Preliminary Assessment of Acid Sulfate Soil Materials in Currency Creek, Finniss River, Tookayerta Creek and Black Swamp region, South Australia

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CSIRO Land and Water Science Report CLW 01/09
January 2009

www.csiro.au

CSIRO Land and Water Science Report series ISSN: 1834-6618

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Cover Photographs

Photographs showing: (i) a typical acid sulfate soil with sulfuric material ($pH < 4$) to a depth of 30 cm in the exposed creek-bed of Currency Creek, near north Goolwa, looking west towards the Adelaide Hills, South Australia and (ii) a small excavated area in a dry wetland adjacent to Finniss River (near FIN36) comprising acid sulfate soil with underlying sulfidic material, which was excavated (as part of the construction of a new dam) and placed on the surrounding edges of the excavation whence it transformed to sulfuric material (comprising sideronatrite with pH value of 2.2). View looking north towards the Finniss River, South Australia.

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ACKNOWLEDGEMENTS

This work was largely funded by the Murray-Darling Basin Authority (MDBA) as part of a larger Murray-Darling Basin (MDB) risk assessment of acid sulfate soils. We also acknowledge the Commonwealth Department of the Environment, Water, Heritage and the Arts for their funding support, which enabled the production of the original acid sulfate soil prediction maps (Fitzpatrick *et al*. 2008b,e). Simon Apte, Doug Beak, Greg Davis, Peter Hairsine, Scott Keyworth, Mike McLaughlin, Mary Mulcahy, Keith Sclater, Chris Smith and Mark Thomas are all thanked for constructive reviews and support.

EXECUTIVE SUMMARY

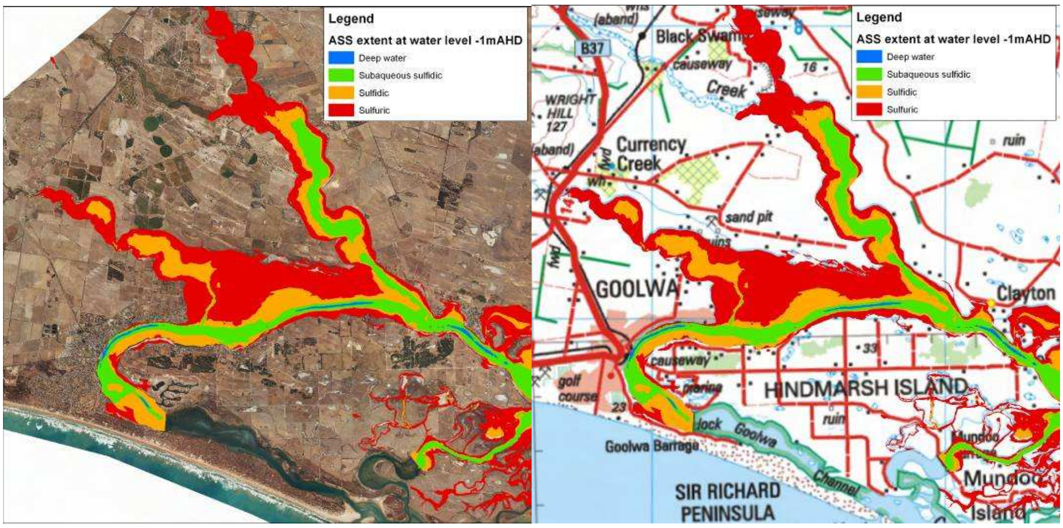
This report presents the results and conclusions from (i) a nine-day program of field work conducted from 18th to 26th November 2008, (ii) previous data (field, laboratory and map data from Fitzpatrick et al. 2008a,b) and (iii) data from a return field trip in December 2008. Together these data are used to assess the potential acidification risks and the extent of acid sulfate soils (ASS) in the lower reaches of Currency Creek and Finniss River, and at Tookayerta Creek and Black Swamp further upstream. These areas, adjacent to Lake Alexandrina in the lower reaches of the River Murray in South Australia, have recently experienced falling and historically low water levels due to drought conditions. The exposure and drying of sulfidic materials can potentially have serious environmental consequences relating to soil and water acidification, metal mobilisation, de-oxygenation of water, or formation of malodours (H_2S, organo-S compounds). Such conditions can exacerbate the oxidation and potential acidification of ASS. This field investigation used field pH and soil morphology to "estimate" the general ASS risk category. The specific aims of this investigation were to:

- Make field assessments of the extent of various ASS materials in the Currency Creek, Finniss River and Tookayerta Creek and Black Swamp regions according to the recent field methodologies agreed with the Murray-Darling Basin Authority (Fitzpatrick *et al*. 2009).

- Identify the main ASS subtypes and ASS hot-spots, and suggest future monitoring and management options based on ASS field data.

In November/December 2008, samples from 12 representative transects or toposequences – mostly across dry wetlands, dry river-beds, dry lake-beds and in-river-channels (originally subaqueous and waterlogged soils) – were collected in the Currency Creek, Finniss River and Tookayerta Creek/Black Swamp region adjacent to Lake Alexandrina. A total of 131 samples were collected and analysed from a wide range of ASS subtypes with sulfidic, sulfuric and monosulfidic materials in sands, clays and peats. Large areas of extremely acidic soils (sulfuric materials: pH < 4.0) were present and confirmed previous predictions (Fitzpatrick *et al*. 2008b) that these areas have a high risk of developing sulfuric materials (i.e. soil pH < pH 4). There is also a high risk of developing more sulfuric materials from existing sulfidic materials, which have not yet oxidised.

The following two maps show the projected extent of sulfuric and sulfidic materials at –1.0m Australian Height Datum (AHD), which closely approximates the extent of these materials identified in this study in late December 2008 when the water level was –0.7m AHD.



At several sites, abundant new occurrences of minerals in salt efflorescences and sub-surface horizons were observed. Bright yellowish green and orange surface efflorescences and pale yellow mottles in subsoils were present and X-ray diffraction analyses showed that these were sideronatrite, schwertmannite and jarosite/natrojarosite minerals, respectively. The pH values of the bright yellowish green surface efflorescences are very acidic (pH < 2) and the orange and pale yellow minerals are acidic (pH < 3–4). The presence of all of these minerals indicates high contents of iron sulfides (principally pyrite) in the original materials. It is predicted that much large quantities of sulfuric acid will be produced in the sulfidic subaqueous ASS to a depth of >50 cm if the river levels continue to drop significantly and the adjacent wet soils are allowed to dry.

Some of the waters in soil pits of the dry river-beds and wetlands of Currency Creek (with deep cracks) and Finniss River (sands) had low pH values ranging from 3.4 to 3.9. Some river waters sampled in Currency Creek and Tookayerta Creek/Black Swamp contain moderate to low concentrations of alkalinity (<117 mg/L and 31 mg/L respectively as HCO_3). Acid sulfate soil influences on the low alkalinity in Currency Creek are likely when compared to the high alkalinity of Lake Alexandrina water (currently in the range 200 to 250 mg/L). This is because the lower Finniss River and, until recently, Currency Creek are contiguous with Lake Alexandrina via the Goolwa channel and should therefore have had similar alkalinities when water levels were higher. Even with the retreat of the lakes sporadic movement of lake water up the lower Finniss and Currency channels occurs through wind activity, “seiching”. The alkalinity of Lake Alexandrina thus helps to maintain the alkalinity of the remnant Currency Creek and Finniss River waters, along with local contributions from ground waters and evapo-concentration.

A full risk assessment requires detailed information on field characteristics, geochemistry, mineralogy and the extent of the various subtypes of ASS present at a site. It also requires analysis and understanding of water transport, flow regimes, lateral transport of acids and solutes and the role of groundwater. However, due to the urgent need to inform the client of the distribution of acidified soils in this region, in this report we will only present data and interpretations on field investigations and some mineralogical data together with recommendations for future monitoring of this environment.

It should be noted that this is a preliminary report. The conclusions drawn in this preliminary report may alter when full acid soil chemistry is completed on the collected samples.

Recommendations

Monitoring is considered an essential component of ASS risk assessments during the current drought, and will be particularly important during rewetting phases when acidity and metal mobilisation may occur. Monitoring frequency should be assessed based on a number of factors including the degree and extent of risk. This is site and scale dependent. Taking into account the area of the Currency Creek, Finniss River and Tookayerta Creek/Black Swamp catchments, it is recommended that monitoring be completed at two levels:

1. Detailed monitoring to be completed at selected “reference sites” every two to three months to determine future changes in acid generation, i.e. increase in sulfuric material with depth and increase in spatial extent during the drying or wetting regimes and mobility. This will involve soil sampling and analyses at specified sites along transects, supported by: (i) morphological, (ii) chemical (e.g. Cr-reducible S, retained acidity and acid neutralising capacity), and (iii) mineralogical observations at each reference site.

