MINERALOGY, BIOGEOCHEMISTRY, HYDRO-PEDOLOGY AND RISKS OF SEDIMENTS, SALT EFFLORESCENCES AND SOILS IN OPEN DRAINS IN THE WHEATBELT OF WESTERN AUSTRALIA

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INTRODUCTION

Salinised land in the wheatbelt of Western Australia (WA) is expected to increase to over 3 million hectares if current trends continue and the construction of open drains has increasingly been seen as a major management option (Ali *et al.* 2004, Dogramaci & Degens 2003). Over 15,000 kilometres of drains have already been constructed in parts of the WA wheatbelt and generally without extensive regional linkages. Unfortunately, most of the drains have been constructed with limited planning, design, and construction guidelines, and usually without an understanding of their effectiveness, stability, or their downstream impacts (Dogramaci & Degens 2003). Initial results in the WA wheatbelt showed that drainage was associated with:

- Formation of hypersaline soils (drain batters) and sodic soils (edge of drain) (Fitzpatrick *et al.* 2003);
- Highly acidic shallow groundwater, which is caused primarily by iron hydrolysis (e.g., Mann (1983)) or ferrolysis (Brinkman 1979) reactions. This situation develops when anoxic water containing dissolved ferrous ions is exposed to air and ferrous ions are oxidised to the ferric ions, which react with water to form reddish-brown precipitates of ferric oxyhydroxides, releasing free hydrogen ions in the process. If the water sample contains a substantial amount of dissolved iron and has a low buffering capacity, the pH of the solution may fall from a value of about 6-7 to 2-3 (George 2002, Rogers & George 2005);
- Formation of sulfidic and sulfuric materials in drains, especially in waterlogged areas in valley floors through the formation of pyrite in sulfidic materials. Drainage of valley floors causes pyrite to oxidise and release substantial amounts of sulfuric acid to form sulfuric materials (Fitzpatrick *et al.* 2003); and,
- High concentrations of metals in the hypersaline groundwater and drain water with low pH (< 4.5) discharging from drains into streams (Fitzpatrick *et al.* 2003, George 2002, Rogers & George 2005).

Despite these problems, as well as the variability in drainage response and the relatively flat landscapes in the wheatbelt, deep drains are increasingly seen as a viable option. Acid groundwater has been debated as the main cause of off-site risk because it has the potential to release metals and elements harmful to flora and fauna that inhabit receiving areas. Misidentification and the application of conventional salinity management practices in areas where acidic groundwaters and sulfidic sediments exist (Fitzpatrick *et al.* 1996) are likely to make the problem worse. Consequently, a research project to quantify the geochemistry of groundwaters and drain sediments in the WA wheatbelt, particularly the Avon Basin, was developed to assess the causes and risks and to identify management options as part of the Engineering Evaluation Initiative (EEI) (Dogramaci & Degens 2003, Rogers & George 2005). Hence, the objectives of this study were to:

- Develop an experimental approach and field sampling program to determine the changes in soil and water characteristics in drains;
- Conduct field work at 21 representative case study sites across the WA wheatbelt;
- Develop detailed and generic conceptual models that encapsulate the various soil-water processes observed at the case study sites;
- Develop a user-friendly set of soil-water indicators and a soil identification key for categorising the drain sediments and soils to assist local advisers to identify signs of soil and water degradation;
- Assess the impacts of deep open drains on the production, export and fate of leachate and minerals; and,
- Develop strategies to appropriately manage the drained soils, acidic water and oxidation products.

METHODOLOGY

The drain waters were sampled for flow, salinity, pH, major metals, trace elements, rare earth elements and other elements such as uranium (Rogers & George 2005). In addition, at 21 representative drain sites the following materials were described and sampled (over 200 samples): sulfidic materials/sediments; sulfuric materials/sediments; gels; salt efflorescences; salt crusts; iron-rich crusts; and, soils (drain batters and saline-sodic soils on the edge of drains). Samples were variously treated and fractionated (sub-samples) according to procedures outlined in the flow diagram (Figure 1). Specialised laboratory analyses (see Figure 1) were

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conducted on selected sub-samples from each site using geochemical (XRF and ICP), mineralogical (XRD and scanning electron microscopy) and chemical methods to determine what biogeochemical and mineralogical processes were taking place in the drains.

