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Final Progress Report for the Australian Research Council Linkage Project LP110100480

FINAL

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Executive Summary

This report principally focuses on the main practicable outcomes of the three year Australian Research Council (ARC) Linkage project LP110100480 'Exploiting Natural Processes to Effectively Remediate Acidified Coastal Environments' which commenced in 2011 with industry partners the Tweed Shire Council, NSW Cane Growers' Association and NSW Sugar Milling Co-operative. The report encapsulates findings presented at the final annual project meeting held in Murwillumbah on the 7th May, 2014.

The main aims of the project were to:

1) Undertake research which identified acid sulfate soil (ASS) hotspots within three catchments in the Tweed Shire and then the most suitable remediation strategies to reduce ASS discharge on a catchment scale - with a focus on exploiting low-cost and long-term natural solutions;

2) Implement on-ground remedial works or changed land/drain management practices identified in (1) above; and

3) Conduct field measurements to determine the efficacy of the remedial works in reducing the discharge of problematic contaminants (particularly iron and aluminium) from the three catchments.

The major outcomes of the project in the three catchments were as follows:

Black's Drain – It was determined that the remediation undertaken by Tweed Shire Council and landholders in 2009/2010 (main drain shallowing and scald capping) has effectively decreased ASS discharge from this catchment by at least a factor of 5 and has been very successful. Recent monitoring in 2014 has indicated that a secondary acid scald in the catchment, revegetated in 2008, was only partially successful and acidic water was also being discharged from further upstream. Although ASS discharge from this site was not detected where the drain entered the Tweed River, further consideration could be given to re-capping and re-vegetating this scald as well as further characterisation of acid sulfate soil issues in the upstream valley east of where the remediation was undertaken.

Christie's Creek – Previous research had identified a hydraulically-isolated cane block that was disproportionally contributing to ASS discharge in this creek. Recommendations to changes in water management have been gradually implemented at this site by the landholder, with the assistance of Tweed Shire Council, over the course of the project. In 2011, partial shallowing of one of the main drains was completed and a liming trail was undertaken. Studies showed that neither were sufficient to overcome poor water quality being discharged into Christies Creek from this site. In April 2014, the pumping regime was modified so that less acidic water would be pumped into the creek with further scope for shallowing of the remainder of the main drains. Monitoring of drain water quality and levels are continuing to assess the impacts of these (and future) changes to the site. Recent observations in 2014 indicated poor water quality in Christies Creek that was unrelated to this site. A secondary ASS 'hotspot' site that had been identified in previous research should be further investigated once work is completed in the hydraulically-isolated cane block.

Clothier's and Reserve Creeks – Field studies between 2012 and 2013 identified a number of problematic ASS sites in the catchment(s) which drain into Cudgen Lake. However, land west of the Pacific Highway draining into Clothiers Creek does not contribute to ASS discharge. The first priority site recommended for remediation was on Reserve Creek just upstream (west) of the pacific highway. Despite attempts of the Tweed Shire Council to engage previous and present landholders into

undertaking remediation at this site, no recommended works have been undertaken. In response, other areas in the catchment contributing to ASS discharge were further characterised. Water quality monitoring, plant sampling, soil surveys and visual observations indicated that it is the drains of Reserve Creek east of the Pacific Highway that are principally implicated in poor water quality. As the drainage is poor through this area of the catchment, flooding regularly results in the biodegradation of water-intolerant plant species and the formation of 'black water' and monosulfidic black ooze (MBO). It also appears that the MBO forms, or becomes trapped in vegetation 'mats' lining the side of the drains. During dry spells, drain water levels recede and the MBO oxidises resulting in the production of acidity and ASS oxidation products. As a result, it is suggested: 1) the blockage downstream be removed to minimise the severity of black water events and the formation of MBO; 2) the vegetation 'mats' be removed regularly through on-going drain maintenance with the spoil being limed as per standard practices and; 3) that long-term solutions to reduce the surface area of ASS in the drains being cyclically oxidised during dry spells. The water quality monitoring stations installed by Tweed Shire Council should remain in Reserve Creek to observe any changes in water quality in response to the on-ground works that are undertaken.

Introduction and Background

In November 2010 it was announced by the Australian Research Council (ARC) that the Linkage project LP110100480 'Exploiting Natural Processes to Effectively Remediate Acidified Coastal Environments' was awarded funding for 3 years for collaborative research between the University of New South Wales (UNSW), the Tweed Shire Council, NSW Cane Growers' Association and NSW Sugar Milling Co-operative. Funding for the project commenced in January 2011 and previous stakeholder meetings were held on the 28th January 2011 and 27th March 2012 at the Tweed Shire Council depot, Murwillumbah and the 20th March 2013 at Craig King's shed, Christies Creek (Figure 1). The results outlined in this report were presented to all stakeholders on the 7th May 2014 at the final meeting of the project which was held in the Mt Warning Room, Murwillumbah Civic Centre, Murwillumbah.

Figure 1: 2nd Annual General Meeting of the project on 20th March at Craig King's shed, Christie's Creek.

At the commencement of the project the three catchments in the Tweed Shire, identified as acid sulfate soil hotspots, were in various stages of investigation and remediation.

Black's Drain, a highly-modified tributary of the Tweed River, was remediated in 2009/2010 as an outcome of the research findings from a previous ARC Linkage project LP0455697 which ran from 2005-2008 (Collins et al. 2009). Major remediation work was conducted by the Tweed Shire Council in collaboration with landholders Jim and Les Dickinson within the pasture section of the catchment (drain infilling, drain widening and shallowing, drain bank revegetation, acid scald capping and liming, stock exclusion, and the construction of packed-bed limestone channels) whilst only minor adjustments to the downstream sugarcane section were made on the Stainlay's property (drain bank revegetation). Significant pre-remediation data existed on this catchment from research activities conducted in LP0455697. The aim of this project was to identify if the remediation works were successful.

Christie's Creek is a coastal catchment dominated by sugar cane cultivation and pasture in the upper catchment and native forest and residential areas in the lower catchment. During the three years prior to the commencement of this project, this catchment had come to the attention of the Tweed Shire Council owing to the occurrence of fish kills, heavy iron flocs and, more recently, arsenic concentrations exceeding ANZECC (2000) water quality guidelines (Kinsela et al. 2009a). The source of the arsenic and indeed other contaminants identified in the catchment (iron and aluminium) was the underlying ASS (Kinsela et al. 2009b). No remediation work at Christie's Creek had been carried out prior to this project, although a limited-scale monitoring program had been established in this catchment in 2009/2010 with the collaboration of landholders Ross Hardy, Ray Dooley, Craig King and Mr and Mrs Colin Love. Based on these field studies, a hydraulically-isolated sugar cane block in the downstream portion of Christie's Creek was selected as the first priority for remediation. Remedial works proposed for this area included a) optimisation of the drain pumping regime discharging into Christie's Creek, and b) drain shallowing of the 2 major drains at least to the invert of the field drains (Kinsela et al. 2011). The aim of this project was to implement the recommended remediation strategies and monitor their effectiveness.

Cudgen Lake (Clothier's & Reserve Creeks) is the coastal catchment immediately south of the Tweed River and has been the subject of previous research and remediation studies (e.g. Australian Research Council LP0219475 & NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004). Cudgen Lake has been subjected to poor water quality over many years, due to the construction of an adjacent golf course and residential development that was abandoned before its completion. This resulted in major fish kills in 1991 and 1998, and an overall degradation of aquatic life. Research from LP0219475 had shown that the problem was mainly due to rain-induced discharges from oxidising ASS in the catchment (Macdonald et al. 2004). The Hot Spot Remediation Program resulted in approximately 6 km of drains being filled and almost 11,000 m^2 of severely degraded 'acid scald' being remediated. Despite these measures, large fish kills continued to occur within Cudgen Lake and adjoining waterways (Perkins 2010). The aims of this project were to identify how successful were aspects of previous remediation programs, (re)identify ASS hot spots within this catchment, develop strategies for their remediation and post-remediation monitoring. This activity was, by far, the largest proposed for the project.

Many of the outcomes from this project have been previously reported (Stroud et al. 2013; Stroud and Collins 2013; Collins et al. 2012). Being the final report, these outcomes are briefly reiterated here as well as the findings of field studies undertaken since the last meeting in March 2013.

UNSW Project Personnel

Funding of the project allowed for the employment of Dr Jackie Stroud (August 2011 – July 2014) as a Research Associate who lead the field studies and the day-to-day management of the project. She also obtained Early Career Funding from UNSW which enabled her to perform laboratory studies including the development of new methods to improve the spatial resolution of field monitoring in ASS (Stroud and Collins 2014a) and studies into the microbial ecology of acid sulfate soils and sulfidic drain sediments (Stroud et al. 2014).

A PhD stipend, funded by the project, was awarded to Miss Yliane Yvanes-Giuliani and she commenced studies into ASS aluminium geochemistry, as a co-tutelle program between UNSW and the University Aix-Marseilles, France, in March 2011. She also obtained an Australian Nuclear Science and Engineering top-up scholarship in July 2011 which has facilitated the use of certain scientific instruments at the Australian Nuclear Science and Technology Organisation (ANSTO). Her expected PhD thesis submission date is September 2014.

