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CHAPTER 15

SPATIAL VARIABILITY IN THE STORAGE OF SULFUR, CARBON AND ACID GENERATION POTENTIAL IN AN INLAND SALINE SULFIDIC WETLAND, LOWER MURRAY RIVER FLOODPLAINS, SOUTH AUSTRALIA

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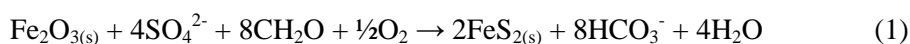
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INTRODUCTION

While acid sulfate soils (ASS) have long been recognised in marine environments (Dent 1986; Dent and Pons 1995; Lin and Melville 1994; Pons *et al* 1982; Van Breemen 1982), they have more recently been identified in inland settings, particularly in landscapes affected by salinisation (Fitzpatrick *et al* 1996). ASS are all soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). In coastal environments these soils are typically composed of a lower horizon with sulfidic material (potential ASS or PASS) overlain by an upper acidic (pH <3) horizon comprising sulfuric material characterised by the formation of jarosite (actual ASS; AASS) resulting from sulfide oxidation (Van Breemen 1982). Due to high carbonate concentrations inland sulfidic sediments are generally less acidic (pH 4-5) upon oxidation (Fitzpatrick *et al* 1996).

Sulfides form in reduced saline environments rich in sulfate and organic carbon, proceeding through a complex series of microbially mediated reactions (Andreae and Jaeschke 1992; Berner 1984; Canfield *et al* 1998; Howarth 1979; Morse *et al* 1987). In ASS, where pyrite is the dominant sulfide, the overall reaction of sulfide formation can be simplified to (Dent 1986):



The formation of sulfides is not sufficient by itself to produce potential acidity because an equal amount of acid neutralising capacity (here as HCO_3^-) is generated. A key step in the formation of potential acidity is the removal of the acid neutralising capacity from soil materials, leaving a net store of potential acidity in the remaining sulfides. In coastal environments carbonate is removed from sediments by tidal flushing (Dent 1986) whereas carbonate remains with sulfides in inland sulfidic materials (Fitzpatrick *et al* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a).

Under reduced conditions sulfidic material remains relatively benign and poses little threat to the surrounding environment (Dent 1986). However, when sulfidic material is exposed to oxidising conditions, pyrite can be oxidised by molecular oxygen and ferric iron (Luther and George 1987; McKibben and Barnes 1986; Moses *et al* 1987; Nordstrom and Southam 1997; Singer and Stumm 1970), producing sulfuric acid and forming sulfuric material. The overall reaction for the complete oxidation of pyrite and hydrolysis of iron produces 4 moles of H^+ for every mole of FeS_2 and can be written as (Dent 1986):



The draining of sulfidic material in many coastal environments has resulted in sulfide oxidation and the development of sulfuric material (Kinsela and Melville 2004; Lin *et al* 2004; MacDonald *et al* 2004; Oborn 1989; Osterholm and Astrom 2002; Smith *et al* 2003; Van Breemen 1982; Ward *et al* 2004). The low pH (<3) of sulfuric material can cause significant environmental damage to surrounding environments and infrastructure directly (e.g. Sammut and Lines-Kelly 1996; White *et al* 1997), and also indirectly by mobilising iron, aluminium and heavy metals (e.g. Astrom and Astrom 1997; Sammut and Lines-Kelly 1996; Sammut *et al* 1996).

Salinity impacts an estimated 25 % of the Lower Murray floodplains area and the area affected is expected to double over the next 50 years (Allison *et al* 1990; Evans and Kellett 1989; Lovering *et al* 1998; Simpson and Herczeg 1994). Sulfate constitutes ~20% of salts in the saline waters of the Murray-Darling Basin (Herczeg *et al* 2001; Jones *et al* 1994; Stephenson and Brown 1989). Recent surveys of wetlands in the Murray-Darling Basin have demonstrated that sulfides are widespread, especially in more saline wetlands (Fitzpatrick *et al.* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a; Sullivan *et al* 2004). Wetlands converted into evaporative saline disposal basins, including the Loveday Basin, have become hyper-saline (Evans 1989; Trehwella 1989). Lamontagne *et al* (2006a) identified the Loveday Basin, which had been partially dried, as having high but variable concentrations of sulfide and carbonate. Currently, the extent of sulfidic material within the Loveday Basin, the effect of water manipulations on the distribution of sulfides and carbonate, and the potential for sediments to become acidic, are unknown.

In this study we have examined the sediments / soils of the Loveday Basin in detail to establish the distribution of sulfur and carbon stores under different water regimes and the potential for sediment / soil acidification upon oxidation. It is hypothesised that (1) sulfur and sulfides will be concentrated in the upper sediments of the basin, (2) water regimes within the basin will control the spatial distribution of sulfur and carbon stores, and (3) the basin has sufficient amounts of carbonate to neutralise the potential acidity stored in the sulfidic material.

Site description

The Loveday Disposal Basin is a 3.3 km² hyper-saline wetland located in the lower Murray River floodplains, South Australia (34°15'S, 140°24'E; Figure 1). The climate is semi-arid, having cool winters and hot dry summers with variable rainfall (100-500 mm y⁻¹) and a high potential evapo-transpiration (~2000 mm y⁻¹) (Hostetler and Radke 1994). Originally a stranded meander lake of the Murray River, the basin sits within the Coonabidgal Clays, a silty clay aquitard, which overlies the Monoman Sand aquifer and abuts the Parilla-Loxton Sand aquifer within the Murray floodplains (Hostetler and Radke 1994). The basin was disconnected from the Murray River via floodgates and converted into an evaporation basin in 1972 to dispose of saline irrigation water for nearby irrigation districts (Evans 1989). Additionally, the basin is inundated during flood events of the Murray River (river height >10AHD; (Hostetler and Radke 1994)) and, sitting below the Cobdogla Irrigation Area groundwater mound to the east and the River Murray to the west (Figure 1), may also receive saline groundwater discharge (Hostetler and Radke 1994). Over three decades the basin has been essentially a terminal site for salts, including sulfate, with the principal loss of water through evaporation (Hostetler and Radke 1994). In addition to sulfate the basin also contains significant accumulations of sulfides (Lamontagne *et al* 2006a). Basin sediments were partially dried in 2000 due to a reduction in irrigation discharge and lack of floods. The basin sediments have since remained partially dry with intermittent wetting and drying due to variable inputs of water from rain events and irrigation and groundwater discharge.

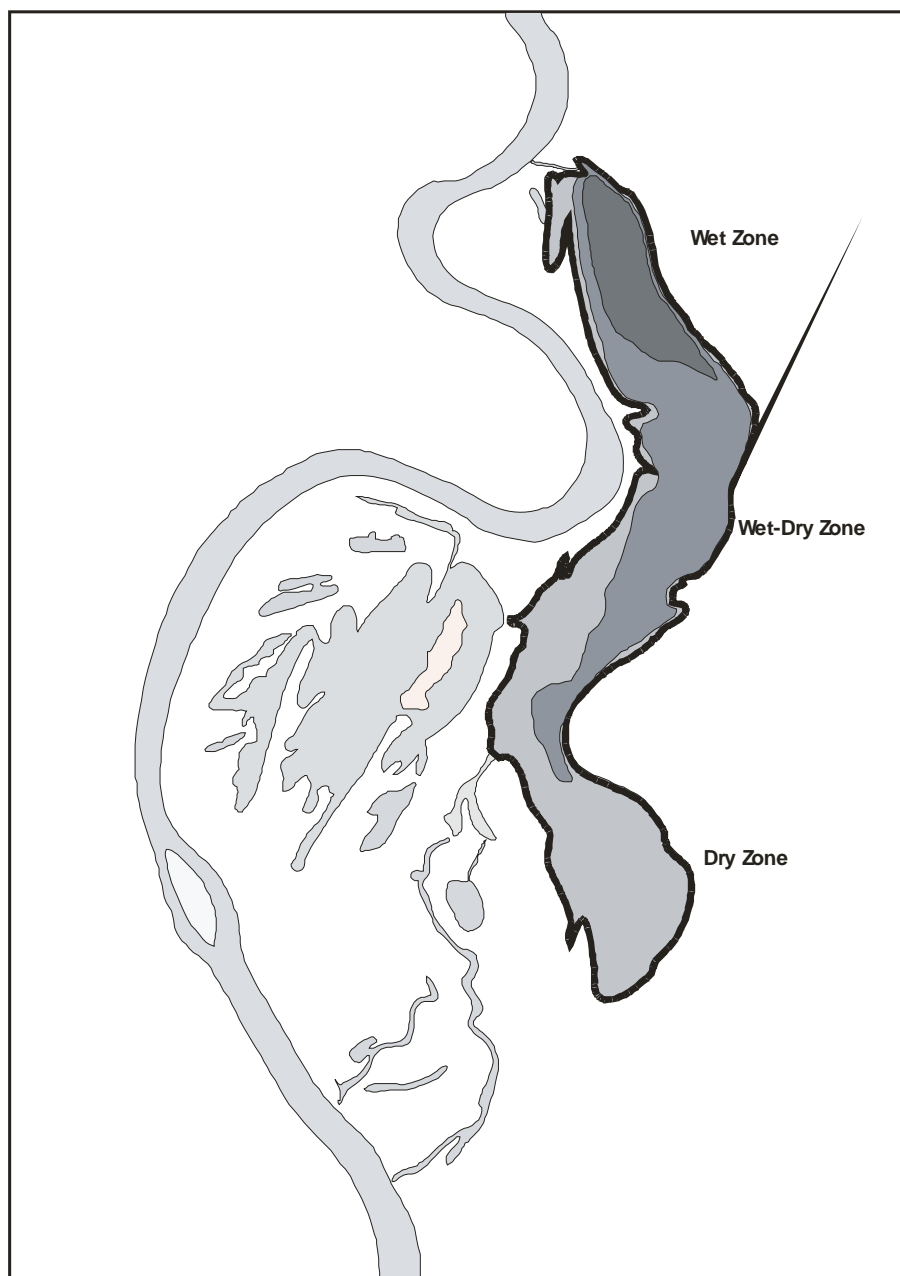


Figure 1 Map of Loveday basin.

