

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

Sylvia Warnecke<sup>A</sup>, Col Ahern<sup>B, C</sup>, Angus McElnea<sup>B, C</sup>, Freeman Cook<sup>D</sup>, Heiner Fleige<sup>E</sup> and Rainer Horn<sup>E</sup>

<sup>A</sup>Institute for Spatial Analysis and Planning in Areas of Intensive Agriculture, University of Vechta, Vechta, Germany, Email [swarnecke@ispa.uni-vechta.de](mailto:swarnecke@ispa.uni-vechta.de)

<sup>B</sup>Queensland Department of Environment and Resource Management, Indooroopilly, QLD, Australia, Email [Col.Ahern@derm.qld.gov.au](mailto:Col.Ahern@derm.qld.gov.au)

<sup>C</sup>CRC CARE, Salisbury South, South Australia 5106, Australia, Email [Col.Ahern@derm.qld.gov.au](mailto:Col.Ahern@derm.qld.gov.au)

<sup>D</sup>CSIRO Land and Water, Indooroopilly, QLD, Australia, Email [freeman.cook@csiro.au](mailto:freeman.cook@csiro.au)

<sup>E</sup>Institute of Plant Nutrition and Soil Science, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, Email [rhorn@soils.uni-kiel.de](mailto:rhorn@soils.uni-kiel.de)

## 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

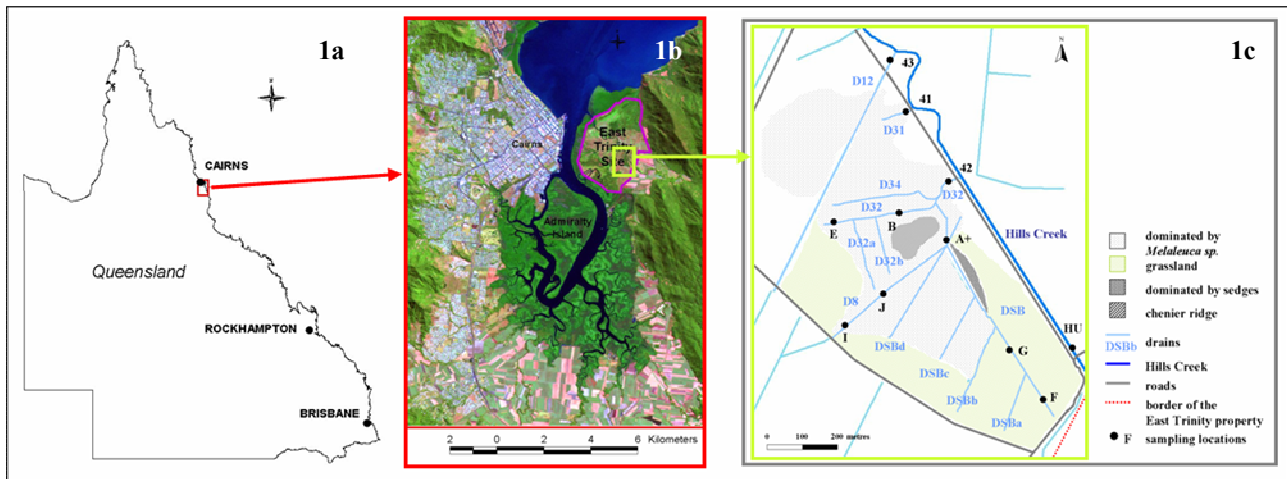
A rigorous management program is crucial to alleviate acid sulfate soils' (ASS) impacts if disturbance has occurred or must be undertaken. A special challenge is presented by broadacre degraded coastal wetlands that have not been under any use for sometimes decades since bunding and drainage, but still 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 15<sup>th</sup> 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 ( $\text{Fe}^{2+}$ ), 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.

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

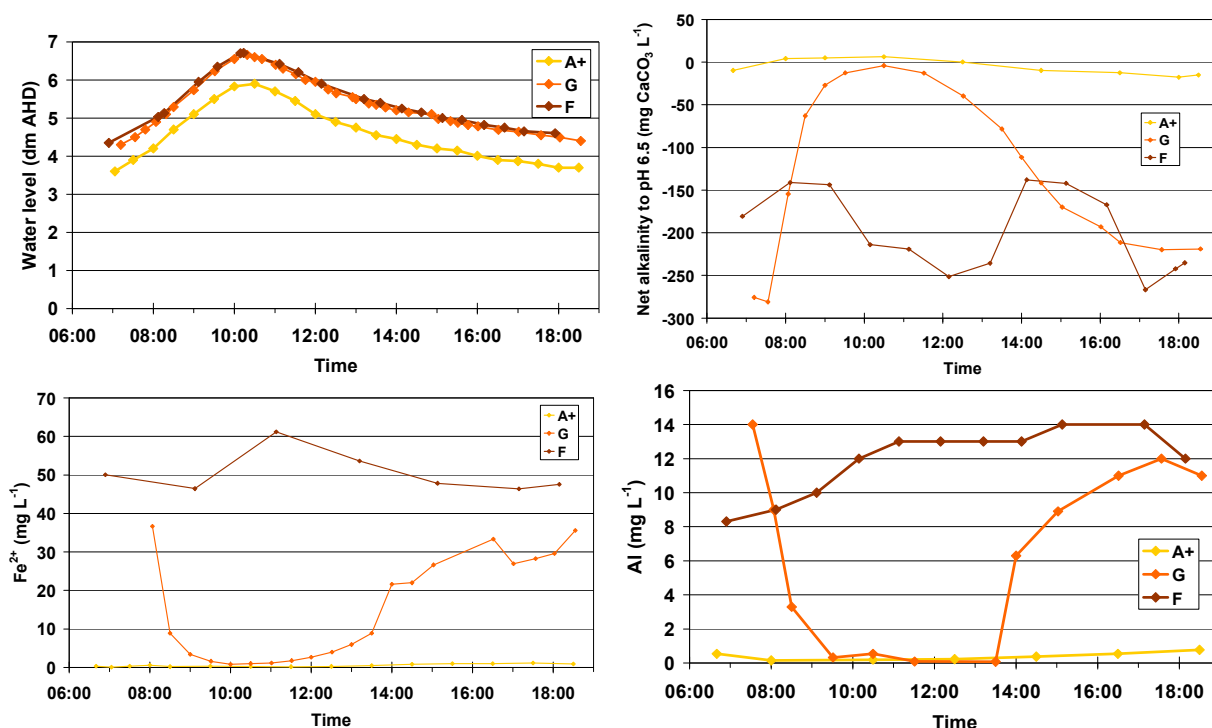
The semi-quantitative Ferrozine test is used for the photometric determination of aqueous ferrous ion ( $\text{Fe}^{2+}$ ). The sub-sample was sucked up into a 60 mL Terumo plastic syringe and filtered with a syringe filter with 0.45  $\mu\text{m}$  pore diameter (Sartorius minisart syringe filters or 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,  $\text{Fe}^{2+}$  and total dissolved Al on 15<sup>th</sup> 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,  $\text{Fe}^{2+}$  concentrations and total dissolved Al concentrations as determined for the sampling locations along DSB during a full tidal cycle sampling day on 15<sup>th</sup> 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  $2.4 \text{ mol H}^+ \text{ m}^{-3}$  (equalling  $120.1 \text{ mg L}^{-1} \text{ CaCO}_3$  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  $\text{Fe}^{2+}$  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.

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