Acidic water discharge criteria for saline aquatic ecosystems in the WA Wheatbelt – a technical discussion paper

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by

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Cover: measuring pH in the Cowcowing Lakes system, (photo courtesy: Paul Shand, CSIRO)

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Summary

Acidity has been recognised as a hazard of rising saline groundwater in the Western Australian Wheatbelt. Increasing interest in using deep open drains to intercept this groundwater requires criteria and/or targets for the management of acidic discharge in pumped or drained water discharged to the environment. This discussion paper reviews the hazards of saline acidic waters, assesses the extent to which various measurements characterise the risks for inland saline waterways and lakes, and recommends interim criteria to guide management of acidic saline waters in the WA Wheatbelt.

Acidic waters pose hazards that extend beyond having low pH. These include the capacity to acidify environments and the toxicity associated with dissolved metals, mostly iron and aluminium. Various measures of acidity hazards include pH, sampling for dissolved metals or measurement of the amount of alkaline material needed to neutralise the waters. This last measure is called 'net acidity' and indicates the balance between acidity due to low pH and dissolved metals and dissolved alkalinity. Net acidity is not measured directly but calculated from measurements of water acidity and alkalinity.

Currently there are no national guidelines for pH or dissolved metals to be readily adapted as interim criteria for the discharge of acidic saline waters to inland saline ecosystems. Guideline values for pH and dissolved metals are available for fresh water and marine aquatic ecosystems, but these apply to waters with aquatic species not common in inland waterways with different composition of salts. There are international and state guidelines for net acidity developed from a chemical basis for fresh and brackish waters. Given the derivation, these guidelines may be equally applicable to saline waters.

It is proposed that discharge criteria for acidic saline waters released to waterways and lakes be based on net acidity and that a maximum threshold of 10 mg $CaCO_3$/L be adopted as an interim guideline level. This recommendation is based on net acidity being readily interpreted, able to reflect acidity and dissolved metal hazards, and the ease of calculating net acidity from field measurements of acidity and alkalinity. The proposed guideline level was derived from recent toxicity testing using aquatic organisms that can be found in inland saline aquatic ecosystems in south-western WA. This level is intended to achieve a high level of confidence of protecting aquatic ecosystems from the effects of acidity and may be relaxed to 20 mg $CaCO_3$/L for lower value ecosystems.

1   Introduction

Dryland salinity due to rising saline groundwater affects around one million hectares of the Western Australian (WA) Wheatbelt and threatens at least an additional two million hectares over the next 20 to 100 years (Cacetta et al. 2010). The rising saline groundwater in many low-relief valley floors is also acidic (pH < 4.5; Shand & Degens 2008) with evidence that this has acidified lakes, waterways and floodplains (Degens et al. 2008a; Degens & Shand 2010). Over 100 000 km^2 of the Wheatbelt is believed to contain aquifers in which the groundwater is saline and acidic (Peiffer et al. 2009; Lillicrap & George 2010). Increasing interest in using deep groundwater drains to mitigate rising shallow watertables (Ruprecht et al. 2004; Kingwell & Cook 2007) has increased the likelihood of the acidic water being discharged directly to floodplain waterways, lakes and wetlands.

Acidic saline waters discharging from drains are chemically similar to acidic mine drainage (AMD) or drainage from acid sulfate soils. The acidic saline waters contain high concentrations of iron and aluminium, although typically more saline than seawater (Degens et al. 2008b; Degens & Shand 2010). High concentrations of trace elements such as manganese, lead, cerium, copper, lanthanum, nickel and zinc can also occur in the waters, although often less than encountered with AMD (Degens et al. 2008b). These trace elements, together with the acidity, present a clear hazard to inland waterways and lakes (Degens 2009; Stewart et al. 2009) similar to that widely understood from investigations of acid mine drainage (AMD; e.g. Gray 1997) and drainage from acid sulfate soils (e.g. Sammut et al. 1995).

The environments where drains might discharge include primary and secondary saline ecosystems in waterways, lakes and wetlands. Assessing and managing discharge to these require environmental criteria and/or targets which have been recognised as a priority strategy of the *Inland Drainage Policy Framework* (Department of Water 2013). These criteria need to be practical to measure but also able to adequately encompass the risks associated with acidic drain waters. Practical treatment options are available for farmers to neutralise acidity and remove trace metals from acidic drain waters (Degens 2009), but these require water quality benchmarks to determine when treatment is required and to what level.

Common measurements of acidity include pH, which most people are familiar with, and the lesser known, net acidity (Kirby & Cravotta 2005). pH is a measure of the concentration of hydrogen ions (H$^+$) and is a master indicator of the acidity status of waters important for both chemical processes and biology living in contact with water. Net acidity is an integrated indicator that includes pH, the dormant acidity associated with dissolved metals found in many acidic waters, and any residual alkalinity (Kirby & Cravotta 2005; see also Glossary). The units of net acidity measurement are expressed as the weight of CaCO$_3$ (pure limestone) needed to neutralise all of the acidity in a litre of the water.

There is uncertainty regarding which characteristics of acidic waters will be most useful in assessing and managing the risks that the waters may pose to receiving environments. The Department of Environment and Conservation recommends that for (fresh) waters with pH < 6 the net acidity be less than 40 mg CaCO$_3$/L (Department of Environment and Conservation 2009), while international approaches (Younger et al. 2002) recommend treatment of all acidity (i.e. net acidity = 0 mg CaCO$_3$/L) to the point of alkalinity being present

(net acidity < 0 mg CaCO$_3$/L to perhaps −50 mg CaCO$_3$/L). A recent review of the impacts of drain waters on wetlands recommended an interim acidity threshold of no less than pH 6 (Jones et al. 2009), but noted that the dissolved metals in the waters (mostly acidic) posed additional uncertain threats. The authors also recommended that further investigations be carried out to assess the toxicity effects of trace metals on species of biota that occur in Wheatbelt wetlands across a range of salinity levels (Jones et al. 2009).

This discussion paper reviews the use of measures of acidic water properties, assesses the extent to which these characterise the hazards associated with the waters, and the benchmark information available to apply the measures to inland saline waterways of the WA Wheatbelt.

2 Acidic saline water – aquatic hazards defined by water properties

2.1 The basic chemistry of acidic waters in Wheatbelt WA

The acidic saline waters in the inland areas of the WA Wheatbelt have characteristics beyond being low in pH. Most of these characteristics are coupled with the affinity of the low pH water for dissolved metals.

High concentrations of dissolved iron (> 50 mg/L) and iron's reaction with oxygen in air are thought to play a key role in lowering the pH in saline groundwater in the WA Wheatbelt (Shand & Degens 2008; Lillicrap & George 2010). Research has also focused on how groundwater came to have containing high iron concentrations but little or no dissolved alkalinity (Peiffer et al. 2009; Lillicrap & George 2010). In the low pH conditions clays in the saline aquifers dissolve and raise the concentrations of aluminium and silicate in groundwater. This has occurred in some areas to the extent that aluminium concentrations are in the order of hundreds of mg/L and often higher than those of iron (Degens et al. 2008b). High concentrations (1–10 mg/L range) of manganese also occur under low pH conditions; however, this appears to be unrelated to acidity across the Wheatbelt since water with pH 2.5–9.2 contains similar concentrations (Shand & Degens 2008; Degens & Shand 2010). The influence of the dissolved metal on acidity is probably also limited by its slow reaction with oxygen to generate hydrogen ions (Younger et al. 2002).

The dissolved metals and low pH influence the behaviour of the acidic waters on discharge to groundwater drains, waterways or lakes. In drains, dissolved iron can continue to react with oxygen in the air, further releasing hydrogen ions (lowering the pH) and forming red precipitates. This reaction becomes sluggish once the water pH falls below about 3.5 (Degens 2009) particularly when no iron-oxidising bacteria are present. Similar effects have also been observed by the author in waterways and lakes where acidic groundwater discharges. In contrast, dissolved aluminium in the acidic waters is not influenced by oxygen but will stay dissolved unless pH increases, generally to > pH 5. These dissolved metals influence the capacity for acidic waters to lower the pH of alkaline waters and soils and is indicated by net acidity. Net acidity is not measured directly, but calculated from measurements of alkalinity and acidity as the subtraction of acidity from alkalinity (Appendices A and B; see Glossary).

