canal widening are considered. For example, in scenario Wo (Figure4c) canals are not widened. This scenario is used as control scenario for comparison with two scenarios W1 and W2. In scenario W1 only the NTL and the QLCC canals are widened to a top width of 50m and deepened to elevation of -2.0 m below Mean Sea Level (Figure 4a). In scenario W2 more secondary canals connected the QLCC to the West Sea are widened (Figure 4b).

Sluice operation for controlling saline water intake and drainage has significant effect on acidity propagation. Model results from scenarios in group 1 showed that scenarios with more frequent intake of saline water are more effective in improving acidity condition because of the increase of alkalinity in canal water. The scenario of opening HP and GR one day a week at the highest difference of tide amplitude of between the East and West Seas can be considered as a most suitable option for sluice operation for both purposes of salinity and acidity control. Furthermore, a significant reduction of acidity in the study area occurs when such sluice operation is combined with the widening of primary and secondary canals that connect these sluices to the West Sea (scenario W2).

## Conclusion

For managing acidity movement in the study area, the process of land use zoning, matching water salinity with requirement, then simulating acidity propagation under effects of salinity control is suitable. Such process helped in analyzing effects on both salinity and acidity by changing sluice operation and/or widening canals. However, the analysis also showed a trade-off in water quality management: moving acidity out of the study area may cause pollution to the area at the West sea side.

## References

Åström M, Österholm P, Bärlund I, Tattari S (2007) Hydrochemical effects of surface liming, controlled drainage and lime–filter drainage on boreal ASS. *WaterAir Soil Pollut.* **179,** 107–116.

Dong TD (2000) VRSAP model and its applications. In ‘Proceedings of the Workshop on Hydrologic and Environmental Modeling in the Mekong Basin. Technical Support Division, Mekong River Commission, Phnom Penh, Cambodia’. (Ed RW Al-Soufi).

Indraratna B, Glamore W, Tularam GA (2002) The effects of tidal buffering on ASS environments in coastal areas of NSW. *Geotech. and Geolog. Engineer.* **20,** 181–199.

Johnston SG, Slavich PG, Hirst P (2005) The effects of controlled tidal exchange on improving drainage water quality in ASS backswamps. *Agricult. Water Manag.* **73,** 87–111.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith D, Martens MA, McElnea AE, Wilbraham ST, van Heel S (2008) Contemporary pedogenesis of severely degraded tropical ASS after introduction of regular tidal inundation. *Geoderma* **149,** 335–346.

Hoanh CT, Tuong TP, Gallop KM, Gowing JW, Kam SP, Khiem NT, Phong ND (2003) Livelihood impacts of water policy changes: evidence from a coastal area of the Mekong river delta. *Water Policy* **5,** 475–488.

Phong ND (2009) Modelling of canal water acidity due to ASS: a case study of the Camau Peninsula, Mekong Delta, Vietnam. PhD thesis, The University of Melbourne, Australia.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in the Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar. Pollut. Bull.* **51,** 149–164.

# Marine disposal of monosulfide from a eutrophic estuary system and the impact on water chemistry

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## Abstract

The sediments of the Peel Harvey Estuary system (PHES) contain accumulations of monosulfidic black ooze (MBO) related to hypereutrophication and discharge from active acid sulfate soils. MBOs may release acidity and contaminants (nutrients, trace metals) when disturbed. We investigated release of acidity during resuspension of MBOs in a laboratory study and during a dredging event in the estuary. Selected samples from the laboratory study were analysed using XANES. In the laboratory study, decreases in pH (approx. 1 pH unit) of MBO suspensions coincided with the re-establishment of oxidizing conditions. Sediment analyses illustrated near-complete oxidation of acid-volatile sulfide (AVS, a proxy for monosulfide). The XANES data supported the chemical AVS analysis, showing the disappearance of peaks corresponding to mackinawite and greigite and appearance of the sulfate peak, consistent with AVS oxidation products. Pyrite and organic S peaks showing minimal changes throughout the resuspension. The data for estuary water quality from dredge monitoring showed consistent transient decreases in $E_h$ at the point of sediment disposal, but pH remained well-buffered. The decreases in $E_h$ were associated with increases in concentrations of ammonium and orthophosphate, with high variability. Laboratory experiments demonstrate the high reactivity of MBOs from the PHES following disturbance, but high variability and buffering in the field may limit the observation of these effects.

## Key Words

Sulfide, sediment, oxidation, pH, redox, resuspension.

## Introduction

Eutrophic estuary systems often contain an abundance of the acid sulfate material "monosulfidic black ooze" (MBO), which is an organic sludge enriched with highly reactive iron-monosulfide. MBO is a natural product formed during bacterially mediated sulfate reduction, and when undisturbed it is recognised as playing an important role in improving water quality by storing acidity and sequestering metals (Macdonald *et al.* 2004; Smith 2004; Smith and Melville 2004). However, contaminant stores in MBOs are temporary and can be released into the water column upon disturbance and oxidation (Smith 2004; Burton *et al.* 2006; Burton *et al.* 2009). Consequently, an understanding of chemical changes during MBO oxidation is critical to effectively manage water quality impacts during their disturbance and disposal. This is particularly important when such systems are subject to disturbance by development and recreation. The Peel Harvey Estuary system (PHES), located 70 km south of Perth in Western Australia has accumulated unusually large amounts of MBO related to contributions from hypereutrophication and active acid sulfate soils in it catchment. The Peel-Harvey MBO also have anomalously high acid-volatile sulfide (AVS, a proxy for monosulfide) contents; four 30 cm cores taken from the South Yunderup boating channel on the North-East of the estuary had AVS concentrations ranging from 33 to 335 µmol/g, with an average of AVS of 209 µmol/g. This study investigates a laboratory resuspension of sediment collected from the South Yunderup channel, and the water chemistry during a dredging event in 2008.

## Methods

### *Laboratory resuspension*

Three cores between 0-20 cm were collected from the South Yunderup boating channel in the PHES and homogenised in the laboratory under a stream of nitrogen gas. Three sediment to water ratios (50 g/L, 100 g/L and 200 g/L) and one control treatment (nil sediment addition) were resuspended in the laboratory with estuary water for two weeks, with humidified compressed air being continuously bubbled through the suspensions. Samples were collected immediately prior to MBO addition (0 hours) and at 0.33, 0.66, 1, 2, 3, 4, 24, 48, 72, 96, 168 and 336 hours and analysed for pH, $E_h$, alkalinity, ferrous iron, dissolved sulfide, orthophosphate, ammonium and dissolved metals. Sediment was analysed for AVS, CRS, elemental S and total extracted metals (Burton *et al.* 2009). Sulfur speciation at 0, 24 and 72 hrs was also investigated using K-edge X-ray absorption spectroscopy (XANES) using the Taiwan Synchrotron. Only the pH, $E_h$, and XANES data will be presented in this paper.

*Field dredge event*

The South Yunderup approach channel was dredged and the sediment disposed of in a submerged area of the estuary in 2008. Five water monitoring events were conducted between July 2008 and September 2008 to investigate the impact of the large scale MBO disturbance on the water chemistry of the estuary. The first site was 100 m upcurrent from the disposal point and was a reference for undisturbed estuary conditions. The second site was at the point of sediment disposal, with the remaining 3 to 4 sites were approximately every 100 m in a transect across the dredge plume moving away from the sediment disposal point. Water was analysed for alkalinity, ferrous iron, dissolved sulfide, orthophosphate, ammonium, dissolved metals, pH, $E_h$, dissolved oxygen and electrical conductivity. Only the pH, $E_h$, ammonium and orthophosphate data will be presented in this paper.

## Results and discussion

During a laboratory resuspension of MBO material from the PHES a decrease in pH in all treatments was observed when the solution reached a redox potential of approximately + 400 mV (Figure 1a). The lower pH following oxidation of a higher mass of MBO reflected the greater acidity produced by oxidising higher quantities of AVS. In the highest sediment to water ratio treatment (200 mg/L) the pH dropped to a minimum of 6.99, before increasing to approximately the same pH that is observed at the end point of the other treatments (Figure 1b). This suggests that while the buffering capacity of the estuarine water prevents the severe acidification events that are observed during the resuspension of MBO in river systems (Sullivan *et al.* 2002).

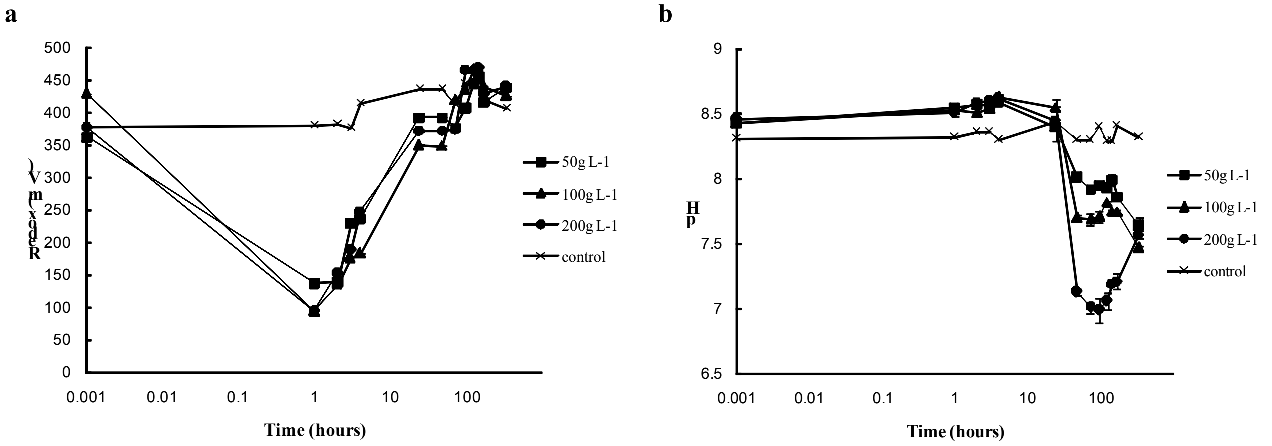

**Figure 1. The a) redox and b) pH of three sediment resuspension treatments and one control (no added sediment) were recorded for a two week period.**

This acidification is consistent with the disappearance of AVS and the appearance of the oxidation product sulfate observed in the peaks measured by XANES at 0, 24 and 72 hrs of resuspension for the 100 g/L treatment (Figure 2a). In a system not limited by oxygen, AVS has almost completely oxidised in all treatments by 24 hrs of resuspension, with the majority being oxidised within the first 4 hrs.

The results from monitoring a dredging disturbance also indicate redox and water quality changes. In the dredge plume, the localized impact zone can be distinguished by the decrease in redox potential at the point of sediment disposal (Figure 3a). The pH, however, is unaffected by distance from disposal site, and the variation observed between sampling dates is representative of normal estuarine processes (Figure 3b).
The localised release of ammonium and phosphate was observed at the sediment disposal point in the dredge plume (Figure 4). The variation of concentrations measured at the disposal point is most likely a result of the heterogeneous nature of the dredge plume and hydrodynamic conditions in the estuary at the time of sampling.

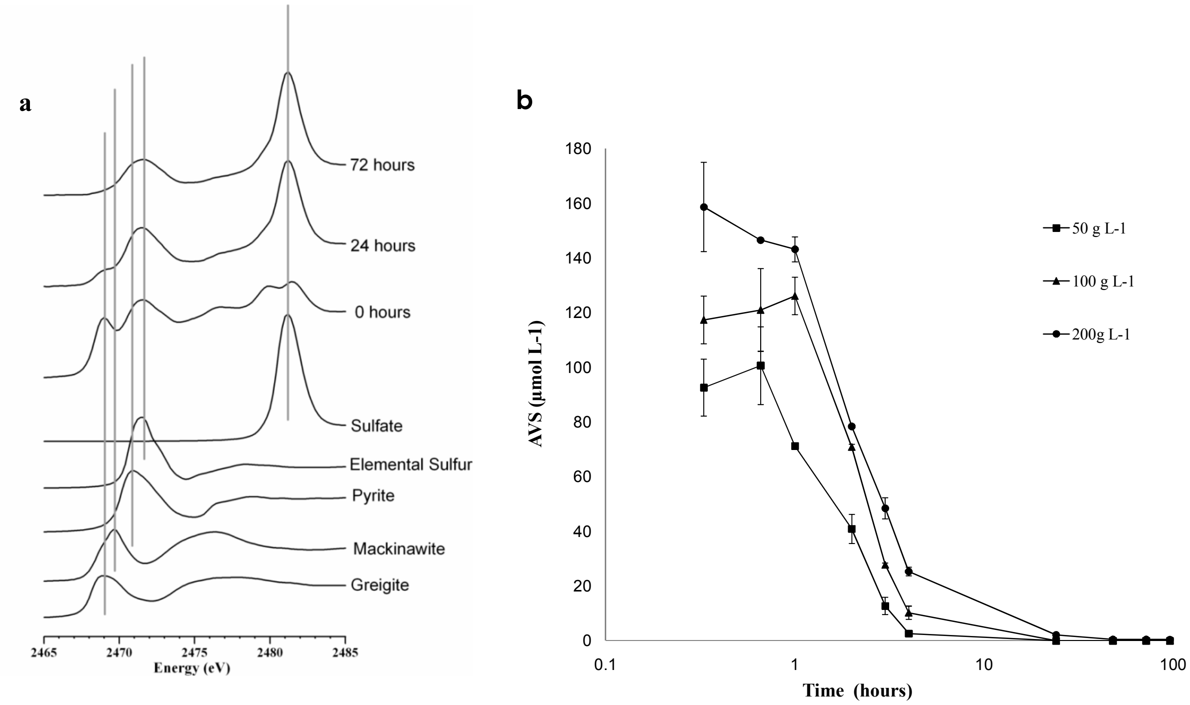

**Figure 2. a) Comparison between the X-ray energy of XANES peaks for reference phases and the XANES peaks in samples collected at three time intervals during the resuspension of 100 g/L of MBO from the Peel Harvey estuary system b) Acid volatile sulfide concentrations of laboratory MBO resuspension for all treatments. Starting (0 hr) concentrations of AVS are 4054 µmol/L for 50 g/L, 8108 µmol/L for 100 g/Land 16217 µmol/L for 200 g/L. These values are not graphed to maintain the clarity of the figure.**

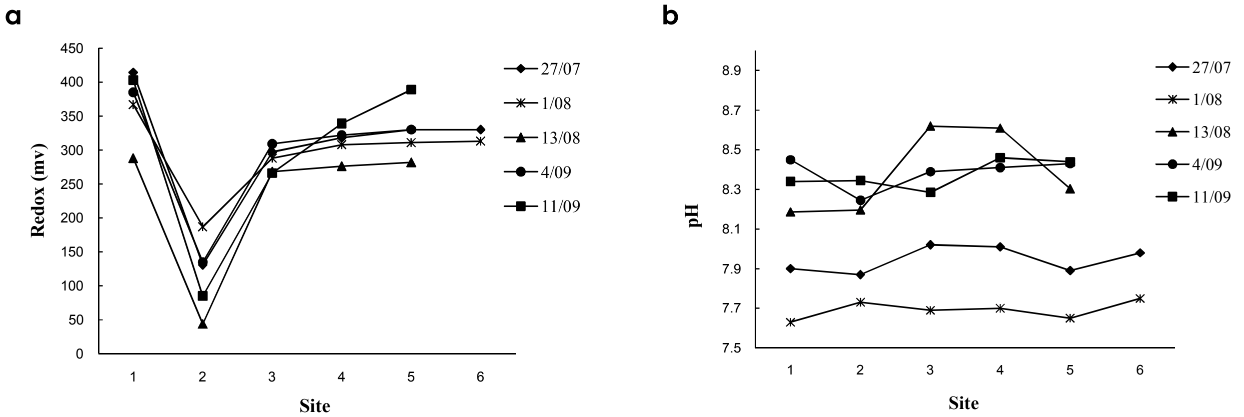

**Figure 3. a) The redox and b) the pH of surface water across a transect of a dredge plume; the sediment disposal point is at Site 2.**

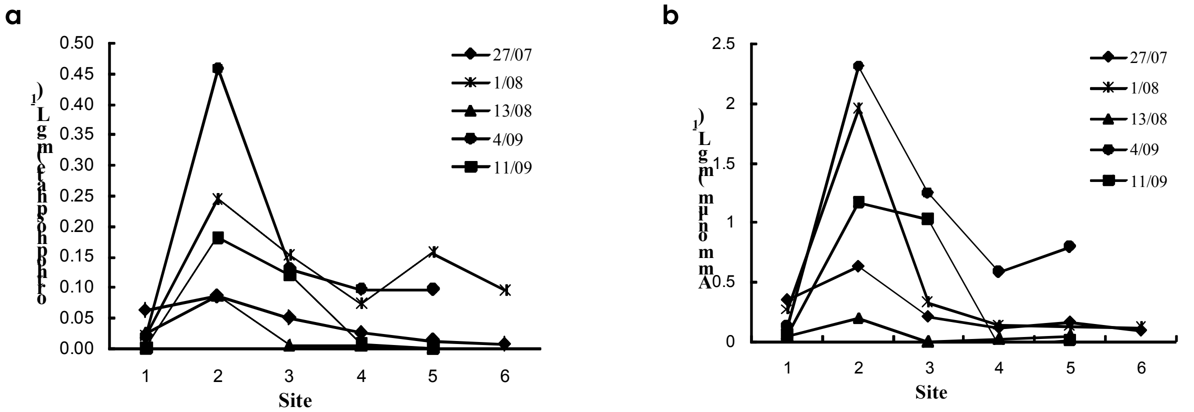

**Figure 4. Concentrations of a) orthophosphate and b) ammonium in surface water across a transect of a dredge plume; the sediment disposal point is at Site 2.**

## Conclusion

Laboratory experiments demonstrate the high reactivity of MBOs from the PHES following disturbance, but high variability and buffering in the field may limit the observation of these effects. Alongside the emphasis on acidification, deoxygenation and metal release during MBO resuspension, it is important to acknowledge the possibility of nutrient release from sediments in eutrophic estuaries.

## References

Brearly A (2005) ‘Ernest Hodgkin's Swanland: estuaries and coastal lagoons of Southwestern Australia’. (University of Western Australia Press: Perth, Western Australia).

Burton ED, Bush RT, Sullivan LA, Hocking RK, Mitchell DRG, Johnston SG, Fitzpatrick RW, Raven M, McClure S, Jang LY (2009) Iron-monosulfide oxidation in natural sediments: resolving microbially-mediated S transformations using XANES, electron microscopy and selective extractions. *Environmental Science & Technology* **43**, 3128-3134

Burton ED, Bush RT, Sullivan LA (2006) Acid-volatile sulfide oxidation in coastal flood plain drains: iron−sulfur cycling and effects on water quality, *Environmental Science & Technology* **40**, 1217-1222

Burton ED, Phillips IR, Hawker DW (2005) Reactive sulfide relationships with trace metal extractability in sediments from southern Moreton Bay Australia, *Baseline/Marine Pollution Bulletin* **50**, 583-608

Bush RT, Sullivan LA, Fyfe D, Johnston S (2004) Redistribution of monosulfidic black oozes by floodwaters in a coastal acid sulfate soil floodplain. *Australian Journal of Soil Research* **43**, 603 – 607

Macdonald BCT, Smith J, Keene AF, Tunks M, Kinsela A, White I (2004) Impacts of Runoff from Sulfuric Soils on Sediment Chemistry in an Estuarine Lake. *Science of the Total Environment* **329**, 115 - 130.

Magni P, Montani S (2006), Seasonal patterns of pore-water nutrients, benthic chlorophyll a and sedimentary AVS in a macrobenthos-rich tidal flat. *Hydrobiologia* **571**, 297-311.

Smith J (2004) Chemical Changes During the Oxidation of Iron Monosulfide-Rich Sediment *Australian Journal of Soil Research* **42**, 659 - 666.

Smith J, Melville MD (2004) Iron Monosulfide Formation and Oxidation in Drain-Bottom Sediments of an Acid Sulfate Soil Environment. *Applied Geochemistry* **19**, 1837 - 1853.

Sullivan LA, Bush RT, Burton ED (2006) ‘Acid sulfate soil development issues in the Peel Region’. (Department of Environment, Western Australia).

Sullivan LA, Bush RT, Fyfe D (2002) Acid sulfate soil drain ooze: distribution, behaviour and implications for acidification and deoxygenation of waterways. In ‘Acid Sulfate Soils in Australia and China’. (Eds C Lin, MD Melville, LA Sullivan) pp. 91-99. Science Press, Beijing

Zimmerman AR, Canuel EA (2000), A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. *Marine Chemistry* **69**, 117-137.

# Mobilisation of arsenic following sea-water inundation of acid sulfate soils

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## Abstract

Tidal seawater inundation of coastal acid sulfate soils can generate Fe- and $SO_4$-reducing conditions in previously oxic sediments. This creates potential for mobilisation of As during the redox transition. We investigate the hydrology, porewater geochemistry, solid-phase speciation and mineralogical partitioning of As across two tidal fringe toposequences and explore the consequences for As. Seawater inundation induced a tidally-controlled redox gradient. Maximum porewater As (~400 µg/L) occurred in the intertidal, redox transition zone between Fe-oxidizing and $SO_4$-reducing conditions. Mechanisms of As mobilisation include the reduction of solid-phase As(V) to As(III), reductive dissolution of As(V)-bearing secondary Fe(III) minerals and competitive anion desorption. There was attenuation of porewater As in the zone of contemporary pyrite reformation. Oscillating hydraulic gradients caused by tidal pumping promote upward advection of As and $Fe^{2+}$-enriched porewater in the intertidal zone, leading to accumulation of As(V)-enriched Fe(III) (hydr)oxides at the oxic sediment-water interface. This creates a natural reactive-Fe barrier, but does not completely retard the flux of porewater As to overtopping surface waters. The accumulated Fe minerals may be prone to future reductive dissolution. A conceptual model of As hydro-geochemical coupling is presented.

## Key Words

Acid sulfate soil, iron, arsenic, sea-level rise, tidal marsh, East Trinity.

## Introduction

Arsenic (As) in water supplies derived from coastal floodplain aquifers degrades the health of millions of people (Smedley and Kinniburgh 2002). It is increasingly recognized that redox transitions caused by inundation of oxic sediments can lead to mobilisation of As. As behaviour in this context is often intimately coupled with the geochemical cycling of Fe (hydr)oxides and sulfide minerals (Root *et al.* 2009). Coastal acid sulfate soils (CASS) often have elevated concentrations of As due to the tendency of As to accumulate in pyrite (Smedley and Kinniburgh 2002). Acid sulfate soils are also usually rich in secondary Fe(III) minerals such as goethite, ferrihydrite, jarosite and schwertmannite (Sullivan and Bush 2004). These Fe(III) minerals are important sorbents for As and can become enriched in As under oxic conditions in both acid sulfate soils and acid mine drainage (Smedley and Kinniburgh 2002).

Seawater inundation has been used as a technique to successfully ameliorate acidity within lowland CASS (Powell and Martens 2005). Seawater inundation initiates a large redox transition which leads to reductive dissolution of Fe(III) minerals and the reformation of sulfide-minerals, including pyrite (Johnston *et al.* 2009a, b). It also introduces tidal pumping to shallow groundwater, which can cause porewater exchange and solute redistribution within intertidal zone sediments. This study examines the potential for As mobilisation, attenuation and hydro-geochemical coupling with Fe and S across a seawater inundation-induced redox boundary in CASS.

## Methods

### *Study site*

The study site, East Trinity, is an ~800 ha Holocene sedimentary coastal plain dissected by several estuarine creeks (145°47’ E, 16°56’ S). A tide-excluding sea wall was constructed and the site was intensively drained in the 1970’s (Powell and Martens 2005). This caused the oxidation of iron-sulfides in former mangrove sediments and the widespread formation of severe acid sulfate soils across the site (Powell and Martens 2005). A remediation program began in 2001–02 that involved tidal inundation of acid sulfate soils up to an elevation of ~0.5 m AHD (AHD is Australian Height Datum, 0 m AHD approximates mean sea level). Tides regularly inundate most of the formerly acidified areas across the site. Two toposequence transects were established to bracket the fringe of the tide-imposed redox gradient (i.e. spanning the supratidal/intertidal zone; 0.6 to 0 m AHD; Figure 1). Both transects have similar stratigraphy, comprised of clay-textured former sulfuric horizons to about 0.7–1.0 m below ground level (bgl), underlain by un-oxidised, sulfidic estuarine muds.

*Hydrology*
Groundwater levels along each transect were measured at 30 minute intervals (±0.01 m) using submersible pressure transducers vented to the atmosphere (Odyssey, ODYPS05) housed in a series of four 50 mm diameter PVC piezometers.