METHODS

Sampling and analysis

Sediments were sampled with a shovel and/or PVC sediment corers from 0-50 cm and with a soil auger from 50-250 cm. Samples from 12 depth profiles were taken at 5 cm increments from 0-50 cm and for each major unit, from 50-250 cm. Samples of surface sediments were taken at another 70 sites from 0-5 cm and 20-25 cm. Samples from 0-50 cm were collected in screw-top polyethylene containers and samples from 50-250 cm collected in zip-lock sample bags, with all samples frozen on dry-ice in the field

and transported to a -20°C freezer. Frozen samples were subsequently freeze-dried and hand- or machine-milled for analysis.

Hand milled samples were analysed for the mineralogy of bulk sediments and density separated clay fractions by Cu K α X-ray diffraction (XRD) on a Siemens D500/D501 series XRD (Moore and Reynolds 1989). Bulk samples were dried at 40°C, hand ground to between 1-10 μ m, spiked with zinc oxide and scanned from 2-70° 2 θ at 2° per minute in 0.02° steps. Oriented magnesium saturated clay fractions were scanned from 2-42° 2 θ , re-scanned from 2-35° 2 θ after glycolation, and scanned again from 2-28° 2 θ after heating at 350°C for 1h. Output files of intensity against 2 θ were analysed with EVATM mineral identification and SIROQUANT mineral quantification softwares.

The concentrations of reduced inorganic sulfur minerals (FeS and FeS₂) were analysed by the acid volatile sulfur (AVS; FeS) method (Fyfe *et al* 2004) and chromium reducible sulfur (CRS; FeS + FeS₂) method (Sullivan *et al* 1999; Sullivan *et al* 2000). AVS was conducted in the field on wet sediments as well as in the laboratory, along with CRS on freeze-dried machine milled samples. These methods liberate the reduced inorganic sulfur fractions as H₂S, which is trapped in a zinc acetate solution as zinc sulfide and quantified from iodometric titration. The AVS fraction has commonly been assumed to represent the monosulfides (amorphous FeS, FeS_{1-x} and Fe₃S₄), but recent studies demonstrate that other sulfur fractions might be included in the extraction and that not all the monosulfides are removed (Rickard and Morse 2005). The authors acknowledge the limitations of this method while referring to this fraction from here on as the “monosulfides” for comparison with other studies that have used this method. As the CRS method measures the total inorganic reduced sulfur (FeS + FeS₂), pyrite (FeS₂) is calculated from the CRS fraction minus the AVS fraction, likewise, for comparison with other studies that have used these methods.

Organic sulfur content was measured by analysing total sulfur in CRS residues, where inorganic reduced sulfur is removed as H₂S and any remaining oxidised sulfur removed by rinsing with Milli-Q. (Nriagu and Soon 1985). Total sulfur was analysed on all samples by X-ray fluorescence (XRF) and total sulfur and total carbon analysed on a suite of 50 samples by LECO-CNS induction furnace analysis (conducted at CSIRO). Carbonate carbon was quantified by a manometric technique (conducted by CSIRO) on all samples, after removal of large shell fragments, with the difference between total carbon and carbonate assumed to be organic carbon. The sulfate fraction was calculated by subtraction of the CRS and organic sulfur from the total sulfur. The presence and amounts of gypsum, pyrite and jarosite were confirmed with a Cambridge 360 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) analyser (Riemer 1998).

Sediment pH and EC were measured on wet sediments in a 1:5 sediment-Milli Q water mix with duplicate samples oxidised with 30 % H₂O₂ (Ward *et al* 2002).

Amounts of sulfur, carbon and acidity

The amounts of sulfur and carbon fractions have been calculated from their average concentrations in each sedimentary unit multiplied by the bulk density of sediments and the volume of each unit.

$$X_A = X_C \times BD \times V_U$$

Where X_A is the amount (weight) of the sulfur or carbon fraction in each unit, X_C is the average concentration (weight/weight) of sulfur or carbon in each unit, BD is the bulk density of sediments (g cm⁻³) and V_U is the volume of each unit. The bulk density of sediments is assumed to be 1.3 g cm⁻³ for sediments below 10 cm and 0.9 g cm⁻³ for sediments above 10 cm (Beavis *et al* 2006).

The acid generation potential (AGP) of each unit has been calculated assuming 2 moles of H⁺ are produced for every mole of CRS and the acid neutralising capacity (ANC) has been calculated assuming 2 moles of H⁺ are consumed for every mole of carbonate. The net acid generation potential (NAGP) of sediments is assumed to be equal to the AGP minus the ANC.

$$NAGP = AGP - ANC$$

Positive NAGP values indicate a net store of acidity whilst a negative NAGP corresponds to an excess of alkalinity in sediments.

RESULTS AND DISCUSSION

Basin sediment characterisation

The mineralogy and grain size distributions of the Loveday Basin's sediments (3.3 km²) are summarised in Tables 1 and 2. The basin sediments are principally homogenous grey (5Y6/1) clays (Coonambidgal Clays; unit C) to a depth of 150 cm composed of kaolinite, illite, muscovite and feldspar overlying quartz-rich light grey (5Y7/2) silts (150-200 cm depth, unit D) and light yellowy grey (5Y8/2) sands (200-250 cm depth; unit E) of the Monoman Sands (Tables 1 and 2). Since the partial drying of the basin in 2000, intermittent wetting and drying of sediments has produced three distinct zones within the surface 30-40 cm of sediments. These zones have been mapped from aerial photographs, LANDSAT image mosaics and field observations and have been termed in this study the Wet Zone, Wet-Dry Zone and Dry Zone, each following topographic contours of the basin (Map Figure 1).

Table 1 Grain size distribution of basin sediments

Grain Size Weight %	A (Wet)	A (Wet-Dry)	A (Dry)	B (Wet)	B (Wet-Dry)	B (Dry)	C	D	E
Silt and Clay (<63um)	98.42	98.61	85.12	94.80	94.40	86.07	87.93	90.11	40.91
Very Fine Sand (63-125um)	0.65	0.84	8.20	1.38	2.24	7.71	5.37	3.71	10.55
Fine Sand (125-250um)	0.50	0.32	5.92	2.10	2.16	5.62	5.16	3.59	39.48
Medium Sand (250-500um)	0.38	0.17	0.47	1.61	0.43	0.44	0.79	0.71	1.13
Coarse Sand (0.5-1mm)	0.04	0.04	0.01	0.03	0.34	0.01	0.35	0.76	0.87
Very Coarse Sand (1-2mm)	-	0.02	-	0.08	0.43	0.14	0.21	0.64	0.75
Gravel (>2mm)	-	-	0.29	-	-	-	0.20	0.49	6.31

Table 2 Bulk mineralogy of basin sediments

Mineral Weight %	A (Wet)	A (Wet-Dry)	A (Dry)	B (Wet)	B (Wet-Dry)	B (Dry)	C	D	E
Quartz	24.0	22.3	43.1	30.3	30.3	39.0	47.1	46.4	56.2
Orthoclase	3.1	3.1	5.6	5.2	4.0	4.4	4.0	3.8	5.1
Albite	2.8	1.8	6.9	7.6	3.4	5.1	5.1	3.1	3.2
Muscovite	0.9	0.8	1.4	0.9	1.2	12.2	5.3	1.0	0.9
Kaolinite	1.9	1.8	1.8	4.8	3.9	5.5	3.7	2.7	2.0
Illite	4.1	12.0	2.5	7.0	7.0	8.0	13.2	5.9	6.2
Montmorillonite	16.0	7.0	10.4	23.3	24.2	7.8	6.4	17.3	15.2
Calcite	3.9	4.6	3.0	0.3	2.9	1.0	3.7	2.7	2.0
Sodium Chloride	7.0	8.8	7.3	3.9	6.3	2.9	1.0	1.5	1.2
Gypsum	8.3	17.3	0.1	0.4	0.5	2.4	0.5	0.3	0.9
Pyrite	2.1	1.4	1.9	4.8	3.3	0.7	-	-	-
Jarosite	-	-	-	-	0.3	-	-	-	-
Amorp. Content	25.8	19.1	15.7	11.4	12.9	11.1	13.5	17.1	8.5

The three zones have been further subdivided into a saline clay unit (0-10 cm depth; unit A) and a mottled clay unit (10-40 cm depth; unit B). The Wet Zone sediments (0.6 km²; pH 7-8) have a permanent water cover with unit B characterised by dark grey clays (5Y4/1) with black (5Y2/1) sulfidic mottles, covered by sulfidic black (5Y2/1) ooze of unit A. The Wet-Dry Zone sediments (1.1 km²; pH 3-7) are currently exposed to the atmosphere in dry periods but intermittently saturated during wet periods, resulting in cyclic wetting and drying. Shrinkage of the clays during drying has produced desiccation cracks (20 cm deep) that have propagated to form polygonal desiccation features (Lamontagne *et al* 2006a). In the Wet-Dry Zone unit B is dark grey (5Y4/1) to dark reddish brown (5YR4/2) and contains prominent red (2.5YR4/8) iron-rich mottles intermingled with black (5Y2/1) sulfidic mottles and isolated pale yellow (5Y8/4) mottles of jarosite associated with pH <4. Unit A of the Wet-Dry Zone is covered in salt efflorescence during dry periods and in sulfidic black (5Y2/1) ooze during wet periods. The Dry Zone sediments (1.7 km²; pH 6-7) are predominantly dry, only forming a water cover during large flood events. In the Dry Zone the grey (5Y6/1) sandy clays of unit B contain reddish brown (2.5YR4/8) iron-rich

mottles, with unit A being predominantly light grey (5Y7/2) dry flocculated sandy clays. The distinct textural characteristics of the basin's three surface zones indicate these areas have either formed under different sedimentary conditions or evolved from the same parent material due to subsequent environmental changes.