Raised pH from mixing acidic saline waters with alkaline surface waters or sediments will trigger changes in water quality due to the behaviour of dissolved iron and aluminium. Neutralisation of acidic iron-rich waters can lead to dissolved iron forming large sludgy precipitates in flowing waters, as the iron reacts with air at higher pH (Younger et al. 2002). This reaction can also lead to fluctuating pH as the iron continues to react with oxygen and release H^+ (lowering pH). If there are significant amounts of dissolved iron present, the acidity released by oxidation and precipitation can overwhelm any alkalinity and return pH to acidic levels. Dissolved aluminium can also form sludgy precipitates when water is

neutralised, as it is more sensitive to changes in pH between 4.5 and 5.5 (Kirby & Cravotta 2005). The iron and aluminium precipitates cause physical changes in water quality by increasing turbidity and physical changes in habitat by smothering the beds of streams and lakes. In addition to these physical effects, the toxicity of the metals changes during neutralisation, with dissolved aluminium often becoming more toxic at pH 4.5–6 (Gensemer & Playle 1999).

The low pH conditions of the saline groundwater enable a range of metals and metalloids to be leached from the ancient regolith of the Wheatbelt and entrained at high concentrations. Metals such as copper, zinc, lead and nickel commonly have elevated concentrations in acidic groundwater (Shand & Degens 2008; Degens & Shand 2010). The solubility of these metals strongly depends on pH because this modifies whether the metals are adsorbed onto clays and iron oxides in aquifers, drains or waterways. Metals such as cadmium, cobalt, chromium and beryllium, and metalloids such as arsenic and selenium can also be dissolved in the acidic waters, but these have only been found in lower concentrations in the WA Wheatbelt (Shand & Degens 2008; Degens & Shand 2010). By contrast, rare earth elements such as cerium and lanthanum can be up to mg/L concentrations in the acidic waters (Degens et al. 2008b).

2.2   Acidic water impacts in a risk framework

Acidic saline water may have various impacts that can be broadly illustrated by considering them in a risk framework. The main risks of untreated acidic water are defined by the hazards to ecosystems, land, human health and infrastructure, and the pathways by which these might be expressed. Water hazards consist of two components: (1) acidity and (2) mobilisation of metals and minor elements. The potential impacts of these depend on how, when and how much acidic water reaches surface environments and the biological or physical receptors in the environment.

Acidic water can pose a hazard to the following receptors:

- aquatic life in often saline lakes, creeks and floodplains
- riparian vegetation
- terrestrial fauna (if water is consumed by native or introduced fauna or agricultural animals)
- human health, where water accumulates in lakes used for recreation
- infrastructure in waterways, such as bridges and culverts.

The effects of exposing each of the potential receptors to acidic waters vary. It is important to note that risks of impacts are greatly diminished if there is no pathway for transporting acidic waters to places where they (waters) can affect surface environments. Similarly, containing the waters also minimises risks to terrestrial fauna and humans if access to the waters is prevented.

This discussion paper focuses on the effects of exposing aquatic ecosystems to acidic waters. These effects are summarised in the following section. The hazards, and consequently risks, of acidic waters to infrastructure and human health are not discussed in

this paper and remain unquantified in the Wheatbelt. The latter may require future consideration in view of increased recognition of risks to human health from acidic waters draining from acid sulfate soils (Ljung et al. 2009).

2.3   Direct effects of acidity on saline aquatic ecosystems

Very little is known of the effects of acidic waters on saline aquatic ecosystems as acidity in saline waters is rare on a worldwide scale (Waiser & Robarts 2009). However, broad understanding can be drawn from the impacts of acidic water on freshwater aquatic ecosystems. Few aquatic species are known to be tolerant to both salinity and acidity (Davis et al. 2003; Halse 2004; Timms 2005) and low pH waters have reduced capacity to support aquatic diversity in waterways and lakes (Jones et al. 2009; Stewart et al. 2009). While pH has been the only acidity-related variable measured in ecological studies of acidic waters, it is quite likely that the dissolved metals also influence aquatic organisms. In freshwater ecosystems, their influence is often more than just the effects of low pH (Sutcliff & Hildrew 1989; Gensemer & Playle 1999) and the same is expected in saline environments.

The following discussion outlines the non-metal (pH related) and metal-related effects of acidic waters on aquatic organisms extrapolating from fresh aquatic ecosystems to inland saline aquatic ecosystems.

2.3.1 Effects of low pH (H⁺ ions)

There is little understanding of direct and indirect acidic impacts on aquatic organisms. Most investigations report on the changes in species abundances in ecosystems following acidification (e.g. Halse 2004; Jones et al. 2009; Stewart et al. 2009) with little understanding of what mediated these impacts.

Lowering the pH of flowing water can directly and immediately affect organisms (including algae, macro-invertebrates and aquatic plants) living in the water and on the beds of lakes and waterways. This can happen when acidic drain waters mix with surface waters and pH drops and dissolved metals (mainly iron and aluminium) control the water's pH behaviour once pH reaches a point where the metals precipitate. The susceptibility of aquatic organisms to low pH waters varies between species (Gray 1997; Jones et al. 2009) as well as on stage of life-cycle (Havas & Rosseland 1995). This is mainly because of varying sensitivity of appendages such as gills or the resistance of organisms with calcareous shells to low pH (Havas & Rosseland 1995; Jones et al. 2009).

The effects of pH on aquatic organisms can also include indirect, often longer-term, effects on habitat and nutrient availability such as changes in the availability of phosphorus and nitrogen due to pH effects on nutrient cycling and nutrient retention in sediments, loss of habitat due to the death of aquatic plants, or changes in predation due to death of predatory species or loss of habitat (Gray 1997). In the Wheatbelt, these effects also likely include loss of refugia by acidification of sediments. Eggs, resting bodies (e.g ephippia) and seed banks in sediments are important refuges from which re-colonisation of surface waters occurs following fresh-flow events (Davis et al. 2003; Sim et al. 2006a, b). Acidification of sediments

is likely to affect the capacity for organisms in the sediments to survive and the suitability of sediments as refugia.

2.3.2 Effects of dissolved aluminium and iron

The toxicity of dissolved metals represents an additional element of acidic water toxicity in addition to that of hydrogen ions (indicated by pH). The influence of dissolved metals such as iron and aluminium consists of maintaining low pH as well as toxicity effects when the acidic waters mix with alkaline waters.

The acid-producing potential of aluminium and iron can present a significant acidification threat to downstream environments. Both metals suppress rises in pH when alkaline substances (such as dissolved bicarbonates, carbonates or hydroxides) are mixed with acidic waters. The dissolved metals are insoluble in neutral to alkaline waters and precipitate as solids that consume alkaline materials. Consequently, when acidic iron- and aluminium-rich waters discharge to aquatic environments, the waters will continue to lower the pH and consume dissolved alkalinity until all of the dissolved metals have reacted and precipitated.

The acid-producing potential of the dissolved metals is indicated in measures of potential acidity. This can be estimated by two approaches – by calculation from analysis of dissolved metals and pH or by titration using a strong alkaline solution. Acidity is calculated from dissolved metal concentrations (as mg/L values) and pH as:

$$Acid_{calc} = 1.79 \times Fe^{2+} + 2.68 \times Fe^{3+} + 5.56 \times Al^{3+} + 1.82 \times Mn^{2+} + 50000 \times 10^{-pH}$$

(after Kirby & Cravotta 2005) where all iron can assumed to be Fe^{2+} when pH > 3.5. Titration of acidic waters with strong alkaline solutions (e.g. sodium hydroxide) can also provide an estimate of potential acidity (see Appendix A), although internationally this is regarded to provide an underestimate of the true acidity which is best indicated by calculated acidity (Kirby & Cravotta 2005). However, for saline waters in the WA Wheatbelt, acidity measured by titration generally overestimates acidity and therefore provides a conservative estimate with minimal risks of underestimating net acidity (see Appendix B).

