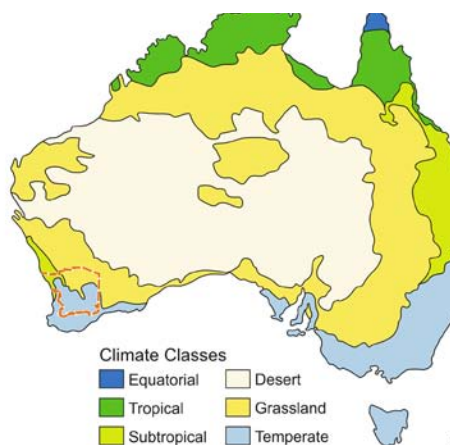


The geochemistry of acid-saline waters and drainage sediments in the Avon Catchment, Western Australian Wheatbelt



Introduction

The relationship between native vegetation clearance and increasing groundwater and surface water salinities is well established in the semi-arid regions of Australia (Allison et al. 1990). The primary cause of dryland salinity in many parts of Australia is due to increased groundwater recharge following native vegetation clearance for annual crops and pastures. This has caused mobilisation of salt stored in the shallow regolith and/or increased groundwater discharge. Salinisation due to rising water tables is a significant management issue in

Figure 1: Location of Australian Wheatbelt east of Perth in Western Australia.

many parts of the West Australian (WA) Wheatbelt (Fig. 1). Engineering options to counter rising saline groundwaters are increasingly being adopted in the WA Wheatbelt (Clarke et al. 2002; Hatton et al. 2003).

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The adoption of engineered drainage solutions to control groundwater levels can be an effective management tool in landscapes affected by dryland salinity. However, hydrological efficiency is highly dependant on near surface regolith properties. Recently, there has been extensive state government agency and landholder interest in using deep (2-3 m) drainage systems as an option to control water table rise (Ali et al. 2004a) (Fig. 2). Over 10,000 kilometres of drains have already been constructed to protect both low-lying land from salinisation and rehabilitate marginally saline lands, and plans are already being assessed for further expansion of drainages on individual properties, and to establish regional integrated drainage systems.

Concerns have been raised by landholders, local government authorities, land management agencies and the general community (Dogramaci & Degens 2003) regarding the potential for drainage systems to discharge acidic, trace element rich waters that may impact on receiving environments. Initial investigations of some major drainage schemes found that these can discharge waters of pH 2-3 with total dissolved solids (TDS) of 30000 to 50000 mg l⁻¹ (TDS of seawater is 34600 mg l⁻¹) at 5-10 ML per day (Ali et al. 2004b).

In order to address these concerns, and provide a robust scientific basis upon which to plan drainage schemes and assess geochemical risks of acid discharge, the Engineering



Figure 2. Typical deep acidic saline drain with in the WA Wheatbelt.

Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project have been commissioned as part of the WA National Action Plan for Salinity and Water Quality (NAPSWQ). Although salinity was originally assumed to be the main potential water quality problem, the realisation

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that acidic groundwaters are common throughout the Wheatbelt (Rogers & George 2005; Shand & Degens 2007) has highlighted that acidity and mobilisation of elements, which may be toxic at high concentrations poses a significant risk. A number of projects are being managed by the Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME) in collaboration with the WA State Government Department of Water, Department of Agriculture and Food and CSIRO Land and Water. The primary aim of these initiatives is to assess the geochemical risks and impacts on receiving environments of deep drainage, and to identify management options for the disposal of acidic waters. This paper outlines the main conclusions of recent investigations (Shand & Degens 2007) including an evaluation of geochemical risks in receiving environments of the Avon catchment into which deep drains discharge.