The clays of the Wet and Wet-Dry Zones are almost identical in mineralogy and grain size distribution (Tables 1 and 2). Both the Wet and Wet-Dry Zones have a large silt-clay grain size fraction of >94% with low quartz (22-30%) and muscovite (0.8-1.4%) contents (the sand size fraction increases in the Wet and Wet-Dry Zone along the basin's eastern side due to input from the adjacent Loxton-Parilla Sands. Additionally, in both the Wet and Wet-Dry Zones, unit A has high gypsum (8-17%) and unit B has high smectite (23-24%) concentrations (Table 2). The Wet and Wet-Dry Zones are distinctly different in grain size and mineralogy from the Dry Zone (Tables 1 and 2). The Dry Zone has a lower silt-clay grain size fraction (85-86%), with greater amounts of sand (5-8%) and higher quartz concentrations (39-43%). Unit B of the Dry Zone also has higher muscovite (12%) and lower smectite (7.8%) concentrations than unit B of the Wet and Wet-Dry Zones (Table 2). The grain size distribution and clay mineralogy indicate that the sediments of the Wet and Wet-Dry Zones have formed from the same parent material, which is distinctly different to the parent materials which have formed the Dry Zone sediments.

The Dry Zone sediments are similar in mineralogy and grain size distribution to the underlying unit C (Table 2). Both sediments have high quartz and muscovite concentrations and lower amounts of smectite. The principal difference between the two units is the higher salt content of the Dry Zone (halite 2.9-7.3%; gypsum 0.1-2.4%). This suggests the Dry Zone sediments are principally the exposed surface of unit C which has accumulated salts due to evaporation of saline waters. However, the different mineralogy and grain size distribution of the Wet and Wet-Dry Zones indicate these sediments are not formed from unit C. The deposition of smectite-rich clays over the coarser quartz- and muscovite-rich unit C is a common sedimentary sequence within flooded wetlands of the lower Murray floodplains often referred to as 'wetland clays'. Although water flow has been restricted between the Loveday Basin and the River Murray for the last 30 years, the basin is still inundated during flood events (river level above 10m AHD; (Hostetler and Radke 1994)), which will deposit the majority of the wetland clays. Gell *et al* (2007) measured the sedimentation rates of the Loveday Basin (Wet Zone) to be >1.0 cm/y above 60 cm depth (post-1958 to 2006) using ¹³⁷Cs isotopes, pollen and optically stimulated luminescence (OSL) techniques. This demonstrates that the majority of the basin's wetland clays (~30-50 cm depth) have been deposited since the basin's conversion into a disposal basin in the 1970's. The regulation of basin waters appears to have promoted the settling of the fine clays, forming the smectite-rich wetland clays that overly unit C in the Wet and Wet-Dry Zones.

The textural features and clay mineralogy of the Loveday Basins sediments reflect the basin's dominant water regimes. The Dry Zone has not accumulated any detectable smectite-rich wetland clays, demonstrating that this area of the basin has not had prolonged water cover since basin water regulation and is probably only inundated under high flood events. The Wet and Wet-Dry Zones are comprised of 30-50cm of smectite-rich wetland clays which indicate, from sedimentation rates (Gell *et al* 2007), that these areas have mostly maintained a permanent water cover since Loveday's conversion into a saline disposal basin in the 1970's. Subsequent intermittent drying of these smectite-rich wetland clays since 2000 has resulted in the formation of the prominent desiccation features and iron-rich mottles of the Wet-Dry Zone. The Wet Zone has maintained a water cover during these dry periods and sediments have remained largely undisturbed with no evidence of oxidation or the formation of desiccation features. The three dominant water regimes of the Loveday Basin have produced these three distinct sedimentary units.

Distribution of sulfur and carbon stores

Sulfur

The Loveday Basin sediments have a wide range of sulfur concentrations and amounts with depth (Figures 2 and 3). The principal forms of sulfur are sulfate (based on XRD analysis showing predominantly gypsum with minor amounts of jarosite), pyrite (CrS-AVS), monosulfides (AVS) and organic sulfur (OS). Total sulfur concentrations are relatively low between 40 cm and 250 cm depths (units C, D and E) ranging from 0.04 to 0.15%S but increase significantly in sediments above 40 cm depth where concentrations in unit B range from 0.04 to 1.51%S and in unit A from 0.08 to 5.74%S. The

basin's sulfur is dominated by sulfate (0.04-5.67% S) which is present in all sediment units. The reduced forms of sulfur, pyrite (<0.002-1.31% S), monosulfides (<0.002-0.42% S) and organic sulfur (0.04-0.08% S), are largely restricted to the sulfur-rich upper 40 cm of basin sediments (Figure 2).

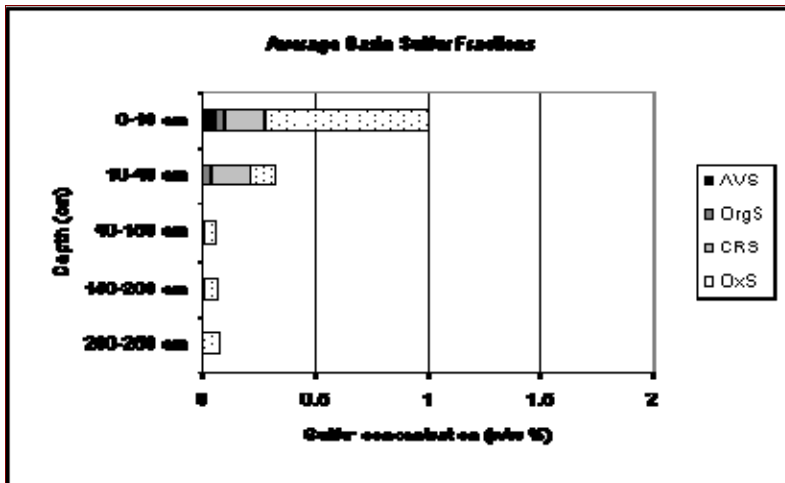


Figure 2 Total basin sulfur concentrations

This sulfur-rich upper 40 cm of sediments, although making up only 5% of the basin's total volume, contains 64% (12.72 kt S) of the basin's sulfur with 52% (7.41 kt S) of sulfate, 90% (3.89 kt S) of pyrite and <95% (0.39 kt S) of monosulfides (Figure 3). The high near-surface sulfate concentrations demonstrate that for most of the basins history sulfate concentrations have been low and sulfate accumulation from the recent evaporative disposal of saline waters has been restricted to the upper 40 cm of sediments, with limited movement into the underlying unit C. Additionally, the restriction of reduced sulfur to the upper 40 cm demonstrate that it is only since the regulation of the basin waters that conditions have been favourable for the formation and preservation of significant amounts of sulfides.

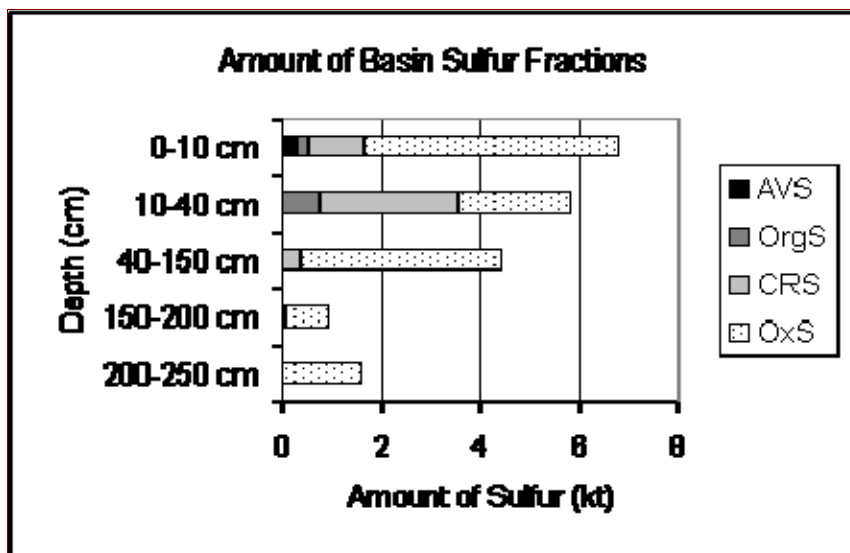


Figure 3 Total basin sulfur amounts

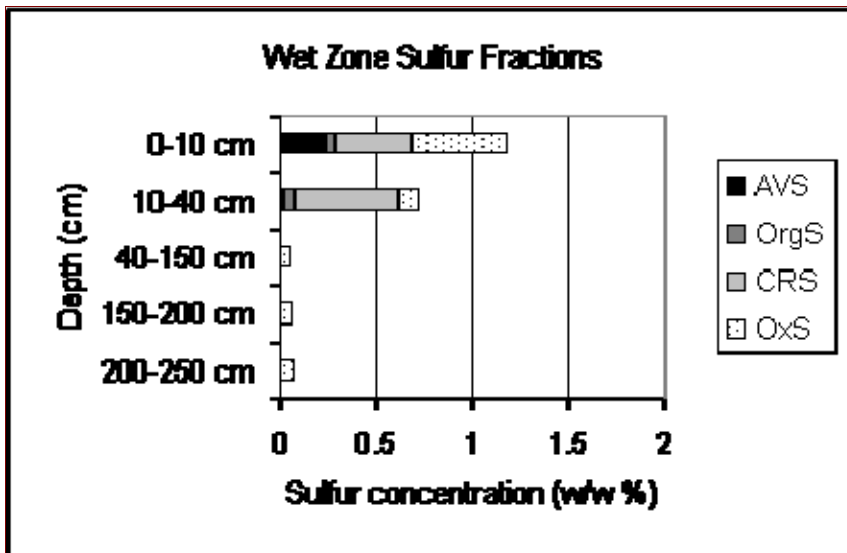


Figure 4. Wet Zone sulfur concentrations

Variations in the form and concentration of sulfur in the sulfur-rich surface 40 cm are distinct between the Wet Zone, Wet-Dry Zone and Dry Zone (Figures 4, 5 and 6). Sulfides are the dominant form of sulfur in the Wet Zone (averaging 0.6%S), present predominantly as pyrite with monosulfides concentrated in unit A (Figure 4). The Wet-Dry Zone also contains significant concentrations of sulfides (averaging 0.2%S) but sulfate, in the form of gypsum and isolated mottles of jarosite, is most prevalent, averaging 1.5%S in unit A (Figure 5). The Dry Zone contains relatively low concentrations of sulfur as sulfate (averaging 0.3%S) and only minor amount of sulfide (averaging 0.04%S), largely in the unit A (Figure 6). These differences between the three zones indicate the three water regimes that have produced the distinct textures and clay mineralogies have also produced distinct distributions of sulfur minerals.