In the WA Wheatbelt, more than 85% of the potential acidity in acidic saline surface waters is due to dissolved aluminium and iron (Fig. 1). These metals can be present at concentrations that are an order of magnitude greater than the concentrations of H^+ as measured by pH.

The aluminium and iron in acidic waters can also have short-term impacts on aquatic organisms in creeks, floodways and lakes where drainage water directly discharges (and evaporates).

In the case of dissolved aluminium, the non-acidic impacts on aquatic organisms are largely due to the formation of toxic ion-complexes (Gensemer & Playle 1999), mostly when acidic waters are partially neutralised by alkaline waters; for example, during mixing with flood waters (Degens et al. 2008a). However, high concentrations of sulfate, calcium and dissolved organic carbon are common in many acidic saline waters in the Wheatbelt (Shand & Degens 2008) and can reduce the toxic effects of the metal (Gensemer & Playle 1999). Fine sludge precipitating from aluminium-rich water after neutralisation may physically clog breathing organs and mouthparts of aquatic insects, although there is no evidence to support

this (Gensemer & Playle 1999). This effect may be similar to that of increased colloidal turbidity in streams.
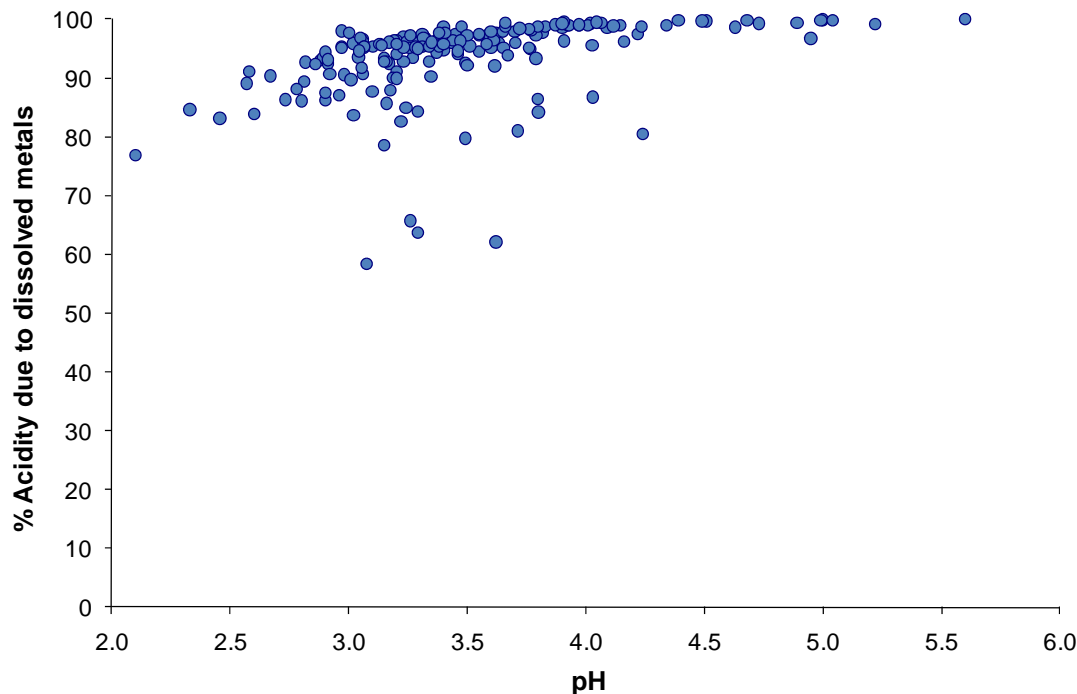
Figure 1 Percentage of total acidity due to dissolved metals in a range of acidic saline drain waters from the WA Wheatbelt (data from Shand & Degens 2008; Degens & Shand 2010)

In contrast, the effects of dissolved iron are more indirect by lowering pH in downstream environments and altering the physical conditions in waterways and lakes. Oxidation of iron can reduce the pH of water in stream sections well downstream of where water discharges, even when the pH first appears to be higher than 6. Delayed oxidation in the Wheatbelt is particularly likely because in the low-gradient slow-moving streams water has limited aeration. Formation of sludges after iron oxidises and neutralises can smother organisms in the water and on the bottoms of lakes and waterways (Phippen et al. 2008). Wind mixing of shallow lakes has been observed by the author to resuspend the often colloidal iron precipitates and increase turbidity. The increased turbidity is likely to directly affect all aquatic organisms (Phippen et al. 2008; ANZECC & ARMCANZ 2000c). A further potential effect of iron oxidation is the reduction in surface waters of oxygen concentrations, which are known to be critical for aquatic life (ANZECC & ARMCANZ 2000c).

Some of the iron-rich sludge forming from acidic waters can also trap acidity in minerals (such as schwertmannite; Sullivan & Bush 2004) that can continue to lower the pH of water for many decades. Formation of sludge may create localised acidic conditions in the sediments that affect mats of algae growing on the bottom of lakes and creeks and on submerged aquatic plants. These organisms are important parts of saline aquatic ecosystems (Davis et al. 2003; Sim et al. 2006 a, b).

2.3.3 Effects of dissolved minor elements

Additional direct toxic effects on aquatic organisms may be caused by other elements such as manganese, copper, nickel, zinc and lead. In fresh waters, these may cause immediate toxic effects on aquatic organisms in waterways and lakes; for example, reduction in growth and reproduction, or even mortality (Wang 1987; Rainbow 1996). However, their relative toxic effects may be masked by low pH and the overwhelming effects of metals such as aluminium and iron. Additional long-term toxicity may be caused by elements, such as lead, which are known to bioaccumulate in some aquatic organisms (e.g. Wang 1987; Gosavi et al. 2004).

3   Existing guidelines and acidity measures

There are currently no national or international guideline limits for acidity of inland saline and brackish ecosystems or common metals such as aluminium and iron in acidic waters. Nationally developed guidelines for protection of species in aquatic ecosystems focus on freshwater and marine ecosystems. The lack of guidance for inland saline ecosystems reflects the paucity of information on toxicity responses of aquatic organisms to various water quality parameters in inland saline waters in primary or secondary salinised ecosystems. The following section discusses whether existing guideline limits for pH and major metal concentrations relevant to acidity impacts can be applied to inland saline aquatic ecosystems.

3.1   pH guidelines

Existing guidance limits for pH vary depending on the ecosystem (wetland or waterway) and expected salinity. National guidance limits recommend pH levels at or near neutral for freshwater lakes or waterways (Table 1) and higher minimum values for marine ecosystems – the nearest comparison point for saline aquatic ecosystems. Guideline pH levels for marine waters may be inappropriate for naturally saline aquatic ecosystems with many exhibiting pH up to two units less than this (Pinder et al. 2004 and see summary in Jones et al. 2009). Further limitations of the marine guidelines lie in the reliance of these on marine monitoring rather than specific species responses (ANZECC & ARMCANZ 2000b).

A recent review of saline aquatic ecosystems in the Wheatbelt recommended a guideline level of pH 6 (Jones et al. 2009), but this did not take into account the likely confounding effects of dissolved metals such as iron and aluminium. These metals can remain in waters with pH 6, particularly following mixing of alkaline and acidic waters, and indicate that use of pH as a single criterion for discharge is likely to underestimate the ecological risks of these metals.

3.2   Dissolved metal guidelines

Guidelines for dissolved aluminium and iron are available for fresh and marine ecosystems, but may not be relevant to inland saline aquatic ecosystems given the differences in ionic composition. At face value the guidelines for marine ecosystems would appear to be more applicable to the Wheatbelt than those for freshwater ecosystems, given the salinity of inland saline waters (Table 1). Many Wheatbelt streams and wetlands generally range from brackish to saline in status (Mayer et al. 2005; Jones et al. 2009). However, the marine guidelines are based on species often absent in the Wheatbelt and developed in marine waters; these can have different ionic strength and composition to Wheatbelt stream and lake waters.