Occurrence and generation of acid waters in the Wheatbelt

Acid saline groundwaters are present over large areas of the Wheatbelt, but are more common in the east where up to 70% of groundwaters sampled have acidic pH (pH 3 – 4.5 (Fig. 3). Such groundwaters were known to occur

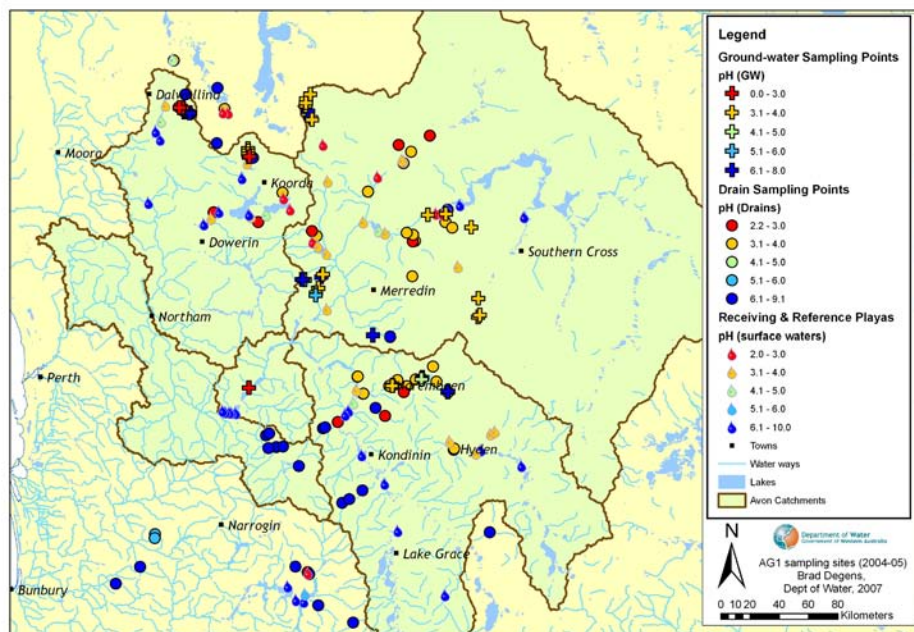


Figure 3. Locations of drain, lake and ground-water sampling sites (classified by sample pH) in the Avon catchment (from Shand & Degens 2007).

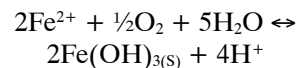
prior to the installation of drains showing that drainage is not the main cause of acidification. Acid hypersaline lakes (Fig. 4) are also a relatively common feature of the Wheatbelt, where the lakes represent strongly evaporated groundwater discharge. Acid hypersaline lakes typically occur in low-lying closed basins and in valley bottoms where they form discontinuous chains (Commander *et al.* 2002). Many of the deep drains installed in the Avon catchment of the Wheatbelt to control groundwater levels are acidic,



Figure 4. Acid hypersaline lake in the Wheatbelt near Koorda.

displaying a similar distribution to acid groundwaters (Fig. 3). The significance of increasing discharge of acidic waters for trace metal mobilisation, and the risk that this poses to aquatic ecosystems, should increasing drainage occur, has only recently been investigated (Shand & Degens 2007).

The origin of acidity in the groundwaters is not known in detail, although it is commonly believed that the oxidation of dissolved iron (Fe) plays an important role in generating acidity (Mann 1983; McArthur *et al.* 1991). This reaction may be more important at the margins of Playa Lakes and drains where reduced iron (Fe^{2+}), present in Fe-rich groundwater, is oxidised to Fe^{3+} , generating acidity (H^+) in the process:



This model by itself is unlikely to explain the occurrence and preponderance of acid groundwater in many parts of the Wheatbelt, since Fe-rich waters are common in many other non-acidic areas. In addition, acidity is required (consumed) in order to dissolve iron initially by reductive dissolution of oxidised Fe, hence it is difficult to attain the low pH values of

groundwaters without an additional strong source of acidity (e.g. sulfide oxidation as found in acid mine drainage). New models are currently being developed based on fractionating alkalinity, e.g. removing alkalinity by the precipitation of calcite from stored acidity, the latter being stored and transported in the water. Such models may explain e.g. the correlation between calcareous soils and gypsum with areas of low pH groundwater.