2. Spatial monitoring on a monthly basis (or when there is a rapid water level change at the sites) sampled in this study, to assess spatial trends, based on visual indicators, morphological descriptions and “indicators” of acid generation. Observations should include physical characteristics of soils (e.g. changes in depth of sulfuric materials, depth of cracking, depth to water) and surface mineralogical characteristics (e.g. visually monitor changes in soil that may indicate sulfide oxidation such as brown-orange precipitates or the presence of indicator minerals such as jarosite, schwertmannite or Magnesium-rich sulfatic salts).

As well as providing a basis for quantitative estimates of acidity, metal mobility and treatment options, the data from the monitoring exercise can be used to confirm the current ASS maps. These maps can be used to illustrate the extent of acidification, to inform decision makers to assist in assessing the risks to local ecosystems.

We recommend that the detailed monitoring program be conducted along at least three transects in both Currency Creek and Finniss River catchments and along at least one transect in the Tookayerta Creek/Black Swamp catchment. However, we recommend that the rapid monitoring be conducted along all 12 transects, which includes all current 39 soil profile sample sites.

Monitoring of the water should be conducted following refilling or inundation to determine any impacts on water quality. This should include alkalinity, pH, SEC, major and trace elements, and nutrients.

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1. INTRODUCTION

This report presents the results and conclusions from field work conducted from 18th to 26th November 2008, (ii) previous data (field, laboratory and map data from Fitzpatrick et al. 2008a,b and (iii) data from a return field trip in December 2008. These data are used to assess the extent of acid sulfate soils (ASS) in the lower reaches of Currency Creek and Finniss River, and at Tookayerta Creek and Black Swamp further upstream, and the potential acidification risks. These areas have recently experienced falling water levels due to drought conditions. Such conditions can exacerbate the oxidation and potential acidification of ASS. This field investigation used field pH and soil morphology to “estimate” the general ASS risk category.

Current drought conditions have had a significant impact on the River Murray corridor, including the many wetlands which form important habitats and ecosystems. These habitats and ecosystems are important for maintaining healthy river system. The extent and importance of ASS in the River Murray, lower lakes and adjacent wetlands has only recently been fully appreciated (Fitzpatrick *et al*. 2008a,b,c,d,e; Shand *et al*. 2008).

The presence of sulfidic materials can potentially have serious environmental consequences relating to soil and water acidification if oxidation occurs, de-oxygenation of water, or formation of malodours (H_2S, organo-S compounds). Previous work by CSIRO Land and Water and others in wetlands, disposal basins and lakes in the Murray Basin has identified occurrences of sulfidic, sulfuric and monosulfidic black ooze materials in a range of ASS in subaqueous soils and sediments (*e.g*., Baldwin *et al*. 2007; Fitzpatrick *et al*. 2006; Fitzpatrick *et al*. 2008a, b, c, d, e; Hicks and Lamontagne 2006; Lamontagne *et al*. 2004; Shand *et al*. 2008). Sulfidic groundwater systems that occur at depth may also impact on receiving environments (Shand *et al*. 2006). Recent studies have also shown potential risks from the remobilisation of metals, especially following oxidation and rewetting, including Al, As, Cd, Co and Ni in oxidised ASS (Simpson *et al*. 2008, Stauber et al. 2008).

A full risk assessment requires detailed information on field characteristics, geochemistry, mineralogy and the extent of the different subtypes of ASS (Fitzpatrick *et al*. 2008) present at a site. It also requires analysis and understanding of water transport, flow regimes, lateral transport of acids and solutes and the role of groundwater. However, due to the urgent need to inform the client of the distribution of acidified soils in this region, in this report we will only present data and interpretations on field investigations and some mineralogical data together with recommendations for future monitoring of this environment.

Phase 1 of this project (field assessment and sampling) is complete, and Phase 2 (laboratory assessment and interpretation) is ongoing (Fitzpatrick *et al.* 2009). A database has been compiled, which includes information on site details (Table 1) and soil characteristics (in preparation). This will be updated as the work program and data collection progresses. The conclusions drawn in this preliminary report may be modified when full chemical analysis is completed on the collected samples.

Figure 1. Locations of all ASS survey sites from Currency Creek (CUR 11 to 26), Finniss River (FIN 20-28; 30-38) and Tookayerta Creek/Black Swamp (FIN 29). Grid interval is 10 km.

The specific aims of this investigation were to:

- Make field assessments of the extent of various ASS materials in the Currency Creek, Finniss River and Tookayerta Creek/Back Swamp regions according to the recent field methodologies agreed with the Murray-Darling Basin Authority (Fitzpatrick *et al*. 2009).
- Identify the main ASS subtypes and ASS hot-spots, and suggest future monitoring and management options based on ASS field data.

1.1. Summary of previous work

Acid sulfate soils are those soils containing iron sulfide minerals (e.g. Pons 1973; Fanning 2002). These soils may either contain sulfuric acid (sulfuric material) or have the potential to form sulfuric acid (sulfidic material), or cause de-oxygenation (monosulfidic black ooze material - MBO), or release contaminants when the sulfidic minerals are exposed to oxygen. Often ASS are formed where there is an abundance of natural organic carbon and sulphate. This occurs in wetlands or marshy areas and in near-marine or saline environments. As water levels decline in Lake Albert and Lake Alexandrina (the Lower Lakes) and the River Murray system below Blanchetown (Lock 1), due to the current, unprecedented drought conditions, the anaerobic sulfidic materials that were once covered by water are now exposed to oxygen at the river and lake margins, and in adjacent wetlands. With continued lowering of water levels, the sulfidic material can become progressively oxidised to greater depths of the soil profile, generating sulfuric material (pH < 4). Potentially, this can adversely impact water quality, ecological systems and public health.

Previous studies by CSIRO Land and Water developed a conceptual model (Figure 2) to describe four sequential drying phases and the development of different ASS Subtypes (Fitzpatrick *et al.* 2008b) that occur. Applying this model, Fitzpatrick *et al*. (2008b,c) integrated locally detailed field survey and laboratory data and used the Australian Soil Classification (Isbell 1996) to derive fourteen subtypes of ASS conforming to the map legend of the Atlas of Australian ASS.

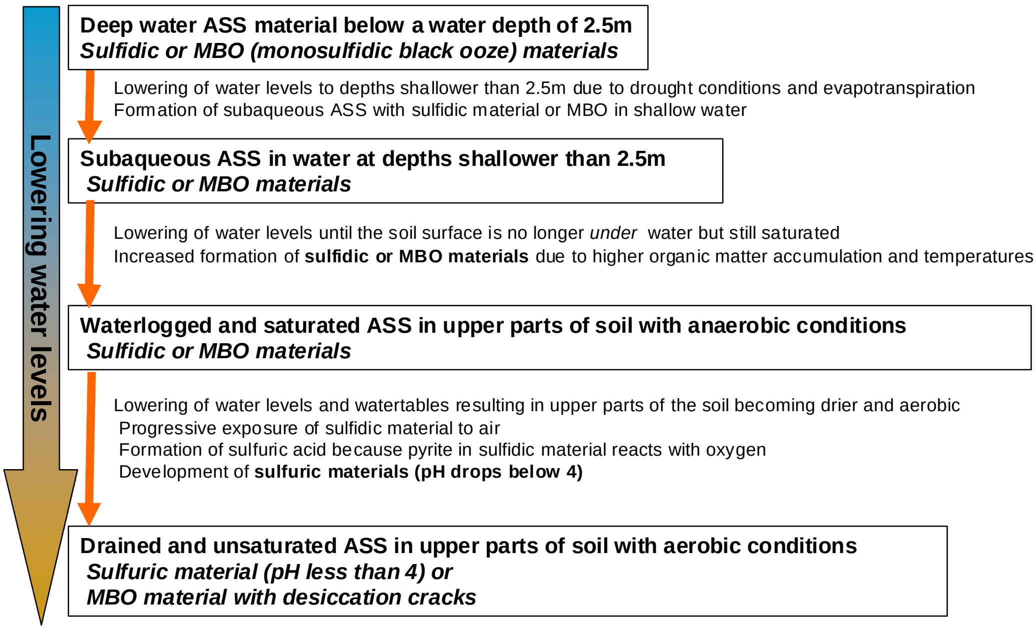

Figure 2. Generalised conceptual model showing the sequential transformation of four Classes of ASS due to lowering of water levels from "deep-water ASS" → "subaqueous ASS" → "waterlogged and saturated ASS" (all containing sulfidic material with high sulfide concentrations and pH > 4) to → "drained and unsaturated ASS" containing sulfuric material (pH < 4) in the upper soil layers (from Fitzpatrick *et al.* 2008a, b, c, d).