Table 1 Existing acidic water guideline limits potentially applicable to inland saline lakes and waterways

	Wetlands	Freshwater waterways [a]		Marine ecosystems [a]	
		95%	80%	95%	80%
pH	7.0 [b]	6.5	6.5	8.0	8.0
Al (µg/L)	N/A	55 (pH > 6.5) [c] 0.8 (pH < 6.5) [d]	150	0.5 [d]	
Fe (µg/L)	N/A	300 [d,e]		1000 (pH > 6) [e] 300 (pH < 6) [e]	
Net acidity (mg CaCO$_3$/L)	N/A	< 40 (when pH < 6) [f] > 0 (pH independent) [g]		N/A	

N/A = not available or not determined

[a] ANZECC and ARMCANZ guideline limits for wetlands in protection of species at different levels of confidence (95% and 80%; ANZECC and ARMCANZ 2000a) except where indicated

[b] Lower guideline limits for protection of species in slightly disturbed south-west wetlands (ANZECC and ARMCANZ 2000a)

[c] Moderate to high reliability species protection level (ANZECC and ARMCANZ 2000c)

[d] Low reliability species protection level (ANZECC and ARMCANZ 2000c)

[e] Department of Environment and Conservation (2010) contaminated water assessment guidelines (species protection levels not specified)

[f] Department of Environment and Conservation (2009) – Acid sulfate soil treatment guideline

[g] International acid water treatment guidance in PIRAMID Consortium 2003; Younger et al. 2002

Marine guidelines for aluminium are based on four crustaceans, one mollusc and two annelids (ANZECC & ARMCANZ 2000c) that have not been reported in reviews of Wheatbelt streams and lakes or wetlands (e.g. Pinder et al. 2004; Jones et al. 2009). The genus of the only marine species (*Nitocra spinipes*) for which aluminium toxicity data is reported (ANZECC & ARMCANZ 2000c) is found in the Wheatbelt (Jones et al. 2009). Reliable data for iron toxicity in marine waters is unavailable, with iron generally an essential element (ANZECC & ARMCANZ 2000c). As discussed previously, toxicity effects for dissolved iron (as Fe^{2+}) are mostly attributed to the physical effects of suspended materials in water columns and on lake/stream beds when the metal oxidises and precipitates (Phippen et al. 2008).

Protection guidelines for marine species assume seawater ionic composition whereas the ionic composition and salinity of saline water in the WA Wheatbelt are quite different. For example, Wheatbelt waters are frequently depleted in K, Ca and SO$_4$ relative to seawater (Shand & Degens 2008; Degens & Shand 2010) even if they have similar salinity. Similarly,

stream salinities can vary from less than 5000 mg TDS/L to more than 50 000 mg/L between winter and summer (Mayer et al. 2005). These differences in background salinity and composition are likely to influence the relative toxicity of low pH and dissolved metals to aquatic organisms – even when considering the same species.

Recent toxicity testing indicated pH guidance limits for aquatic organisms tested in seawater may be more conservative than for the same organisms tested in inland saline waters. A marine amphipod (*Allorchestes compressa*) and a brine shrimp (*Artemia salina*) tolerated pH less than 5 in saline waters from Dumbleyung (Ecotox Services Australasia 2011) whereas marine organisms are not known to be tolerant of such low pH in seawater (McMahon & Doyle 1997). This difference was probably due to the differences in ionic composition between inland saline waters and seawater.

National guideline levels for freshwater aquatic ecosystems may be transiently applicable to inland waters in the WA Wheatbelt during and immediately following large flood events. The existing limits (Table 1) may apply to ephemeral ecosystems when salinity is less than 2500 mg/L (ANZECC & ARMCANZ 2000a). However, the hardness of the water during this period (due to Ca and Mg) is likely to be a key factor influencing the aquatic toxicity of dissolved metals such as aluminium, with higher concentrations known to reduce toxicity (Gensemer & Playle 1999).

3.3   Net acidity guidelines

Guidelines for treatment of acidic waters recommend the use of net acidity as a trigger limit for managing the hazards (Table 1). Net acidity is a value calculated from measurements of alkalinity and acidity as:

Net acidity = acidity – alkalinity

Alkalinity can be directly measured by a field drop-test titration kit or laboratory analysis (see Appendix A). Acidity can similarly be measured with a field drop-test titration kit (see Appendix A), although is more accurately found by calculation from dissolved metals and pH (see Section 2.3.2; Appendix B).

International guidelines recommend treatment of waters containing net acidity to less than zero so that the waters contain alkalinity (PIRAMID Consortium 2003; Younger et al. 2002). In contrast, Department of Environment and Conservation guidelines (2009) recommend treatment of waters to less than 40 mg $CaCO_3$/L when pH < 6 (Table 1). The basis for the DEC guideline is not clear.

Use of net acidity as a guideline is based on chemistry theory, using the inorganic acidifying components of low pH waters (Kirby & Cravotta 2005) to provide a simple indicator for identifying and treating acidic water problems. While initially developed for drainage of water from acid-generating mines (Younger et al. 2002) this has subsequently been adopted to the similar acidic waters discharging from acid sulfate soils (Department of Environment and Conservation 2009). Recent national guidance for acid sulfate soils considers net acidity in soils, but not waters (EPHC & NRMMC 2011).

Net acidity guidelines are based on managing the acidity risks of the waters coupled mainly with H^{+}, dissolved iron and aluminium but **have not** been verified with toxicity testing using

either marine or freshwater organisms. The original 0 mg CaCO$_3$/L net acidity guideline (Table 1) was developed for acidic fresh and brackish waters, but is equally likely to be applicable to saline acidic waters. This is because the chemical properties of saline acidic surface waters are similar to those of acidic fresh waters associated with acid mine drainage and acid sulfate soils (Degens et al. 2008b). The higher salinity of acidic saline waters does not influence the net result of acid–base reactions and would only modify the solubility and rates of reactions of various dissolved elements in the waters.

3.4   Determining guidelines for inland aquatic ecosystems

Determining guideline limits for protecting aquatic ecosystems from the effects of acidic saline waters requires assessing the sensitivity of multiple aquatic species to contaminants (ANZECC & ARMCANZ 2000c). The results of multiple toxicity tests are used to establish the range of species sensitivities to toxins. This information is used to derive guidance values by calculating the concentration at which species protection can be achieved with known levels of confidence (90%, 95% or 99% as has been previously adopted ANZECC & ARMCANZ 2000a). Toxicity testing requires assessing biological responses to individual dissolved metals (such as aluminium) at a range of concentrations for a range of saline waters (to isolate the influences of other constituents in the waters on metal toxicity). The choice of test organisms also requires consideration – particularly as these need to represent different trophic levels in WA Wheatbelt waterways and lakes. The choice is likely to be challenging given the reported variations in species composition between aquatic ecosystems in the Wheatbelt (Pinder et al. 2004; Jones et al. 2009). Furthermore, the development of toxicity tests requires organisms that can be reliably cultured under laboratory conditions and have easily identifiable responses to toxins.

Clearly, species- and metal-specific guidelines present challenges for including a representative suite of organisms for the range of water chemistries in the Wheatbelt. Achieving them will require a concerted and exhaustive effort.

The above review indicates that direct measures of acidic water toxicity using pH may indicate some risks the water poses to saline aquatic ecosystems but can underestimate other risks associated with trace dissolved metals or downstream acidification. Assessing the risks of dissolved metals requires toxicity testing and adoption of routine dissolved metal analysis. The primary environmental risks of acidic waters are encompassed in the capacity for the water to acidify aquatic environments (indicated by net acidity measurements). Focusing on this perhaps offers a more achievable, practical path to developing discharge criteria for acidic saline waters in the Wheatbelt than pH and metal-specific investigations.

4 Proposed interim criterion to manage acidic water hazards

Management of acidic water hazards for inland saline ecosystems requires measures that reflect the acidity and dissolved metal hazards, can easily be done in the field, and are readily interpreted. Assessment of the pros and cons of current measures of acidic water hazards outlined in the earlier sections is provided in Table 2. This provides the basis for the following discussion.