*Solid-phase sampling*
Replicate soil cores were obtained by gouge-auger from selected sampling locations. Cores were immediately sectioned and sub-samples sealed in air-tight polyethylene bags, completely filled with soil and frozen after collection until analysis. Near-total As [$As_{Tot}$] was extracted by hot aqua-regia digestion (APHA 1998) and measured by ICP-MS (Perkin-Elmer ELAN-DRCe). Duplicate analysis performed on twelve percent of samples had a precision within 8%. Fe-rich surficial sediment (0–0.01 m) was also sampled from across the study area and frozen. Jarosite pedofeatures from former sulfuric horizons were removed with a scalpel from air-dried bulk soil. Pyrite was enriched by density separation with *s*-tetrabromoethane from a bulk sample (~0.5 kg) of unoxidised sulfidic sediment. Arsenic K-edge X-ray absorption near-edge structure (XANES) spectra were collected on beamline 20B at the Photon Factory, Tsukuba Japan. Duplicate spectra were collected from selected natural samples and reference standards in fluorescence mode using a 32 element array Ge solid-state detector. The spectral background was subtracted using a polynomial fit and the edge jump height normalized to unity.

*Porewater geochemistry*
Porewaters were sampled during April 2008 via equilibration dialysis using 1.5 m long peepers. This is described in detail by Johnston *et al*. (2009c). Porewater filtrate (0.45 µm) was preserved with $HNO_3$ and stored in the dark at 4 °C for subsequent analysis of total As by ICP-MS (Perkin-Elmer ELAN-DRCe), operated in DRC mode to optimize interference removal. Five percent of samples were analysed in duplicate and had a precision within 6%.

## Results and discussion

Tidal inundation frequency increased downslope and was accompanied by mostly sub-oxic Eh (<200 mV) in tidally inundated former sulfuric horizons. There was enrichment of As within key Fe mineral phases. Jarosite was enriched by a factor of ~4 (75 µg/g) compared to bulk soil (Table 1). The sulfidic sediment-derived dense mineral fraction (comprised mainly of pyrite and some marcasite), was enriched in As by more than an order of magnitude compared to bulk soil (Table 1). In addition, surface Fe-rich accumulations (0–0.01 m; 5 to 40% Fe w/w) also had elevated As contents (1–6x) (Table 1), with $As_{Tot}$ positively correlated ($r^2 = 0.34$, α 0.05) with poorly crystalline Fe (data not shown).

**Table 1. As in transect soils and key Fe fractions, mean (±standard deviation).**

| Location/soil fraction (*n*) | Near-Total extract (µg/g) |
|---|---|
| Transect 1 & 2 soils (*110*) | 18.3 ±6.5 |
| Jarosite (*4*) | 75.7 ±14.7 |
| Surface Fe(III)-rich accumulations (3*4*) | 36.1 ±26.3 |
| Pyrite (*2*) | 279.0 ±24.9 |

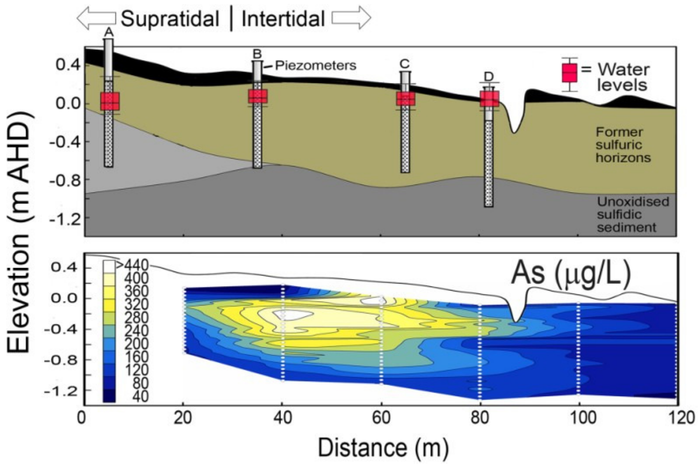

**Figure 1. Transect 1 stratigraphy, hydrology and porewater As concentrations.**

There was a distinct zone of As mobilisation in the porewaters at both transects, where concentrations exceeded 400 µg/L (Figure 1). The zone of maximum porewater As was spatially associated with former sulfuric horizons near the intertidal limit and most of this aqueous As (~80%) was As(III) (speciation data not shown). There were also very high concentrations of porewater $Fe^{2+}$ (~2000 mg/L) in this same zone, consistent with reductive dissolution of secondary Fe(III) minerals. There was a significant positive relationship between As and $Fe^{2+}$ in the zone of mobilisation ($r^2 = 0.71$, α 0.01, Figure 2). This is consistent with reductive dissolution of As-enriched Fe(III) minerals being a key process responsible for As mobilisation.

There was also a strong positive correlation between As and $HCO_3^-$ at the same locations ($r^2 = 0.63$, α0.01, Figure 2). Bicarbonate competes with As for adsorption sites and this may be an additional mechanism responsible for elevated porewater As. Anaerobic carbon metabolism via Fe reduction also generates $HCO_3^-$ and hence there is potential for coupling of both processes. Porewater As decreased towards the lower sections of both transects in the zone of contemporary pyrite reformation (~100 m). Dissolved As can be effectively sequestered by iron-sulfide minerals through surface complexation and co-precipitation and this is a likely mechanism of attenuation.

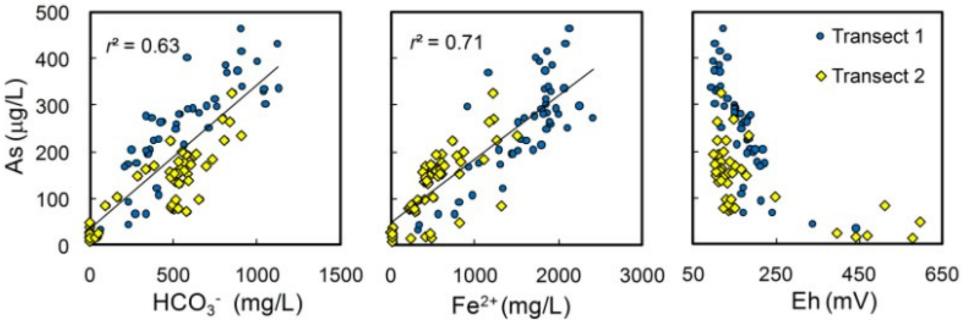

**Figure 2. Relationships between porewater As and $HCO_3^-$, $Fe^{2+}$, and redox potential (SHE) from Transect 1 and 2 at 60 m distance.**

The coupling of a redox transition triggering As mobilisation with physical forcing processes is an important feature of seawater inundation of CASS. Tidal forcing causes highly dynamic groundwater behaviour which generates oscillating horizontal hydraulic gradients (Figure 3). During the ebb-tide phase, the development of seaward hydraulic gradients promotes upward advection and seepage of As-and $Fe^{2+}$-rich porewater along the intertidal slope, followed by Fe oxidation and the precipitation of As(V)-enriched Fe(III) mineral phases.

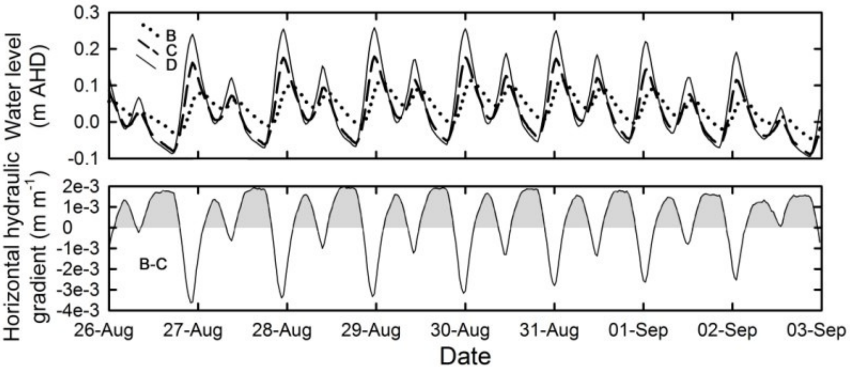

**Figure 3. Transect 1 time-series groundwater levels and corresponding horizontal hydraulic gradients between piezometers B-C. Periods of effluent (seaward) horizontal hydraulic gradients are shaded grey.**

Arsenic K-edge XANES analysis revealed distinct down-profile and downslope trends in solid-phase As speciation, consistent with the seawater-induced redox gradient (data not shown). The XANES spectra indicate that an FeAsS-like phase was an important reservoir for As in the original, un-drained parent material. Solid-phase As in both jarosite and surficial Fe(III)-rich material was mainly As(V). In former sulfuric horizons at 20 m and 60 m (Transect 1) the XANES data revealed a mixture of As(V) and As(III). In contrast, the XANES spectra for samples from the surface and in the former sulfuric horizon at 100 m, display edge positions consistent with As(III) or As sulfides. XANES data demonstrate that seawater inundation of CASS is leading to reduction of solid-phase As(V) to As(III), and the subsequent reformation of As sulfides within former sulfuric horizons.

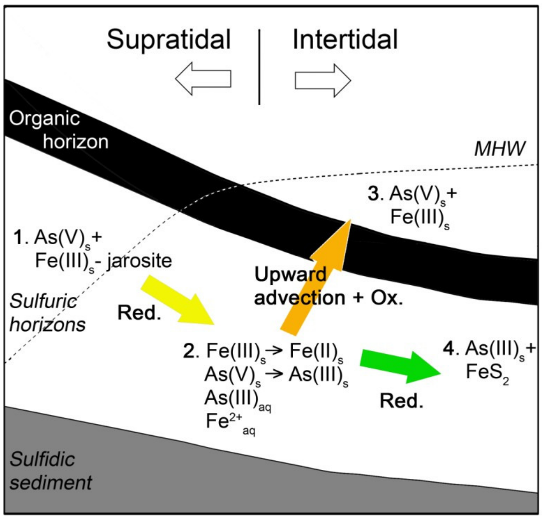

**Figure 4. Conceptual model of As hydro-geochemistry across a tidal, seawater inundated CASS toposequence. MHW is mean high water.**

## Conclusion

Seawater inundation of a CASS toposequence has caused a major shift in the solid and aqueous-phase speciation, distribution and partitioning of As. While there is evidence of considerable As mobilisation, it appears to be spatially localized between two distinct geochemical regimes. As behaviour is intimately bound with the fate of Fe and S. Results are synthesised in a conceptual model which represents As hydro-geochemistry across the seawater inundation fringe (Figure 4). The oxidation of As-rich pyrite in the drained sulfidic parent material led to (1) the formation of acid sulfate conditions with preferential enrichment of As(V) in secondary Fe(III) minerals (e.g. jarosite). Seawater inundation (2) initiates reducing conditions stimulating As mobilisation by several processes including a) reductive dissolution of As-bearing secondary Fe(III) minerals, b) reduction of As(V) to As(III), and c) competitive anion desorption by $HCO_3^-$. Tidal pumping facilitates upward advection (3) of $Fe^{2+}$ and As(III)-rich porewaters in the intertidal zone, where subsequent oxidation in surficial sediments results in the accumulation of tertiary Fe(III)-minerals enriched in As(V). Further downslope (4) there is attenuation of porewater As in the zone of contemporary pyrite re-formation, where solid phase As occurs predominantly in the form of As(III).

## References

APHA (1998) ‘Standard methods for the examination of water and wastewater’. 20th Ed. (American Public Health Association – American Water Works Association. Baltimore, USA)

Johnston SG, Bush RT, Sullivan LA, Burton ED, Smith D, Martens MA, McElnea AE, Ahern CR, Powell B, Stephens LP, Wilbraham ST, van Heel S. (2009a) Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coast. and Shelf Science* **81**, 257–266.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith CD, Martens MA, McElnea AE, Wilbraham ST (2009b) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335–346.

Johnston SG, Burton ED, Bush RT, Keene AF, Sullivan LA, Isaacson L (2009) Pore water sampling in acid sulfate soils: a new peeper method. *Journal of Environmental Quality* **38**, 2474–2477.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in the Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* **51**, 149–164.

Root RA, Vlassopoulos D, Rivera NA, Rafferty MT, Andrews C, O’Day PA (2009) Speciation and natural attenuation of arsenic and iron in a tidally influenced shallow aquifer. *Geochimica Cosmochimica et Acta* **73**, 5528–5553.

Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **17**, 517–568.

Sullivan LA, Bush RT (2004) Iron-precipitate accumulations associated with waterways in drained coastal acid sulfate soil landscapes of eastern Australia. *Marine and Freshwater Research* **55**, 727–736.

# Mobility and storage of metals, metalloids and trace elements in disturbed acid sulfate soils from a tidal estuary in South Australia

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## Abstract

In Australia, acid sulfate soils (ASS) are widespread in both coastal and inland settings where they pose environmental hazards from acidification and metal mobilisation. In this study, three saturated soil-sediment profiles from distinct positions in a disturbed tidal ASS landscape were hydrogeochemically characterised. The soil profile geochemical data and surface water chemistry were compared in order to find evidence of metal, metalloid and trace element mobilisation. The results showed that concentrations of Cu, Ni, Pb, Zn, S, Al, Mg and Fe were elevated in the near-surface, oxidised layers of sulfuric materials of the ASS profile and were marginally elevated within nearby hyposulfidic material in circum-neutral stream sediments. Metals and metalloids, including Ni, Zn, Al and Fe, were leached to pore waters in sulfuric materials from which a range of salt efflorescences had precipitated. Acidic drain waters also contained elevated Al, Fe and other major cations and anions, but did not contain detectible concentrations of trace elements. Nearby circum-neutral stream waters only contained elevated concentrations of Fe. Leaching of trace metals was greatest at the surface of exposed sulfuric materials where salt efflorescences had formed. Covering sulfuric materials with mulch, soil or water could reduce metal mobilization by limiting salt precipitation at the surface.

## Key Words

Sulfidic, sulfuric, monosulfide, pore water, metals, salt efflorescence.

## Introduction

This study focussed on soil geochemical and hydrogeochemical data to find evidence of sources and pathways of metals, metalloids and trace elements in a coastal acid sulfate soil landscape located at Gillman, South Australia (Figure 1). Tidal influences were cut off from the Gillman area in 1954 when a bund wall was constructed to reclaim the area for agricultural and industrial purposes, causing sulfidic sediments to oxidise. Three soil-sediment profiles located at different positions along a toposequence were studied (Figure 2). The traverse covered former supra-tidal soils containing sulfuric materials and former tidal soils in which monosulfidic materials had developed. Vertical profiles of trace elements, focussing on toxic elements, were compared for soils, pore waters and load limits in surface waters of nearby streams and drains.

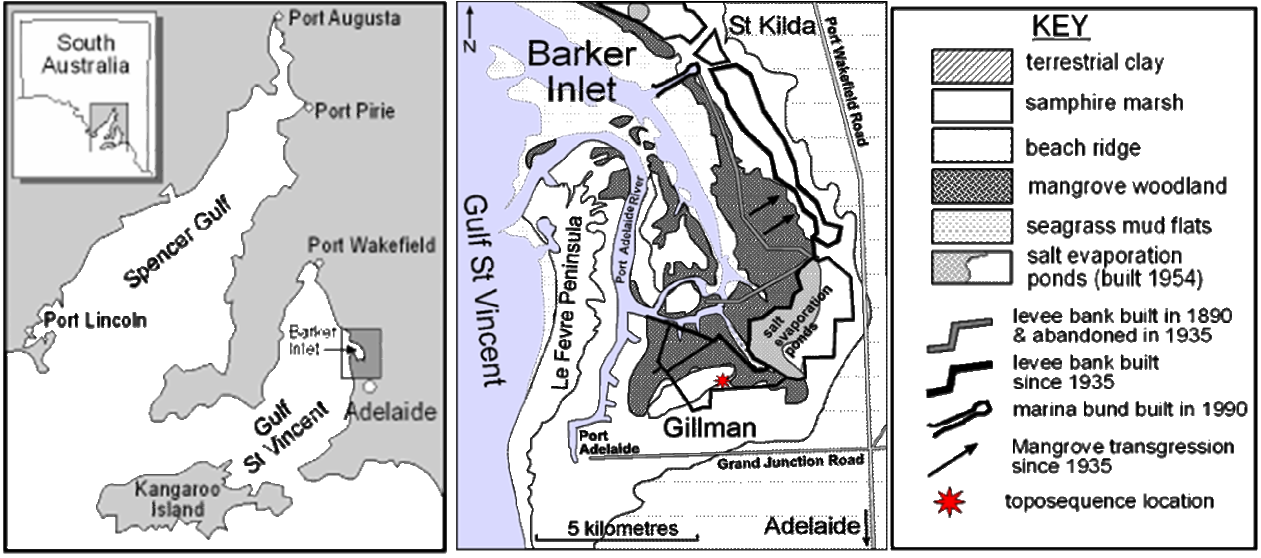

**Figure 1. Barker Inlet, originally a tidal estuary, is located 20 km north of Adelaide, South Australia. This figure depicts the pre-European environment, overlain by a network of tidal barriers that were since installed. Toposequence 'A' (Figure 2) is located at Gillman where inter-tidal mangrove woodlands and supra-tidal samphire salt marsh were reclaimed for agriculture and industry in the 1950s. The land was soon abandoned due to severe acidification, salinity and storm-water ponding (from Fitzpatrick *et al.* 2008, Thomas 2010).**

## Methods

Soil chemistry was determined from selected layers in soil-sediment profiles BG 15 and BG P 5 (Figure 2). Total major and trace element analyses were determined on the < 2mm fraction of 11 bulk soil samples using X-ray fluorescence spectroscopy (XRF). Soil pore waters were collected using peepers; multi (35) chambered dialysis samplers, which have semi-permeable membranes that separate receiver solution from sediment and soil solution (e.g. van Oploo *et al.* 2008). Peepers were installed in saturated soil-sediments in February 2003 and left to equilibrate for 8 weeks. Water samples were analysed for major anions and cations and selected trace elements by ICP-OES. Mineralogy was determined by powder x-ray diffraction (XRD).

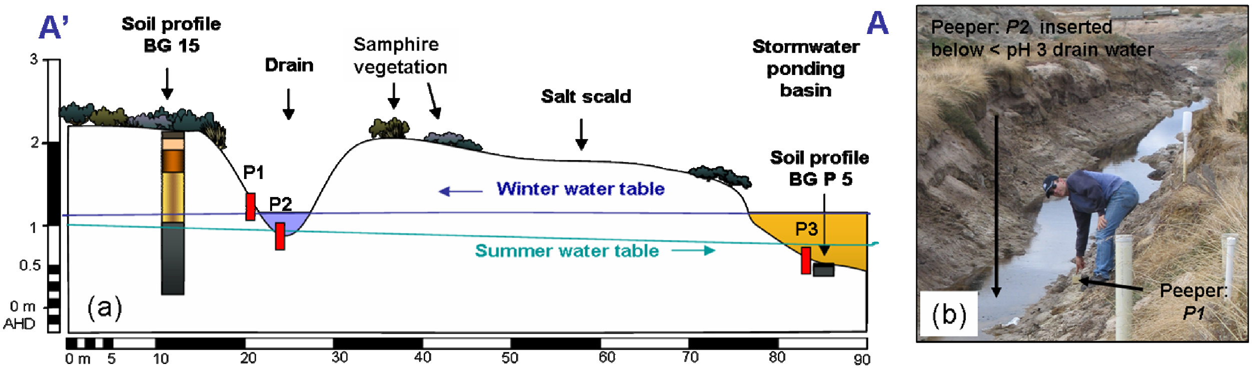

**Figure 2. Schematic cross-section showing localities of soil-sediment profiles and peepers (P1, P2 and P3) along toposequence A'-A. The drain was excavated in August 2002 and was not open to the stormwater ponding basin.**

## Results

### *Soils*

Metal concentrations (Cu, Ni, Pb and Zn) were elevated at the surface of soil-sediment profile BG 15 and marginally elevated at the surface of profile BG P 5 (Table 1). The source of metals was likely anthropogenic (e.g. Fitzpatrick *et al.* 2008, Thomas 2010). The soil pH (1:5) of profile BG 15 decreased with depth to a minimum pH of 2.3 at 110 cm, just above the summer water table. Below this depth soil pH gradually increased to pH 4.2 at the base of the profile. Soil EC was highest just above the water table, between 65 and 110 cm depth, at the level where salt efflorescences had accumulated on the drain wall (Figure 3). The soil pH and EC of subaqueous profile BG P 5 were relatively consistent with increasing depth (Table 1). Profile BG 15 comprised sulfuric materials and hypersulfidic materials (Fitzpatrick *et al.* 2008; Sullivan *et al.* 2009; Thomas, 2010). Sulfuric materials occurring between 30 cm and 120 cm depth contained significant acidity, in the form of titratable actual acidity (TAA) and retained acidity. Potential sulfidic acidity was highest between 95 cm and 120 cm, with chromium reducible sulfur ($S_{CR}$) concentrations up to 6.88 %, adding to a positive net acidity of 5000 mol $H^+$/t (Figure 3).

Subaqueous profile BG P 5 did not contain sulfuric materials. However, it did contain hyposulfidic materials (Sullivan *et al.* 2009): it did not experience a drop in pH by at least 0.5 unit to 4 or less after incubation, and monosulfidic materials. Occurrence of sulfidic materials was greatest between 0 cm and 5 cm with an acid volatile sulfur content of 1.15 % (AVS) and a reduced inorganic sulfur content of 0.95 % $S_{CR}$. The acid neutralising capacity (ANC) of most soil layers was not sufficient to neutralise the potential acidity, resulting in a positive net acidity (Figure 4).