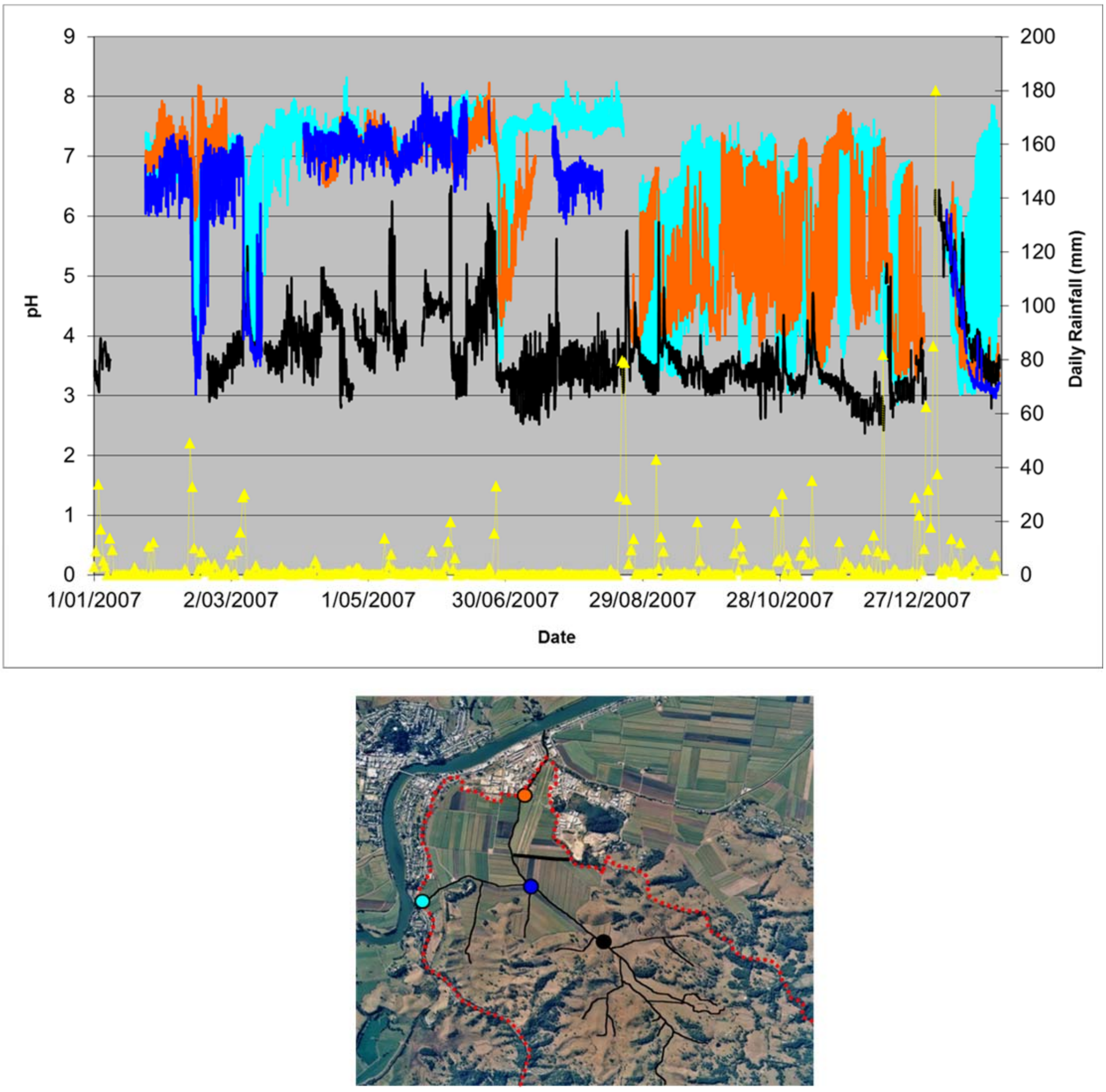
Dr Richard Collins was lead chief investigator (CI) of the project and contributed to both laboratory and field research activities of Jackie and Yliane. His role (at 0.2 FTE) in the project was not remunerated from project funding.

Results

Black's Drain

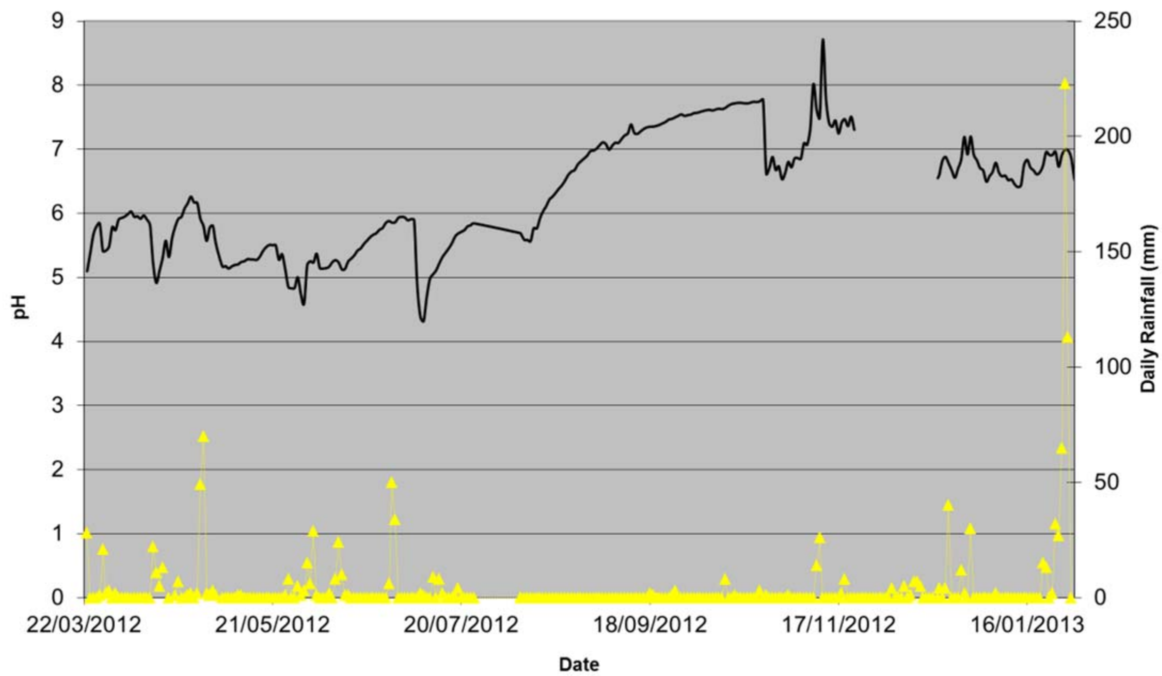
Figure 2 is an example of long-term water quality monitoring data from Black's Drain pre-remediation. One of the main conclusions from this data was that the water quality, in this case pH, was consistently poor at the water quality monitoring station (WQM) sited in the upper-most part of the catchment, having an average yearly pH of 3.7 for 2007. Further drain water sampling during two rainfall events corroborated these findings (Collins et al. 2009).

Figure 2: Drain water pH values and 24 hr rainfall totals during 2007 at various sites along Black's Drain. The data are colour-coded to the sites shown in the aerial image below the graph (Collins et al. 2009).



Water quality monitoring at the same site during 2012, two years after remediation, showed a marked improvement in drain water pH with an average pH of 6.3 measured over the course of one year (Figure 3). Rainfall event sampling in Black's Drain was also undertaken in November 2011 and February 2013. Typically ASS discharge events after rainfall result in either (initially high pH) iron or (low pH) aluminium events. The former generally occurs during the wet season while the latter typically occurs after a prolonged dry spell. Pre-remediation data captured an 'aluminium' and an 'iron' discharge event (Table 1). The results clearly showed that there was an ASS problem in this catchment. In Table 1 are also results from rainfall event sampling post-remediation in 2011 and 2013. The event in 2011 was expected to be an 'iron' event, but it can be seen in Table 1 that the concentration of iron being discharged was 22-fold less than the comparable pre-remediation 'iron' event. The rainfall event monitored in 2013 was expected to be an 'aluminium' event as the preceding months had been very dry. However, no appreciable quantities of aluminium were measured, but there was some iron discharge. Nevertheless, the iron concentration was still ~7 fold less than the comparable 'iron' pre-remediation event in 2008.

Figure 3: Drain water pH values in Black's Drain for one year during 2012/2013 at the site marked in black in Figure 2.



Based on these results it was concluded that the remediation activities undertaken in 2009/2010 were extremely successful. Recent monitoring, however, in March/April 2014 (Hamish Brace, pers. comm., 2014) indicated that a secondary acid scald in the catchment (Figure 4), that was revegetated by the Tweed Shire Council in 2008, was only partially successful. Low pH values were also recorded in Black's Drain receiving water from further upstream (i.e. the remediated site and an upstream valley east to this site). Previous studies during the Australian Research Council project LP0455697 have shown that water draining from the eastern upstream valley is also affected by acid sulfate soil discharge. Although water quality was still good where Black's Drain entered the Tweed River, further consideration could be given to re-capping and re-vegetating this scalded site as well as further characterising the acid sulfate soil issues in the upstream valley east to the main drain where remedial works were undertaken in 2009/2010.

Table 1: Aluminium and iron export during rainfall events from Black's Drain before and after remediation in 2009/2010. The metal export, expressed as a concentration here, was determined by dividing the total quantity of metal exported by the total volume of water discharged over the measuring period (7-10 days). This was required to be able to directly compare rainfall events.

Date of event	Metal export (tonnes/GL)	
	Aluminium	Iron
Pre-remediation		
August 2007	9	2
January 2008	4	55
Post-remediation		
November 2011	~0	2.5
February 2013	~0	8

Figure 4: Aerial image of the upper catchment of Black's Drain indicating the site of the acid scalded area. The industrial estate is just north of the scald.

Christie's Creek

As detailed in the reports of Kinsela et al. (2009b) and Kinsela et al. (2011), recommended remediation activities at the hydraulically-isolated cane block involved drain shallowing of the two major drains and modifications to the employed water pumping regime into Christie's Creek. A compromise was reached with the landholder to initially shallow a portion of the major drain running east-west, stabilise the drain batters of the major north-south drain and to conduct a liming trial (Kinsela and Collins 2011). It can be seen from Figure 5 that the liming trial did not result in an improvement in soil pH. However, a marked (visual) improvement in drain sediment quality was observed where drain shallowing of the major east-west drain had been undertaken (Figure 6), e.g. no observation of ASS oxidation products.