4.1 Proposed criterion and guideline value

Net acidity is proposed as a criterion to provide the best management of hazards where drains discharge acidic water to lakes and waterways in the WA Wheatbelt. Net acidity provides an integrated indicator of toxic concentrations of dissolved metals as well as pH. The indicator provides a practical benchmark that can be calculated in the field from measurements using simple drop-test kits (see Degens 2009) without the need for calibration (as is regularly needed with pH probes) or laboratory analysis (Table 2). While pH provides a robust, widely understood measure of the acidic status of water, it does not indicate the stability of the water chemistry. Water pH can be unstable depending on whether or not the water is in equilibrium with the atmosphere, (often) unlikely in groundwater or groundwater drains. Furthermore, pH does not indicate the buffering capacity of the water or the capacity for various acidifying reactions to be driven by any dissolved metals (Table 2).

A net acidity threshold of less than 10 mg $CaCO_3$/L is proposed as interim guideline value to minimise the risks of acidic waters to primary and secondary saline ecosystems in the WA Wheatbelt. A higher value of 20 mg $CaCO_3$/L might be applicable for highly disturbed ecosystems.

The guideline value is supported by recent toxicity testing with partially neutralised saline drain waters showing that the net acidity where there is no effect (no observable effect concentration/NOEC) on four species of salt-tolerant organisms ranged from 0 to 30 mg $CaCO_3$/L (Table 3; Ecotox Services Australasia 2011). A guideline value of 10 mg $CaCO_3$/L represents the lower 95% confidence interval of the mean no-effect concentrations for the tested species, whereas a guideline value of 20 mg $CaCO_3$/L represents the upper 95% confidence interval. It was notable for all species that none survived when net acidity concentrations exceeded 75 mg $CaCO_3$/L (Ecotox Services Australasia 2011). Basing the guideline value on no-effect concentrations is consistent with the approach recommended in national water quality guidelines (ANZECC & ARMCANZ 2000c).

Toxicity testing for the criterion was conducted using water from three acidic saline drains neutralised to varying degrees with sodium bicarbonate. The drain waters had salinities of 39–40 g TDS/L and initial net acidities of 350–513 mg $CaCO_3$/L. Toxicity tests carried out with the waters **after** mixing, aeration and settling of any precipitated metal sludge. Therefore the tests reflect the toxicity of residual dissolved acidity in the waters rather than of suspended or sludge materials produced after neutralisation.

Table 2 Summary of pros and cons of acidic water indicators

Indicator	Pros	Cons
pH	Easily measured in the field for immediate decision making Widely understood in terms of significance for receiving environments (particularly interpreting toxicity)	Calibration required before measurement Calibration relies on chemical solutions that need to be replaced routinely Does not indicate stability of acidic/non-acidic conditions and potential buffering capacity Limited in measuring amount of neutralisation required to mitigate acidity risks
Acidity	Indicator easily measured in the field for immediate decision making No calibration of measurement required Allows immediate determination of maximum amount of neutralisation required to mitigate acidity risks	Uses chemicals that need to be replaced routinely Does not indicate stability of acidic/non-acidic condition as a sole measure Not in common use
Net acidity	Indicator easily calculated in the field from acidity and alkalinity Reliant on field measurements where no calibration required Reflects likely equilibrium acidic/non-acidic condition of the water Allows immediate field determination of amount of neutralisation required to mitigate acidity risks Locally relevant information available to interpret aquatic toxicity	Uses chemicals that will routinely need to be replaced Not in common use
Dissolved metals	Provides accurate indication of dissolved metals enabling assessment of discharge risks Possible to interpret aquatic toxicity with additional species information Can provide accurate estimation of acidity and therefore minimum amount of neutralisation required to mitigate acidity risks	Cannot be measured in the field Sampling and laboratory analysis required Not in common use

Table 3 Summary of toxicity test results for neutralised acidic saline (39–40 g TDS/L) drain waters and acidified stream water from the WA Wheatbelt (adapted from Ecotox Services Australasia 2011)

Toxicology test	Water[1]	EC$_{50}$ or IC$_{50}$[2]	EC$_{10}$ or IC$_{10}$[3]	NOEC$_{NA}$[4]	NOEC$_{pH}$[5]
		---------- Net acidity (mg CaCO$_3$/L) --------			
48 hr acute (survival) toxicity test with the brine shrimp *Artemia salina*	BY	20 (17–22)	17 (16–19)	10	5.9
	BC	30 (26–34)	26 (25–26)	10	6.1
	FC	7 (0–11)	4 (0–6)	0	6
	C	N/A	N/A	−10	5
48 hr acute (survival) toxicity test with the ostracod *Platycrysis bauera*	BY	18 (16–20)	17 (16–17)	10	5.9
	BC	36 (32–40)	29 (28–34)	35	5.7
	FC	7 (0–11)	4 (0-6)	0	6
	C	N/A	N/A	−10	5
72 hr micro-algal growth inhibition toxicity test using *Dunaliella salina*	BY	28 (24–34)	20 (0–22)	20	5.6
	BC	44 (34–53)	22 (6–30)	35	5.7
	FC	32 (28–36)	17 (0–20)	15	5.6
	C	N/A	N/A	−10	5
48 hr acute (survival) toxicity test with the marine amphipod *Allorchestes compressa*	BY	25 (23–27)	21 (18–28)	20	5.6
	BC	37 (30–45)	35 (35–35)	35	5.7
	FC	18 (16–26)	15 (9–24)	15	5.6
	C	N/A	N/A	−10	5.1

[1] Test waters – sodium bicarbonate (NaHCO$_3$) neutralised saline drain waters from Beynon Road, Dumbleyung (BY), Beacon (BC) and Fence Road, Dumbleyung (FC). Coblinine River water, Dumbleyung (C) acidified with hydrochloric acid to pH 4.7, 5.1, 5.6, 6 and 6.4

[2] Statistically-derived net acidity concentration (with 95% confidence interval in brackets) at which 50% of organisms affected (EC$_{50}$) or inhibited (IC$_{50}$ for the micro-algal test only) by net acidity in the test waters

[3] Statistically-derived net acidity concentration (with 95% confidence interval in brackets) at which 10% of organisms affected (EC$_{10}$) or inhibited (IC$_{10}$ for the micro-algal test only) by net acidity in the test waters

[4] NOEC$_{NA}$ = net acidity concentration in test series where no effect/inhibition occurred on test organisms (note: negative net acidity indicates that water contains alkalinity exceeding acidity)

[5] NOEC$_{pH}$ = pH in test series where no effect/inhibition occurred on test organisms

Acidification and aquatic toxicity effects on the environment are expected to be minimal where drain water is discharged with net acidity <10 mg $CaCO_3$/L provided that the water has had time to react with air to allow any metals to precipitate and settle as sludge prior to discharge.

Use of field tests with limited accuracy may constrain the practicality of applying the guideline limits for net acidity. The resolution of detection of some field kits can be as much as 20 mg $CaCO_3$/L for acidity (see Appendix A) and 5 mg $CaCO_3$/L for alkalinity which reduces the accuracy of detecting a net acidity of less than 10 mg $CaCO_3$/L. However, using the low range methods for these kits can often provide more accurate measures that should be able to resolve this level of net acidity. A value of 20 mg $CaCO_3$/L may be more practical to measure in the field than 10 mg $CaCO_3$/L and perhaps could be considered after trialling the criterion.

Toxicity testing also showed that net acidity calculated from dissolved metals was better in indicating the toxicity of the waters to aquatic organisms than pH alone. Where dissolved metals were present, the pH at which there were no effects on the test organisms ranged from 5.6 to 6.1 whereas in the **absence of dissolved metals** in the acidified Coblinine River water the organisms were not affected at pH 5.0–5.1 (Table 3). It was evident that sensitivity of organisms to low pH can vary depending on the presence of dissolved metals and therefore is less reliable as an indicator of acidic water toxicity than net acidity.

The proposed interim guideline is similar to criteria used to manage acidity in freshwaters from acid sulfate soils (Department of Environment and Conservation 2009) and internationally for acid mine drainage (Younger et al. 2002; PIRAMID Consortium 2003). Furthermore, the interim guideline is consistent with earlier proposals that acidic saline waters should be treated to at least 0 mg $CaCO_3$/L, preferably with excess alkalinity, to minimise environmental risk (Degens 2009 after Younger et al. 2002). Previous guideline limits for acidity were based on chemical theory (as discussed earlier), whereas the present recommendation is supported by the first toxicity testing involving net acidity in saline waters with salt-tolerant aquatic organisms.