Geochemistry of the acid waters

Samples were collected from groundwater boreholes, drains and lakes (receiving environments) in the Avon

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catchment to assess the potential risks that the drains may impose on receiving environments. All samples were filtered in the field through $0.45\ \mu\text{m}$ membrane filters and either acidified with ultrapure HNO_3 or retained unacidified and stored at 5°C , depending on the analysis performed. On-site measurements of pH, specific electrical conductance (SEC), temperature and Eh were taken at many sites (when possible). Drain/creek flow was also estimated whenever possible. The concentrations of major and minor cations and sulfate were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Anion analyses were completed using ion chromatography and colorimetry (APHA 1998).

Drain flow was highly variable (from $30\ \text{l s}^{-1}$ to less than $0.1\ \text{l s}^{-1}$) over the study area, and generally decreased with increasing age of the drain. In some cases, drains ceased to flow once the water table fell below the base of the drains. However, the impact often extended to distances greater than 200 m (Ali et al. 2004a) depending on the local geology and hydrogeology. During periods of low flow, the salinity of drain water increased and pH generally decreased.

The pH data for surface waters and groundwater

displays a bimodal distribution (Fig. 5). The pH was generally lower in the eastern Wheatbelt than in the western and central Wheatbelt, and most drains were typically saline (Fig. 5). Major element concentrations and TDS display large variations, typically over several orders of magnitude. High TDS surface waters are present in both acidic and alkaline surface waters and groundwaters (Fig. 6), although the former have much higher TDS, largely due to evaporation. Sodium displays a strong positive correlation with Cl ($r^2=0.99$) but the other major elements correlate poorly with Cl indicating gains or losses relative to seawater (Fig. 7). The surface waters in particular have low ratios of Ca, Mg and SO_4 to Cl relative to seawater consistent with removal processes such as mineral precipitation (e.g. calcite, gypsum, halite) and/or removal through redox processes (e.g., reduction of sulfate to sulfide).

Most minor and trace elements vary over several orders of magnitude. Nearly 50% of the samples have F concentrations exceeding the WHO guideline value of $1.5\ \text{mg l}^{-1}$ (Fig. 8). Nutrients and total organic carbon were measured only in surface waters but reached high concentrations: $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and TOC had maxima of 1.4, 11, 45

