Occurrence, genesis and environmental significance of schwertmannite in re-flooded Acid Sulfate Soils in the Lower Murray Reclaimed Irrigation Area

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Introduction

The Lower Murray Reclaimed Irrigation Area (LMRIA) comprises approximately 5,000ha of flood-irrigated agricultural land located on the floodplain of the River Murray between Mannum and Lake Alexandrina (Figure 1). These river flood plains were developed for agriculture (Dairy, Beef and Fodder) between 1881 and 1940 (Taylor and Poole 1931). From 1940, the construction of levee banks along the river channel, as well weirs along the River and barrages at the river mouth allowed farming to thrive, as water levels became more stable and periodic flooding was minimised. The regulation of the river also raised the water level of the River channel to approximately 1-1.5 m above that of the flood plains. The rise in river level allowed the use of flood irrigation on the now agricultural land behind the levee banks. This type of irrigation is successful due its low capital and energy costs, and effect in reducing soil salinisation (EPA, 2009; Mosley and Fleming 2010).

Reduced inflows to the River Murray from approximately 2006 to early 2010, however, resulted from persistent drought in the Murray-Darling Basin. In the wetlands between Lock 1 (upstream from Mannum at Blanchetown) and Wellington near the entrance to Lake Alexandrina, the combination of decreasing water levels and gently sloping near-shore beds caused large expanses of previously inundated sediments and subaqueous soils to be exposed (Fitzpatrick *et al*. 2008a,b; 2009). The impacts on the Dairy Swamps were not realised until high pool levels led to mobilisation of acidity and metals into drains around the irrigation areas. Acid sulfate soils with sulfuric materials occurring mostly at depth from approximately 70 cm to over 4 m in the LMRIA dairy swamps were identified at three sites (Figure 1). In addition, bright reddish-orange plumes of fine iron-rich precipitates were found coating vegetation and the base of drains, associated with extremely acidic drain water (pH 2.5 – 3.5) at four sites (Figures 1 and 2). This drain water is returned to the Lower River Murray via pumping, hence it is important to determine the nature and environmental significance of the precipitates.

Results and discussion

Occurrences

Mineralogical analysis by X-ray diffraction (XRD) of the reddish-yellow (orange) precipitates from the acid drain water was used to document the occurrence of the iron oxyhydroxysulfate mineral schwertmannite [$Fe_8O_8(OH)_6SO_4$], which is an indicator of extreme acidic geochemical water/soil conditions (pH < 3.5) (Bigham *et al.* 1996). Geochemical speciation calculations (PHREEQC) using the dissolved metal and major ion concentrations supported the XRD results as the saturation index (SI) exceeded zero for schwertmannite in many drains. The schwertmannite-rich iron precipitates were also found to contain high concentrations of metals [Al (max: 81,900 mg/kg) > As (max: 99 mg/kg) > Zn (max: 164 mg/kg) > Cu (max: 89 mg/kg) > Pb (max: 20 mg/kg)] due to co-precipitation/scavenging of these elements during formation of schwertmannite. Precipitates also contained high concentrations of P (max: 5890 mg/kg), Ni (max: 131 mg/kg), Cr (max: 26 mg/kg), Co (max: 70 mg/kg), B (max: 56 mg/kg) and Mn (max: 271 mg/kg); where max = maximum concentrations after HCl dissolution.

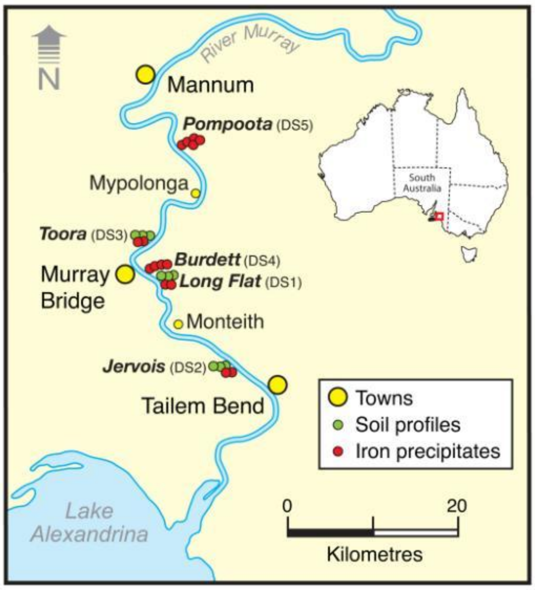

Fig. 1. Map of Murray Reclaimed Irrigation Area (LMRIA) showing distribution of 3 selected representative soil profile sites at Toora, Long Flat and Jervois and Iron precipitates from drains at Pompoota, Toora, Burdett, Long Flat and Jervois, used for assessment of Acid Sulfate Soil (ASS).