**Table 1. Selected soil chemical properties for soil-sediment samples from profiles BG 15 and BG P 5.**

| Profile | Layer | Depth (cm) | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | $SO_3$ | MgO | CaO | $K_2O$ | $P_2O_5$ | Sr | Cd | Cr | Cu | Ni | Pb | Zn | pH | EC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | from | to | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (1:5) | dS/m |
| BG 15 | OA | 0 | 5 | 55.63 | 14.93 | 8.79 | 0.05 | 0.14 | 2.82 | 0.52 | 2.95 | 0.31 | 77 | 1.5 | 96 | 25 | 18 | 112 | 131 | 8.03 | 0.75 |
| | A | 5 | 15 | 58.71 | 16.73 | 7.35 | 0.04 | 0.12 | 2.33 | 0.39 | 2.91 | 0.18 | 69 | 1.5 | 103 | 13 | 15 | 27 | 51 | 7.57 | 1.05 |
| | 2Ey1 | 25 | 30 | 76.43 | 9.54 | 4.00 | 0.01 | 0.37 | 0.92 | 0.27 | 1.82 | 0.06 | 45 | 1.5 | 63 | 7 | 3 | 11 | 26 | 4.42 | 3.04 |
| | 2Ey2 | 30 | 40 | 72.55 | 11.02 | 4.94 | 0.01 | 0.47 | 1.09 | 0.25 | 2.11 | 0.06 | 51 | 1.5 | 72 | 9 | 4 | 13 | 30 | 3.98 | 5.20 |
| | 3Bg | 40 | 65 | 63.05 | 14.83 | 4.30 | 0.01 | 0.59 | 1.53 | 0.24 | 2.69 | 0.09 | 58 | 1.5 | 82 | 13 | 6 | 8 | 34 | 3.37 | 8.83 |
| | 4Bgj | 65 | 95 | 37.80 | 9.60 | 10.70 | 0.01 | 1.90 | 1.28 | 0.33 | 3.16 | 0.09 | 67 | 1.5 | 58 | 11 | 2 | 18 | 25 | 3.15 | 23.90 |
| | 5Bigj | 95 | 110 | 26.24 | 3.14 | 12.29 | 0.00 | 2.63 | 1.25 | 1.02 | 1.61 | 0.04 | 61 | 1.5 | 21 | 7 | 5 | 3 | 11 | 2.26 | 45.15 |
| | 6Bg2 | 120 | 150 | 89.58 | 3.66 | 0.76 | 0.00 | 0.76 | 0.29 | 0.13 | 1.02 | 0.01 | 30 | 1.5 | 46 | 5 | 1 | 1 | 6 | 4.12 | 3.89 |
| | 7Bg1 | 150 | 170 | 74.66 | 10.17 | 3.81 | 0.01 | 2.61 | 1.15 | 0.18 | 1.78 | 0.03 | 42 | 1.5 | 116 | 19 | 9 | 9 | 30 | 4.24 | 4.87 |
| BG P5 | Oge1 | 0 | 5 | 73.53 | 7.72 | 5.73 | 0.01 | 0.76 | 1.08 | 0.47 | 1.67 | 0.08 | 79 | 1.5 | 64 | 17 | 3 | 26 | 92 | 7.01 | 5.06 |
| | Oge2 | 15 | 20 | 77.68 | 8.29 | 2.82 | 0.01 | 0.74 | 0.99 | 0.22 | 1.76 | 0.07 | 77 | 1.5 | 62 | 14 | 5 | 22 | 48 | 7.49 | 4.46 |
| | | LLD (ppm) | | 29 | 24 | 10 | 5 | 8 | 36 | 20 | 16 | 5 | 1 | 3 | 2 | 1 | 2 | 2 | 2 | | |

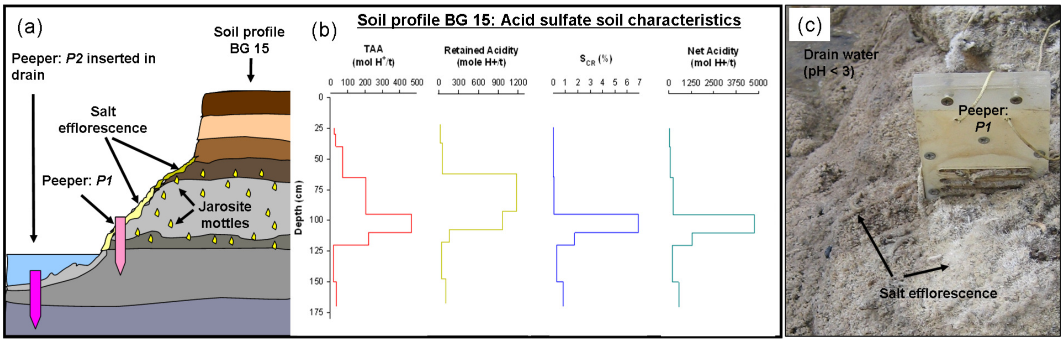

**Figure 3. (a) – schematic cross section of the drain showing position of peeper P1 within the drain wall and peeper P2 in the bottom of the drain. (b) – down profile (to scaled with (a)) ASS characteristics (TAA, retained acidity, $S_{CR}$% and net acidity) for profile BG 15. (c) – salt efflorescences on the surface around peeper P1.**

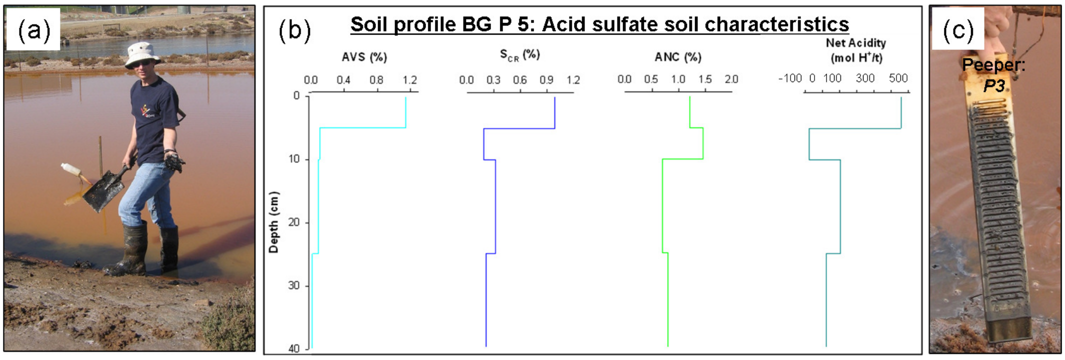

**Figure 4. (a) – photo showing iron floc in surface water of the storm water ponding basin and disturbed monosulfidic material that formed at the sediment surface. (b) – acid sulfate soil characteristics (AVS, $S_{CR}$%, ANC and net acidity) of profile BG P 5. (c) – peeper P3 removed from the pond (profile BG P 5).**

*Pore waters and surface waters*

Soil pore water chemistry collected by peeper P1, located in the oxic-acidic drain wall at profile BG 15 showed considerable variation in pH and EC as well as anions, cations and trace element concentrations from the surface to a depth of 35 cm (Figure 5). Most anion, cation and trace element concentrations were highest near the surface and decreased with depth, with Ca and Sr showing the opposite trend. Metals (Zn, Ni, Fe, and Al) were particularly elevated near the surface, where salt efflorescence occurred.

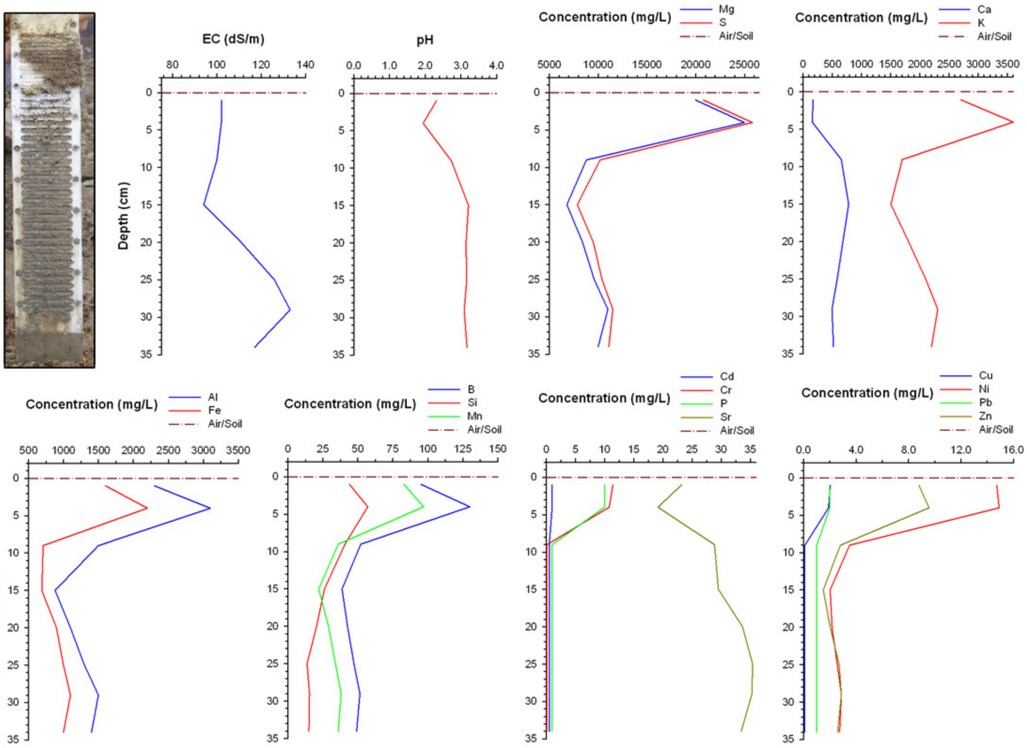

**Figure 5. Down profile pore water chemistry collected by peeper P1, located within the drain wall.**

Soil pore water chemistry collected by peeper P2, located in the oxic-acidic drain sediment, showed a trend for pH and EC similar to peeper P1, however the concentration of most trace elements fell below detection limits (Table 2). Calcium increased with depth below the water/sediment interface in P2. Drain surface water concentrations were generally higher than in P2 pore waters (Table 2). Soil pore water chemistry collected by peeper P3, located in the reducing-circum-neutral bottom sediment of the stormwater pond showed an increasing trend for pH and EC and major cations and anions with depth. Concentrations were considerably lower than in the oxic-acidic environments, with most trace elements being below detection limits (Table 2). Surface water concentrations were generally higher than in P3 pore waters, particularly Fe (Table 2).

**Table 2. Maximum, minimum and mean values for selected pore water and surface water chemistry.**

| **Peeper sample data** | | **Si** | **Al** | **Fe** | **Mn** | **S** | **Mg** | **Ca** | **K** | **P** | **B** | **Cd** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** | **pH** | **EC** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Porewater** | | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | | dS/m |
| ***P1*** | max | 57.1 | 3100 | 2200 | 97.0 | 25800 | 25000 | 780 | 3600 | 10 | 130.0 | 1.0 | 11.4 | 2.0 | 14.9 | 2.0 | 9.6 | 3.21 | 133.0 |
| (n=9) | min | 13.7 | 880 | 690 | 22.0 | 7870 | 6800 | 150 | 1500 | 1 | 38.7 | 0.5 | 0.1 | 0.1 | 2.0 | 1.0 | 1.5 | 1.94 | 94.0 |
| | mean | 27.5 | 1609 | 1133 | 45.7 | 13141 | 12178 | 504 | 2233 | 3 | 61.7 | 0.6 | 0.1 | 0.5 | 5.4 | 1.2 | 3.9 | 2.88 | 111.3 |
| ***P2*** | max | 36.8 | 900 | 840 | 29 | 8800 | 8200 | 1100 | 1800 | 1 | 37 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 3.88 | 112.6 |
| (n=31) | min | 0.1 | 28 | 330 | 2.5 | 3800 | 4100 | 550 | 1200 | 1 | 14 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 2.01 | 79.7 |
| | mean | 21.8 | 648 | 707 | 21 | 7325 | 6950 | 679 | 1606 | 1 | 30 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 2.55 | 94.1 |
| ***P3*** | max | 0.1 | 1 | 47 | 0.1 | 1200 | 1400 | 410 | 340 | 1 | 1.0 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 8.19 | 55.2 |
| (n=33) | min | 0.1 | 1 | 1 | 0.1 | 690 | 940 | 260 | 230 | 1 | 1.0 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 6.62 | 39.1 |
| | mean | 0.1 | 1 | 7 | 0.1 | 879 | 1085 | 328 | 276 | 1 | 1.0 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 7.36 | 44.9 |
| **Surface water** | | | | | | | | | | | | | | | | | | | |
| ***P2*** (n=4) | mean | 44.3 | 995 | 870 | 30.9 | 9350 | 8700 | 540 | 1900 | 1 | 40.5 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 1.95 | 95.7 |
| ***P3*** (n=2) | mean | 9.4 | 10 | 260 | 2.5 | 735 | 915 | 300 | 233 | 1 | 1.0 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 6.50 | 53.1 |
| | LLD | 0.2 | 2 | 2 | 0.2 | 10 | 10 | 10 | 10 | 2 | 2 | 0.2 | 0.2 | 0.2 | 0.4 | 0.2 | 0.2 | 0.01 | 0.1 |

### *Salt efflorescences and iron oxyhydroxide minerals*

Salt crusts formed on the exposed pit face by the wicking and evaporation of soil solution containing $Na^+$, $Cl^-$ and $SO_4^{2-}$. White "fluffy" salt crust consisting of halite, gypsum and pentahydrite ($MgSO_4.5H_2O$) occurred where soil pH, clay and carbonate content was higher, in the upper 30 cm of drain wall. Some goethite (FeOOH), occurred between 5 and 30 cm as yellowish orange mottles. Lower in the profile (between 30-75cm) a thicker (5-10 mm thick) creamy white to yellow crust formed on acidic quartz sands and was dominated by halite, gypsum and starkeyite ($MgSO_4.4H_2O$). Thick agglomerations (5-30 mm thick) of yellowish green salts comprising tamarugite [$NaAl(SO_4)_2.6H_2O$], sideronatrite [$Na_2Fe(SO_4)_2(OH).3H_2O$], jarosite and pentahydrite ($MgSO_4.5H_2O$) formed where TAA, retained acidity and potential sulfidic acidity was greatest (Figure 3). These largely soluble salts dissolve during rain events and contribute to acidity and metal content in drainage waters. The salt minerals are indicators of subsurface biogeochemical soil-water processes (e.g. pH, Eh, EC and parent mineralogy) operating in this landscape (e.g. Fitzpatrick *et al.* 1997).

## Conclusion

Sulfuric acid that has been produced in profile BG 15 should remain in the soil profile due to the low hydraulic gradient of the area, unless this is altered by drains or pumping. Open drains allow soluble sulfate-containing minerals that are a store of Na, Ca, Mg, Cl, Sr and $SO_4$ and metals (e.g., Al, Fe, Zn, Ni) to precipitate in oxic-acidic conditions and may present an environmental hazard to connected water bodies following rainfall. The salts (containing Fe and S) may also contribute to the formation of the monosulfidic materials in water bodies lower in the landscape where soil conditions are reducing and circumneutral.

## References

Fitzpatrick RW, Self PG (1997) Iron oxyhydroxides, sulfides and oxyhydroxysulfates as indicators of acid sulphate surface weathering environment. In 'Soils and Environment: Soil Processes from Mineral to Landscape Scale. Advances in GeoEcology 30'. (Eds K Auerswald, H Stanjek , JM Bigham) pp. 227-240. (Catena Verlag: Reiskirchen, Germany).

Fitzpatrick RW, Thomas BP, Merry RH (2008) Acid Sulfate Soils in Gulf St Vincent. In 'Natural History of Gulf St Vincent'. (Eds SA Shepherd, S Bryars, IR Kirkegaard, P Harbison, JT Jennings) pp. 106-120. (Royal Society of South Australia Inc., Adelaide, South Australia).

Sullivan LA, Fitzpatrick RW, Bush RT, Burton ED, Shand P, Ward NJ (2009) Modifications to the classification of acid sulfate soil materials. Southern Cross GeoScience Tech Report 309.

Thomas BP (2010) Coastal acid sulfate soil-landscape relationships in temperate climates: Linking soil processes to hazard management in the Barker Inlet, Gillman area, South Australia. PhD Thesis, Adelaide University, Earth and Environmental Science Dept.

van Oploo P, White I, Ford P, Melville MD, Macdonald BCT (2008) The use of peepers to sample pore-water in acid sulfate soils. *Eur. J. Soil Sci.* **59,** 762-770.

# Monolithic lysimeters as tools to study the composition of pore and drainage waters responding to high water table in boreal acid sulphate soil

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## Abstract

Impacts of high water table on the quality of pore and discharge waters in an acid sulphate soil (*Sulfic Cryaquepts*) were studied using ten PVC lysimeters (200 dm$^3$, diameter 50 cm, height 100 cm). Each lysimeter contained a monolith of undisturbed soil horizons B, BC and C equipped with the system for water supply and for continuous measurements of soil moisture, temperature, bulk electrical conductivity and redox potential. Elemental composition and other quality parameters of pore and discharge waters were analysed. The water balance of lysimeters was calculated from the water supply, ground water level and measured discharge. The experimental treatments were: cropped high (HWC) and low (LWC) water table treatments, and uncropped high water table treatment (HWB). Water table elevation induced reducing conditions in the soil both in summer (HWC) and in winter (HWC, LWC) despite low temperatures (< +10 ºC). Reducing conditions gave rise to high iron concentrations in pore and discharge waters as opposed to the lowered concentrations of aluminium. The cumulative iron loads from HWC (17.8 kg/ha) exceeded those from LWC (1 kg/ha). The Al loads from LWC (3.6 kg/ha) exceeded those from HWC (2.2 kg/ha), even if less water discharged from LWC than from HWC.

## Key Words

Acid sulphate soil, redox potential, pore water quality, discharge water quality, lysimeter

## Introduction

The acidity and high metal concentrations of discharge waters from cultivated acid sulphate soils have deteriorated the water quality in recipient waters in Finland (Åström 2005; Roos 2006). For this reason, a research project was established to investigate the impact of high water table on the quality of pore and drainage waters, and on the growth of reed canary grass, a perennial bioenergy crop. Lysimeters have been used for a long time in studies on water flow and leaching of elements in agricultural soils (Goss 2009). They are also the most practical tool to study the impacts of controlled ground water level on acid sulphate soils at near field scale. Acid sulphate soils have distinct soil horizons from the well-structured A horizon down to the massive C horizon, soil redox status varying from oxidized to reduced, respectively. In order to get undisturbed horizons into the lysimeter a simple method to take monoliths from acid sulphate soil was developed. We report here the methods for monitoring soil redox status in different soil horizons, the initial response of redox potential and the pore and discharge waters quality to the water table elevation in boreal conditions at the beginning of the experiment.

## Material and methods

Ten monolithic lysimeters were taken from a poldered cultivated acid sulphate soil of the University of Helsinki at Viikki in southern Finland (60° 13.4' N, 25° 0' E) in summer 2008. The soil presented in Table 1 is classified as *Sulfic Cryaquepts* according to Soil Taxonomy (Yli-Halla 2008, Mokma *et al.* 2000). In the field, the B horizon is actual acid sulphate soil. The transition horizon (BC) is located at the depth of the subsurface drainage pipes at about 1 m below soil surface and the reduced C horizon (potential acid sulphate soil) is constantly water-logged. The results presented here are from the beginning of the experiment to the end of year 2008. The study will be continued to the end of year 2010 so that it will comprise a total of two hydrological years and two harvested yields.

**Table 1. Selected physical and chemical properties of the soil sampled into the lysimeters.**

| Horizon | Depth in a lysimeter (cm) | pH | Clay (%) | Total S (g/kg) | Oxalate extractable Al (g/kg) | Oxalate extractable Fe (g/kg) | Carbon (%) | Redox potential in the field $E_h$ (mV) |
|---|---|---|---|---|---|---|---|---|
| Ap | 0 - 20 | 6.4 | 33 | 0.4 | 1.6 | 4.7 | 3.8 | 500 |
| Bgjc | 20 - 50 | 3.8 | 61 | 4.2 | 4.1 | 13.2 | 1.9 | 500 |
| BCgc | 50 - 80 | 4.2 | 57 | 4.6 | 2.5 | 11.7 | 2.5 | 300 |
| C | 80 - 100 | 6.5 | 59 | 14.9 | 1.7 | 2.2 | 2.8 | 75 |

The lysimeter body was a PVC tube 50 cm in diameter, 100 cm in length and with 4.5 mm wall thickness. The technique for sampling the lysimeters by a special cutting tool and an excavator was developed in the pre-experiment in 2007. Soil monoliths were dug up from the depths between 70 cm to 150 cm, so that they finally comprised of a 60-cm of structured actual acid sulphate soils layer and 20-cm of massive potential acid sulphate soils layer (sulphidic materials). After sampling, the bottom of lysimeters was sealed with a PVC cap. The monoliths transported into a greenhouse compartment with wire-net walls and glass roof, where controlled treatments could be carried out. The turfs (20-cm thick) of one-year old reed canary grass grown on a non-acid soil were planted on the top of cropped monoliths, whereas the uncropped lysimeters were filled with 20 cm layer of non-acid topsoil material. In order to facilitate high water level treatment, the lysimeters were made waterproof up to 1 m hydraulic pressure. All access holes were made watertight. The drainage tubes were installed at the depth of 70 cm in all lysimeters. The overflow height was defined according to the water table treatment. The ground water table in each lysimeter was controlled by an external water supply tube, and monitored through two observation pipes connected to the depths of 70 and 90 cm.

The experiment consisted of eight cropped and two uncropped lysimeters. The water table treatments were high (HW) or low (LW) water table. The treatments started on 22.7.2008 when the water table was raised in the high water table treatments (HWC and HWB) to a level 20 cm below the soil surface, whereas in the LWC treatment it was allowed to drain freely to the depth of 65 cm. In order to prevent shrinkage of soil in LWC and the possibility of consequent preferential sidewall flow of water during the later experiment, the water table of LWC was raised to 30 cm from the soil surface at the beginning of January 2009 for four months. Because the lysimeters were not buried into the ground, they were exposed to the boreal climate as a whole. To mimic soil temperatures in the field, the lysimeters were equipped with insulation and heater against frost in winter and with sunshades in summer, so only the top of lysimeters were subjected to open air temperatures.

The water supply tubes were filled daily to the levels corresponding to the desired water table depths. In addition, the lysimeters were watered from above at three-day intervals with amounts corresponding to the mean monthly long-term precipitation at a local weather station. The daily water consumption of a lysimeter was measured from the water level in the water supply tube. The water balance of a lysimeter was determined from the irrigation (P), the discharge (Q) and the water consumption and water table change in a lysimeter (ΔS). The evapotranspiration was calculated from equation 1.

$$E = P - Q - \Delta S \qquad (1)$$

An automatic data acquisition system for soil redox potential consisted of a common Ag/AgCl reference electrode (Inlab 301), a saturated KCl salt bridge (Linebarger 1975) and a Agilent 34980A datalogger (input impedance 10 GΩ) scanning the Pt electrodes at 10-minute intervals. Soil redox potential was measured continuously at a known buffer solution (220 mV, Schott) and at five soil depths: 10 cm (A), 30 cm (B), 50 (B) and 70 cm (BC) and 90 cm (C). Air temperature was measured by the datalogger with thermocouples in open air, under the heat insulation or solar shades, and among plant canopy. The measured redox potentials ($E_m$) were converted to temperature-corrected $E_h$ values (SHE) using equation (2).

$$E_h = E_m + 199 - 55 + 0.7\,\{(273 + t) - 298\}\ (\text{mV}) \qquad (2)$$

Soil moisture content, temperature and bulk electrical conductivity were measured continuously at 10-min intervals with 5TE probes and data loggers (Degacon Em50) in three soil horizons (A, B, BC). Soil pH was measured manually with an ISFET electrode through access holes. Soil water was sampled by pore water extractor (Rhizon, MOM) to plastic vacuum tubes. Total and filtered (0.45 µm) discharge water were sampled to plastic bottles cleaned with acid. Part of pore and discharge water samples were used for pH and EC measurements. The elemental composition of water samples was analysed by ICP-OES (Thermo Scientific, ICAP 6000). The cumulative discharge was calculated by summing all discharges from a lysimeter, and the cumulative loads by summing the weekly products of measured elemental concentration and discharge.

## Results

Temperature varied from + 25 to – 5 ºC during the study period. At the beginning of experiment, soil temperatures followed the air temperatures at all depths because the insulation and solar shade was not installed. In winter, insulation and heater kept soil temperatures between +3 and + 7 ºC (Figure 1).