A series of conceptual process models for each of the lakes (Alexandrina and Albert) and lower River Murray systems were applied to:

- explain the sequential formation and transformation of sulfidic material to sulfuric material in various subtypes of ASS (5,500 BC to the extreme drought conditions of 2006-2008),
- explain and predict new occurrences of minerals, their formation and transformation (e.g. pyrite to sideronatrite; sideronatrite to schwertmannite; pyrite to natrojarosite), and
- predict the impacts of further drought on ASS oxidation and impacts.

Combined bathymetry, soil and vegetation mapping in a GIS framework was used to help predict the distribution of different subtypes of ASS according to three predictive scenario maps (Fitzpatrick *et al*. 2008a,b), which in Figure 3 depict sequential changes in ASS materials at different water levels in Lake Alexandrina.

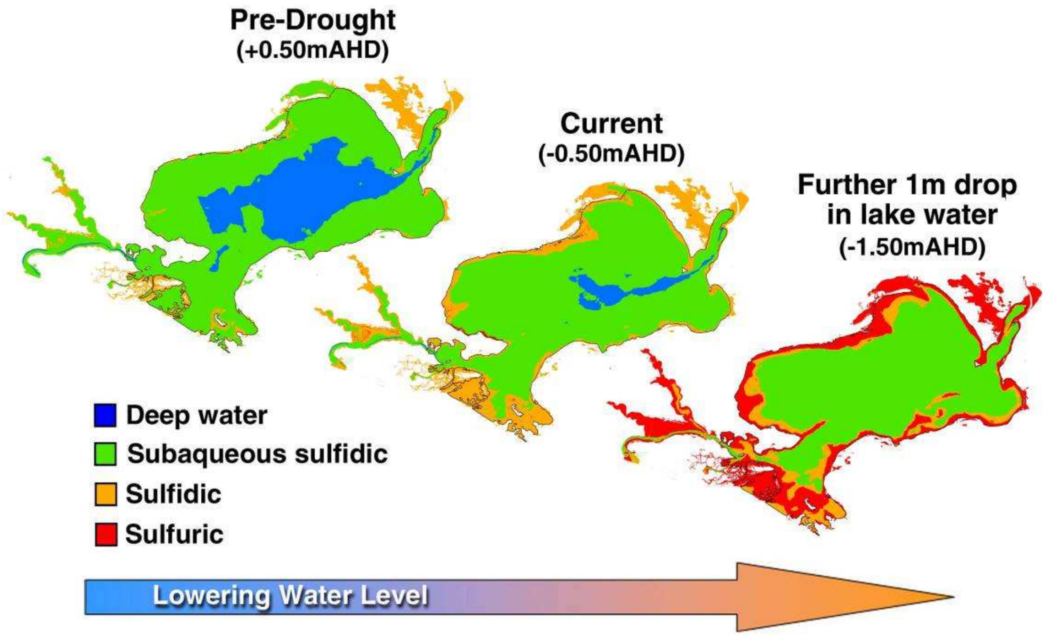

Figure 3. Predictive scenario maps depicting changes in ASS materials at different water levels in Lake Alexandrina for +0.5 m Australian Height Datum (AHD) (pre-drought), -0.5 m AHD (approximate level during early 2008), and -1.5 m AHD (an extreme case, should low lake inflows persist) (From Fitzpatrick *et al.* 2008b).

These predictive ASS maps are constantly being revised as new information becomes available through site visits, field testing and the availability of new spatial data sets (Fitzpatrick *et al*. 2008b; p. 59).

High sulfide contents were previously measured in a subaqueous sulfidic soil in the Finniss River at site AA26 adjacent to FIN26 (Figure 1) (see FIN26; Figure 5), which also had relatively low acid neutralising capacity in the upper soil layers (*i.e.*, low carbonate concentrations (Fitzpatrick *et al*. 2008b; p. 118).

Field studies combined with the maps and predictive models were used to conclude that most of this region could produce sulfuric material if the water level fell to -1.5 m AHD (see predictive scenario shown in the ASS maps in Figures 14 and 15).

2. FIELD AND LABORATORY METHODS

Sampling strategy

Between 18th and 26th November 2008, we assessed and sampled 131 soil layer samples in the Currency Creek, Finniss River and Tookayerta Creek/Black Swamp region adjacent to Lake Alexandrina (Figure 1). These samples were taken from 39 regionally representative sub-aqueous, waterlogged and drained soil profiles, to assess current and potential impacts of acid sulfate soils (ASS) during the current extreme drought conditions.

The guiding principles for the selection of the site subset shown in Figure 1 included that the profiles were: part of a sufficient geographic spread of survey sites for the study area (river channels, wetlands); and that those selected were deemed regionally representative in terms of hydrological, biogeochemical and morphological properties.

These sites were also easily accessible at the time the study was undertaken. As such, these sites should form the basis for any future monitoring program.

2.1. Field sampling of soils and waters

Field sampling and assessment were completed in November and December 2008. A total of 131 samples were collected from 38 soil profiles (20 from Currency Creek, 17 from Finniss River and 1 from Tookayerta Creek/Black Swamp) (Figure 1). At each survey site, global positioning system coordinates and site location descriptions were recorded (Table 1). The locations of these sites are shown in Figure 1. All soil profiles were described to about 100 cm depth, soil samples collected and where water was observed, water samples were collected. Detailed soil morphological descriptions will be presented in a subsequent report along with the laboratory information. Soil morphology was described in the field (*e.g.*, colour, consistency, structure and texture) according to McDonald *et al*. (1990). Multiple samples from each layer were taken, including:

- two sets of chip tray samples placed in individual tray compartments, one for desk top morphological reference and archiving in the CSIRO Land and Water soil archive, and the other for incubation (ageing) experiments;
- bulk (~500 g) samples for peroxide pH analysis and bulk storage, placed in thick sealable plastic bags;
- two sets of samples each placed in 70 ml screw top plastic jars, one for XRD (powder X-ray diffraction) and XRF (X-ray fluorescence spectrometry) analyses, and the other for chromium reducible sulfur (S_{CR}) analyses (Fitzpatrick *et al.* 2008b; 2009).

Water samples were collected for chemical analyses at several sites (Table 1 and one sample from the soil cracks below 43 cm in the wetland close to the Finniss River (FIN20). Dissolved oxygen (DO) pH, and redox potential (Eh) were measured on-site using a calibrated YSI multi-parameter meter and electrodes. Other on-site measurements included temperature (T ^{o}C), specific electrical conductance (SEC or EC) and alkalinity (by titration, see methods below). Samples were collected for major and trace chemical analyses in 125 ml polyethylene bottles. Those for major and trace element analysis were filtered through 0.45 µm membrane filters and the aliquot for cation and trace elements were acidified to ca. 0.2 % v/v HCl to minimise adsorption onto container walls.

2.2. Soil types

Site descriptions are presented in Table 1. Soil colour, texture, structure and consistency are valuable field indicators for soil identification and appraisal. Soil type can determine potential impacts on ASS formation during desiccation or inundation, and likely products of oxidation based on acid generating and acid neutralising characteristics. Sandy or quartz-rich soils are often more at risk of acidification because they have little capacity to neutralise acidity, whereas clay-rich soils have ability to neutralise acidity through dissolution of clay minerals. Individual soil profiles often show variations in layer textures, contributing to the complexity of interpreting likely ASS behaviour at each site.

Table 1. Locality, depth to water table and surface condition of samples from Currency Creek, Finniss River and Tookayerta Creek/Black Swamp.

