GEOCHEMISTRY OF DRAINS IN TILLEY SWAMP, UPPER SOUTH-EAST, SOUTH AUSTRALIA

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INTRODUCTION

To manage an expected increase in land area affected by dryland salinity and flooding in the upper South East of South Australia, an extensive system of drains has been constructed to intercept both saline ground water and fresher surface waters. Saline water is to be delivered to temporary storage in Morella Basin and nearby areas such as Tilley Swamp, or discharged to the Coorong. Fresher surface waters are expected to be directed to wetlands to improve environmental condition. Tilley Swamp is an interdune area running parallel to and just inland to the east of the Coorong. It trends approximately NNW-SSE and is approximately 40 km long and 4 km wide. A natural drainage course runs along the western side of the interdune. A drain that is about 2.5 to 3 m deep was constructed towards the eastern side of the interdune flat. It intercepts ground water and conveys saline waters from the extensive southern part of the network across the length of Tilley Swamp to Morella Basin. Vegetation of the area includes extensive areas of *Melaleuca halmaturorum* (coastal paperbark), pasture species, and *Gahnia* spp. (cutting grass) with samphire species in permanent saline areas along the natural drainage course.

The drain constructed through Tilley Swamp provides an opportunity to observe the geochemical and pedological properties of materials within the drains, both recent (active acid sulfate soil weathering features) and relict (post-active acid sulfate soil weathering features; Fanning 2002), consider their value as environmental indicators and to evaluate the probable response of the soil materials to future inundation. Important materials that develop in the drains during periods of low flow are thin layers of sulfidic materials, monosulfidic black ooze (MBO), salt efflorescences and iron oxyhydroxide minerals on drain walls.

Figure 1. A general view of Tilley Swamp looking east across the interdune to a low dune ridge midway to the major dune ridge in the distance. Regrowth melaleuca is present on the left and pasture with samphire occurs in low-lying, saline areas on the right. The drain and sites TS 23 and TS 24 are on the far (eastern side of the interdune flat.

METHODOLOGY

A detailed description of the field and laboratory analytical work is given in Merry and Fitzpatrick (2005). A general view across Tilley Swamp is shown in Figure 1 and the sampling sites in Figure 2. Morella Basin is the smaller, northern part with Tilley Swamp extending away to the SSE. Drain materials were sampled from locations TS2, TS11, TS16, TS23 and TS24. Sampling took place in May 2005 when water levels in the drain were very low and before the winter rains had begun, so salt efflorescences were common on the drain walls. Soil and sediment materials sampled were analysed for $pH_{1:5}$, $EC_{1:5}$, cations and anions in 1:5 soil:water extracts (but not carbonate and bicarbonate). Selected samples were analysed for organic carbon, carbonate carbon (as $CaCO_3$), total S and for EC, anions and cations on saturation extracts. Other selected samples were analysed mineralogically by X-ray diffraction and for 26 elements by X-ray fluorescence spectrometry.