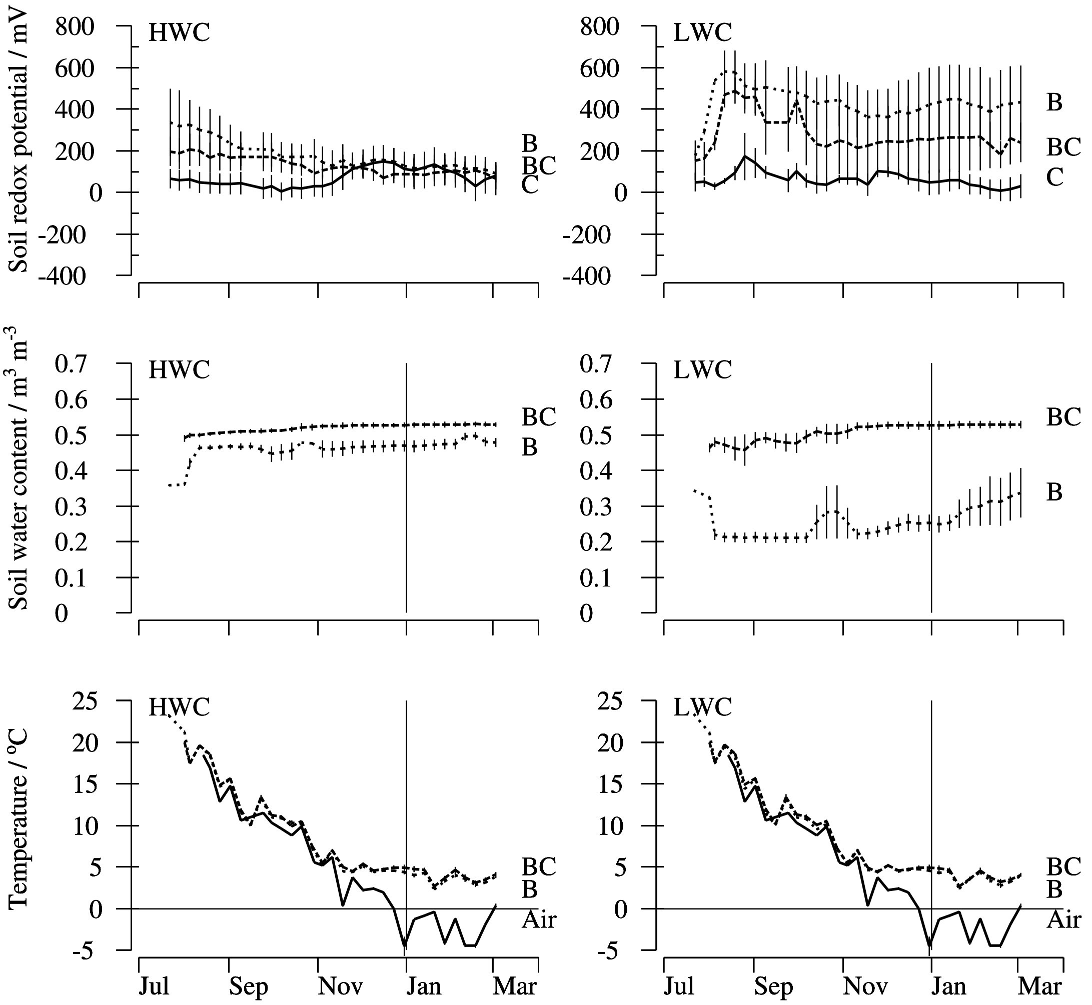
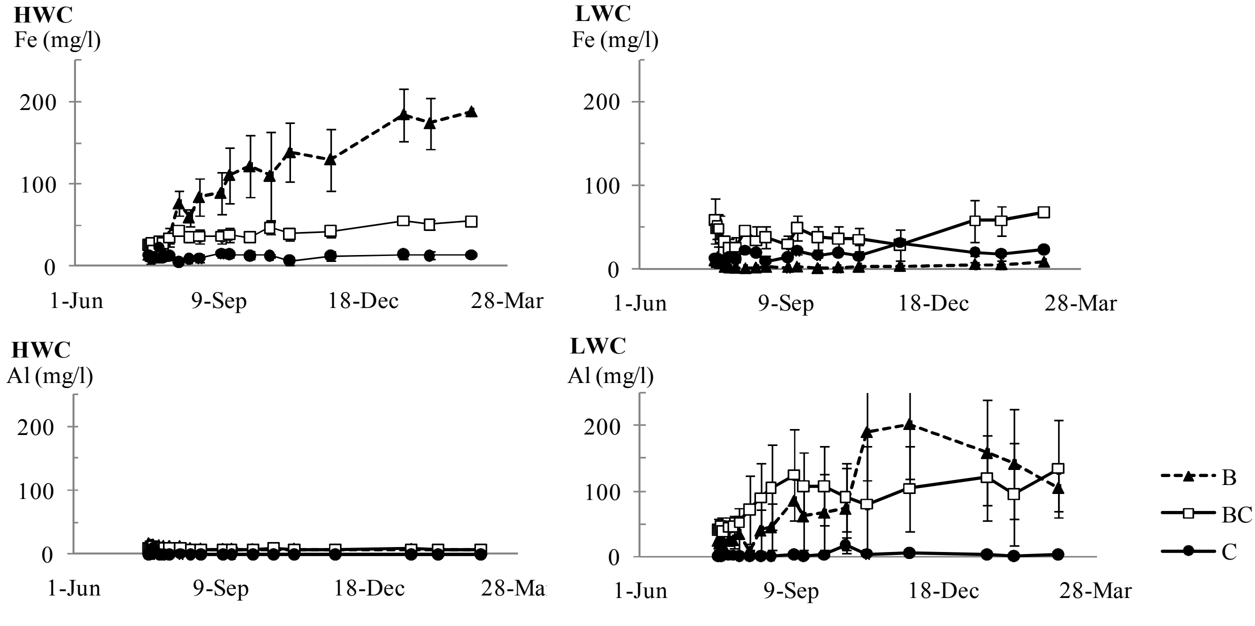


**Figure 1. Temporal variation of redox potential and moisture content in the different soil horizons in HWC and LWC in July 2008 - March 2009. The error bars represent standard errors of the mean.**

The redox status varied from oxic in the plough layer (Eh c. 500 mV) to reduced in the C horizon (Eh < 300 mV). At the beginning of experiment, all subsoil horizons were reduced. In HWC, the C horizon remained always reduced, and the saturation by water induced reduced conditions also in the horizons B and BC (Figure 1). In LWC, the C horizon remained always reduced, but the BC and B turned oxic within two weeks from treatment start.

The elemental composition of pore water differed between soil horizons but in a given horizon the differences were minor in all lysimeters in the beginning of the experiment. Elevation of water table induced changes in the pore water composition, the variation in the oxidized horizons being high as compared to that in the reduced horizons (Figure 2). The concentrations of Fe and Al responded to the reduction of soil horizons dissimilarly. For instance, in B horizon, the mean concentration of Fe rose up to 188 ± 30 mg/l in the HWC treatment but remained low at 8 ± 4 mg/l in the LWC treatment. On the contrary, the maximum Al concentration was smaller in HWC (7± 2 mg/l) than that in LWC (203 ± 92mg/l).

The timing and volume of water discharge differed between the treatments. In the beginning of the experiment, the volume of discharge water was larger in LWC treatment, probably because of free drainage and preferential flow through the macropores and fractures induced by soil shrinking. The evapotranspiration of reed canary grass exceeded the amount of watering so that during the growing period there was no discharge from HWC treatment. In autumn, the volume of discharge was multiplied. The variation in Fe and Al concentrations was higher in LWC than in HWC (Table 2).



The error bars represent std.errors of means

**Figure 2. The Fe and Al concentrations in the pore water of soil horizons B, BC and C in HWC and LWC.**

**Table 2. Total elemental discharge loads and concentrations in the lysimeter experiment in autumn 2008.**

| | Total load (kg/ha) | | | Mean concentration (mg/l) | | |
|---|---|---|---|---|---|---|
| | HWC | LWC | $F_{(1,6)}$ | HWC | LWC | $F_{(1,6)}$ |
| Fe | 17.8 ± 7.8 | 1.0 ± 0.8 | 4.57 ($p < 0.01$) | 39.4 ± 0.4 | 6.4 ± 0.2 | 14.7 ($p \approx 0.08$) |
| Al | 2.2 ± 0.8 | 3.6 ± 1.5 | 0.70 ($p > 0.40$) | 4.9 ± 0.1 | 22.4 ± 0.6 | 3.5 ($p > 0.1$) |

Treatment effects were tested by F-test (the significance in parenthesis). Replicates n = 4. Measurement period 22 Jul – 31 Dec 2008.

## Discussion

High water table in a cropped acid sulphate soil induced reduced conditions in saturated soil horizons in the temperature range of +3 – +20 °C. The response of Fe and Al concentrations in the pore and discharge waters to the reduction was asymmetric; Fe concentration increased while Al concentration decreased. Although the ferric oxides are very sparingly soluble in water, the microbially catalysed reduction enhanced the dissolution at favourable conditions. The B horizon is rich in ferric oxides and supposedly the roots of reed canary grass at that depth provide easily decomposable organic matter to the microbes. This is the probable reason for the extremely high Fe concentrations in the pore water in the B horizon of HWC. In LWC, the B horizon is very acidic (pH 3.8) resulting to dissolution of Al oxides. This fact accounts for the high Al concentration in the pore water in the B horizon of LWC. In the first 0.5-yr of the experiment, the high Al and Fe concentrations in the discharge water in LWC and HWC, respectively, stem from their high concentrations in B horizon.

## References

Åström M, Sundtröm R, Holmberg M, Storberg K (2005) pH of streams in western Finland - a perspective from the Middle Ages into the mid 21st century. *Agricultural and Food Science* **14**, 5-13.

Goss MJ, Ehlers W (2009) The role of lysimeters in the development of our understanding of soil water and nutrient dynamics in ecosystems. *Soil Use and Management* **25**, 213-223.

Linebarger RS, Whisler FD, Lance JC (1975) New Technique for Rapid and Continuous Measurement of Redox Potentials. *Soil Science Society of America Journal* **39**, 375-377.

Mokma DL, Yli-Halla M, Hartikainen H (2000) Soils in a young landscape on the coast of southern Finland. *Agricultural and Food Science in Finland* **9**, 291-302.

Roos M, Åström M (2006) Gulf of Bothnia receives high concentrations of potentially toxic metals from acid sulphate soils. *Boreal Environment Research* **11**, 383-388.

Yli-Halla M, Mokma DL, Wilding LP, Drees LR (2008) Morphology, Genesis and Classification of Acid Sulphate Soils of Finland. In ' Proceedings of the Joint Conference of the 6th International Acid Sulfate Soil Conference and the Acid Rock Drainage Symposium'(Ed C Lin, S Huang, Y Li), pp. 224-228. (Guangdong Press Group: Guangzhou).

# Quantifying retained acidity in acid sulfate soil materials: An evaluation of routine methods

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## Abstract

Retained Acidity is an important aspect of acid sulfate soil (ASS) but techniques for the quantification of this property have not yet been systematically assessed. In this study, the utility of routine techniques for quantifying the Retained Acidity fraction will be examined. The relatively insoluble minerals such as jarosite and schwertmannite are major contributors to Retained Acidity in ASS. Known quantities of synthetic and natural jarosites and schwertmannite will be added to two non-acid sulfate soil samples plus to one quartz sand sample. By using $S_{NAS}$ in the chromium suite and $S_{RAS}$ in the SPOCAS suite (Ahern *et al.* 2004), the Retained Acidity fraction of the spiked samples will be assessed. The method introduced by Li *et al*. (2007) and the acidified ammonium oxalate method (Regenspurg *et al.* 2004) will be undertaken to recover the added jarosite and schwertmannite, respectively. The mineralogy of the samples will be characterized by X-ray diffraction (XRD). In the second part of this study, the potential interference from other common sulfate minerals, $CaSO_{4.}2H_2O$ (gypsum) and $BaSO_4$ (barite) will be examined.

## Key words

Sulfidic soils, Schwertmannite, Jarosite, Soil tests

## Introduction

Retained Acidity is one of the main components of the Existing Acidity in the Acid Base Account (ABA) method of Ahern *et al*. (2004) for ASS. The Retained acidity fraction is generally associated with the insoluble sulfate salts such as schwertmannite, jarosite, natrojarosite and other iron, aluminium hydroxysulfates. These secondary minerals naturally exists in highly acidic (pH < 4) ASS materials, and continue to release acidity as they weather by hydrolysis (Ahern *et al.* 2004; Burton *et al.* 2007; Wang *et al.* 2006). The hydrolysis of secondary minerals is generally a slow process and the acidity generated is considered to be in a less available form than readily soluble or exchangeable sources of acidity (Ahern *et al.* 2004; Fitzpatrick *et al.* 2009). In practice, both the Retained Acidity and Actual Acidity fractions are operationally defined fractions, dependent on the specific analytical approach used for their quantification.

Often the Actual Acidity fraction in the Existing Acidity represents the dominant and most available pool of acidity in acidified and oxidised ASS and hence has been studied extensively. Nevertheless, in oxidised soils and soils with little or no sulfide, the Retained Acidity fraction can be a significant source of acidity (McElnea *et al.* 2004). The kinetics and processes of acidity generation by the Retained Acidity fraction is not as well known as that of pyrite oxidation, yet the data to hand indicates that this acidity fraction could add substantial amounts of acidity to the soil in the long run. For this reason the risk of acidity production by the Retained Acidity store in soils must be taken into account to manage the acidification risk posed by ASS materials. Consequently, an accurate quantification of the major insoluble minerals such as schwertmannite, jarosite etc. is a particularly important factor which should be considered when developing management strategies. Despite this fact, there has not been any rigorous research published on the reliability of the currently available methods to date. The present study aims to conduct a systematic analysis of each method in the recovery of the two major minerals (jarosite and schwertmannite) in the retained acidity fraction.

Insoluble sulfate minerals such as gypsum and barite (which do not produce the acidity) could affect the estimation of sulfur associated with acidifying minerals when measured after the peroxide digestion (Sullivan *et al.* 1999 and reference therein). Thus, the second part of this study will focus on the potential interferences caused by gypsum and barite on the currently available methods for assessing Retained Acidity.

## Assessment Methods

Assessment methods will consist of the following:

i. $S_{NAS}$ – This is the difference of $S_{HCl(4M)}$ - $S_{KCl}$

ii. $S_{RAS}$ - The sulfur measured by 4M HCl extraction on the soil residue remaining after peroxide digestion and TPA titration of the SPOCAS method.

iii. Schwertmannite is generally analysed by using the acidified ammonium oxalate method (Carlson and Schwertmann 1981) which is described in a later section of this paper.

iv. Jarosite will be recovered by the method described by Li *et al*. (2007).

v. XRD – to characterize the synthesised solid.

Some of the possible problems and the interferences that could affect the final result of the analyses of above mentioned methods are described below.

*$S_{NAS}$ (Net acid soluble sulfur)*

$S_{NAS}$ gives an overall estimation of the retained acid soluble sulfur fraction of the sample yet, it does not account for the individual contribution of the different insoluble sulfate minerals present in the sample. The acidity that could be generated from this fraction is estimated based on the following assumption.

1 mole of jarosite gives 3 moles of $H^+$

Nonetheless, as the $S_{NAS}$ is not only derived from jarosite but could also be derived from other relatively insoluble sulfates such as schwertmannite, iron and aluminium hydroxyl sulfates the validity of the above assumption is questionable. Clearly, prior knowledge of the mineralogy of the ASS materials may be essential to the development of the appropriate stoichiometry for acidity estimations using this method.

*$S_{RAS}$ (Residual acid soluble sulfur)*

The $S_{RAS}$, is measured by extracting the washed soil residue after the peroxide digestion with 4M HCl (Ahern *et al*. 2004). Nevertheless, Ward *et al*. (2002) found that the peroxide digestion could provide necessary conditions for the formation of jarosite including low pH (2-4), higher concentrations of sulfate and iron (which originate from pyrite oxidation) and $K^{+}$. Hence, the estimated sulfur concentration at the end of this procedure may be an overestimation or underestimation of the exact amount present in the sample.

*Schwertmannite recovery method*

Experiments have shown that the oxalate dissolution in the dark dissolves schwertmannite and ferrihydrite completely leaving goethite and jarosite as a solid precipitate. However, some researchers have found that, this method doesn't completely dissolve schwertmannite in sediments (Gagliano 2004).

*Jarosite recovery method*

One of the limitations of this method is to keep the temperature below 550°C (Li *et al.* 2007). According to Li *et al*. (2007), sulfate in jarosite could release as $SO_3$ when the temperature is above 550°C. Though the overall temperature in the oven is set to 550°C, there is a possibility of generating greater temperatures in microenvironments of jarosite due to the ignition of organic matter in the sample (Henderson *et al.* 2007). Thus, the final estimated quantity of jarosite may not represent the actual concentration as some of the jarositic sulfur could have been removed as $SO_3$ during pyrolysis.

## Experimental methods and procedure

Two non-acid sulfate soil sample sets were collected from 2 sites in north-eastern NSW (Tukean Swamp on the Richmond River catchment and Shark Creek on the Clarence River catchment). Within 24hr of sampling, two soil samples were put in the oven at 80° C for two weeks until a constant weight was reached. Clean quartz sand samples will be used for comparison.

Synthetic/natural jarosites and schwertmannite ranging in proportions up to 20 %, will be added to two non-acid sulfate soil samples and the quartz sand sample. The homogenised samples will then be analysed as soon as possible (1hr) using the methods described earlier. A similar procedure will be undertaken to assess the potential interferences of gypsum and barite. Each sample will be analysed in triplicate.

*Recovery and synthesis methods*

*Retained Acidity recovery methods*
$S_{NAS}$ – Chromium Suite (Ahern *et al.* 2004)
$S_{RAS}$ – SPOCAS Suite (Ahern *et al.* 2004)

*Jarosite recovery method* (Li *et al.* 2007)
Jarosite in a sample can be extracted by three sequential steps which are outlined below.

i. Argon purged water extraction- This step takes ~ 3 minutes, and removes the soluble sulfate salts such as gypsum, epsomite and melanterite. The extract is then analysed for Fe, Mg, Ca etc. using ICP.

ii. Pyrolysis- The residue remaining after the extraction in the first step, is then roasted at 550ºC for 1hr. During this step all reactive sulfides are removed.

iii. 4M HCl extraction- The residue is then treated with 4M HCl for 30 minutes, and the extract is analysed for insoluble sulfate salts such as jarosite using ICP.

*Schwertmannite recovery method* **(**Carlson and Schwertmann 1981)
Schwertmannite recovery in the soil samples will be assessed using the method originally introduced by Carlson and Schwertmann (1981). In this method, schwertmannite in the sample (~0.05g) is dissolved completely by extracting with 0.05L acidified ammonium oxalate solution (pH 3) in the dark for 15 minutes. This extraction separates the schwertmannite from goethite and jarosite since schwertmannite is soluble in acid ammonium oxalate with respect to those two minerals. The stoichiometric composition of the dissolved schwertmannite will be then determined by assessing the Fe and S concentrations in the extracts using flame AAS and ICP-AES respectively. The Fe:S ratio in the extract can be further used to verify the complete dissolution of schwertmannite which is typically in the range of 5-8 (Regensberg *et al.* 2004 and reference therein)

*Synthesis of schwertmannite* (Regenspurg *et al.* 2004)
Synthesis of schwertmannite will be carried out according to the method of Pentinghaus (Regenspurg *et al.* 2004).

*Synthesis of jarosite* **(**Baron and Palmer 1996).
Jarosite will be synthesized according to the method of Baron and Palmer (1996).

## Conclusion

Methods for the assessment of Retained Acidity, despite being a critical component of the acidity risk assessment of acid sulfate soil materials, have not yet been critically assessed in a systematic fashion for acid sulfate soil materials and the common acidity containing minerals that do not readily dissolve (such as jarosite and schwertmannite). This issue is well known to scientists and land managers who work with acid sulfate soils. This paper firstly examines some of the potential limitations of the existing methods for estimating retained acidity and secondly outlines an approach that will be used to systematically assess the efficacy of existing methods for assessing Retained Acidity.

## References

Ahern CR, McElnea AE, Sullivan LA (2004) 'Acid Sulfate Soil Laboratory Methods Guidelines: In Queensland Acid Sulfate Soils Manual.' (Department of Natural Resources, Mines, Energy: Queensland, Australia).

Baron D, Palmer CD (1996) Solubility of jarosite at 4-35°C. *Geochimica et Cosmochimica Acta* **60**, 185-196.

Burton ED, Bush RT, Sullivan LA, Mitchell DRG (2007) Reductive transformation of iron and sulfur in schwertmannite-rich accumulation associated with acidified coastal lowlands. *Geochimica et Cosmochimica Acta* **71**, 4456-4473.

Carlson L, Schwertmann U (1981) Natural ferryhydrides in surface deposits from Finland and their association with silica. *Geochimica et Cosmochimica Acta* **45**, 421-429.

Fitzpatrick RW, Grealish G, Shand P, Simpson SL, Merry RH, Raven MD (2009) Acid sulfate soil assessment in Finnis river, Currency creek, Black swamp and Goolwa channel, South Australia.26/09.

Gagliano WB (2004) Biogeochemical charcterization of a constructed wetland for acid mine drainage treatment. PhD, Ohio State University, Ohio, USA.

Henderson SP, Sullivan LA, Bush RT, Burton ED (2007) Schwertmannite transformation to hematite by heating: Implications for pedogenesis, water quality and $CO_2$/$SO_2$ export in acid sulfate soil landscapes. *Geochimica et Cosmochimica Acta* **71 (suppl.1)**, A394.

Li J, Smart RStC, Schumann RC, Gerson AR, Levay G (2007) A simplified method for estimation of jarosite and acid-forming sulfates in acid mine wastes. *Science of the Total Environment* **373**, 391-403.

McElnea AE, Ahern CR, Manders JA, Smith CD (2004) Variability of acid sulfate soil chemistry at east trinity remediation site, far north Queensland, Australia. In 'ISCO 2004-13th International Soil Conservation Organisation Conference'Brisbane, Australia.

Regenspurg S, Brand A, Peiffer S (2004) Formation and stability of schwertmannite in acidic mining lakes. *Geochimica et Cosmochimica Acta* **68**, 1185-1197.

Sullivan LA, Bush RT, McConchie D, Lancaster G, Haskins PG, Clark MW (1999) Comparison of peroxide-oxidisable sulfur and chromium-reducible sulfur methods for determination of reduced sulfur in soil. *Australian Journal of Soil Research* **37**, 255-265.

Wang H, Bigham JM, Tuovinen OH (2006) Formation of schwertmannite and its transformation to jarosite in the presence of acidophilic iron-oxidizing microorganisms. *Materials Science and Engineering* **26**, 588-592.

Ward NJ, Sullivan LA, Bush RT, Lin C (2002) Assessment of peroxide oxidation for acid sulfate soil analysis. 1.Reduced inorganic sulfur. *Australian Journal of Soil Research* **40**, 433-442.

# Reductive dissolution of natural jarosite in a tidally inundated acid sulfate soil: geochemical implications

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## Abstract

Jarositic pedofeatures are a significant mineralogical indicator of the weathering conditions in ASS wetland environments. The geochemical processes in the reductive dissolution of natural jarosite are presented for a tidally inundated acid sulfate soil (ASS) of northeastern Australia. The extent of reductive dissolution of jarosite was determined from mineral micromorphology and by identifying differences in geochemical weathering along a toposequence. With increasing pH and decreasing Eh under tidal inundation, reduction of Fe(III) minerals occurred and jarosite became increasingly unstable. Direct evidence from scanning electron microscopy (SEM) and x-ray diffractometry (XRD) identified mineral structure and composition consistent with jarosite. Natural jarosite from the intertidal zone exhibited features associated with dissolution. Molar ratios of Fe to K indicated increasing depletion of K in natural jarosite downslope. Results provide important insights to the observed and predicted variability and stability of jarosite with tidal inundation.

## Key Words

K-jarosite, coastal ASS, elemental composition, seawater inundation, remediation, East Trinity.

## Introduction

The ferric sulfate mineral jarosite ($KFe_3(SO_4)_2(OH)_6$) is formed from pyrite oxidation and precipitates as pore fillings and coatings in soils under strongly oxidising and acidic conditions. Its presence is commonly observed as pale yellow mottles (Munsell soil colour 2.5Y 6/8) in the sulfuric horizon of acid sulfate soils (ASS). Natural jarosite crystals exhibit a classic euhedral ortho-rhomboidal morphology, with K, Na and $H_3O^+$ combining in the alkali position of the lattice structure (Brophy and Sheridan 1965). While the compositional variability of jarosite in ASS has not been published extensively, K-jarosite has been reported as the most abundant form (van Breemen 1973). In addition, the elemental composition of jarosite can provide an indication of the antecedent soil porewater conditions, and hence reflect the environment of precipitation (Dutrizac 1983). The substitution of Na into the lattice structure indicates increasing reactivity and solubility of jarosite, as jarosite rich in Na is considered less stable than K-jarosite (Gasharova *et al.* 2005). Jarosite is considered stable only under relatively oxidised (Eh >400 mV) and acid (pH 2 to 4) conditions. At higher pH values, jarosite is metastable with respect to goethite and slowly hydrolyses to fine-grained iron oxide, FeOOH. Hydrolysis is generally enhanced by leaching and by supply of bases.

It is well established that the metastable Fe(III) oxides which form in sulfuric horizons are prone to reductive dissolution when subjected to reducing conditions. This can lead to large increases in $Fe^{2+}$ and concomitant increases in pH (e.g. van Breemen and Harmsen 1975). However, to our knowledge, there are few field-based studies in coastal ASS landscapes specifically examining the reductive dissolution of jarosite. This study will contribute to the present knowledge of jarosite behaviour by examining the mineralogical variability with tidal inundation in ASS. This has important implications for environmental rehabilitation and management of these coastal ASS landscapes.

## Methods

### *Study site*

The study site was located in a Holocene sedimentary coastal plain at East Trinity near Cairns in northeastern Australia (145°48′ E, 16°56′ S), and covers an area of 940 ha. It experiences a tropical monsoonal climate with summer-dominant rainfall and a maximum tidal range in Trinity Inlet of around 3.2 m. Extensive drainage and clearing of vegetation for agriculture in the early 1970s caused oxidation of pyrite-rich, estuarine sediments and subsequent development of severely acidic soils. Various parts of the site have undergone remediation from 2001, which consisted of the reintroduction of regular tidal inundation to the previously drained ASS (Johnston *et al.* 2009a; Powell and Martens 2005). For this study, sampling sites were located along an established transect in the upper reaches of Firewood Creek sub-catchment and selected to represent a topographic sequence spanning the supratidal to intertidal zones (0.6-0.0 m AHD).

The transect was located upstream from the tidal floodgates and has experienced regular but attenuated tidal inundation for the preceding 5 years (i.e. since 2003).