Site ID Number	Easting zone 54H	Northing zone 54H	Depth to Water Table (cm)	Surface Condition	Surface Earth Cover (Vegetation)	Location Notes
CUR11	302384	6070538	-10	water	water	in water 4 m from shore
CUR12	302365	6070521	not reached	sealed	bare, few weeds	15 m from shore
CUR13	302272	6070678	80	cracking	bare	80 m from shore
CUR14	302218	6070463	not reached	sealed	weeds	250 m from shore, 10 m from step up bank
CUR15	305343	6071064	not reached	sandy, firm	bare	shore edge of water
CUR16	305395	6070954	-10	water	water	80 m from shore
CUR17	305334	6071123	not reached	sealed, peaty	bare	old beach shoreline
CUR18	305224	6071431	not reached	sandy, firm	bare	midway to steep up into reeds
CUR19	305152	6071684	not reached	sandy, firm	few reeds nearby	mid/high 40 m before step up
CUR20	298356	6073698	-40	water	water	2 m into water channel
CUR21	298352	6073708	60	sealed	bare	near reeds, 20 m from water
CUR22	298350	6073695	not reached	sealed	bare	1 m from water edge
CUR23	298538	6073748	1	sealed	bare	water edge
CUR24	298557	6073753	-30	water	water	30 m from shore
CUR25	298414	6073793	not reached	sealed, salt crust	bare	high, 20 m from step up to reeds
CUR26	301098	6072836	-20	water	water	20 m from shore
CUR27	301049	6072909	not reached	sealed, sandy	bare	80 m from water edge and 10 m from reeds
CUR28	301047	6072912	not reached	sealed, sandy	bare	10 m from CUR27 site
FIN20	305780	6073935	45	cracking	bare	clear area between islands of reeds
FIN21	305888	6073941	55	cracking	bare	clear area between islands of reeds, and where white crystals occur
FIN22	305945	6074053	-10	water	water	10 m from edge of *Phragmites*

Site ID Number	Easting zone 54H	Northing zone 54H	Depth to Water Table (cm)	Surface Condition	Surface Earth Cover (Vegetation)	Location Notes
FIN23	305748	6074053	not reached	cracking	bare	10 m from edge of *Phragmites*
FIN24	305756	6074049	not reached	cracking	bare	paired site with FIN23
FIN25	305810	6074047	55	soft, peaty	bare	shore edge with water currently 50 m out
FIN26	303084	6079608	30	sealed, salt	bare	below edge of river bank, sampled previously when water was here. Site under jetty
FINx	305720	6073883	0	water	water	measurement in excavated house dam
FIN27	306196	6075060	not reached	sealed, soft	bare	low, 50 m from water
FIN28	305974	6075099	not reached	cracking, hard	bare	mid, in backswamp channel
FIN29	302739	6076943	-20	water	reeds	side of valley where black swamp occurs
FIN30	307978	6073636	-30	water	water	low, 15 m into water from shore
FIN31	308016	6073669	60	sealed, sandy	bare	mid, on old shoreline 50 m from water edge
FIN32	308051	6073691	85	loose, sandy	reeds	high, in reeds before step up
FIN33	306784	6076264	not reached	loose, sandy	Phragmites	high
FIN34	306777	6076255	not reached	sealed	bare	mid to high, 10 m from FIN23
FIN35	306748	6076232	50	peaty, soft	bare	mid to high, 10 m from shoreline
FIN36	306736	6076216	-20	water	water	low, 10 m from shoreline
FIN37			not reached	sealed, sandy	bare	mid, where
FIN38	304329	6079422	45	peaty, soft	bare	high, 5 m from reeds and step-up
FIN39	304300	6079424	-3	water	water	low, 5 m from water edge

Where: Site Identification Number (CUR – currency creek area, FIN – Finniss river area), site co-ordinates (WGS 84 Zone 54), depth to water table (soil surface is '0', if value is '-ve' then water level is above surface), soil surface condition, surface earth cover (either water, vegetation type or bare – no vegetation), plus additional notes on the location (such as position from water).

2.3. Laboratory soil analysis methods

The general flowchart for soil sample collection and analysis is shown on Figure 4. Air was excluded as far as possible from the samples. On return to the laboratory the soils were stored at 4℃ until analysed. Samples (soils and salts) for XRF and detailed sulfide analysis (S_{CR}) for acid-base accounting were dried at 80℃. Moisture contents were recorded and bulk densities estimated (Fitzpatrick *et al*. 2009).

Samples have been submitted for sulfide analysis (Cr-reducible S; Ahern *et al*. 2004). The oven dried samples and air dried/moist samples in the chip trays are being stored for the long-term (archived) to allow for additional analysis, if required. The samples in the chip tray for incubation (ageing) experiments are being used to follow the course of potential acidification and to assess if these soils have the potential to generate or neutralise potential acidity (Fitzpatrick *et al*. 2008b; 2009).

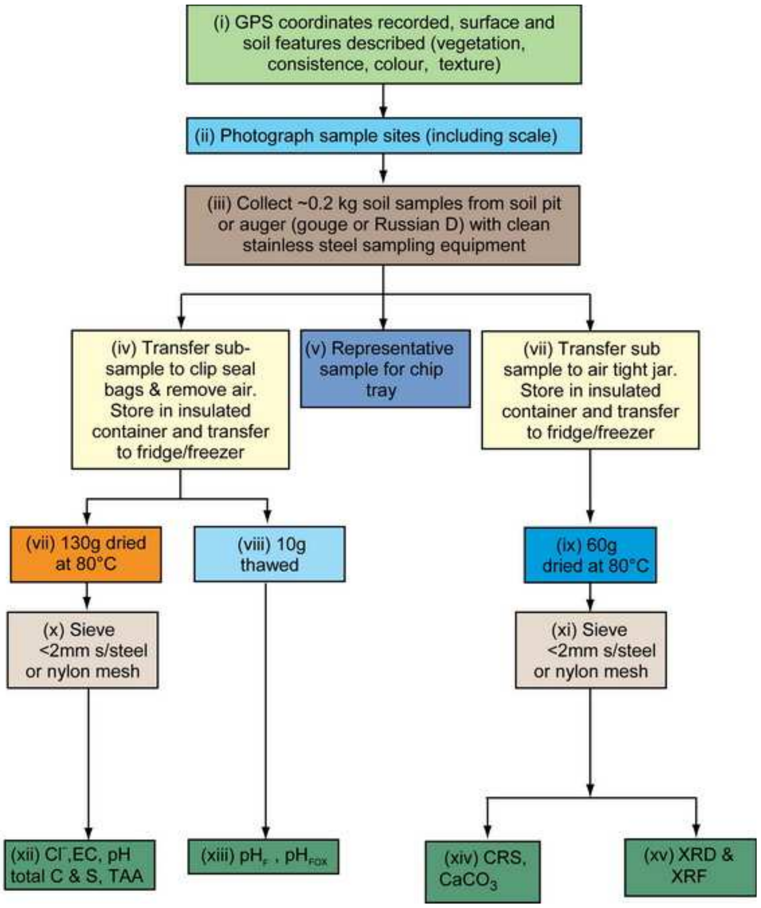

Figure 4. General flow chart for soil sampling and analysis.

2.3.1. Methodologies used to assess acid generation potential

In order to assess the acid generation potential (AGP) of acid sulfate soils, a range of methodologies are used. This requires several parameters to be measured, as highlighted in Figure 4 (e.g. Fitzpatrick *et al.* 2008b; 2009; Ahern *et al.* 1998; 2004). An important consideration is also the mineralogical make-up of the soils (e.g. X-ray diffraction data as provided in Appendix 1), which may either enhance or neutralise acid generating potential. These parameters also need to be combined with field observations and placed into the geological and hydrogeological setting, so that laboratory-scale data can be extrapolated and interpreted at the landscape scale.

3. RESULTS

3.1. Soil morphology and pH based on field investigations

Field interpretations

The decrease in water levels in Currency Creek and Finniss River systems since the original baseline study was conducted in August 2007 by Fitzpatrick *et al*. (2008b) has now exposed significant new quantities of subaqueous and waterlogged soils, and formed large areas of ASS with sulfuric materials (Figures 5 to 13). Hence, the current risk of soil acidification in this region is high. In several areas, the pH of the upper soils is < 2 and the pH of standing water in the cracks of some soils is < 4.8. In summary, the area has a mixture of ASS sub-types (Table 2).

At the time of the most recent sampling (November 2008) of a previously sampled site (AA 26) at the Finniss River, large tracts of the channel margins had been exposed, allowing sampling and characterisation of materials further into the exposed dry river-bed (Figure 5; see Appendix 1 for XRD analyses). A strong sulfidic-sulfuric smell was evident at this and most other sites.