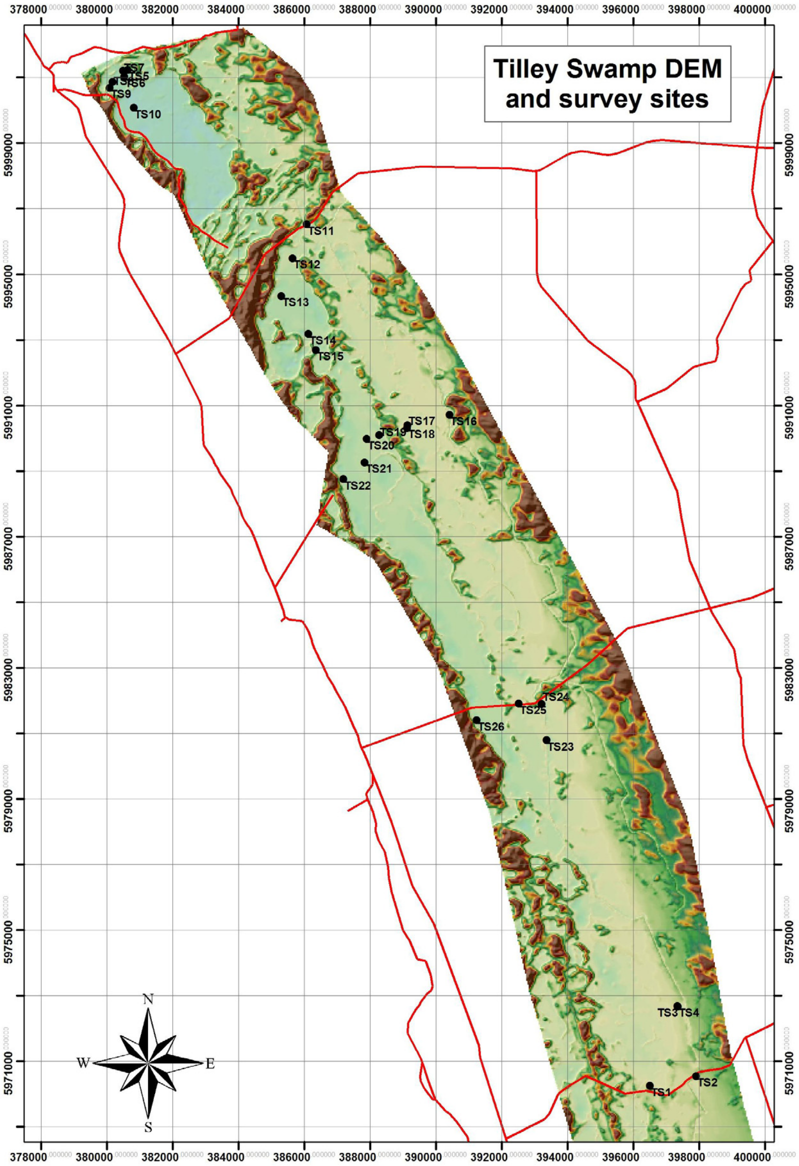

Figure 2. Topographic map of Tilley Swamp and Morella Basin (the north-eastern most, low lying area) with locations of sampling sites.

RESULTS AND DISCUSSION

Sulfidic materials adjacent to drains

Distinct redox depletions (Schoeneberger *et al.* 2002) with olive, green, blue and grey colours were observed on the sides of drains between 50 and 120 cm above a hard carbonate layer (Figure 3). These redox depletions develop in the wet and moist clayey subsoils affected by surface and groundwater. Sulfidic material (Isbell 1996) was identified in black mottles located just above the water-air interface in the drain between 250 and 300 cm (Figures 3 and 4). The amount of sulfidic material increased below the hard carbonate layer (120-150 cm). The requirements for these high rates of sulfate reduction and sulfide (pyrite, FeS_2) accumulation in the sulfidic material are: (i) high concentrations of sulfate in the groundwater and (ii) saturated soils and sediments in the drains for periods long enough to favour anaerobic conditions, and (iii) availability of labile carbon to fuel microbial activity. Sulfidic materials were also observed in dune-swale systems in the Upper South East by Fitzpatrick and Merry (1999).

	
	0 – 5cm: Very dark grey (10YR 3/1d), highly organic, melaleuca roots, sandy loam. 5 – 20 cm Very dark grey (10YR 3/1d), organic, with many shells, sandy loam.
	20 cm B2k horizon: Dark grey (10YR 4/1 m) calcareous, shelly (1-4 mm) 50 cm
	50 cm B3 horizon: Light olive grey (5Y 6/2 m) with redox depletions/mottles (yellowish-greenish-grey to olive), clay loam grading to light clay with increasing depth. 120 cm
	120 -150 cm: Hard carbonate / calcrete layer (see close-up view in Figure 4)
	150 – 160 cm Salt efflorescences (e.g. TS2 Figure 7) and iron oxyhydroxides (e.g. TS2 Figure 6) in eroded cavities between the hard carbonate layer and underlying mottled clays below hard calcrete.
	150 – 200 cm: dark green (5GY4/1m), black (2.5Y2/0) mottles, medium clay. 200 - 250 cm: black (2.5Y2/0) mottles (sulfidic material) that increase in concentration with depth below carbonate layer to above the water-air interface in the drain (close-up view in Figures 4 & 5). 300 cm
	300 – 350 cm black (2.5Y2/0) Monosulfidic Black Ooze (MBO) near and below the water level (close-up view in Figures 4 and 5).