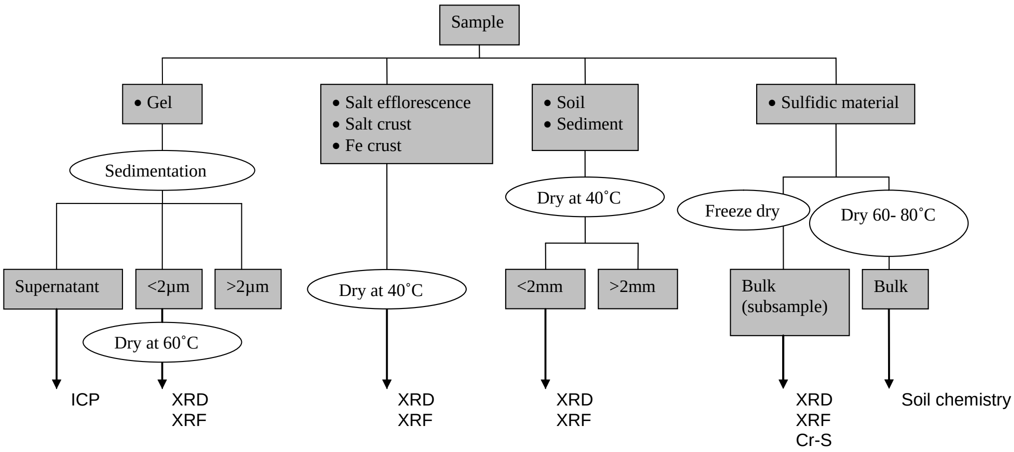

Figure 1: Flow diagram summarising the preparation and fractionation of various sub-samples and the analytical methods used to characterise the mineralogy, geochemistry and chemistry of sub-samples. Where: XRD = X-ray diffraction, XRF = X-ray fluorescence, ICP = Inductively coupled plasma analyses, Soil chemistry = pH, EC, organic carbon, carbonate content, exchangeable cations and SAR.

All the descriptive field information and laboratory data was stored in a web-based data-base, which was specifically designed as a framework for the acquisition, collation and communication of all information (Baker & Fitzpatrick 2005, Fitzpatrick *et al.* 1996). The following information is stored in the web-based data-base: (i) Site locality map; (ii) site summary web page; (iii) additional web pages that were included in the data set; (iv) 3-dimensional, interpretive models; (v) profile/sample summary pages; (vi) data summary pages; (vii) Scanning Electron Microscopy (SEM) microphotographs; (viii) chip tray photographs; (ix) XRF data; (x) XRD data; and, (xi) XRD spectra (see flow diagram and examples outlined in Figure 2 of Baker & Fitzpatrick (2005)). This new approach permitted the easy collation of geological, soil, hydrological, geochemical and mineralogical data to help construct 22 cross-section diagrams and mechanistic models of soil-regolith and water processes for each case study site.

DISCUSSION

Salinity and acidity of drain waters

Most drains were typically very saline with conductivity in the range 60-100 dS/m (approximating TDS of 38 to 64 ppt). Low pH is widespread, with more than half of the drains sampled in October 2004 being less than pH 3. Drain pH decreases during summer, probably due to iron oxidation of groundwaters and/or sediments (Rogers & George 2005). Results indicated two broad groups of drain pH and salinity. The pH was lowest east of a line from Dalwallinu to Dumbleyung (pH less than 3.5) and highest (pH greater than 6) in the western and central WA wheatbelt, though there were few drains flowing in this area. Only a few sporadic high pH (alkaline) samples were taken from drains in the eastern areas. Data show that in most eastern drains with a low pH (less than 4.5), iron, aluminium, cobalt, copper, zinc, lead, uranium and a range of other trace elements and rare earth elements all elevated.