New occurrences of surface salt efflorescence minerals and sub-surface mottles minerals were observed at several sites. Bright yellowish green and orange surface efflorescences (Figures 5, 6, 7, 8, and 10) and pale yellow mottles (Figures 6, 7, 8 and 9) in subsoils were present. X-ray diffraction analyses showed that these were jarosite, sideronatrite, schwertmannite and tamarugite minerals, respectively (Appendix 1). The pH values of the bright yellow efflorescences indicate high acidity (pH < 2) and the orange minerals are acidic (pH < 3 – 4). Their presence indicates previously high contents of pyrite or monosulfides in the original materials. The white fluffy salt efflorescences comprised mixtures of mainly Mg-sulfate minerals (e.g. hexahydrite $MgSO_4.6H_2O$, epsomite $MgSO_4.7H_2O$, gypsum and traces of halite).

Soil pH values below about pH 5 result in the decomposition of soil minerals, including clays. These can release (usually logarithmically increasing with decreasing pH) of potentially toxic elements such as aluminium. For example, tamarugite $[NaAl(SO_4)_2.6H_2O]$ with pH values of 1.6 to 2.5 overlying clayey sulfuric material was identified at site FIN 26 – see Figure 5). The yellow colour associated with the organic material changes to orange away from the organic matter as the acid becomes neutralised by chemical reactions in the adjacent soils (Figure 10).

Selected photographs of ASS for a wide range of sites at Currency Creek and Finniss River are shown in Figures 5 to 13.

Table 2. Summary of ASS sub-types.

Creek/River	Dominant ASS sub-types: sulfuric materials	Dominant ASS sub-types: sulfidic materials
Currency Creek	Sulfuric soil (sandy)* Sulfuric cracking clay soil**	Sulfidic soil (sandy)* Sulfidic cracking clay soil**
Finniss River	Sulfuric cracking clay soil	Sulfidic cracking clay soil
Tookayerta Creek / Black Swamp	Currently none	Sulfidic organic soils Monosulfidic organic soils

*Dominant (above 70%); **Subdominant (<%).

Finniss River catchment

(a) (b)

(c) (d)

Figure 5. Changes in water level in the Finniss River at Watsons Landing, which is the sampling site furthest upstream on the western side of the Finniss River (labelled as FIN 26 in Figure 1). a) August, 2007 showing the whole river ponded with water. A sulfidic subaqueous clayey soil was sampled under 80 cm of water at the end of the jetty and labelled as sample AA 26; Sulfidic organic clayey soil was sampled in the *Phragmites* four metres from the bank/waters edge and labelled as sample AA27 (see Fitzpatrick *et al*. 2008b pp. 99 and 118 for morphological and chemical data respectively). b) November 2008 showing substantial lowering of water levels to produce mainly waterlogged or saturated ASS (sulfidic cracking clay soil – end of jetty). c) January 8th 2009 showing further lowering of water levels to expose a clayey dry river-bed with cracks and salt efflorescences (sulfuric cracking clay soil). d) November 2008 showing close-up photograph of the dry clayey river-bed adjacent to the *Phragmites* in the river bank. White fluffy salt efflorescences (comprising mixtures of mainly Mg-sulfate minerals [hexahydrite $MgSO_4.6H_2O$, epsomite $MgSO_4.7H_2O$] and gypsum) and bright yellowish green coloured iron oxyhydroxysulfate minerals comprising sideronatrite [$Na_2Fe(SO_4)_2.OH.H_2O$], tamarugite [$NaAl(SO_4)_2.6H_2O$ with pH values of 1.6 to 2.5 overlying clayey sulfuric material (sulfuric cracking clay soil) (see Appendix 1 for XRD).

Figure 6. Sulfuric cracking clay soil in dry wetland bed of Finniss River (Sites FIN 20 and 21 on Figure 1) showing thick layers (pale yellow mottles/ precipitates) of jarosite in the cracks (pH 3.3) and the water in the large cracks with a pH of 3.54 (Table 3).

Figure 7. Sulfuric cracking soil in dry wetland bed of the Finniss River (Sites FIN 23 and 24 on Figure 1) showing thick precipitates and layers of schwertmannite (pH 3 -4) .

Figure 8. Acid sulfate soil in the clayey dry river-bed of the Finniss River (Site FIN 28 on Figure 1) showing a soil pit with black sulfidic material (iron sulfides) at depth (> 60 cm) overlying sulfuric material with pale yellow mottles surrounding old *Phragmites* root channels in a dark grey matrix consisting of jarosite (right hand side) overlying a cracked surface layer comprising mainly the bright orange mineral, schwertmannite (Appendix 1), which has a pH ranging between 3 and 3.6.

Currency Creek Catchment

Figure 9. ASS profile adjacent to Goolwa North (Site CUR12 on Figure 1): sulfuric cracking clay soil (vertosol) in dry river-bed of Currency Creek showing pale yellow mottles of jarosite in grey clay matrix between 10 cm to 30 cm) (photo on right hand side).

Figure 10. Sulfuric soils (sandy) in the dry river-bed of Currency Creek (Sites CUR15 and 16 on Figure 1).

Figure 11. Sulfuric soil (sand over clay) in dry river-bed of Currency Creek showing: jarosite mottles (pH 3.3) and pH of 3.96 in the water in the soil pit. (Sites CUR 24 and 23 on Figure 1).

Figure 12. Sulfuric soil (sandy) in dry river-bed of Currency Creek showing: jarosite mottles (pH 3.3) in soil pit with surface salt and Fe-efflorescences of schwertmannite (pH 3 -4 bright orange colour) and sideronatrite (pH 2.5 and bright yellow colours). (Site CUR 27 and 28 on Figure 1).

Figure 13. Sandy sulfidic subaqueous soil in Currency Creek showing black monosulfidic black ooze (MBO) beneath green algal mat. (Site CUR 22 on Figure 1).

Spatial distribution of ASS with sulfuric and sulfidic materials

The decrease in water levels in the rivers since the baseline study in August 2007 (Fitzpatrick *et al*. 2008b) has now exposed significant areas of previously subaqueous soil, leading to oxidation of ASS and the formation of large areas of ASS with sulfuric materials (Figure 3). The present occurrence of ASS with sulfuric material is spatially extensive in the dry river-beds and dry wetlands in Currency Creek and Finniss River systems. Hence, the current risk of soil acidification in this region is high. In several areas, the pH of the upper soils are < 2 and the pH of standing water in some soils is < 4.8. A full compilation of the data will be provided in the final report. In summary, the area has a range of ASS sub-types (Table 2).

Risks associated with metal mobilisation upon wetting are also considered potentially high. In some cases, these ASS will potentially pose a serious threat to surrounding ecosystems and river water quality. Future risks of deoxygenation from monosulfidic materials are considered moderate to high due to their potential to form on re-wetting. Most of the subaqueous soil materials sampled in Currency Creek, Finniss River, Tookayerta Creek and Black Swamp are predicted to contain high contents of pyrite with an ASS hazard risk ranging from moderate to severe. Based on the amount of acidic hydroxysulfate minerals, it is likely that large quantities of sulfuric acid will be produced in the subaqueous ASS to a depth of > 50 cm if the river levels continue to drop and the adjacent wet soils are allowed to dry.