Net acidity encompasses the major metal risks associated with dissolved aluminium and iron in acidic waters and the influence these have on water pH. While net acidity does not capture the risks associated with trace elements (e.g. lead, copper and zinc) sometimes dissolved in acidic waters, recent bicarbonate neutralisation tests indicate that these can be greatly decreased during neutralisation (Ecotox Services Australasia 2011). This is attributed to the adsorption onto iron and aluminium precipitates that form once iron- and aluminium-rich waters are neutralised (McDonald et al. 2006).

4.2   Why pH alone is limited

The use of the pH criterion alone can be too conservative and could lead to failure to ensure that there are no acidity hazards associated with Wheatbelt waters. Toxicity tests suggested that pH exceeding 6.1 might be a suitable indicator that acidity risks associated with net acidity are minimised (Table 3); however, it is still possible for waters at this pH to contain net acidity. Meta-analysis of more than 750 surface water and groundwater samples taken across the Wheatbelt in previous work (Shand & Degens 2008; Degens & Shand 2010)

indicated that 14% of the 91 waters with pH > 6 contained net acidity exceeding 10 mg $CaCO_3$/L (Fig. 2). This may seem an acceptable error rate, but some of these waters (groundwater and drainage water) could contain net acidity exceeding 200 mg $CaCO_3$/L that would otherwise be unidentified and unmanaged if using pH criterion alone.

A further limitation of relying on pH to define discharge criteria is that 70% of waters between pH 5 and 6 would be deemed as being at risk of acidification – when these have no acidification risks. This error means that extra costs would be incurred in treating and managing waters for acidity for no gain.

This discussion indicates that measuring pH alone is probably not sufficiently conservative to manage the majority of risks associated with acidic drainage waters in the Wheatbelt.
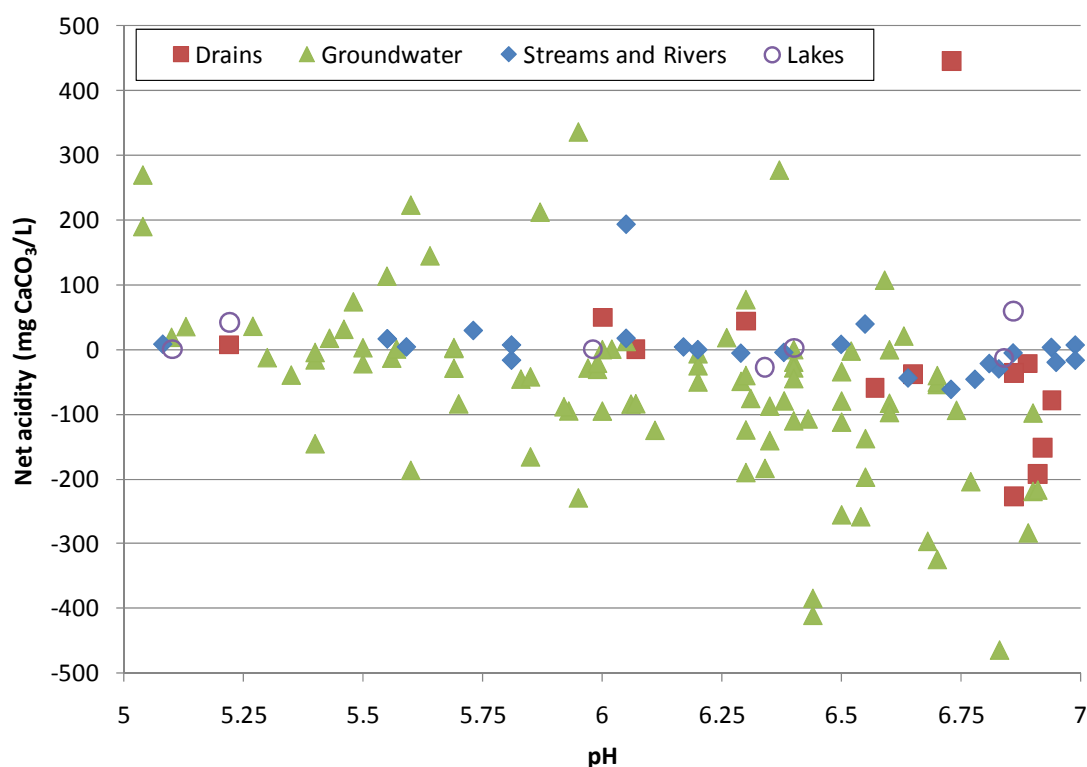
Figure 2 Net acidity of waters with field pH 5–7 collected from drains, groundwater bores and surface sites (lakes, streams and rivers) in areas with acidity issues in the Wheatbelt (data from Shand & Degens 2008; Degens & Shand 2010)

4.3   Hazards that the proposed criteria do not capture

Management to minimise net acidity captures most of the hazards associated with acidic waters, but not those from minor metals or metalloids. These include metals such as cadmium, copper, lead, manganese, nickel and zinc or metalloids such as arsenic. These can sometimes be present after neutralisation, although in most cases they can be removed with the iron and aluminium precipitates (Degens 2009). Manganese can be an exception.

As with dissolved aluminium and iron, there are no reliable guidelines for concentrations of minor metals and metalloids in inland saline waters. The ANZECC and ARMCANZ (2000a) guidelines for marine ecosystems provide a broad interim basis for assessing toxicity (see

Degens 2009 for a list). These indicate that the toxicity of minor metals and metalloids varies depending on the element; generally, copper > lead > cadmium > zinc > nickel (ANZECC & ARMCANZ 2000c). There is some uncertainty regarding the toxicity of manganese in marine ecosystems (ANZECC and ARMCANZ 2000c). However, recent tests with neutralised drain waters showed no toxic responses to residual concentrations of manganese, lead and copper (Ecotox Services Australasia 2011) that were above ANZECC and ARMCANZ (2000a) guideline values for marine ecosystems. This indicates that the ANZECC and ARMCANZ values (2000a) are conservative and applying them to neutralised discharge waters will result in a conservative level of protection for saline aquatic ecosystems.

4.4   Application

It is anticipated that net acidity will be calculated from measurements of acidity and alkalinity of groundwater or drainage water that might be discharged to waterways or lakes. For groundwater, the measurements should be made using freshly collected samples of shallow groundwater seepage into test pits or water pumped from bores. If net acidity exceeds 10 mg $CaCO_3$/L, discharge of this water without treatment may result in harmful effects on the ecology of receiving lakes and waterways.

Discharge of water with net acidity less than 10 mg $CaCO_3$/L is unlikely to result in harmful effects provided that the water has been sufficiently aerated and enough time allowed for completion of any neutralising reactions. This caveat ensures that the physical effects of metal precipitate formation (increased turbidity or smothering of bed sediments) on the receiving environments are minimised in waters where significant acidity occurs in conjunction with alkalinity (usually very iron-rich alkaline waters). This can be achieved by constructing ponds to promote aeration and sludge settling from drain waters prior to discharge. Details of suitable pond designs are provided in PIRAMID Consortium (2003) and Younger et al. (2002).

The management responses for waters exceeding the guideline will depend on the level of acidity and the receiving environment. For drainage or groundwater pumping systems, management could include:

- treatment of acidity using in-drain or end-of-drain systems (Degens 2009)

- containment and evaporation in constructed ponds (and treatment of seepage)

- retention and evaporation in lakes with periodic neutralisation by flood waters (see Degens & Shand 2010)

or

- retention and evaporation in lakes with augmented treatment capacity.

Further details of these options are provided in the proposed guidelines for treating acidic drain water (Degens 2009).

Appendices

Appendix A — Assessment of fundamental risk factors for acidic waters

Estimating total acidity

Total acidity can be measured in the field in samples immediately following collection using kits involving simple drop-tests or more accurate metered dosing. This measurement is sometimes called 'phenolphthalein acidity' or 'mineral and organic acidity'. The basic measurement involves taking a sample with a calibrated container, adding a solution or powder that colourimetrically indicates pH (phenolphthalein) and adding a dilute mixture of sodium hydroxide of known concentration until the colour changes indicating that a certain end-point pH has been reached. The standard method involves measuring the volume of sodium hydroxide solution added to reach a stable pH of **8.3** in the water sample (indicated by the colour changing from colourless to purple). *Note that titrating to pH = 4.5 only indicates mineral acidity or free acidity.*

With waters highly coloured with tannins or other organic compounds the colour change signalling the pH end point may be difficult to see. It may be necessary to use a pH probe to detect when the pH reaches 8.3.