Sulfidic materials (Isbell 2002)

These occurred in almost all the drain sediments (Figures 2b & 2c) and mostly consist of accumulations of iron sulfide minerals, one of the end products of the process of sulfate reduction (i.e., the use of SO_4^{2-} instead of O_2 during microbial respiration). Sulfate reduction is a natural process that occurs in virtually all the drains. However, the quantities or thickness of sulfidic material that accumulate in the rains is a function of many factors. The key requirements for high rates of sulfate reduction and sulfide accumulation are: (i) a high concentration of sulfate in surface or groundwater; (ii) saturated soils and sediments for periods long enough to favour anaerobic conditions; and, (iii) the availability of labile carbon to fuel microbial activity. Saline groundwaters in the wheatbelt generally contain quite large concentrations of sulfate. Thus, drains that intercept saline groundwater should be expected to accumulate some sulfides in their sediments over time, especially if they are permanently flowing or waterlogged. Two forms of iron sulfide minerals are of importance from an environmental point of view: monosulfides (FeS); and, pyrite (FeS_2). Soils and sediments rich in monosulfides (or "black ooze") tend to be very dark and soft. Monosulfides can react rapidly (minutes to hours) when they are disturbed (that is, when exposed to oxygen; Sullivan *et al.* 2002). Pyrite will tend to occur as more discrete crystals in the sediment matrix and will react more slowly when disturbed (over days to years).

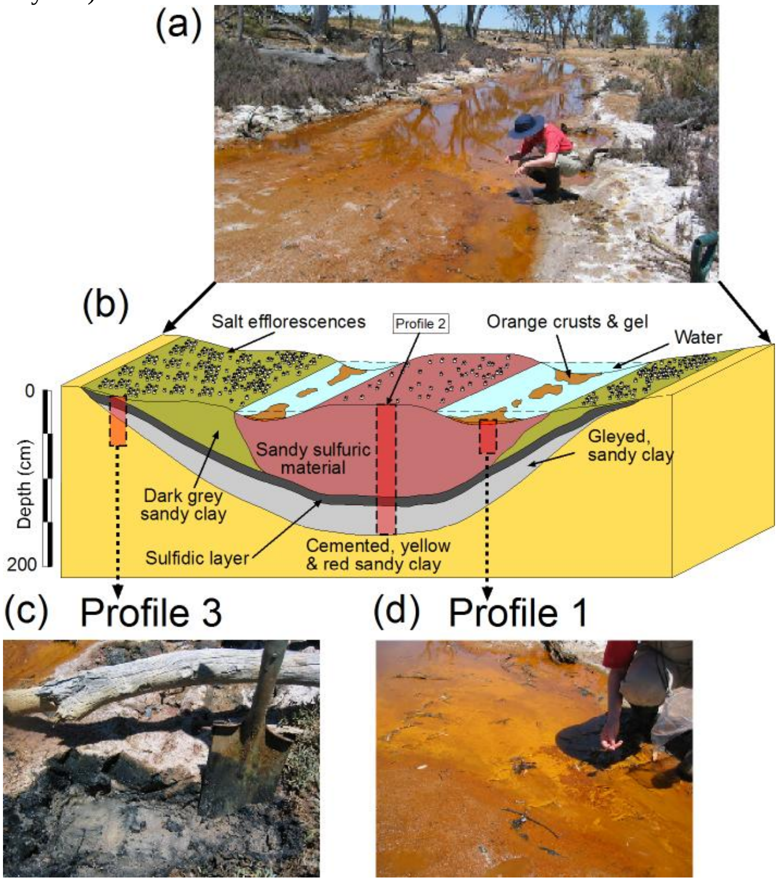

Figure 2: Schematic cross-section or hydro-toposequence (2b) through a drain showing various white salt efflorescence zones on the edge of the drain (2a), layers of black sulfidic material in profiles 3 (2c), 2 and 1; orange coloured sulfuric materials in profiles 1 and 2 from the centre of the drain (2d) and underlying soil-regolith materials (2b). Profile 3 (2c) on edge of the drain has white salt efflorescences overlying a mixture of uniform black, sulfidic material and monosulfidic black ooze, which in turn overlies mottles of black, sulfidic material in a yellowish-greenish-grey to olive mottled clay. Soil profile 1 (2d) near the centre of the drain has orange coloured iron oxide crusts and gels (mostly akaganéite with some schwertmannite) that scavenge metals and form by oxidation of pyrite in the underlying layer of sulfidic material.