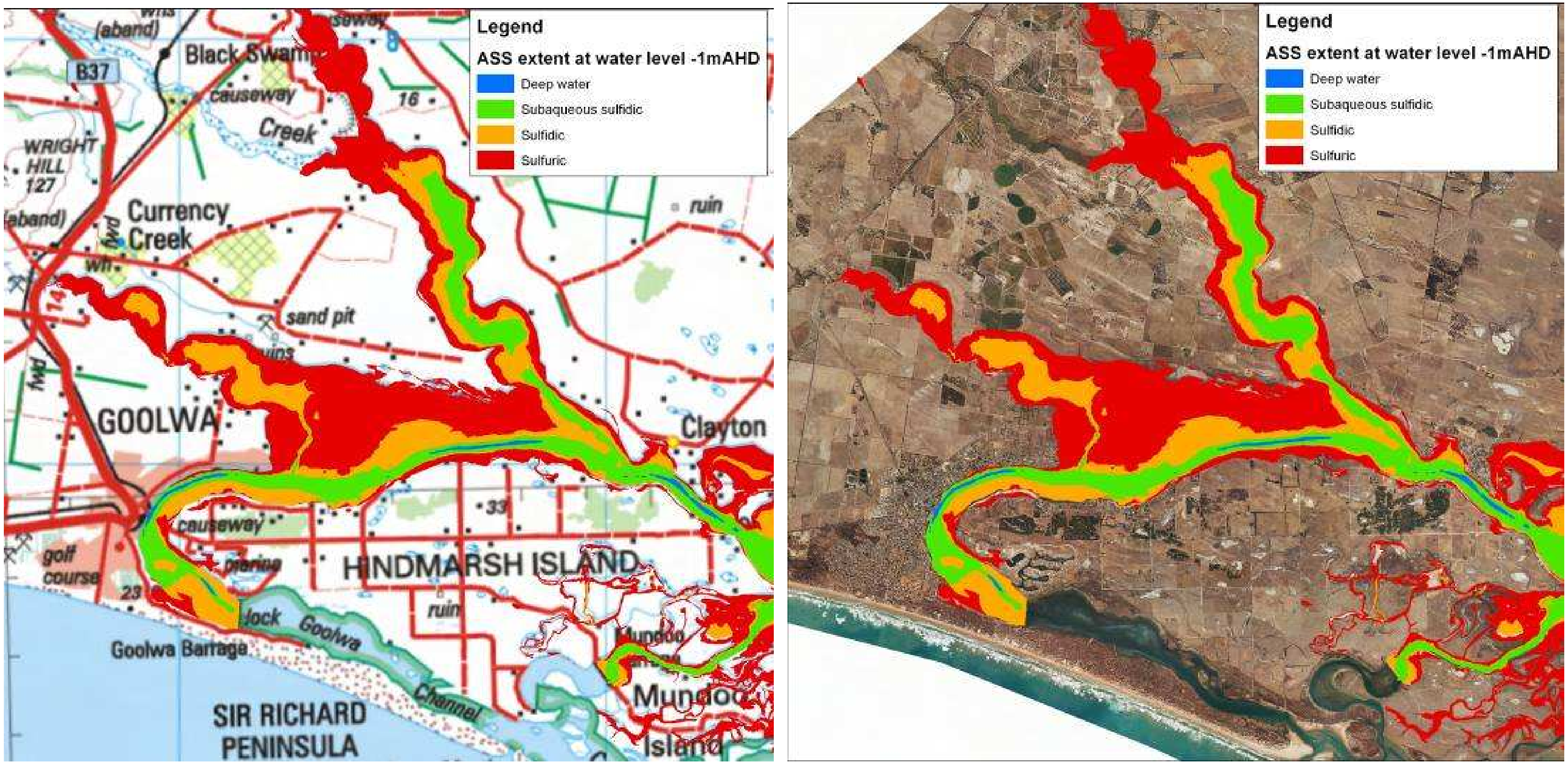

Figure 14. Maps depicting predicted occurrences of ASS Subtypes for Lake levels at -1.0 m AHD (based on Fitzpatrick *et al.* 2008b), which closely approximate the current distribution of sulfuric and sulfidic materials, verified from field work along 12 transects in late November 2008.

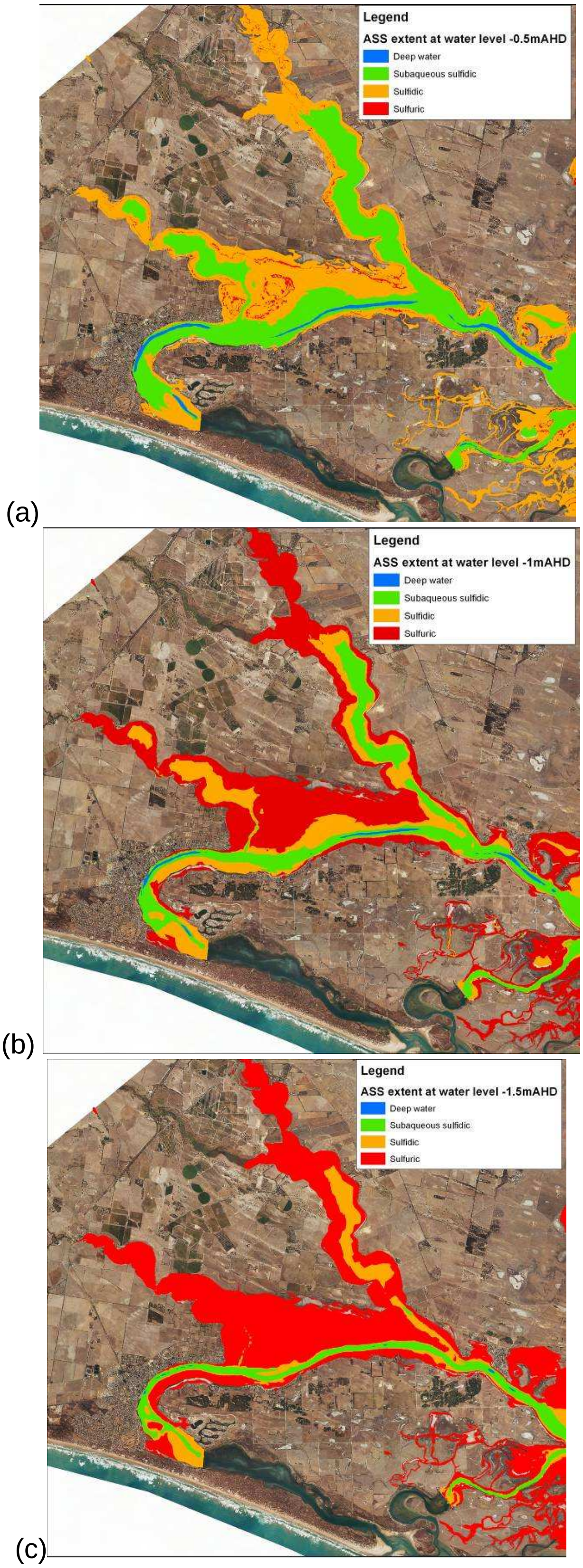

Figure 15. Maps depicting the occurrences of various acid sulfate soil subtypes for: (a) water levels at - 0.5 m AHD (February, 2008) when the soils were originally mapped; (b) previously predicted occurrence at -1.0 m AHD, which closely relates to present levels and confirmed in this study; and (c) predicted occurrence for a future scenario of -1.5 AHD (Modified from Fitzpatrick *et al.* 2008b).

3.2. Mineralogy

The mineralogy of selected soils was determined by X-ray diffraction (XRD) (see Appendix 1 for mineral identification interpretation inserted on each X-ray diffraction pattern). The physical manifestation of the minerals in the field is shown in Figures 5 to 13.

3.3. Water Chemistry

Seventeen water samples were collected from 15 of the study sites (Table 1): ten sites from the creeks and rivers in the channels, one from cracks in the dried wetland, and four from soil pits and data are shown in Table 3.

Table 3 Field parameter data for water samples.

Sample	**T**	**SEC or EC**	**DO**	**pH**	**Eh**	**AlkalinityHCO_3**	**Site notes**
units	^{o}C	µS/cm	mg/L		mV	mg/L	
CUR11a	19.28	23377	10.05	6.98	398	n.d.	Currency Creek, 10 cm deep
CUR11b	21.51	23591	9.77	8.06	347	175	plastic bag sample collected from CUR11A location
CUR16	20.34	13290	13.4	8.67	466	183	Currency Creek, 10 cm deep
CUR20	18.01	5465	9.79	8.14	319	280	Currency Creek, 40 cm deep
CUR21	18.94	8024	3.48	6.56	190	n.d.	Water in pit, water table 60 cm
CUR23	18.44	27388	1.75	3.96	594	0	Water in pit, water table 15 cm
CUR24	20.8	21669	14.25	6.75	503	n.d.	Water in pit, water table 30cm
CUR26	22.97	18388	14.12	8.62	463	117	Currency Creek, 20 cm deep
FIN20	17.06	34192	3.88	3.54	541	0	Water in cracks, water table 43 cm
FIN21	21.68	34354	10.6	5.29	336	0	Water in pit, water table 55cm
FIN22	26.94	6942	9.63	8.0	375	146	Finniss river water, 10 cm deep
FINx	27.09	4085	0.5	7.64	211	262	Dam near house
FIN29a	24.57	1174	7.65	7.66	255	28	Wet grass area of Black Swamp 20 cm deep
FIN29b	20.72	994	8.5	7.13	272	31	Water sample collected in grass area of Black Swamp, 20 cm deep
FIN30	20.07	11294	11.52	8.56	275	162	Finniss River water, 30 cm deep
FIN36	24.83	11438	10.82	8.49	300	131	Finniss River water, 20 cm deep
FIN39a	31.7	10395	11.8	7.84	304	n.d.	Finniss River water, 3 cm deep
FIN39b	32.59	20860	10.3	8.89	282	145	Finniss River water, 3 cm deep

[1] n.d.: not determined.