Figure 5: Soil pH (1:5 soil:water ratio) before and after (approx. 1 yr) a liming trail at 1 tonne/acre at Christies Ck in the peaty surface soil and the acidic sub-surface acid sulfate soil. (n = 6 for all samples).

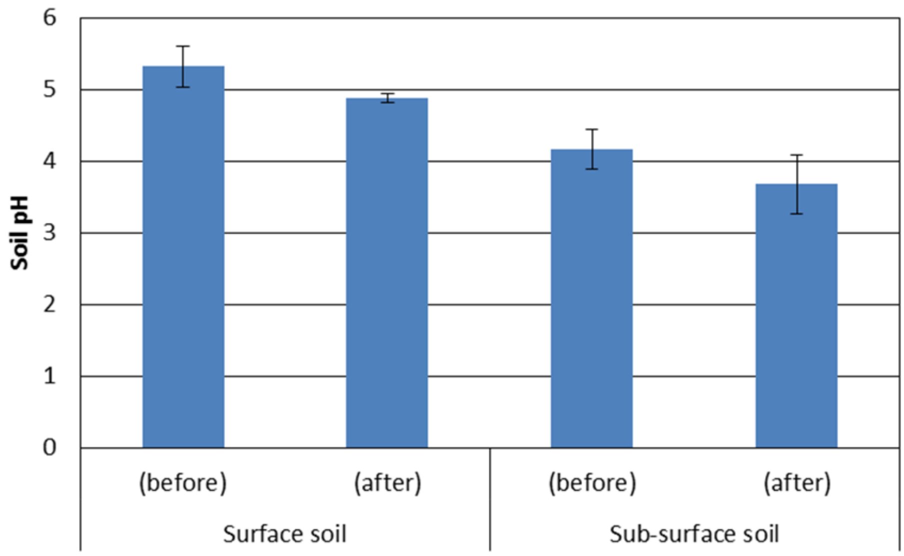
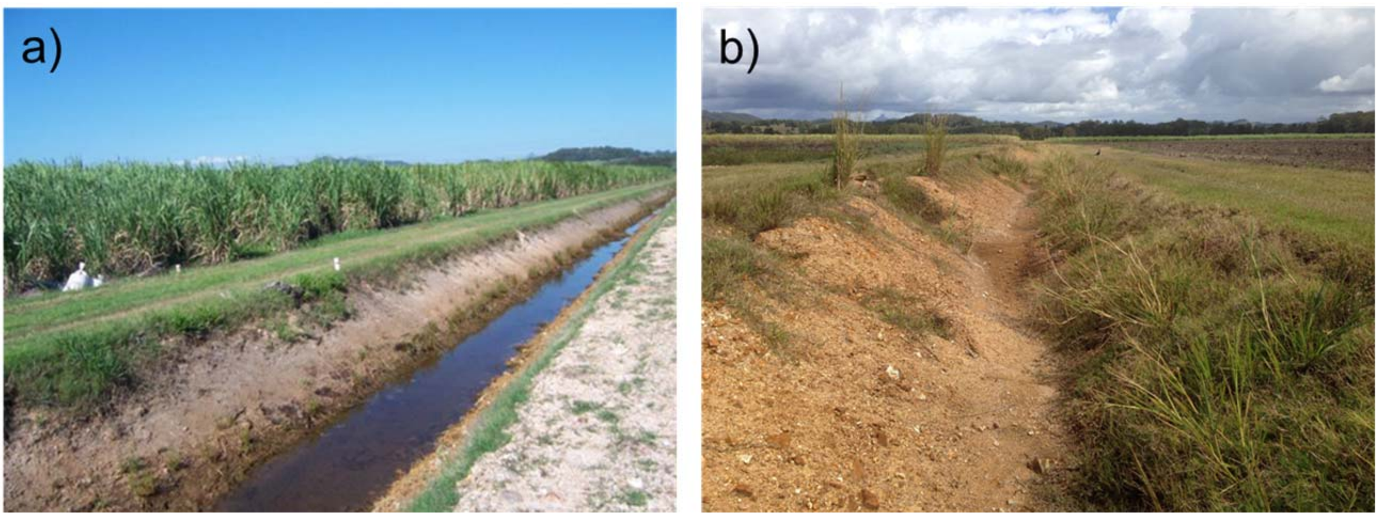


Figure 6: The major east-west drain (looking east) of the hydraulically-isolated cane block in Christie's Creek before (a) and after (b) drain shallowing. No ASS oxidation products are observed on the drain sediments after shallowing and the drain banks are revegetating.



Despite the improved appearance of the drain where it had been shallowed, drain water pH was still periodically acidic during 2013/2014 when rainfall totals exceeded approximately 50 mm/24 hr (Figure 7). This result was somewhat expected based on the field studies reported in Kinsela et al. (2009b) where a strong correlation between groundwater and drain water levels in this cane block was observed (i.e. pumping was drawing out acidic groundwater into the field drains and subsequently the main drains, e.g. Figure 8).

Figure 7: Average daily drain water pH values and 24 hr rainfall totals during 2013/2014 at the hydraulically-isolated cane block at Christie's Creek. Gaps in the data are due to equipment failure.

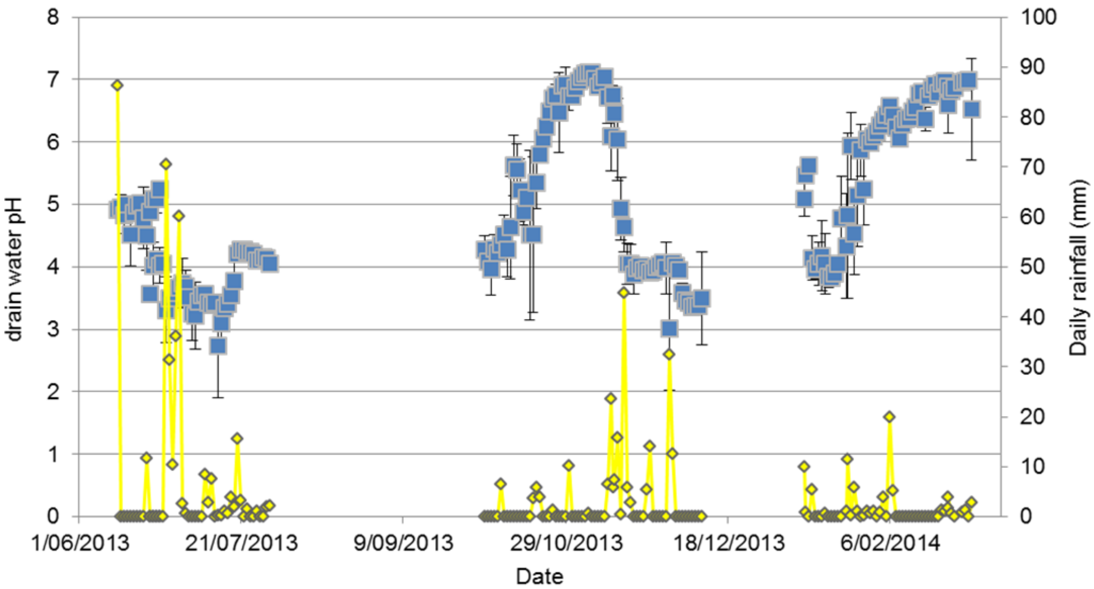


Figure 8: Water running from a field drain into the pumped major east-west drain, before shallowing, in the hydraulically-isolated cane block in Christie's Creek (from Kinsela et al. 2009b).

In April 2014, the water pumping regime for this cane block was modified so that pumping into Christie's Creek automatically ceases when the water level in the main drain reaches the bottom of the base of the deepest field drain. This effectively decreases the soil depth through which poor quality groundwater is pumped by 300 mm (i.e. drain water levels will now be 300 mm higher than previously when pumping stops). The field drains are approximately 800 mm deep on this cane block and the deepest field drain is ~ 100 mm deeper than the majority of field drains. Therefore, the changed pumping regime will cease pumping at approximately 900 mm from the ground surface – more than adequate for drainage that cane requires. As a result, there is future scope to raise the drain water level at which pumping ceases by at least another 200-300 mm without adversely impacting upon cane growth (R. Quirk, pers. comm.). This pumping regime should allow for sufficient drainage for the cane and, at the same time, reduce the amount of poor quality water being pumped into Christie's Creek unnecessarily (which would mostly occur at later pumping times after the surface water has been removed and there is less dilution from surface run off into the drains). Further works have also been planned with the landholder to continue to shallow the main drains and this is strongly recommended. In this scenario, the aim is keep as much of the ASS oxidation products in the soil and to minimise the pumping of drain water into Christie's Creek when it is likely to be at its worst. Drain water quality is continuously being monitored by the Tweed Shire Council as well as drain water levels. With this equipment in place it will be possible to determine drain water quality during pumping and non-pumping regimes and assess the benefits arising from the changed pumping practices when compared to previous studies at this site (Kinsela et al. 2009b).

A recent fish kill in Cudgera Creek (into which Christie's Creek discharges near Hasting's Point) was reported in March/April 2014. Later in May 2014 Christie's Creek was observed to be loaded with orange/red, and supposedly iron-rich, floc (Figure 9), but only in the northern arm of Christie's Creek. This floc was traced to upstream of Ray Dooley's land suggesting that there are additional ASS hotspots within the catchment of Christie's Creek that require further detailed ASS investigation/characterisation. According to the field studies of Kinsela et al. (2010), water quality within Christie's Creek at 'Site 2' (Figure 10) was relatively poor and was not related to upstream run off from 'Site 1'. Given that the hydraulically-isolated cane block was the first remedial priority, no further studies have been undertaken at 'Site 2' in this project. The reported fish kill and photo in Figure 9 suggests that, once action on the cane block has been accomplished, further attention should be given to 'Site 2'.