Monosulfidic Black Ooze

Monosulfidic Black Ooze (MBO) is readily observed in the surface sediments of most drains (Figures 2b & 2c). The high nutrient environment, especially at the edges of drains, and the activity of algae and micro-organisms cause reduction and formation of black, smelly iron monosulfides and other sulfides. Erosion of organic rich topsoils and influx of ground-water with low redox potentials (reducing) into the drains were also likely to contribute to MBO formation. MBO is very reactive if exposed to oxygen, but provided the materials remain anoxic and undisturbed they are relatively non reactive. If flushed out of the drain as floodwaters scour drain channels they will oxidise and may become acidic. However, in some drains the ubiquitous carbonates of calcium, magnesium and sodium in drain water may neutralise the acid.

Sulfuric materials

When sulfidic materials are drained and exposed to air, they oxidise and produce sulfuric acid (e.g., Dent & Pons 1995). If the amount of acidity produced exceeds the buffering capacity of water and sediments, acidification occurs. Prior to draining, materials that can cause acidification are called sulfidic materials (i.e., potential acid sulfate soil materials or PASS). Once sulfidic materials are drained they may transform to sulfuric materials (i.e., actual acid sulfate soil materials or AASS).

The occurrence of bright yellow natrojarosite mottles in some of the clay-rich sulfuric horizons is indicative of acid conditions in the range pH 3.5-4. Similarly, the occurrence of orange coloured mottles, gels and crusts (Figures 2a & 2d) are indicative of schwertmannite and akaganéite, which form from the oxidation of ferrous iron in acid conditions in the range pH 4-5. Many of these minerals occurred in drains above the ground-water level, indicating that there is a store of acidity in soil profiles that could contribute to future, if not current drainage acidity.

Sulfate-containing salt efflorescences and oxyhydroxysulfate minerals

A predominance of sulfate-containing evaporite minerals occur in the drains because of the specific chemical composition and pH of inflowing drainage waters containing Na, Ca, Mg, Cl, Ba and SO_4. The saline groundwaters enriched in sulfate (with other elements sourced from mineralised zones) seeping through soils, anaerobic conditions and organic carbon in saturated soils yield pyrite-enriched sulfidic material containing pyrite framboids through anaerobic bacterial reduction of sulfate. When sulfidic materials are eroded and exposed to air, pyrite is oxidised producing sulfuric acid with mineral dissolution followed by precipitation of the following sulfate-containing minerals in varied environments:

- Pentahydrite, starkeyite, bischofite, bassanite, carnallite, rozenite, barite, halite and gypsum in sandy sulfuric horizons with pH <3.0;
- Natrojarosite and jarosite in clay-rich sulfuric horizons with pH 3.5-4; and,
- Eugsterite, bloedite, thenardite, glauberite, gypsum, thenardite, mirabilite, schwertmannite, lepidocrocite, akaganéite and colloidal poorly crystalline/pseudoboehmite-like (white) precipitates in sulfidic materials with pH >5.

Movement and accumulation of soluble salts is typical of drains, but the salt crusts in the WA wheatbelt contain an assemblage of previously unrecorded types of sulfate-containing evaporite minerals as detected by XRD and SEM. This is caused by the unique geochemistry of the drainage environment. The components of the evaporite minerals were derived by leaching of oxidized iron sulfides and then precipitated as specific minerals at various stages during the drying/evaporation of the drained soils. These sulfate-containing salt minerals accumulate steadily in the lower parts of drains immediately below/under the carbonate-rich or calcrete layers and above the sulfidic layers (Figure 2d) because of limited lateral movement of water to carry the soluble salts away in the drains. The significance of the minerals found in these salt efflorescences is that they reflect annual geochemical cycling in the drain environment. In this case there is an annual cycle of evapoconcentration and metal accumulation during summer followed by dissolution of the salts and loss to drainage waters during winter rainfall. A change in mineral composition will indicate a change in the nature of the salts entering the system from drain or ground waters.