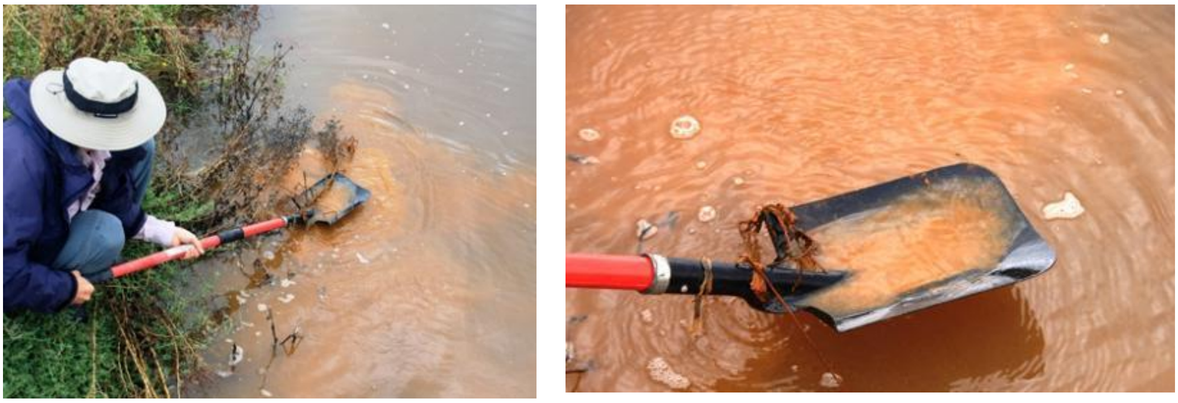

Fig. 2. Acidic (pH 2.5 – 3.5) iron rich drain water in Burdett drain near Murray Bridge (Long Flat), LMRIA in April 2011, comprising the reddish-yellow (orange) coloured precipitate schwertmannite, which forms between pH 2.5 and 3.5.

Genesis

To understand the genesis of schwertmannite in the LMRIA a series of three soil landscape cross-sections, in the form of conceptual soil-regolith toposequence models were constructed (Figure 3; Fitzpatrick *et al.* 2012).

a) **During pre-drought (pre-2007)** water tables were maintained from irrigation, river and groundwater flows [Figure 3 (a)].

The build up of hypersulfidic material (sulfidic materials capable of severe acidification) in the saturated soil profiles at depth is due to stable water level conditions and availability of sufficient iron, sulfate and organic material. Under these saturated conditions (pre-drought), hypersulfidic material did not pose an immediate threat of acidification and metal release.

The top metre of these clayey organic-rich soils was prevented from forming significant amounts of sulfuric material due to the continuous wetting and drying cycles associated with flood irrigation over the last 100 years and also a build up of ANC. Acidic soils were not identified pre-drought in the LMRIA (EPA 2008; Fitzpatrick et al. 2008a).

b) **Drought (2008-early 2010)** caused severe soil cracking and oxidation of pyrite minerals. Productive non-acid sulfate soils at surface (0-15cm) above hyposulfidic soils (15-50cm) and deeper hypersulfidic soils (>50cm) [Figure 3 (b)].

The exposure and drying of hypersulfidic material caused a number of serious environmental impacts related to Acid Sulfate Soils (ASS) to be realised for the first time in the LMRIA between Mannum and Wellington. This study of ASS along three transects in the LIMRIA (Figure 1) and investigations of associated acidic drainage waters/Fe-precipitates in former irrigation bays (where cattle are still grazing) identified deep sulfuric soil material with prominent natrojarosite in mottles of cracking clay soils. This situation from the LMRIA with low water tables was due mainly to the pool levels in the River Murray during the 2006 to 2010 drought and the inability of irrigators to access water or much of their water allocation. The low water table level under the floodplain during the drought has resulted in oxidation of previously undisturbed hypersulfidic material in ASS to form deep (> 1.5 m) Acid Sulfate Soils with sulfuric material (e.g. Fitzpatrick *et al*. 2008a,b; 2009).

c) **Post-drought reflooding and irrigation (2011)** caused mobilisation of acidity (H^+), metals and metalloids, controlled by hydrological conditions. [Figure 3 (**c**)].

The rising river and groundwater levels since late 2010, and some recommencement of irrigation in 2011 mobilised soil acidity, caused surface water acidification (pH 2.5 – 3.5) and precipitation of the bright reddish-orange plumes of fine iron-rich precipitates comprising mainly schwertmannite, which was also found coating vegetation and the base of drains (Figure 2). The drains in these irrigation areas also receive regional groundwater inputs and require drainage (via pumping back to river) to avoid back-flooding of pastures.