Cudgen Lake (Clothier's and Reserve Creeks)

During the NSW Environmental Trust ASS Hot Spot Remediation Program conducted from 2000-2004 a number of remediation activities were undertaken throughout the catchments draining into Cudgen Lake, i.e. Clothier's and Reserve Creeks (Tweed Shire Council 2004). The nature of these activities are summarised in Figure 11. Bearing this in mind, the first aim of this project for these catchments was to re-investigate, on a catchment scale, how effective these works have been and, further, to clarify if other hot spots were present. Initially, two additional water quality monitoring stations were installed in Reserve and Clothier's creeks on (or near) the western side of the Pacific Highway in 2012 to monitor water quality from the uppermost areas of the catchments (Figure 11). The results indicated that Clothier's Creek to the west of the Pacific Highway contributes little to ASS discharge (Figure 12). Similarly, water upstream from the junction where Reserve Creek splits into two drains, running north and east, appeared to be of good quality, suggesting that the drain infilling activities undertaken on Harry Boyd's cane farm in 2004 have contributed to improved water quality.

Figure 9: Christie's Creek, 10th May 2014 at the main floodgate (see Figure 9 for location of floodgate).

Figure 10: Aerial image of the Christie's Creek catchment showing 'Site 2' from Kinsela et al. (2010).

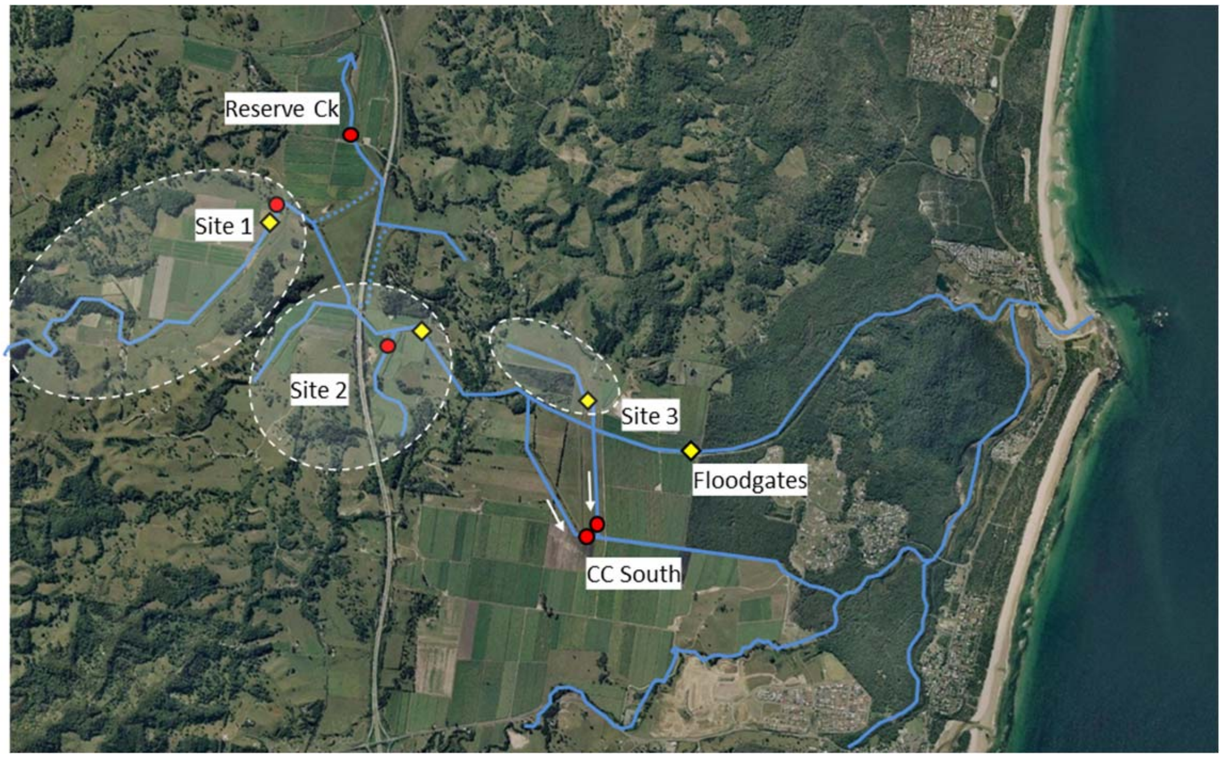


Figure 11: Aerial image of Clothier's and Reserve Creek catchments showing the remediation activities completed during the Cudgen Lake acid sulfate soil hot spot remediation project (Tweed Shire Council 2004). The coloured circles indicate sites of water quality monitoring stations for which the data can be seen in Figure 12.

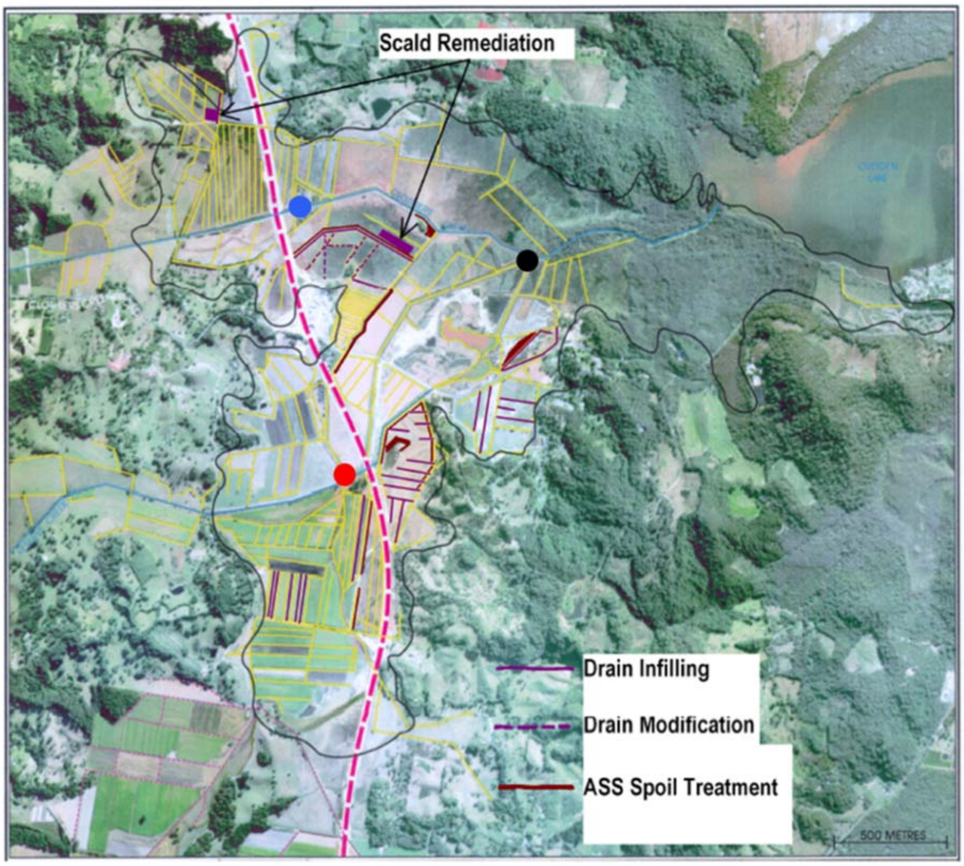
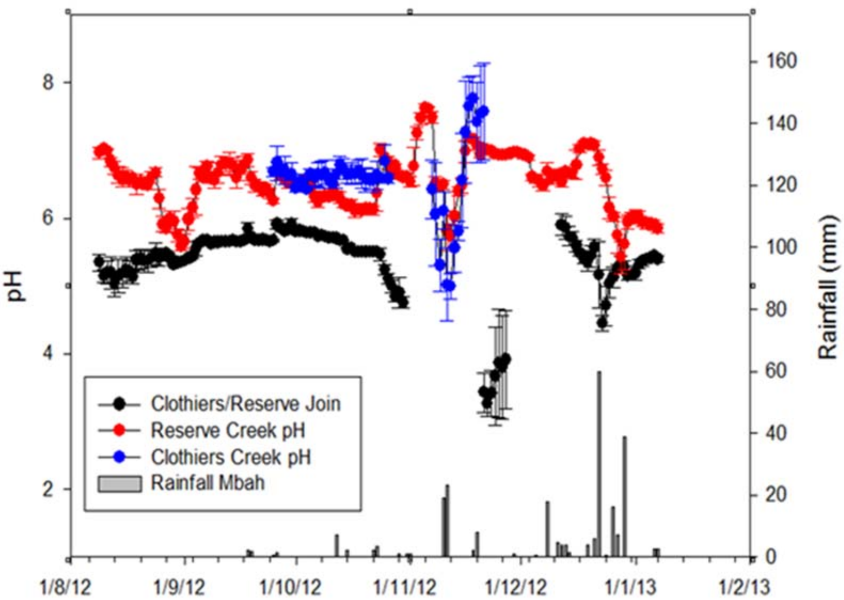
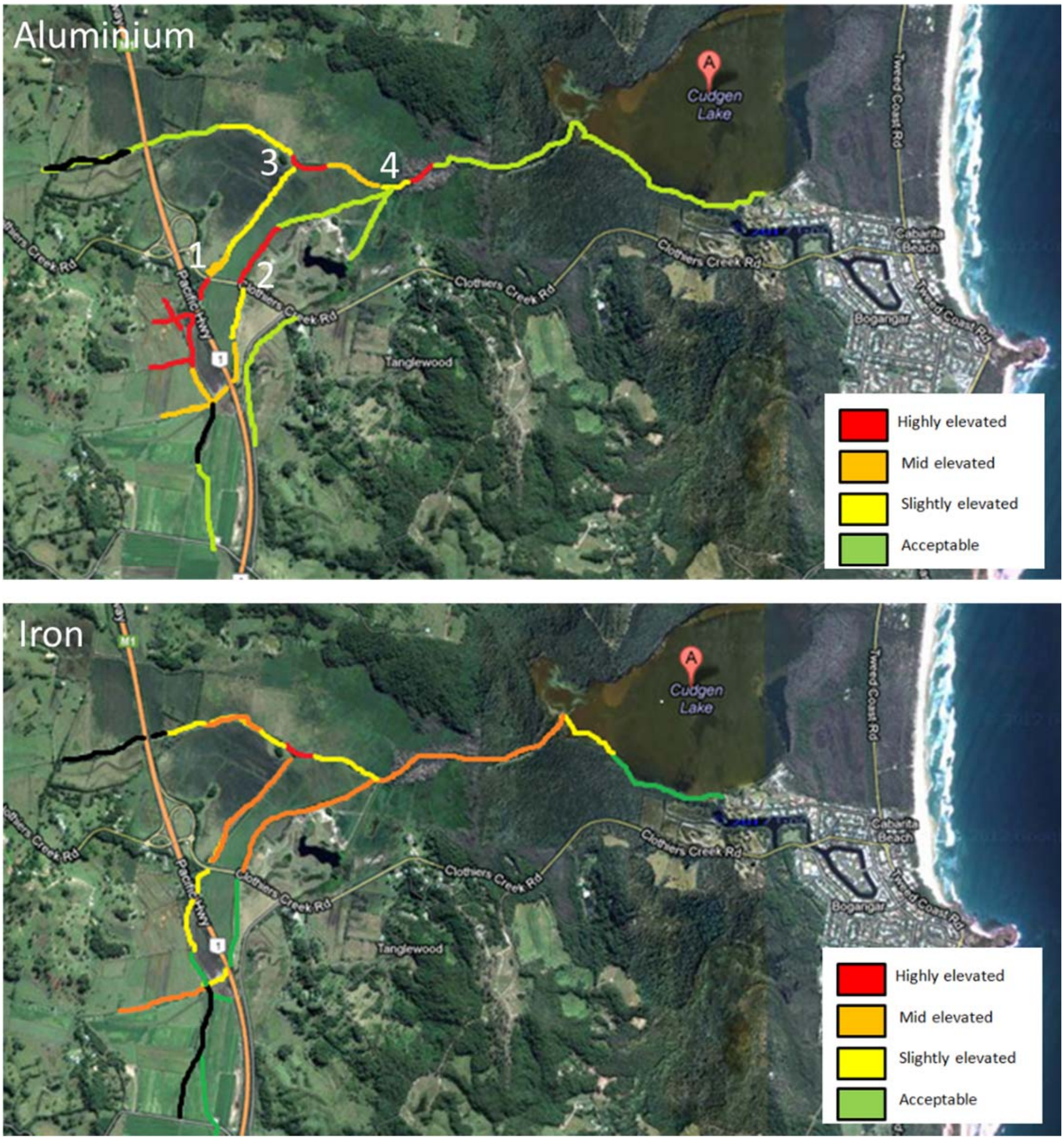