These minerals range in morphology from thin, powdery and very transient efflorescences to thicker, more persistent, soil-cementing crusts. Formation of these complex salts of sulfates of Fe, Al, Na, Pb, Ca, As, Zn, Mg, jarosites, oxyhydroxysulfates and oxyhydroxides are indicative of rapidly changing local environments and variations in redox, pH and rates of availability of S and other elements. As such, these evaporite minerals are indicators of soil-water processes operating in specific landscapes. A detailed understanding of these minerals and biogeochemistry in acid sulfate soils and sediments reveals important dual applications for land management and mineral exploration.

EVALUATION OF POTENTIAL RISKS FOR WA WHEATBELT DRAINS

The significance of sulfate-containing evaporite minerals

Sulfate-containing evaporite minerals found in salt efflorescences in drains are significant in that these are an integrated indicator of complex geochemical conditions in the drains and play a critical role in drain erosion processes by salt fretting. These soluble sulfate-containing minerals play important roles in the transient storage of components (Na, Ca, Mg, Cl, Sr and SO_4), which will dissolve during rainfall and contribute to formation of the saline monosulfidic black ooze in the drains. The metals concentrated within these salts (e.g., Al, Fe, Zn, As and Pb) also indicate a significant environmental risk since many are in a position to be flushed (potentially in concentrated pulses) into receiving environments by rainfall events.

Sulfidic materials and acidification

Accumulation of significant sulfidic materials increases the risk of additional acidification in the drainage waters not associated with ground-water discharge. Acidification could be an issue locally where carbonates are absent or spatially separated from groundwaters. Discharge of low redox potential groundwater (Figure 2a & 2b) has been readily identified as a source of acidity, however the contribution of this source compared with sediment sources over the life of the drain is not clear. The discharge of low redox groundwater to drains can produce environmental impacts similar to that of disturbed sulfidic materials (i.e., deoxygenation and acidification) because the waters are rich in dissolved iron and manganese.

Acidification and elevated metal concentration

Accumulations of metals within the sulfidic materials further compounds the off-site risks posed by the drains. In addition to lowering pH, disturbance and oxidation of sulfidic materials during flow events will lead to significant, short-term pulses in dissolved metal concentrations in surface waters, including toxic species such as Al, Fe and other metals (e.g., Cu or Cr, see Figures 2a & 2d). Drains sampled in eastern areas were typically acid and contained large amounts of Fe, Al, salt, metals (Cr, Mn, As) and the rare earth elements La and Ce. The increase in solubility of metals combined with hydrological variability of the drains under acidic conditions may be more harmful to biota than the low pH itself.

The effect of Anthropogenic burning

Burning in one drain is dramatic because it resulted in the formation of abundant, irreversibly fused, particulate and discrete artifacts, which blocked a drain pipe.

CONCLUSIONS

As a result of the data analysis from this paper and the wider project (e.g., Rogers & George 2005), the following management and assessment guidelines are suggested:

- Drains need to be kept free of sediments to both sustain their hydraulic effect (lowering of water tables) and prevent additional acidification and biogeochemical reactions within them (i.e., formation of sulfidic and sulfuric materials). Formation of 'new' sediment profiles in drains characterised by iron sulfide minerals occurs over a period of months, and has potential to generate some additional acid through sulfide oxidation if drain sediments dry out. These sediments are also hydrologically and chemically unstable, accumulate metals and can potentially result in pulses of metal export occurring from the drains;
- Organic material (such as dead vegetation) should be prevented from entering drains for the same reasons (hydraulic and geochemical impacts);
- Subsoils that contain calcretes, silcretes and red-brown hardpans are at less risk of erosion, sedimentation, dissolution and related problems than clay-rich, sodic subsoils, and sandy materials;
- Pilot excavations should be assessed before drain construction to determine the risk of acid groundwater and trace element issues;
- Drain designs should prevent erosion and the transport of acids and related organic and metal-rich deposits (plus sediment) to receiving environments especially during flood events;
- An assessment of the impact of acid and trace element-rich drain discharges on receiving environments (lake/river systems, evaporation basins) is critical; and,
- Processes involved in sequestration of metals in drain sediments can be exploited to develop management strategies that will reduce metal export and off-site impacts of the acidity exported by the drains.

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