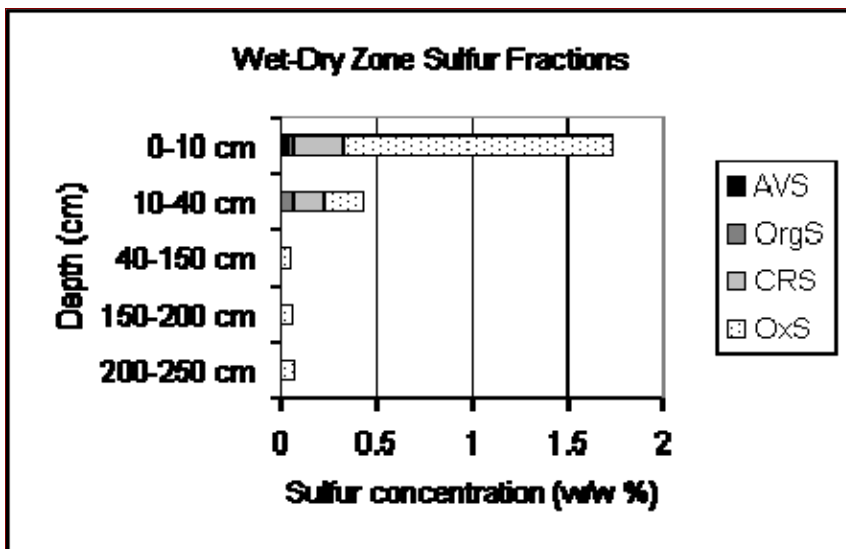


Figure 5. Wet-Dry Zone sulfur concentrations

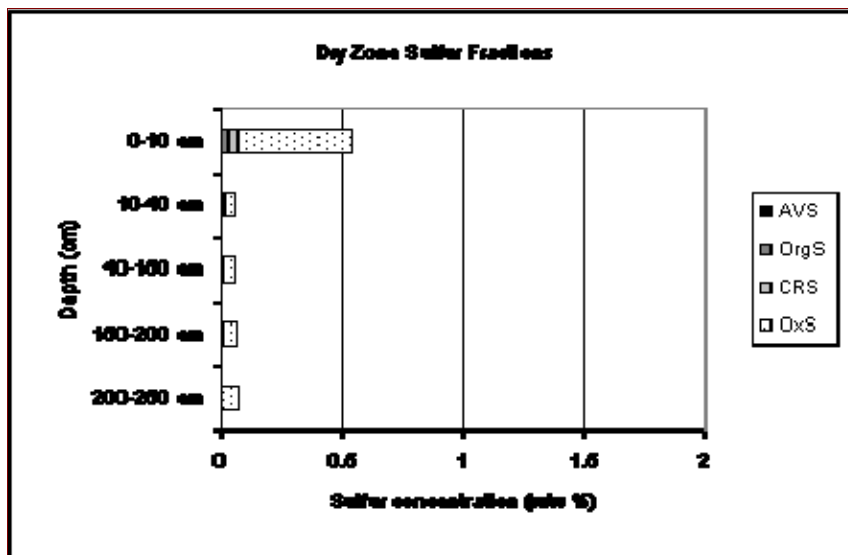


Figure 6. Dry Zone sulfur concentrations

Whilst the spatial range in sulfate and sulfide concentrations is relatively low within the Wet and Dry Zones, concentrations within the Wet-Dry Zone are highly variable (Figures 7 and 8). Low sulfate (<1%) and sulfide (<0.2%) concentrations are consistent throughout the Dry Zone at both 0-10cm and 10-40cm depths. Sulfate accumulation may be restricted in the Dry Zone as the flooding of the basin to the elevation of the Dry Zone sediments is infrequent (Hostetler and Radke 1994) and significantly reduces the basin salinity (Lamontagne *et al* 2006b), lowering sulfate concentrations. Additionally, the infrequent flooding of this zone and exposure to the atmosphere would limit the formation and preservation of sulfides (Dent 1986). This indicates that the predominantly dry conditions of the Dry Zone have produced the consistently low sulfate and sulfide concentrations observed. Within the Wet Zone, sulfate concentrations are consistently below 1% at both 0-10cm and 10-40cm and sulfides are consistently greater than 0.2%S at 0-10cm, increasing at 10-40cm depth. This indicates that sulfate reduction and the preservation of sulfides are consistently high across the entire Wet Zone, where a permanent water cover has been present. In contrast to the Wet and Dry Zones, sulfate and sulfide concentrations across the Wet-Dry Zone range over two orders of magnitude (<0.01-5.67%S and <0.01-1.1%S respectively), suggesting the heterogeneity is due to the wetting and drying of sediments.