Figure 12: Drain water pH at the sites marked in Figure 11.



Two sample-intensive field studies were undertaken during 2012-2013 to further characterise the ASS discharge dynamics downstream (east) of the two water quality monitoring stations described above. The first involved the collection of 350 water lily samples along Clothier's and Reserve Creeks to the entrance of Cudgen Lake. The water lilies were analysed for aluminium and iron concentrations as it was hypothesised that these plants absorb these metals proportional to the long-term average metal concentration in the drain waters – and so could be used as a bio-indicator of metal pollution (and hence ASS hotspots). From these results, it was deduced that several aluminium hotspots existed principally in Reserve Creek, whereas bioavailable iron was elevated in the entire catchment generally east of the Pacific Highway and north of Clothier's Creek Road (Figure 13).

Figure 13: Water lily aluminium and iron concentrations in Clothier's and Reserve Creeks. The numbered sites represent where auto-samplers were placed for monitoring a rainfall event in January/February 2013.



Secondly, a rainfall event was monitored in January/February 2013 where a combination of auto-samplers and grab sampling was carried out to corroborate the location of acidity plumes and quantify metal discharge loads from both Clothier's and Reserve Creeks. The locations of the auto-samplers are shown in Figure 13. Aluminium and iron discharge through Clothier's Creek measured at site 3 was minimal during this rainfall event (Table 2) confirming the results shown in Figures 12 and 13. The quantities of aluminium exported through sites 1 and 2 were very high (Table 2) and also largely agreed with the spatial distribution of highly elevated aluminium concentrations in the water lilies, being *in situ* or downstream to these areas. Very high quantities of iron were also exported through (or generated at) sites 2 and 4, the latter being downstream from the former where the southern arm of Reserve Creek connects with Clothier's Creek. The iron was associated with the appearance of 'black water' which typically occurs after heavy rainfall events, prolonged flooding and the biodegradation of water-intolerant plant species. It would, therefore, appear that the catchment has two water quality issues: iron/black water loads from stagnant drainage across the whole catchment and; acidity/aluminium from Reserve Creek.

Table 2: Total exported aluminium and iron at various sites along Clothier's and Reserve Creeks during a rainfall event in January/February 2013. Site locations are shown in Figure 13.

Location	Metal exported (tonnes)	
	Aluminium	Iron
Site 1	26	13
Site 2	10	127
Site 3	<0.05	0.2
Site 4	0.2	57

Priority Site 1

The above-mentioned studies were described in detail by Stroud et al. (2013) and, based on these results, a priority site for on-ground works was identified at Site 1006, Clothiers Creek Road, Condong, 2484 for which was provided a recommended approach to remediation and changed land management practices (Stroud and Collins 2013). The former back swamp is used for cattle grazing, is isolated from all water sources (except direct rainfall) and has an extensive network of drains. There seems to be no hydrological function for the drains as the drainage outlets to Reserve Creek are approximately 0.5 m above ground level through the surrounding bund wall (Figure 14).

Furthermore, a total of 95% drains cut through the actual acid sulfate layer (which is <0.5 m below the ground surface) providing a groundwater source of acidity into the shallow drains and possibly through the soil surface during flooding, and this water is trapped onsite by the bund wall with drainage outlets 0.5 m above ground level leading to extensive scalding near levee outlets (Figure 14). Drain water and surface standing water was measured at circa pH 2.5 – 3.5 on the lower pasture, with elevated aluminium (2 - 11 mg/l) concentrations, average 8 mg/l. The soil has high actual acidity and elevated retained acidity, with 144 tonnes of acidity/tonne soil, requiring 10.8 kg lime/tonne soil (dry weight).

Figure 14: Water control structure embedded in the bund wall at the lower end (east) of the paddock at Site 1006, Clothiers Creek Road, Condong, 2484.

In conforming with the NSW Department of Trade and Industries Grazing and Dairy Industry Guidelines (NSW ASSMAC 1998) and the Acid Sulfate Soils Remediation Guidelines for Coastal Floodplains in New South Wales (Tulau 2007) it was recommended that a wet pasture be established at this site with:

- Modification of the extensive (ca. 5.2 km) network of drains (main source of acidity), specifically the in-fill of 1.2 km of priority drains and shallowing 4 km of the remaining drains.
- Dam modification to allow the spring water and runoff to shallow flood (ca. <15 - 20 cm) 19 ha of priority remediation paddocks (this level of shallow flooding is needed to support wet grazing plant species).
- Planting paddocks with suitable grazing species, e.g. water couch (*Paspalum distichum*) to improve organic matter levels and provide a wet pasture grazing source.

Attempts in early 2013 to engage the landholder at the time to work with the Tweed Shire Council to undertake these works failed. The property was sold later in 2013 and the new owners were also approached about discussing the findings from this project. As of May 2014, there has been no positive response from the new owners of the property. In light of this reaction, other areas in the catchment contributing to ASS discharge were further investigated in the final stages of the project to define remedial actions.

Priority Site 2

Based on the results obtained in Figure 13 and Table 2, field surveys were undertaken in early 2014 on land north of points 1 and 2 on Figure 13, the 'RTA land', and around the two major drains of Reserve

Creek east of the Pacific Highway. The RTA land was previously identified as a remediation priority as part of the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004 (Tweed Shire Council, 2004). Extensive works were carried out in this program which included infilling 10,000 m² of scalded areas and 1 km of drains. The acid scald on the RTA land was capped with treated fill (average 20 kg lime per tonne of soil) sourced from clean and ASS spoil from the banks of Clothier's Creek (Tweed Shire Council, 2004).

As can be seen in Figure 15, the remediated scald area was fully vegetated, in agreement with the outcomes reported from the program (Tweed Shire Council, 2004). Soil sampling indicated that there was no evidence of actual acid sulfate soils and a saturated, blue clay PASS was observed to occur ~ 60 cm below the soil surface (Stroud and Collins 2014b). It was, therefore, concluded that the remediation of the scalded area was successful and unlikely to be the cause of acid sulfate discharge events that are currently being detected in Reserve Creek. The undulating and well-vegetated area south-west of the scald site (Figure 11) was also investigated and no deep field drains, that were indicated in (Tweed Shire Council, 2004), could be located. However, four N-S soil transects through this section of land showed that actual acid sulfate soils were present, occurring at an average depth of 31 cm from the soil surface (Stroud and Collins 2014b). While this area of land is therefore a potential source of acidity, aluminium and iron, the lack of deep field drains to provide a rapid conduit to Reserve Creek would suggest that its contribution to ASS discharge would be minimal.