*Soil collection and handling*

Four duplicate cores were collected at selected distances (20, 40, 60, 80 and 100 m) along the transect. Soil descriptions (texture, colour, etc.) were undertaken in the field for stratigraphy (see Figure 3a). Soils and sediments were rapidly sectioned into specified depth intervals (from 0–0.05, 0.05–0.15 m depth, and thereafter in 0.10 m increments) to a depth of at least 1.25 m for analysis of the solid fraction. Field measurements of pH ($pH_F$) and Eh ($Eh_F$) were made immediately on duplicate cores by direct probe insertion using calibrated Intermediate Junction Ag/AgCl combination pH and ORP electrodes with a saturated KCl reference solution. Eh measurements were corrected to the Standard Hydrogen Electrode (SHE). Samples from the equivalent depth intervals were bulked and placed into air-tight, sealable polyethylene bags, completely filled with material (i.e. no enclosed air). All soil and sediment samples were stored frozen until analysis to minimise possible oxidation of reduced species. Soil porewaters were also sampled at selected distances along the transect using a peeper equilibration dialysis method. Measurements of pH and Eh were made immediately using calibrated electrodes. Jarositic pedofeatures were collected from the sulfuric horizon (0.20-0.50 m depth) at corresponding distances. Samples were dried in a $N_2$ atmosphere at 20 °C, and jarositic pedofeatures were carefully removed by hand, minimising the inclusion of clay material and organic matter. These fragments were stored separately in air-tight plastic vials for morphological characterisation. A portion of the resultant samples were prepared for mineralogical and geochemical analysis by gently grinding and sieving to <63 μm, then stored in air-tight plastic vials.

*Geochemical analyses*

Frozen samples were thawed under $N_2$ and homogenised with a spatula for geochemical analysis of the solid fraction. Gravimetric moisture content (θg) was determined by oven-drying sub-samples at 105 °C until a constant mass. A portion of soil samples were oven-dried at 85 °C for at least 24 h and gently ground. Aqueous extractions were undertaken in duplicate on 2 g oven-dry soil using a 1:5 soil to water ratio. Water-soluble cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $Fe^{2+}$) and anions ($SO_4^{2-}$) were determined in filtered (0.45 μm) aqueous extracts using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; Perkin-Elmer DV4300). Water soluble $Cl^-$ was also determined in aqueous extracts using flow injection analysis (FIA; Lachat QuikChem 8000). Total C was determined gravimetrically on oven-dry materials using a LECO CNS-2000 Carbon, Nitrogen and Sulfur Analyzer. Near-total Fe and S were determined on oven-dry materials by hot aqua-regia digestion (3:1 $HCl:HNO_3$, 95 °C, 1 h) using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Perkin-Elmer Optima ELAN-DRCe).

*Mineralogical analyses*

The mineralogical composition of the dried jarositic pedofeatures was identified by X-ray powder diffraction (XRD). The diffractograms were obtained with a Bruker D4-Endeavor diffractometer, with a 2.2 kW CoK radiation source and a Lynx Eye detector. The diffractograms were comprised of randomly oriented aggregates of the mineral fraction. Samples were scanned stepwise from 15° to 80° 2θ using 0.05° steps and a 4 s count time. Scanning electron microscopy (SEM) and elemental analysis (energy dispersive X-ray, EDX) of jarositic pedofeatures were carried out with a Leica 440. Material was carefully sampled from pedofeatures under a light microscope, then mounted on aluminium stubs and coated in carbon. Microanalysis was carried out after internal calibration with an OXFORD microprobe ISIS system.

## Results

Prior to re-establishing tidal inundation, soils along the toposequence were described as having distinct sulfuric horizons in the upper 1 m with pedofeatures typical of ASS, including jarosite and Fe(III) oxides mottles (Johnston *et al.* 2009b). Following regular tidal inundation over 5 years, ASS materials were transformed from Hydraquentic Sulfaquepts to Typic Sulfaquents (Johnston *et al.* 2009b). Soil geochemical characteristics of the former mineral sulfuric horizon (0.10–0.70 m depth; GBj) are shown in Table 1. Reducing conditions were evident in the lower intertidal zone (i.e. at lower elevation), and these soils were characterised by greater concentrations of soluble $Na^+$ and $Cl^-$, reflecting seawater influence, and increasing soluble $K^+$ contents. The abundance, size and prominence of jarosite mottles were lower in the intertidal ASS compared with the supratidal ASS. This is consistent with circumneutral pH and moderately reducing Eh, indicating that the geochemical conditions for the intertidal ASS lie outside the stability field for jarosite (Table 1, Figure 1).

**Table 1. Soil geochemical characteristics of the mineral sulfuric horizon (0.10–0.70 m depth) along the toposequence examined in this study. Data shown is the mean of n=7 depth intervals.**

| Zone | Supratidal | Supratidal | Intertidal | Intertidal | Intertidal |
|---|---|---|---|---|---|
| Distance (m) | 20 | 40 | 60 | 80 | 100 |
| Field $pH_F$ | 4.5 | 4.2 | 5.4 | 6.1 | 6.1 |
| Field $Eh_F$ (mV) | 589 | 517 | 217 | 103 | 143 |
| Soluble $Cl^-$ (mmol/kg) | 65 | 107 | 251 | 444 | 451 |
| Soluble $SO_4^{2-}$ (mmol/kg) | 20 | 21 | 19 | 11 | 11 |
| Soluble $Na^+$ (mmol/kg) | 7 | 12 | 27 | 45 | 48 |
| Soluble $K^+$ (mmol/kg) | 1.2 | 1.4 | 1.9 | 2.7 | 2.8 |
| Soluble $Fe^{2+}$ (mmol/kg) | 0.31 | 0.30 | 0.64 | 0.06 | 0.06 |
| Total Fe (mmol/kg) | 487 | 493 | 600 | 410 | 330 |
| Total S (mmol/kg) | 282 | 369 | 337 | 171 | 126 |

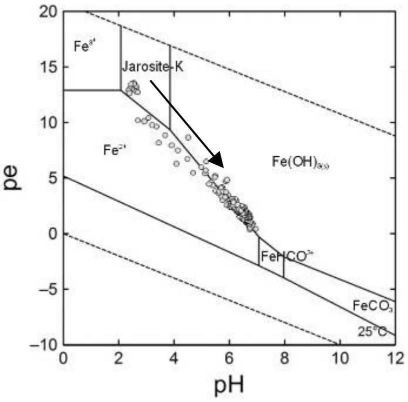

**Figure 1. pE-pH diagram for tidally inundated ASS, based on porewater pH and Eh along the toposequence. Stability fields of Fe species are shown. Direction of arrow indicates increasing tidal inundation (i.e. with lower elevation).**

The pe-pH diagram (Figure 1) describes the geochemical conditions for various stable Fe mineral phases. Porewater pH and Eh were shown to lie close to the Fe(II)/Fe(III) boundary (Figure 1), suggesting that the reduction of Fe(III) minerals is controlling soil geochemical conditions with increasing tidal inundation. Various Fe(III) oxide minerals (including ferrihydrite, schwertmannite and goethite) that form in ASS sulfuric horizons have been shown to undergo reductive dissolution after reflooding (e.g. van Breemen and Harmsen 1975). Under increasing pH and decreasing Eh conditions typical of tidally inundated ASS, jarosite is increasingly unstable (Figure 1).

The natural yellow precipitates from the former sulfuric horizon along the toposequence were identified as jarosite from X-ray diffractograms (Figure 2a). Crystal morphologies evident from scanning electron photomicrographs were consistent with jarosite, and exhibited a classic euhedral ortho-rhomboidal form (Figure 2b, c). Figure 2b shows that jarosite from the supratidal zone (i.e. at 20 m upslope on transect) was generally inter-grown euhedral crystals >1 µm with clearly defined edges and planar surface features. In contrast, jarosite from the intertidal zone (i.e. at 100 m downslope on transect) exhibited features consistent with dissolution, including smaller, sub-rounded crystals with clearly visible etch pits (Figure 2c).

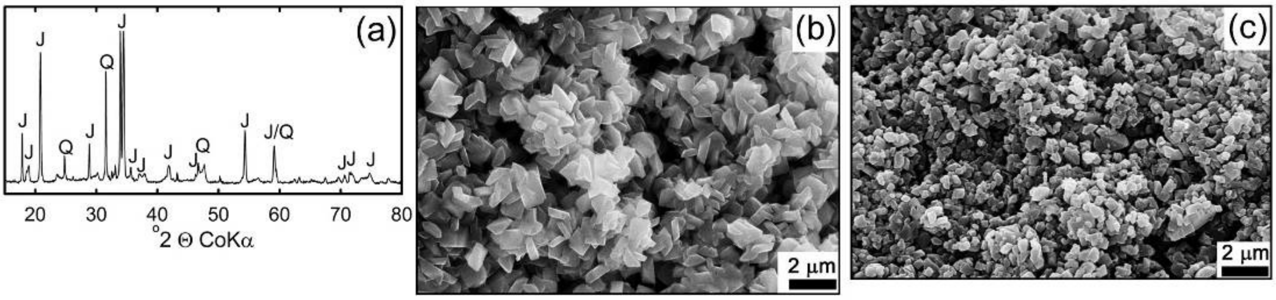

**Figure 2. Representative X-ray diffractogram of jarositic pedofeatures (a), and scanning electron photomicrographs of natural jarosite from 20 m (supratidal zone) (b) and 100 m (intertidal zone) (c) along the toposequence.**

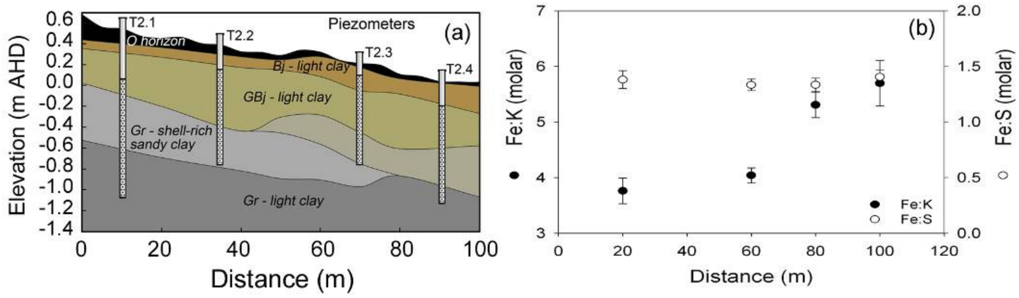

**Figure 3. Stratigraphic cross-sectional profile along the toposequence (a). Horizon boundaries are described after Dent (1986). Relationship between elemental composition of jarosite from SEM-EDX and distance (m) (b). Molar ratios of Fe:K and Fe:S (± standard deviation) are shown.**

The elemental composition of the jarositic pedofeatures was confirmed by SEM-EDX. Jarosite from the supratidal zone displayed mean elemental ratios for K:Fe:S of 0.79:3:2.17 (n=26), which is relatively close to the ideal stoichiometry of 1:3:2. However, whilst molar ratios of Fe to S remained stable in the natural jarosite along the toposequence, Fe to K ratios indicated increasing depletion of K downslope with tidal inundation (Figure 3b). This depletion was strongly correlated with elevation (Figure 3a). These data are consistent with the findings of Smith *et al*. (2006), who demonstrated selective loss of K relative to Fe during dissolution of jarosite. Other studies have also reported incongruent dissolution of jarosite and retention of Fe relative to K (e.g. Jones *et al.* 2006; Welch *et al.* 2008).

## Conclusion

Direct evidence from scanning electron microscopy (SEM) and x-ray diffractometry (XRD) identified jarosite in the former sulfuric horizon of tidally inundated ASS. Under reducing soil conditions, natural jarosite from the intertidal zone exhibited features consistent with dissolution. Molar ratios of Fe to K indicated increasing depletion of K in natural jarosite downslope. Results provide important insights to the observed and predicted variability and stability of jarosite with tidal inundation.

## References

Brophy GP, Sheridan MF (1965) Sulfate studies IV: the jarosite-natrojarosite-hydronium jarosite solid solution series. *American Mineralogist* **50**, 1595-1607.

Dent D (1986) 'Acid sulphate soils: a baseline for research and development.' (International Institute for Land Reclamation and Improvement (ILRI): Wageningen, The Netherlands).

Dutrizac JE (1983) Factors affecting alkali jarosite precipitation. *Metallurgical Transactions B: Process Metallurgy* **14B**, 531-539.

Gasharova B, Göttlicher J, Becker U (2005) Dissolution at the surface of jarosite: an in situ AFM study. *Chemical Geology* **215**, 499-516.

Johnston SG, Bush RT*, et al.* (2009a) Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine Coastal and Shelf Science* **81**, 257-266.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith D, McElnea AE, Martens MA, Wilbraharn S (2009b) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335-346.

Jones EJP, Nadeau T, Voytek MA, Landa ER (2006) Role of microbial iron reduction in the dissolution of iron hydroxysulfate minerals. *Journal of Geophysical Research* **111**, G01012.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* **51**, 149-164.

Smith AML, Hudson-Edwards KA, Dubbin WE, Wright K (2006) Dissolution of jarosite [KFe3(SO4)(2)(OH)(6)] at pH 2 and 8: Insights from batch experiments and computational modelling. *Geochimica et Cosmochimica Acta* **70**, 608-621.

van Breemen N (1973) Soil forming processes in acid sulphate soils. In 'Proceedings of the international symposium on acid sulphate soils'. (Ed. H Dost) pp. 66-129. (International Institute for Land Reclamation and Improvement: Wageningen, The Netherlands).

van Breemen N, Harmsen K (1975) Translocations of iron in acid sulfate soils: I. Soil morphology, and the chemistry and mineralogy of iron in a chronosequence of acid sulfate soils. *Soil Science Society of America Proceedings* **39**, 1140-1148.

Welch SA, Kirste D, Christy AG, Beavis FR, Beavis SG (2008) Jarosite dissolution II-Reaction kinetics, stoichiometry and acid flux. *Chemical Geology* **254**, 73-86.

# Reductive sulfur biomineralisation in a re-flooded acid-sulfate soil landscape

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## Abstract

We quantified the in-situ rates of dissimilatory $SO_4^{2-}$-reduction and the resulting S biomineralisation products in an acid-sulfate soil landscape which had been re-flooded by controlled tidal inundation. $SO_4^{2-}$-reduction was confined to the near-surface, formerly-drained soil layers and occurred at rates up to ~300 nmol/cm$^3$/day. Elemental S was the dominant short-term product of $SO_4^{2-}$-reduction, and was present at up ~40 $\mu mol_S$/g. It was generally more abundant than iron-monosulfides or iron-disulfides in recently re-flooded soil layers. However, as expected, iron-disulfides were increasingly significant in soil layers that had experienced long-term inundation (i.e. 40-80 $\mu mol_S$/g formed over ~5 years).

## Key Words

Acid-sulfate soils, elemental sulfur, iron, iron-sulfide, East Trinity.

## Introduction

The process of contemporary iron-sulfide formation in re-flooded acid-sulfate soils (ASS) consumes acidity and can sequester potentially-toxic trace elements (Burton *et al.* 2008a). Iron sulfide biomineralisation therefore offers an attractive site remediation outcome when drained ASS are inundated and reverted to wetlands. However, little quantitative information exists on either the in-situ rates of microbial dissimilatory $SO_4^{2-}$-reduction or the abundance of the resulting biomineralisation products during ASS wetland re-establishment. This limits the ability to accurately predict iron-sulfide biomineralisation, and to develop management strategies to optimise ASS remediation. The objective of this study was to examine reductive sulfur biomineralisation in a re-flooded ASS landscape that had been reverted to a tidal wetland. Specifically, we quantified the in-situ rates of dissimilatory $SO_4^{2-}$-reduction and the abundance of associated reduced inorganic S species in relation to tidal inundation.

## Methods

### *Study site*

The study site is an 800 ha coastal wetland located at East Trinity in north-eastern Australia. In the 1970's, a sea-wall with tide-gates was constructed in order to exclude tidal inundation and thereby drain the wetland soils. This caused iron-sulfide oxidation and severe acidification. In 2001-02, a program of lime-assisted tidal exchange was initiated in order to remediate the acidified soil layers. The tidal exchange component of this approach has involved incremental tidal inundation across the formerly drained site.

### *Field methods and analyses*

A transect was established at the tidal inundation front (Figure 1). Groundwater levels were measured using Odyssey (ODYPS05) pressure transducers, housed in 50 mm diameter PVC piezometers. Soil samples (0.1 m intervals, to 1.5 m below the soil surface) were collected at 5 positions along the transect using a gouge-auger. The samples were immediately transferred into 50 mL centrifuge vials with no headspace and stored at 4ºC until return to our laboratory within 2-3 days. In-situ $SO_4^{2-}$-reduction rates were determined using the S-35 incubation method (Jakobsen and Postma 1999). This involved collecting undisturbed soil sub-samples using 3 mL polypropylene syringes with the distal end removed. These sub-samples were retrieved from an intact soil profile held within a gouge-auger. The samples were injected with 150 to 200 kBq of $^{35}SO_4^{2-}$, incubated at ambient temperature for 24 hrs and then mixed with 20% Zn acetate and frozen. The S-35 labelled samples were subjected to the 3-step RIS extraction procedure described below. The accumulation of S-35 in each RIS fraction was determined by liquid-scintillation counting.

Soil porewaters were recovered by centrifugation and analysed for pH, Eh, $Fe^{2+}$ and $SO_4^{2-}$ as per Burton *et al.* (2008a). Solid-phase Fe was extracted with deoxygenated 1 M HCl for 1 hour, followed by extraction with a citrate-buffered dithionite solution. The concentration of Fe(II) and Fe(III) in the 1M HCl, and total Fe in the dithionite extract were quantified via the 1,10-phenanthroline method. Solid-phase RIS species were analysed using the 3-step extraction method of Burton *et al.* (2009). This involved (1) extraction of iron-monosulfides as acid-volatile sulfide (AVS) using 6 M HCl / 0.1M ascorbic acid (2) extraction of elemental S by shaking with toluene followed by quantification via HPLC, and (3) the recovery of iron-disulfides as Cr(II)-reducible S using the diffusion method of Burton *et al.* (2008b).

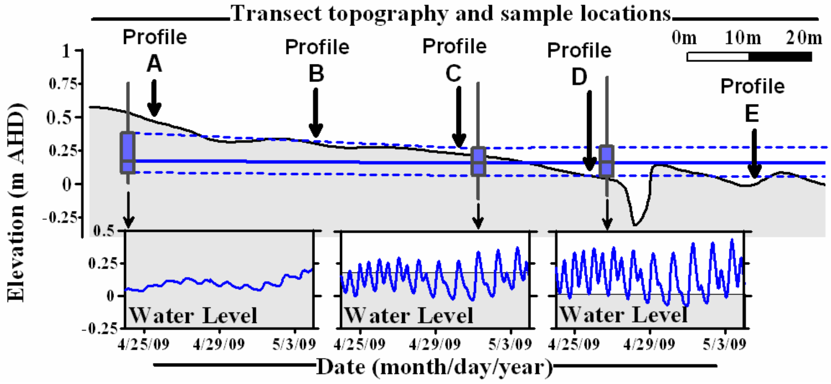

**Figure 1. Topographic and hydrological features of the inundation-front transect. The blue line in the upper panel denotes the median groundwater level ± the lower and upper quartile (interpolated from 3 piezometers, shown as the box-and-whisker plots). The solid-blue line in the lower panels shows the groundwater level, recorded at 30 minute intervals in each of the 3 piezometers.**

## Results

The surface elevation of the transect studied here spanned < 0 m to ~0.6 m AHD. The median groundwater levels were 0.1-0.2 m AHD. However, these levels displayed significant short-term fluctuations due to tidal influence (Figure 1). At the lower end of the transect (i.e. near Profile E), the soil surface was for the most time covered by tidal surface waters. In contrast, towards the upper end of the transect, the soil surface was only infrequently inundated. The incremental nature of tidal inundation at the study site means that the transect reflects a temporal progression of increasing inundation duration from Profile E to Profile A. The near-surface depth intervals at Profile A and B had not been subject to considerable tidal inundation and had low pH and high Eh (Figure 2). In contrast, the whole soil profile at the lower end of the transect had experienced regular or continuous tidal inundation for >12 months. As a result, the pore water pH ranged from approx. pH 5 to 7 (Figure 2). This represents a substantial increase in pH when compared against the severely acidic conditions which existed prior to tidal inundation (Powell and Martens 2005; Johnston *et al.* 2009).

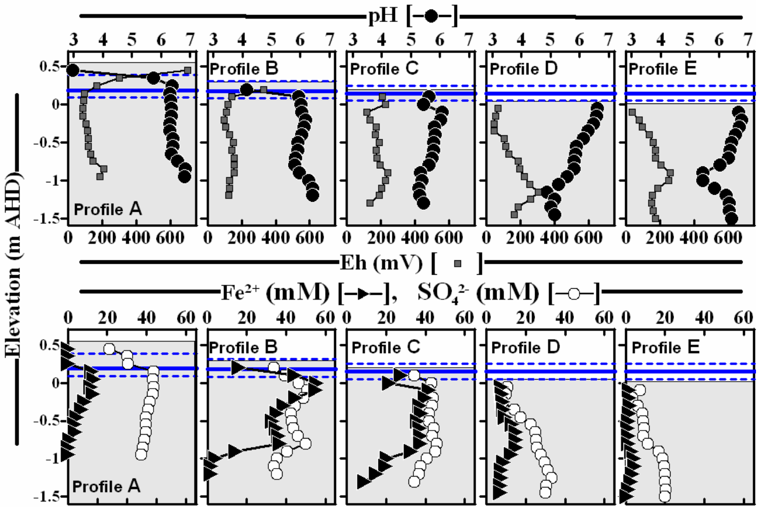

**Figure 2. Selected porewater propertes across the inundation-front transect. The blue lines show the median groundwater level (solid-line) ± the lower and upper quartile (dashed lines).**

The Fe$^{2+}$ concentrations were extremely large (10 – 60 mM) within re-flooded soil layers (i.e. +0.1 to -0.7 m AHD) at Profile A, B and C (Figure 2). This is a result of reductive dissolution of Fe(III)-bearing minerals, such as jarosite, goethite and schwertmannite. The importance of Fe(III)-reduction is evident by the decreasing concentrations of both labile (1 M HCl-extractable) and crystalline (dithionite-extractable) solid-phase Fe(III) in the surface 0 – 0.6 m depth intervals towards the lower end of the transect (Figure 3). This decrease is accompanied by increases in 1M HCl-extractable Fe(II) (Figure 3), which suggests that the low pore-water $Fe^{2+}$ concentrations in the 0 – 0.6 m depth interval at Profile D and E are due to precipitation of Fe(II) minerals such as siderite ($FeCO_3$) and mackinawite (FeS).

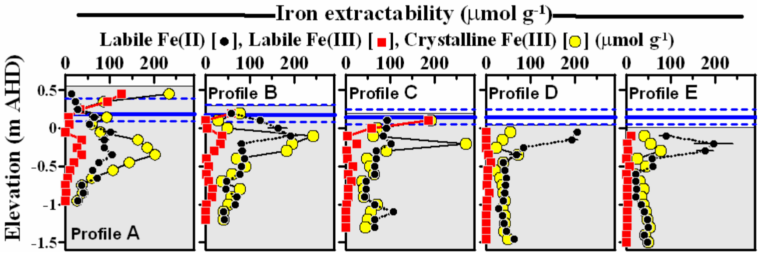

**Figure 3. Iron extractability across the inundation-front transect. The blue lines show the median groundwater level (solid-line) ± the lower and upper quartile (dashed lines).**

Within the un-oxidised estuarine sediment (below -0.7 to -0.9 m AHD), RIS speciation was dominated by $FeS_2$ (Figure 4). In the shallower, previously-drained soil layers, RIS speciation comprised a mixture of AVS, elemental S and $FeS_2$. Given the site's history, the presence of RIS in these shallow soil layers is a consequence of recent reductive S biomineralisation. At Profile E (which has experienced prolonged and continuous tidal inundation over several years), $FeS_2$ was the most abundant RIS species, except in the surface 0 – 0.1 m depth interval. In contrast, elemental S and (to a lesser extent) AVS were the dominant biomineralisation products in the near-surface soil layers at Profiles A to D (see bottom panel in Figure 4).