INLAND ACID SULFATE SOIL SYSTEMS ACROSS AUSTRALIA

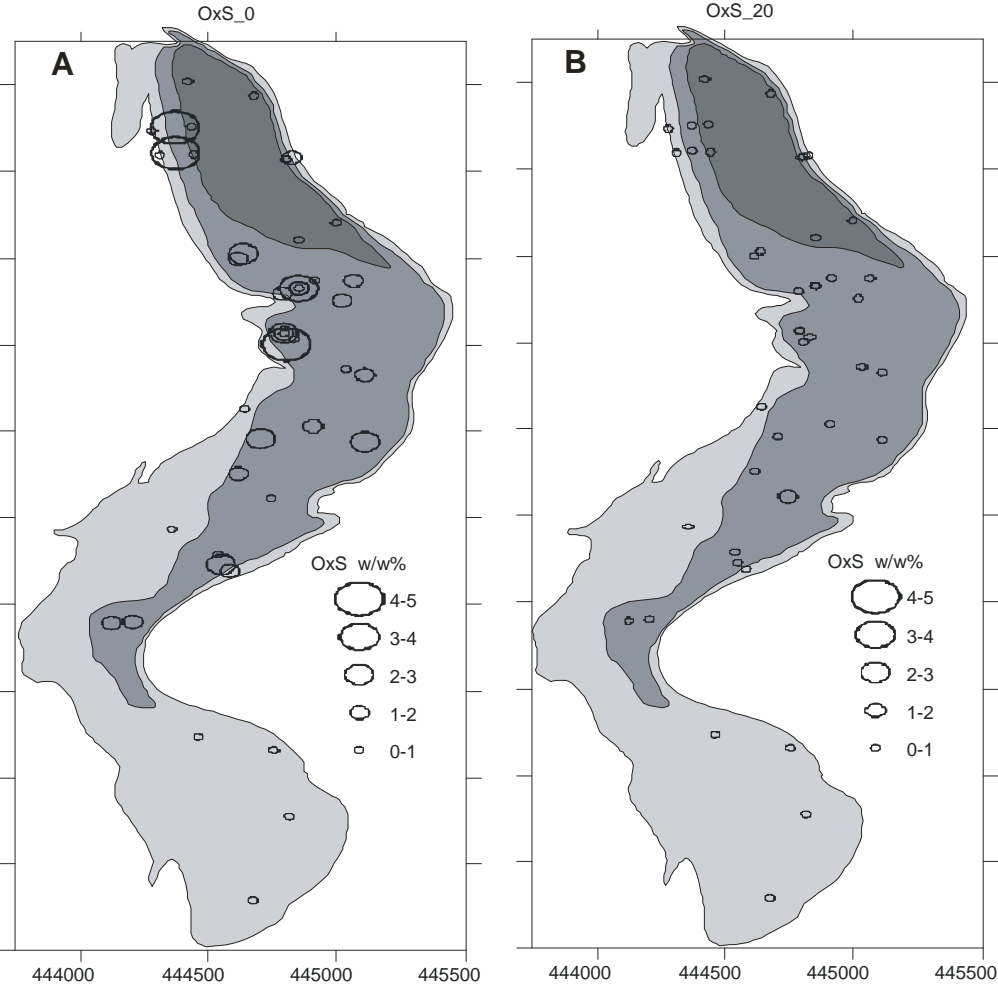


Figure 7 Sulfate concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

INLAND ACID SULFATE SOIL SYSTEMS ACROSS AUSTRALIA

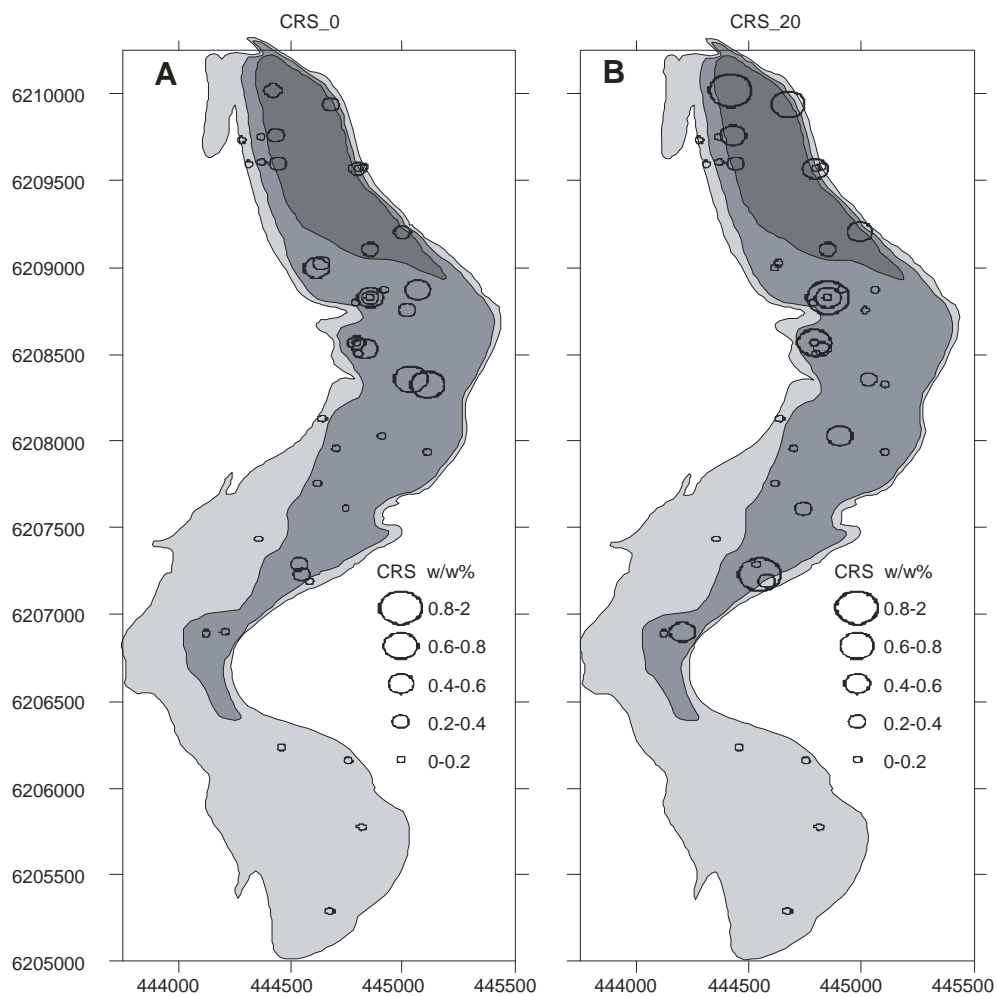


Figure 8 Sulfide concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

The Wet-Dry Zone was formed under similar conditions to the Wet Zone prior to sediment drying since 2000 and has accumulated wetland clays and high concentrations of sulfide (up to 1%S). Like the Wet Zone, with a largely permanent water cover for 30 years, the Wet-Dry Zone most likely had sediments with relatively homogenous low sulfate and high sulfide concentrations. This would indicate that the localised higher sulfate concentrations at the surface of the Wet-Dry Zone relative to the Wet Zone represent an increase in sulfate (Figures 7 and 8) and the localised lower sulfide concentrations of the Wet-Dry Zone relative to the Wet Zone represent a decrease in sulfides (Figures 7 and 8). An increase in sulfate and decrease in sulfide concentrations during the wetting and drying of the saline sulfidic sediments can be explained by the oxidation of sulfide upon exposure to the atmosphere and the evaporative concentration of sulfate in surface salt efflorescence since sediment drying in 2000. The variable distribution of sulfate and sulfides in the Wet-Dry Zone indicates that the accumulation of sulfate salts and the oxidation of sulfides during wetting and drying phases do not proceed evenly throughout the sediments. These observations show that, whilst predominantly dry and predominantly wet sediments have consistent distributions of sulfate and sulfide, the wetting and drying of sulfidic sediments produce highly variable distributions of sulfate and sulfide.

Carbon

The sediments also have a broad range of organic carbon and carbonate concentrations which range from <0.002 to 3.89%C and from <0.005 to 1.69%C respectively. Organic carbon concentrations are relatively low below 40 cm depth (units C, D and E), ranging from <0.002 to 0.32%C, but it increases in concentration in the upper 40 cm from 0.11 to 3.89%C (Figure 9). Carbonate is generally in high concentrations (averaging 0.6%C) in units D and E whilst the majority of unit C has low carbonate

concentrations (averaging 0.05% C; Figure 9). The basin's carbonate concentrations increase in the upper 40 cm of sediments, averaging 0.14% C in unit B and 0.38% C in unit A (Figure 9). The amounts of carbonate and organic carbon are given in Figures 10. Like sulfur, carbon concentrations in the upper 40 cm of the basin show distinct differences between the three water regimes. The average organic carbon and carbonate concentrations follow similar trends to sulfide concentrations through these zones with generally high concentrations in the Wet Zone (2.3% C and 0.5% C respectively; Figure 11) which decrease in the Wet-Dry Zone (1.75% C and 0.2% C respectively; Figure 12) and are much lower in the Dry Zone (0.8% C and <0.1% C respectively; Figure 13). The consistently organic-rich wetland clays of the Wet and Wet-Dry Zones demonstrate that the high water levels that trapped the fine clays have also trapped organic carbon. These distinct trends indicate that the amount and distribution of organic carbon and carbonate, like those of sulfate and sulfide, are controlled by the prevailing water regime.

