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 (Figure 1). 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 and other surface 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 pedological, geochemical and mineralogical properties of materials within the drain, 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 (Dent and Pons 1995; Isbell 2002), monosulfidic black ooze (MBO), salt efflorescences and iron oxyhydroxide minerals on drain walls.

The aim of this study is to use hydro-pedological, mineralogical and biogeochemical information to help understand the soil-water process in the open drains and assist in their management.

Materials and Methods
Samples were variously treated and fractionated (sub-samples). Specialised laboratory analyses were conducted on selected sub-samples from each site using X-ray fluorescence (XRF), ICP-MS, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray Absorption Spectroscopy (S K-edge and Fe K-edge XAS) and laboratory chemistry to determine what biogeochemical and mineralogical processes were taking place in the drains.

RESULTS AND DISCUSSION
A detailed description of the field and laboratory analytical work is given in Merry and Fitzpatrick (2005) and Fitzpatrick and Merry (2005). A general view of a representative cross section through a drain in Tilley Swamp is shown in Figure 2. At each site the following materials were described and sampled: (i) monosulfidic black ooze (Sullivan et al 2002), (ii) sulfidic materials (Isbell 2002), (iii) yellowish Fe-rich mottles, (iv) white salt efflorescences and crusts on the walls of drain, (v) reddish–brown Fe-rich gels and precipitates and (vi) calcrete layers (Figure 2). These six materials were generally evident within the drains and were used to indicate six different geochemical process zones (Figure 2).

Tilley Swamp is a calcareous, saline environment with ground water commonly within 3 metres of the soil surface (Figure 2). Under conditions of low flow, sulfidic material (mottles) and monosulfidic black ooze (MBO) forms, but is not found in soils away from the drain (Figure 2). 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.

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.
We have constructed 3D (Figure 2) and 4D mechanistic models of soil-regolith and water processes using the toposequence approach (soil landscape cross-sections; Fitzpatrick et al. 1996), that explain and predict processes giving rise to the production, export and fate of leachate and minerals in the open drains. The main materials and key processes that these materials indicate are discussed and summarised for each of the six zones shown in Figure 2 as follows:

Zone 1: Oxidation of monosulfides in the monosulfidic black ooze causes oxygen depletion of drainage waters.

Zone 2 and 3: Oxidation of pyrite and ferrous iron within the zone of active watertable fluctuation forming:
- Sulfuric acid, which causes dissolution and removal of carbonates from soil layers
- Goethite-rich mottles in an olive gleyed matrix (post active acid sulfate soil materials).

Zone 4: Soluble sulfate/chloride-containing minerals in efflorescences (Figure 3) were also identified in localised areas in the drains. The salt efflorescences are produced by evaporation of ground and capillary waters. Pedogenic eugsterite [Na$_4$Ca(SO$_4$)$_3$.2H$_2$O] has been identified for the first time in Australia. These evaporite minerals reflect the unique geochemical reactions resulting from the combination of groundwater, drainage water and drained soils. Hence, under these more alkaline conditions (and also observed in the Iraq marshlands) where Na/Ca ratio >4, eugsterite, gypsum and thenardite (i.e. Na-Ca-sulfate salts) will form. In contrast, under acidic conditions (e.g. Western Australian wheatbelt drains) where Na/Ca ratio <4, bloedite and pentahydrate (i.e. Na-Mg-sulfate salts) form (Fitzpatrick et al. 2005).
Figure 3. Scanning electron microscope (SEM) images of salt efflorescences from Zone 4 containing minerals with high levels of sodium, calcium, chloride and sulfate ions.
Zone 5: We identified various types of hydrated oxyhydroxides (ferrihydrite), oxyhydroxides (goethite), oxides (hematite, manganese oxides), Fe-sulfides and Fe-monosulfides (Figure 4) in various localities in the drains. Oxidation and concentration of ferrous iron in the upper ten centimetres of the capillary zone formed ferrihydrite, goethite and manganese oxides with ankerite and Mg-calcite. The Fe and Mn-oxides most likely scavenged high total concentrations of arsenic (5000 mg/kg) and phosphorus (1200 mg/kg). These oxides are ubiquitous in many soils and are known to take up arsenate and phosphate (Fordham and Norrish 1979).

**Figure 4.** Scanning electron microscope (SEM) images of reddish layer from Zone 5 containing ferrihydrite, goethite, ankerite, Mg-calcite and Mn-oxides with high concentrations of arsenic (5000 mg/kg) and phosphorus (1200 mg/kg)
CONCLUSIONS

Minerals in efflorescences containing soluble sulfate and chloride play important roles in the transient storage of components (Na, Ca, Mg, Ba, Sr, Cl, Br, I and SO$_4$). They can detach soil during crystal growth and degrade drain walls. They will dissolve during rainfall and contribute to formation of saline monosulfidic black ooze in drains.

We conclude that the Fe-oxyhydroxide and Mn-oxide minerals, and sulfate/carbonate containing minerals in salt efflorescences, are indicative of changing local environments with variations in redox, pH and rates of availability of S and other elements. As such, they provide insight to the drain geochemistry and can be used as indicators of environmental change that can also be used to help understand and manage this system.

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REFERENCES