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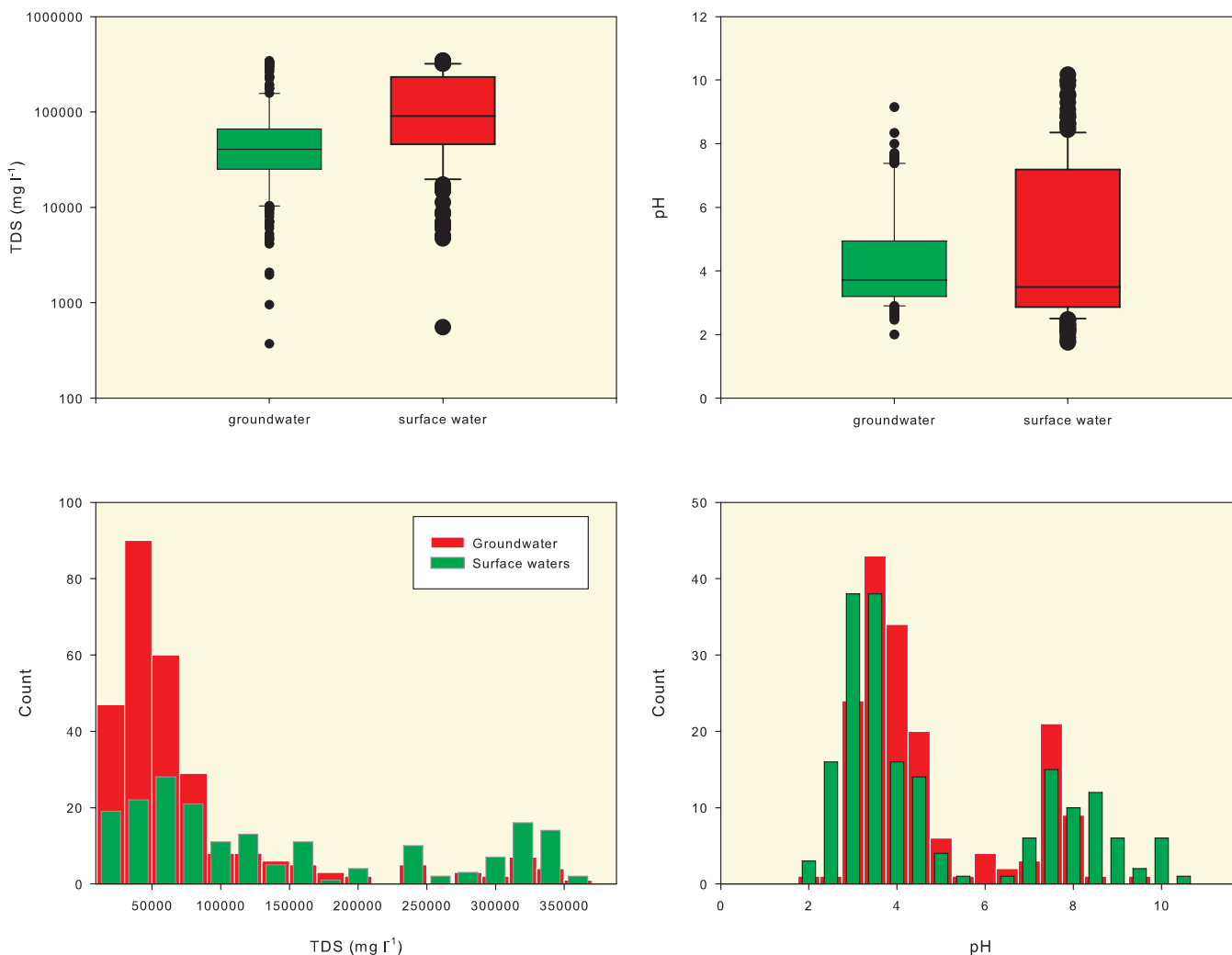


Figure 5. Boxplots (displaying median, interquartile ranges and outliers) and histograms for TDS (left) and pH (right) in surface waters and groundwaters sampled in the Avon catchment.

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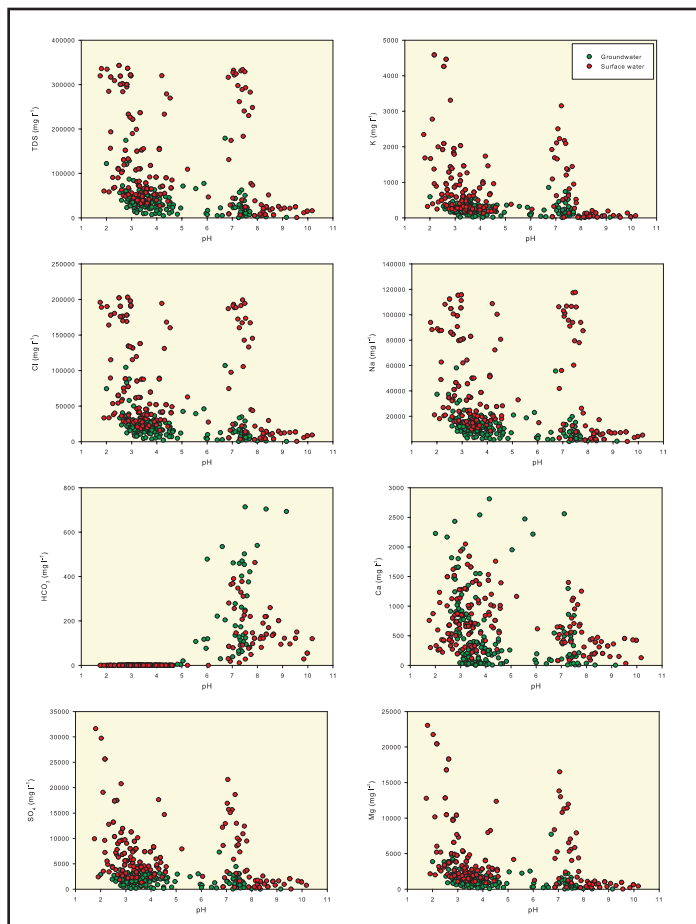