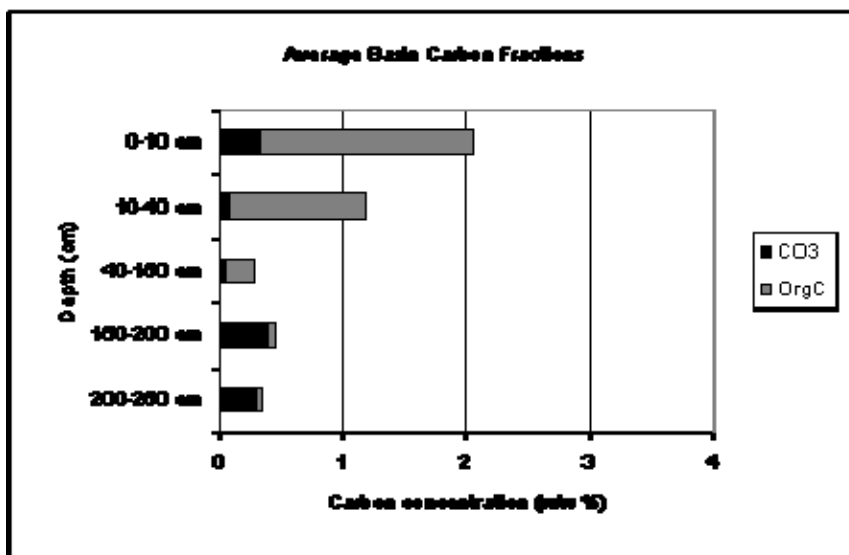


Figure 9. Total basin carbon concentrations

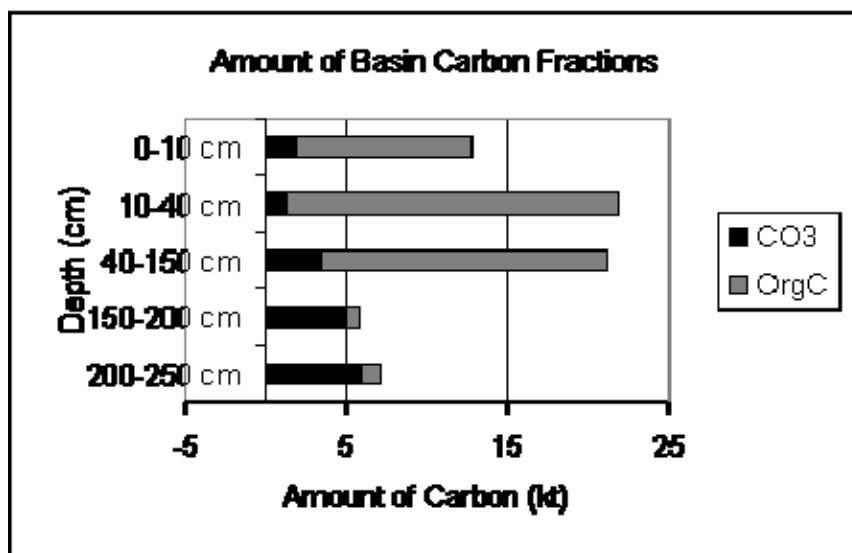


Figure 10. Total basin carbon amounts

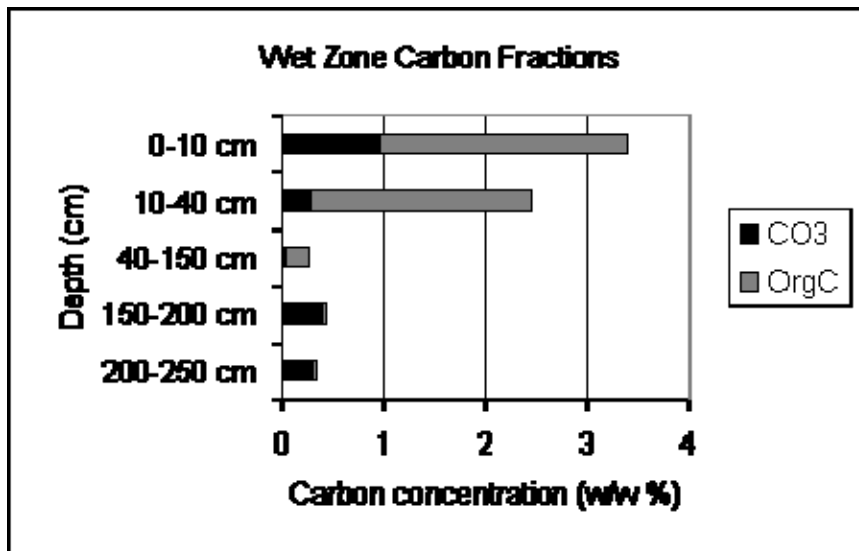


Figure 11. Wet Zone carbon concentrations

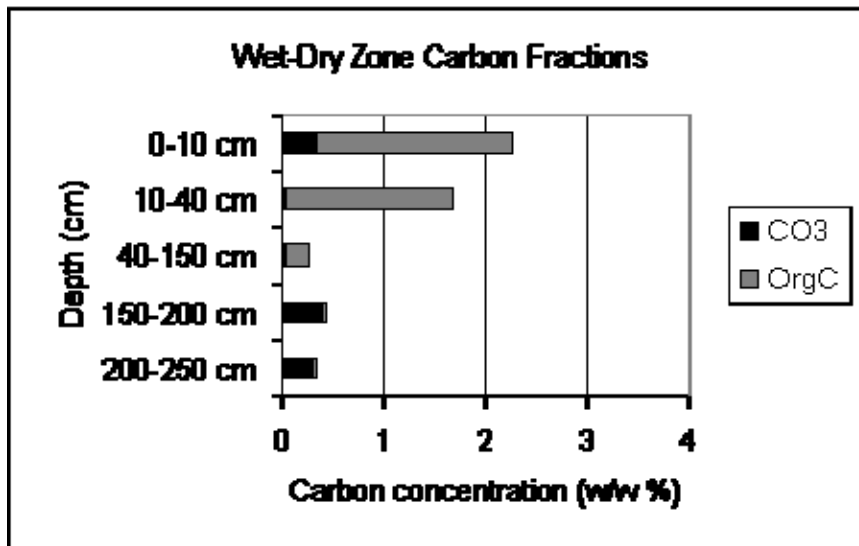


Figure 12. Wet_Dry Zone carbon concentrations

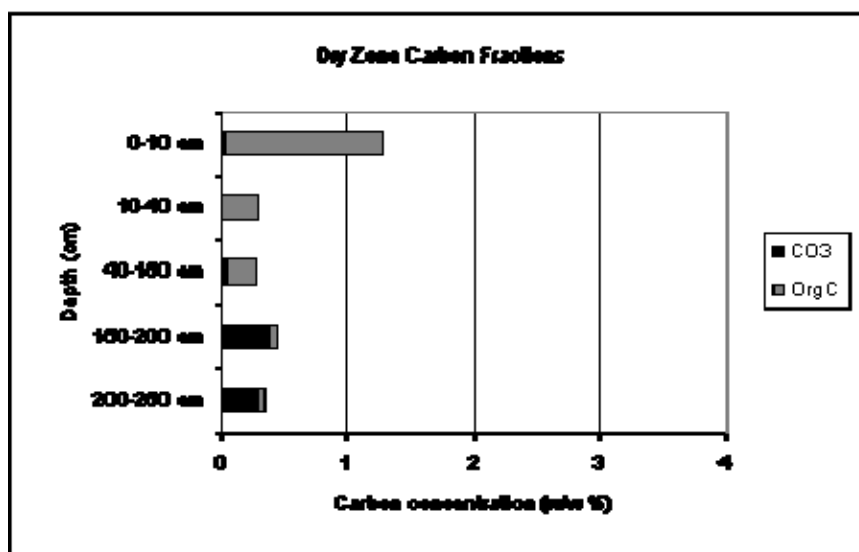


Figure 13. Dry Zone carbon concentrations

The concentrations of carbonate are spatially relatively consistent within the Wet and Dry Zones and, as for sulfate and sulfides, highly variable in the Wet-Dry Zone (Figure 14). The consistently low concentrations of carbonate in the Dry Zone are, like for sulfate, most likely related to the low salinity and infrequency of flooding events that reach these sediments. The consistently high concentrations of carbonate in the Wet Zone are most likely due to a combination of precipitation of carbonate from saline waters and mineralisation of organic carbon through sulfate reduction. The spatially variable carbonate concentrations of the Wet-Dry Zone are largely lower than those of the Wet Zone. This is unusual as carbonate, like sulfate, would be expected to have accumulated in the Wet-Dry Zone due to evaporation. The variable and considerably lower carbonate concentrations imply that wetting and drying of sediments has leached carbonate from the Wet-Dry Zone.

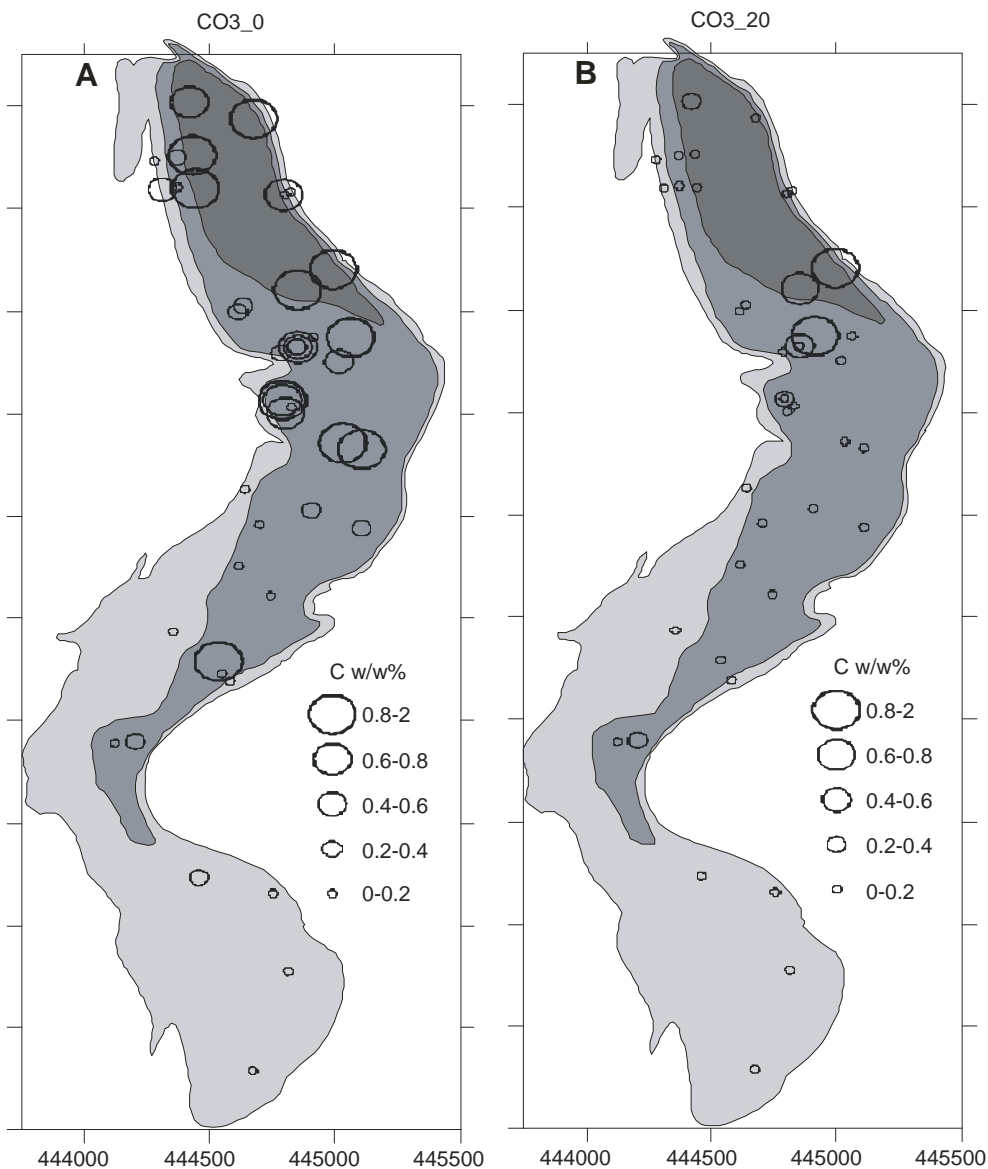


Figure 14
Carbonate concentrations of unit A (0-10 cm) and unit B (10-40 cm) through the Wet, Wet-Dry and Dry Zones.

ACIDIFICATION POTENTIAL

Distribution of sulfide versus carbonate

The spatial distribution of sulfide relative to carbonate controls the potential for the acidification of sediments (Dent 1986). The concentrations of sulfide against carbonate have been plotted for units A and B of the three water regimes (Figures 15 A-C) and for units C, D and E across the basin (Figure 15 D). The trigger value for sulfide concentrations in fine textured coastal ASS (0.1%S as sulfide) has been plotted as a dashed line. According to the coastal ASS guidelines, sediments with higher sulfide concentrations than this value would require further investigation. Plotted as a solid line is where the acid generation potential (AGP) of sulfides equals the acid neutralising capacity (ANC) of carbonate. Any value to the left of this solid line has greater AGP than ANC and may become acidic upon oxidation. The Loveday Basin sediments largely follow a trend of high sulfide concentrations matched with high carbonate concentrations. In units C, D and E and throughout the Dry Zone sulfide concentrations are consistently below the coastal ASS trigger value, with sufficient carbonate concentrations to counter any acidity (Figure 15 C and D). The Wet Zone has high sulfide concentrations but also proportionally high concentrations of carbonate (Figure 15 A).