Figure 3: Soil profile in the drain at site TS11 (Figure 2) showing evidence of active (i.e. black, sulfidic material in mottles above the water-air interface in the drain between 250 to 300 cm and Monosulfidic Black Ooze (MBO) near and below the water level at 300 cm and post-active acid sulfate soil weathering conditions (i.e. iron oxyhydroxide minerals formed below hard calcrete, which is better expressed in site TS2 Figure 6) (from Merry and Fitzpatrick 2005).

Figure 4: Close-up view of the lower portion between 120 to 350 cm of the soil profile at site TS11 shown in Figures 3 and 5 (from Merry and Fitzpatrick 2005).

Monosulfidic black ooze (MBO)

During periods of low flow, water in the drains has a chemical composition close to that of the groundwater, although this may change or be diluted during winter and spring when more surface water is carried. Typically, this low-flow water contains about 400 mg/L of S, alkalinity (as $CaCO_3$) of 530 mg/L and a sodium adsorption ratio of about 25 (DWLBC analyses). Soils in Tilley Swamp typically contain between 200 and 4,500 mg/kg of S, which is much greater than most agricultural soils, and carbonate minerals were present in all samples. The groundwater is anoxic and sufficient organic matter is present in the drains at low flow for biologically controlled reduction to occur and produce monosulfidic black oozes (MBO), which accumulate at the bottom of the drain (Sullivan *et al.* 2002). The wet and moist subsoils affected by the groundwater table are already reducing and the soils exhibit olive, green, blue and grey colours. Black, mottled soil in the lower drain side had a redox potential of -50 mV (300 cm; site TS24), and have high organic carbon contents of 1 to 2% or more (e.g., site TS11, Figures 3, 4 and 5). Chromium reducible sulfur analyses indicate concentrations of about 0.3% in reduced (MBO) materials in the drains and lower concentrations, between 0.03 and 0.05%, in the reduced soils affected by ground waters. In this saline environment, these materials show no unusual concentration of any of the other elements for which analysis was completed.

Figure 5. Black monosulfides (MBO) near the water level in the drain at site TS11.

Post-active acid sulfate soil weathering

The soil and drain materials are predominantly calcareous with equivalent calcium carbonate concentrations as high as 80% and high S concentrations. However, a common feature of the soil profiles is a decrease in soil Ca, Mg and Sr (present mainly as carbonates) at the depth in the profile of the probable historic position where reduced groundwater becomes oxidised. Formation of sulfuric acid during oxidation has removed the carbonate minerals from these layers. No soil materials were observed where all carbonate had been removed by this acid production, but equivalent $CaCO_3$ contents as low as about 1% between 70 and 200 cm were observed at site TS11 (e.g. Figure 3).

At site TS2, located at the eastern side and southern end of Tilley Swamp (Figure 2), this apparent removal of carbonate was also observed. However, the soil profile showed a strong accumulation of ferruginised sand at depths between 140 and 160 cm, immediately below about 10 cm of very hard carbonate that contained shell material (Figure 6). XRD analysis showed that the layer is dominantly quartz with minor amounts of goethite, magnesian calcite and ankerite ($CaFe(CO_3)_2$ with Mg and Mn substitution). Iron concentrations reached 15% in the upper part of the layer. These iron-rich materials have since been observed in drain exposures on the eastern side of the next interdune flat to the east of Tilley Swamp. An additional feature of this layer of iron accumulation is that it has accumulated very high concentrations of arsenic (to about 5,000 mg/kg) and phosphorus (to about 1200 mg/kg). Limited As and P analysis of subsoils from the area indicate concentrations generally below detection for As (<0.4 mg/kg) and between 170 and 500 mg/kg for P. Iron oxyhydroxides are known scavengers of arsenate and phosphate in oxidised environments. This soil layer is interpreted as having resulted from oxidation of sulfide and reduced iron at the top of the groundwater surface producing acid which has removed much of the carbonate minerals, and formed goethite which then adsorbed arsenate and phosphate, also from the groundwater as there is no other known source and agriculturally applied P could not penetrate the overlying calcrete. It is likely that these processes have happened over a long period of time as the age of the interdune materials is at least 100,000 years (Murray-Wallace *et al*. 2001).