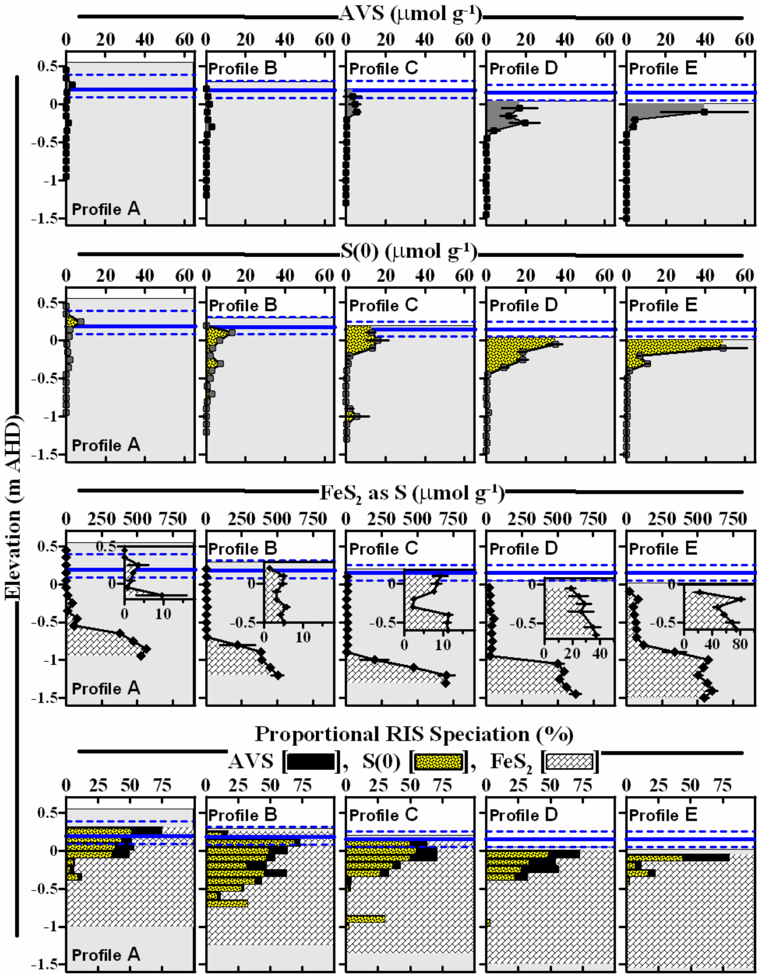

**Figure 4. Distribution of RIS species across the inundation-front transect. The blue lines show the median groundwater level (solid-line) ± the lower and upper quartile (dashed lines).**

In-situ $SO_4^{2-}$-reduction was confined to the shallow, re-flooded soil layers (Figure 5). The rates were generally greatest near the soil surface, consistent with a ready supply of labile organic C. The exception to this trend was the surface 0-20 cm depth at Profile A, which was above the upper quartile of groundwater level and thus still relatively oxidising (Figure 5). The actual rates of $SO_4^{2-}$-reduction were up to ~300 nmol /cm$^3$/day, which is comparable to organic-rich salt marsh sediments. In terms of transect position, the rates were highest in the near-surface soil layers at Profiles B, C and D, and were lower towards both the upper (Profile A) and lower (Profile E) ends of the transect. At the upper end, this can be explained by the groundwater level being well below the O-horizon, which would limit the C supply necessary for $SO_4^{2-}$-reduction. In contrast, the $SO_4^{2-}$-reduction rates at the lower end of the transect (i.e. Profile E) appear to be limited by small pore-water $SO_4^{2-}$ concentrations. Profile E is almost continuously inundated and as a consequence does not experience the same degree of $SO_4^{2-}$ re-supply via tidal pumping that exists towards the middle of the transect (i.e. Profile C and D).

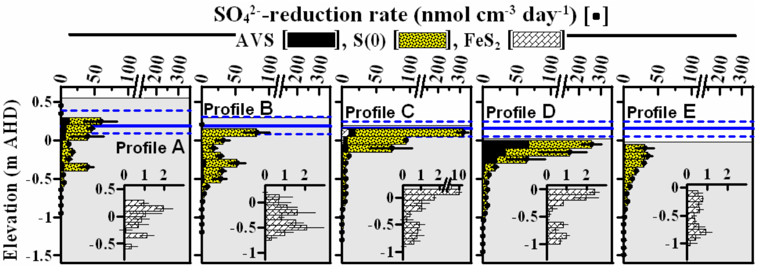

**Figure 5. In-situ rates of sulfate-reduction. The blue lines show the median groundwater level (solid-line) ± the lower and upper quartile (dashed lines).**

Figure 5 shows that elemental S was the most important short-term product of $^{35}SO_4^{2-}$-reduction (Figure 5). The importance of elemental S as a short-term biomineralisation product is consistent with the abundance of elemental S in the shallow, formerly drained soil layers (bottom panel in Figure 4). In the soils examined here, the abundance of elemental S can be explained by oxidation of $H_2S$ (the initial product released by $SO_4^{2-}$-reduction) by reaction with Fe(III) minerals (Burton *et al.* 2006).

Although not a major short-term product of $SO_4^{2-}$-reduction, the S-35 incubations provide strong evidence for rapid $FeS_2$ formation in the shallow, formerly drained soil layers (see insets in Figure 5). Interestingly, this short-term formation of $FeS_2$ was quite considerable at depths below the near-surface maximum in total $SO_4^{2}$reduction rates. As a result, the contemporary accumulation of $FeS_2$ is not concentrated near the soil surface, unlike the near-surface accumulation of AVS and elemental S (Figure 4).

## References

Burton ED, Bush RT, Sullivan LA (2006) Elemental sulfur in drain sediments associated with acid sulfate soils. *Applied Geochemistry* **21**, 1240 – 1247.

Burton ED, Bush RT, Sullivan LA, Johnston SG, Hocking RK (2008a) Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* **253**, 64 – 73.

Burton ED, Sullivan LA, Bush RT, Johnston SG, Keene AF (2008b) A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* **23**, 2759-2766.

Burton ED, Bush RT, Sullivan LA, Hocking RK, Mitchell DRG, Johnston SG, Fitzpatrick RW, Raven M, McClure S, Jang LY (2009) Iron-monosulfide oxidation in natural sediments: Resolving microbially-mediated S transformations using XANES, electron microscopy and selective extractions. *Environmental Science & Technology* **43**, 3128-3134.

Jakobsen R, Postma D (1999) Redox zoning, rates of sulfate reduction and interactions with Fe-reduction and methanogenesis in a shallow sandy aquifer, Romo, Denmark. *Geochimica et Cosmochimica Acta* **63**, 137 – 151.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith D, Martens MA, McElnea AE, Wilbraham ST, van Heel S (2009) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335 – 346.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in the Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* **51**, 149–164.

# Remediating coastal acid sulfate soils by tidal inundation: geochemical hysteresis of iron

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## Abstract

The effects of restoring marine tidal inundation to a severely degraded acid sulfate soil landscape were investigated. Tidal inundation stimulated Fe and $SO_4^{2-}$ reduction, leading to internal alkalinity generation and the reformation of considerable quantities of pyrite within former sulfuric horizons. After ~five years of regular tidal inundation the amount of acidity within former sulfuric horizons had decreased dramatically. However, the change in hydrology and geochemistry initiated by tidal inundation has had profound consequences for the fate, mobilisation, redistribution and transformation of Fe minerals in the landscape. The transition to mainly reductive pedogenesis has mobilised a store of previously immobile secondary Fe(III) minerals (e.g. jarosite). Tidal pumping is driving upward advection of mobile $Fe^{2+}$. Oxidation of $Fe^{2+}$ near the soil-surface water interface leads to surficial accumulation of poorly-crystalline Fe(III) minerals, which display a mineralisation sequence related to tidal zonation. A conceptual representation of this hysteresis in iron geochemistry is presented.

## Key Words

Acid sulfate soil; iron; sea-level rise; tidal marsh; East Trinity.

## Introduction

An innovative technique to mitigate the negative environmental consequences of coastal acid sulfate soils (ASS) is the partial or complete inundation of ASS by tidal marine waters (Powell and Martens 2005; Johnston *et al.* 2009a, b). Tidal inundation ameliorates acute soil acidity by supplying bicarbonate alkalinity, and by stimulating upward migration of the redox boundary which generates an internal supply of bicarbonate alkalinity via iron and sulfate reduction (Johnston *et al.* 2009b).

ASS are typically rich in meta-stable, secondary Fe(III) minerals that formed after the oxidation of pyrite (e.g. jarosite, schwertmannite; Sullivan and Bush 2004). Re-establishing tidal inundation in an Fe(III)-rich ASS landscape generates considerable potential for reductive dissolution of Fe(III) mineral phases. Tidal pumping of shallow groundwater can be a powerful mechanism for porewater exchange and solute movement within intertidal zone sediments and its introduction may lead to subsequent mobilisation and redistribution of aqueous Fe. The biogeochemical cycling of Fe is closely linked with that of sulfur and a variety of important / toxic trace elements (e.g. arsenic), and thus changes in iron behaviour are likely to have consequences for these elements. We investigate and describe some of the effects of marine tidal inundation upon the behaviour and geochemistry of iron in ASS.

## Methods

### *Study site*

The study site, East Trinity, is situated in northern Australia near Cairns. It consists of an ~800 ha Holocene sedimentary coastal plain dissected by several estuarine creeks (145°47’ E, 16 °56’ S). A tide-excluding sea wall was constructed around the site in the 1970’s (Powell and Martens 2005). Tide exclusion combined with intensive drainage caused the oxidation of iron-sulfides in mangrove sediments, leading to widespread formation of severe acid sulfate soils across the site (Powell and Martens 2005). A remediation program commenced in 2001–02, which has involved incrementally increasing tidal inundation of acid sulfate soils up to an elevation of ~0.5 m AHD (AHD is Australian Height Datum, 0 m AHD approximates mean sea level). Tides now regularly inundate most of the formerly acidified areas across the site.

### *Hydrology*

Groundwater levels along each transect were measured at 30 minute intervals (±0.01 m) using submersible pressure transducers vented to the atmosphere (Odyssey, ODYPS05) housed in a series of four 50 mm diameter PVC piezometers.

### *Solid-phase sampling*

Replicate soil cores were obtained by gouge-auger from selected sampling locations. Cores were immediately sectioned and sub-samples sealed in air-tight polyethylene bags, completely filled with soil and frozen after collection until analysis. Field pH ($pH_F$) and redox potential ($Eh_F$) were determined on additional duplicate cores by direct insertion of freshly calibrated electrodes. Fe-rich surficial sediment (0–0.01 m) was also sampled from a variety of locations within the study area and frozen. The elevation of all sample points was surveyed to AHD.

Samples were thawed under $N_2$, homogenised and analysed sequentially in duplicate for reactive Fe fractions and speciation according to Kostka and Luther (1994). Poorly crystalline solid-phase Fe(II) and Fe(III) were extracted with 0.5M HCl on 1–2 g wet sub-samples [$Fe_{HCl}$]. The centrifuged residue was then extracted with a citrate-buffered dithionite solution [$Fe_{DCb}$]. The sum of $Fe_{HCl}$ and $Fe_{DCb}$ is reported as $Fe_{Ex}$ and largely represents the Fe pool available for reductive transformations over biologically relevant timescales. A separate portion of sample was dried at 85 °C and crushed to pass a 0.5 mm sieve. These dried and crushed samples were digested for near-total Fe using hot aqua-regia (1:3 $HNO_3$:HCl, 110 °C, 1:60 soil:solution, 1 h digest) and filtered (0.45 µm) aliquots analysed for Fe by inductively coupled plasma mass spectroscopy (ICP-MS; APHA 1998) using a Perkin-Elmer ELAN-DRCe instrument. Selected samples were examined via XRD using a Bruker D4 Endeavor fitted with a Co X-ray source and Lynx-Eye detector. Samples were scanned from 15º– 80º 2θ with a 0.05º 2θ step-size and a 4 second count-time and analysed using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Karlsruhe, Germany).

*Porewater geochemistry*

Porewaters were sampled during April 2008 via equilibration dialysis using 1.5 m long peepers. This is described in detail by Johnston *et al*. (2009c). Porewater was analysed for $Fe^{2+}$ and total Fe using the 1,10-phenanthroline method (APHA 1998).

## Results and discussion

Soil pH increased substantially (2–3 units; Figure 1) in former sulfuric horizons subject to tidal inundation for approximately five years. Following tidal inundation there was a significant relationship between elevation and pH, with sites exposed to longer tidal inundation showing the greatest increases (Figure 1).

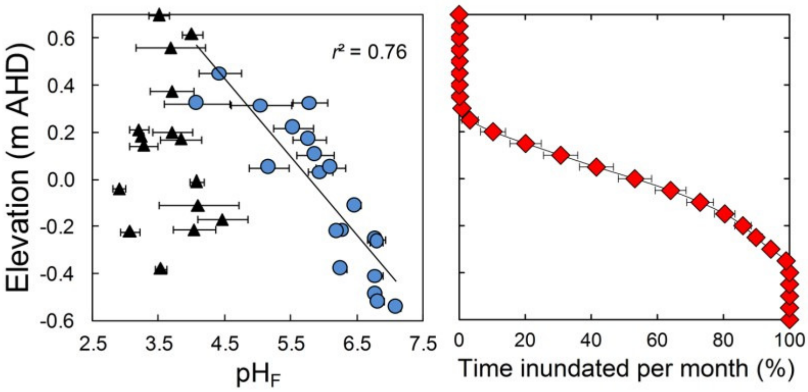

**Figure 1. (a) Changes in the relationship between the mean (±std. error) soil $pH_F$ of sulfuric horizons and surface elevation, prior to tidal inundation (2001-02; triangles), and after 5+ years of tidal inundation (2007-08; circles). (b) tidal inundation frequency relative to surface elevation during 2008.**

The redox transition caused by tidal inundation has initiated extensive reductive dissolution of Fe(III) minerals, including jarosite. This has resulted in very high concentrations of porewater aqueous $Fe^{2+}$ (>2000 mg $L^{-1}$) in former sulfuric horizons in the upper-intertidal zone (Figure 2).

This mobile $Fe^{2+}$ is able to be re-distributed according to the prevailing tidally-influenced hydrology. Tidal pumping in the fringing aquifer generates oscillating hydraulic gradients which drive upward advection of $Fe^{2+}$-enriched porewater during the ebb-tide phase. This is followed by oxidation of $Fe^{2+}$, precipitation and subsequent accumulation of Fe(III) minerals in surficial tidal sediments (Figure 3a,b,c). Fe(III)-precipitates at the sediment surface-water interface are poorly crystalline and displayed a mineralisation sequence that is related to tidal zonation (Figure 3d). Schwertmannite ($Fe_8O_8(OH)_6SO_4$) was the dominant Fe mineral phase in the upper-intertidal zone at mainly low pH (3–4). This was followed by increasing lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) at circumneutral pH within lower-intertidal and subtidal zones (Figure 3d).

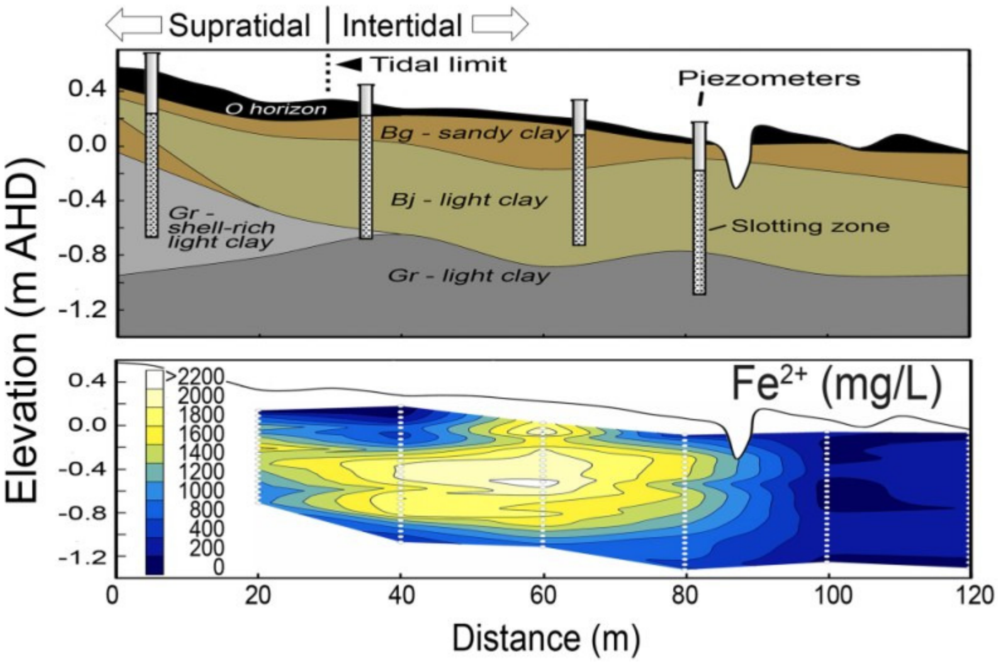

**Figure 2. Stratigraphy and porewater $Fe^{2+}$ concentrations across a tidally inundated acid sulfate soil toposequence.**

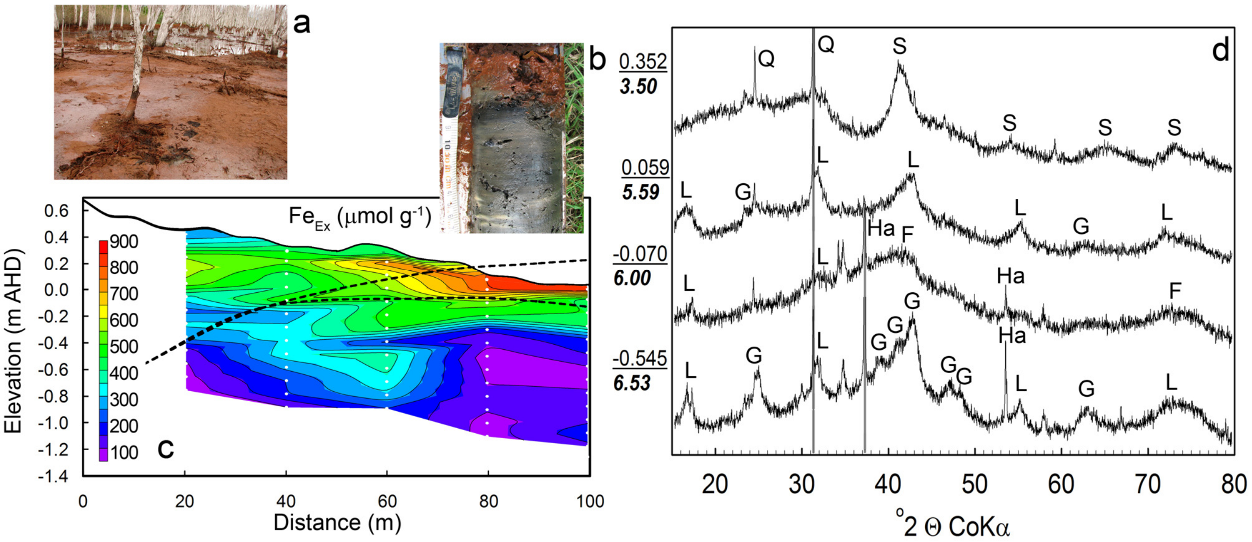

**Figure 3. Surface accumulations (a), (b) of poorly crystalline Fe(III) minerals; (c) surface enrichment of poorly crystalline reactive Fe fractions ($Fe_{Ex}$) within the intertidal zone at Transect 2. Dashed lines represent tidal water table minima and maxima at time of sampling; (d) representative X-ray diffractograms of Fe-rich surficial (0-1 cm) accumulations. Underline text on y-axis is surface elevation (m AHD) at the point of sample collection and bold italic is $pH_F$. S, schwertmannite; Q, quartz; G, goethite; L, lepidocrocite; F, ferrihydrite; Ha, halite.**

The surficial enrichment of poorly crystalline Fe(III)-minerals has a range of geochemical consequences. Poorly crystalline Fe(III)-minerals provide an effective substrate for adsorption / co-precipitation of trace metals and is likely to influence their long-term accumulation. In addition, poorly crystalline Fe can promote the formation of elemental sulfur ($S^0$) and acid volatile sulfides (AVS) in surficial sediments at the expense of pyrite formation (Burton *et al.* 2007).

The onset of mass reductive dissolution of Fe in combination with tidal pumping has effectively mobilised a large store of previously immobile secondary Fe(III) minerals. Whilst the neutralisation of acidity has caused the soil pH to return to a status similar to the original, pre-drainage condition, there is a hysteresis in the geochemical trajectory of remediation with respect to Fe. This can be represented conceptually (Figure 4a) where, **(1)** corresponds to a natural, pyrite-rich, anoxic, inter-tidal mangrove environment with circumneutral pH and a low proportion of reactive Fe ($Fe_R$:$Fe_{Tot}$). The exclusion of tides and drainage of sediment leads to **(2)**, where the oxidation of pyrite and formation of secondary Fe (III) minerals was associated with increased

$H^+$ and some increase in reactive Fe. The reintroduction of tidal inundation **(3)**, has caused the neutralisation of acidity, but surficial enrichment of reactive-Fe. Increasing pyritisation of this reactive Fe pool is likely over time, but the kinetics of this process are uncertain. Corresponding field data from the East Trinity site is shown in Figure 4b, for surficial sediments (0–0.1 m) under natural **(1)** and drained **(2)** conditions and after the reintroduction of tidal inundation **(3)**.

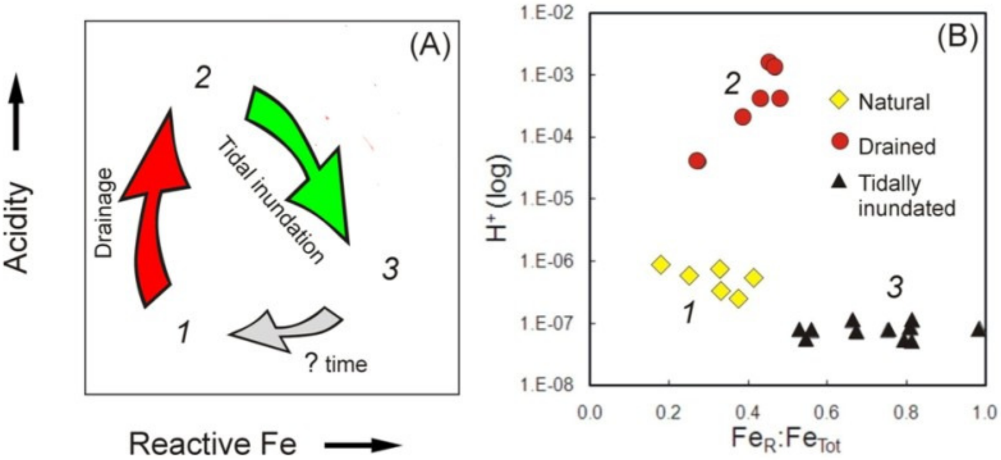

**Figure 4. Conceptual representation of hysteresis in tidal remediation of ASS with respect to changes in acidity and the reactive-Fe fraction in surficial sediments**

## Conclusion

This study demonstrates that marine tidal inundation can be effective at raising the pH of soils through internal generation of alkalinity via Fe / S reduction. However, interactions between topography and tides exert a fundamental hydrological control on the geochemical zonation, redistribution and subsequent mineralogical transformations of Fe within the landscape. These transformations involving Fe underpin important aspects of the geochemical trajectory of remediation, including the behaviour of co-associated trace elements and the formation of reduced inorganic sulfur species. A clear understanding of the behaviour of Fe is critical in evaluating the transferability of this remediation technique.

## References

APHA (1998) Standard methods for the examination of water and wastewater, 20th Ed. (American Public Health Association – American Water Works Association. Baltimore, USA)

Burton ED, Bush RT, Sullivan LA, Mitchell DRG (2007) Reductive transformation of iron and sulfur in schwertmannite–rich accumulations associated with acidified coastal lowlands. *Geochimica et Cosmochimica Acta* **71**, 4456–4473.

Johnston SG, Bush RT, Sullivan LA, Burton ED, Smith D, Martens MA, McElnea AE, Ahern CR, Powell B, Stephens LP, Wilbraham ST, van Heel S. (2009a) Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coast. and Shelf Science* **81**, 257–266.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith CD, Martens MA, McElnea AE, Wilbraham ST (2009b) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335–346.

Johnston SG, Burton ED, Bush RT, Keene AF, Sullivan LA, Isaacson L (2009) Pore water sampling in acid sulfate soils: a new peeper method. *Journal of Environmental Quality* **38** (6), 2474–2477 doi:10.2134/jeq2009.0135

Kostka JE, Luther GW (1994) Partitioning and speciation of solid phase Fe in saltmarsh sediments. *Geochimica et Cosmochimica Acta* **58**, 1701–1710.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in the Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* **51**, 149–164.

Sullivan LA, Bush RT (2004) Iron-precipitate accumulations associated with waterways in drained coastal acid sulfate soil landscapes of eastern Australia. *Marine and Freshwater Research* **55**, 727–736.