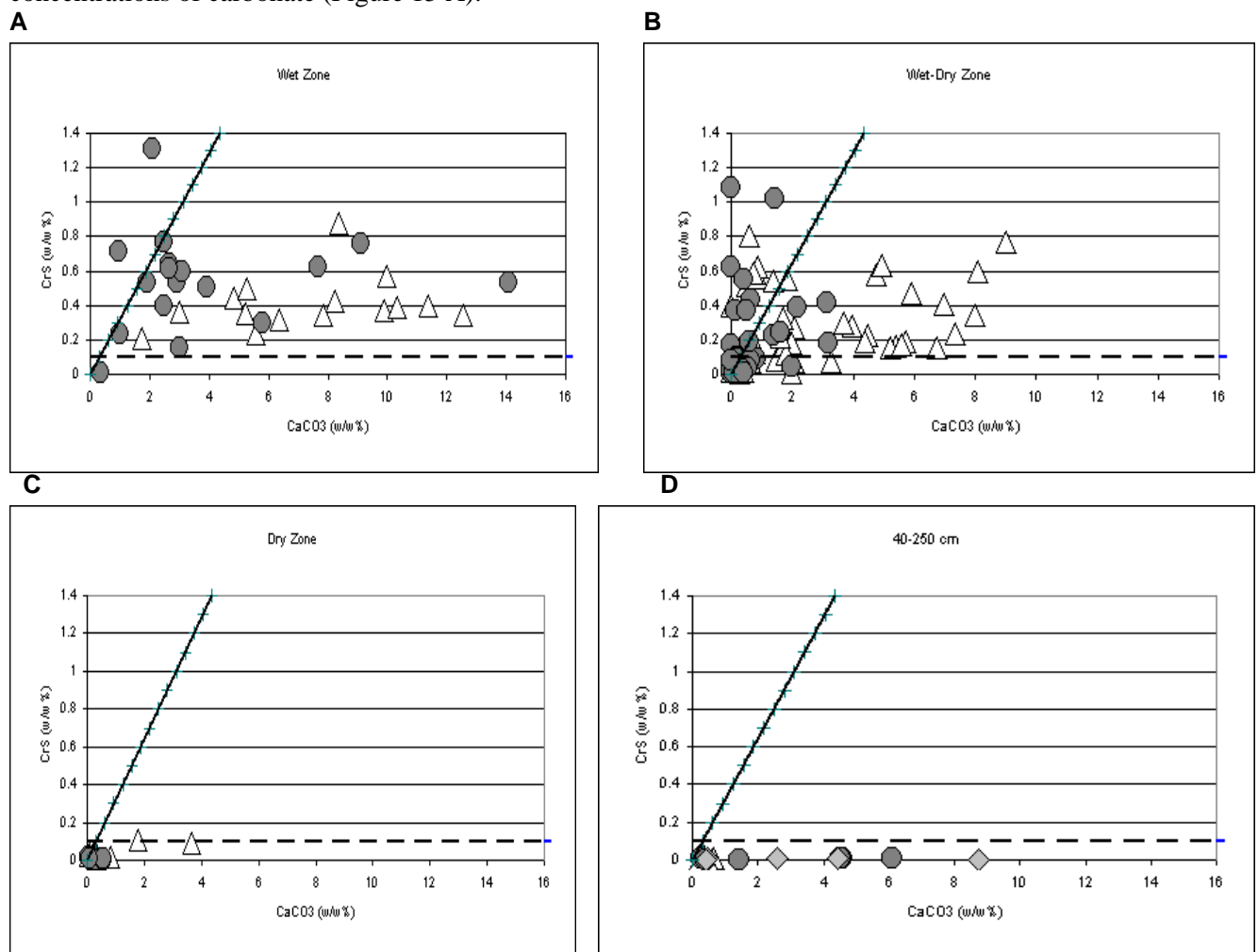


Figure 15. Concentration of sulfide (CRS) vs carbonate (CaCO₃). A-C saline clay (triangles) and mottled clay (circles). D Coonambigal Clays (triangles), Monoman Sands (circles and diamonds) Coastal ASS trigger value (0.1%S; Dashed line). AGP = ANC (Solid line).

However, in the Wet-Dry Zone high sulfide concentrations are not always associated with high carbonate concentrations. In this zone, 61 out of the 105 samples measured have greater AGP than ANC, mostly from unit B, and have the potential to become acidic if oxidised (Figure 15 B). Although the majority of the basin's sulfidic sediments have high carbonate concentrations, some localised areas of the Wet-Dry Zone have high sulfide and low carbonate concentrations. These areas of the basin often contain localised

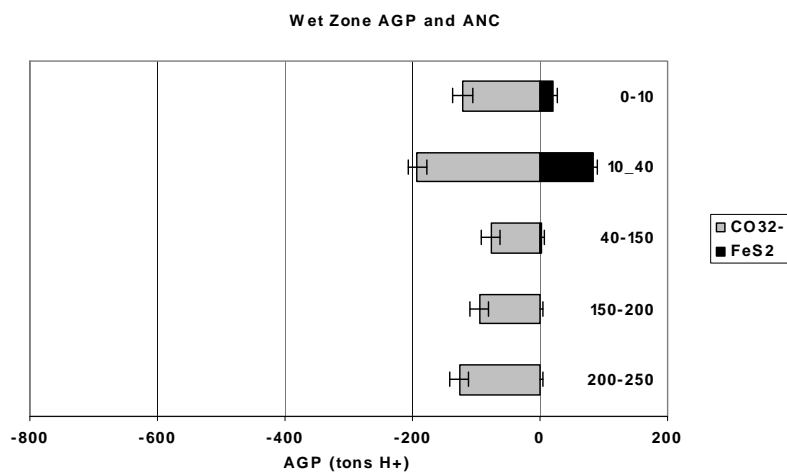
acid ‘hot spots’ (pH 3-4) associated with mottles of jarosite, demonstrating that acidification, although only on a small scale, does occur in these sediments.

The lower concentrations of sulfides and carbonate of the Wet-Dry Zone compared with the Wet Zone indicate that the wetting and drying of sediments has removed sulfide and carbonate (discussed above). The difference in the distribution of sulfides and carbonate in the Wet-Dry Zone indicate they are removed by different processes or at different rates. Carbonate is readily solubilised in waters that are under-saturated in carbonate or at the mixing interface of two waters that are saturated with respect to carbonate (Gledhill and Morse 2006). These conditions for carbonate dissolution appear to be met during wetting and drying in parts of the Wet-Dry Zone sediments flushing carbonate from localised areas, principally from unit B. Sulfide as pyrite is highly insoluble in waters, even when under-saturated, but readily dissolves upon oxidation (Bierens De Haan 1991). The wetting and drying of the Wet-Dry Zone sediments has periodically exposed sediments to the oxidising atmosphere, when sulfide oxidation appears to occur locally. The difference in the processes of sulfide and carbonate dissolution under wetting and drying conditions appears to have locally separated sulfides and carbonate in the Wet-Dry Zone, leading to the current heterogeneity.

Net acid generation potential

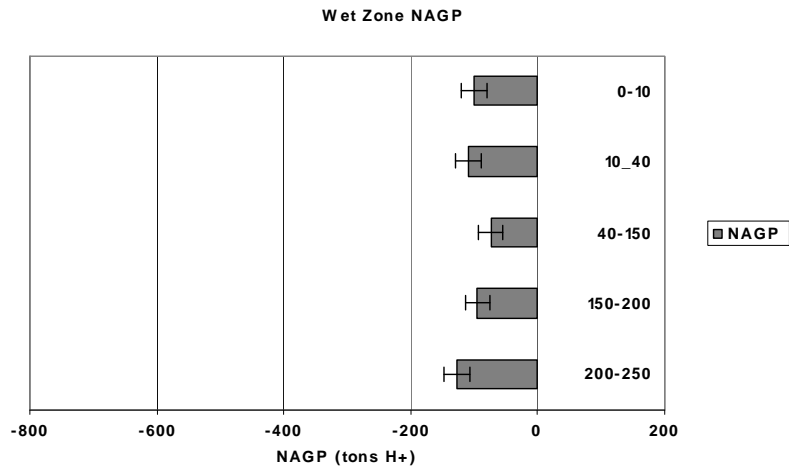
The net acid generation potential (NAGP) has been estimated for each of the basin’s units by subtracting the AGP (calculated from the total amount of sulfide) from the ANC (calculated from the total amount of carbonate). All of the basin’s units, including the sulfide-rich upper 40 cm of sediments, are calculated to have no NAGP (Figure 16 A-H). The negative NAGP values for the basin are an indication of the potential alkalinity that would remain if sulfides were completely oxidised. The high AGP of the Wet Zone is matched with high ANC (Figures 16 A and B) whilst the low ANC of the Dry Zone is proportional to the low AGP (Figures 16 E and F). Conversely, the Wet-Dry Zone has high AGP and only moderate ANC in the mottled clay unit (10-40 cm), resulting in an overall NAGP of -0.89 t H^+ (Figure 16 C and D). Although this unit is calculated to be neutral, the net alkalinity is less than the standard error, indicating that these sediments may have the potential to become acidic if sulfides were completely oxidised. This demonstrates that the separation of sulfides and carbonate in localised areas may be significant enough to produce an NAGP in larger areas of sediment. However, combining the three zones together, the basin as a whole has excess ANC to counter the total AGP (Figure 16 G and H). Although the basin has a high level of internal variability, the basin overall has excess alkalinity, and basin-wide acidification is unlikely.