Commonly available test kits include HACH (drop-test kit: 4–500 mg $CaCO_3$/L Model AC-6 Catalogue No. 2223-01 or digital pipette kit for acidity and alkalinity 10–4000 mg $CaCO_3$/L Model AL-DT Catalogue No. 20637-00), Hanna Instruments (syringe titration test kit: 0–500 mg $CaCO_3$/L Model HI 3820) or the Acid Solutions test kit.

The accuracy of the test kits varies. The HACH drop-test kit typically has an accuracy of ± 20 mg $CaCO_3$/L when titrating total acidity in the high range (0–400 mg/L) but can have an accuracy of ± 5 mg $CaCO_3$/L in the low range (0–100 mg/L) titrating a 23 mL volume using phenolphthalein to detect the end point rather than bromocresol green–methyl red. In contrast, the Hanna kits have an accuracy of ± 5 mg $CaCO_3$/L in the 0–500 mg/L range and ± 1 mg $CaCO_3$/L in the 0–100 mg/L.

Acidity is most accurately found by calculation from dissolved metals and a measurement of pH in the field. This requires collecting a water sample and sending it for laboratory analysis of dissolved metals. A brief comparison of in-field measurements with acidity calculated from laboratory analyses in saline waters is covered in Appendix B. Samples filtered in the field through 0.45 µm filter paper and preserved with nitric acid need to be submitted for analysis of dissolved iron, aluminium and manganese (contact laboratories to determine the best approach). Acidity from these analyses and a measurement of pH in the field is calculated using the equation:

$$\text{Acid}_{calculated} = 1.79 \times Fe^{2+} + 2.68 \times Fe^{3+} + 5.56 \times Al + 1.82 \times Mn + 50000 \times 10^{-pH}$$

where Fe, Al and Mn are concentrations of dissolved elements in mg/L. This calculation requires consideration of the extent to which iron is present as Fe^{2+} or Fe^{3+}. It is often easier to assume dominance of one form; for example, if pH is less than 3.5 and the water is well aerated most iron is likely to be present as Fe^{3+}, in which case 0 is used as the concentration

of Fe^{2+}. For higher pH water, it is safer to assume that dissolved iron is present as Fe^{2+} (also see notes below and Glossary).

Estimating alkalinity

Alkalinity is best measured on samples taken in the field using kits involving simple drop-tests. Samples can also be bottled and sent to a laboratory for later analysis by a similar method to that used in the field. Immediate measurement in the field is generally more reliable than measurement in a laboratory because the alkalinity in samples can change during storage and transport.

The basic measurement of alkalinity involves a chemical test in the field of adding a strong acid to a fixed volume of sample until certain pH is reached. The sample is collected in a calibrated container, added to a larger jar to which a pH indicator (e.g. bromocresol green–methyl red) is added and a dilute mixture of sulfuric acid (of known concentration) slowly added until the colour changes. For the indicator used, the change is from green to pinkish red when the pH of the sample reaches **4.5**. The volume of sulfuric acid added to the sample is recorded and used to calculate the amount of alkalinity in the sample consumed by lowering the pH to 4.5. If the sample is already less than pH 4.5 (that is the colour changes instantly to pinkish red) there is no measureable alkalinity.

Commonly available test kits include HACH (drop test kit: 5–400 mg $CaCO_3$/L Model AL-AP MG/L Catalogue No. 24443-01 or digital pipette kit for acidity and alkalinity 10–4000 mg $CaCO_3$/L Model AL-DT Catalogue No. 20637-00), Hanna Instruments (syringe titration test kit: 0–300 mg $CaCO_3$/L Model HI 3811) or the La Motte test kit (P&T Dropper Pipette Alkalinity test No. 4533; 50–200 $CaCO_3$/L). These range in accuracy from 1 to 5 mg $CaCO_3$/L for generally low range tests up to 100 mg $CaCO_3$/L and up to 20 mg $CaCO_3$/L for higher range tests.

Estimating flow

An estimate of flow is essential for calculating instantaneous acidity loads and providing the hydrological context to measurements of water chemistry. Flow estimation basically involves measuring the cross-sectional area of flowing water and the average velocity of this flow. To achieve high accuracy, this normally involves detailed measurements of depths and flow velocities. Nonetheless, the same basic approach can provide order-of-magnitude estimates.

Basic flow estimation is calculated as: Q = V x A.

where Q is flow in m^3/s, V is average velocity in m/s and A is cross-sectional area (m^2).

Choose a straight section of drain (or a culvert) with constant width, depth and shape to measure the flow. Avoid sections where water ponds. Measure the width and average depth of the section and calculate the cross-sectional area. Where the channel is box shaped, cross-sectional area is calculated as: width x depth. The cross-sectional area of V-shaped channels is ½ x width x depth, and of semi-circular channels is ⅔ x width x depth. Culverts can be a good place to take measurements, but only if flows within them do not bank up.

Velocity can be measured by timing a floating object over a set distance (measured or paced) and taking 85% of this value to estimate the subsurface velocity.

If flow measurements are to be made consistently at a site, the reliability of estimates can be improved by installing a small V-notch weir where the theoretical relationship between depth of flow and discharge can be used to estimate flow or where flow can be measured by the time to fill a bucket (Younger et al. 2002; PIRAMID Consortium 2003).

Care needs to be taken with extrapolating point measurements of flow to estimate discharge over time in drains. For example, significant under- and over-estimation can occur if using a single measurement of flow to estimate daily discharge particularly if rain has fallen.

Appendix B — Comparison of net acidity determined by test kit with laboratory analysis

The international convention is that net acidity be determined by calculation using analysis of dissolved metals and dissolved alkalinity (Younger et al. 2002; PIRAMID Consortium 2003; Kirby & Cravotta 2005). This is generally using the equation:

Net acidity = $acidity_{calc}$ – alkalinity

Where: $Acidity_{calc}$ = 1.79 x Fe^{2+} + 2.68 x Fe^{3+} + 5.56 x Al^{3+} 1.82 x Mn^{2+} + 50000 x 10^{-pH}

(after Kirby & Cravotta 2005).

Alkalinity = alkalinity determined/calculated by strong acid (usually H_2SO_4) titration to pH 4.5.

$Acidity_{calc}$ requires measurements of soluble aluminium, iron and manganese concentrations (in mg/L or ppm) and so sampling and analysis of dissolved metals. While more accurate, this rules out immediate in-field assessment of acidity hazards.