# Sulfidisation processes in a reactive Fe-enriched acid sulfate soil, northeastern Australia

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## Abstract

Solid phase Fe and S fractions were examined in a formerly severely acidified acid sulfate soil (ASS) wetland undergoing remediation via tidal inundation. Considerable diagenetic enrichment of reactive Fe(III) oxides (HCl- and dithionite-extractable) occurred near the soil surface (0–0.05 m depth). Extremely large concentrations of reactive Fe were determined up to 3,590 µmol/g and accounted for ~90% of the total Fe pool. This major source of reactive Fe exerts a substantial influence on sulfidisation processes and the formation, speciation and transformation of reduced inorganic S (RIS) in tidally inundated ASS. Following tidal inundation over the past 5 years, acid volatile sulfide (AVS; up to 57 µmol/g) and elemental sulfur ($S^0$; up to 41 µmol/g) were the dominant fractions of RIS in near surface soils. AVS-S to pyrite-S ratios exceeded 2.9 near the surface, indicating that abundant reactive Fe favoured the accumulation of AVS minerals and $S^0$ over pyrite. While the large availability of reactive Fe may limit the transformation of AVS minerals and $S^0$ to pyrite during early diagenesis, over longer time scales it can also promote the sequestration of S within pyrite. These findings provide an important understanding of sulfidisation processes occurring in reactive Fe-enriched, tidally inundated ASS landscapes.

## Key Words

Reactive iron, reduced inorganic sulphur, pyritisation, tidally inundated, remediation, East Trinity.

## Introduction

Cycling of Fe and S are key processes in the biogeochemistry of intertidal estuarine sediments (e.g. Canfield 1989; Morse and Rickard 2004). In these sedimentary environments, bioauthigenic pyrite ($FeS_2$) is a major sink for reduced S and its formation via the process of sulfidisation has been studied extensively (e.g. Berner 1970; Boesen and Postma 1988). Drainage of sulfide-rich, estuarine materials is known to cause rapid oxidation of pyrite, leading to severe acidification and the development of acid sulfate soils (ASS). An innovative approach to remediating ASS landscapes is to restore tidal inundation (Johnston *et al.* 2009a; Powell and Martens 2005). Tidal inundation radically alters the geochemical conditions of soils, promoting microbially-mediated reduction of Fe(III) and $SO_4^{2-}$. Re-establishing tidal inundation in ASS can cause reductive dissolution of these minerals within the soil profile and lead to substantial enrichment of the reactive Fe fraction near the soil surface (Johnston *et al.* 2009b). Reactive Fe is a key component in the formation of iron sulfide minerals, and is defined as that Fe which readily reacts with dissolved sulfides (Berner 1970; Canfield 1989). The abundance of solid phase Fe and its reactivity with sulfides is a major factor influencing the formation of reduced inorganic S (RIS) species, and hence the degree of sulfidisation (DOS) (Boesen and Postma 1988), in coastal marine and estuarine sediments. The exceptional enrichment of reactive Fe in a tidally inundated ASS wetland of far north Queensland provides an ideal opportunity to investigate the composition and transformation of RIS species where Fe is not limiting.

## Methods

### *Study site*

The study site was located in a Holocene sedimentary coastal plain at East Trinity near Cairns in northeastern Australia (145°48′ E, 16°56′ S), and covers an area of 940 ha. It experiences a tropical monsoonal climate with summer-dominant rainfall and a maximum tidal range in Trinity Inlet of around 3.2 m. Extensive drainage and clearing of vegetation for agriculture in the early 1970s caused oxidation of pyrite-rich, estuarine sediments and subsequent development of severely acidic soils. Various parts of the site have undergone remediation from 2001, which consisted of the reintroduction of regular tidal inundation to the previously drained ASS (Johnston *et al.* 2009a; Powell and Martens 2005). For this study, sampling sites were located within Firewood Creek sub-catchment and selected to represent an intertidal ASS mudflat, experiencing frequent but attenuated tidal inundation for the preceding 5 years.

*Soil collection and handling*

Six duplicate cores were collected within the intertidal ASS mudflat and rapidly sectioned into specified depth intervals. Field measurements of pH ($pH_F$) and Eh ($Eh_F$) were undertaken immediately on each undisturbed core by direct probe insertion using calibrated electrodes. Soil samples were bulked and placed into air-tight, sealable polyethylene bags, completely filled with material and stored frozen until analysis.

*Soil chemical analysis*

Soil samples were thawed under $N_2$ and homogenised for analysis of the solid fraction. Gravimetric moisture content ($\theta_g$) was determined by oven-drying sub-samples at 105 °C. Water-soluble $SO_4^{2-}$ was determined turbidimetrically using a spectrophotometer, and water soluble $Cl^-$ by flow injection analysis (FIA) using a Lachat QuikChem 8000 instrument, in filtered (0.45 µm), aqueous (1:5 soil to water) extracts. Total C was determined gravimetrically on oven-dry materials using a LECO CNS-2000 Carbon, Nitrogen and Sulfur Analyzer. Near-total Fe and S were determined on oven-dry materials by hot acidic digestion (1:1 $HNO_3$:HCl, 1 h, 95°C) in 1:100 soil to solution extracts measured by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin-Elmer ELAN-DRCe instrument.

Operationally-defined solid phase reactive Fe and RIS fractions were extracted sequentially in triplicate from moist 1–2 g soil sub-samples. Poorly crystalline Fe(II) and Fe(III) were extracted with 0.5 M HCl for 1 h. In the remaining soil, crystalline Fe was extracted with citrate-dithionite for 4 h. Fe concentrations were determined by the 1,10-phenanthroline method using spectrophotometry, with the addition of hydroxylammonium chloride for total Fe. The cold, dilute HCl and dithionite extractions are selective for poorly crystalline Fe(III) (oxyhydr)oxides (e.g. ferrihydrite, lepidocrocite) and readily reducible, crystalline Fe(III) oxides (e.g. goethite, hematite), respectively (Kostka and Luther 1994). Together, these extractions provide an estimate of the reactive Fe pool present in the soils. AVS-S was determined by cold diffusion and measured by iodometric titration (Burton *et al.* 2009). In the remaining soil, $S^0$-S was determined by toluene extraction and measured by cold cyanolysis in acetone using spectrophotometry (Burton *et al.* 2009). Subsequently, CRS-S was determined by cold diffusion and measured by iodometric titration (Burton *et al.* 2008). AVS-S provides an estimate of the reactive sulfide pool, and CRS-S is a widely used proxy for pyrite.

## Results and discussion

*General soil characteristics*

Soil profile descriptions of the intertidal ASS mudflat revealed a fine-grained, organic soil A horizon (0.0–0.1 m depth, 10YR 2/1), overlying a former sulfuric horizon (0.05–1.1 m depth), which was underlain by reduced, sulfidic materials (1.1–1.5 m depth, 2.5Y 4/1) and comprised predominantly of silty, light clays. Following tidal inundation, these formerly severely acidified ASS were classified as Typic Sulfaquents. Soil pH was circumneutral with a mean $pH_F$ range from 6.50 to 7.14, and measured $Eh_F$ values were indicative of moderately reducing conditions, with a mean redox potential from +1 to +141 mV in tidally inundated ASS (Table 1). Molar ratios of water-soluble Cl:$SO_4$ (Cl:$SO_{4W}$) reflected the modern supply of marine salts, as indicated by mean EC values ranging from 5.4 to 8.6 dS/m.

**Table 1. General soil characteristics of the tidally inundated ASS profiles examined in this study. Values shown are $\bar{x}$ of $n$=6 samples.**

| Depth (m) | $\theta_g$ (g/g) | $pH_F$ | $Eh_F$ (mV; SHE) | $EC_W$ (dS/m) | Molar Cl:$SO_{4W}$ | Total C (µmol/g) | Total Fe (µmol/g) | Total S (µmol/g) |
|---|---|---|---|---|---|---|---|---|
| 0.00–0.05 | 1.20 | 7.11 | 1 | 8.59 | 11 | 3867 | 2545 | 187 |
| 0.05–0.15 | 0.79 | 7.14 | 17 | 5.34 | 9 | 2348 | 1092 | 108 |
| 0.15–0.25 | 0.76 | 7.02 | 12 | 5.42 | 9 | 1565 | 630 | 132 |
| 0.25–0.35 | 0.75 | 6.87 | 49 | 5.95 | 10 | 1277 | 404 | 145 |
| 0.35–0.45 | 0.83 | 6.80 | 74 | 6.59 | 10 | 1360 | 345 | 131 |
| 0.45–0.55 | 0.81 | 6.69 | 92 | 6.87 | 10 | 1485 | 298 | 125 |
| 0.55–0.65 | 0.80 | 6.65 | 133 | 7.76 | 10 | 1722 | 251 | 116 |
| 0.65–0.75 | 0.82 | 6.50 | 141 | 8.42 | 10 | 1801 | 257 | 106 |

Large concentrations of total C were evident in surface soils (0–0.05 m depth, up to 4,806±546 µmol/g), which decreased to a minimum in the former sulfuric horizon (Table 1). Similarly, total Fe (up to 3,258±640 µmol/g) and S (up to 241±24 µmol/g) contents were greatest in the surface soils. However, the total Fe pool far exceeded the pool of total S throughout the soil profiles of the tidally inundated ASS.

*Solid phase reactive Fe and RIS fractionation*

Solid phase reactive Fe fractions of soil profiles for tidally inundated ASS are shown in Figure 1a. Of these fractions, HCl-extractable Fe(II) was most abundant in the surface sediments (0–0.05 m depth), with concentrations up to 1,243±289 µmol/g. These values were considerably greater than HCl-extractable Fe(III) at the same depth interval, with maximum concentrations of 583±124 µmol/g. Maximum dithionite-extractable Fe concentrations of 908±383 µmol/g also occurred in the surface sediments (0–0.05 m depth). AVS-Fe represented only a small proportion (generally < 5%) of total Fe in tidally inundated ASS (up to 57 µmol/g). Pyrite-Fe was also present at relatively small concentrations (7–30 µmol/g) and consequently comprised a small proportion of total Fe. Amounts of these iron sulfide mineral phases were overshadowed by extraordinarily large concentrations of reactive Fe fractions (HCl- plus dithionite-extractable fractions less AVS-Fe).

The reactivity of iron minerals with sulfide is of major importance for the formation of RIS species. Reactive Fe comprised almost 90% of the total Fe in the upper 0.35 m of tidally inundated ASS, and decreased to 50–80% of total Fe below this depth. The degree of pyritisation (DOP) estimates the amount of Fe available for reaction with sulfide over geologic time (Berner 1970). However, in sediments that contain a significant fraction of AVS, the DOP value can underestimate the availability of reactive Fe during early diagenesis. In these sediments, the effect of reactive Fe availability on sulfide accumulation may be described by the degree of sulfidisation (DOS) (Boesen and Postma 1988): In the tidally inundated ASS, DOS values were small (~3%), indicating that sulfidisation was not limited by the availability of reactive Fe in surface materials.

A large proportion of the total S pool (generally > 40%) was composed of RIS. Solid phase RIS fractions of soil profiles for tidally inundated ASS are shown in Figure 1b. Maximum AVS-S concentrations of 57±5 µmol/g occurred in the surface soils (0–0.05 m depth), and decreased with depth. Similarly, $S^0$-S was generally most abundant in the surface soils, with concentrations of 41±12 µmol/g. The formation of $S^0$ via $SO_4^{2-}$ reduction (Thode-Andersen and Jørgensen 1989) is an important pathway leading to the formation of pyrite and involving FeS clusters (Berner 1970; Morse and Rickard 2004). Pyrite-S contents generally increased with depth from 14±6 µmol/g (0.05–0.15 m depth) to 60±9 µmol/g (0.65–0.75 m depth). In most estuarine sedimentary systems, pyrite generally dominates the RIS fractions, with AVS and $S^0$ typically comprising only a minor fraction of total RIS (Morse and Rickard 2004). However, AVS-S and $S^0$-S were the dominant forms of RIS in tidally inundated ASS, comprising up to 50% of the total RIS (Figure 1b).

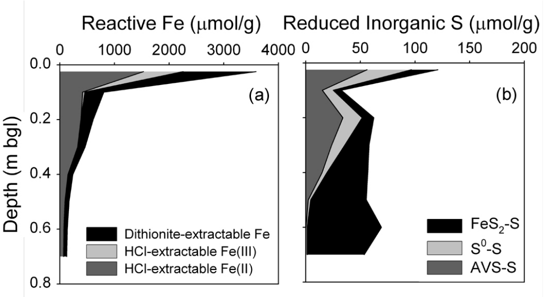

**Figure 1. Speciation of solid phase reactive Fe (a) and RIS (b) in a selected tidally inundated ASS profile.**

Over time, AVS and $S^0$ may be progressively transformed to the more geologically stable pyrite, resulting in decreasing AVS-S to pyrite-S ratios (Morse and Rickard 2004). The tidally inundated ASS were characterised by high AVS-S to pyrite-S ratios in the surface soils (up to 2.94), indicating a low degree of conversion of AVS minerals to pyrite. These high ratios are considered anomalous, given conditions were conducive to pyrite formation. A number of biogeochemical parameters may explain the favoured AVS accumulation relative to that of pyrite (e.g. Thode-Andersen and Jørgensen 1989); however, it is most likely that the ratios observed in tidally inundated ASS occur as a result of the abundant reactive Fe favouring S sequestration in FeS (Canfield 1989).

*Implications of enriched reactive Fe for sulfidisation*

Our results suggest that very large concentrations of reactive Fe in tidally inundated ASS have exerted a substantial influence on sulfidisation processes and RIS speciation in the near surface materials. Strong positive relationships were observed between poorly crystalline Fe and AVS-S (r=0.86; *n*=48) and $S^0$-S (r=0.59; *n*=48) concentrations, significant at the 0.01 level, and are shown in Figure 2. This is consistent with abundant reactive Fe favouring the accumulation of AVS minerals and $S^0$ relative to that of pyrite in these soils. It also suggests that the accumulation of pyrite in tidally inundated ASS may be occurring slowly under the described geochemical conditions. The kinetics of RIS formation and speciation may reflect the relatively short time scale of remediation via tidal inundation (~5 y) at this site. The contemporary situation differs significantly from the adjacent environment (intertidal ASS mudflat cf. mangrove wetland), as there is now a far greater pool of reactive Fe in surface soils. This increase in the availability of reactive Fe has profound consequences for the coupled cycling of Fe and S, and is likely to cause a distinct hysteresis during the short-term accumulation of AVS minerals and $S^0$ and the reformation of pyrite over the longer term.

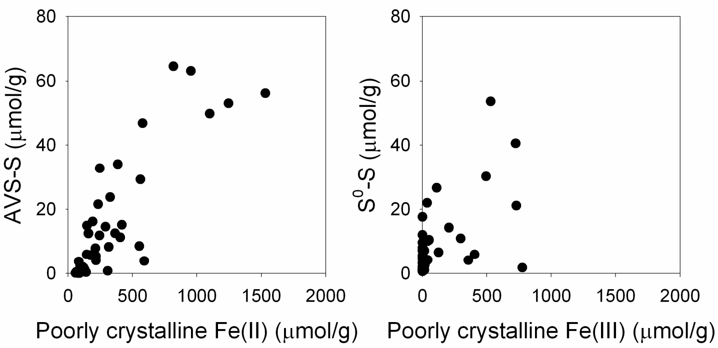

**Figure 2. Bivariate relationships of solid phase AVS-S (r=0.86) and $S^0$-S (r=0.59) with poorly crystalline Fe in tidally inundated ASS.**

## Conclusion

Large availability of reactive Fe favoured formation and accumulation of AVS and $S^0$ relative to pyrite, despite geochemical conditions being conducive to pyrite formation. This appears to be related to the shorter time scale of tidal inundation of ASS and is a consequence of early diagenesis. Reactive RIS fractions in surface soils are likely to oxidise rapidly and cause acidification were tidal inundation ceased. However, enrichment of reactive Fe suggests enhanced S sequestration within pyrite over the longer term.

## References

Berner RA (1970) Sedimentary pyrite formation. *American Journal of Science* **268**, 1-23.

Boesen C, Postma D (1988) Pyrite formation in anoxic environments of the Baltic. *American Journal of Science* **288**, 575-603.

Burton ED, Bush RT, Sullivan LA, Hocking RK, Mitchell DRG, Johnston SG, Fitzpatrick RW, Raven M, McClure S, Jang LY (2009) Iron-monosulfide oxidation in natural sediments: resolving microbially mediated S transformations using XANES, electron microscopy, and selective extractions. *Environmental Science & Technology* **43**, 3128-3134.

Burton ED, Sullivan LA, Bush RT, Johnston SG, Keene AF (2008) A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* **23**, 2759-2766.

Canfield DE (1989) Reactive iron in marine sediments. *Geochimica et Cosmochimica Acta* **53**, 619-632.

Johnston SG, Bush RT, Sullivan LA, Burton ED, Smith D, Martens MA, McElnea AE, Ahern CR, Powell B, Stephens LP, Wilbraham ST, van Heel S (2009a) Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine Coastal and Shelf Science* **81**, 257-266.

Johnston SG, Keene AF, Bush RT, Burton ED, Sullivan LA, Smith D, McElnea AE, Martens MA, Wilbraham S (2009b) Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* **149**, 335-346.

Kostka JE, Luther GW (1994) Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta* **7**, 1701-1710.

Morse JW, Rickard D (2004) Chemical dynamics of sedimentary acid volatile sulfide. *Environmental Science & Technology* **38**, 131A-136A.

Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* **51**, 149-164.

Thode-Andersen S, Jørgensen BB (1989) Sulfate reduction and the formation of $^{35}$S-labelled FeS, $FeS_2$, and $S^0$ in coastal marine sediments. *Limnology and Oceanography* **34**, 793-806.

# The effect of oven drying and grinding on the partitioning of copper and nickel in acid sulfate soil materials

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## Abstract

A sequential extraction procedure was applied to an acid sulfate soil profile to investigate the effect of sample preparation on the partitioning of copper and nickel. The samples were either used as collected (field condition) or subjected to the standard sample preparation, commonly applied to soils to be stored for subsequent analysis (i.e. oven drying and grinding). This effect was investigated both in the oxidised zone and unoxidised zones of the soil profile. Both sets of samples (i.e. oxidised and reduced) showed a substantial loss in the $HNO_3$-extractable fraction in the dried and ground soil materials, and in the reduced materials there was with a corresponding increase in the copper and nickel recovered in the $MgCl_2$ and HCl fractions. Based on these findings, it is recommended that when assessing metal partitioning, acid sulfate soil samples be analysed in their field condition.

## Key Words

Acid sulfate soils; metals; sample preparation; sequential extraction procedure

## Introduction

When analysing soils for metal content, the most common method of sample preparation is to sieve, then air-, oven-, or freeze-dry the soil; the dried material is then sieved and ground (Ahern *et al.* 2004; Klitzke and Lang 2007). Dried, ground soils are homogenous by nature, and the material is relatively stable over extended periods of time (Rao *et al.* 2008). By contrast, the analysis of field condition soils has a number of difficulties, including the inherent heterogeneity of soil materials, variable soil moisture content, as well as the need for a larger soil sample mass. For these reasons, dried, ground soils are often chosen for total metal analysis in preference to field condition soil samples (Furman *et al.* 2007; Rao *et al.* 2008).

The availability (in terms of the toxicity and mobility) of a given metal is linked to its geochemical form. Because of this, total metal concentrations give little indication as to the bioavailability, and hence toxicity of a metal (Gleyzes *et al.* 2002). When analysing a soil for the total metal content, the soil condition is not important – the aim of the procedure is to recover the maximum amount of a given metal present in the soil. When looking at partitioning and the various forms of the metal, sample preparation can have a potentially significant affect on the metal partitioning.

By gaining an understanding of how solid phase metals are stored in the soil some predictions can be made as to the present and future mobility and toxicity, and thus an assessment of potential environmental risk can be made. Sequential extractions can be useful in assessing phase associations of metals and other toxicants of interest. This approach, however, provides results that are only as representative as the samples being analysed. Acid sulfate soils contain a variety of soil redox conditions, from oxidising to reduced. As such, the mineralogy of redox sensitive components such as iron, sulfur and manganese, affect other metals present in the soil profile. The standard soil pretreatment of drying and grinding can potentially have a significant impact on the mineralogy of soils containing reduced minerals, and thus change the portioning of metals and other contaminants within the soil (Bordas and Bourg 1998).

The aim of this study was to assess whether metal partitioning, as measured by a sequential extraction procedure, was affected by the common pretreatment of drying and grinding.

## Methods

### *Sample Collection*

The study site is situated near Port Macquarie, NSW (31°25’38”S, 152°51’05” E). A pit was dug to 2.4 meters, and sampled in 13 depth increments, 7 situated in the oxidised zone and 6 in the unoxidised zone. Samples to be analysed as field condition were packed into acid-washed 150ml polypropylene containers, with no headspace, while soils to be dried, sieved and ground (standard treatment) were placed in sealed plastic bags, with the air extruded, and then transported frozen.

*Sample Analysis*

All glass- and plastic-ware was soaked in 10% (v/v) nitric acid and rinsed with deionised (Milli-Q) water before use. All reagents were analytical grade and solutions were prepared using Milli-Q water. Both sample pretreatments were subject to the same sequential extraction procedure (Table 1). The supernatant from each extraction step was analysed for copper and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-AES: Perkin-Elmer DV4300) or inductively coupled plasma-mass spectrometry (ICP-MS: Perkin-Elmer Optima 4000/30DV), calibrated using commercially available standards. Samples were first analysed using ICP-AES, and samples containing metal concentrations less than the detection limit were then analysed by ICP-MS.

**Table 1. Summary of the six step sequential extraction procedure used to assess metal fractionation.**

| Fraction | Treatment<br>(extractant, duration of extraction; or method) |
|---|---|
| 1. Exchangeable ($MgCl_2$) | 1M $MgCl_2$, 1 hour |
| 2. Acid Soluble (HCl) | 1M HCl, 4 hours |
| 3. Organic (Pyro) | 0.1M Sodium Pyrophosphate, 16 hours |
| 4. Crystalline oxide (CBD) | 0.35M Acetic Acid/0.2M sodium citrate buffer with 50g/L sodium dithionite, 4 hours |
| 5. Pyrite Bound ($HNO_3$) | Conc. $HNO_3$, 4 hours |
| 6. Residual (Res) | EPA method 3050, (hot acid and peroxide method) |

## Results and Discussion

Drying and grinding the soil affects the metal partitioning in both the oxidised and the unoxidised soil materials (Figure 1). In most cases, drying and grinding results in a greater percentage of the nickel or copper being extracted in the more environmentally available fractions (that is exchangeable and acid soluble). The exception to this was nickel extracted from the oxidised zone. This is a function of the far greater total amount of nickel extracted following the drying and grinding of the soil materials (average in the dried and ground samples was 24mgkg$^{-1}$, as opposed to 17mgkg$^{-1}$ in the field condition samples). Most of this “extra” nickel is recovered in the residual fraction, as a function of the drying and grinding, thus altering the partitioning patterns calculated through the percentage recovery.

In both the oxidised and the unoxidised soils, the field condition soils have a much larger proportion of the total metal in the $HNO_3$-extractable fraction. In this $HNO_3$ extracttion, metals are recovered through the dissolution of pyrite and other reduced sulfide minerals. Pyrite is stable under reducing conditions, and thus oxidation of the reduced materials can lead to an increase in the amount of a metal in more available fractions (Bordas and Bourg 1998), – this was observed in this study. The decrease in the amount of $HNO_3$-extractable copper and zinc in the samples is commensurate with the increase in $MgCl_2$- and HCl-extractable copper and zinc in the oven dried and ground samples.

There was a substantial decrease in pyrophosphate-extractable copper following drying and crushing of the soil materials. This was observed in both the oxidised and reduced soil samples. Copper has a strong affinity for organic matter (McLaren and Crawford 1973), and the oxidation of the organic matter can lead to metal release from more environmentally available phases (Stephens *et al.* 2001). The opposite is obseved for nickel, with a slight increase in the proportion of nickel extracted with pyrophosphate in the oven dried sediments. Nickel does not have such a strong association with the organic fraction, and this increase may be due to the oxidation of more recalcitrant organic fractions, made available in pyrophosphate during the drying and grinding process.

The percentage recovery of both copper and nickel was observed to increase in residual fraction following the drying and grinding procedure. This is most like likely due to the greater surface area of the soil material, the exposure of previously protected mineral surfaces, as well as oxidation through the drying process. Sample grinding may also expedite the oxidation of the soil materials.