A

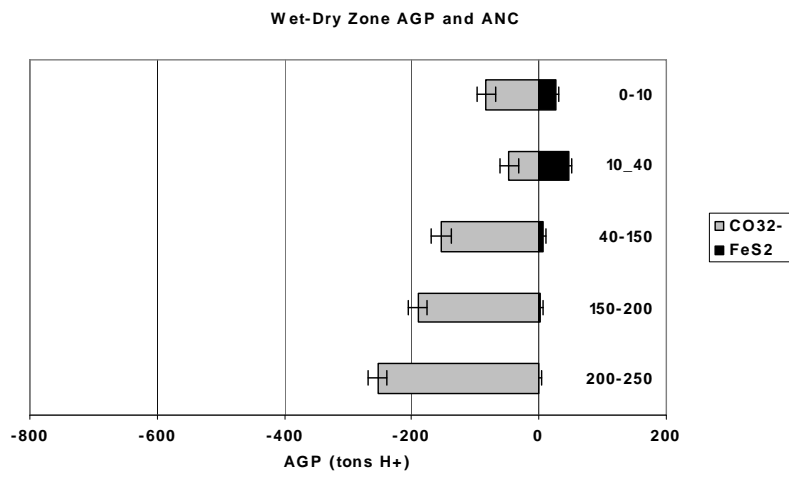


B

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C



D

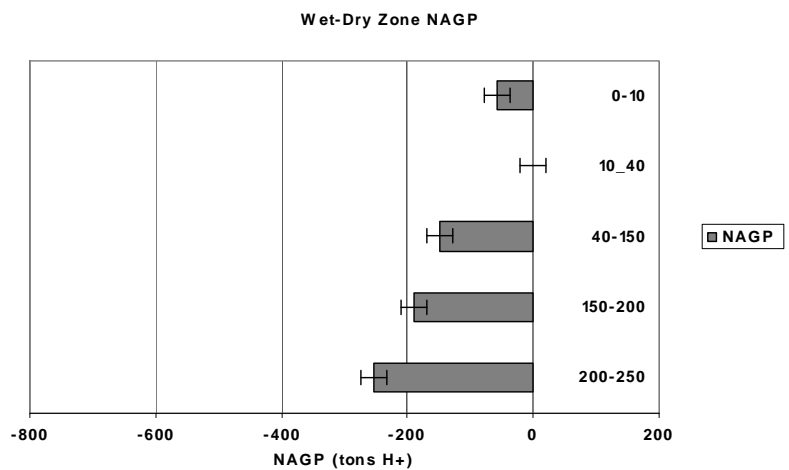
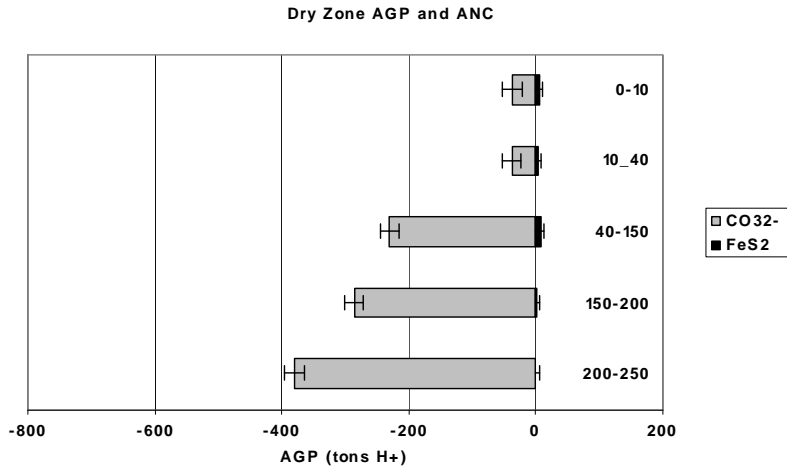


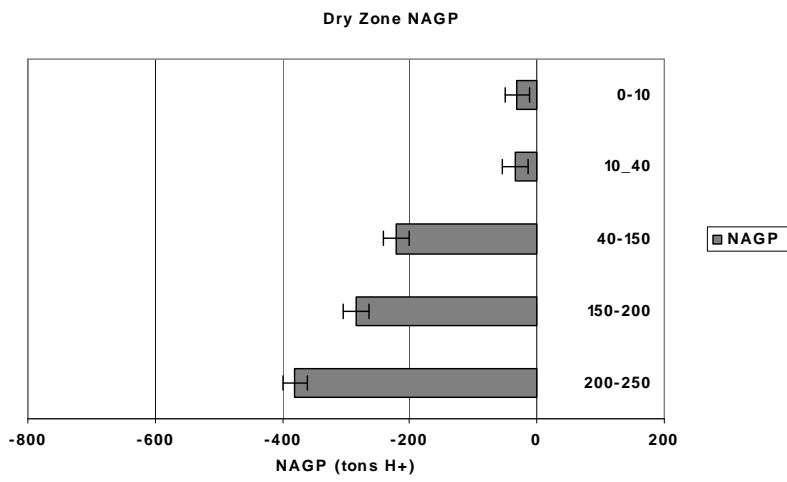
Figure 16 A-D. AGP and ANC (calculated from the amounts of sulfide and carbonate) and the resulting NAGP (AGP-ANC).

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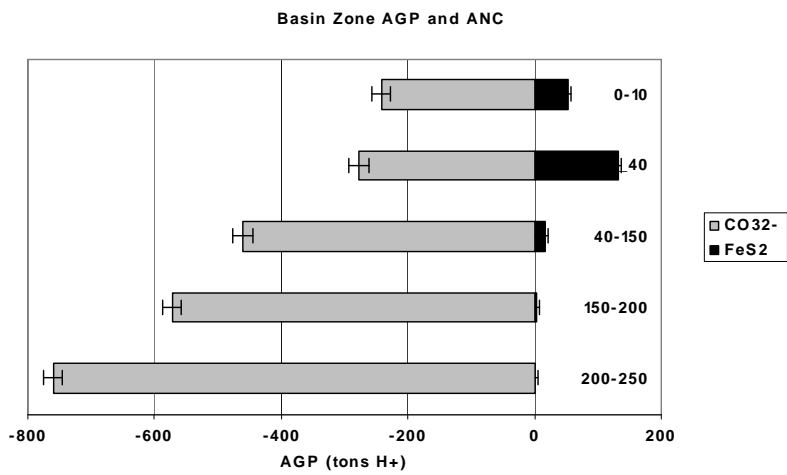
E



F



G



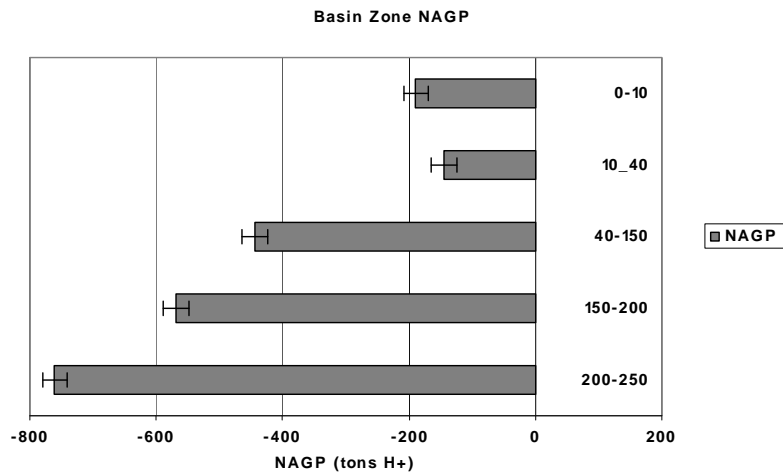


Figure 16 E-H. AGP and ANC (calculated from the amounts of sulfide and carbonate) and the resulting NAGP (AGP-ANC).

Acid sulfate soils

The sulfidic sediments/materials of the Loveday Basin, like other recent inland sulfidic sediments/materials, are intimately linked with sulfate-rich saline waters (Fitzpatrick *et al* 1996; Hall *et al* 2006; Lamontagne *et al* 2006a). Inland sulfidic materials/sediments typically form at the interface of sulfate-rich saline waters and organic-rich surface sediments. These sediments have high carbonate concentrations and, without sediment acidification, are characterised by schwertmannite rather than jarosite, characteristic of coastal ASS (Fitzpatrick *et al* 1996). Whilst the sulfidic sediments of the Loveday Basin have formed through similar processes to other inland sulfidic sediments, the basin has also developed acidic areas similar to coastal ASS. The oxidation of sulfides in carbonate-poor areas of the basin has resulted in the formation of acidic sulfuric horizons rich in jarosite (AASS) overlying unbuffered sulfidic sediments (PASS), which is a characteristic sediment profile of coastal ASS (Dent 1986). The principal difference between the basin sediments and coastal ASS is the spatial scale. Where coastal ASS have up to metres of sulfidic and sulfuric sediments (Fitzpatrick *et al* 1996) the basin's sulfur-rich sediments are restricted to 40 cm depth. Additionally, the basin's small acidic areas are surrounded by carbonate-rich sediments and the basin as a whole can not be classed as an ASS by the coastal ASS definition (Pons 1973). However, the development of acidic areas, although currently only small in the Loveday Basin, demonstrate that, under the correct conditions, there is the potential for ASS to develop from inland sulfidic sediments. This study has demonstrated an association between the wetting and drying of inland sulfidic sediments and the formation of acidic sediments. Other sulfidic wetlands and disposal basins along the Murray-Darling Basin floodplains may be disturbed by wetting and drying due to drought, increased irrigation efficiency or managed water level manipulation (i.e. for the mitigation of salinity or the reintroduction of 'natural' wetting and drying regimes) and could be at risk of forming ASS. The processes involved in the separation of sulfides and carbonate have not been investigated in this study but appear to be linked to the different solubilities of sulfides and carbonate during wetting and drying conditions.

CONCLUSIONS

After 35 years operating as a saline disposal basin, high sulfur and carbon concentrations are restricted to the surface 40 cm of the Loveday Basin. This accumulation is principally within organic-rich sulfidic wetland clays, the majority of which have been deposited over the same time period. The distribution and form of sulfur and carbon within the surface 40 cm of basin sediments show distinct trends between the basin's dominant water regimes of predominantly dry (Dry Zone), predominantly wet (Wet Zone) and intermittent wetting and drying (Wet-Dry Zone). Due to infrequent flooding, the Dry Zone has not accumulated wetland clays and has low concentrations of organic carbon, carbonate and sulfur, principally as sulfate. In the Wet and Wet-Dry Zones, where water levels have remained high for around 30 years, the sedimentation of the organic-rich wetland clays and the concentration of sulfate by evaporation have produced a substrate for sulfate reduction, resulting in high sediment sulfide concentrations. Water levels have remained high in the Wet Zone and here the wetland clays have maintained consistently high concentrations of organic carbon, carbonate and sulphides, with low concentrations of sulfate. Wetting and drying of these sulfidic wetland clays in the Wet-Dry Zone since 2000 has produced highly variable concentrations of sulfur and carbon due to localised sulfide oxidation and the redistribution of sulfate and carbonate. Within the Wet-Dry Zone high sulfide concentrations are not always associated with high carbonate concentrations, most likely due to their different solubilities, resulting in small pockets of sediment with potential and actual acidity. However, as a whole, the Loveday Basin has excess ANP from carbonate to buffer the AGP from sulfides and, as long as the basin remains a closed system to carbonate, large scale acidification is unlikely. The distinct patterns between the three zones shown in this study demonstrate that the water regime controls not only the sediments' texture but also the form and distribution of sulfur and carbon and the sediments' NAGP. Management options for inland sulfidic sediments that incorporate water manipulations need to assess the potential for the separation of carbonate and sulfides and any resulting sediment acidification.

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