Site descriptions are given in Table 1 (site notes) and physico-chemical data in Table 3. It should be noted that some chemical parameters and concentrations show short (event based) and medium temporal (e.g. seasonal) variations. This summary represents only a snapshot during the period of sampling.

The channel waters in the Currency Creek and Finniss River were both alkaline (pH 7.84 and 8.89) with very high SEC or EC values (23,591 and 18,388 µS/cm Table 3). The pH of the water in Black Swamp was 7.13. Alkalinity (as HCO_3) was also high in the western part of

Currency Creek (175 to 280 mg/L HCO_3) and the waters were oversaturated with dissolved oxygen (DO). However, downstream at site CUR26, the alkalinity decreased to 117 mg/L. The water in the cracks and in the soil pits was very acidic and oxidising (Eh of > 500 mV), typical of strongly oxidising conditions found associated with sulfuric materials. As expected the water also had very high SEC.

4. CONCLUSIONS

This study aimed to verify the presence (or absence) of ASS in the Currency Creek, Finniss River and Tookayerta Creek/Black Swamp areas, assess the risks of any ASS found, and to determine the surface water quality of waters present in the area (Table 3). The combined methodologies of peroxide testing, acid-base accounting (ABA) and soil incubation/ageing form the basis for a comprehensive risk assessment, representing a robust and tested methodology framework. This field investigation used field pH and soil morphology to “estimate” the general ASS risk category. Samples have also been submitted for laboratory analyses to quantify the amount of acidity (acid base accounting – see Fitzpatrick et al. 2008b; 2009). Although overall risks are low to very high, specific risk categories may be defined. Specific risks addressed are acidification, metal mobilisation and deoxygenation, and these are summarised in Table 4.

Table 4. Estimated risk categorisation for the various risks associated with the subtypes of ASS identified.

Risk Class	**Acidification**	**Metal mobilisation**	**De-oxygenation of water**
Monosulfidic organic soils	Low	Low-moderate	High
Sulfidic cracking clay soil	Low	Low	Low
Sulfidic organic soils	Low-moderate	Low-moderate	Low
Sulfidic soil (sandy)	Low - moderate	Low - moderate	Low
Sulfuric cracking clay soil	High	High	Low
Sulfuric soil (sandy)	Very high	Very high	Low

The highest risk of acidification is clearly related to the soils and sediments, which already contain sulfuric material. There is significant potential for acidification of soils with sulfidic materials but the risk of this occurring is low to moderate provided they are kept under anaerobic conditions. Metal mobilisation is likely to be most significant in sulfide-containing soils, which have undergone oxidation. Sulfide minerals scavenge trace metals and may therefore release these metals during oxidation.

De-oxygenation of waters is commonly associated with disturbance of monosulfidic black ooze (MBO) materials. The discharge of waters to the Finniss River could present a local risk if MBO materials are disturbed.

Note:
At the time of writing this report, chemical analyses which help define the acidity status of these soils had not been completed. The field and other observations reported here are expected to be confirmed by the chemical analyses and will add greater detail with respect to the full extent of actual and potential acid production.

5. RECOMMENDATIONS

Monitoring is considered an essential component of ASS risk assessments during the current drought, and will be particularly important during rewetting phases when acidity and metal mobilisation may occur. Monitoring frequency should be assessed based on a number of factors including the degree and extent of risk. This is site and scale dependent. Taking into account the area of the Currency Creek, Finniss River and Tookayerta Creek/Black Swamp catchments, it is recommended that monitoring be completed at two levels:

> (i). Detailed monitoring to be completed at selected “reference sites” every two to three months to determine future changes in acid generation, i.e. increase in sulfuric material with depth and increase in spatial extent during the drying or wetting regimes and mobility. This will involve soil sampling and analyses at specified sites along transects, supported by: (i) morphological, (ii) chemical (e.g. Cr-reducible S, retained acidity and acid neutralising capacity), and (iii) mineralogical observations at each reference site.
>
> (ii). Spatial monitoring on a monthly basis (or when there is a rapid water level change at the sites) sampled in this study, to assess spatial trends, based on visual indicators, morphological descriptions and “indicators” of acid generation. Observations should include physical characteristics of soils (e.g. changes in depth of sulfuric materials, depth of cracking, depth to water) and surface mineralogical characteristics (e.g. visually monitor changes in soil that may indicate sulfide oxidation such as brown-orange precipitates or the presence of indicator minerals such as jarosite, schwertmannite or Magnesium-rich sulfatic salts).

As well as providing a basis for quantitative estimates of acidity, metal mobility and treatment options, the data from the monitoring exercise can be used to confirm the current ASS maps. These maps can be used to illustrate the extent of acidification, to inform decision makers to assist in assessing the risks to local ecosystems.

We recommend that the detailed monitoring program be conducted along at least three transects in both Currency Creek and Finniss River catchments and along at least one transect in the Tookayerta Creek/Black Swamp catchment. However, we recommend that the rapid monitoring be conducted along all 12 transects, which includes all current 39 soil profile sample sites.

Monitoring of the water should be conducted following refilling or inundation to determine any impacts on water quality. This should include alkalinity, pH, SEC, major and trace elements, and nutrients.

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http://www.clw.csiro.au/publications/science/2008/sr12-08_withmaps.pdf
http://www.clw.csiro.au/publications/science/2008/sr12-08_nomaps.pdf

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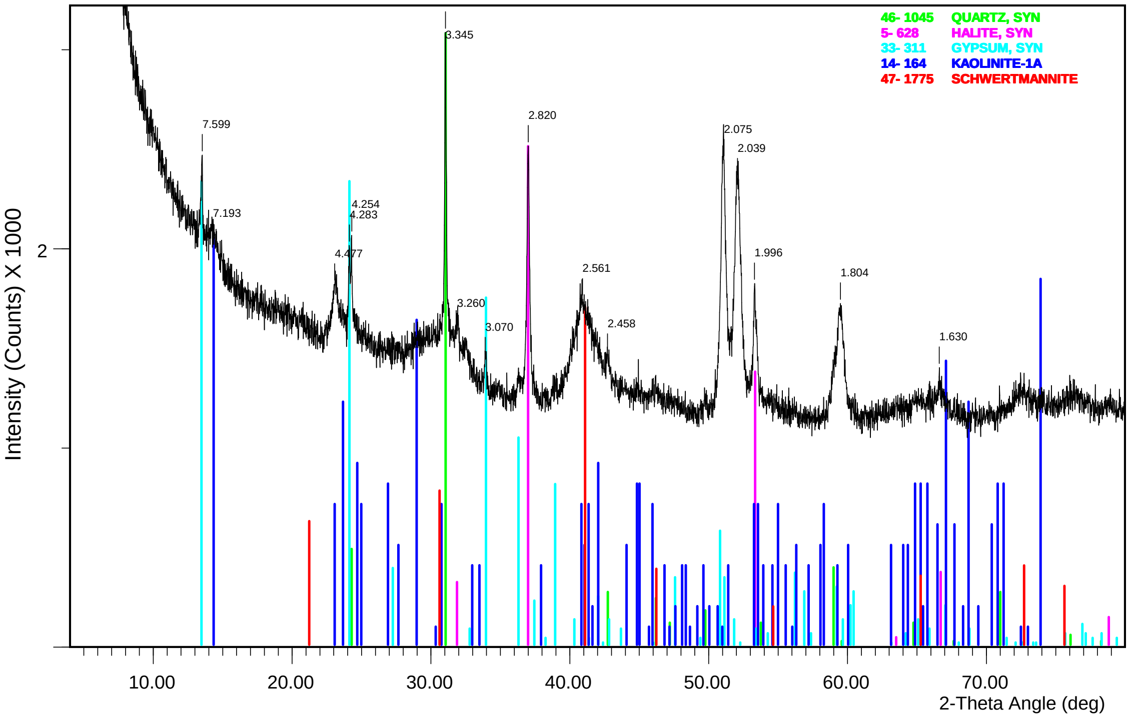
7. APPENDIX 1. X-RAY DIFFRACTION DATA OF SELECTED SAMPLES FROM FINNISS RIVER