A less reliable method is to measure acidity by titration with a strong alkaline solution (such as sodium hydroxide). This approach is not generally recommended internationally because it can underestimate acidity (Kirby & Cravotta 2005). However, in the acidic saline waters found in the WA Wheatbelt, acidity determined by titration generally overestimates acidity, resulting in an overestimation of net acidity. This is illustrated in analysis of net acidity using calculated acidity ($Acidity_{calc}$) and measured acidity ($Acidity_{meas}$) for acidic drain waters neutralised with bicarbonate solution (used in the testing by Ecotox Services Australasia 2011). A notable point is that the difference diminishes as waters approach net acidity of 0 mg $CaCO_3$ (Fig. 3).
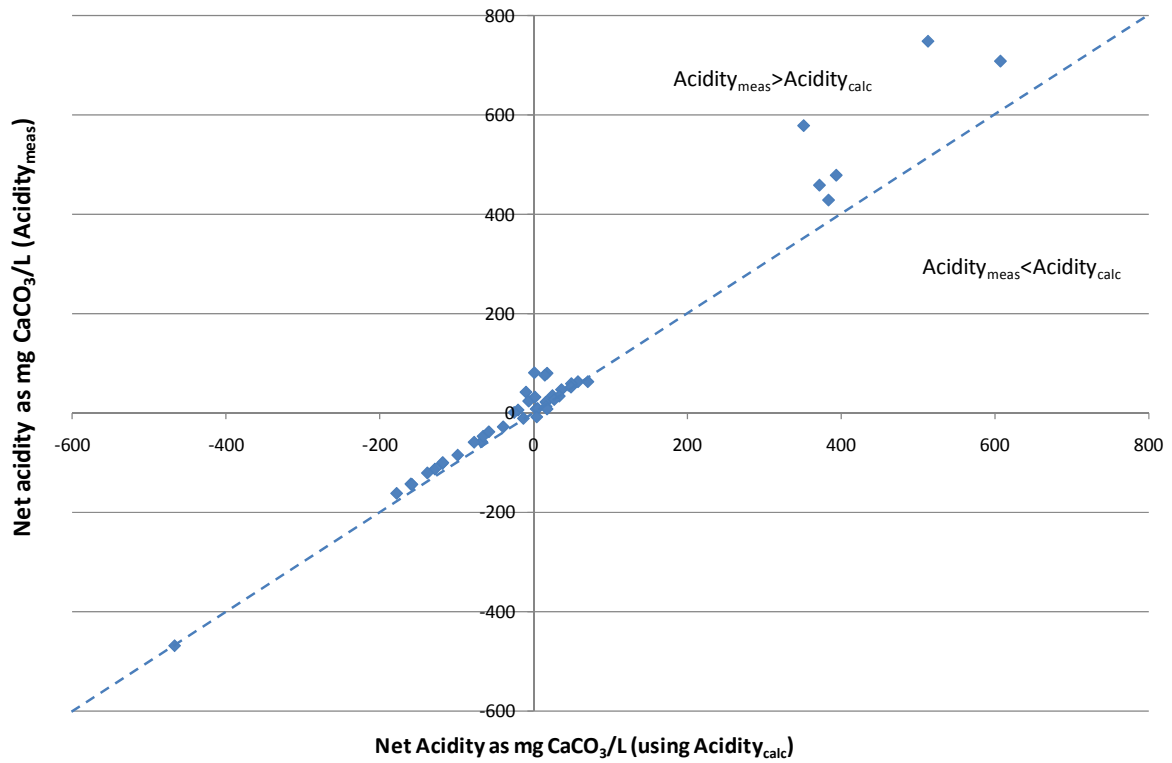
Figure 3 Deviation between net acidity based on acidity measured using a field test kit (Acidity$_{meas}$; also similar to acidity by laboratory titration) and calculated acidity (Acidity$_{calc}$) for a range acidic waters neutralised with bicarbonate

Glossary

Acidity

The amount of acidity associated with all dissolved ions in a solution expressed as an amount of pure calcium carbonate needed to neutralise these. This includes hydrogen ions (as measured by pH) and commonly 'free' dissolved metals such as aluminium, iron and manganese. Other dissolved metals such as lead and zinc only begin to make a significant contribution to this acidity at high concentrations (> 1 mg/L) – rare in acidic Wheatbelt water (Degens et al. 2008b). Organic acids may also contribute to acidity in some natural water, particularly those originating from peat wetlands but their contribution is insignificant. Acidity can be found by measuring the amount of sodium hydroxide (NaOH/caustic soda) needed to raise the pH of a litre of the solution to 8.3 (Kirby & Cravotta 2005). Acidity can also be more reliably calculated from measurements of pH, soluble aluminium, iron and manganese concentrations (in mg/L or ppm) using the formula (after Kirby & Cravotta 2005):

$Acid_{calc} = 1.79 \times Fe^{2+} + 2.68 \times Fe^{3+} + 5.56 \times Al^{3+}\ 1.82 \times Mn^{2+} + 50000 \times 10^{-pH}$

Note that when water pH exceeds 3.5, most of the dissolved iron is likely to be present at Fe^{2+} with iron as Fe^{3+} probably only present in significant concentrations when water pH is less than 3.5 (Langmuir 1997). From this equation, simple 'rules of thumb' are that every g/L of dissolved aluminium requires 5.6 g $CaCO_3$/L to neutralise, every g/L of iron (as ferrous iron) requires 1.8 g $CaCO_3$/L to neutralise and every g/L of manganese requires 1.8 g $CaCO_3$/L to neutralise.

Acid mine drainage (AMD)

Outflow of acidic, usually metal-rich, water from mine environments usually as a result of changes in geochemistry and hydrology associated with mining geological formations containing sulfide ores.

Alkalinity

Largely the concentration of bicarbonate (HCO_3^-) in most water (except when pH > 8.3 when the amount of carbonate or CO_3^{2-} is more dominant) and can be measured in any water with pH > 4.5 by measuring the amount of hydrochloric acid (HCl) needed to lower pH of a litre of the solution to 4.5 (see Kirby & Cravotta 2005). Sometimes alkalinity is due to ions other than bicarbonate, such as dissolved silicate, phosphate or ammonia (Langmuir 1997), but only if in relatively high concentrations (i.e. tens of mg/L).

Bioaccumulate

Concentration and storage of, usually, organic (e.g. persistent hydrocarbons) or inorganic (e.g. metals) contaminants within organisms often by organisms consuming others that have accumulated these.

Criterion	A standard or test on which a judgment or decision can be based.
Dissolved metal	Concentration of metals that remains in water after being filtered through 0.45 µm filter membrane.
Metal acidity	Term applied to the acidity due to dissolved metals in acidic water (commonly aluminium, iron and to a lesser extent manganese in Wheatbelt water).
Net acidity (or net acidic)	This property of water accounts for dissolved alkalinity (such as bicarbonate or carbonate) in describing the degree of acidity in water. Some groundwater and water from treatment systems at pH > 4.5 can contain both dissolved acidity (as mineral acidity) and alkalinity. Net acidity = acidity_{calc} – alkalinity measured in each case as units of $CaCO_3$ equivalent/L. See also – Acidity and Alkalinity.
No observable effect concentration (NOEC)	The highest concentration of contaminants in a toxicity test series at which test organisms are unaffected compared with organisms in a control (untreated) treatment.
pH	This is a measure of the concentration of hydrogen ions (H^+) in water, measured on a scale of 1 to 14, where the mid-point 7 is neutral. In technical terms, pH values are calculated as the negative of the base-10 logarithm of the hydrogen ion concentration. In practical terms, this means that each unit change in pH represents a 10-fold change in hydrogen ion concentration so that, for example, a fall in pH from 4 to 3 represents a 10-fold increase in hydrogen ion concentration. The measure also applies to soils and muds, but only because pH is measured in the water held in the pores of these materials (i.e. it is not possible to measure pH in a dry soil).
Primary salinity	Land and water salinity occurring in a landscape as a result of natural hydrological processes unaffected by human change in the landscape.
Regolith	All the soil and geological materials above fresh bedrock (including transported unweathered rocks).

Salinity (water)   This is a measure of the total soluble (or dissolved) salt (TDS) in water. This is sometimes measured by weighing the residue after completely drying a sample of filtered water. This material is often mostly a mix of predominantly sodium, calcium, potassium, magnesium as chloride, sulfate and bicarbonate (for alkaline waters) salts expressed as a weight per volume of water (mg/L).

Salinity can also be calculated by summing the major ions (as in this report) or estimated from measurements of electrical conductivity (EC) by normalising to a measurement equivalent to water at 25 °C (often called temperature compensation) and converting to TDS by multiplying the temperature compensated EC by 5.072 for EC 0–261 mS/m, by 5.889 for EC 261–1701 mS/m and by 7.820 for EC greater than 1701 mS/m.

Secondary salinity   Land and water salinity caused by changes in the hydrology of a landscape due to human activities (e.g. clearing perennial vegetation). In south-western WA, clearing perennial vegetation has typically increased recharge to groundwater causing rising watertables, increased mobilisation of salts and increased discharge of groundwater to soil, waterways and lakes.

Toxicity (or toxicological)   Potential for a constituent in waters (also soils/sediments or air) that with increasing concentration causes chemical or physical stress in an organism by disrupting the natural biochemistry, physiology or behaviour of the organism.

Wheatbelt   Agricultural zone of south-west Western Australia used mainly for broadacre cropping and sheep farming generally occurring in the area where annual rainfall is between 500 mm and 320 mm.

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