Figure 6. Iron minerals formed below hard calcrete at site TS2. This layer (post-active acid sulfate soil layer) contains 15% iron (quartz, goethite and ankerite minerals are present) and has “scavenged” high concentrations of arsenic and phosphorus

Sulfate-containing salt efflorescences

Salt efflorescence or evaporite deposits sampled from the drain walls (Figure 7) proved to be an assemblage of sulfate-containing minerals, mostly thenardite (Na_2SO_4), eugsterite ($Na_4Ca(SO_4)_3.2H_2O$), gypsum ($CaSO_4.H_2O$), halite (NaCl), bloedite ($Na_2Mg(SO_4)_2.4H_2O$) and possibly barite ($BaSO_4$). This is caused by the somewhat unique geochemistry of the combined groundwater, drainage water and drained soils in the Tilley Swamp region. Geochemical analyses of these saline soil materials indicate high concentrations of sulfate, magnesium, calcium and sodium ions (Appendix Table A7 in Merry & Fitzpatrick 2005).

Sulfides produced in bottom sediments and at the base of the drain react with the oxygen in the air to form sulfuric acid. The acid either drains into the drain or reacts with carbonates and salts in specific layers within the soils to form sulfates – precipitating dissolved iron, calcium, magnesium, sodium and other elements such as arsenic. The components (Na, Ca, Mg, Cl, Ba and SO_4) of the evaporite minerals were derived by leaching by oxidized iron sulfides and then precipitation as specific minerals (eugsterite, thenardite, bloedite and gypsum) at various stages during the drying/evaporation of the drained soils (Figure 7).

Capillarity results in movement of the groundwater to the exposed surfaces of the drain where evaporation results in precipitation of salt efflorescences. Their chemistry indicates oxidising environments, with a predominance of sulfate minerals (apart from halite) and usually a physical separation from oxidised iron minerals.

It is possible that the appearance of these minerals in the drain walls has been driven by the generation of acid dissolving the more soluble soil constituents, at least in the lower parts and by capillarity and evaporation from the drain surfaces in the upper parts.

Figure 7. Close-up view of salt efflorescences in eroded cavities between the hard carbonate layer and underlying iron-rich mottled clays at site TS2, depth 140 cm.

Similar observations have been made of salt efflorescences in the Great Konya Basin in Turkey by Driessen and Schrool (1973), in Spain by Gumuzzio *et al.* (1982) and in drained, alkaline sulfidic marshes in southern Iraq by Fitzpatrick (2004). Gumuzzio *et al.* (1982) reported that the mineralogical composition varied, with the winter type being characterised by mirabilite-thenardite-epsomite and a summer type constituted thenardite-bloedite. The significance of the minerals found in these salt efflorescences is that they appear each summer and are environmental indicators. A change in the minerals found will indicate a change in the nature of the salts entering the system from the drain or ground waters.

CONCLUSIONS

Tilley Swamp is a calcareous, saline environment with ground water commonly within 3 metres of the soil surface. Under conditions of low flow, sulfidic material (mottles) and monosulfidic black ooze (MBO) forms, but is not found in soils away from the drain. These sulfides remain benign in a reduced environment, but can quickly cause oxygen depletion of the water when re-suspended during periods of higher, turbulent flow. This is not thought to be of environmental significance in these drains.

The depletion of carbonate minerals in some soil layers due to acid formation has occurred over a long period of time (i.e. Post-active acid sulfate soil weathering conditions) but we have not yet observed sites where carbonate is totally removed. Under these circumstances, rapid acidification of remaining soil materials would be expected. High concentrations of As and P, observed in layers of iron oxyhydroxide accumulation are related to the layers with carbonate depletion on the eastern side of the interdune flats, and thought to have resulted from long-term scavenging by the iron oxyhydroxides. The common occurrence of salt efflorescences on drain surfaces provides a window on seasonal geochemical processes that could be used as environmental indicators.

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