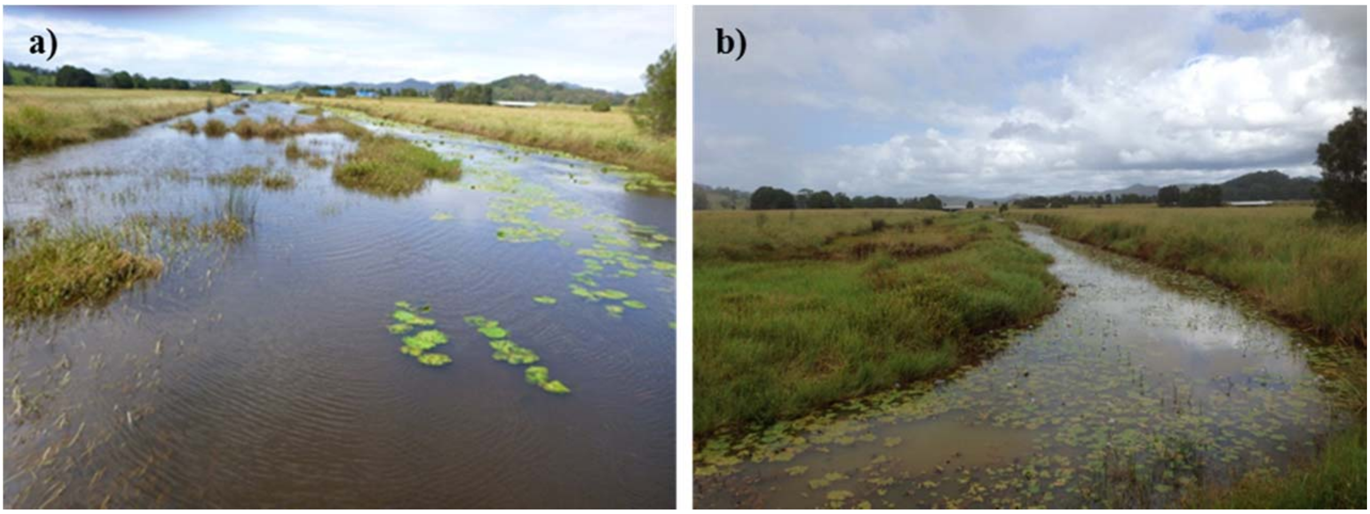
Figure 15: The acid scald on the 'RTA land': a) before and; b) after remedial works undertaken through the NSW Environmental Trust ASS Hot Spot Remediation Program (Tweed Shire Council, 2004) and; c) present day.

During the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004, ASS spoil, assumed to be from drain cleaning activities, along the banks of the northern arm of Reserve Creek and at its junction with Clothier's Creek were also treated (limed) (Figure 11). The spoil at the latter site is largely unvegetated (Figure 16) with pH values ranging from 3.7 to 4.7. Laboratory analysis of a composite sample (n = 3) showed this material had a net acidity of 69 moles H^+/tonne requiring a liming rate of 5.2 kg $CaCO_3$/tonne of ASS spoil. Assuming that the ASS spoil along the northern arm of Reserve Creek, east of Clothier's Creek Road, has similar properties, it would be expected that this ASS spoil provides a local source of acidity to Reserve Creek during rainfall and very large flooding events. While its contribution to ASS discharge is difficult to accurately ascertain, the relatively small area of this spoil in conjunction with the dilution that rainfall and large flooding events would provide, tends to suggest that it would be a minor contributor.

No remediation was undertaken on land adjacent to the southern arm of Reserve Creek that is east of the Pacific Highway during the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004 (Figure 11). The land adjacent to Reserve Creek, and upstream from Clothier's Creek Road to the Pacific Highway, is heavily vegetated (Figure 17) but cattle have never been observed grazing on this land for a number of years. The field drains indicated in Figure 11 could also not be located during field surveys.

Figure 16: ASS spoil at the junction of Clothier's Creek and the northern arm of Reserve Creek that was treated during the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004 (Tweed Shire Council, 2004).

Figure 17: The southern arm of Reserve Creek looking south-west from Clothier's Creek Road during: a) flooding in January 2013 and; b) non-flood conditions. Note the shallow shelf in the drain which is exposed during non-flood conditions.

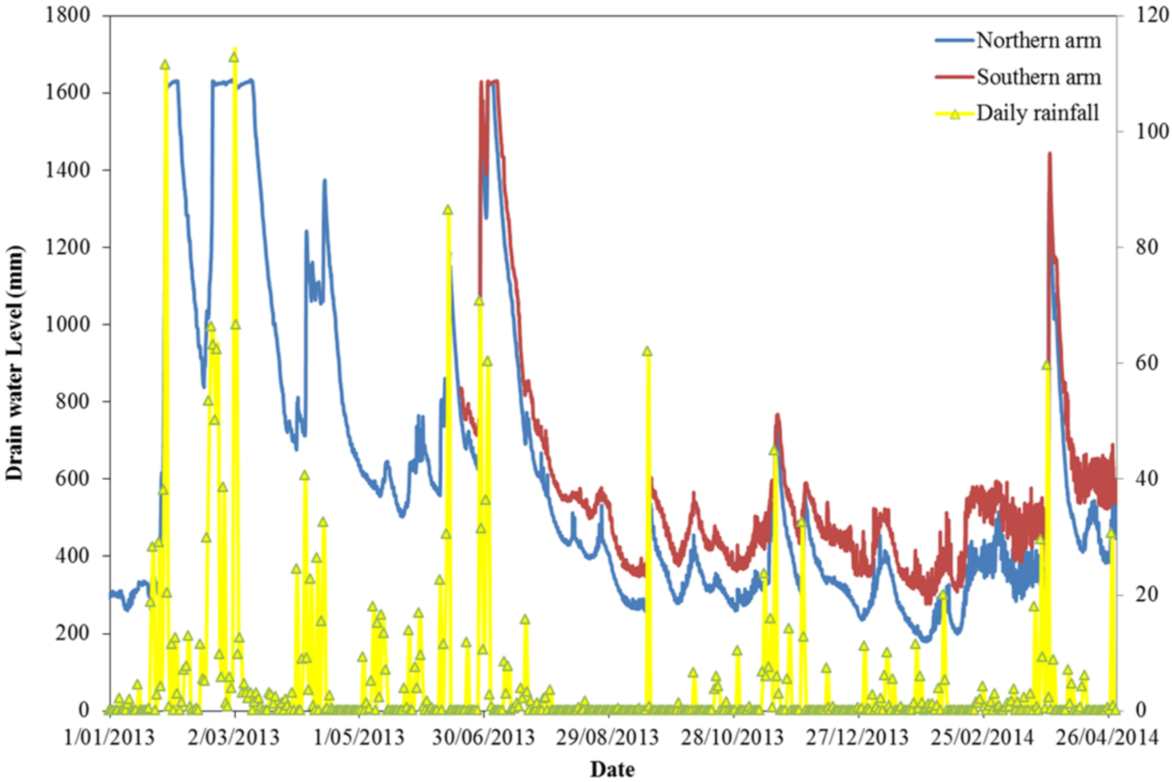


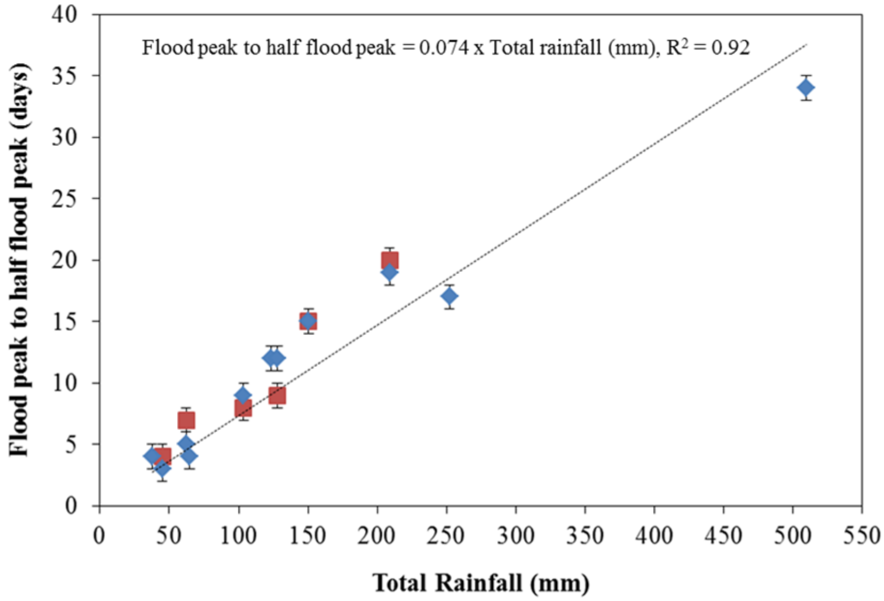
The southern arm of Reserve Creek is very wide east of the Pacific Highway (e.g. Figures 17a and 18c) and unevenly deep between the Highway and Clothier's Creek Road so that approximately 2/3 of the drain base area is routinely exposed during non-flood conditions (Figure 17b). In agreement with the findings of the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004 (Tweed Shire Council, 2004), it is possible that this shelf is a recurring source of acidity and metals, providing cyclical conditions suitable for the formation of monosulfidic black ooze (MBO) and black water (during flooding) and its subsequent air exposure and generation of ASS discharge (non-flood conditions). However, the vegetation itself appears to be water-tolerant and, therefore, resistant to degradation and the formation of black water. In fact, oxidised MBOs are observed along the banks of the entire length of both arms of Reserve Creek east of the Highway during non-flood conditions (Figure 18). The abundance of MBO in the drains in this area and the lack of deep field drains in adjacent land, providing a rapid conduit for ASS discharge into Reserve Creek(s), indicates that the ASS problems measured in the drains are actually derived *in situ* (i.e. in the drains themselves).

Figure 18: Oxidised monosulfidic black ooze drain sediments (a) and sediment/vegetation mats (b) along the banks of the northern arm of Reserve Creek east of Clothier's Creek Road which are also observed in the southern arm of Reserve Creek (c), looking north-east from Clothier's Creek Road.