Figure 6. Relationship of TDS and major element concentrations to pH in surface waters and groundwaters of the Avon catchment.

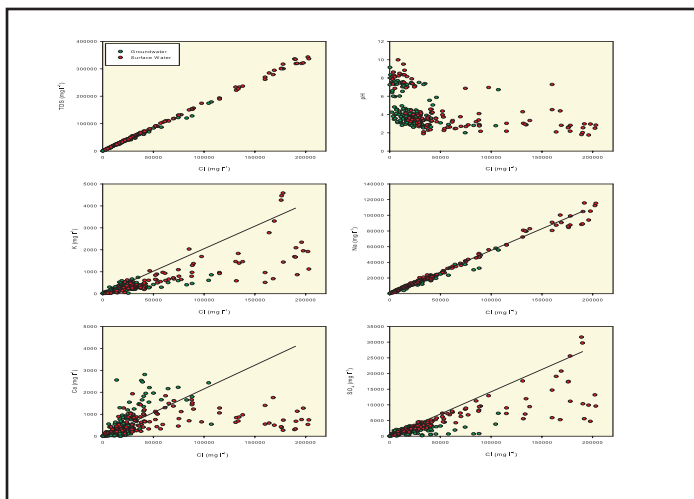


Figure 7. Relationship of TDS, pH and major element concentrations to Cl in surface waters and groundwaters of the Avon catchment. Solid line is seawater dilution line.

and 255 mg l⁻¹, respectively. The redox-sensitive elements Fe and Mn are present at high concentration in the waters, in general being higher at lower pH. Aluminium concentrations also display a wide range, reaching maximum concentrations greater than 1000 mg l⁻¹ at low

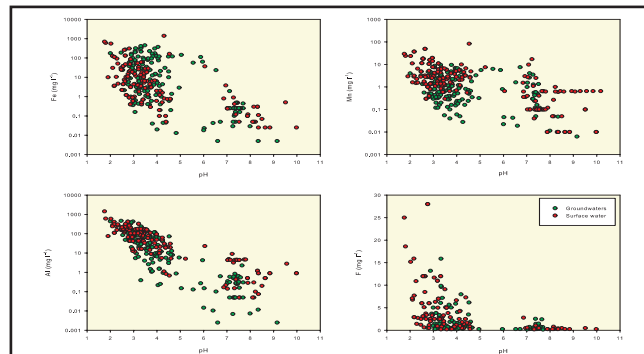


Figure 8. Concentrations of minor and trace elements in waters of the Avon catchment plotted against pH. Note log scales for Fe, Mn and Al.

pH. Many metals, including Fe and Mn are more soluble and mobile under acidic conditions (Stumm & Morgan 1996). The acid nature of both surface waters and groundwaters has allowed a number of trace elements to reach mg l⁻¹ concentrations including Co, Cr, Cu, Ni, Pb, U, Y and the rare earth elements (REE), many above national drinking water guideline values (Fig. 8). A number of elements which are rarely present in waters such as Th, Pd and Tl have elevated concentrations above typical baseline values. The concentrations of many trace elements are more typical of highly polluted waters, and much higher than those expected in non-industrial or mining areas (Nordstrom 2007; Shand & Edmunds 2008).