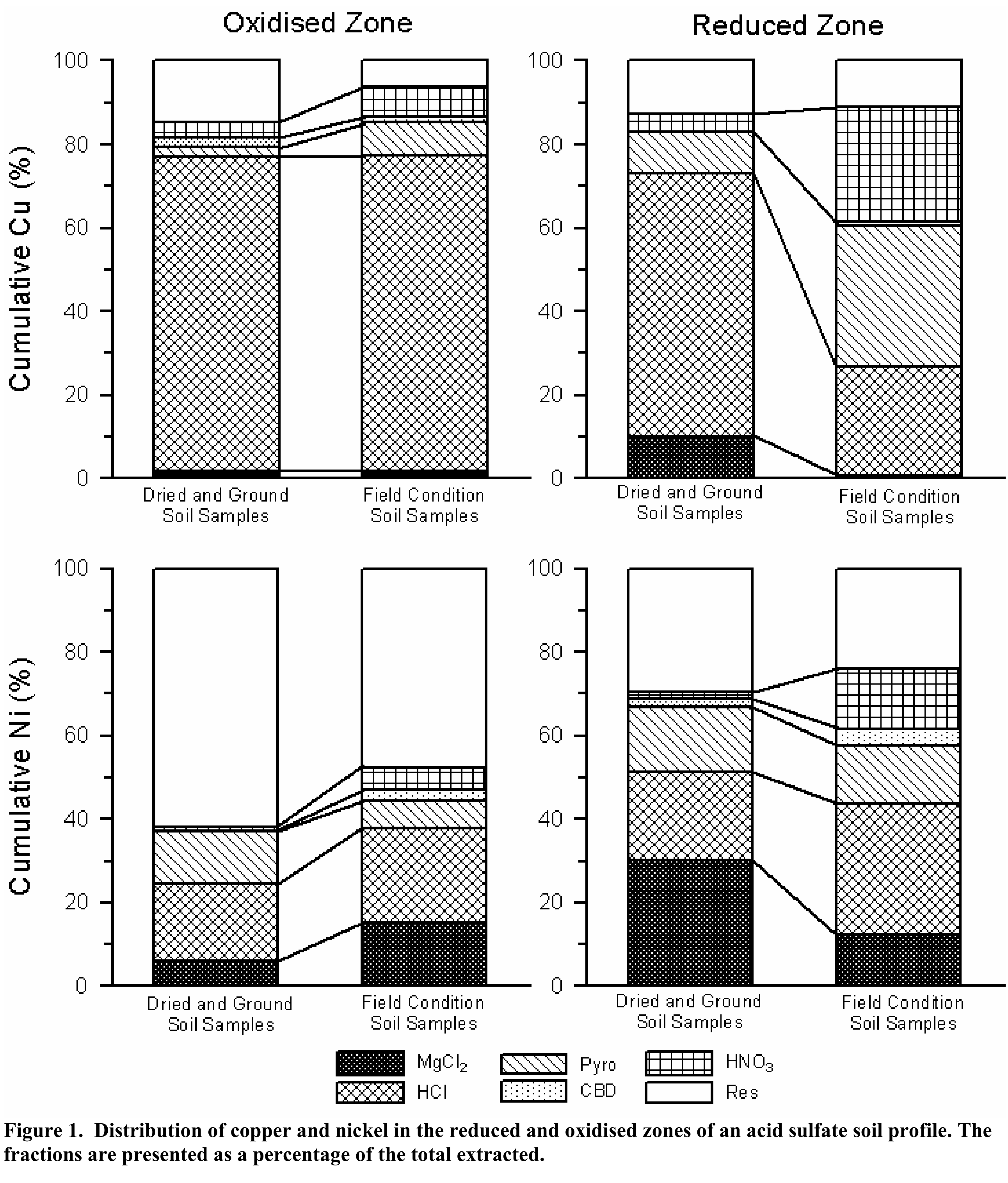

**Figure 1. Distribution of copper and nickel in the reduced and oxidised zones of an acid sulfate soil profile. The fractions are presented as a percentage of the total extracted.**

## Conclusion

Drying and grinding significantly affected the determination of metal partitioning in the examined soil materials. This was especially apparent in the reduced materials, where there was a decrease in the $HNO_3$ (pyrite) extractable fractions, and a redistribution to the $MgCl_2$- and HCl-extractable fractions, both more readily available forms. The results indicate that the use of dried and ground soil materials has the potential to overestimate the biological impact of metals in a soil material, and marginalise the effect of metals associated with reduced sulfide phases (i.e. pyrite). Based on these findings, it is recommended that soil samples be used in field condition when assessing the potential impact of metals in acid sulfate soil landscapes.

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## References

Ahern CR, McElnea AE, Sullivan LA (2004) Acid Sulfate Soils Laboratory Methods Guidelines. In 'Queensland Acid Sulfate Soils Manual'. *(*Department of Natural Resources, Mines and Energy: Indooroopilly, Queensland, Australia).

Bordas F, Bourg AM (1998) A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load. *Water Air and Soil Pollution* **103**, 137-149.

Furman O, Strawn DG, McGeehan S (2007) Sample drying effects on lead bioaccessibility in reduced soil. *Journal of Environmental Quality* **36**, 899-903.

Gleyzes C, Tellier S, Astruc M (2002) Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trends in Analytical Chemistry* **21(6-7)**, 451-467.

Klitzke S, Lang F (2007) Hydrophobicity of soil colloids and heavy metal mobilization: Effects of drying. *Journal of Environmental Quality* **36**, 1187-1193.

McLaren RG, Crawford DV (1973) Studies on soil copper 1. The fractionation of copper in soils. *Journal of Soil Sciences* **24(2)**, 172-181.

Rao CRM, Sahuquillo A, Sanchez JE (2008) A review of different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water, Air and Soil Pollution* **189**, 291-33.

Stephens SR, Alloway BJ, Parker A., Carter JE, Hodson ME (2001) Changes in the leachability of metals from dredged canal sediments during drying and oxidation. *Environmental Pollution* **114**, 407-413.

# The effects of increasing salinity on exchange processes in coastal lowland acid sulfate soils

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## Abstract

10 coastal lowland acid sulfate soils (CLASS) from floodplains in eastern Australia were subjected to increasing seawater concentrations to determine the effects of exchange processes on metal desorption due to increasing ionic strength. Soils were subjected to one of six treatments; 0%, 10%, 20%, 50%, 80% or 100% seawater diluted in deionised water. pH decreased with increasing seawater concentration. In general, concentrations of Al, Cd, $Fe^{2+}$ and Mn increased in soils sampled from levees, organic and mineral sulfuric horizons with increasing salinity. Increasing trace metal concentrations with increasing seawater concentration is attributed to both exchange processes and pH effects. The increasing ionic strength of the seawater treatments displaced trace metals and protons adsorbed on sediments. These processes have implications for rapid water quality changes in CLASS environments when subjected to seawater inundation.

## Key Words

Climate change, sea level rise, desorption

## Introduction

Coastal lowland acid sulfate soils (CLASS) frequently contain high concentrations of acidity and trace metals. These soils commonly occur in large, low elevation (0-1 m Australian Height Datum; AHD) backswamp basins on coastal floodplains in eastern Australia. In these backswamp locations, the mineral sulfuric horizon is frequently close to the surface (< 1 m) capped by a thin layer of fluvial sediments and hence, can be an important contributor to surface water quality due to upward capillary and advection processes. Increasing ionic strength as a result of seawater inundation will alter decomposition and geochemical processes in sediments, surface- and groundwaters. In particular, the addition of seawater can increase the concentrations of aqueous $Fe^{2+}$, Al and Si (Mkadam *et al.* 2006; Portnoy and Giblin 1997) and decrease pH (Wright *et al.* 1988). Previous studies have shown that reflooding of CLASS can result in reductive mobilisation of a number of trace metals, which has implications for water quality in these areas (Burton *et al.* 2008).

Due to the low elevation and location of these backswamp basins, which are at, or below sea level, there is a high susceptibility to pulses of saline water caused by saltwater intrusion, storm surge, king tides and rising sea levels. This risk will increase in the future with predicted increases in sea level and extreme events due to climate change. This study aims to determine the effects of increasing ionic strength on exchange processes and trace metal desorption caused by increasing salinity in CLASS sediments.

## Materials and Methods

### *Site Description and Field Sampling*

Soils were sampled from three CLASS backswamp located on estuarine Holocene sediments; Tuckean (Tuck), Rocky Mouth Creek (RMC) and Shark Creek (SC), in the sub-tropical region of eastern Australia. The Tuckean and Rocky Mouth Creek backswamps are located in the mid-estuary of the Richmond River. The Shark Creek backswamp is located in the lower Clarence River estuary.

Bulk soils were sampled from three horizons at each site; levee, organic and mineral sulfuric horizons. Each levee horizon was sampled from the 0 – 0.1 m depth and was located on a natural levee of the CLASS backswamp. The organic horizon was sampled from the 0 – 0.1 m depth and located in the CLASS backswamp. An additional organic horizon was sampled in a forest dominated by tea tree (*Melaleuca quinquenervia*) at the SC site (termed SC Melaleuca). The mineral sulfuric horizon was sampled from the same location as the organic horizon, and characterised by the presence of jarosite. This horizon occurred at a depth of 0.6-0.8 m at the Tuck and SC sites, and 0.7-0.9 m at the RMC site. Samples were placed into polyethylene bags and stored at 4°C until analysis.

*Sample Preparation and Laboratory Analysis*

Bulk soils were oven-dried at 40°C for 48 hours and lightly crushed to pass through a 2 mm sieve. Soil pH, EC and soluble cations were determined on 1:5 soil: water extracts (Rayment and Higginson 1992). Exchangeable cations were extracted with 1:5 soil:2M $BaCl_2/NH_4Cl$ (Rayment and Higginson 1992). Where the $EC_{1:5} \geq 0.3$ dS/m, soluble salts were removed by washing three times with an ethanol/glycerol solution. Soluble and exchangeable cations were determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Samples were subjected to one of six treatments; 0, 10, 20, 50, 80 or 100 % synthetic seawater. The synthetic seawater consisted of the major cations and anions found in natural seawater (Cavanaugh 1975). 5 g of soil was extracted with synthetic seawater at a ratio of 1:10. Samples were shaken on an orbital shaker for four hours, centrifuged and filtered through a 0.45 µm filter. The extracts were analysed for pH and EC. Major cations and trace metals were determined on the extracts by ICP-MS. Aqueous Fe speciation was determined using 1, 10-phenanthroline (APHA 2005). $Fe^{3+}$ was determined from the difference between total Fe and $Fe^{2+}$ following reduction with hydroxylammonium chloride.

## Results and Discussion

The bulk soil characteristics are shown in Table 1. The levee soils had higher pH and lower EC compared to the organic and mineral sulfuric soils from the same site. The organic and mineral sulfuric soils were saline and acidic with high concentrations of soluble and exchangeable Al.

**Table 1. Soil characteristics prior to treatment.**

| Horizon | Site | $pH_{1:5}$ | $EC_{1:5}$ (dS/m) | Soluble | | | | Exchangeable | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Al | Cd | Fe | Mn | Al | Cd | Fe | Mn |
| | | | | | (mmol/kg) | | | | $(cmol_c/kg)$ | | |
| Levee | RMC | 5.68 | 0.06 | 7.07 | nd | 3.49 | 0.25 | 22.0 | 0.01 | 0.00 | 283.06 |
| | Tuck | 4.96 | 0.08 | 1.81 | nd | 0.68 | 0.31 | 370.8 | 0.00 | 0.00 | 46.68 |
| | SC | 5.57 | 0.08 | 3.00 | nd | 1.71 | 0.19 | 20.4 | 0.09 | 0.00 | 51.15 |
| Organic | RMC | 3.68 | 1.26 | 122.76 | nd | 0.53 | 2.23 | 2045.7 | 0.00 | 0.00 | 4.07 |
| | Tuck | 3.99 | 0.98 | 28.94 | nd | 1.47 | 3.68 | 990.2 | 0.01 | 0.00 | 11.10 |
| | SC | 4.43 | 0.53 | 2.49 | nd | 0.21 | 0.78 | 541.8 | 0.01 | 0.00 | 11.74 |
| | SC Melaleuca | 3.61 | 1.85 | 44.61 | nd | 1.86 | 6.85 | 1150.3 | 0.01 | 13.83 | 18.85 |
| Mineral sulfuric | RMC | 3.31 | 1.58 | 95.08 | nd | 1.79 | 2.26 | 1791.4 | 0.00 | 0.61 | 4.13 |
| | Tuck | 3.26 | 1.56 | 58.47 | nd | 5.12 | 5.10 | 1309.9 | 0.00 | 19.57 | 9.39 |
| | SC | 3.96 | 0.33 | 0.69 | nd | 0.09 | 0.53 | 852.4 | 0.00 | 0.00 | 7.74 |

EC was lowest in the 0% seawater treatment in all horizons at all sites, and increased following treatment with increasing seawater concentration due to the addition of soluble salts (Figures 1a, 1b and 1c). In the levee sediments, pH decreased with increasing seawater concentration, reaching a minimum with the 20% treatment (Figure 1). In the mineral sulfuric sediments, samples from Shark Creek showed a similar trend, decreasing with increasing seawater concentration to a minimum in the 20% treatment. Conversely, pH in sediments from RMC and Tuck showed little change between treatments. Similarly, in the organic horizon, the pH of sediments from RMC and Tuck showed little change between treatments, while those from RMC and SCM decreased with increasing seawater concentration to a minimum with the 20% seawater treatment.

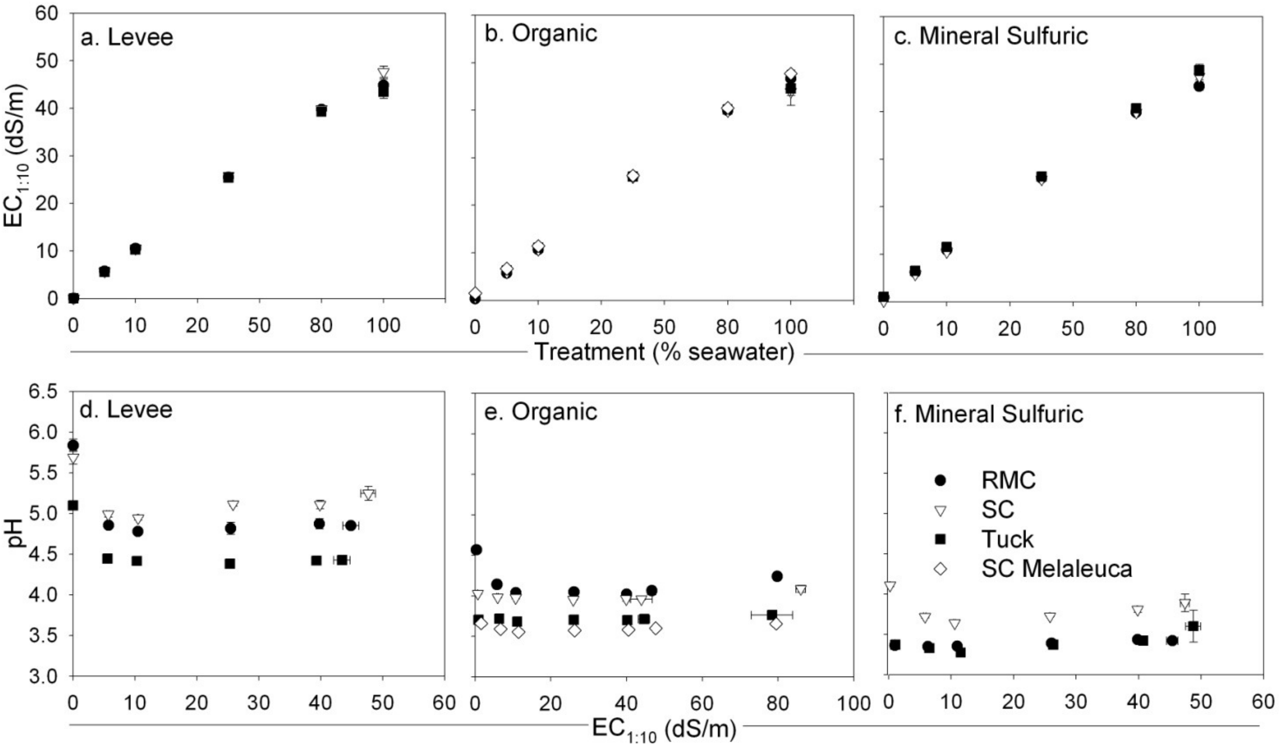

**Figure 1. $EC_{1:10}$ of soil extracts following treatment with seawater in sediments from a) levee; b) organic, and c) mineral sulfuric horizons; and $pH_{1:10}$ of soil extracts following treatment with seawater in sediments from d) levee; e) organic, and f) mineral sulfuric horizons. Error bars indicate standard deviation.**

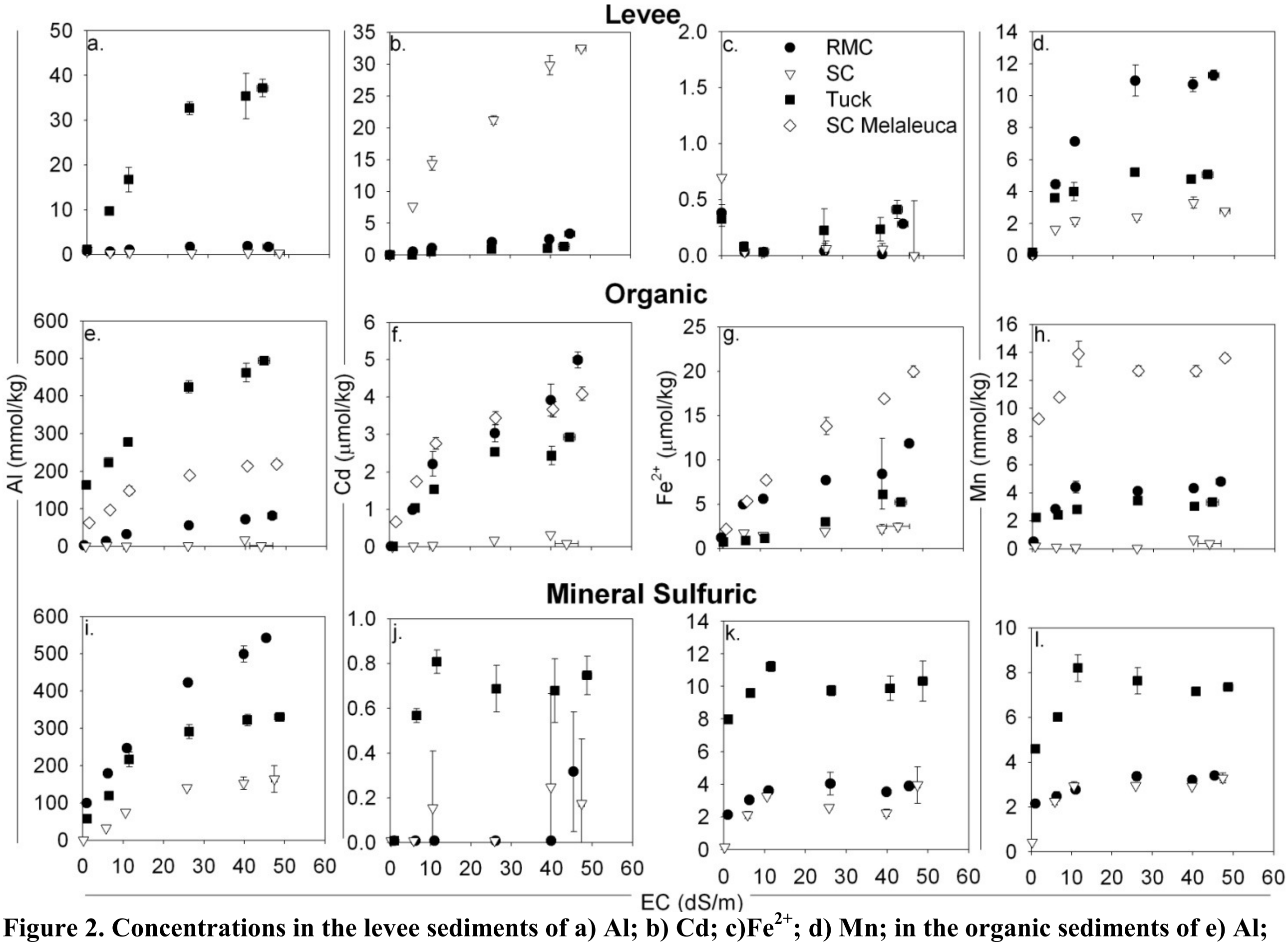

**Figure 2. Concentrations in the levee sediments of a) Al; b) Cd; c)$Fe^{2+}$; d) Mn; in the organic sediments of e) Al; f) Cd; g)$Fe^{2+}$; h) Mn; and mineral sulfuric sediments of i) Al; j) Cd; k)$Fe^{2+}$; l) Mn following treatment with seawater . Error bars indicate the standard deviation.**

In the levee sediments, Al concentrations increased with increasing EC at RMC and Tuck sites (Figure 2a). The Tuck site had the highest exchangeable Al concentrations in the levee sediments compared to RMC and SC sites. Cd concentration increased with increasing salinity, and was at least six times higher compared to other horizons at the same site. Similarly, in the levee sediments at the RMC and Tuck sites, Cd concentrations increased with increasing salinity but were substantially lower than that found at the SC site (Figure 2b). Concentrations of Mn increased with increasing seawater concentration to 50% seawater at all sites in the levee sediments (Figure 2d).

In the organic horizon sediments, Al concentrations increased with increasing salinity and were substantially higher than the concentrations found in the levee soils at the same site (Figure 2e). Cd concentrations increased with increasing salinity at the SC and SC Melaleuca sites (Figure 2f). At the RMC and Tuck sites, Cd concentrations increased with salinity to the 50% seawater treatment. Similarly, $Fe^{2+}$ concentrations increased with increasing salinity (Figure 2g). The organic soils have the potential to release much more iron into solution compared to the other horizons. These soils released the highest concentrations of $Fe^{2+}$ to solution, despite having generally lower soluble $Fe^{2+}$ concentrations (Table 1). Mn concentrations generally increased with increasing salinity to the 20% seawater treatment in the organic horizon sediments (Figure 2h).

In the mineral sulfuric sediments, Al concentrations increased with increasing salinity and were an order of magnitude higher than the levee sediments from the same site (Figure 2i). $Fe^{2+}$ concentrations increased with increasing salinity to 20% seawater at all sites (Figure 2k). Cd concentrations were generally lower in the mineral sulfuric sediments than the organic sediments at the same site (Figure 2j). Mn concentrations in this horizon showed a similar pattern to that found in the organic horizon sediments, increasing with salinity to 20% seawater treatment.

Increasing seawater concentration resulted in decreases in pH in all sediments. This is attributed to the displacement of adsorbed protons on the exchange surface. The higher ionic strength solution displaces those ions adsorbed on the surface of the soil particles. We suggest that the desorption of some pH dependent species such as Al and Fe are also partially driven by the decline in pH in addition to increasing ionic strength of the treatment solution. Similarly, the specific adsorption of Cd is also strongly pH dependent.

These exchange processes have implications for water quality in these environments. CLASS are highly susceptible to seawater inundation as a result of climate change induced sea level rise, while seawater intrusion at depth will impact on the mineral sulfuric sediments. The experimental results show that the initial addition of marine derived salts will result in a decrease in pH and increase in trace metals, even at low salt concentrations such as that found in brackish waters in estuarine environments.

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## References

APHA (2005) 'Standard methods for the examination of water and waste water.' (American Public Health Association, American Wastewater Association, World Environment Fund: Washington DC, USA).

Burton ED, Bush RT, Sullivan LA, Johnston SG, Hocking RK (2008) Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* **253**, 64-73.

Cavanaugh GM (1975) 'Formulae and methods VI of the Marine and Biological Laboratory Chemical Room, 6th Edition.' (Marine Biological Laboratory: Woods Hole).

Mkadam KM, Yonaha T, Al VA, Tokuyama A (2006) Dissolved aluminum and silica release on the interaction of Okinawan subtropical red soil and seawater at different salinities: Experimental and field observations. *Geochemical Journal* **40**, 333-343.

Portnoy JW, Giblin AE (1997) Biogeochemical effects of seawater restoration to diked salt marshes. *Ecological Applications* **7**, 1054-1063.

Rayment GE, Higginson FR (1992) 'Australian Laboratory Handbook of Soil and Water Chemical Methods.' (Inkata Press: Australia).

Wright RF, Norton SA, Brakke DF, Frogner T (1988) Experimental verification of episodic acidification of freshwaters by sea salts. *Nature* **334**, 422-424.