Acid events have been recorded in these sections of Reserve Creek since 1990 (Tweed Shire Council, 2004) and black water events, to the author's knowledge, at least since 2008. The latter events have possibly been exacerbated since 2009 when a fire near the creeks' entrance to Cudgen Lake resulted in a blockage of fallen trees. Anecdotally, this event has increased flooding times in the area from days to weeks (C. King, pers. comm., 2014) and has severely affected upstream cane farming profitability. Data collected on drain water levels during 2013 certainly supports the view that current flooding times do extend into the weekly range (Figure 19) but, there are no comparable data with which to compare before the blockage. A reasonably strong correlation was obtained between total rainfall (over a number of days) and the time required for drain water levels in the northern and southern arms of Reserve Creek to recede to levels ½ of the peak (flood) height (Figure 19) indicating that an average rainfall event of 100 mm would take ~7.4 days to recede from the (flood) peak to half of this value.

Figure 19: Relative drain water level heights in the northern and southern arms of Reserve Creek as measured at Clothier's Creek Road and corresponding Daily rainfall values (from Kingscliff). The bottom graph shows the relationship between total rainfall (sometimes over a number of days) and the time it takes for drain water levels to drain from their peak height to half peak height (from Stroud and Collins 2014b).





Overall, the findings of these studies indicate that improvements in the quality of water draining into Cudgen Lake necessitate modifications to drainage through the northern and southern arms of Reserve Creek north-east of the Pacific Highway. Based on the results in Table 2, it appears that the largest ASS issue is black water formation in the southern arm that has probably intensified since fallen trees downstream have restricted flow into Cudgen Lake. The simplest and most cost-effective way to limit black water formation would, therefore, be to remove these trees further downstream and restore hydrological flows to previous levels. This would minimise the extent, duration and severity of black water events by limiting: 1) the time water remains stagnant facilitating vegetation biodegradation and the formation of black water and MBO and so, in turn; 2) the volume of water that is affected by black water which ultimately drains into Cudgen Lake.

It is expected, however, that restoring historical flow levels through Reserve Creek would result in drains that are drier more often and so result in greater air exposure, oxidation and acidification of any sulfidic sediments present. Given that this process is already observed along the drain banks under the current poor drainage conditions (Figure 18), restoring hydrological flows would also require that the vegetation 'mats' lining the side of the drains, that accumulate MBO, be removed and the spoil treated as per standard practices. In addition, long-term solutions are required to reduce the surface area of ASS sediments in Reserve Creek, with the priority being the southern arm, that are seasonally oxidised during dry spells. Given the length of the southern arm of Reserve Creek from the Pacific Highway to its junction with Clothier's Creek (~1.7 km) and its width (~25 – 30 m), it is clear that any drain modifications are likely to be costly. Furthermore, there is existing infrastructure, i.e. both Clothier's Creek Road and the drain culverts, that will restrict the range of drain modifications that could be implemented (if these are not to be altered).

Drain modifications that reduce the surface area of exposed ASS sediments long-term would typically involve either: 1) drain shallowing so that ASS sediments are not exposed or; 2) maintaining the same depth but making the drain less broad. Given that the ASS layer is close to the soil surface in this area (< 0.6 m), the former option is possibly not achievable without impacting upon flow. Furthermore, this would require changes to the heights of the drain culverts at Clothier's Creek Road. Although drain narrowing may also negatively impact upon flows, the removal of any existing bund walls or treated ASS spoil along the drain would allow greater flooding of the adjacent low-lying land and so provide greater capacity for receiving upstream floodwaters. At this stage, however, the entire length of the southern arm of Reserve Creek requires further characterisation, as does the resources available, to determine the most effective long-term solution to minimise ASS discharge from this area into Cudgen Lake. Finally, the water quality monitoring stations that are currently installed along Reserve Creek should remain in place to monitor changes in water quality in response to any on-ground works that are undertaken.

Conclusions

Post-remediation monitoring at Black's Drain has shown that the remediation carried out in 2009/2010 has been very successful in reducing ASS discharge from this catchment. A partially remediated acid scald site in this catchment is still contributing to ASS discharge but is currently of secondary importance and could be further re-capped and re-vegetated when funding is available. Implementation of on-ground works at Christie's Creek was delayed by adverse weather conditions and difficulties in coordinating with the landholder. Almost all of the recommended drain management works have now been implemented with final drain shallowing to be undertaken in the near future. This site is currently equipped with water quality monitoring equipment to evaluate the success of these works and changed water pumping activities on minimising ASS discharge into Christies Creek. Focus should now be shifted to other areas in this catchment that are disproportionately contributing to ASS problems. Field studies indicated that the remediation activities undertaken in the NSW Environmental Trust ASS Hot Spot Remediation Program 2000-2004 were largely successful, but severe ASS problems still exist in the Reserve Creek catchment. Two priority sites for on-ground works were identified. A detailed remediation program for the first site was developed, but due to the refusal of past and present landholders these works have not been undertaken. The second area identified involves the drains east of the Pacific Highway and extensive drain modifications are likely to be needed to reduce the impact of ASS from this area. Further drain characterisation and consultation between stakeholders is required before a detailed plan of on-ground works can be prepared.

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Publications

Peer-reviewed Journal Articles (abstracts of published articles are provided in Appendix A)

1) Stroud JL and RN Collins (2014a) Improved detection of coastal acid sulfate soil hotspots through biomonitoring of metal(loid) accumulation in water lilies (*Nymphaea capensis*). *Sci. Total Environ. 487:500-505.*
2) Yvanes-Giuliani Y, TD Waite and RN Collins (2014a) Exchangeable and secondary mineral reactive pools of aluminium in coastal lowland acid sulfate soils. *Sci. Total Environ. 485-486:232-240.*
3) Stroud JL, A Low, RN Collins and M Manefield (2014) Metal(loid) bioaccessibility dictates microbial community composition in acid sulfate soil horizons and sulfidic drain sediments. *Environ. Sci. Technol. In review.*
4) Yvanes-Giuliani Y, D Fink, J Rose and RN Collins (2014b) Isotopically exchangeable aluminium in coastal lowland acid sulfate soils. *In preparation.*
5) Yvanes-Giuliani Y, D Fink, J Rose and RN Collins (2014c) Lability of iron- and aluminium-natural organic matter complexes as assessed by Donnan dialysis and isotope exchange. *In preparation.*

Reports

6) Stroud J and R Collins (2014b) Remediation recommendations: Reserve Creek sites adjacent to Clothiers Creek Road. *UNSW Water Research Centre publication 2014/4, The University of New South Wales, Sydney, NSW 2052, Australia. In preparation.*
7) Collins R and J Stroud (2014) Final Progress Report for the Australian Research Council Linkage Project LP110100480. *UNSW Water Research Centre publication 2014/3, The University of New South Wales, Sydney, NSW 2052, Australia. p. 29.*

8) Stroud J and R Collins (2013) Remediation recommendations: 1006, Clothiers Creek Road, Condong, 2484. *UNSW Water Research Centre publication 2013/2, The University of New South Wales, Sydney, NSW 2052, Australia. p.14.*
9) Stroud J, Y Yvanes-Giuliani and R Collins (2013) 2012 Annual Progress Report for the Australian Research Council Linkage Project LP110100480. *UNSW Water Research Centre publication 2013/1, The University of New South Wales, Sydney, NSW 2052, Australia. p.17.*
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11) Kinsela A and R Collins (2011) Suggested remedial works for Christies Creek to reduce the discharge of aluminium and iron from acid sulfate soils. Final Report, version 2. *UNSW Water Research Centre publication 2011/10, The University of New South Wales, Sydney, NSW 2052, Australia. p.25.*
12) Kinsela A, W Glamore and R Collins (2011) Suggested remedial works for Christies Creek to reduce the discharge of aluminium and iron from acid sulfate soils. Final Report, version 1. *UNSW Water Research Centre publication 2011/4, The University of New South Wales, Sydney, NSW 2052, Australia. p.25.*

Conference Presentations

13) Stroud JL and RN Collins (2014) Bioavailability of metals in acid sulfate soil wetlands: implications for remediation. *4th National Acid Sulfate Soils Conference, Perth, Australia, May 2014.*
14) Stroud JL, A Low, RN Collins and M Manefield (2014) Metal(loid) bioaccessibility dictates microbial community composition in acid sulfate soil horizons and sulfidic drain sediments. *4th National Acid Sulfate Soils Conference, Perth, Australia, May 2014.*
15) Stroud JL and RN Collins (2014) Improved detection of coastal acid sulfate soil hotspots through biomonitoring of metal(loid) accumulation in water lilies (*Nymphaea capensis*). *4th National Acid Sulfate Soils Conference, Perth, Australia, May 2014.*
16) Stroud JL, A Low, M Manefield and RN Collins (2014) Iron and sulfur cycling bacteria in acid-impacted coastal sulfidic sediments. *4th National Acid Sulfate Soils Conference, Perth, Australia, May 2014.*
17) Stroud JL and RN Collins (2012) Arsenic concentrations and speciation in acid sulfate environments. *Understanding the Geological and Medical Interface of Arsenic, As 2012 – 4th International Congress: Arsenic in the Environment, 27-28.*
18) Stroud J and RN Collins (2012) Arsenic and trace metals in acid sulfate environments. *7th International Acid Sulfate Soil Conference, Vaasa, Finland, August 2012.*
19) Yvanes-Giuliani Y, D Fink, J Rose, TD Waite and RN Collins (2012) Labile and exchangeable metal concentrations in Australian coastal acid sulfate soils: mechanisms controlling metal mobility. *7th International Acid Sulfate Soil Conference, Vaasa, Finland, August 2012.*
20) Stroud J and RN Collins (2012) Characterisation of arsenic and trace metals in acid sulfate environments. *Goldschmidt 2012, Montreal, Canada, June 2012.*
21) Yvanes-Giuliani Y, D Fink, J Rose, TD Waite and RN Collins (2012) Mobilization of exchangeable aluminium in acid sulfate soils (ASS) *Goldschmidt 2012, Montreal, Canada, June 2012.*
22) Yvanes-Giuliani Y, D Fink, J Rose, TD Waite and RN Collins (2012) Use of ^{26}Al and Accelerator Mass Spectrometry (AMS) to study Al geochemistry in Acid Sulfate Soils. *Heavy Ion Accelerator Symposium on fundamental and applied science, Canberra, Australia, April 2012.*