Geochemical processes occurring in drains

The discharge of acid groundwater to artificial drains, and subsequent reactions, has led to a complex and dynamic geochemical environment. The oxidation of reduced soluble Fe²⁺ in drains to insoluble Fe³⁺ oxy-hydroxides is commonly strikingly visible (Fig. 9) and often lead to a



Figure 9. Iron oxy-hydroxide minerals covering the base of a stream, note also the abundance of salt efflorescences adjacent to the stream caused by evaporation of capillary water. The efflorescences are generally present during summer months but are washed into the stream during rainfall periods, producing a pulse of increased salinity.

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further decrease in pH. The elements Fe and Al are pH sensitive and act as stores of acidity in solution, releasing H⁺ during the precipitation of oxyhydroxide minerals by hydrolysis reactions. These minerals commonly form gels in the environment, which are efficient scavengers of trace metals (e.g., As, Cr, Sn, Th, V, Cd, Cu, Mo), but the fine colloidal nature of these materials places them at risk of being suspended and flushed from the drains even at low flow velocities. The association of the metals with the precipitates and gels is not well documented in the drains of the study area, but it is probable that these materials could act as transporting media for metals from the drains if not well managed.

A wide range of minerals actively form in the drain environment (Fitzpatrick et al. 2007). Iron sulfide minerals (pyrite and monosulfides) are commonly encountered immediately beneath the oxidised sediment surface where conditions are reducing, causing sulfate to be reduced to sulfide. The key requirements for high rates of sulfate reduction and sulfide accumulation are: (i) high concentrations of sulfate in surface water or groundwater, (ii) saturated, reducing iron-rich soils and sediments, and (iii) the availability of labile carbon to fuel microbial activity (Berner 1984). Disturbance of these sulfide-rich sediments, in particular if they form monosulfidic black oozes, in drains can lead to severe deoxygenation and acidification. (Sullivan et al. 2002).

A remarkable range of other mineral precipitates and gels were found in the drains (Table 1), indicative of the

Mineral Name	Chemical Formula
akaganéite	Fe ³⁺ O(OH, Cl)
bassanite	2(Ca) ₂ (SO ₄)·(H ₂ O)
barite	BaSO ₄
bischofite	MgCl ₂ ·6H ₂ O
bloedite	Na ₂ Mg(SO ₄) ₂ ·4H ₂ O
boehmite	AlO(OH)
carnallite	KMgCl ₃ ·6(H ₂ O)
eugsterite	Na ₄ Ca(SO ₄) ₃ ·2(H ₂ O)
glauberite	Na ₂ Ca(SO ₄) ₂
gypsum	CaSO ₄ ·2(H ₂ O)
halite	NaCl
jarosite	KFe ³⁺ (SO ₄) ₂ (OH) ₆
lepidocrocite	FeO(OH)
mirabilite	Na ₂ SO ₄ ·10(H ₂ O)
natrojarosite	Na Fe ³⁺ (SO ₄) ₂ (OH) ₆
pentahydrate	MgSO ₄ ·5(H ₂ O)
rozenite	Fe ²⁺ SO ₄ ·4(H ₂ O)
schwertmannite	Fe ³⁺ ₁₆ O ₁₆ (OH) ₁₂ (SO ₄) ₂
starkeyite	MgSO ₄ ·4(H ₂ O)
thenardite	NaSO ₄

Table 1 Chemical compositions of minerals found in the drains of the Australian Wheatbelt.

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range of geochemical conditions occurring. Bright yellow natrojarosite mottles in some of the clay-rich sulfuric horizons are indicative of acid conditions in the pH range 3.5-4. Similarly, the occurrence of orange-coloured mottles, gels and crusts are indicative of schwertmannite and akaganéite, which form from the oxidation of ferrous iron under acidic conditions in the pH range 4-5. Saline and subaqueous soils with sulfuric material may also occur in receiving lakes. Other precipitates include evaporite minerals, those being found to date in the drains and lakes include pentahydrate, 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 >4-5.