FIN28.1



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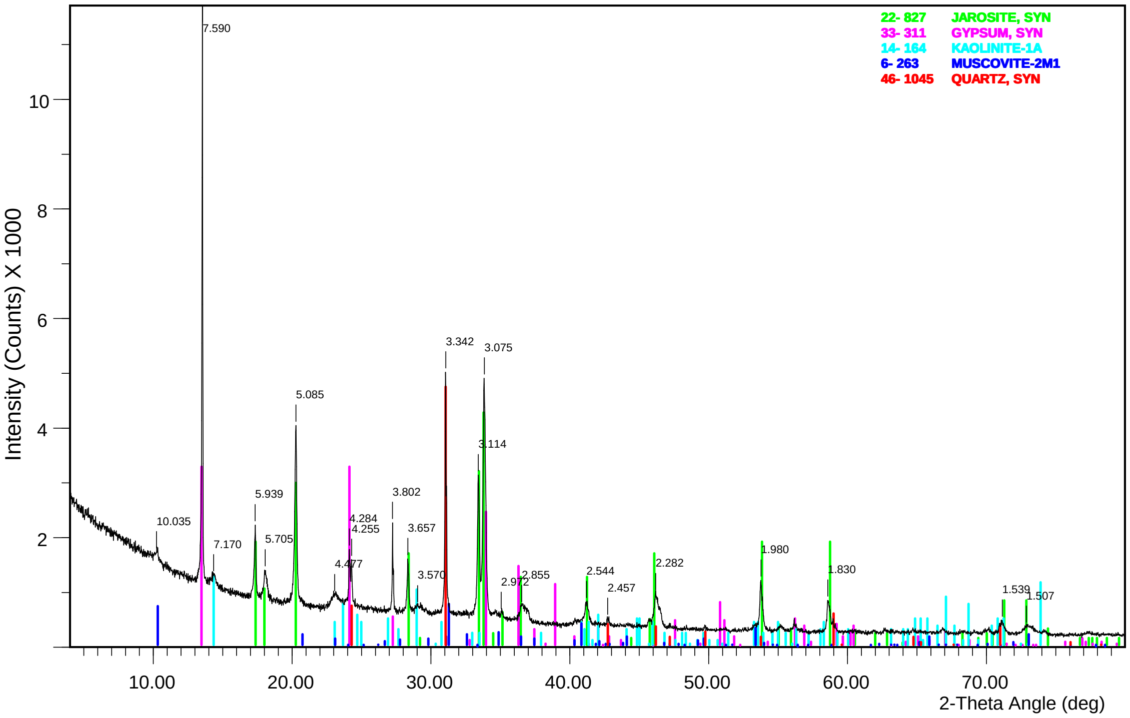

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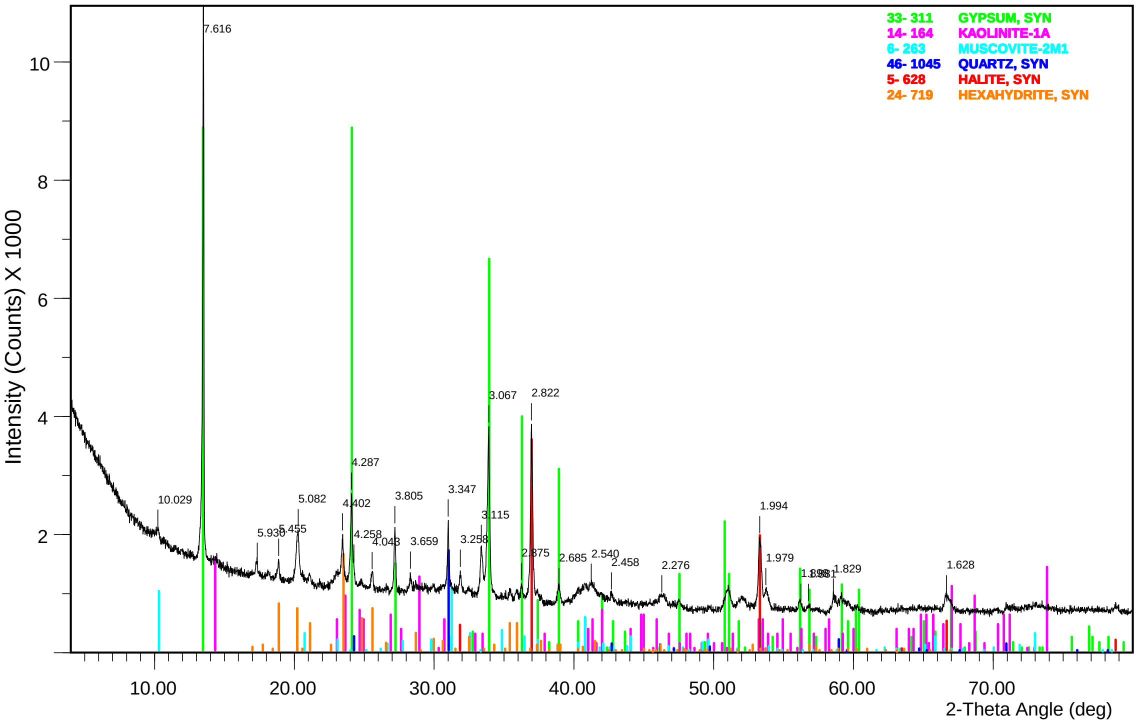

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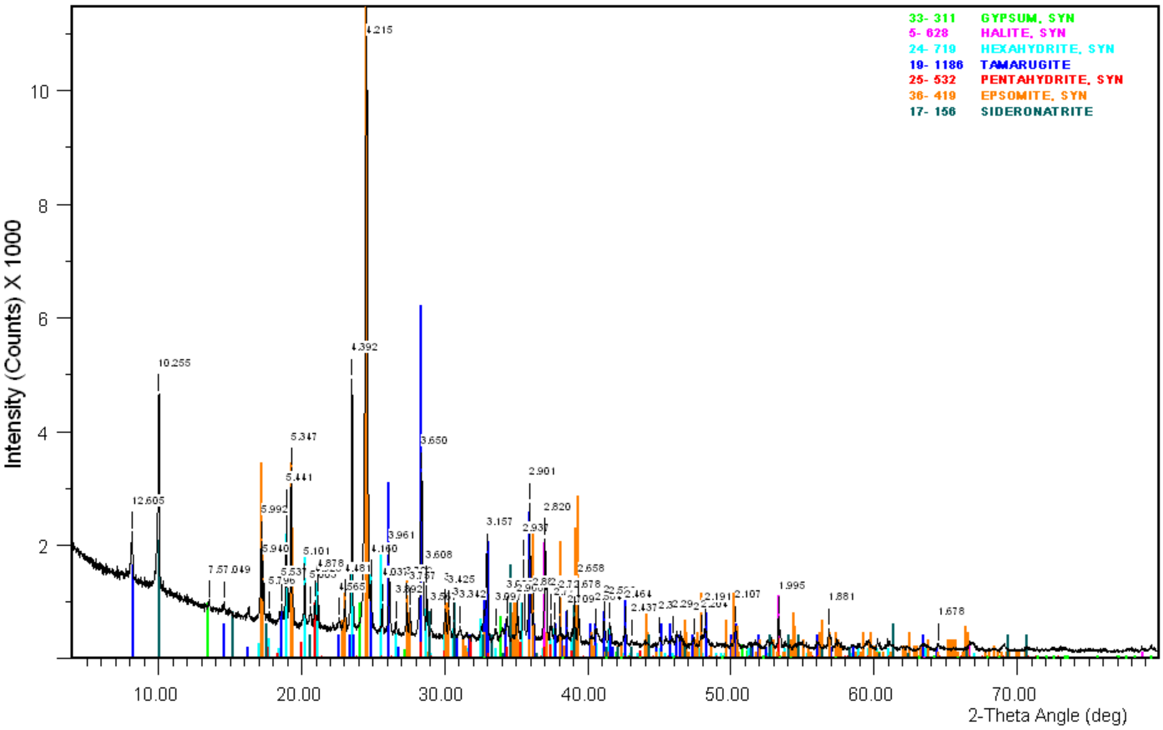

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