23) Yvanes-Giuliani Y, D Fink, J Rose, TD Waite and RN Collins (2012) Partitioning of aluminium in acid sulfate soils and implications for remediation. *3rd National Acid Sulfate Soils Conference, Melbourne, Australia, March 2012.*
24) Stroud J and RN Collins (2012) Assessment of arsenic and metal bioavailability in drain waters from acid sulfate environments. *3rd National Acid Sulfate Soils Conference, Melbourne, Australia, March 2012.*
25) Yvanes-Giuliani Y, J Rose, TD Waite and RN Collins (2011) Partitioning of aluminium in acid sulfate soils and implications for remediation. *19th Annual RACI Analytical and Environmental Divisions Research and Developments Topics Conference for 2011, La Trobe University, Melbourne, Australia, December 2011.*

Local Presentations

26) Stroud J, Y Yvanes-Giuliani and R Collins (2014) Final Annual General Meeting for LP110100480. *Presented to the Tweed Shire Council, NSW Cane Growers' Association, NSW Milling Co-operative and local landholders, Murwillumbah, 7th May 2014.*
27) Collins R (2013) Acid sulfate soil remediation at Black's Drain 2005-2013. *Presented to the Tweed River Committee, Murwillumbah, 12th June 2013.*
28) Stroud J, Y Yvanes-Giuliani and R Collins (2013) 2nd Annual General Meeting for LP110100480. *Presented to the Tweed Shire Council, NSW Cane Growers' Association, NSW Milling Co-operative and local landholders, Craig King's Shed, Christie's Creek, 20th March 2012.*
29) Collins R, J Stroud and Y Yvanes-Giuliani (2012) 1st Annual General Meeting for LP110100480. *Presented to the Tweed Shire Council, NSW Cane Growers' Association, NSW Milling Co-operative and local landholders, Murwillumbah, 27th March 2012.*
30) Collins R (2011) Exploiting natural processes to effectively remediate acidified coastal environments – project commencement. *Presented to the Tweed Shire Council, NSW Cane Growers' Association, NSW Milling Co-operative and local landholders, Murwillumbah, 27th January 2011.*

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31) Collins R (2013) Engineering solutions to remediate coastal acid sulfate soils in north-eastern New South Wales. *Poster for the Australian Synchrotron Open Day, Melbourne, Australia, 13th October 2013.*

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Kinsela A and R Collins (2011). Suggested remedial works for Christies Creek to reduce the discharge of aluminium and iron from acid sulfate soils. Final Report, version 2. *UNSW Water Research Centre publication 2011/10, The University of New South Wales, Sydney, NSW 2052, Australia. p.25.*

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Stroud JL and RN Collins (2014a). Improved detection of acid sulfate soil hotspots using the water lily Nymphaea Capensis. *Science of the Total Environment 487:500-505.*

Stroud J and R Collins (2014b) Remediation recommendations: Reserve Creek sites adjacent to Clothiers Creek Road. *UNSW Water Research Centre publication 2014/4, The University of New South Wales, Sydney, NSW 2052, Australia. <u>In preparation</u>.*

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Appendix A

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Contents lists available at ScienceDirect

Science of the Total Environment

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Exchangeable and secondary mineral reactive pools of aluminium in coastal lowland acid sulfate soils

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HIGHLIGHTS

- Exchangeable Al concentrations are very high in coastal acid sulfate soils.
- Al–organic matter complexes form a significant fraction of exchangeable Al.
- Dissolved organic matter increases aqueous Al concentrations at pH values >5.
- 0.2 M $CuCl_2$ can be considered an alternative to 1 M KCl to measure exchangeable Al.

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ABSTRACT

The use of coastal floodplain sulfidic sediments for agricultural activities has resulted in the environmental degradation of many areas worldwide. The generation of acidity and transport of aluminium (Al) and other metals to adjacent aquatic systems are the main causes of adverse effects. Here, a five-step sequential extraction procedure (SEP) was applied to 30 coastal lowland acid sulfate soils (CLASS) from north-eastern New South Wales, Australia. This enabled quantification of the proportion of aluminium present in 'water-soluble', 'exchangeable', 'organically-complexed', 'reducible iron(III) (oxyhydr)oxide/hydroxysulfate-incorporated' and 'amorphous Al mineral' fractions. The first three extractions represented an average of 5% of '*aqua regia*' extractable Al and their cumulative concentrations were extremely high, reaching up to 4000 $mg \cdot kg^{-1}$. Comparison of Al concentrations in the final two extractions indicated that 'amorphous Al minerals' are quantitatively a much more important sink for the removal of aqueous Al derived from the acidic weathering of these soils than reducible Fe(III) minerals. Correlations were observed between soil pH, dissolved and total organic carbon (DOC and TOC) and Al concentrations in organic carbon-rich CLASS soil horizons. These results suggest that complexation of Al by dissolved organic matter significantly increases soluble Al concentrations at pH values > 5.0. As such, present land management practices would benefit with redefinition of an 'optimal' soil from pH ≥5.5 to ~4.8 for the preservation of aquatic environments adjacent to organic-rich CLASS where Al is the sole or principle inorganic contaminant of concern. Furthermore, it was observed that currently-accepted standard procedures (i.e. 1 M KCl extraction) to measure exchangeable Al concentrations in these types of soils severely underestimate exchangeable Al and a more accurate representation may be obtained through the use of 0.2 M $CuCl_2$.

1. Introduction

Extensive areas of low-lying (<2 m of the mean sea level) floodplains around coastlines ranging from warm-climate (e.g. Australia) to cold-climate (e.g. Northern Europe) zones have been drained for agricultural use (Boman et al., 2010; Dent and Pons, 1995; Stone et al., 1998). This artificial drainage has induced the oxidation of pyrite present within these Holocene marine sulfidic sediments resulting in the generation of acid and the formation of so-called coastal lowland acid sulfate soils (CLASS). Consequently, acidified waters, aluminium, iron and trace metals are periodically released from these soils resulting in the severe degradation of surrounding aquatic environments (Dent and Pons, 1995; Fältmarsch et al., 2008; Macdonald et al., 2007).

The discharge of drainage waters containing high concentrations of aluminium occurs regularly in rivers worldwide affected by CLASS and other surrounding waterways (Jones et al., 2011; Kinsela and Melville, 2004; Macdonald et al., 2007; Roos and Åström, 2005; Rosicky et al., 2004a). For example, concentrations of Al in pore and surface waters of up to 50 and 40 $mg \cdot L^{-1}$, respectively, have been reported in the Tweed River catchment, north-eastern NSW, Australia (Jones et al., 2011). Aluminium concentrations up to 124 and 100 $mg \cdot L^{-1}$ have also

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Improved detection of coastal acid sulfate soil hotspots through biomonitoring of metal(loid) accumulation in water lilies (*Nymphaea capensis*)

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HIGHLIGHTS

- Water lilies in acid sulfate environments accumulate aluminium, iron and arsenic.
- Acid sulfate soil discharge generates a diverse suite of bioavailable metal(loid)s.
- Biomonitoring identified hotspots within a large catchment.
- Correlations *in-planta* included Si:Al and S:Fe.

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ABSTRACT

Anthropogenically disturbed coastal acid sulfate soils along the east coast of Australia, and worldwide, periodically result in the discharge of acid waters containing high concentrations of metals. Identifying priority sites (hotspots) within a catchment for acid sulfate soil remediation activities typically involves long-term monitoring of drainwater chemistry, including the capture of data on unpredictable rain-induced groundwater discharge events. To improve upon this monitoring approach, this study investigated using the water lily (*Nymphaea capensis*) as a biomonitor of drainage waters to identify hotspots in three acid sulfate soil impacted catchments (83 km^2) in north-eastern New South Wales, Australia. In one catchment where the location of hotspots was known, water lily lamina concentrations of a suite of metal(loid)s were significantly ($p < 0.05$) higher than plants collected from an unpolluted 'reference' drainage channel, thus validating the concept of using this species as a biomonitor. A catchment-scale water lily sampling program undertaken in catchments with unidentified hotspots revealed within catchment variation of plant metal concentrations up to 70-fold. High resolution maps produced from these results, therefore, provided strong evidence for the location of potential hotspots which were confirmed with measurements of drainwater chemistry during rain-induced groundwater discharge events. Median catchment lily accumulation was ca. 160 mg Al kg^{-1} and 1300 mg Fe kg^{-1}, with hotspots containing up to 6- and 10-fold higher Al and Fe concentrations. These findings suggest that biomonitoring with *N. capensis* can be an important tool to rapidly identify priority sites for remediation in acid sulfate soil impacted landscapes.

1. Introduction

Acid sulfate soils cover 40 000 km^2 of coastal areas in Australia, with up to 1 million km^2 worldwide (White et al., 2007). Coastal acid sulfate soils form when the pyrite (FeS_2) naturally present in the soil is oxidised and the acidity generated exceeds the neutralisation capacity of the soil. Rain-induced groundwater discharge from these soils into waterways is acidic and metalliferous (principally iron (Fe) and aluminium (Fe)), causing between 1 and 5 acute pollution events per year (weather dependent). These events can cause massive fish; worm, vegetation and bivalve kills (Sammut et al., 1995) and outbreaks of epizootic ulcerative syndrome (Callinan et al., 2005); and pose potential health risks for populations using these groundwaters for irrigation and recreational purposes (Appleyard et al., 2006).

Acid sulfate soil pollution is a diffuse source (oxidised sub-soil layer) but 'hotspots' occur within a catchment as a result of hydrogeochemical interactions, that is, rainwater percolates through to the actual acid sulfate soil layer, and the hydraulic gradient of the site determines the groundwater flow outlet(s) to the waterways. To date, hotspots are principally detected during rain-events (>60 mm rain in

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