The processes that give rise to the variable mineral assemblages play a major role in influencing transport of acidity and trace metals from the drains and vary with season and drain age. Furthermore, identifying the processes has enabled development of practical management options to mitigate the risks that drain discharge poses to receiving environments. In order to facilitate the transfer of information on drain and water geochemistry, an interactive web-based database has been constructed (Baker & Fitzpatrick 2005). This website incorporates a visual

aid designed to allow rapid and effective communication of data and information at a range of scales (regional to microscopic).

Receiving environments

Many acid drains discharge to saline sites, principally playas in the floodways of the main palaeodrainage systems (Dogramaci & Degens 2003; de Broekert & Coles 2004; Ali et al. 2004b). Acid drainage discharge to playa lakes can result in acidification of surface waters and the sediments and soils surrounding the playa lakes. However, in some cases lake waters and sediments may have been acidic prior to discharge, in which case the impacts are dependent on the magnitude of drain discharge compared with regional ground-water discharge. Concentrations of Al, Fe and trace metals including Pb, Ni, Co and U are often higher in the surface waters of sites receiving acidic drainage. This acidification and associated increased in trace metal solubility may result in impacts on aquatic ecosystems, including loss of habitat and reduced ecosystem functioning during playa lake filling events, and should form an integral part of future research in the region.

The discharge of acid drain water into alkaline waters in receiving environments allows the possibility for neutralisation of acidity. Geochemical modelling using the PHREEQC geochemical code was undertaken. This modelling indicates that the neutralisation of acidity in the drain waters in receiving environments is unlikely to occur until the volumes of alkaline waters are in the order of more than 25-99 times that of the incoming acid drainage waters. It will therefore be necessary to implement further remediation strategies in the absence of such volumes of alkaline waters being continuously available.

Management implications of acid drain water

The widespread occurrence of acid groundwaters and surface waters in the Wheatbelt containing high concentrations of potentially toxic elements requires care to be taken in managing and linking deep drains installed for salinity reduction. Drains also need to be designed and managed to minimise turbulent flow to minimise the flushing of precipitates and gels (frequently containing trace metals) and disturbance of sulfidic sediments (being a store of acidity and trace metals). In particular, entry of surface waters from catchments to the drains should be avoided without measures to contain flow velocities. Drains should also be designed to maximise hydrological residence times as the formation of precipitates will contribute to maximising retention of trace metals within the systems.

Management of trace metal mobility and acid release will need to be considered when maintenance cleaning of sediments from drains is carried out. This might include mixing with sediments from alkaline drain spoils, placement within depressions on drain spoils (allowing drying and containment but including contact with alkaline spoils) or collection and containment in a site with low risk of off-site impacts (i.e. outside of a surface water flow path).

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It is vital for all landholders, community groups, drainage contractors and local governments to be aware of the many impacts that could result from the occurrence of sulfuric materials and disturbance of sulfidic materials, as these have important consequences for environmental, engineering, economic, and quality of life perspectives. Disturbance and oxidation of sulfidic material can have negative impacts including: destruction of wetlands, acidification and deoxygenation of waterways and increased incidence of fish kills and disease, contamination of valuable groundwater resources, mobilisation and accumulation of heavy metals, corrosion and destabilisation of roads, concrete and steel infrastructure, stimulation of blooms of blue-green algae, decrease in the agricultural productivity of land, increased odour problems and increased mosquito and arbovirus incidence.

Future work

The work completed in the Avon catchment is now being extended to other parts of the Wheatbelt. Following a review of potential acid neutralisation techniques for acid drains in the Wheatbelt (Douglas & Degens 2006), pilot treatment sites have recently been established to investigate low-cost, practical treatment options for acidic drainage waters. Future research will focus on the geochemical processes and efficiency of the treatment sites. The trials will focus on simple engineering structures using either carbonate neutralisation (being the most widely available, low cost

material currently available in the Wheatbelt) or sulfate reduction systems using locally available carbon sources.

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