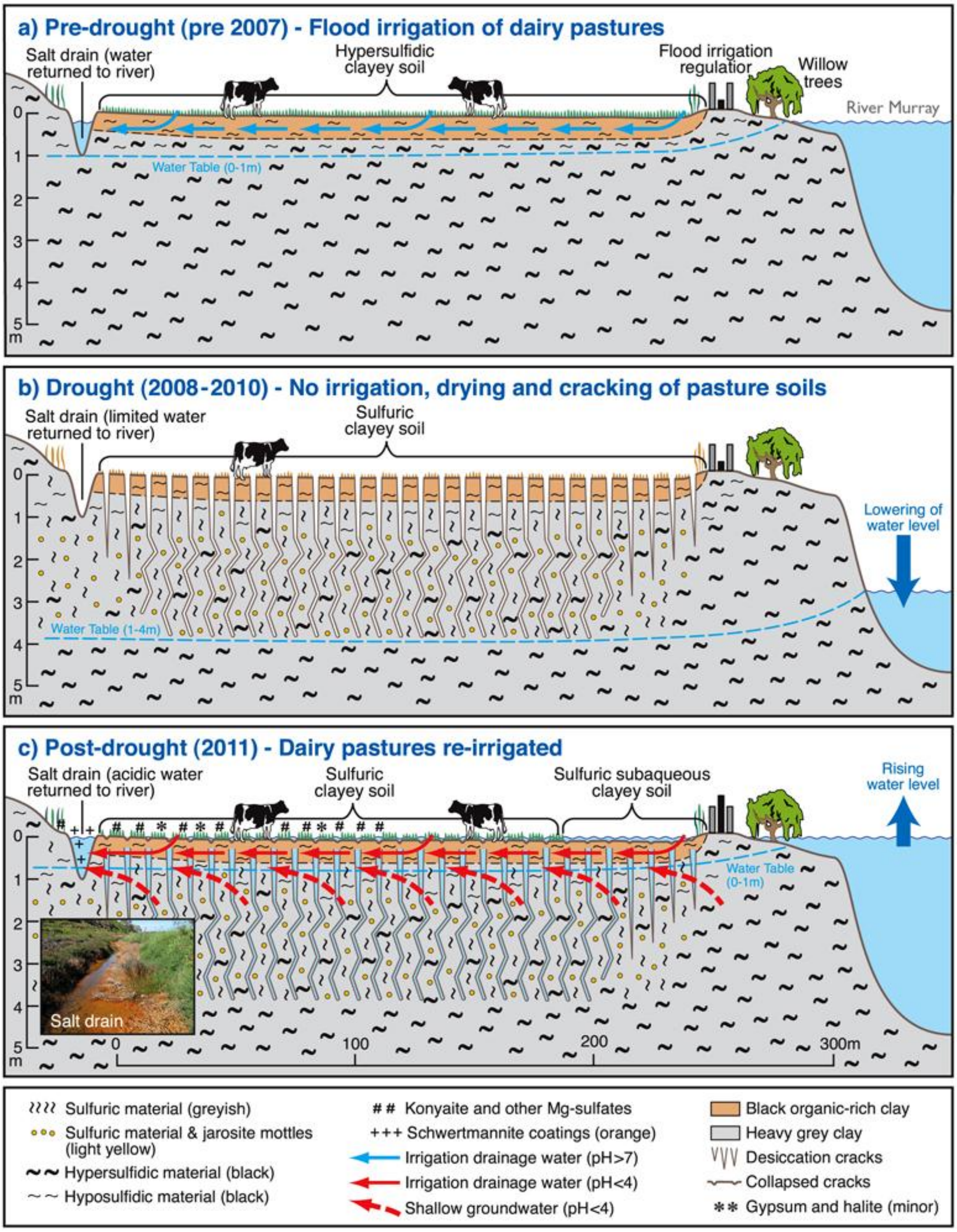

Fig. 3. Generalised soil-regolith conceptual model illustrating the role of climate variation (drought triggered and reflooding), environmental conditions imposed by humans (e.g. modifications from barrages, isolating wetlands, weirs and irrigation) and water conditions (subaqueous, waterlogged, dried and rewetted) that play a vital role in the alteration of soil geochemical processes and sequential transformation of ASS subtypes. Note: both vertical and lateral cracking occurred, which provided significant preferential flow pathways from the soil beneath the pasture to the drains. Inset photo in (c) shows surface precipitates of the iron-rich orange-coloured mineral, schwertmannite and other salt efflorescences (e.g. Konyaite: $Na_2Mg(SO_4)_2$. $5H_2O$ and Hexahydrite: $MgSO_4$ $6H_2O$) in paddocks near Toora (2nd September, 2011).

Conclusions and Environmental significance

The occurrence and formation of schwertmannite is due to the formation of sulfuric material between 0.7 and 4 m of soil profiles with large cracks in clay soils followed by rising river and groundwater levels since late 2010, and some recommencement of irrigation in 2011, which mobilised soil acidity, caused surface water acidification (pH 2.5 – 3.5) and precipitation of schwertmannite.

Schwertmannite is a metastable phase and has been shown to transform to goethite over the timescale of weeks to months (Bigham *et al.* 1996). As the drain water is pumped back to the River Murray dilution of the acidic, sulfate and iron rich drain water occurs. This dilution and pH neutralisation would likely promote dissolution of schwertmannite and release of associated trace elements (Acero *et al.* 2006). The environmental fate and ecological impacts of schwertmannite being discharged into the River Murray clearly warrants further study.

Acknowledgments

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